Surface chemical and tribological investigations of phosphorus-containing lubricant additives

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SURFACE CHEMICAL AND TRIBOLOGICAL INVESTIGATIONS OF
PHOSPHORUS-CONTAINING LUBRICANT ADDITIVES

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH
for the degree of
Doctor of Technical Sciences

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2003
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1. Summary / Zusammenfassung

Summary

The replacement of existing non-ecologically compatible friction modifiers and extreme-pressure additives (mostly metal- and Cl-containing) by more environmentally benign alternatives is an important challenge for industry over the next decade. In order to achieve this objective, it is necessary to understand how these non-ecological additives work, and to be able to predict how other molecules would function under similar conditions.

The focus of the present work is to elucidate the action mechanism of these additives by investigating both the macroscopic tribo-behavior and the microscopic structure of a tribo-stressed surface. First, the tribological performance of commercially available, metal-free additives (amine phosphate, dithiophosphate and phosphorothionate) and a metal-containing additive (ZnDTP) were examined with flat-on-disk type tribometry under a wide variety of experimental conditions. From the tribological tests, the additives were found to reduce friction in boundary lubrication - even at room temperature - and to prevent occurrence of stick-slip events. Amine phosphate, a mixture of phosphoric acid ester and alkyl amine, was found to show the most pronounced reduction of friction coefficient. Phosphoric acid ester was found to work particularly well in reducing friction, whereas alkyl amine appeared to do nothing but work as a neutralizer.

Following tribological tests, surfaces on which some kind of lubrication films were presumably present were precisely analyzed with imaging and small-area XPS analysis, compared with both frozen pure additives and additives adsorbed on surfaces that were produced under a wide variety of conditions of surface-treatment or adsorption.

From imaging XPS analysis on a surface following tribological testing with amine phosphate, the elemental distribution around the contact area was clearly observed, indicating formation of a lubrication film in the contact area. From small-area XPS analysis, the contact area was found to consist of high concentrations of iron and organic phosphate with some iron oxide, and the non-contact area was found to consist mainly of the adsorbed organic phosphate and iron (oxy-) hydroxide. A surface after the tribological test with phosphoric acid ester was found to have similar characteristics, although the two additives appeared to have a different preference for the surface state with which they react. In other words, amine phosphate appeared to react preferentially with a metal surface while phosphoric acid ester appeared to react preferentially with an oxide surface.
The identification of the different chemical states of the elements, particularly phosphorus, was possible only on the basis of the XPS data collected on standard and reference compounds, i.e. pure, un-reacted additives (frozen on gold), iron oxides, and iron oxides with adsorbed additives. A two-dimensional chemical-state plot (Wagner chemical-state plot) was employed to distinguish between the different chemical states of phosphorus (organic, iron phosphate, polyphosphate etc.) so that the adsorbed or the tribo-stressed surfaces could be clearly distinguished.

Finally, the reaction mechanisms of the two additives were proposed in accordance with the XPS analysis results of the tribo-films, the adsorption films and the frozen pure additives. The difference of adsorbability or reactivity between amine phosphate and phosphoric acid ester could be reasonably well understood by considering the theory of hard and soft acids and bases.

Zusammenfassung


Die genaue Identifikation des unterschiedlichen chemischen Zustands der Elemente, insbesondere des Phosphors, war nur auf der Basis der XPS-Daten von Standards und Referenzproben, z.B. reinen, unreagierten Additiven (im gefrorenen Zustand auf Gold) oder auf Eisen bzw. Eisenoxid adsorbierten Additiven möglich. Im zweidimensionalen chemischen Zustandsdiagramm (Wagner chemical state plot) konnte der Bindungszustand des Phosphors (organisch, Eisenphosphate, Polyphosphate etc.) sowohl im Bereich der reinen Adsorption als auch im tribologisch beanspruchten Bereich klar identifiziert werden.

Auf der Basis der Theorie "hard and soft acids and bases" wird für Aminphosphat und Phosphorester ein Reaktionsmechanismus postuliert, welcher die XPS-Resultate der untersuchten Referenzproben, der adsorbierten Additive und der tribologisch gebildeten Reibungsfilme erklären kann.
2. Introduction

2.1 General remarks

Lubricants usually contain a variety of additives of different chemical functionalities to meet many service requirements. Among them are friction modifiers (FM), extreme pressure (EP) additives and anti-wear (AW) additives. Several chemical compounds are available for use as additives which will impart new properties to the lubricant or improve the existing properties. However, these additives must be compatible with one another as well as with the base-stock.

The recent trend is toward the use of multifunctional additives which are able to impart more than a single property to the lubricants. Phosphorodithionate and dithiocarbamate complexes of molybdenum, zinc, antimony, titanium, copper and other transition metals are two such classes of additives which have found extensive use as AW additive or EP additives in lubricants for various applications. However due to environmental restrictions and operational reasons, the use of these metal phosphorodithionate complexes has been brought into question on account of problems of toxicity, waste disposal, filter clogging, pollution, etc.

The recent AW and EP additive technology for both automotive and industrial applications is based on ashless sulfur-phosphorus chemistry. A number of ashless compounds based on derivatives of dialkylphosphorodithioic acids have been reported in recent literature as AW / EP additives.

On the other hand, from the point of view of fundamental research regarding lubricant additives, the recent advances in the metallic surface analysis method, including EPMA and XPS, fortunately have brought new findings about the behavior of the additive on the frictional surface. In-situ measurement of the frictional surface also helped in elucidation of the action mechanism. Thus, the focus is more toward mechanism study using such highly sensitive surface analytical tools. In this chapter, first various existing lubricant additives will be reviewed and then surface analytical studies in tribology will be reviewed.

2.2 Extreme pressure and anti-wear additives

An EP / AW additive is a lubricant additive that prevents seizure and decrease wear-out during friction. It is added in lubricants that are used in boundary conditions, where the lubrication film is apt to break due to the partial high pressure and the high temperature. The main usage of the EP / AW additives is for gear oil, cutting oil, engine oil or machine oil. Under the boundary lubrication condition, the EP / AW additives generate some chemical
changes and form a surface protection film called a boundary lubrication film, on a metal surface. Therefore, it is necessary that the functional group in the molecule can react with the metal surface. It is also necessary that the additives decompose or react on the metal surface and are able to form a boundary lubrication film promptly on the surface. Moreover, the boundary lubrication film is required to be relatively soft and ductile, and also to be mechanically and chemically stable. Some compounds that contain sulfur, chlorine, phosphorus and some complex compounds combining some of these elements can meet the demands. Since every boundary lubrication film that is generated by these compounds has different physical properties, two kinds or more are often combined to obtain these synergistic effects.

It was formerly known that sulfurized fatty oils and lead soap were effective EP / AW additives. In the 1930's when hypoid-gear spread for rear axles of cars, a lot of compounds were gradually developed. From around 1940, reports concerning the reaction mechanism of EP / AW additives started to appear and a lot of patents also appeared, including for tricresylphosphate (TCP) and zinc dialkyldithiophosphate (ZnDTP). Since then, an EP / AW additive containing phosphorus, sulfur and chlorine (1959) and an EP / AW additive containing phosphorus and sulfur (1961) have been developed, and a lot of new compounds are still being reported [1].

It is accepted that the research on the action mechanism of the EP / AW additives started from the “iron sulfide theory” of Baxter [2] (1939) and “the chemical polishing theory” of Beek [3] (1940). However, 40 years after these works, a lot of researchers are still working on this matter, and thus the research of the action mechanism of EP / AW additives can be regarded as both an old and a new subject. Although there is considerable agreement about the action mechanisms of various EP / AW additives, there are many objections regarding the details.

2.2.1 Types of extreme pressure and anti-wear additives

In general, EP / AW additives are classified into the following four types by chemical compositions: the sulfur compound type, the chlorine compound type, the phosphorus compound type and the organo-metallic compound type. Typical EP / AW additives are shown in Table 2.2.1. Sulfurized fatty oils and sulfurized olefin are famous as the sulfur compound type EP / AW additives, which are used in the gear oil together with the phosphorus compound type EP / AW additives and also used in the cutting oil alone or together with the chlorine compound type EP / AW additives. As chlorine compound type EP / AW additives, chlorinated paraffin is mainly used and chlorinated fatty oils or chlorinated
2. Introduction

esters are also used in some cases. As for phosphorus compound type EP / AW additives, TCP and the amine phosphate are typically used in machine oils and gear oils, respectively. ZnDTP, which is often used in engine oil or hydraulic fluid, is famous as the organo-metallic compound type EP / AW additive. Molybdenum dialkyldithiocarbamate (MoDTC) also attracts attention, but rather as a friction modifier (FM) additive for engine oils.
### Table 2.2.1 Typical EP / AW additives

<table>
<thead>
<tr>
<th>Sulfur compound type</th>
<th>Sulfurized fatty oil</th>
<th>Sulfurized terpene</th>
<th>Sulfurized olefin</th>
<th>Sulfide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine compound type</td>
<td>Chlorinated paraffin</td>
<td>Chlorinated fatty oil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphorus compound type</td>
<td>Phosphite</td>
<td>Phosphate</td>
<td>Amine phosphate</td>
<td></td>
</tr>
<tr>
<td>Organo-metallic compound type</td>
<td>Dialkyldithiophosphate</td>
<td>Dialkyldithiocarbamate</td>
<td>Naphtanate</td>
<td></td>
</tr>
</tbody>
</table>

#### Sulfur compound type

- **Sulfurized fatty oil**
  - CH₃ — (CH₂)x — C — C — O — CH₂ — (CH₂)y — CH₃

- **Sulfurized terpene**
  - H₂C — C — CH — CH₂ — C — CH₃

- **Sulfurized olefin**
  - CH₃
  - CH₂ — C — S — S — CH₂ — C — CH₂
  - CH₃

#### Chlorine compound type

- **Chlorinated paraffin**
  - Cl
  - Cl
  - Cl

- **Chlorinated fatty oil**
  - Cl
  - Cl
  - Cl

#### Phosphorus compound type

- **Phosphite**
  - (C₆H₄O)₃P

- **Phosphate**
  - (CH₂ — O)₃P — O
  - (C₈H₁₆O)₃P — O

- **Amine phosphate**
  - [RO]₂P — OH — NH₂R’
  - [RO]₂P — S — R’O — P — OH — NH₂R’

#### Organo-metallic compound type

- **Dialkyldithiophosphate**
  - RO — P — S — Zn — S — OR
  - RO — P — S — Mo — O

- **Dialkyldithiocarbamate**
  - R — N — C — S — S — Zn — S — C — N — R
  - R — N — C — S — Mo — S — N — R

- **Naphtanate**
  - R — (CH₂)ᵥ — C — O — Pb — O — C — (CH₂)ᵦ — R
2.2.2 Studies of action mechanism

a) Sulfur compound type

As sulfur compound type EP / AW additives, sulfurized fatty oils and sulfurized olefin are used in practice, whereas alkyl or benzyl mono-sulfide and disulfide are often used for investigation for understanding the action mechanism of sulfur compound type EP / AW additives since they have simple chemical structures. The action mechanism of the sulfur compound type EP / AW additives was originally proposed by Davey et al. [4] and then refined by Forbes et al. [5], illustrated in Fig.2.2.1. In the proposed mechanism, a sulfur compound type EP / AW additive (disulfide or mono-sulfide) physically adsorbs on an iron surface first, and then reacts and form an iron sulfide film, which can reduce frictional wear and prevent seizure. The mono-sulfide directly forms the iron sulfide film after physisorption, whereas the disulfide forms the iron sulfide film through formation of an iron mercaptide. Anti-wear property under a mixed lubrication condition is dependent on the ease of physisorbing and decomposing of the S-S bond, that is the ease of formation of the iron mercaptide, while anti-seizure property under a boundary lubrication condition is dependent on the ease of forming the iron sulfide film. Davey and Forbes et al. said that the wear and seizure mechanism of sulfur compound type EP / AW additives such as mono-sulfide, disulfide, sulfoxide and sulfone, can be explained by their theory [6,7]. In other words, tribological performance of the sulfur compound type EP / AW additives is dependent on their chemical structure, where the ability of adsorption of their functional groups, the stability of the S-S bond and C-S bond dominate the performance. As Forbes [8] himself pointed out, however, it should be emphasized that there was no evidence that pure iron sulfides were the load-carrying layers and these layers were more likely to be complex mixtures of iron-sulfur, and possibly carbon-oxygen compounds. In fact, Dacre et al [9] mentioned that anti-wear property should be dependent on the physisorption speed from the viewpoint of iron mercaptide. Hiley [10] showed from their experiments using polysulfide that anti-wear and anti-seizure performance increase, as with higher multi-sulfide.

Next, as to the boundary lubrication films, some examples of analysis results for compounds formed on frictional surfaces by sulfur compound type EP / AW additives are listed in Table 2.2.2. As shown in the table, some results showed that the boundary lubrication film consists of only iron sulfide, however most results showed that it consists of iron sulfide, iron oxide and iron sulfate. Furthermore, some research showing the importance of oxygen for the additive action has been reported recently. Tomaru et al. [11] indicated that oxygen dissolved in the lubricant plays an important role for the formation of a moderate iron sulfide film. Moreover, Sakai et al. [12] showed results which suggest that the existence of a little amount of iron oxide is desirable so that the sulfur compound type EP / AW additive acts...
effectively. Therefore, it should be accepted that the boundary lubrication film consists of iron sulfide and iron oxide or a complex compound of sulfur-oxygen-iron, as Godfrey [13] expected from his experiments using pure sulfur.

\[ \text{FeS} + 2\text{R} \rightarrow \text{FM} \]  

\[ \text{FeS} + 2\text{R} \rightarrow \text{EP} \]

**Fig.2.2.1 Action mechanism of sulfur compound type EP / AW additives**

**Table 2.2.2 Boundary lubrication films formed by sulfur compound type EP / AW additives**

<table>
<thead>
<tr>
<th>Authors</th>
<th>EP / AW additives</th>
<th>Generated films on the frictional surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toyoguchi et al</td>
<td>DBDS</td>
<td>FeSO₄ (low load): Fe₃O₄, α-Fe₂O₃, Fe₃S₄ (high load)</td>
</tr>
<tr>
<td>Piggott et al</td>
<td>Diethyl trisulfide</td>
<td>FeS₂</td>
</tr>
<tr>
<td>Coy et al</td>
<td>DBDS, disulfide</td>
<td>FeS, Fe₃C, Fe₃O₄</td>
</tr>
<tr>
<td>Bird et al</td>
<td>DBDS</td>
<td>Iron sulfide, Iron oxide</td>
</tr>
<tr>
<td>Sakamoto et al</td>
<td>Sulfurized olefin</td>
<td>FeS, Fe₂S₄, FeO, Fe₃O₄</td>
</tr>
<tr>
<td>Sakai et al</td>
<td>DBDS</td>
<td>FeS, Fe₂S₄, FeO, Fe₃O₄</td>
</tr>
<tr>
<td>Mori et al</td>
<td>Di-t-dodecyl poly</td>
<td>α-Fe₂O₄</td>
</tr>
<tr>
<td></td>
<td>sulfide</td>
<td>Iron oxide, Iron sulfate, Iron sulfide</td>
</tr>
</tbody>
</table>

**b) Chlorine compound type**

It is considered that the action mechanism of chlorine compound type EP / AW additives means that they heat-decompose and form a boundary lubrication film of iron chloride (FeCl₂, FeCl₃, FeOCl) on a surface of iron, resulting in the prevention of wear and seizure owing to its stratified structure. This chemical reaction equation is described as follows [21-29]:

\[ RCl_x + Fe \rightarrow FeCl_2 + RCl_{x-2} \]
Tysoe et al revealed that in the EP regime, chlorinated hydrocarbons thermally decompose on iron forming a film comprising a layer of iron chloride which can also incorporate nano-size carbon particles in accordance with the above equations [23-29]. As chlorine compound type EP / AW additives show good lubricity or anti-seizure property in a tribologically severe condition at a wide range of temperature, they are used especially in the field of metal forming processes such as for cutting oils or for press forming oils. On the other hand, they are not used so much in other fields, since they have quite a high hydrolysis property and their boundary lubrication films are apt to hydrolyze themselves into iron hydroxide or iron oxide [31]. Moreover nowadays use of chlorine-containing chemicals is being restricted with regards to the influence on the human body.

**c) Phosphorus compound type**

Investigations of the action mechanism of the phosphorus compound type EP / AW additive are conducted mainly by using aryl or alkyl phosphate and phosphide. TCP is the most used among them. In an early research work, Beek et al [3] proposed the theory of “chemical polishing” by a low melting point eutectic mixture of Fe-Fe₃P. Although some reports [31] supported the chemical polishing theory by proving the formation of iron phosphide on a frictional surface, the majority considered that their experimental conditions were so severe that the iron phosphate film formed first on the surface changed to an iron phosphide film through an iron pyro-phosphate. Therefore, it is generally considered that the action mechanism of phosphorus compound type EP / AW additives does not agree with the chemical polishing theory. In Table 2.2.3, analysis results of boundary lubrication films formed on frictional surfaces by phosphorus compound type EP / AW additives are shown. As shown in the table, iron phosphate was detected in most of the reports, and thus “the iron phosphate theory” is generally accepted nowadays. In 1958, Donovan et al [32] surmised the iron phosphate theory from the static corrosion test for the first time. Then in 1965 Godfrey [33] supported the theory from tribotests using Fe₂P paste and analysis of a real frictional surface. This work was quite unique from the point of view that both study of classical tribological performance and surface analytical study were covered and both results were correlated. They showed that a boundary lubrication film formed on a steel surface by TCP was a mixture of FePO₄ and FePO₄-H₂O and no iron phosphide (Fe₂P) was detected. To prove the abovementioned results, they conducted tribotests using FePO₄-H₂O and Fe₂P pastes respectively and compared the friction coefficients and worn surfaces. As a result, they proved that friction and wear behavior with the FePO₄-H₂O paste lubricant were similar to
those with TCP, while those with the Fe2P paste lubricant were clearly different from the other two lubricants. The behavior of the friction coefficient with those lubricants is illustrated in Fig.2.2.2. Their results also indicated that formation of the iron phosphate film was due to thermal decomposition of the TCP. Barcraft [34] also showed at more or less the same time as Godfrey that iron phosphate film was formed as the boundary lubrication film by hydrolysis. As a result, the iron phosphate theory based on the following action mechanism that Barcraft advocated has been supported up to now:

1. Adsorption of the organic phosphate to the surface of iron
2. Formation of the organic acid phosphate by hydrolysis
3. Formation of the organic phosphate by reaction of organic acid phosphate and surface of iron
4. Generation of inorganic iron phosphate

This mechanism agrees with the results showing that the anti-seizure performance of a phosphorus compound type EP / AW additive depends on the chemical structure, that is, reactivity with the steel surface. There were some reports supporting hydrolysis for the decomposition mechanism. Gauthier et al [35] found iron phosphate and organic phosphorus compounds on a frictional surface after wear tests using TCP, as shown in Table 2.2.3. TCP decomposes to the phosphoric acid ester by frictional heat generation and then directly reacts with the steel surface, resulting in formation of the boundary lubrication film of the iron phosphate, which prevents wear-out. When the boundary lubrication film decreases in thickness and is less than a certain critical value, the organic phosphate generated by decomposition of TCP is polymerized and forms an organic polyphosphate compound, which also prevents wear-out. In conclusion, there are a lot of reports that support the iron phosphate theory as the action mechanism of the phosphorus compound type EP / AW additive. Both hydrolysis and thermal decomposition are possible for the process of the iron phosphate formation, when thinking about its behavior on a frictional surface. Although it is not clear which is predominant, both can occur. Friction polymer can also be generated at the same time. Moreover, a synergistic action of the oxidation iron as well as the sulfur compound type EP / AW additives can be predicted.
Table 2.2.3 Boundary lubrication films formed by phosphorus compound type EP / AW additives

<table>
<thead>
<tr>
<th>Authors</th>
<th>EP / AW additives</th>
<th>Generated films on the frictional surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nakamura et al [36]</td>
<td>Tributyl phosphide</td>
<td>( \text{Fe}_2\text{P}, \text{FeP}_2, \text{FePO}_4\cdot2\text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Godfrey [33]</td>
<td>TCP</td>
<td>( \text{FePO}_4, \text{FePO}_4\cdot2\text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Barcroft et al [34]</td>
<td>Triphenyl phosphate</td>
<td>Arylacid phosphate, Iron phosphate</td>
</tr>
<tr>
<td>Yamamoto et al [37]</td>
<td>TCP</td>
<td>( \text{Fe}_3\text{P} )</td>
</tr>
<tr>
<td>Montes [35]</td>
<td>TCP</td>
<td>( \text{Fe}_3(\text{PO}_4)_2, \text{FePO}_4, \text{C}_x\text{H}_y )</td>
</tr>
<tr>
<td>Yamamoto et al [38]</td>
<td>TCP, Trioctyl phosphate</td>
<td>( \text{FePO}_4, \text{FeO-Fe}_2\text{O}_4 )</td>
</tr>
<tr>
<td>Gauthier et al [35]</td>
<td>TCP</td>
<td>( \text{Fe}_3(\text{PO}_4)_2(\text{PO}_4\text{C}_x\text{H}_y)_n )</td>
</tr>
<tr>
<td>Mori et al [20]</td>
<td>Tri-oleyl Phosphite</td>
<td>Iron phosphate</td>
</tr>
</tbody>
</table>

Fig. 2.2.2 Frictional behavior of TCP, \( \text{FePO}_4\cdot2\text{H}_2\text{O} \) paste and \( \text{Fe}_2\text{P} \) paste [33]

**d) Organo-metallic compound type**

Zinc dialkyldithiophosphate (ZnDTP) is the most famous organometallic compound type EP / AW additive, and organic molybdenum compounds (molybdenum dialkyldithiophosphate and dialkyldithiocarbamate) are also often used as friction modifier (FM) additives for engine oil. A lot of research has been reported concerning the action mechanism of ZnDTP, including the thermal decomposition mechanism. Dorinson [39] and Rounds [40] advocated a theory that sulfur and phosphorus in ZnDTP directly react with a steel surface, resulting in the formation of a boundary lubrication film, which, however, is not
accepted by the majority. Recently many discussions have centered on the “frictional polymer theory”, derived originally from the thermal decomposition investigation of Feng [41], where the boundary lubrication film is formed through the formation of frictional polymer on a steel surface, as illustrated in Table 2.2.4 (A). Brazier et al [42] also estimated the polymer described in Table 2.2.4 (B). Then, Coy [43] and Bird et al [44] supported the formation of the polymer, but did not estimate its chemical structure. The analysis results of the film on the surface were often different from their estimations as shown in Table 2.2.4 (D). Later, Barcraft et al [45] brought the “double function theory” into the aforementioned frictional polymer theory by investigating the thermal decomposition mechanism by means of a “hot wire method” using three different types of ZnDTP. Their work revealed that ZnDTP gradually forms the polymer film by the thermal decomposition as temperature rises not only on steel surface but also on surfaces of other materials, as shown in the Fig.2.2.3. The work also revealed that the composition of the generated polymer film differs depending on the temperature, as listed in Table 2.2.5. The estimated chemical structure of the generated polymer in their report was that of over 600 degree centigrade. As a result, they understood that the polymer generated over 200°C can work to prevent wear. Moreover, when a lubrication condition becomes severe, it decomposes further by frictional heat, resulting in formation of iron sulfide and iron phosphate films. Therefore one of the most promising mechanisms of the ZnDTP action is the “frictional polymer theory”, where ZnDTP decomposes and form a polymer, which first works to prevent wear, and then further decomposes in the more severe condition to form the iron sulfide or iron phosphate, which works to prevent seizure. It is considered that anti-seizure or anti-wear performance of ZnDTP depends on its chemical structure, that is, the structure and length of the alkyl chains.

As far as the organic molybdenum compounds are concerned, there are two compounds that are actually used in industries, dithiophosphate and dithiocarbamate, as shown in Table 2.2.1. However there have been very few reports regarding the action mechanism of the molybdenum dithiophosphate. Martin et al [46] confirmed the formation of molybdenum disulfide (MoS$_2$) by using a new experimental strategic approach, that is, first elaborating selected chemisorbed surface films of the additive on a steel surface by using a classical chemisorption test in the lubricant and second, by running tribo tests on the previous film formed, but in an ultra high vacuum chamber. There are also some reports that proved the formation of MoS$_2$ in the case of MoDTC [47].
2. Introduction

Table 2.2.4 Change of estimated structure of the friction polymer formed by ZnDTP

<table>
<thead>
<tr>
<th>Estimated structure of the friction polymer</th>
<th>Estimated structure of the friction polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) (Zn:P:S=1:2:3) [41]</td>
<td>(B) (Zn:P:S=1:2:2) [42]</td>
</tr>
<tr>
<td>(C) (Zn:P:S=1:2:0.25) [45]</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Surface analysis of the frictional surface</th>
<th>Surface analysis of the frictional surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loeser et al [48]</td>
<td>Zn : P : S = 1 : 5 : 0.76</td>
</tr>
<tr>
<td>Farbes et al [49]</td>
<td>Zn : P : S = 1 : 1.9 : 0.31 (AW region)</td>
</tr>
<tr>
<td></td>
<td>1 : 1.9 : 2.0 (EP region)</td>
</tr>
<tr>
<td></td>
<td>1 : 2.1 : 5.1 (high load)</td>
</tr>
<tr>
<td>Bird et al [44]</td>
<td>Zn : P : S = 1 : 1.3 : 0.38</td>
</tr>
</tbody>
</table>

Fig. 2.2.3 The polymer formation rate of ZnDTP [45]
(V: The polymer film formation rate, μm/s)
2.3 Surface analytical studies in tribology

The beneficial contribution of chemical analysis in the progress of chemistry, which is one of the natural sciences, is great. At the same time, surface analysis plays an important role in the development of surface chemistry.

The surface analysis can be divided into chemical analysis and apparatus-based analysis, and apparatus-based analysis can be further classified into (1) spectral analysis, (2) electrochemical analysis, (3) thermal analysis, and (4) separate analysis. Many surface analysis methods belong mainly to spectral analysis and in accordance with the requirement for a higher level and continuous analysis, rapid progress based on the theoretical and technological developments in analytical chemistry has occurred in recent years.

Plans directed at an increase in performance of materials and the resolution of apparatus in studies and developments in such fields as chemistry, semiconductors, and metalworking made it necessary to perform the characterization of solid surfaces. The accomplishment of this task requires the application of surface analysis methods that would be sensitive to information about solid surfaces and have appropriate spatial resolution in addition to apparatus-based analytical methods. In the field of tribology, surface analysis is extremely effective in the clarification of tribochemical reactions occurring on frictional surfaces. Indeed, many surface analysis methods were used to characterize the boundary lubrication films in the studies mentioned in the previous section (2.2).

Methods of surface analysis that are most widely used in the tribology field are: Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and secondary ion mass spectroscopy (SIMS). The SIMS is subdivided into dynamic SIMS (D-SIMS), that has been used for a long time and is based on large incident ion currents, and static SIMS (S-SIMS), that is based on small incident ion currents. In addition to the above four analytical methods, the electron probe microanalysis (EPMA), the scanning probe microscopy (SPM), the Fourier transform infrared spectroscopy (FT-IR), and the Raman spectroscopy (Raman)
are often used for studies in tribology.

2.3.1 Outline of surface analysis methods in tribology

a) Excitation quanta and detection quanta

Excitation quanta and detection quanta for main surface analysis methods are shown in Table 2.3.1. The specific feature of surface analysis methods is that information collected by the analysis is limited to the solid surface under consideration. In cases where excitation quanta and detection quanta are large and detection quanta are electrons or ions, in a solid body, a short mean free path of inelastic scattering takes place. In cases where detection quanta are photons, information obtained covers a region in the order of a micrometer in depth because the interactions of electrons and ions with a solid body are usually comparatively weak. However, the FT-IR can be realized as a total reflection absorption method by using the critical angle of total reflection and a high-sensitivity reflection method using light polarization; therefore, it can be used as a sensitive surface analysis technique that allows to obtain information about monomolecular layers. The SPM established as an analytical method in recent years allows the detecting of phenomena (tunnel current, intermolecular force, and friction force) generated in sliding contact of atomic order between solids by using a probe with a tip about 10 nm in radius.

<table>
<thead>
<tr>
<th>Excitation quantum</th>
<th>Electron</th>
<th>Ion</th>
<th>Photon</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron</td>
<td>AES</td>
<td></td>
<td>EPMA</td>
<td></td>
</tr>
<tr>
<td>Ion</td>
<td>SIMS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Photon</td>
<td>XPS</td>
<td></td>
<td>IR, Raman</td>
<td>SPM</td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

b) Obtained information

Information obtained by the surface analysis can be divided into (1) information about composition, (2) information about morphology, (3) information about structure, and (4) information about electronic state. The relationship between obtained information and main surface analysis methods is shown in Fig.2.3.1 and a review of peculiarities of respective analytical methods is given in Table 2.3.2. As is evident from the figure and table, XPS is a method that allows analysis of the electronic state and the composition simultaneously. Thus, as the electronic state is closely related to the structure, in some cases the structure can be estimated by analogy with the electronic state. The reason that XPS is an effective analytical
2. Introduction

tool in tribology is due to the large extent of information that can be obtained. The S-SIMS to a certain extent allows determination of the structure of a cross-section of a sputtered layer by the mass analysis of ion fragments.

![Diagram of surface analysis methods](image)

**Fig.2.3.1 Main surface analysis methods in tribology and obtainable information**

<table>
<thead>
<tr>
<th>Analytical method</th>
<th>Depth of analysis</th>
<th>Width of analysis</th>
<th>Analysis of distribution</th>
<th>Analysis in direction of depth</th>
<th>Composition</th>
<th>Morphology</th>
<th>Structure</th>
<th>Electronic state</th>
<th>Quantitative accuracy</th>
<th>Limits of detection</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>XPS</strong></td>
<td>&lt; Several nm</td>
<td>Common: 1- Several mm Micro: 0.1um-</td>
<td>-</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>-</td>
<td>++</td>
<td>&lt; 10%</td>
<td>0.02 - Several atom</td>
</tr>
<tr>
<td><strong>AES</strong></td>
<td>&lt; several nm</td>
<td>Common: 1- 500 µm Micro: 0.02mm-</td>
<td>+++</td>
<td>+++</td>
<td>++</td>
<td>++</td>
<td>(SEM)</td>
<td>-</td>
<td>-</td>
<td>++</td>
</tr>
<tr>
<td><strong>D-SIMS</strong></td>
<td>&lt; 10nm</td>
<td>Common: 0.1- 1mm Micro: 0.1µm-</td>
<td>++</td>
<td>+++</td>
<td>++</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>Several</td>
<td>+++</td>
</tr>
<tr>
<td><strong>S-SIMS</strong></td>
<td>&lt; 0.1 nm</td>
<td>Common: 0.1- 1mm Micro: 1µm-</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>Several</td>
<td>+++</td>
</tr>
<tr>
<td><strong>EPMA</strong></td>
<td>1 µm&lt;</td>
<td>Common: 2- 500mm Micro: 0.5µm-</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>(SEM)</td>
<td>-</td>
<td>-</td>
<td>+++</td>
</tr>
<tr>
<td><strong>Raman</strong></td>
<td>Several nm &lt;</td>
<td>Common: 1- 100µm Micro: 0.5µm-</td>
<td>+</td>
<td>++</td>
<td>-</td>
<td>-</td>
<td>++</td>
<td>-</td>
<td>Several</td>
<td>++</td>
</tr>
<tr>
<td><strong>IR</strong></td>
<td>Several nm &lt;</td>
<td>Common: 0.1- Several mm Micro: 10µm-</td>
<td>+</td>
<td>++</td>
<td>-</td>
<td>-</td>
<td>++</td>
<td>-</td>
<td>Several</td>
<td>++</td>
</tr>
</tbody>
</table>

In addition, the surface analysis methods allow the determination of the in-plane distribution (mapping) and the distribution in depth (depth profiling) at the appropriate spatial resolution in relation to the above four types of information.
The determination of the in-plane distribution can be accomplished by different analytical methods: (1) the excitation electron scanning method (scanning type method), (2) the specimen displacement method, and (3) the method making use of a lens and a detector with position resolution (projection type). The AES is used in this case (1). The AES using a field radiation type electron gun has an in-plane resolution of about 20 nm. The EPMA can be used in case (1) and case (2) depending on the measured surface area, but since X-ray is used for the electron detection, its in-plane resolution is of submicron order. The FT-IR and the Raman are used in case (2) and their in-plane resolution is theoretically about a half of the wavelength used, amounting to about a few micrometers. The XPS, the S-SIMS and the D-SIMS can be used in cases (1), (2), and (3), depending on the manufacturer of the equipment used. When the XPS is of the projection type, its in-plane resolution is a few micrometers and when it is of the scanning type, its in-plane resolution is 10 um. The in-plane resolution of the S-SIMS is of the micrometer order and that of the D-SIMS is of the submicron order. In any case, the resolution of a submicron is normally narrow enough for the analysis of the frictional surface since the width of a wear scar or a scratch track is normally more than a submicron.

The in-depth analyses in which the depth of detection is taken into consideration are linear and performed as follows: (1) a specimen produced by the ion sputtering is cut off, (2) the angle of radiation of excited quanta or the angle of taking detected quanta is changed, and (3) cross-sectional specimens are prepared. In case (1), the AES and the D-SIMS are used. These methods allow the in-depth analysis to be performed up to about a few micrometers. The in-depth resolution determined by dividing the width of interface by the thickness of the sputtered layer is about a few percent. The XPS is used in cases (1) and (2), but when used in case (1), the surface area is greater than in the AES, but its in-depth resolution is lower. In addition, if a sputtered surface can be chemically modified, the chemical state in depth direction cannot be discussed. The FT-IR and the Raman are used in cases (2) and (3), but in case (2), their in-depth resolution is not very high and the depth of detection varies significantly from some nanometers to some micrometers, depending on measurement conditions. The EPMA is used in case (3) and its in-depth resolution is of the micrometer order. Moreover, this method allows the performance of analysis to a depth of up to a few millimeters.

c) Sensitivity, accuracy, and precision

In surface analysis, sensitivity, accuracy and precision are very important factors. Here sensitivity means extent of detectable concentration. Both accuracy and precision relate to error of measurement, where accuracy means extent of accidental error, whereas precision means extent of systematic error.
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Now, sensitivity is an important factor in selecting an analytical method. When analyzing the in-depth distribution of impurities in a solid body, the SIMS allows the detection of elements even at concentrations of the ppb order. This is possible because of a high peak-to-background ratio (P/B ratio). Also, a preliminary concentration treatment of specimens is not necessary, which indicates directly at the perfection of the instrumental analysis. However, the yield of secondary ions can be easily changed by matrix components; therefore, the quantitative accuracy and the precision are within a few tens of percents.

The analytical accuracy is determined by the stability of the equipment, such as a source of excitation, a spectrometer (including mass-spectrometer), and a detector, and the efficiency of generation of detected quanta and the stability of physical and chemical phenomena used in measurements. In particular, the stability of a source of excitation plays an important role in measurements that take a long time. With recent technological progress, the in-depth analysis becomes a simpler task even in the case of using a field radiation type electron source. For example, a relative quantitative error in the XPS and the AES in the case of using a standard specimen (Au-Cu alloy) is about 2-6% [50] and about 3-10% [51], respectively.

The precision of instrumental analyses including surface analysis is generally somewhat inferior, but the preparation of standard samples and modifications of equipment by using standard samples promote a gradual improvement in this direction. In the case of applying the relative sensitivity coefficient to equipment when using actual specimens, a relative error amounts to 5-20% [51]. However in the case of quantitative analysis on a frictional surface, the morphology and homogeneity of the surface should be carefully taken into account for the accuracy of the analysis.

2.3.2 In-situ analysis in tribology

Since most of the surface analysis methods require ultrahigh vacuum (UHV) conditions, even now the analysis is performed mainly on test specimens after their testing. However, it cannot necessarily be said that the surface under friction is characterized by this method. In other words, tribo reaction ongoing under friction cannot be observed by this method. Therefore, in recent years, in the field of tribology, the in-situ analysis has started to be used to obtain basic information about mechanisms of reactions between additives and test specimens on sliding surfaces more directly. Martin et al. investigate the action mechanism of MoS$_2$ by combining XPS, AES and a tribometer [52]. This technique is available only for solid lubricants. On the other hand, for liquid lubricants like EP, FM, AW additives, methods for in-situ analyzing of boundary lubrication films by using the FT-IR micro reflection method have been reported [53, 54].
2.4 Aim and organization of the thesis

Despite many empirical studies and the progress of surface analytical tools in the tribology field, the boundary lubrication films have generally been poorly characterized and thus the mechanism of film growth and removal (wear) is largely unknown. This is particularly true for metal-free additives, which are increasingly being used as an environmentally friendlier alternative to heavy metal containing ones.

The focus of this work is to investigate the chemical composition of tribo-films formed on a steel surface by commercially available metal-free oil additives under a variety of tribo-conditions, and thus to understand the chemical mechanism more deeply. To achieve these objectives, the tribological performances were investigated with a simple pin-on-disk tribotesting, while the generated tribo-films were characterized with small area and imaging XPS, which is considered to be one of the most promising approaches to understand additive action as mentioned above, and then both informations were correlated in this work. Moreover, the additives and the steel surface both before and after the reaction were also characterized with XPS and compared with each other in order to identify the chemical change of additives and steel surfaces due to tribo-reaction. Furthermore, the tribo-films were compared with adsorbed film of the additives on various steel surfaces, paying special attention to the oxidation state of the surface.

As to the organization of this dissertation, the detail of the experimental procedures and their basic theories will be described in chapter 3. The characterization of the pure additives and various conditions of the steel surfaces will be described in chapter 4, and their tribological behaviors will be described in chapter 5. The characterization of the adsorbed films will be described in chapter 6 and their tribo-films will be characterized in chapter 7. Then, in chapter 8 the film formation mechanism and lubrication mechanism of the boundary lubrication films will be discussed. Chapter 9 will provide a brief summary of findings.
2. Introduction

Table 2.4.1 The organization of the thesis

<table>
<thead>
<tr>
<th>Tribological information</th>
<th>Surface analytical information</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Tribological results (Chapter 5)</td>
<td>correlate</td>
</tr>
<tr>
<td>- Boundary lubrication film characterization (Chapter 7)</td>
<td></td>
</tr>
<tr>
<td>- Adsorbed film characterization (Chapter 6)</td>
<td>compare</td>
</tr>
<tr>
<td>- Pure additive characterization (Chapter 4)</td>
<td></td>
</tr>
<tr>
<td>- Disk surface characterization (Chapter 4)</td>
<td></td>
</tr>
</tbody>
</table>

References

2. Introduction

2. Introduction


3. Experimental

3.1 Base oil and additives

3.1.1 Base oil

Commercial pure poly-alpha-olefin (PAO) with viscosity of 31 cSt at 40 °C shown in Fig.3.1.1 was used without further purification or treatments as the base oil of lubricants for tribological tests. PAO is widely used as base oil of lubricant since it is chemically stable and thus is hardly decomposed even at high temperature. Alpha olefins are straight chain hydrocarbons with a reactive olefinic tail [1]. The monomers produced commercially by fractionation of oligomerised ethylene are polymerized to yield branched chain hydrocarbons. These hydrocarbons have long chain alkyl group on alternate carbons with a polymer chain length dependent on the number of monomer units incorporated. Viscosity increases and volatility decreases with polymer chain length. The length of the alkyl branches depends on the chain length of the original alphaolefin. Viscosity index improves and pour point increases with increasing chain length of the alkyl branches. The best compromise is obtained by starting with 1-decene. Polydecenes form the largest segment of the polyalphaolefin market.

\[
R_1 \quad (\text{CH} - \text{CH}_2 \text{)}_n
\]

Fig.3.1.1 Constitutional formula of Polyalphaolefin

3.1.2 Additives [2]

Commercially available four typical lubricant additives, which are either extreme pressure (EP) additives or anti-wear (AW) additives, were used in this work to understand action mechanism of lubricant additives on boundary lubrication. They were mono/dialkylphosphoric acid neutralized with dialkylaminel amine (amine phosphate), diisopropyl dithiophosphoryl-alkylpropionate (dithiophosphate), nonylated triphenyl phosphorothionate, butylated triphenyl phosphorothionate, and Zinc dialkyldithiophosphate (ZnDTP) and all of them were supplied by Ciba Specialty Chemical Ltd. (Basel, Switzerland). The additives used in this work were the chromatographically purified main components of
3. Experimental

the technical products.

Physical and chemical properties of the additives are listed in Table 3.1.1. All the information in the table was provided by the supplier. As listed in the table, all the additives are viscous liquid at room temperature and have slight yellow color. All of them are easily soluble in PAO.

Constitutional formulas of the additives are shown in Fig. 3.1.2. As shown in the figure, these commercial additives have rather complex structures, however their functional groups are simple and similar to each other as shown in Fig. 3.1.3. Amine phosphate has a phosphate with one or two free acid, -OH, as a functional group, and two or one alkyl groups. Since it is acid type phosphate, it is neutralized with dialkylamine. Nonylated triphenyl phosphorothionate and butylated triphenyl phosphorothionate have the monothiophosphate as a functional group. The hydrocarbon groups connected to the oxygen atom of the thiophosphate are phenyl, nonylphenyl and butylphenyl, respectively. Dithiophosphate has dithionated phosphate as a functional group and its alkyl chain connected to the oxygen atom is isopropyl and its alkyl chain connected to the sulfur atom is alkylpropionate. ZnDTP has two dithiophosphate groups and both of which are connected to the zinc atom as illustrated in the figure. Its alkyl chains connected to the oxygen atom of the dithiophosphate are secondary alkyl groups. It is believed that in a boundary lubrication, functional groups of EP or AW additives play the most important role for formation of boundary lubrication films. Thus, although their shape and length of alkyl chain are not same, it is thought that one can discuss the difference of tribo-film formation or tribological performances with these four additives.
### Table 3.1.1 Physical and chemical information of the additives

<table>
<thead>
<tr>
<th></th>
<th>Amine phosphate</th>
<th>Dithiophosphate</th>
<th>Nonylated triphenyl phosphorothionate</th>
<th>Butylated triphenyl phosphorothionate</th>
<th>ZnDTP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Element</strong></td>
<td>C</td>
<td>H</td>
<td>P</td>
<td>S</td>
<td>Zn</td>
</tr>
<tr>
<td></td>
<td>70.84</td>
<td>42.49</td>
<td>75.44</td>
<td>47.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.97</td>
<td>7.36</td>
<td>9.62</td>
<td>8.23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.69</td>
<td>10</td>
<td>4.25</td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>20.84</td>
<td>4.47</td>
<td>8.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.46</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>9.49</td>
</tr>
<tr>
<td><strong>Appearance</strong></td>
<td>clear, viscous, colorless to yellow liquid</td>
<td>clear, slightly yellow to yellow liquid</td>
<td>clear, highly, viscous, slightly yellow, liquid</td>
<td>Pale yellow oil</td>
<td>clear, highly, viscous, slightly yellow, liquid</td>
</tr>
<tr>
<td><strong>Refractive Index nD20</strong></td>
<td>1.450-1.470</td>
<td>1.488-1.495</td>
<td>1.52-1.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Density at 20deg</strong></td>
<td>g/ml</td>
<td>0.89-0.93</td>
<td>1.09-1.12</td>
<td>0.99-1.03</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>max 0.4, typical 0.3</td>
<td>max 0.2, typical 0.1</td>
<td>max 0.1</td>
<td></td>
</tr>
<tr>
<td><strong>Viscosity at 40deg</strong></td>
<td>mPa.s</td>
<td>1800-2600mPa.s, typical 2200</td>
<td>4-6.5 mm2/s, typical 5.0</td>
<td>2500-3500mm2/s, Typical 3000</td>
<td>56mm2/s</td>
</tr>
<tr>
<td><strong>Water content</strong></td>
<td>%</td>
<td>max 0.4, typical 0.3</td>
<td>max 0.2, typical 0.1</td>
<td>max 0.1</td>
<td></td>
</tr>
<tr>
<td><strong>Halogens</strong></td>
<td>ppm</td>
<td>max 25, 15</td>
<td>max 80, 50</td>
<td>max 250; typical 100</td>
<td></td>
</tr>
<tr>
<td><strong>Solubility in</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mineral oil</td>
<td>%</td>
<td>3</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>2</td>
</tr>
<tr>
<td>PAO</td>
<td></td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>1</td>
</tr>
<tr>
<td>rape seed oil water</td>
<td>%</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
</tr>
<tr>
<td>water</td>
<td>%</td>
<td>&lt;0.01 at 20deg</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td><strong>Total base number</strong></td>
<td>mg KOH/g</td>
<td>92-100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Pourpoint</strong></td>
<td>%</td>
<td>&lt;0.0, -6deg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Vapour pressure at 25deg</strong></td>
<td>Pa</td>
<td>9.00E-05</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td><strong>Melting point</strong></td>
<td></td>
<td>0-10</td>
<td>&lt;0</td>
<td>&lt;0</td>
<td>&lt;0</td>
</tr>
<tr>
<td><strong>Boiling point</strong></td>
<td></td>
<td>300</td>
<td>180</td>
<td>&gt;300</td>
<td></td>
</tr>
<tr>
<td><strong>Flashpoint DIN 51758</strong></td>
<td>deg</td>
<td>135</td>
<td>114</td>
<td>108</td>
<td>162</td>
</tr>
<tr>
<td><strong>Ignition DIN 51794</strong></td>
<td>deg</td>
<td>310</td>
<td>280</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ph-value at 1% in water</strong></td>
<td>deg</td>
<td>4.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Thermal decomposition</strong></td>
<td>deg</td>
<td>350</td>
<td>&gt;250</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3. Experimental

Fig. 3.1.2 Constitutional formula of the additives

Fig. 3.1.3 Functional group of the additives
3. Experimental

3.2 Tribological Tests

3.2.1 Theory [3]

a) The laws of friction

Friction is the resistance to motion which is experienced whenever one solid body slides over another. The resistive force, which is parallel to the direction of motion is called the 'friction force'. If solid bodies are loaded together and a tangential force is applied, then the value of the tangential force which is required to initiate sliding is the 'static friction force'. The tangential force required to maintain sliding is the 'kinetic (or dynamic) friction force'. Kinetic friction is generally lower than static friction.

It has been found experimentally that there are two basic laws of friction, which are obeyed over a wide range of conditions. There are, however, a number of notable exceptions. It should be stressed at this point that the two laws of friction are empirical in nature and no basic physical principles are violated in those cases where the laws of friction are not obeyed. The first law states that friction is independent of the apparent area of contact between the contacting bodies, and second, that the friction force is proportional to the normal load between the bodies. Thus a brick can be slid as easily on its side as on its end and if the load between two sliding bodies is doubled then the friction force is doubled. These laws are often referred to as 'Amontons laws' after the French engineer Amontons who presented them in 1699 [4]. Coulomb (1785) introduced a third law, that kinetic friction is nearly independent of the speed of sliding, but this law has a smaller range of applicability than the first two.

The second law of friction enables ones to define a coefficient of friction. The law states that the friction force $F$ is proportional to the normal load $W$. That is

$$F \propto W$$

Therefore

$$F = \mu W$$

where $\mu$ is a constant known as the 'coefficient of friction'. It must be stressed that $\mu$ is a constant only for a given pair of sliding materials under a given set of ambient conditions and varies for different materials and conditions.

Nearly all surfaces are rough on a microscopic scale and true contact is obtained over a small fraction of the apparent contact area. Furthermore the real area of contact is independent of the apparent area of contact. Thus the first law of friction is explained since friction is related to the real area of contact.

When two bodies are rubbed together, some form of interaction takes place at the contacting surfaces resulting in a resistance to relative motion. Most friction theories assume
that the resistive force per unit area of contact is a constant. Thus
\[ F = AS \] (3.2.3)
where \( F \) is the friction force, \( A \) is the real area of contact, \( S \) is the constant force per unit area, resisting relative motion, that is, the specific friction force.
If the assumption that \( S \) is a constant can be justified, then the value \( A \) will be important. For a single spherical contact or an array of similar spheres all at the same height under loading conditions which produce elastic deformation only
\[ A \propto W^{2/3} \] (3.2.4)
For a surface on which the contact is wholly plastic, or for a surface whose asperity height distribution can be represented by an exponential function, or for a surface whose asperity height distribution is gaussian, it can be written with sufficient accuracy
\[ A \propto W \] (3.2.5)
Many practical surfaces have an asperity height distribution that is close to gaussian.

There are only three mechanisms which can cause appreciable loss of energy, that is, friction at the interacting surfaces. They are adhesion, plowing on a softer surface with a harder asperity, and energy loss due to elastic deformation (elastic hysteresis). The elastic hysteresis effect of steel pairs is almost negligible and its plowing effect is also small enough to neglect compared to the adhesion.

When metal surfaces are loaded against each other they make contact only at the tips of the asperities. Because the real contact area is small, the pressure over the contacting asperities is assumed high enough to cause them to deform plastically. This plastic flow of the contacts causes an increase in the area of contact until the real area of contact is just sufficient to support the load, Fig3.2.1. Under these conditions, for an ideal elastic-plastic material [5]
\[ Ap_o = W \] (3.2.6)
where \( A \) is the real area of contact, \( p_o \) is the yield pressure of the metal and, \( W \) is the normal load. It can be written
\[ F = As = Ws/p_o \] (3.2.7)
and
\[ \mu = F/W = s/ p_o \] (3.2.8)
It is reasonable to take \( s \) equal to \( s_o \) the critical shear stress, and both \( p_o \) and \( s_o \) must refer to the softer of the two metals.
Now
\[ \mu = s_o / p_o \] (3.2.9)
It was assumed that $A$ was defined by the yield pressure of the softer metal $p_o$ and the normal load $W$. This is approximately true for static contact but in the case of friction, where a tangential force is also applied, yielding must take place as a result of the combined normal and shear stresses. Thus, the real contact area in the case of friction becomes considerably larger than static contact. This phenomenon is called ‘junction growth’ and described as follows [6].

$$A^2 = \left(\frac{W}{p_o}\right)^2 + \alpha \left(\frac{F}{p_o}\right)^2$$ (3.2.10)

$W/p_o$ is the area of contact derived from the simple theory in which only the effect of normal load is considered, and the additional term $\alpha (F/p_o)^2$ represents the increase caused by the shear or friction force.

When some kind of lubricant is applied on rubbing surfaces, there must be a thin lubrication film with critical shear stress $s_f$ at the junction. It can be also assumed that $s_f = cs_o$ where $s_o$ is the critical shear stress for the metal and $c$ is less than unity. While $F$ and $A$, have values such that $F/A < s_f$, then junction growth will proceed as described previously for uncontaminated metals. However, when $F/A = s_f$ then the lubrication film will shear, junction growth will end, and gross sliding will occur [5]. Therefore

$$s_f/p = c/\left[\alpha (1 - c^2)\right]^{1/2}$$ (3.2.11)

The coefficient of friction $\mu = (F/W) = (s_fA/pA)$. Therefore

$$\mu = c/\left[\alpha (1 - c^2)\right]^{1/2}$$ (3.2.12)

As $c$ tends to 1 then $\mu$ tends to infinity in agreement with results obtained for unlubricated metals. Thus a small amount of weakening at the interface by lubrication produces a drastic reduction in $\mu$.

**b) Lubrication mechanism** [7]

Oil is often used as a lubricant to reduce friction force. When lubricated by an oil type
3. Experimental

lubricant, its lubrication mechanism is categorized into three regions depending on thickness of the lubricating film. Fig. 3.2.2, which is well known as the Stribeck curve [8], illustrates the relationship between friction coefficient and normalized lubricating film thickness in case of liquid lubrication. The three regions are called hydrodynamic lubrication region, mixed lubrication region, and boundary lubrication region.

![Stribeck curve](image)

**Hydrodynamic lubrication**

Where lubricating film thickness is high enough to separate two sliding surfaces, this lubrication region is called hydrodynamic lubrication region since friction force between the surfaces is determined by hydrodynamic theory. Its friction coefficient is calculated by Reynolds’ Equation where the friction coefficient increases as pressure (load) increases or viscosity increases or sliding velocity increases.

**Mixed lubrication**

If the load applied between the two surfaces increases, or the sliding speed reduced, the oil wedge separating the bearing surfaces will eventually diminish in volume until the film thickness becomes the same order as the height of the larger surface asperities. Any further reduction in film thickness will cause surface asperities to penetrate and disturb the laminar conditions of flow in the lubricant. This state is often called thin film or mixed lubrication to describe a condition where the two surfaces are separated from each other, partly by
hydrodynamic forces and partly by thin layers of lubricant adhering to the surface contours. It is an indeterminate state in which the strict laws of hydrodynamic lubrication are no longer fully applicable.

**Boundary lubrication**

A further increase in bearing load or reduction of sliding speed causes the bulk of the lubricant film to be squeezed out until a film of only a few molecular-layers thick is left between the sliding surfaces. This state of lubrication was first systematically investigated by Hardy [9], who coined the term boundary lubrication to describe the surface frictional behavior of certain organic compounds derived from petroleum products of natural origin such as paraffins, alcohols and fatty acids. Today the term boundary lubricant is frequently extended to cover other types of lubricants, e.g. surface films, solid mineral lubricants, which do not function hydrodynamically. The transition from hydrodynamic lubrication through mixed lubrication to boundary lubrication is a gradual one and mixed states of lubrication probably exist over a wide range of rubbing and sliding conditions found in engineering practice.

True boundary lubrication can, strictly speaking, only exist when sliding speeds are so low and contact pressures so high that the existence of load-supporting hydrodynamic wedges of the lubricant are physically impossible. Mixed and boundary states of lubrication are always present during the running-in process of lubricated moving surfaces of new machinery. Running-in is, in effect, a carefully controlled process of deliberately induced wear in which the peaks of surface roughness continually penetrate the normal lubricant film until it is smoothed away. Some remarkable aspects of frictional behavior under boundary lubrication condition can be summarized very briefly as follows [2]:

1. Boundary lubrication depends on the nature of the under-lying layer of metal as well as on the properties of the lubricant.
2. Lubricant layers only a few molecules thick can provide effective boundary lubrication.
3. The bulk viscosity of a fluid lubricant appears to have no significance in its boundary frictional behavior.
4. The frictional force is almost independent of the sliding velocity, provided the motion is smooth and the sliding velocity is insufficient to cause a rise in bulk temperature.
5. Friction and surface damage depend on the chemical composition of the lubricant and/or the products of reaction between the lubricant and the solid surface.
6. The frictional behavior may be influenced by surface roughness, temperature, and contaminants.
c) Extreme pressure lubricants

Extreme pressure lubricants are a class of lubricants to which certain active chemicals or chemical groups have been added. These additions are termed E.P. additive and the active chemicals which are in general use are chlorine (chlorinated esters, etc.), sulphur (sulphurized fats and oils, etc.) and phosphorus (tricresyl phosphate, etc.). Through chemical reactions with the metal surfaces these additives form solid surface films of metallic chlorides, metallic sulfur compound and metallic phosphorus compound. These boundary films have relatively low shear strength so that rubbing between the interacting surfaces occurs in the additive film and thus protects the underlying metal. The melting-points of the E.P. layers are high so they will remain attached to the base metal even under extreme conditions of temperature.

d) Friction measurement

Any apparatus for measuring friction must be capable of supplying relative motion between two specimens, of applying a measurable normal load and of measuring the tangential resistance to motion. There are a large number of methods available and the final choice will depend largely on the exact conditions of rubbing contact under investigation.

Where continuous friction measurement is required over a period of time then a complicated approach must be used. Here one specimen, usually a disc or a cylinder, is driven continuously, while a second specimen, nominally stationary, is loaded against it. Commonly used combinations is pin-on-disc or -cylinder. The arrangement of pin on disk type tribotest is shown in Fig. 3.2.3.

![Fig. 3.2.3 Arrangement of pin on disk tribometer](image)

The loading of the stationary specimen can be by simple deadweight or, if the experimental conditions demand it, by some more complicated method such as hydrostatic or magnetic loading. The measurement of the friction force is usually accomplished by
mounting the nominally stationary specimen so that a very small tangential movement, proportional to the frictional force, occurs. This small movement is measured and recorded. For a precise measurement of friction coefficient, great care must be taken in ensuring cleanliness during these tests, since small amounts of contamination can significantly affect the measured friction, and this is why so much emphasis is placed on controlled atmosphere tests.

3.2.2 Apparatus

The tribological measurements were performed with a pin on disk type tribometer as illustrated in Fig. 3.2.4, where its contact geometry was flat on flat (chip-on-disk) type. The size of the chip was 3.5mm in width, 3.5mm in length and 1.0mm in height, while the size of the disk was 23.0mm in diameter and 5.0mm in height. The tribo pair was made of the same steel material (52100) and their surfaces were mechanically polished to mirror-like finish. The detail conditions of the tribo pair will be mentioned later. In addition, the tribo pair was immersed in lubricant during the tribotest in order to minimize oxidation of the tribo film formed on the rubbed surface and also to cool the sliding surfaces down to room temperature with the lubricant.

![Fig.3.2.4 A schematic diagram of tribometers](image)

Pin on disk type tribometers have been widely used as a simple tribometer in many tribological investigations. In most cases their contact geometry were ball on flat type, since scattering of the data due to unevenness of the surface of the tribo-pair can be minimized by using commercial bearing balls whose surface have mirror surface. Also high contact pressure can be obtained with the ball on disk type tribometer, which is suitable for investigation of wear of materials or evaluation of tribological performance of lubricants under boundary lubrication. However, a contact area obtained with ball on disk tribometer is relatively small, and its contact pressure is considered to be uneven as described in
Fig. 3.2.5(A), which may cause inhomogeneous tribo films. Therefore, when a surface rubbed with a ball is analyzed with XPS, information obtained is apt to be the average of inhomogeneous tribo-film in the analysis area, which may make one difficult to relate the analytical results with the tribological conditions of the experiment.

On the other hand, as described in Fig 3.2.5 (B), the flat on flat type tribometer gives relatively homogeneous contact pressure so that the tribo film on the rubbed surface can be regarded also homogeneous. Therefore one can relate the obtained results with the tribological conditions. To obtain homogeneous contact pressure with flat on flat tribometer, however, the roughness control of the surface is very important.

Two tribometers, made by Swiss Center of Electronics and Microtechnologies, Inc. (CSEM) and made by Center for Tribology Inc. (CETR), are used to ensure that tribological results are independent from formation of apparatus. They make the same relative movement between the chip and the disk, although these two tribometers have completely different configurations and functions.

**a) CSEM tribometer**

The appearance of CSEM tribometer is shown in Fig. 3.2.6. A flat shaped indenter, a chip, is loaded on to a disk sample with a precisely known weight. A chip holder is mounted on a stiff lever, designed as a frictionless force transducer. As the disk is rotating, resulting frictional forces acting between the chip holder and the disk are measured by very small...
deflections of the lever. The CSEM tribometer facilitates the determination and study of friction behavior of steel surfaces with varying time, contact pressure, velocity, lubricants, and so on. The frictional forces were simultaneously recorded to an analog recorder.

Fig. 3.2.6 CSEM tribometer [10]

1) Eccentric, 2,3) Control levels, 4,5) Counterweights, 6) Cantilever, 7) Locking screw for the pin holder, 8) Pin holder, 9) Gas supply line, 10) Friction radius adjustment, 11) Friction radius locking lever

b) CETR tribometer

The appearance of CETR tribometer is shown in Fig. 3.2.7. A flat shaped indenter, a chip, is loaded on to a disk sample with vertical linear motion system. The load sensor provides feedback to the closed-loop vertical motion control, which ensures constant load during testing. As the chip holder is rotating, resulting frictional forces acting between the chip holder and the disk are measured by very small deflections of a torque meter. The CETR tribometer facilitates the determination and study of friction behavior of steel surfaces with varying time, contact pressure, velocity, temperature, lubricants, and so on. The CETR tribometer is fully controlled by a personal computer and its digital data can be stored in the computer.
3. Experimental

![Image of CETR tribometer](image)

**Fig. 3.2.7 CETR tribometer [11]**

1) Vertical liner motion system, 2) Pin holder, 3) Pin :chip holder, 4) Disk, 5) Disk holder :lubricant cup

**c) High temperature tribometer**

CETR tribometer was used for tribotests at high temperature. The lower specimen holder of CETR tribometer was modified, where whole lubricant/disk holder is heated up with pipe heaters mounted at the bottom of the holder as illustrated in Fig.3.2.8. The temperature was controlled at the set point by measuring temperature of disk surface by a thermo-couple and providing feedback to the heaters. Tests were performed at 150, 175, and 200 °C.

![Diagram of high temperature tribotest](image)

**Fig. 3.2.8 Schematic view of high temperature tribotest**
3.2.3 Experimental conditions

a) Ambient tribological tests

The tribological measurements were performed with a flat on flat (chip on disk) tribometer using steel/steel tribo-pairs. The load was kept constant at 10N while the velocity was varied stepwise from 1 to 10,000 mm/min. This procedure resulted in Striebeck-like curves which can then be compared so as to evaluate the relative performance of the oils. The steel was mechanically polished and the final Ra roughness was 0.01 µm for the flat and less than 0.01 µm for the disk. The steel pair was immersed in lubricant during the tribo-test. The test conditions are shown in Table 3.2.1.

| Running in: | 2000 revolutions at 287mm/min |
| Velocity:  | 1.43 mm/min--> 2.86 mm/min--> 4.30 mm/min--> |
|           | 5.74 mm/min--> 8.61 mm/min--> 11.5 mm/min--> |
|           | 17.2 mm/min--> 31.6 mm/min--> 86.2 mm/min--> |
|           | 172 mm/min--> 253 mm/min--> 316 mm/min--> |
|           | 547 mm/min--> 747 mm/min, |
| Load:     | 10N (pressure: 8.16 x 10^5Pa) |
| Temperature: | R.T., isothermal |
| Lubricant supply: | Immersed Condition |
| Atmosphere: | Air |
| Relative Humidity: | 40-60% |
| Rubbing surfaces: | 100Cr6 Steel (US 52100) |
| Roughness: | Disk :Ra < 0.01 µm |
|           | Chip :Ra = 0.01 µm |

b) High Temperature Tribotests

High temperature tribotests were performed to investigate influence of temperature on reaction between additives and a steel surface. Its setting and experimental conditions were the same as ambient tribological tests mentioned above except for the cases of experimental temperature. Tests were performed at 150, 175, and 200 °C. A was started with ‘running in process’ 15 minutes after the temperature of the steel surface reached at set value.
3.2.4 Materials

a) Lubricants

The polyalpha olefin was used as the base oil and the additives used were mono/dialkylphosphoric acid neutralized with dialkylamine amine, diisopropyl dithiophosphoryl-alkylpropionate, nonylated triphenylphosphorothionate, butylated triphenylphosphorothionate and Zinc dialkyldithiophosphate. Each lubricant used for tribotests contained additive equivalent in 3.0x10^{-3} atm% phosphorus (2.00wt% for amine phosphate, 0.94wt% for dithiophosphate, 2.21wt% for nonylated triphenyl phosphorothionate, 1.12wt% for ZnDTP).

Although some additives have rather high viscosity, the viscosity of each lubricant is more or less same as that of polyalpha olefin, 31 mm²/sec at 40 °C, because the concentrations of the additives are quite low. (Refer to Table 3.1.1)

<table>
<thead>
<tr>
<th>Additive</th>
<th>M.W.</th>
<th>wt% in PAO</th>
<th>P atm % in PAO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine phosphate</td>
<td>659</td>
<td>2.00</td>
<td>3.04 x 10^{-3}</td>
</tr>
<tr>
<td>Phosphoric acid ester</td>
<td>266</td>
<td>0.82</td>
<td>3.04 x 10^{-3}</td>
</tr>
<tr>
<td>Alkyl amine</td>
<td>381</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>Nonylated triphenyl</td>
<td>729</td>
<td>2.21</td>
<td>3.04 x 10^{-3}</td>
</tr>
<tr>
<td>phosphorothionate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butylated triphenyl</td>
<td>392</td>
<td>1.19</td>
<td>3.04 x 10^{-3}</td>
</tr>
<tr>
<td>phosphorothionate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dithiophosphate</td>
<td>310</td>
<td>0.94</td>
<td>3.04 x 10^{-3}</td>
</tr>
<tr>
<td>ZnDTP</td>
<td>368</td>
<td>1.12</td>
<td>3.04 x 10^{-3}</td>
</tr>
</tbody>
</table>

b) Steel disk and chip

Compositions of steel disk and chip

The material of tribo-pair used was 52100 (US standard) tool steel, whose composition is shown in Table 3.2.3.

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.95</td>
<td>0.17</td>
<td>0.20</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>1.30</td>
<td>&lt;0.30</td>
<td>&lt;0.25</td>
</tr>
<tr>
<td>-1.05</td>
<td>-0.37</td>
<td>-0.45</td>
<td></td>
<td></td>
<td></td>
<td>-1.65</td>
<td></td>
</tr>
</tbody>
</table>
3. Experimental

Polishing of steel disk
Disks were polished up to nanoscale order by a polishing machine to avoid influence of disk roughness on tribotest results, 3D morphological image of disk surface obtained by optical interferometric profilemeter is shown in Fig. 3.2.9. The histogram of surface roughness of polished disks was shown in Fig. 3.2.10, where the average surface roughness of the disk is 4.1 nm.

The polishing procedure is summarized as follows:

1) Polished on emery paper SiC #320, #500 and #1000 with water : 10 sec each,
2) Polished with diamond paste 10-15 µm, and 4-8 µm : 30 sec each,
3) Polished with diamond paste 1 µm : 20 min,
3. Experimental

Polishing of steel chip

Since chips are too small to polish with a polishing machine, the chips were first embedded in a disk shape bakelite at 150 °C, and then polished by a polishing machine. The average surface roughness of chips is 37.2 nm and slightly rougher than that of a disk. Nevertheless, one can regard it as a milled like surface. 3D morphological image of a chip surface is shown in Fig. 3.2.11 and the histogram of surface roughness of polished chips is shown in Fig. 3.2.12. The polishing procedure is summarized as follows.

1) Embedded in a disk shape bakelite at 150 °C.
2) Polished on an emery paper SiC #800 with water : 20 sec
3) Polished on an emery paper SiC #1200 with water : 2 min
4) Polished on an emery paper SiC #2500 with water : 4 min
5) Polished with diamond paste 6 µm : 4 min

3D morphology of a chip is shown in Fig. 3.2.9
c) **Standard chemicals as reference compound**

X-ray photoelectron spectroscopy (XPS) spectrum of standard chemicals were accumulated in order to obtain reference peak positions and curve fitting parameters for analysis of pure additives, adsorbed films formed on steel surface, and boundary lubrication film formed on steel surfaces. The standard chemicals shown in table 3.3.2 were used without further purification. The standard chemicals, which are in powder state, were pressed into a pellet prior to introducing into the XPS chamber so as to avoid any trouble during a measurement. Although the pellet sample seemed to be coated with organic contamination, they were measured without sputtering cleaning.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Supplier</th>
<th>Product No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Phosphide</td>
<td>Alfa</td>
<td>22951</td>
</tr>
<tr>
<td>Iron phosphide</td>
<td>Alfa</td>
<td>39341</td>
</tr>
<tr>
<td>Iron (III) phosphate</td>
<td>Alfa</td>
<td>31106</td>
</tr>
<tr>
<td>Iron (III) pyrophosphate</td>
<td>Alfa</td>
<td>18224</td>
</tr>
<tr>
<td>Zinc phosphate hydrate</td>
<td>Sterem Chemicals Inc.</td>
<td>93-3020</td>
</tr>
<tr>
<td>Iron (III) sulfate</td>
<td>Aldrich Chemicals Co.</td>
<td></td>
</tr>
<tr>
<td>Iron (II) sulfide</td>
<td>Berder &amp; Hobein</td>
<td>12312</td>
</tr>
<tr>
<td>Sodium phosphite</td>
<td>ETH</td>
<td>01-438</td>
</tr>
<tr>
<td>Sodium phosphate</td>
<td>ETH</td>
<td>01-438</td>
</tr>
<tr>
<td>Calcium hydrophosphate</td>
<td>ETH</td>
<td>01-324</td>
</tr>
</tbody>
</table>

### 3.3 XPS analysis

#### 3.3.1 Theory [12]

**a) Principle of XPS analysis**

Surface analysis by XPS is accomplished by irradiating a sample with monoenergetic soft x-rays and analyzing the energy of the detected electrons. Mg Kα (1253.6 eV) or Al Kα (1486.6 eV) x-rays are usually used. These photons have limited penetrating power in a solid on the order of 1-10 micrometers. They interact with atoms in the surface region, causing electrons to be emitted by the photoelectric effect. The emitted electrons have measured kinetic energies given by:
3. Experimental

\[ KE = h\nu - BE - \Phi_s \]  \hspace{1cm} (3.3.1)

where \( h\nu \) is the energy of the photon, \( BE \) is the binding energy of the atomic orbital from which the electron originates, and \( \Phi_s \) is the spectrometer work function.

The binding energy may be regarded as the energy difference between the initial and final states after the photoelectron has left the atom. Because there is a variety of possible final states of the ions from each type of atom, there is a corresponding variety of kinetic energies of the emitted electrons. Because each element has a unique set of binding energies, XPS can be used to identify and determine the concentration of the elements on the surface. Variations in the elemental binding energies (the chemical shifts) arise from differences in the chemical potential and polarizability of compounds. These chemical shifts can be used to identify the chemical state of the materials being analyzed.

In addition to photoelectrons emitted in the photoelectric process, Auger electrons may be emitted because of relaxation of the excited ions remaining after photoemission. In the Auger process (Figure 3.3.1), an outer electron falls into the inner orbital vacancy, and a second electron is simultaneously emitted, carrying off the excess energy. The Auger electron possesses kinetic energy equal to the difference between the energy of the initial ion and the doubly charged final ion, and is independent of the mode of the initial ionization. Thus, photoionization normally leads to two emitted electrons, a photoelectron and an Auger electron. The sum of the kinetic energies of the electrons emitted cannot exceed the energy of the ionizing photons.

Fig.3.3.1 A schematic diagram of photoelectron (a) and Auger electron (b) emission process
3. Experimental

Probabilities of electron interaction with matter far exceed those of the photons, so while the path length of the photons is in the order of micrometers, that of the electrons is in the order of tens of angstroms. Thus, while ionization occurs to a depth of a few micrometers, only those electrons that originate within tens of angstroms below the solid surface can leave the surface without energy loss. These electrons which leave the surface without energy loss produce the peaks in the spectra and are the most useful.

The electrons leaving the sample are detected by an electron spectrometer according to their kinetic energy. The analyzer is usually operated as an energy window, referred to as the pass energy, accepting only those electrons having an energy within the range of this window. To maintain a constant energy resolution, the pass energy is fixed. Incoming electrons are adjusted to the pass energy before entering the energy analyzer. Scanning for different energies is accomplished by applying a variable electrostatic field before the analyzer. This retardation voltage may be varied from zero up to and beyond the photon energy. Electrons are detected as discrete events, and the number of electrons for a given detection time and energy is stored and displayed.

b) The nature of the spectrum

The spectrum is displayed as a plot of the number of electrons versus electron binding energy in a fixed, small energy interval. The position on the kinetic energy scale equal to the photon excitation energy minus the spectrometer work function corresponds to a binding energy of 0 eV with reference to the Fermi level. Therefore, a binding energy scale with 0 at that point and increasing to the left, is customarily used.

Several types of peaks are observed in XPS spectra. Some, photoelectron lines and Auger lines, are fundamental to the technique and are always observed. Others, X-ray satellites, X-ray ghost lines, shake-up lines, multiplet splitting, energy loss lines and valence lines/bands, are dependent upon the exact physical and chemical nature of the sample. A third type is the result of instrumental effects. The following describes the various spectral features that are likely to be encountered:

(1) Photoelectron Lines.

The most intense photoelectron lines are relatively symmetrical and are typically the narrowest lines observed in the spectra. Photoelectron lines of pure metals can, however, exhibit considerable asymmetry due to coupling with conduction electrons. Peak width is a convolution of the natural line width (the lifetime of the "hole" resulting from the photoionization process), the width of the x-ray line which created the photoelectron line and the instrumental contribution to the observed line width.

(2) Auger Lines.

These are groups of lines in rather complex patterns. There are four main Auger series
that is observable in XPS. They are the KLL, LMM, MNN and NOO series, identified by specifying the initial and final vacancies in the Auger transition. The KLL series, for example, includes those processes with an initial vacancy in the K shell and final double vacancy in the L shell. Because Auger lines have kinetic energies which are independent of the ionizing radiation, they appear on a binding energy plot to be in different positions when ionizing photons of different energies (i.e., different x-ray sources) are used. Core-type Auger lines (with final vacancies deeper than the valence levels) usually have at least one component of intensity similar to the most intense photoelectron line.

A characteristic survey spectrum (or wide scan spectrum) is presented in Fig.3.3.2. High-resolution spectra of specific features observed in the survey spectrum are shown in Fig.3.3.3. The survey spectrum of a mechanically polished clean surface of 5200 steel (US standard) has been annotated specifically for this example. First, the background can be observed in the survey spectrum. The number of counts attributed to the background increases with increasing binding energy. This is the inelastic scattering. After each photoemission event, there is a cumulative background signal associated with photoelectrons that have lost energy due to inelastic collisions in the solid, but that still have sufficient energy to escape the work function of the surface. There is a continuum of energies of such electrons ranging between the photoemission KE and zero KE since the collision events reducing the KE of the photoelectron do not have discrete energies. Rising prominently above the background signal two types of peaks are observed in the survey spectrum. There are photoemission peaks associated with core-level photoionization events and X-ray-induced Auger electron emission peaks. If binding energy referencing has been performed, peaks can be readily identified from their positions using tabulations of binding energy values. In the survey spectrum, photoemission peak of iron coming from the substrate of 5200 steel, oxygen coming from its oxide layer and carbon coming from organic contaminant on the top are observed. Auger lines (FeLMM, OKLL, CKLL) are also observed in the survey spectrum. Much additional detail can be observed in the high-resolution spectra in Fig3.3.3. From the peak shape, it is apparent that each spectrum is composed of a number of sub-peaks. These sub-peaks are identified in the figure.
3. Experimental

![Survey Spectrum](image)

**Fig. 3.3.2** A survey spectrum of mechanically polished surface of 52100 steel.

![High-resolution Spectra](image)

(a) C1s  
(b) O1s  
(c) Fe2p3/2

**Fig. 3.3.3** High-resolution spectra of mechanically polished surface of 52100 steel.
C) Chemical information

As the core photoelectron of an element has a unique binding energy, which seems like a fingerprint, almost all elements except for H and He can be identified via measuring the binding energy of its core photoelectron. Furthermore, the binding energy of core photoelectron is very sensitive to the chemical environment of element. The same atom is bounded to the different chemical species, leading to the change in the binding energy of its core photoelectron. The variation of binding energy results in the shift of the corresponding XPS peak, ranging from 0.1eV to 10eV. This effect is termed as "chemical shift", which can be applied to studying the chemical status of element in the surface.

Chemical shifts occur with Auger lines as well as with photoelectron lines. The chemical shifts are different from those of the photoelectron lines, but they are sometimes more pronounced. This can be very useful for identifying chemical states, especially in combination with photoelectron chemical shift data. If data for the various chemical states of an element are plotted with the binding energy of the photoelectron line on the ordinate and the kinetic energy of the Auger line on the abscissa, a two-dimensional chemical state plot can be obtained.

With chemical states displayed in two dimensions, the Auger parameter method becomes very powerful as a tool for identifying the chemical components in the case that the direct interpretation based on the chemical shift of photoelectron or Auger electron alone. The kinetic energy of the Auger line is plotted against the binding energy of the photoelectron line, with the latter plotted in the -x direction (kinetic energy is still, implicitly, +x). The kinetic energy of the Auger electron, referred to the Fermi level, is easily calculated by subtracting from the photon energy the position of the Auger line on the binding energy scale. With this arrangement, each diagonal line represents all values of equal sums of Auger kinetic energy and photoelectron binding energy. The Auger parameter $\alpha$ is defined as,

$$\alpha = KE_A - KE_P = BE_P - BE_A$$  \hspace{1cm} (3.3.2)

or as the difference in binding energy between the photoelectron and Auger lines. This difference can be accurately determined because static charge corrections cancel. With all kinetic and binding energies referenced to the Fermi level, and recalling that:

$$KE = h\nu - BE$$  \hspace{1cm} (3.3.3)

then

$$KE_A + BE_P = h\nu + \alpha$$  \hspace{1cm} (3.3.4)

or the sum of the kinetic energy of the Auger line and the binding energy of the photoelectric line equals the Auger parameter plus the photon energy. A plot showing Auger kinetic energy versus photoelectron binding energy then becomes independent of the photon energy. In general, polarizable materials, especially conductive materials, have a high Auger parameter, while insulating compounds have a lower Auger parameter.
3. Experimental

d) Quantitative analysis

As discussed above, the complete XPS spectrum of a material contains peaks that can be associated with the various elements (except H and He) present in the outer approximately 10 nm of that material. The area under these peaks is related to the amount of each element present. So, by measuring the peak areas and correcting them for the appropriate instrumental factors, the percentage of each element detected can be determined. This is true for the surface that is homogeneous in the analysis volume, but is incorrect for the surface that is inhomogeneous in the analysis volume like a surface with less than monolayer coverage of adsorbate, a surface with a thin top layer and a surface with multilayers.

First, for a sample that is homogeneous in the analysis volume, the number of photoelectrons per second in a specific spectra peak is given by:

\[ I = nf\sigma\theta\lambda AT \]  

(3.3.5)

where \( n \) is the number of atoms of the element per cm of the sample, \( f \) is the x-ray flux in photons/cm\(^2\)-sec, \( \sigma \) is the photoelectric cross-section for the atomic orbital of interest in cm\(^2\), \( \theta \) is an angular efficiency factor for the instrumental arrangement based on the angle between the photon path and detected electron, \( y \) is the efficiency in the photoelectric process for formation of photoelectrons of normal photoelectron energy, \( \lambda \) is the mean free path of the photoelectrons in the sample, \( A \) is the area of the sample from which photoelectrons are detected, and \( T \) is the detection efficiency for electrons emitted from the sample. From Equation 3.3.5:

\[ n = I/f\sigma\theta\lambda AT \]  

(3.3.6)

The denominator in Equation 3.3.6 can be defined as the atomic sensitivity factor, \( S \). Considering a strong line from each of two elements, then:

\[ \frac{n_1}{n_2} = \frac{(I_1/S_1)}{(I_2/S_2)} \]  

(3.3.7)

This expression may be used for all homogeneous samples if the ratio \( S_1/S_2 \) is matrix-independent for all materials. It is certainly true that such quantities as \( \sigma \) and \( \lambda \) vary somewhat from material to material (especially \( \lambda \)), but the ratio of each of the two quantities \( \sigma_1/\sigma_2 \) and \( \lambda_1/\lambda_2 \) remains nearly constant. Thus, for any spectrometer, it is possible to develop a set of relative values of \( S \) for all of the elements. Multiple sets of values may be necessary for instruments with multiple x-ray sources at different angles relative to the analyzer. A general expression for determining the atom fraction of any constituent in a sample, \( C_X \), can be written as an extension of Equation 3.3.7:

\[ C_X = \frac{n_X}{\Sigma n_i} = \frac{I_X/S_X}{\Sigma I_i/S_i} \]  

(3.3.8)

As for the surface that is inhomogeneous in the analysis volume, Fig 3.3.4 shows three important situations encountered in surface analysis. At the tip a diagram of an adsorbed layer is shown. Here, atoms (or molecules) are distributed at less than monolayer coverage leaving some substrate surface exposed. Profile (1) in Fig.3.3.4 shows the concentration profile of
such a system, namely, fractional concentration beyond the surface but no penetration inside the surface layer. Species adsorbed at submonolayer coverage can be present either as separate atoms or as islands. The middle part of Fig.3.3.4 shows a thin layer, at least several monolayers thick. It is well defined and overlays the surface of the substrate. The concentration profile for this type of system may differ. For example, in Profile (2), one has a wafered situation where the concentration of the surface material drops to zero abruptly. In Profile (3), however, the concentration varies continuously in an exponential fashion, into the bulk of the substrate. These models also apply to species distributed in the substrate. The third situation, depicted in Fig.3.3.4 at the bottom, is for a multiplayer system. Here, one encounters stacked layers. Again, the distribution can vary. For example, in Profile (4), two materials, A and B, overlay the substrate C in a wafer-like fashion. In Profile (5), Material A overlays C with some overlap between them; Material B is concentrated at the interface. From Fig.3.3.4, it is apparent that there are two important parameters in surface analysis by XPS: first, the concentrations of species either at a surface or at an interface; second, the distribution of species as a function of depth. The detail of each model can be found somewhere else [13].

**Adsorbed layer**

![Adsorbed layer](image)

**Thin layer**

![Thin layer](image)

**Multi-layered system**

![Multi-layered system](image)

Fig.3.3.4 Three situations for consideration in quantitative analysis for inhomogeneous surfaces

Here, considering briefly a surface with a uniform thin layer, where a thin surface film of thickness \( t \) (at least several atomic layers) overlays a substrate \( m \), the equation for intensities from the substrate \( I_s \) and the layer \( I_l \) as a function of thickness are,
3. Experimental

\[
\text{Is} = I_s^0 k \exp(-t/\lambda) \quad (3.3.9)
\]
\[
\text{Io} = I_o^0 k \exp(1 - \exp(t/\lambda)) \quad (3.3.10)
\]

where

\( \text{Is} \) and \( \text{Io} = \) substrate and thin layer intensities, respectively,

\( I_s^0 \) and \( I_o^0 = \) substrate intensity at \( t = 0 \) and thin layer intensity at \( t = \text{infinity} \), respectively

\( k = \) proportionality constant

\( \lambda = \) mean free path value

Next, considering the surface uniform multi layers (three layer), where a thin top layer of thickness \( l \) and a thin middle layer of thickness \( t \) and a substrate, the equations for their intensities as a function of thickness are,

\[
\text{Is} = I_s^0 k \exp(-t/\lambda) \exp(-l/\lambda) \quad (3.3.11)
\]
\[
\text{Io} = I_o^0 k \exp(1 - \exp(t/\lambda)) \exp(-l/\lambda) \quad (3.3.12)
\]
\[
\text{It} = I_t^0 k (1 - \exp(-l/\lambda)) \quad (3.3.13)
\]

where subscript \( t \) means top layer. The detail of the three layer model used in the present work is described in section 6.6 and 7.3.

e) Angle resolved XPS profiles [13]

By varying the take-off angle \( \Theta \), i.e. the angle between sample surface and detector (being 0° when measuring parallel to the surface), one can adjust the depth of observation. The dependence of intensity with the take-off angle is given by

\[
\frac{I_s}{I_o} = 1 - \exp\left(-\frac{d}{\lambda \sin \Theta}\right) \quad (3.3.14)
\]

The mean free path length of an electron (\( \lambda \)) with a given kinetic energy is constant for a certain material and has been determined for a number of materials [8]. When detecting vertical to the surface, the maximum depth (\( d \)) at which electrons are still detected is achieved. As the take off angle is decreased, this depth is decreased and the measurement gets more and more surface sensitive. If however the place of interest is more than approximately 30Å below the surface (limited due to the range of values of \( \lambda \)), sputtering of the surface with ions becomes necessary so as to remove the top material. By alternatively measuring and sputtering, a chemical depth profile of more than 3nm can be achieved. However, sputtering may result in significant chemical modification of the surface to be analyzed.
3. Experimental

3.3.2 Apparatus

All spectra in this work were obtained using a Model 5700 MultiTechnique ESCA system, Physical Electronics Inc., (PHI). A schematic diagram of the apparatus (Fig. 3.3.2) illustrates the relationship of major components, including the electron energy analyzer, the X-ray source, and the ion gun used for sputter etching. The electron energy analyzer incorporated into 5700 ESCA system is a Concentric Hemispherical Analyzer (CHA) type. 5700 ESCA system has a monochromated Aluminum X-ray source and a dual-anode X-ray source. The monochromatic X-ray source is located perpendicular to the analyzer axis, and the standard X-ray source is located at 54.7 degree relative to the analyzer axis. Electron take-off angle can be varied from nearly 0 up to 90 degree, measured with respect to the surface plane.

![Fig.3.3.5 A schematic diagram of the PHI Model 5700 Multi Technique ESCA system](image)

3.3.3 Experimental Conditions

a) Small area XPS

In order to understand reaction between additives and steel surfaces, small area XPS analysis were performed on steel disks following various treatments; adsorbed with pure additives, tribo-stressed with lubricants containing additives as well as pure additives and standard chemicals. All survey spectra scan were taken at pass energy of 183.7 eV. The detail scan of peaks of interest was, in most cases, obtained with a pass energy of 23.5 eV. Since lower pass energy showed more structure for some materials, the narrow spectra were
3. Experimental

necessary to accurately determine the energy, shape and spin-orbit splitting of strong lines in some cases. On insulating samples, a high-resolution spectrum was taken of the adventitious hydrocarbon on the surface of the sample to use as a reference for charge correction. 285.0 eV was adapted for binding energy for adventitious carbon, which was generally accepted. The analyzed area was, in most cases, a circle with diameter of 0.4mm, which was obtained with the combination of No.3 aperture and minimum area mode setting in software at 5700 ESCA system.

<table>
<thead>
<tr>
<th>Table 3.3.1 Small area XPS analysis conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray source: Al Kα(1486.6eV), Mg Kα (1253.6eV), Twin anode source, 15keV x 23.3mA</td>
</tr>
<tr>
<td>Analyzer: High Resolution Spectra</td>
</tr>
<tr>
<td>Pass Energy: 23.5 eV</td>
</tr>
<tr>
<td>Step size: 0.125eV</td>
</tr>
<tr>
<td>(FWHM Ag 1.1eV)</td>
</tr>
<tr>
<td>- Survey Spectra</td>
</tr>
<tr>
<td>Pass Energy: 183.7 eV</td>
</tr>
<tr>
<td>Step size: 0.4eV</td>
</tr>
<tr>
<td>Aperture: 0.4mm diameter</td>
</tr>
</tbody>
</table>

b) Imaging XPS

Imaging XPS analysis was performed mainly on the tribo-stressed steel surfaces to distinguish chemical differences between tribo-stressed area and non-stressed area.

Imaging XPS is accomplished by sweeping the analysis position and recording the signal as a function of deflection. In a sense, this is a reverse electron gun where, instead of directing the gun at differing pints on a surface, the signals from differing points are steered into the lens and analyzer. Physically, this is done by electrostatic deflection plates placed in the nose of the lens. PHI 5700 ESCA system equipped Multi Channel Detector (MCD) system for acquiring XPS images and there are two modes for acquiring XPS images with it; unscanned mode and scanned mode. The fastest mode of XPS image is its unscanned mode. Each channel is assigned a specific energy width that depends upon the choice of pass energy. Data is collected in sixteen detector channels simultaneously. This energy spectrum is stored with each pixel of the image. When coupled with an ability to redefine the peak and background channels, multiple chemical state maps can be generated from a single image acquisition. When sixteen channels are not sufficient to separate chemical states, MCD is used in scanned mode. Any number of data points may be defined to enhance the energy resolution of the spectra. Each detector channel is swept through all energies, hence the output is dependent...
upon the energy per step which is defined independently of the pass energy. Because significantly more data is acquired, scanned mode maps take longer than unscanned maps.

In this work, scanned mode was used to obtain XPS images. The mapped area was mostly square with a size of 2 mm x 2.82 mm with 32 x 32 pixels, where its take-off angle is 45 degrees. (2 mm x 2 mm square size when 90 degrees)

c) Angle resolved XPS

In order to investigate the structure and thickness of reaction film (adsorbed films or tribo films), angle resolved XPS analysis was performed on steel disks adsorbed with pure additives or tribo-stressed with lubricants containing additives. Depth profiling information can be obtained by varying the take-off angle and film thickness can be determined by measuring at least two angles. In this work, spectra were collected at take off angles of 15, 30, 45, 60, 75, 80 degrees.

3.3.4 Data processing and curve fitting algorithm

**Background subtraction [13]**

The accurate removal of the background contribution to a spectrum is a process that must be carried out with care since, except in the case of the trivial removal of a horizontal background, it may involve distortion of the data when incorrectly carried out. Any background removal will alter absolute peak intensities and will cause problems with any quantification model that must be defined with respect to clear background conditions. There is no definite way to remove a background and the whole process is still controversial.

A rather crude removal of the background may be achieved by removal of a linear background drawn as a straight line between the first and last set of points in a spectrum. The correct choice of a first and last set of points, or a suitable average over them, has a critical effect upon the resulting background. Such a process is best not carried out directly but may be included in the curve-fitting process. This means that the original data are not altered and if a non-linear background has been removed, as described below, then such a linear background would be expected to be horizontal.

The removal of a non-linear background requires a complete understanding of the processes that give rise to background electrons. Such a process will involve inelastic electron ejection processes, but the background must be distinguished from any peaks, which may be broad and difficult to distinguish, that may arise for specific elastic processes such as satellite peaks of various sorts and Auger electron peaks. In addition any angular dependence of the background (which may be machine dependent since β factors will differ for different
3. Experimental

...machine) and inhomogeneities in the material may cause problems. The problems that may arise from plasmon losses and asymmetric broadening being confused with the inelastic background has been pointed out. The most common method of non-linear background subtraction, often called the Shirley method, considers the background at any point due to inelastically scattered electrons, is assumed to arise solely from the scattering of electrons of higher kinetic energy and is thus proportional to the integrated photo-electron intensity to higher kinetic energy. In the present work, Shirley method is used. In Fig.3.3.6, as an example, a spectrum after linear background subtraction and non-linear background subtraction (Shirley) are shown, where the shape of spectra clearly differ each other. In this particular spectrum, the spectrum after linear background subtraction shows negative value of intensity, which happen more often with linear background subtraction than Shirley one.

![Fig.3.3.6 Spectra after Shirley and linear background subtraction](image)

**Curve fitting**

The curve fitting algorithm used in this work was the following Gaussian- Lorentzian sum formula and asymmetric Gaussian- Lorentzian sum formula. The asymmetric one was used only for curve fitting of Fe2p3/2, while the symmetric one was used for all the other
regions. The asymmetric Gaussian-Lorentzian formula is a combination of the regular Gaussian-Lorentzian and an exponential tail formula. The exponential tail formula is applied only to the higher binding energy side of the peak, thereby giving the peak an asymmetric shape. It is the product of an exponential function and a Gaussian-Lorentzian combination determines the shape of the symmetric portion of the peak. The shape of the exponential tail is determined by the tail length parameter. Tail scale, a scaling parameter, is then applied to the tail to properly size the tail to the symmetric portion of the curve.

- Gaussian-Lorentzian:

\[
B(X_i, Q) = H \left\{ 1 - \exp \left( -\ln(2) \frac{(X_i - PP)^2}{FWHM} \right)^2 + \frac{(1 - PG)}{1 + \left( \frac{2(X_i - PP)}{FWHM} \right)^2} \right\} \quad (3.3.15)
\]

- Asymmetric Gaussian-Lorentzian:

\[
B(X_i, Q) = H \left\{ 1 - \exp \left( -\ln(2) \frac{(X_i - PP)^2}{FWHM} \right)^2 + \frac{(1 - PG)}{1 + \left( \frac{2(X_i - PP)}{FWHM} \right)^2} + Tail \right\} \quad (3.3.16)
\]

where,

\[
Tail = TS \left\{ 1 - \exp \left( -\ln(2) \frac{(X_i - PP)^2}{FWHM} \right)^2 \right\} \exp \left( \frac{-6.9}{TL} \frac{2(X_i - PP)}{FWHM} \right)^2 \quad \text{if } X_i \geq PP
\]

\[
Tail = 0 \quad \text{if } X_i < PP \quad (3.3.17)
\]

and where,

- \( B(X_i, Q) \) functional value at energy point \( X_i \),
- \( X_i \) binding energy value for data point \( i \),
- \( PP \) binding energy of the peak’s center,
- \( H \) height of the peak at its center,
- \( FWHM \) full width at half maximum of the peak,
- \( PG \) percent Gaussian (where 0 is 0% and 1.0 is 100%)
- \( TL \) tail length in half width at half maximum of the peak,
- \( TS \) tail scale factor.

In Fig.3.3.7 example of curve fitting for a steel surface adsorbed with amine phosphate whose detail is described in 3.1.2 are shown. O1s spectrum in Fig3.3.7 (a) is fitted with
Gaussian- Lorentzian with FWHM of 1.55eV and Gaussian ratio of 80%. Fe2p3/2 spectrum in Fig.3.3.7 (b) is fitted with Asymmetric Gaussian-Lorentzian with FWHM of 1.38eV and Gaussian ratio of 40% for metal peak, FWHM of 2.8eV and Gaussian ratio of 60% for oxide peak, and FWHM of 3.4eV and Gaussian ratio of 60% for phosphate. The metal peak has also a tail. In the case of an asymmetric spectrum like Fe2p3/2, not only curve fitting parameters but also type of background affect curve fitting result as peak positions or number of peaks. If correct fitting parameters or appropriate background are not adopted, the results obtained (peak positions or number of peaks) can be completely wrong. Whereas a symmetric spectrum like O1s is dominantly affected by curve fitting parameters, but not so much by background.

(a) O1s

(b) Fe2p3/2

Fig. 3.3.7 O1s and Fe2p3/2 spectrum of a steel surface adsorbed with amine phosphate
3. Experimental

3.3.5 Experimental procedure

a) Characterization of pure additives

It is of great importance to characterize pure additives with XPS prior to the characterization of adsorbed or tribo-stressed steel surfaces with additives. Chemical change of the additives due to chemisorption or tribo chemical reaction can be distinguished only by characterizing initial and final state of additives (that is, additive before reaction and reaction film) and by comparing them carefully.

The pure additives used were characterized by means of small area XPS. The additive was dropped on the sputter-cleaned gold plate and frozen at -180 degrees centigrade with liquid nitrogen in the preparation chamber of XPS. After frozen completely, the sample was introduced to the sample holder in the main chamber of XPS, which was also cooled down to -180 degrees centigrade with liquid nitrogen so the sample would not vaporize during acquisition. Then, XPS spectra of the samples were collected with a standard setting described in 3.3 section. The thickness (or height) of the frozen droplet is high enough (more than 1mm) compared to the depth of observation by XPS (few nm) so that influence of interaction between the additive and the sputtered gold plate can be ignored.

b) Characterization of adsorbed films on steel surfaces

The interaction of the selected additives on steel surfaces depends on their surface conditions as well as their constitutional formulas. Therefore, it is necessary to investigate physical and chemical adsorption of the selected additives on various states of steel surfaces, e.g. sputter cleaned metal surface, oxidized surface, contaminated surface with organic film for understanding their tribo chemical reactions.

In this work, interactions of the selected additives on steel surfaces were investigated by adsorbing the additives on various states of steel surfaces as described above and characterizing the films formed on the steel surfaces by means of XPS.

First, a disk prepared for tribological tests originally were washed with 30 ml acetone in a 50 ml beaker using ultrasonic bath (USB) for 5 minutes and then washed with 30 ml cyclohexane in a 50 ml beaker using USB. Then, for adsorption on sputter cleaned metal surface, the washed disk was introduced to the XPS chamber and removed its oxide layer by sputtering with Ar ion gun at 3keV for 2 mm x 2 mm raster size. After sputtering the disk was taken out of XPS chamber and transferred to a glove box without exposing the disk to air by using a ‘transfer cell’. The glove box has N2 atmosphere and its H2O and O2 concentration were controlled to below 1 ppm. The transfer cell is a sealed container and fits the preparation chamber of the XPS so that the disk was transferred from the XPS to the cell in vacuum. Then,
the transfer cell, in which the disk was kept in vacuum was transferred to the glove box and opened there. The disk was then transferred from XPS to the glove box without exposing it to air. In the glove box the disk was immersed in an additive for 24 hours and then washed twice with 30 ml cyclohexane using USB for 5 minutes each. The adsorbed disk was transferred from the glove box to the XPS using the transfer cell, in which N$_2$ gas was filled. Then, the film formed on the steel disk surface was characterized with XPS.

For adsorption on oxide surface, the disk was cleaned and sputtered with the same procedure described above. The sputtered disk was taken out of the XPS and exposed to air for 10 seconds. It can be thought that the re-oxidized surface was fully oxidized but it has very few organic contamination layers on top which can be different from the case of as-machined surface. The re-oxidized disk was immersed in an additive for 24 hours, and then washed with the same procedure and characterized with XPS.

For adsorption on as-machined surface, the disk was cleaned with the same procedure and then immersed in an additive for 24 hours. After 24 hours, the disk was washed with the same procedure and characterized with the XPS.
3. Experimental

Fig. 3.3.8 Adsorption test procedures
3. Experimental

c) Characterization of tribo-fims

Rubbing surfaces have peculiar aspects from the chemical and physical point of view, where the temperature rises due to friction and the surface composition may also change dynamically due to deformation of the material or plowing effect of friction. Thus, the film formed by a lubricant additive on a steel surface under tribo stress is considered to be different from just the adsorption film. Small area XPS analysis and Imaging XPS analysis were performed on both the tribo-stressed area and the not stressed area of the samples.

First, a disk and a chip for a tribological test were washed with 30 ml aceton in a 50 ml beaker using USB for 5 minutes and then washed with 30 ml cyclohexane in a 50 ml beaker using USB. A tribological test using the cleaned tribo pairs was conducted with a lubricant containing one of the selected additives at various velocities, obtaining Stibeeck curve. After the tribological test, the tribo-stressed disk was washed twice with 30 ml cyclohexane in a 50 ml beaker using USB for 5 minutes each and then, characterized with XPS.

References

4. Characterization of pure additives

4.1 Introduction

In many cases the information provided by XPS is contained in a spectrum that consists of a number of overlapping peaks, often of different peak shapes and intensities. In this situation the peak positions can sometimes be determined in a qualitative manner by derivative spectra. Once approximate peak positions and peak shapes have been found the data can be fitted by curve fitting methods. Therefore, curve fitting parameters such as peak position, full width with at half maximum (FWHM) and ratio between Gaussian and Lorentzian, which are characteristic of a XPS machine and should be used for all the data, must be determined prior to analysis of the additives, steel surface adsorbed or tribo-stressed with the additives. The parameters can be obtained by processing reference materials that have simple body. In this work, first standard materials listed in Table 3.3.2, which are expected to be involved in the pure additives, steel surface adsorbed or tribo-stressed with the additives, will be characterized with XPS to determine the parameters. Next, the baseoil, the selected additives will be characterized one by one using the fixed parameters.

4.2 Base oil

In most industrial applications, lubricant additives are contained in a base oil for a small amount. The additives are often reactive, whereas the base oil should generally be inactive against oxidation, decomposition, polymerization and so on. Furthermore, the base oil should be purified to some extent, since impurity in the base oil can prevent the additives from functioning. Lubricants used in tribological tests in this work also consist of majority of a base oil and a small amount of one of the additives like the industrial applications, thus the base oil (PAO) was characterized with XPS so as to confirm its purity (and stability).

A survey spectrum of frozen poly alpha olefin is shown in Fig.4.2.1. Only carbon and slight oxygen signals can be seen and no other elements, for instance due to contamination, are found. Its surface atomic composition was found to be 98.3% carbon and 1.7% oxygen. These values are close to the expected values based on the stoichiometry (100%).

The C1s high-resolution spectrum of frozen poly alpha olefin deposited on a sputtered-clean gold plate is shown in Fig.4.2.2, where the series of big solid dots represents the original spectrum, the dot-lines represent the individual fitting peaks, the solid line represents sum of the individual peaks and the light solid line represents error between the original spectrum and the sum. As shown in the figure, the spectrum gives the best fit with
two peaks: 285.0eV and 285.9eV using FWHM of 1.25eV. The lower peak (285.0eV) is assigned to hydrocarbon, which includes CH$_3$-, -CH$_2$- and –CH<, and the higher peak (285.9eV) is attributable to oxygenated hydrocarbon, that is, low-level oxidation of alkyl chain of the sample [11]. As can be seen in the curve fit summary shown in Table 4.2.1, the intensity ratio of the hydrocarbon and the low-level oxidized one are found to be 94.5% and 5.5%, respectively. Apart from the low-level oxidation, poly alpha olefin used in this work is in good purity and can be assumed that there is nothing in it to affect lubricity of the additives.

<table>
<thead>
<tr>
<th></th>
<th>C1s</th>
<th>O1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity factor</td>
<td>0.314</td>
<td>0.733</td>
</tr>
<tr>
<td>Atomic ratio (%)</td>
<td>98.3</td>
<td>1.7</td>
</tr>
</tbody>
</table>

![Fig. 4.2.1 Survey spectrum of frozen poly alpha olefin](image1)

![Fig. 4.2.2 C1s high-resolution spectrum of frozen poly alpha olefin](image2)
4. Characterization of pure additives

<table>
<thead>
<tr>
<th>Table 4.2.1 Curve fit summary</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Binding Energy (eV)</td>
</tr>
<tr>
<td>FWHM (eV)</td>
</tr>
<tr>
<td>Intensity ratio (%) (measured)</td>
</tr>
<tr>
<td>Intensity ratio (%) (expected)</td>
</tr>
</tbody>
</table>

4.3 Phosphorus containing additives

4.3.1 Amine phosphate

A survey spectrum generated for frozen pure amine phosphate deposited on a sputtered clean gold plate is shown in Fig. 4.3.1. Carbon, oxygen, phosphorus and nitrogen element were found on the surface of the frozen additive, which agrees with its stoichiometry illustrated in Fig.3.1.2. No other elements such as sodium or potassium owing to contamination were found on the sample. The surface atomic composition of frozen amine phosphate was found to be 85.2% carbon, 9.5% oxygen, 2.4% phosphorus, and 2.9% nitrogen, where the values were corrected for the sensitivity factors from the spectrometer manufacturer. These values are close to the expected values based on the stoichiometry (86.0 % carbon, 9.3% oxygen, 2.4% nitrogen, and 2.3% phosphorus) under assumptions that the amine phosphate congealed homogeneously and no contamination condensed or covered the surface of the frozen sample. This analysis was repeated several times and the experimental values were found to vary by 10%.
4. Characterization of pure additives

![Graph showing data points and curves]

Fig.4.3.1 Survey spectrum of frozen amine phosphate

High-resolution spectra for C1s, O1s, P2p and N1s measured on frozen amine phosphate deposited on sputter-cleaned gold plate are shown in Fig. 4.3.2. Their curve-fitting results after non-linear background subtraction are also shown in Fig. 4.3.2 and summarized in Table 4.3.1. Since X-ray irradiation may induce decomposition of a frozen additive sample, acquisition time could not be taken long enough to have a good signal / noise ratio in some samples. The C1s spectrum shown in Fig.4.3.2 (A) gives the best fit with two peaks; 285.0eV and 286.7eV. The lower main peak (285.0eV) is assigned to hydrocarbon, which includes CH₃-, -CH₂- and –CH<, and the higher peak (286.7eV) is assigned to –C-O- and –C-N-. The relative intensities of the hydrocarbon and the higher peak are found to be 91.0% and 9.0% respectively, which is in good agreement with the expected values based on the stoichiometry (90.0% and 10.0% respectively). The O1s spectrum shown in Fig.4.3.2 (B) also gives the best fit with two peaks; 530.7eV and 532.5eV, although there are three different types of oxygen environment in a molecule according to the stoichiometry. The lower peak (530.7eV) is assigned to –P-OH and –P=O, and the higher peak (532.5eV) is assigned to –P-O-C-. The relative intensities of these peaks are found to be 51% for –P-OH and –P=O, and 49% for –P-O-C-, which is in good agreement with the expected values based on the stoichiometry. The detail of the oxygen environment will be discussed later. In Fig.4.3.2 (C), the P2p signal of pure amine phosphate and its curve-fitting results are illustrated. The spectrum showed the best fit with a pair of P2p3/2 and P2p1/2, since phosphorus signal shows multiple splitting with a delta energy of 0.9eV. Its P2p3/2 binding energy (133.2eV) corresponds to that of phosphate. In Fig. 4.3.2 (D), the N1s signal of amine phosphate and its curve-fitting results are illustrated. The signal showed the best fit with two peaks; 399.1eV and 401.2eV. The
higher peak (401.2eV) is assigned to reacted alkyl amine with phosphoric acid ester and the lower peak (399.1eV) is assigned to non-reacted alkyl amine. Since most of phosphoric acid ester and alkyl amine interact with each other as an acid-base reaction, whose detail appears later, most of alkyl amine is positively charged and, as a result, it showed higher binding energy (401.2eV). The relative intensities of non-reacted and reacted amine are found to be 9% for non-reacted and 91% for reacted amine, which is in good agreement with the expected values based on information provided by the supplier. The relative atomic concentrations of amine phosphate are found to be 84.8% carbon, 10.0% oxygen, 2.9% nitrogen and 2.3% phosphorus, which agrees with the expected values based on the stoichiometry (86% carbon, 9.5% oxygen, 2.4% nitrogen and 2.3% phosphorus).

Table 4.3.1 Curve-fitting results of key element of amine phosphate

<table>
<thead>
<tr>
<th>Element</th>
<th>Cls</th>
<th>Ols</th>
<th>Nls</th>
<th>P2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding Energy(eV)</td>
<td>C(1)</td>
<td>C(2)</td>
<td>O(1)</td>
<td>O(2)</td>
</tr>
<tr>
<td></td>
<td>C-C</td>
<td>C-O</td>
<td>C-N</td>
<td>POH</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.7</td>
<td>1.7</td>
<td>1.55</td>
<td>1.55</td>
</tr>
<tr>
<td>Intensity ratio (measured)</td>
<td>91</td>
<td>9</td>
<td>51</td>
<td>49</td>
</tr>
<tr>
<td>Intensity ratio (expected)</td>
<td>90</td>
<td>10</td>
<td>54</td>
<td>46</td>
</tr>
<tr>
<td>Relative atomic concentration (measured)</td>
<td>84.8</td>
<td>10.0</td>
<td>2.9</td>
<td>2.3</td>
</tr>
<tr>
<td>Relative atomic concentration (expected)</td>
<td>86.0</td>
<td>9.5</td>
<td>2.4</td>
<td>2.3</td>
</tr>
</tbody>
</table>
To understand the O1s curve-fitting results of amine phosphate, it is necessary to consider oxygen state changes caused by chemical interaction between the two constituents of amine phosphate. As can be seen in the constitutional formula illustrated in Fig.3.1.2, amine phosphate consists of alkyl amine and phosphoric acid ester which has free acid group. These two compounds are likely to react with each other as described in equation 4.3.1 in accordance with acid-base reaction, where the hydrogen atom attached to the hydroxyl group of phosphoric acid ester is transferred to alkyl amine. As a result, phosphoric acid ester is
4. Characterization of pure additives

negatively charged where two oxygen atoms (-P=O and -P-OH) reach an equivalent state, while alkyl amine is positively charged [12].

\[
\begin{align*}
R-O \quad \text{P} & \quad \equiv \quad \text{O} \\
R-O \quad \text{P} \quad \text{OH} & \quad + \quad \text{NHR}_2^+ \\
\rightarrow & \\
R-O \quad \text{P} & \quad \equiv \quad \text{O} \\
\text{R-O} & \quad \text{P} \quad \text{O} \\
& \quad + \quad \text{NH}_2\text{R}_2^+
\end{align*}
\] (4.3.1)

Considering the phosphate in detail, the phosphorus has a sp\(^3\) hybrid orbital and connects to two of OR, OH and O with each of 4 bonds as illustrated in Fig.4.3.2. The bond between the oxygen and the phosphorus is considered to be a coordinate bond due to high electronegativity of the oxygen. Accurately speaking, the bond between the oxygen and the phosphorus is not a mere coordinate bond but a sort of double bond of \(\sigma\) bond and \(\pi\) bond called \(d\pi-p\pi\) bond. In the \(d\pi-p\pi\) bond, electron donating from \(p\) orbital of the coordinating oxygen to \(d\) orbital of the phosphorus takes place.

\[
\begin{align*}
\text{P} & \quad \text{O} \quad \text{OR} \\
\text{OH} & \quad \text{OR} \\
\rightarrow & \\
\text{P} & \quad \text{OR} \\
\text{OR} &
\end{align*}
\]

Fig.4.3.3 Schematic diagram of amine phosphate on chemical bond state

Since hydrogen atom in OH group of amine phosphate is transferred to amine side due to ionic bonding, the bond between the oxygen of the OH group and the phosphorus is considered to be the same as the double bond mentioned above. Therefore, the two bonds (-P=O and -P-OH) are regarded as being in equivalent states as mentioned above [13].

\[
\begin{align*}
\text{R} & \quad \delta^- \quad \text{O} \quad \delta^- \\
\text{P} & \quad \delta^+ \\
\text{R} & \quad \delta^- \quad \text{O} \quad \delta^- \quad \delta^+ \\
\rightarrow & \\
\text{R} & \quad \delta^- \quad \text{O} \quad \delta^- \quad \delta^+ \\
\text{P} & \quad \delta^- \\
\text{R} & \quad \delta^- \quad \text{O} \quad \delta^- \\
\rightarrow & \\
\text{R} & \quad \delta^- \quad \text{O} \quad \delta^- \quad \delta^+
\end{align*}
\] (1) (2)

Fig.4.3.4 Schematic diagram of amine phosphate on electron density
In the Fig.4.3.4 electron density change of these oxygen atoms and the phosphorus atom is illustrated. Before the reaction between phosphoric acid ester and alkyl amine, all the oxygen atoms connected to the central phosphorus have negative charges and the phosphorus and the hydrogen atom of –OH group have positive charges as described in Fig4.3.4 (1). Then, the hydrogen is transferred to alkyl amine side owing to the reaction with alkyl amine, and as a result, the oxygen of –OH is negatively charged slightly more, while the oxygen coordinate bonded with the phosphorus, which has a higher negative-charge than the oxygen of –OH group, is slightly reduced its negative charge as they reach an equivalent state. The oxygen of -C-O-P- is barely affected by the reaction in terms of electric charge, while the positive charge of the phosphorus becomes slightly higher as whole phosphoric acid ester is negatively charged due to removal of the hydrogen. As far as their binding energy is concerned, changes to higher negative charge or lower positive charge cause binding energy to shift toward low and changes in the opposite direction cause binding energy to shift toward high. The electron density change and binding energy shift of the atoms in amine phosphate are summarized in Table 4.3.2.

<table>
<thead>
<tr>
<th>Atom</th>
<th>E.D.</th>
<th>B.E.</th>
<th>E.D.</th>
<th>B.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>(δ⁺P)₁</td>
<td>lower</td>
<td>(δ⁺P)₂</td>
<td>higher</td>
</tr>
<tr>
<td>-OH</td>
<td>(δ⁻-OH)₁</td>
<td>lower</td>
<td>(δ⁻-OH)₂</td>
<td>lower</td>
</tr>
<tr>
<td>=O</td>
<td>(δ⁺=O)₁</td>
<td>higher</td>
<td>(δ⁺=O)₂</td>
<td>higher</td>
</tr>
<tr>
<td>CO*P</td>
<td>(δ⁺CO*P)₁</td>
<td>-</td>
<td>(δ⁺CO*P)₂</td>
<td>-</td>
</tr>
</tbody>
</table>

E.D.: Electron Density  
B.E.: Binding Energy

### 4.3.2 Phosphoric acid ester

It is of great importance to investigate phosphoric acid ester and alkyl amine individually in order to know the chemical state of atoms in amine phosphate before the reaction and also to understand the aforementioned chemical state under the interaction between them.
Therefore, they were characterized with XPS individually. Each component were separated from amine phosphate and purified by the supplier.

A survey spectrum of frozen pure phosphoric acid ester deposited on a sputtered-clean gold plate is shown in Fig.4.3.5. Only carbon and oxygen and phosphorus are detected in the sample and no other elements such as nitrogen coming from alkyl amine are detected. Its relative atomic concentrations are 65.4% carbon, 28.4% oxygen and 6.3% phosphorus, where the values were corrected for the sensitivity factors from the spectrometer manufacturer. These values are close to the expected values based on the stoichiometry (67.5% carbon, 26.0% oxygen and 6.5% phosphorus) under assumptions that the sample congealed homogeneously and no contamination condensed or covered the surface of the frozen sample. This analysis was repeated several times and the experimental values were found to vary by 10%.

![Survey spectrum of frozen phosphoric acid ester](image)

Fig.4.3.5 Survey spectrum of frozen phosphoric acid ester

C1s, O1s and P2p high-resolution spectra of pure phosphoric acid ester are shown in Fig. 4.3.6. Their curve-fitting results after non-linear background subtraction are also shown in the figure and the summary of the curve fit is listed in Table 4.4.3.

As can be seen in Fig4.3.2 (A), the C1s spectrum gives the best fit with two peaks; 285.0eV and 286.8eV. The lower main peak (285.0eV) is assigned to hydrocarbon, which includes \( \text{CH}_3^-\), -\( \text{CH}_2^-\) and -\( \text{CH}<\), and the higher peak (286.8eV) is assigned to -\( \text{C-O}<\). These binding energies showed good accordance with those of amine phosphate. The intensity ratio of the hydrocarbon and the higher peak are found to be 84.7% and 15.3% respectively, which is in good agreement with expected value based on the stoichiometry (90.0% and 10.0%
4. Characterization of pure additives

O1s spectrum of pure phosphoric acid ester and its curve-fitting peaks are shown in Fig. 4.3.6 (B), where the spectrum gives the best fit with two peaks; 532.2 eV and 533.5 eV, although the constitutional formula illustrated in Fig. 3.1.2 gives three different types of oxygen environment: -P-O-C-, -P=O, -P-OH. The lower peak (532.2 eV) of the acid is assigned to oxygen of P=O and the higher peak (533.5 eV) is assigned to that of –P-O-C- and –P-OH. The state of pure phosphoric acid ester is considered to be similar to phosphoric acid ester in amine phosphate before the acid-base reaction as described in Fig. 4.3.4 (1). Therefore, the oxygen of –P-OH is considered to have higher binding energy than –P=O and, as a result, –P-O showed more or less the same binding energy as –P-O-C-. All the oxygen in pure phosphoric acid ester showed higher binding energy by approximately 1.5 eV than phosphoric acid ester in amine phosphate. This is owing to fact that phosphoric acid ester in amine phosphate is negatively charged due to acid-base reaction, while pure phosphoric acid ester is electrically neutral.

The P2p spectrum of pure phosphoric acid ester and its curve-fitting results are illustrated in Fig. 4.3.6 (C). The spectrum showed best fit with a pair of P2p3/2 (134.5 eV) and P2p1/2 (135.4 eV), that are assigned to phosphate. Pure phosphoric acid ester showed higher binding energy than that in amine phosphate. This is also caused by the difference of electrical environment as mentioned above. That is, phosphoric acid ester in amine phosphate is negatively charged, while pure phosphoric acid ester is not. As a result, the binding energy of pure phosphoric acid ester is higher than that in amine phosphate.

The relative atomic concentrations of amine phosphate are found to be 64.2% carbon, 29.3% oxygen and 6.5% phosphorus, which agrees with the expected values based on the stoichiometry (67.5% carbon, 26.0% oxygen and 6.5% phosphorus).
4. Characterization of pure additives

Fig. 4.3.6 High-resolution spectrum of phosphoric acid ester (frozen)
4. Characterization of pure additives

Table 4.3.3 Curve-fitting results of key element of phosphoric acid ester

<table>
<thead>
<tr>
<th>Element</th>
<th>C1s</th>
<th>O1s</th>
<th>P2p</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C(1)</td>
<td>C(2)</td>
<td>O(1)</td>
</tr>
<tr>
<td>C-C</td>
<td>285.0</td>
<td>286.8</td>
<td>532.2</td>
</tr>
<tr>
<td>C-O</td>
<td></td>
<td></td>
<td>1.55</td>
</tr>
<tr>
<td>P=O</td>
<td></td>
<td></td>
<td>84.7</td>
</tr>
<tr>
<td>P-O-C POH</td>
<td></td>
<td></td>
<td>90</td>
</tr>
</tbody>
</table>

4.3.3 Alkyl amine

A survey spectrum of frozen pure alkyl amine deposited on a sputtered-clean gold plate is shown in Fig.4.3.5. Oxygen and silicon signals were detected in the sample besides the expected elements, carbon and nitrogen. Their relative atomic concentrations are 89.4% carbon, 3.5% carbon, 4.7% nitrogen and 2.5% silicon. The ratio between the carbon and the nitrogen 89.4%/4.7% is in good agreement with the expected value based on the stoichiometry (96.3% carbon, 3.7% nitrogen). Silicon and oxygen signals are considered to come from SiO2, which came in alkyl amine liquid as a contamination during the purification process. This was confirmed also by the supplier. Since it was hardly possible to eliminate the SiO2 contamination completely, characterization by high-resolution XPS spectra were conducted without further treatment on the sample assuming that no significant chemical interaction between SiO2 contamination and the sample occurs.
C1s spectrum of pure alkyl amine and its curve-fitting results are illustrated in Fig.4.3.8 (A). The spectrum showed the best fit with two peaks; 285.0eV and 285.9eV. The lower peak (285.0eV) is assigned to hydrocarbon and the higher peak (285.9eV) is assigned to –C-N-. The intensity ratio of these two peaks is found to be 84.0% and 16.0% respectively, which agrees with the expected value based on the stoichiometry (92.0% and 8.0% respectively).

N1s spectrum of pure alkyl amine and its curve-fitting results are illustrated in Fig.4.3.8 (B). The spectrum showed best fit with the only one peak (399.2eV) and the peak is assigned to –NH<. Moreover, the binding energy of the peak is in good agreement with that of non-reacted amine in amine phosphate, which is reasonable since pure alkyl amine is considered to be under non-reacted condition.

The relative concentrations of alkyl amine measured are found to be 96.6% carbon and 3.4% nitrogen, which is in good agreement with the expected values based on the stoichiometry (96.3% carbon and 3.7% nitrogen).
4. Characterization of pure additives

![Graph A: C1s spectrum](image1)

![Graph B: N1s spectrum](image2)

Fig. 4.3.8 High-resolution spectrum of alkyl amine (frozen)

Table 4.3.4 Curve-fitting results of key element of alkyl amine

<table>
<thead>
<tr>
<th>Element</th>
<th>C1s</th>
<th>N1s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C(1)</td>
<td>C(2)</td>
</tr>
<tr>
<td>C-C</td>
<td>285.0</td>
<td>285.9</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Intensity ratio (measured)</td>
<td>84</td>
<td>16</td>
</tr>
<tr>
<td>Intensity ratio (expected)</td>
<td>92</td>
<td>8</td>
</tr>
<tr>
<td>Relative atomic concentration (measured)</td>
<td>96.6</td>
<td>3.4</td>
</tr>
<tr>
<td>Relative atomic concentration (expected)</td>
<td>96.3</td>
<td>3.7</td>
</tr>
</tbody>
</table>
4. Characterization of pure additives

4.4 Phosphorus and sulfur containing additives

4.4.1 Nonylated triphenyl phosphorothionate

A survey spectrum of frozen pure nonylated triphenyl phosphorothionate deposited on a sputtered-clean gold plate is shown in Fig.4.4.1. Carbon, oxygen, phosphorus and sulfur elements were found on the surface of the frozen additive, which agrees with its stoichiometry illustrated in Fig.3.1.2. No other elements such as sodium or potassium owing to contamination were found on the sample. The surface atomic composition of frozen nonylated triphenyl phosphorothionate was found to be 90.3% carbon, 6.2% oxygen, 2.2% phosphorus, and 1.4% sulfur, where the values were corrected for the sensitivity factors from the spectrometer manufacturer. These values are close to the expected values based on the stoichiometry (90.0% carbon, 6.0% oxygen, 2.0% phosphorus and 2.0% sulfur) under assumptions that nonylated triphenyl phosphorothionate congealed homogeneously and no contamination condensed or covered the surface of the frozen sample. This analysis was repeated several times and the experimental values were found to vary by 10%.

![Fig.4.4.1 Survey spectrum of nonylated triphenyl phosphorothionate (frozen)](image)

High-resolution spectra for C1s, O1s, P2p and S2p measured on frozen nonylated triphenyl phosphorothionate deposited on a sputter-cleaned gold plate are shown in Fig.4.4.2. Their curve-fitting results after non-linear background subtraction are also shown in Fig.4.4.2 and summarized in Table 4.4.1. The C1s spectrum shown in Fig.4.4.2 (A) gives the best fit with two peaks; 285.0eV and 286.7eV. The lower main peak (285.0eV) is assigned to hydrocarbon and a carbon in benzene ring, and the higher peak (286.7eV) is assigned to
-C-O-. The relative intensities of these two peaks are found to be 89.4% for hydrocarbon and a carbon in benzene ring and 10.6% for -C-O-, which is in good agreement with the expected value based on the stoichiometry (93.7% and 6.7% respectively). The O1s spectrum shown in Fig.4.5.2 (B) also gives the best fit with two peaks: 532.1eV and 533.7eV, although there is only one state of oxygen atom in a molecule according to the stoichiometry. The lower peak (532.1eV) is considered to be low-level oxidation of its alkyl chain, and the higher peak (533.7eV) is assigned to –P-O-C-. The relative intensities of these peaks are found to be 27.1% for the low-level oxidation, and 72.9% for –P-O-C-. In Fig.4.4.2 (C), the P2p spectrum and its curve-fitting results are illustrated. The spectrum showed the best fit with a pair of P2p3/2 and P2p1/2, since phosphorus spectra show multiple splitting with delta energy of 0.9eV. Its P2p3/2 binding energy (134.2eV) is assigned to (R-O-)3P=S. In Fig.4.4.2 (D), the S2p spectrum and its curve-fitting results are illustrated. The spectrum showed the best fit with a pair of S2p3/2 and S2p1/2, since sulfur spectra also show multiple splitting with delta energy of 1.2eV. Its S2p3/2 binding energy (163.3eV) is assigned to (R-O-)3P=S. The relative atomic concentrations of nonylated triphenyl phosphorothionate are found to be 88.7% carbon, 7.3% oxygen, 2.3% phosphorus and 1.7% sulfur, which agrees with the expected values based on the stoichiometry (90.0% carbon, 6.0% oxygen, 2.0% phosphorus and 2.0% sulfur).
4. Characterization of pure additives

Fig. 4.4.2 High-resolution spectrum of nonylated triphenyl phosphorothionate (frozen)
## Table 4.4.1 Curve-fitting results of key element of nonylated triphenyl phosphorothionate

<table>
<thead>
<tr>
<th>Element</th>
<th>C1s</th>
<th>O1s</th>
<th>P2p</th>
<th>S2p</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C(1)</td>
<td>C(2)</td>
<td>O(1)</td>
<td>O(2)</td>
</tr>
<tr>
<td></td>
<td>C-C</td>
<td>C-O</td>
<td>Low level oxidation</td>
<td>-C-O-P-</td>
</tr>
<tr>
<td>Binding Energy (eV)</td>
<td>285.0</td>
<td>286.7</td>
<td>532.1</td>
<td>533.7</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.7</td>
<td>1.7</td>
<td>1.55</td>
<td>1.55</td>
</tr>
<tr>
<td>Intensity ratio (measured)</td>
<td>89.4</td>
<td>10.6</td>
<td>27.1</td>
<td>72.9</td>
</tr>
<tr>
<td>Intensity ratio (expected)</td>
<td>93.3</td>
<td>6.7</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Relative atomic concentration (measured)</td>
<td>88.7</td>
<td>7.3</td>
<td>2.3</td>
<td>1.7</td>
</tr>
<tr>
<td>Relative atomic concentration (expected)</td>
<td>90.0</td>
<td>6.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

### 4.4.2 Butylated triphenyl phosphorothionate

A survey spectrum generated for frozen pure butylated triphenyl phosphorothionate deposited on a sputtered-clean gold plate is shown in Fig.4.4.3. Carbon, oxygen, phosphorus and sulfur elements were found on the surface of the frozen additive, which agrees with its stoichiometry illustrated in Fig.3.1.2. No other elements such as sodium or potassium owing to contamination were found on the sample. The surface atomic composition of frozen butylated triphenyl phosphorothionate was found to be 82.5% carbon, 11.0% oxygen, 3.2% phosphorus, and 3.3% sulfur, where the values were corrected for the sensitivity factors from the spectrometer manufacturer. These values are close to the expected values based on the stoichiometry (85.6% carbon, 8.6% oxygen, 2.9% phosphorus and 2.9% sulfur) under assumptions that butylated triphenyl phosphorothionate congealed homogeneously and no contamination condensed or covered the surface of the frozen sample. This analysis was repeated several times and the experimental values were found to vary by 10%.
4. Characterization of pure additives

High-resolution spectra for C1s, O1s, P2p and S2p measured on frozen butylated triphenyl phosphorothionate deposited on a sputter-cleaned gold plate are shown in Fig.4.4.4. Their curve-fitting results after non-linear background subtraction are also shown in Fig.4.4.4 and summarized in Table 4.4.2.

The C1s spectrum shown in Fig.4.4.4 (A) gives the best fit with two peaks; 285.0eV and 286.7eV. The main peak (285.0eV) is assigned to hydrocarbon and a carbon in a benzene ring, and the higher peak (286.7eV) is assigned to -C-O-. The relative intensities of the hydrocarbon and the higher peak are found to be 84.7% and 15.3% respectively, which is in good agreement with the expected value based on the stoichiometry (90.0% and 10.0% respectively).

The O1s spectrum shown in Fig.4.4.4 (B) also gives the best fit with only one peak; 533.9eV, which is in good agreement with the stoichiometry. In the case of butylated triphenyl phosphorothionate, the peak due to low-level oxidation, which was observed in nolylated triphenyl phosphorothionate, was not observed. This is probably due to the fact that oxidation of alkyl chain takes place less with butylated triphenyl phosphorothionate, since it has shorter alkyl chain than nolylated triphenyl phosphorothionate.

In Fig.4.4.4 (C), the P2p spectrum and its curve-fitting results are illustrated. The spectrum showed the best fit with a pair of P2p3/2 and P2p1/2 with delta energy of 0.9eV. Its P2p3/2 binding energy (134.5eV) can be assigned to (R-O-)3P=S.

In Fig.4.4.4 (D), the S2p spectrum and its curve-fitting results are illustrated. The spectrum showed the best fit with a pair of S2p3/2 and S2p1/2 with delta energy of 1.2eV. Its P2p3/2 binding energy (162.7eV) can be assigned to (R-O-)3P=S.
4. Characterization of pure additives

The relative atomic concentrations of butylated triphenyl phosphorothionate are found to be 85.6% carbon, 8.6% oxygen, 2.9% phosphorus and 2.9% sulfur, which agrees with the expected values based on the stoichiometry (77.6% carbon, 14.4% oxygen, 4.0% phosphorus and 4.0% sulfur).

Fig. 4.4.4 High-resolution spectrum of butylated triphenyl phosphorothionate (frozen)
4.4.3 Dithiophosphate

A survey spectrum generated for frozen pure dithiophosphate deposited on a sputtered-clean gold plate is shown in Fig.4.4.5. Carbon, oxygen, phosphorus and sulfur elements were found on the surface of the frozen additive, which agrees with its stoichiometry illustrated in Fig.3.1.2. No other elements such as sodium or potassium owing to contamination were found on the sample. The surface atomic composition of frozen dithiophosphate was found to be 61.5% carbon, 22.6% oxygen, 5.6% phosphorus, and 10.3% sulfur, where the values were corrected for sensitivity factors from the spectrometer manufacturer. These values are close to the expected values based on the stoichiometry (61.1% carbon, 22.2% oxygen, 5.6% phosphorus and 11.1% sulfur) with the assumptions that dithiophosphate congealed homogeneously and no contamination condensed or covered the surface of the frozen sample. This analysis was repeated several times and the experimental values were found to vary by 10%.
4. Characterization of pure additives

Dithiophosphate used has a relatively complex structure where there are two functional groups in the molecule: dithiophosphate and carbonyl. The structure of dithiophosphate and five types of carbon environment (1 – 5), three types of oxygen environment (A – C) and two types of sulfur environment (α and β) that may be possible to resolve using XPS are illustrated in Fig. 4.4.6 and the anticipated atomic % contributions are summarized in Table 4.4.3. As can be seen in the figure, five types of carbon environment would be a hydrocarbon (1), the carbon connected to the oxygen of dithiophosphate (2), the carbon connected to the sulfur of dithiophosphate (3), the carbon in the carbonyl (4) and the carbon connected to the oxygen of the carbonyl. Three types of oxygen environment would be the oxygen of dithiophosphate (A), the double-bonded oxygen in the carbonyl (B) and the single-bonded oxygen in the carbonyl (C). Two types of sulfur would be the double-bonded sulfur in the dithiophosphate (α) and the single-bonded sulfur in dithiophosphate (β).

![Survey spectrum of dithiophosphate (frozen)](image)

**Fig. 4.4.5** Survey spectrum of dithiophosphate (frozen)

<table>
<thead>
<tr>
<th></th>
<th>C 1s</th>
<th>O 1s</th>
<th>P 2p</th>
<th>S 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity factor</td>
<td>0.314</td>
<td>0.733</td>
<td>0.525</td>
<td>0.717</td>
</tr>
<tr>
<td>Atomic ratio (%)</td>
<td>61.5</td>
<td>22.6</td>
<td>5.6</td>
<td>10.3</td>
</tr>
</tbody>
</table>

**Fig. 4.4.6** The structure of dithiophosphate
Table 4.4.3 Carbon, oxygen and sulfur atomic compositions for dithiophosphate

<table>
<thead>
<tr>
<th>Group type</th>
<th>No. of atom/molecule</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Hydrocarbon</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>-C-O-P-</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>-C-S-</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>-C*(=O)O-C-</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>-C (=O)O-C*</td>
<td>1</td>
</tr>
<tr>
<td>Oxygen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>-C-O-P-</td>
<td>2</td>
</tr>
<tr>
<td>B</td>
<td>-C(=O*)O-C-</td>
<td>1</td>
</tr>
<tr>
<td>C</td>
<td>-C(=O)O*-C</td>
<td>1</td>
</tr>
<tr>
<td>Sulfur</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α</td>
<td>&gt;P(=S*)S-</td>
<td>1</td>
</tr>
<tr>
<td>β</td>
<td>&gt;P(=S)S*-C-</td>
<td>1</td>
</tr>
</tbody>
</table>

High-resolution spectra for C1s, O1s, P2p and S2p measured on frozen dithiophosphate deposited on sputter-cleaned gold plate are shown in Fig. 4.4.7. Their curve-fitting results after non-linear background subtraction are also shown in Fig. 4.4.7 and summarized in Table 4.4.4.

As illustrated in Fig. 4.4.7 (A), the C1s spectrum gives the best fit with three peaks: 285.0eV, 286.6eV and 288.8eV, although there are five types of oxygen environment in a molecule as illustrated in Fig. 4.4.6. Considering electronegativity, a carbon atom in the hydrocarbon is the least electronegative and a carbon atom in –C*(=O)OC- is the most electronegative. A carbon atom in -C-S-, -C-O-P- and -C(=O)OC*- are between them and are also considered to have close electronegativity. Therefore, the lowest peak (285.0eV) is assigned to hydrocarbon (type 1), and the middle peak (286.6eV) is assigned to -C-O-P-, -C-S- and -C(=O)OC*- (type 2, 3, 5). The highest peak (288.8eV) is assigned to -C*(=O)OC- (type 4). The relative intensities of the peaks are found to be 64.4%, 29.6% and 6.0% respectively, which is in good agreement with expected value based on the stoichiometry (54.5%, 36.4% and 9.1%). The O1s spectrum shown in Fig. 4.4.7 (B) also gives the best fit with three peaks: 532.2eV, 532.9eV and 533.5eV, which agrees with the stoichiometry. It is considered that double-bonded oxygen in ester group (type B) is the most electronegative and it becomes smaller in the order of –C-O-P- (type A), the single-bonded oxygen in ester group (type C). Therefore, the lowest peak (532.2eV) is assigned to -C (=O*)OC- (type B), and the middle peak (532.9eV) is assigned to -C-O-P (type A) and the higher peak (533.5eV) is assigned to -C (=O)O*C- (type C). The relative intensities of these peaks are found to be 25.0% for the type B oxygen, 50.0% for the type A oxygen and 25.0% for the type C oxygen. In Fig. 4.4.7 (C), the P2p spectrum and its curve-fitting results are illustrated. The spectrum showed the best fit with a pair of P2p3/2 and P2p1/2. Its P2p3/2 binding energy (133.5eV) is assigned to
4. Characterization of pure additives

(R-O-)$_2$P(=S)S-. In Fig. 4.4.7 (D), the S2p spectrum and its curve-fitting results are illustrated. The spectrum showed the best fit with two pairs of S2p3/2 and S2p1/2. Since the double-bonded sulfur in dithiophosphate ($\alpha$) is considered to be more electronegative than the single-bonded sulfur in dithiophosphate ($\beta$, the lower S2p3/2 peak (162.1 eV) is assigned to $-P(=S*)S$- (type $\alpha$) and the higher S2p3/2 peak (163.5 eV) is assigned to $-P(=S)*C-$ (type $\beta$). The relative atomic concentrations of dithiophosphate are found to be 61.9% carbon, 22.2% oxygen, 5.6% phosphorus and 10.3% sulfur, which agrees with the expected values based on the stoichiometry (61.1% carbon, 22.2% oxygen, 5.6% phosphorus and 11.1% sulfur).

Fig. 4.4.7 High-resolution spectrum of dithiophosphate (frozen)
4. Characterization of pure additives

### Table 4.4.4 Curve-fitting results of key element of dithiophosphate

<table>
<thead>
<tr>
<th>Element</th>
<th>C1s</th>
<th>O1s</th>
<th>P2p</th>
<th>S2p</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C(1)</td>
<td>O(1)</td>
<td>P(2)</td>
<td>O(3)</td>
</tr>
<tr>
<td>Type 1</td>
<td>Binding Energy (eV)</td>
<td>285.0</td>
<td>286.6</td>
<td>288.8</td>
</tr>
<tr>
<td>Type 2-5</td>
<td>FWHM (eV)</td>
<td>1.7</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Type Oxidation</td>
<td>Intensity ratio (measured)</td>
<td>64.4</td>
<td>29.6</td>
<td>6.0</td>
</tr>
<tr>
<td>Type C</td>
<td>Intensity ratio (expected)</td>
<td>54.5</td>
<td>45.5</td>
<td>0</td>
</tr>
<tr>
<td>Type α</td>
<td>Relative atomic concentration (measured)</td>
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<td></td>
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<tr>
<td>Type β</td>
<td>Relative atomic concentration (expected)</td>
<td>61.1</td>
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<td></td>
</tr>
</tbody>
</table>

4.5 Metal, phosphorus and sulfur containing additives

#### 4.5.1 Zinc dialkyl dithiophosphate

A survey spectrum generated for frozen pure Zinc dialkyl dithiophosphate (ZnDTP) deposited on a sputtered-clean gold plate is shown in Fig.4.5.1. Carbon, oxygen, phosphorus and sulfur elements were found on the surface of the frozen additive, which agrees with its stoichiometry illustrated in Fig.3.1.2. No other elements such as sodium or potassium owing to contamination were found on the sample. The surface atomic composition of frozen dithiophosphate was found to be 64.8% carbon, 14.3% oxygen, 5.2% phosphorus, 11.0% sulfur and 4.7% zinc, where the values were corrected for sensitivity factors from the spectrometer manufacturer. These values are close to the expected values based on the stoichiometry (59.3% carbon, 14.8% oxygen, 7.4% phosphorus, 14.8% sulfur and 3.7% zinc) with the assumptions that dithiophosphate congealed homogeneously and no contamination condensed or covered the surface of the frozen sample. This analysis was repeated several times and the experimental values were found to vary by 10%. 

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4. Characterization of pure additives

Fig. 4.5.1 Survey spectrum of ZnDTP (frozen)

High-resolution spectra for C1s, O1s, P2p, S2p and Zn2p3/2 measured on frozen ZnDTP deposited on a sputter-cleaned gold plate are shown in Fig. 4.5.2. Their curve-fitting results after non-linear background subtraction are also shown in Fig. 4.5.2 and summarized in Table 4.5.1. As illustrated in Fig. 4.5.2 (A), the C1s spectrum gives the best fit with two peaks: 285.0 eV and 286.7 eV. The lower peak (285.0 eV) is assigned to hydrocarbon, which includes CH\textsubscript{3} and -CH\textsubscript{2}-, and the higher peak (286.7 eV) is assigned to -C=O-. The relative intensities between the two peaks are found to be 77.6% and 22.4% respectively, which is in good agreement with the expected value based on the stoichiometry (12.5% and 87.5% respectively). The O1s spectrum shown in Fig. 4.5.2 (B) gives the best fit with one peak: 533.1 eV, which agrees with the stoichiometry. In Fig. 4.5.2 (C), the P2p spectrum and its curve-fitting results are illustrated. The spectrum showed the best fit with a pair of P2p3/2 and P2p1/2. Its P2p3/2 binding energy (133.5 eV) is assigned to (R-O-)=P(=S)S-. In Fig. 4.5.2 (D), the S2p spectrum and its curve-fitting results are illustrated. The spectrum showed the best fit with a pair of S2p3/2 and S2p1/2. The S2p3/2 binding energy (162.6 eV) includes both -P(=S*)S- and -P(=S*)S*-C-. In Fig. 4.5.2 (E), the Zn2p3/2 spectrum and its curve-fitting results are illustrated. The spectrum showed the best fit with one peak: 1022.5 eV. The peak is assigned to -S-Zn-S-. The relative atomic concentrations of ZnDTP are found to be 64.5% carbon, 14.8% oxygen, 5.5% phosphorus, 11.1% sulfur and 4.2% zinc, which agrees with the expected values based on the stoichiometry (59.3% carbon, 14.8% oxygen, 7.4% phosphorus, 14.8% sulfur and 3.7% zinc).
4. Characterization of pure additives

![Graphs of C1s, O1s, P2p, S2p, and Zn2p3/2 with binding energies and intensity in arbitrary units.]

Fig. 4.5.2 High-resolution spectrum of ZnDTP (frozen)
Table 4.5.1 Curve-fitting results of key element of ZnDTP

<table>
<thead>
<tr>
<th>Element</th>
<th>C1s</th>
<th>O1s</th>
<th>P2p</th>
<th>S2p</th>
<th>Zn2p3/2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C(1)</td>
<td>C(2)</td>
<td>&gt;P=S</td>
<td>&gt;P=S-C-</td>
<td></td>
</tr>
<tr>
<td>Hydrocarbon</td>
<td>285.0</td>
<td>288.3</td>
<td>533.1</td>
<td>133.5</td>
<td>162.6</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.7</td>
<td>1.7</td>
<td>1.55</td>
<td>1.7</td>
<td>1.88</td>
</tr>
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<td>Intensity ratio (measured)</td>
<td>77.8</td>
<td>22.2</td>
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<td>Intensity ratio (expected)</td>
<td>87.5</td>
<td>12.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>Relative atomic concentration (measured)</td>
<td>64.5</td>
<td>14.8</td>
<td>5.5</td>
<td>11.1</td>
<td>4.2</td>
</tr>
<tr>
<td>Relative atomic concentration (expected)</td>
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<td>14.8</td>
<td>7.4</td>
<td>17.8</td>
<td>3.7</td>
</tr>
</tbody>
</table>

4.6 Stability of the additives

X-ray induced sample damage is a common problem during the XPS analysis of materials, and can cause the spectrum to change with exposure time. Organic polymers exhibit a wide range of damage rates, for example, aromatic materials such as polystyrene degrade almost imperceptibly slowly, whereas halogen-containing polymers degrade fairly quickly [11]. The same phenomena were observed with the frozen additives used in this work. The degradation with X-ray exposure time was clearly observed with amine phosphate and ZnDTP, while it was not recognized with nonylated triphenyl phosphorothionate, butylated triphenyl phosphorothionate and dithiophosphate.

The degradation can be estimated from some parameter characteristic of the sample and measurable from the XPS spectrum. In most cases the parameter was related to the atomic composition or the spectrum shape; for example, with a polymer sample containing only carbon, hydrogen and oxygen, the parameter would be O/C atom ratio. For a polymer sample containing unsaturated hydrocarbons the parameter would be the area ratio of the C1s shakeup peak to the main peak and for a polymer sample with saturated hydrocarbon the parameter would be FWHM of the C1s line. In the case of the frozen additive samples in this work, the degradation was pronounced with the O1s spectrum but it was not distinguishable from the other regions. The degradation appeared on the shape of the O1s spectrum in the case of amine phosphate. In Fig4.6.1 (A), its O1s spectrum obtained using aluminum monochromated source are shown. The monochromated source causes relatively little sample heating and thus the sample degradation can be regarded as negligible. The O1s spectrum of amine phosphate acquired for 0.67 minutes using the unmonochromated aluminum Kα source following 12.0 minutes of X-ray exposure is shown in Fig4.6.1 (B), and the O1s
4. Characterization of pure additives

The spectrum of amine phosphate acquired for 3.3 minutes using the unmonochromated aluminum Kα source following 52.0 minutes of X-ray exposure is also shown in Fig4.6.1 (C). The O1s spectrum obtained with monochromated source, Fig.4.6.1 (A), can be fitted with two peaks and the area ratio of these two peaks are more or less the same. The spectrum with short exposure (12.0 minutes) of unmonochromated X-ray, Fig.4.6.1 (B), shows similar spectrum shape and can be fitted two peaks which have more or less the same area ratio, thereby implying that the sample with which the Fig4.6.1 (B) was obtained was not damaged by the X-ray irradiation. On the other hand, in the case of the O1s spectrum acquired following 52.0 minutes of exposure of unmonochromated X-ray the area ratio of the peak with lower binding energy decreased and also FWHM of these two peaks became wider. (12.0 min: FWHM=1.6, 52.0 min: FWHM=2.15) These changes are surely considered a degradation of the sample due to X-ray irradiation.

Fig.4.6.1 The O1 spectra of amine phosphate under various conditions of X-ray source
4. Characterization of pure additives

The degradation of the additives can be regarded as decomposition of the molecule due to X-ray irradiation, that is, dissociation of a weak bond in the molecule due to energy of X-ray $h\nu$. Strictly speaking, the bond to dissociate must be discussed according to bond dissociation energy of each bond in the molecule, however it can be presumed that in the case of the amine phosphate the double-bonded oxygen dissociatively changed to single-bond since its $\pi$ bond is considered to be weakest, and the free oxygen reacted with the alkyl chain of alkyl amine of amine phosphate as shown in the Fig.4.6.2.

![Fig.4.6.2 The degradation process of amine phosphate](image)

The similar degradation phenomena were observed with ZnDTP. The degradation of ZnDTP was also most pronounced with the O1s spectrum whereas it was hardly distinguishable from the other regions. The O1s spectrum of ZnDTP acquired for 0.67 minutes using the unmonochromated aluminum K\(\alpha\) source (anode power = 350 W, anode voltage = 15.0 kV) following 12.0 minutes of X-ray exposure is shown in Fig4.6.3 (A), and the O1s spectrum of ZnDTP acquired for 3.3 min using the unmonochromated aluminum K\(\alpha\) source following 52.0 minutes of X-ray exposure is also shown in Fig4.6.3 (B). The spectrum with short exposure (12.0 minutes) of unmonochromated X-ray, Fig.4.6.3 (A) can be fitted only one peak which agrees with the stoichiometry discussed in the section 4.5, whereas, in the O1s spectrum acquired after 52.0 minutes of exposure of unmonochromated X-ray, Fig.4.6.3 (B), another peak appeared in the lower binding energy side of the main peak. This new peak increased as the X-ray exposure time increased.
4. Characterization of pure additives

Fig. 4.6.3 The O1 spectra of ZnDTP under two different X-ray exposure time

(A) 12 min with unmonochromated source  
(B) 52 min with unmonochromated source

The dissociation process of ZnDTP has been proposed by many researchers, for example, J.J. Dickert proposed the reactive dissociation mechanism of ZnDTP under the boundary lubrication conditions, in which the shape of oxygen, sulfur, phosphorus and zinc spectra should change drastically. The results obtained in this work, however, showed that the changes appeared only in the shape of O1s spectrum and the binding energy of the S2p spectrum. (The binding energy of S2p3/2 with short exposure of X-ray was 162.7 eV, while that with long exposure of X-ray was 162.5 eV) Therefore, the X-ray induced degradation of ZnDTP in this work is considered to be relatively small compared with the dissociation process proposed by J.J Dickert, and it can be presumed that the dissociation occurred at the bond between the carbon and the oxygen, which is considered to be the weakest bond, and then the free oxygen remains as a negative ion as illustrated in Fig. 4.6.4. As a result, the small peak appeared in the lower binding energy side to the main peak of the O1s spectrum for the degraded sample and also the small chemical shift due to transfer of electrons from the ionized oxygen to the double-bonded sulfur via the central phosphate was recognized.
4. Characterization of pure additives

The degradation speed of the additives can be estimated from a plot of $Xt/Xo$ vs $t$, where $X$ is area ratio of one peak in O1s and $t$ is X-ray exposure time. That is, $Xt$ and $Xo$ represent intensity of one peak after $t$ minutes of exposure to X-ray and initial intensity, respectively. Fig. 4.6.5 shows plots of $Xt/Xo$ vs $t$ for amine phosphate and ZnDTP. In the case of amine phosphate, $X$ is intensity of the lower peak, where the initial value $Xo$ is assumed to be 0.5. In the case of ZnDTP, $X$ is intensity of the main peak, where $Xo=1.0$. As can be seen in the figure, $Xt/Xo$ of ZnDTP decreases linearly as X-ray exposure time $t$ increases, while $Xt/Xo$ started decreasing after approximately 60 minutes of X-ray exposure in the case of amine phosphate. The figure also reveals that the degradation rate of ZnDTP seems to be higher than that of amine phosphate.

![Fig. 4.6.4 The degradation process of ZnDTP](image)

![Fig. 4.6.5 Plots of $Xt/Xo$ vs $t$ for amine phosphate and ZnDTP](image)
4.7 Conclusion

The base oil and the selected additives were characterized with XPS by freezing them. The results obtained are summarized as below.
1) The XPS analysis of the base oil revealed that it is slightly oxidized.
2) Characterization of the selected additives by means of XPS agreed well with their stoichiometry.
3) Amine phosphate was found to exist in different state from the constitutional formula usually described, due to acid-base interaction between phosphoric acid ester part and amine phosphate part.
4) Some of the additives, amine phosphate and ZnDTP had degradation problem during measurements due to X-ray irradiation.

References

Appendix  - Reference chemicals

Curve fitting parameters of the reference chemicals are summarized in Table (1), where C1s peak produced by adsorbed, adventitious carbon, which is considered as a hydrocarbon, was assigned 285.0eV and all other binding energies were referenced to it in order to correct charging shift. All the carbon spectra gave good fits with the use of a combination of 75% Gaussian and 25% Lorentzian fitting routine. The best fits for all of the spectra yielded FWHM values of 1.7eV. All the oxygen spectra (O1s) gave good fits with the use of a combination of 80% Gaussian and 20% Lorentzian fitting routine. The best fits for all of the spectra yielded FWHM values of 1.55eV. Iron spectra (Fe2p3/2) can be fitted only by using an asymmetric shape. Metallic state of iron gave good fits with the tail parameter value of 0.45 for tail length and 60 for tail scale, FWHM value of 1.385 and Gaussian ratio value of 60%. Oxidized state and phosphate state of iron gave good fits with FWHM value of 2.8 and 3.4 eV respectively, and Gaussian ratio value of 40% for the both. Phosphorus spectra (P2p) showed multiple splitting where the area ratio between 2p1/2 and 2p3/2 is 0.5 and the binding energy separation ($\Delta E$) is 0.9eV. All the phosphorus peaks gave good fits with FWHM value of 1.7 and Gaussian ratio of 75%. Sulfur spectra (S2p) also showed multiple splitting with the area ratio of 0.5 and the binding energy separation of 1.2eV. All the sulfur peaks gave good fits with FWHM value of 1.88 and Gaussian ration of 75%. All the zinc spectra (Zn2p3/2) gave good fits with FWHM value of 2.2eV and Gaussian ration of 75%.

| Table (1) Curve fitting parameters of the reference chemicals |
|--------------------------|----------|----------|----------|----------|
|                        | FWHM    | %Gaussian| Tail parameter | $\Delta E$ | Ratio |
|                        |         |          | Tail length | Tail scale |       |
| C1s                    | 1.7     | 75       |             |           |       |
| O1s                    | 1.55    | 80       |             |           |       |
| Fe 2p3/2               | Metal   | 1.38     | 40          | 0.45      | 60    |
|                        | Oxide   | 2.8      | 60          |           |       |
|                        | Phosphate | 3.4   | 60          |           |       |
| P2p                    | 1.7     | 75       | 0.9         | 0.5       |       |
| P2s                    | 2.8     | 75       |             |           |       |
| PKLL                   | 2.2     | 50       |             |           |       |
| S2p                    | 1.88    | 75       | 1.2         | 0.5       |       |
| Zn2p3/2                | 2.2     | 75       |             |           |       |

The binding energies of the reference chemicals are summarized in Table (2), where Auger lines are listed in kinetic energy. Most of the peak positions show good agreement with those with references. The C1s signal always has a multicomponent character. The main
4. Characterization of pure additives

Contribution comes from the contamination at 285.0 eV, and –COH or –COC- (286.6 eV) and –COO- (288.0 eV) in small amounts are also detected. The O1s signal also tends to show a multicomponent character due to adsorption of H₂O (533.2 eV) or oxidation of the samples in some cases, besides peaks of main components.

Table (2) XPS results of the reference chemicals

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
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<td>C1s</td>
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<td></td>
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</tr>
<tr>
<td>Carbide</td>
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<td>283.9</td>
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<tr>
<td>Hydro carbon</td>
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<tr>
<td>-COH, -COC-</td>
<td>286.6</td>
<td>286.5</td>
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</tr>
<tr>
<td>-COO-</td>
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<tr>
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<td>Iron phosphide</td>
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<td></td>
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<tr>
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<td>P2s</td>
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<td>Zinc phosphide</td>
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<td></td>
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<td>Phosphorus red</td>
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<td>Zinc orthophosphate</td>
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<td></td>
<td></td>
</tr>
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<td>Iron phosphate</td>
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<td>Iron pyrophosphate</td>
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<tr>
<td>Zinc phosphate</td>
<td>191.4</td>
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<td></td>
</tr>
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</table>

* Auger lines are in kinetic energy (eV).
## Table (2) XPS results of the reference chemicals

<table>
<thead>
<tr>
<th></th>
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<td>Iron phosphide</td>
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<td>Zinc ortho phosphate</td>
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<td>Iron phosphate</td>
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<td></td>
<td>Iron pyro-phosphate</td>
<td>1849.9*</td>
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<td></td>
<td>Zinc phosphate</td>
<td>1849.8*</td>
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<td>Magnetite</td>
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<td>[9]</td>
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<td>712.6</td>
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<td>[10]</td>
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<tr>
<td></td>
<td>Iron pyro-phosphate</td>
<td>713.0</td>
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<tr>
<td></td>
<td>Iron sulfate</td>
<td>713.1</td>
<td>712.1</td>
<td></td>
<td>[4]</td>
</tr>
<tr>
<td>S2p3/2</td>
<td>Iron sulfate</td>
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<td>168.8</td>
<td></td>
<td>[4]</td>
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<td>SKLL</td>
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<td>Zn2p3/2</td>
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<td>1022.8</td>
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<td>Zinc phosphide</td>
<td>1023.0</td>
<td>1020.9</td>
<td></td>
<td></td>
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</tbody>
</table>

* Auger lines are in kinetic energy (eV).

The three phosphorus spectra (P2p, P2s, and PKLL) show similar behavior of chemical shift, where the phosphides show lower binding energy and the phosphates show higher binding energy. As far as phosphate is concerned, phosphate, pyro-phosphate and ortho-phosphate show nearly same binding energy for P2p, P2s and PKLL. Fe2p3/2 peak positions of the reference chemicals show good agreement with reference values except for iron sulfate, which has 1.0eV difference between this work and the reference. Binding energy of metal iron was obtained by using a steel disk for the tribotest whose oxide layer on the surface was removed by iron sputtering, while the other data were obtained from pellet samples. As far as sulfur and zinc peaks are concerned, accuracy of the data obtained in this work can hardly be discussed since only some information was obtained from references.
5. Tribological performance

5.1 Introduction

It is well known that lubricant additives as EP or AW additives reduce friction, prevent seizure and reduce wear in a boundary lubrication condition. Their effectiveness has been evaluated usually with classical tribotesting. In this chapter, pin-on-disk type tribotest were conducted with the selected additives in order to evaluate macroscopic tribological effectiveness and then influence of roughness of rubbing surface, temperature, load and running-in conducted prior to a main running on friction coefficient are also investigated.

5.2 Running-in

Prior to running, the various pairs of tribo surfaces in a new industrial machine are not mated together. There may be slight initial misalignments and there will certainly be high spots on all surfaces [1]. The initial higher friction leads to higher than normal sliding temperatures; therefore, running-in process is often carried out prior to normal run [2]. Running-in is the process of removing high spots and mating the tribo surfaces; also the surfaces work-harden and become more wear resistant. During this period wear is higher than in normal running as the high spots cause more asperity contacts and the higher temperatures usually cause higher wear rates. If running-in proceeds satisfactorily the high spots are removed by adhesive wear and by plastic deformation. The wear gradually increases the real area of contact until it equals the design contact area, and the contact pressure drops. Frictional losses decrease during this period thus reducing the surface temperatures. The wear rate decreases due to all the above causes until it reaches the normal steady-state wear rate. However, if the initial misalignments are sufficiently high, the apparent bearing surface area might be so low as to cause the pressure to be higher than one-third of the hardness. In this case, the wear rate is excessively high as the real contact area may not grow sufficiently to reduce the pressure to less than H/3, that is, to reduce the wear rate to normal levels, before large-scale damage or even seizure has occurred.

Now, to investigate influence of running-in on tribological results and to achieve a better running-in, the following two procedures have been done with CSEM tribometer:

a. 4000 revolutions at 20rpm
b. 1500 revolutions at 2rpm

As shown in Fig.5.2.1, after the 20 rpm-part, the friction coefficient was steady at about 0.15. During the second part, however, the value dropped to 0.05 after about 10 hours. After
the running-in, the velocity was changed frequently (calibrating plotter), resulting of course in different friction coefficients. However afterwards, the friction coefficient at 2 rpm was again at about 0.06 and started falling gradually.

Although a running-in has been done and a steady value has been achieved, after measuring at other velocities one still gets a more or less strong running-in effect when changing to other (lower) velocities.

Considering asperity contacts during the running-in, the number of asperity contacts in the rubbing interface at 20rpm should be lower than that at 2rpm, since the former lubrication film is considered to be thicker than the latter one owing to hydrodynamic lubrication effect. Consequently, even if a steady state is obtained with running-in at 20rpm, once new running-in at lower velocity (2rpm) is conducted, friction coefficient will move toward a new steady state since it causes new asperity contacts which do not occur at 20rpm.

Therefore, running-in should be done at the similar condition or a bit more severe condition as the normal run. In the case of the present work, it is difficult to determine one optimal velocity of running-in since the test covers wide range of velocity, however, it is considered that as long as once velocity is used for all the experiments, performance of the selected additives can be evaluated.

\[ \text{Friction coefficient versus velocity} \]

**Fig.5.2.1 Friction chart during running-in process**

### 5.3 Apparatus

A plot of friction coefficient versus velocity obtained with the CSEM tribometer and the CETR tribometer for the lubricant containing no additives and the lubricant containing amine phosphate are shown in Fig.5.3.1, where roughness of chips used were 0.01µm in Ra and all the other experimental conditions were also kept the same. The two plots show the same behavior as Stribeck curve, where the velocity is used as X-axis instead of Stribeck number, normalized film thickness. The two curves show good agreement on the velocity border.
between boundary lubrication region and mixed lubrication region, approximately 20mm/min, and the other velocity border between mixed lubrication region and hydrodynamic lubrication region, approximately 200mm/min. Besides overall behavior of the curves, the figure proves that their values of friction coefficient also show good agreement throughout the velocity for both of the lubricants. Moreover both of the tribometers showed the same behavior in regard to stick-slip events. Both of the tribometers generated stick-slip events at low velocity for the lubricant containing no additives, while no stick-slip events were observed with lubricants containing the additive.

To ensure compatibility of the two tribometers, friction coefficients at 3mm/min in velocity obtained with the two tribometers for various lubricants are compared in Table 5.3.1, which is a summary of Fig.5.3.3 and Fig.5.3.4 illustrated below. The table revealed that the two tribometers show the same order of friction coefficient for selected lubricants although there are often only small differences in their lubricity performance.

These results prove that the two tribometers can generate the same results with good precision in terms of average value of friction coefficient, since their contact geometry and relative movement are exactly same.

![Fig. 5.3.1 Strubeck curve obtained with two different tribometers](image)
Table 5.3.1 Friction coefficient in boundary lubrication region for selected lubricants

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Friction coefficient at 10mm/min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CSEM tribometer</td>
</tr>
<tr>
<td>No additives</td>
<td>0.5</td>
</tr>
<tr>
<td>Amine phosphate</td>
<td>0.14</td>
</tr>
<tr>
<td>Dithiophosphate</td>
<td>0.42</td>
</tr>
<tr>
<td>Nonylated triphenyl phosphorothionate</td>
<td>0.40</td>
</tr>
<tr>
<td>Butylated triphenyl phosphorothionate</td>
<td>0.34</td>
</tr>
<tr>
<td>ZnDTP</td>
<td>0.33</td>
</tr>
</tbody>
</table>

The difference between the two tribometers which might cause some differences in results is stiffness of the apparatuses, especially stiffness of the pin and the pin holder, since stiffness of the pin or the pin holder strongly affect occurrence of stick-slip events [3]. Rabinowicz reported the relationship between amplitude of friction coefficient and velocity for various spring constants as Fig.5.3.2 using a simple friction tester [4]. The figure illustrates that amplitude of stick-slip event increases and it occurs from higher velocity in correspondence to the ratio, the spring constant per unit load, decreases. In the case of this work, stiffness of the tribometers, especially stiffness of pin and pin holder, corresponds to the spring constant of Rabinowicz’s experiments. Thus stick-slip events are more apt to occur as the stiffness of the apparatuses decrease.
Stick-slip events were observed with both tribometers when the lubricant containing no additives were used. Next, amplitudes of friction coefficient during the stick-slip events are shown in Table 5.3.2. The result shows that amplitude of friction coefficient for CETR tribometer is twice as much as that of CSEM tribometer, consequently the stiffness of CETR tribometer is considered to be half of that of CSEM tribometer. This indicates that stick-slip events can be observed more often with CETR tribometer than CSEM tribometer.

<table>
<thead>
<tr>
<th>Table 5.3.2 Amplitude of friction coefficient at 10mm/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amplitude of friction coefficient</td>
</tr>
<tr>
<td>CSEM tribometer</td>
</tr>
<tr>
<td>CETR tribometer</td>
</tr>
</tbody>
</table>

5.4 Additive performance

Plots of the friction coefficient versus velocity for selected additives are shown in Fig. 5.4.1, where the graph (a) shows results obtained with CSEM tribometer and the graph (b) shows results obtained with CETR tribometer. Each data point represents the average of at least three different experiments and all the experimental conditions including roughness of chips were kept the same as the previous experiments. Both of the results show good agreement on shape of Striebeck curves [5, 6] of the lubricants and also their friction coefficients.

The figures show that the additives reduce the friction coefficient at low velocities and prevent the occurrence of stick-slip events, while the lubricant containing no additives shows high friction coefficient and stick-slip event. Phosphorus acid ester additive, amine phosphate, shows the most pronounced reduction of friction coefficient in boundary lubrication region, while the ester additives containing both sulfur and phosphorus (S-P ester additive), dithiophosphate, butylated and nonylated triphenyl phosphorothionate and ZnDTP, show slightly higher friction coefficient than amine phosphate. In general, when an extreme pressure additive reacts and forms effective boundary lubrication film, friction coefficient is below 0.2 at highest [7]. Therefore, it seems that the S-P ester additives do not work as an extreme pressure additive in boundary lubrication region under these experimental conditions. This can be reasonable since surface temperature of each experiment carried out at room temperature is considered to be too low for the S-P ester additives to react and form an effective boundary lubrication film, while phosphoric acid ester additive, amine phosphate, can be reactive under these experimental conditions due to its acid function group.
Fig. 5.4.1 Stribeck curve for selected lubricants
(A) obtained with CSEM tribometer, (B) obtained with CETR tribometer
(a) No additives, (b) Amine phosphate, (c) Dithiophosphate, (d) Nonylated triphenyl phosphorothionate, (e) Butylated triphenyl phosphorothionate, (f) ZnDTP
5. Tribological performance

Judging from the tribological results shown in Fig.5.4.1, amine phosphate, a mixture of phosphoric acid ester and alkyl amine, reduces friction in boundary lubrication region by most likely reacting with steel surface resulting in formation of lubrication film even at room temperature. Thus, to understand which component of the compound reduces friction, each component of amine phosphate, the phosphoric acid ester and the alkyl amine, was examined separately. Fig.5.4.2 shows a plot of the friction coefficient for 1.18wt% phosphoric acid ester and the 0.82wt% alkyl amine of amine phosphate in PAO, which is equivalent with the acid ester and the amine of 2% amine phosphate, respectively.

The lubricant containing only the acid ester shows a lower friction coefficient than the compound, amine phosphate, in the boundary lubrication region, while the lubricant containing the only alkyl amine shows even a higher friction coefficient than the lubricant containing no additives. Those results indicate that the phosphoric acid ester part of amine phosphate reacts with the steel surface resulting in formation of a lubrication film which can lower the friction coefficient significantly. On the other hand, the alkyl amine part of amine phosphate does not work to reduce friction in this experimental condition, though some of alkyl amines are reported to be a good friction modifier.
5. Tribological performance

Fig. 5.4.2 Stribeck curve for phosphoric acid ester and alkyl amine of amine phosphate
(A) obtained with CSEM tribometer, (B) obtained with CETR tribometer
(a) No additives, (b) Amine phosphate, (c) Phosphoric acid ester, (d) Alkyl amine
5.5 Roughness

The classical theory of adhesive friction developed by Bowden and Tabor [7] assumes that friction is generated by adhesion at contacting asperity peaks. Providing the adhesive stress is not too great, the pressure at the contacting peaks is equal to the hardness or indentation pressure of the softer material in the friction couple. Since the hardness has an essentially constant value of about three times the flow strength of the material, the total real area of contact and hence the friction force is proportional to the normal load. This is the well known Amontons-Coulomb law which is usually expressed through a constant friction coefficient. While the constant coefficient of friction model is very useful in the analysis of many mechanical systems, it is of limited value in modeling friction at lubricated interfaces. Wilson [12] has pointed out that a variety of different lubrication regimes can occur at the interface. In most of these, all or part of the interface load is carried by pressure in the bulk lubrication film. Only in the boundary regime is the load carried by asperity contacts, which also generate friction through shear of boundary films. Even in this regime, the high interface pressures may result in changes in the effective hardness of asperities, and which also can be affected by type of lubricant. Thus, the real area of contact will no longer be proportional to load and the Amontons-Coulomb law will break down. In this section, the influence of surface topography on tribological results is studied as a function of roughness.

A plot of friction coefficient versus velocity with two different roughness of chips for selected additives are shown in Fig.5.5.1, where figure (a) shows a plot obtained using chip with a roughness of Ra 0.05µm and figure (b) shows a plot obtained using a chip with a roughness of Ra 0.6µm. Both of the plots show a similar tendency in the shape of their curve and order of their friction coefficients, that is, at low velocity the lubricant containing no additives shows the highest friction coefficient, the lubricant containing amine phosphate shows the lowest and the other lubricants falls between them. At high velocity, over 600mm/min, friction coefficient of the lubricant containing no additives is lower than that of the lubricants containing additives, which is not observed in the Stribeck curve of 0.01µm chips, which is shown in Fig.5.4.1.

It seems as in the case of rough chips, such as Ra 0.6µm or 0.05µm, Stribeck curve obtained using the lubricant containing additives do not reach hydrodynamic lubrication region even at the highest velocity during the experiments. This is considered to be due to high roughness, that is, some asperity contacts still take place even at high velocity in the case of a rough chip.

This can be interpreted by thinking running-in effect. Each experiment started from low velocity and went to higher velocity in a step by step procedure, thus the lubricant containing no additive caused wear of asperities in the boundary lubrication region, as well as in the
5. Tribological performance

running-in process, resulting in very low roughness. Consequently, the lubricant with no additives shows a very low friction coefficient at high velocity. On the other hand, wear of asperities did not take place with the lubricant containing additives as much as the lubricant containing no additives, and thus a high friction coefficient was observed with the combination of the rough chip and the lubricants with additives.

Fig. 5.5.1 Stribeck curve for various roughness of chips

Roughness of chip (A) Ra=0.05µm, (B) Ra=0.6µm

(a) No additives, (b) Amine phosphate, (c) Dithiophosphate, (e) Nonylated triphenyl phosphorothionate
5. Tribological performance

Otherwise high velocity, friction coefficient for selected lubricants shows the same tendency in terms of performance of additives. Now, to investigate the effect of roughness on friction coefficient in the boundary lubrication region quantitatively, the relationship between friction coefficient at 8 mm/min for selected lubricants and roughness of chips is plotted in Fig. 5.5.2. The figure shows that friction coefficient decreases slightly as the roughness of a chip increases. This is often acceptable for realistic situations in industries although in most simple theoretical models the friction coefficient is regarded as independent of the surface roughness.

![Fig. 5.5.2 Effect of roughness Ra on friction coefficient](image)

- (a) No additives, (b) Amine phosphate, (c) Dithiophosphate, (d) Nonylated triphenyl phosphorothionate, (e) ZnDTP

The results shown in Fig. 5.5.2 can be interpreted by taking a factor of real contact area into the simple boundary lubrication model with liquid lubrication [13-19] as illustrated in Fig. 5.5.3. The normal load $W$ is described as follows,

$$ W = p_r A_r + q A_q $$

(5.5.1)
where, \( p_r \) is normal pressure applied on the real contact area \( A_r \), and \( q \) is hydrostatic pressure of the lubricant acting on area \( A_q \) that the lubricants are trapped.

Since shearing stress acting on the area \( A_q \) can be ignored, the apparent friction force \( F \) is described as follows,

\[
F = \frac{\tau_r A_r}{p_r A_r + q A_q} \tag{5.5.2}
\]

Based on the assumption that hydrostatic pressure is generated on all areas except contacting area \( A_r \), that is, \( A_q = A_o - A_r \), where \( A_o \) is the apparent contact area, friction coefficient \( \mu \) in the apparent contact area, is described as follows,

\[
\mu = \frac{F}{P} = \frac{\tau_r A_r}{(p_r A_r + q A_q)} = \frac{\mu_r}{1 + (A_o / A_q - 1) (q / p_r)} \tag{5.5.3}
\]

where, \( \mu_r \) is friction coefficient on the real contact area. \( \tau_r \) is shearing stress acting on the real contact area.

It is obvious from the equation 5.5.3 that the apparent friction coefficient \( \mu \) is affected by the real contact area \( A_r \). In Fig.5.5.4, the relationship between the apparent friction coefficient in boundary lubrication and the real contact area is illustrated, where it is assumed that \( q / p_r = 0.2 \). The friction coefficient increases as the real contact area increases.
Next, the relationship between the real contact area and roughness should be clarified in order to understand the Fig. 5.5.2. When the real contact area of two contacting surfaces is considered, a simplification that a single rough surface contacts with a perfectly smooth surface is often made, although in general, all surfaces have roughness. Furthermore, it should be assumed that there is no interaction between separate asperities, that is, the displacement due to a load on one asperity does not affect the heights of the neighboring asperities.

If the separation between the smooth surface and reference plane is \( d \), then there will be contact at any asperity whose height was originally greater than \( d \), as shown in Fig 5.5.5. If the \( \phi(z) \) is the probability density of the asperity peak height distribution, then the probability that a particular asperity has a height between \( z \) and \( z + dz \) above the reference plane will be \( \phi(z)dz \).

Thus, the probability of contact for any asperity of height \( z \) is

\[
prob(z > d) = \int_d^\infty \phi(z)dz
\]  

(5.5.4)
5. Tribological performance

Fig. 5.5.5 Contact between a smooth plane and a rough surface [18]

Since prob(z>d) is equal to A_r / A_0, the real contact area A_r is described as follows, by assuming that the histogram obtained for the all-ordinate distribution of a ground surface has a gaussian distribution.

\[ A_r = A_0 \int_{d}^{\infty} \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{z^2}{2\sigma^2}} dz \]  

(5.5.5)

where, standard deviation \( \sigma \) is the parameter for expressing the roughness of the surface, that is the roughness increases as \( \sigma \) increases. Now, since it is evident that \( A_r \) increases as \( \sigma \) decreases, it can be concluded that the real contact area \( A_r \) increases as the roughness of a surface Ra decreases.

In conclusion, the decrease of the friction coefficient as an increase of roughness, as shown in Fig.5.5.2, is due to decrease of real contact area.

5.6 Temperature

The opinion that an increase in temperature at contacting asperities in the loaded area can change critically the situation from effective lubrication to high wear and seizure is probably as close to unanimity as any in the field. Only the mechanism of its action is in doubt in some circumstances. Also, temperature can act in so many ways and is so intimately involved in the various interactions.

A simple load carrying criterion that is dependent only on the temperature in the contacting asperities between the surfaces in the loaded area was first suggested as early as 1937 and is still widely used with no modification [21]. Then, it has been applied to explain transitions from effective to ineffective lubrication in testing machines [22-27], gears and so
on [28-33]. Essentially it states that for a non-additive oil configuration load support breaks down in a given bearing when the temperature in the contacting asperities exceeds a temperature characteristic of the oil, commonly called the transition temperature. The temperature in the contacting asperities is the bulk temperature plus the temperature rise caused by frictional action between the surfaces. This temperature rise (often called “flash temperature”) depends on the friction, the load and the velocity. The temperature in the contacting asperities depends, therefore, on these variables and on factors determining heat flow into and out of the contacting asperities. In spite of its long history, the temperature rise concept of film breakdown has not yet been unequivocally proved [34].

Temperature increase can affect the processes at the interface in several different ways. On one hand, it can cause disorientation and desorption of physically absorbed films or decomposition of compounds; on the other hand, it can supply activation energy for chemisorption or chemical reaction. It can influence friction and film breakdown by modifying the crystal structure of the surface and by lowering the viscosity of the interfacial film material. The interplay of all these effects is only just beginning to be understood.

If the temperature rise generated during a friction test is too large, the temperature rise in contacting asperities can not be ignored, in consequence, it is of great difficulty to know the real interfacial temperature unless it is measured directly with good precision. In this section, to understand if the tribo-reaction of amine phosphate takes place at room temperature or at high temperature due to frictional temperature rise (flash temperature), the mean temperature rise of the sliding surface was roughly estimated by modified Archard’s model [8-11] as follows. As illustrated in Fig.5.6.1, the surface C slides over the surface B, where the contact area is a circle with radius of a, and the surface B is deformed plastically.

The quantity of heat generated at the interface is

\[ Q = Q_B + Q_C \]  \hspace{1cm} (5.6.1)

where \( Q_B \) and \( Q_C \) represent quantity of heat transferred to the surface B and C respectively. When the sliding velocity \( V \) of the surface C is slow enough for both of the surfaces to reach stationary state, the temperature rise \( T \) at the surface B and C are described as follows,

\[ T_B = \frac{Q_B}{4aK_B}, \quad T_C = \frac{Q_C}{4aK_C} \]  \hspace{1cm} (5.6.2)

where, \( K_B \) and \( K_C \) are heat conductivity of surface B and C, respectively. At the interface, both temperature rise can be considered the same, thus,

\[ T = T_B = T_C = \frac{Q}{4a(K_B + K_C)} \]  \hspace{1cm} (5.6.3)

Now, the quantity of heat generated at the sliding surfaces \( Q \) is described with normal load \( W \), friction coefficient \( \mu \), sliding velocity \( V \) as follows,

\[ Q = \mu WV \]  \hspace{1cm} (5.6.4)

As a consequence, the temperature rise \( T \) in boundary lubrication region can be described below,
5. Tribological performance

\[ T = \frac{\mu WV}{4a (K_B + K_C)} \]  
(5.6.5)

Now, when the velocity \( V \) is high and \( Va/2K \) is beyond 5, the surface temperature becomes lower due to cooling, the temperature rise of the surfaces is

\[ T = \frac{Q}{a} (4K_B + 3.25K_C (Va / \kappa_C)^{1/2}) \]  
(5.6.6)

where \( \kappa_C \) is temperature conductivity of the surface C. when \( Va/2K \) is beyond 100, the quantity of heat \( Q \) is transferred almost only to the surface C and thus the temperature rise of the surfaces is described as below,

\[ T = \frac{Q(\kappa_C /Va)^{1/2}}{3.25aK_C} \]  
(5.6.7)

![Fig.5.6.1 Schematic diagram of the contact area](image)

In Fig.5.6.2, mean temperature rise of apparent contact area and temperature rise at a single contact area of an asperity versus velocity in case of dry friction are shown, where other conditions besides lubrication were kept the same. In this calculation, it was assumed that the contact area of a single asperity was a circle with a radius of 0.1\( \mu \)m and its contact pressure was equivalent to its yield stress. Physical properties used for both materials, B and C are those of steel, which are shown in Table 5.6.1. The figure shows that mean temperature rise of apparent contact area is negligible under such low normal load conditions. The temperature rise at each contacting asperity is also considered to be small in case of these lubricated experiments, since the temperature rise is considered to become negligible as soon as it reaches a hydrodynamic lubrication region. In any case, temperatures at which ester type additives start a reaction are far higher than the surface temperatures.

Therefore, it is natural to consider that the reduction of a friction coefficient in a boundary lubrication region by adding those S-P ester additives, Dithiophosphate, butylated and nonylated triphenyl phosphorothionate and ZnDTP, is due to their adsorption on sliding surfaces preventing some of metal-to-metal contact like friction modifiers.
5. Tribological performance

In the mixed lubrication region, 20mm/min – 200mm/min, friction coefficient plunged as velocity increases since a ratio of boundary friction area, which dominates friction coefficient, decreases dramatically due to increase of lubrication film thickness.

In a hydrodynamic lubrication region, friction coefficient of each lubricant are quite low and similar values since the lubrication film is thick enough to separate two surfaces and thus, additives no longer affect the friction coefficient in this region.

| Table 5.6.1 Physical properties of steel and the parameters for the calculation |
|----------------------------------|-----------------|
| Heat conductivity $K_B$, $K_C$  | 42 W/mK         |
| Density $\rho$                  | 7800 kg/m$^3$   |
| Heat capacity $c$               | 420 J/kgK       |
| Temperature conductivity $\kappa$ | $\kappa = K/\rho c$ |
| Radius of contact area $a$      |                 |
| Apparent contact area           | 2.0 mm          |
| Single asperity                 | 1.0 $\mu$m      |
| Normal load                     |                 |
| Apparent contact area           | 10.0 N          |
| Single asperity                 | $9.24 \times 10^{-4}$ N (yield stress) x (contact area) |

Fig.5.6.2 Effect of sliding velocity on mean temperature rise at the sliding surface

Since the temperature rise can be ignored in the present work as mentioned in the previous section, one can regard the bulk temperature as the real interfacial temperature. Therefore, the reaction temperature dependence of the additives can be obtained from the
tribological results and the bulk temperature.

In Fig.5.6.3, a plot of the friction coefficient of the lubricant containing amine phosphate versus velocity for various temperatures is shown. The friction coefficients at a high temperature shows lower values than the friction coefficient at room temperature in the low velocity, while high temperatures show higher friction coefficients than room temperature in the high velocity. The high friction coefficient at high temperature in the high velocity can be explained by taking the decrease of the viscosity into account. At high temperature over 100 degrees centigrade, the viscosity of the lubricants becomes extremely low and thus the lubrication condition does not reach the hydrodynamic lubrication region and is in the boundary lubrication region even in the high velocity.

![Friction Coefficient vs Velocity Graph](image)

Fig. 5.6.3 Tribological test at high temperature

In Fig.5.6.4, the relationship between friction coefficient of the lubricant containing amine phosphate in the low velocity, 3.0mm/min, and the temperature is shown. The lubricant shows minimum friction coefficient at approximately 120 degrees centigrade. In general, extreme pressure additives are chemically inert at low temperatures and become active over its reaction temperature in which the additives form inorganic layers that are easily worn away. Therefore, if the surface temperature goes too high, the surface becomes corroded and rough, causing high friction.

As far as amine phosphate is concerned, since amine phosphate is considered to be chemically active in room temperature, it can be considered that the inorganic reaction film is
5. Tribological performance

formed at room temperature and its thickness increases according as the temperature increases, resulting in a decrease of its friction coefficient.

The increase of its friction coefficient over 120 degrees centigrade can be due to its corrosion effect mentioned above. However, interpretation of the phenomena requires looking into other aspect such as an investigation of the films formed at various temperatures.

![Graph showing friction coefficient vs. temperature](image)

Fig. 5.6.4 Tribological test at high temperature

5.7 Conclusion

Pin-on-disk type tribotests were carried out using lubricants containing the selected additives at various conditions in order to evaluate their effectiveness as a lubricant additive. The results are summarized as below.

The additives reduce the friction at low velocities and prevent the occurrence of stick-slip events, while the lubricant containing no additives shows high friction coefficient and stick-slip events. Amine phosphate, which is mixture of phosphorus acid ester and alkyl amine, shows the most pronounced reduction of friction coefficient in the boundary lubrication region, while the ester additives containing both sulfur and phosphorus (dithiophosphate, alkylated triphenyl phosphorothionate, and ZnDTP) show a slightly higher friction coefficient than amine phosphate. It seems that the ester additives containing both
sulfur and phosphorus do not work as an extreme pressure additive in the boundary lubrication region under these experimental conditions, while amine phosphate can be reactive under these experimental conditions owing to its acid functional group.

References

5. Tribological performance

6. Characterization of adsorbed films on steel surfaces

6.1 Introduction

To understand interaction between the additives and steel surfaces, it is necessary to grasp the individual characteristics first of all and then to distinguish the change due to their interactions, that is, adsorption. In chapter 4, the characteristics of the additives were investigated precisely with XPS. In this chapter various steel surfaces will be characterized first and then adsorbed films of the additives on the steel surfaces will be investigated. In general, a steel surface has complex multi-layers, which are the substrate of bulk materials, the deformed layer, oxide layer, adsorbed gas layer and the adsorbed organic compound layer on top as illustrated in Fig.6.1.1 [1]. The interaction, adsorption, between additives and steel surfaces is strongly dependent on the state of the steel surface. Thus, interaction between the additives and various state of steel surfaces were investigated, such as a sputtered cleaned surface, a sputtered and re-oxidized surface, a plasma cleaned surface and an as-received surface. As far as the additives are concerned, as it was found in chapter 5 that amine phosphate reduces friction the most in boundary lubrication even at room temperature, implying that it adsorbs or reacts with the steel surface and then forms a lubrication film at room temperature, it is focused on amine phosphate and its constituent molecules, phosphoric acid ester and alkyl amine here.

![Fig.6.1.1 A cross section of a steel surface (an example) [1]](image)

6.2 Steel surfaces

6.2.1 Sputtered steel surface

A steel disk for a tribological test washed with acetone and cyclohexane using an ultrasonic bath (see 3.5 for the detail of cleaning procedure) was introduced in the XPS chamber and sputtered its surface with Ar ion gun for 10 minutes at the energy of 15keV for
2mm x 2mm raster size. The surface was measured by XPS immediately after the sputtering.

In Fig.6.2.2 a survey spectrum of the sputtered steel surface are shown, where carbon, oxygen, chromium, manganese, iron and small amount of argon were detected on the surface. The surface compositions corrected for the sensitivity factors provided by the spectrometer manufacturer were obtained as follows: 8.5% for carbon, 1.9% for oxygen, 1.5% for chromium, 1.8% for manganese and the rest for iron, with the assumption that the over layers were removed by sputtering and only the homogeneous substrate existed. The surface composition values agree with the expected values listed in Table 3.1.3 (note their units, mass %) except for argon and silicon concentrations. It is surmised that the argon signal came from the argon ion for sputtering. As to high-resolution spectra, only Fe spectra showed a good signal to noise ratio and can be analyzed with curve fitting. The high-resolution Fe2p3/2 spectrum of the sputtered clean steel surface and its curve fitting results are shown in Fig.6.2.3. The figure shows that only metal iron (Peak Position: 707.0eV, FWHM:1.38eV, %Gaussian: 40%, Tail length: 0.45, Tail scale: 60) existed on the surface and no other peaks such as oxide or hydroxide.

![Fig.6.2.2 A survey spectrum of a sputtered clean steel surface](image)

![Fig.6.2.3 A Fe2p3/2 high-resolution spectrum of a sputtered clean steel surface](image)
In the adsorption tests on a sputtered clean steel surface described later, the sample sputtered with an argon ion gun was transferred to the nitrogen atmospheric glove box and then followed by the adsorption procedure described in “3.3.5 Adsorption tests”. In other words, the sample was exposed to atmospheric nitrogen gas, which probably contains some contamination gas such as oxygen gas or H\(_2\)O gas before the adsorption test. Therefore, the following test and XPS measurements were conducted in order to characterize the disk surface just before the adsorption test. A washed clean disk was sputtered with an argon ion gun of XPS and then transferred to the nitrogen atmospheric glove box using the vacuum transfer cell. The cell was then opened in the glove box so that the sputtered sample was exposed to the nitrogen atmosphere. After one minute of exposure of the sample to nitrogen atmosphere, the sample was transferred to the XPS chamber using the nitrogen atmospheric transfer cell and then measured.

A survey spectrum of the disk surface is shown in Fig.6.2.4, where small amounts of carbon, oxygen, argon and nitrogen signals were detected besides an iron signal. The peak of C1s, O1s and N1s seems to be higher than those of sputtered clean steel surface shown in Fig.6.2.2. It is thought that the oxygen signal is attributable to its oxidation due to the contamination oxygen gas in the nitrogen atmosphere, and the carbon signal is attributable to organic contaminant in the glove box. As to the argon and nitrogen signals, it is thought that the argon signal is attributable to the embedded argon ion in the disk and the nitrogen signal is attributable to the adsorbed nitrogen gas on the disk surface. C1s, O1s, Fe2p3/2 and N1s high-resolution spectra of the disk surface and their curve fitting results are illustrated in Fig.6.2.5. The C1s spectrum (A) gives the best fit with four peaks, where the peak of 283.3eV is assigned to carbide from the substrate, the peak of 285.0eV is assigned to hydrocarbon, the peak of 286.6eV is attributable to –C-OH or –COC- from organic contamination and the peak of 288.5eV is attributable to –C=O from the organic contamination too. The O1s spectrum (B) gives the best fit with four peaks, where the peak of 529.9eV is assigned to oxide, the peak of 531.6eV is assigned to oxyhydroxide, the peak of 532.7eV is attributable to –C-OH or –COC- from the organic contamination and the peak of 534.3eV is considered to be attributable to adsorbed H\(_2\)O gas. The Fe2p3/2 spectrum (C) gives the best fit with two peaks, where the peak of 706.8eV is assigned to metal iron from the substrate and the peak of 710.2eV is assigned to iron (III) oxide. These results reveal that the sputtered clean surface was slightly oxidized and covered with organic layer even under such an isolated condition. The N1s spectrum (D) gives the best fit with two peaks, where the peak of 397.4eV is attributable to nitrogen gas adsorbed on the reactive steel surface, while source of the peak of 399.4eV is not clear but it is possible that the peak is attributable to amine phosphate existing as a contamination in the glove box.
6. Characterization of adsorbed films on steel surfaces

Fig. 6.2.4 A survey spectrum of the surface sputtered and exposed to nitrogen gas in the glove box

Fig. 6.2.5 High-resolution spectra of the surface sputtered and exposed to nitrogen gas in the glove box
6. Characterization of adsorbed films on steel surfaces

6.2.2 Re-oxidized steel surface

A steel disk for a tribological test washed with acetone and cyclohexane using an ultrasonic bath was introduced in the XPS chamber and sputtered its surface with Ar ion gun for 10 minutes at the energy of 15keV for 2mm x 2mm raster size. The sputtered disk was then taken out of the chamber and exposed to the air for one minute in order to be re-oxidized. The purpose of this procedure was to generate an oxidized steel surface that has very few organic coating layers, which may affect adsorption behavior of the additives. The re-oxidized disk was then introduced in the XPS chamber again and characterized.

A survey spectrum of the surface is shown in Fig.6.2.6. Strong signal of carbon, oxygen and iron were detected and small peak of argon was also detected on the sample, implying that a thick oxide layer was generated on the surface and an organic contamination layer also covered the surface. High-resolution spectrum of C1s, O1s and Fe2p3/2 for the re-oxidized steel surface and their curve fitting results are illustrated in Fig.6.2.7. The C1s high-resolution spectrum (A) gives the best fit with four peaks, where the lowest peak, 283.3eV is assigned to carbide from the substrate, 285.0eV is assigned to hydrocarbon of the organic contamination, 286.6eV is assigned to –C-OH or –COC-, which is also attributable to the organic contamination, and 288.8eV is assigned to carboxylate type carbon, which is also attributable to the organic contamination.

The O1s spectrum (B) gives the best fit with three peaks, where the lowest peak 530.0eV is assigned to oxide, mainly Fe$_2$O$_3$, 531.6eV is assigned to oxyhydroxide, FeOOH, and the highest peak 532.9eV is attributable to –C-OH from the organic contamination layer. The Fe2p3/2 high-resolution spectrum (C) gives the best fit with three peaks. The peak of 706.9eV is assigned to metal iron, the peak of 710.2eV is assigned to iron (III) oxide and the higher peak 711.8eV is assigned to oxyhydroxide.

![Fig.6.2.6 A survey spectrum of the re-oxidized steel surface](image-url)
6. Characterization of adsorbed films on steel surfaces

6.2.3 Plasma-cleaned steel surface

The plasma cleaner is a widely used cleaning system of a surface, which can remove residue and strongly bound hydrocarbon layers thereby improving wettability, chemical adhesiveness. The plasma cleaner is a compact electrodeless device that utilizes radio frequency to excite an argon, nitrogen, oxygen or air gas, which creates plasma. The plasma created is a partially ionized complex gas composed of electrons, ions, free radicals, photons of various energies and gas atoms. The glow discharge or plasma produces an energized gas flow that can modify the physicochemical characteristics of solid surfaces without affecting the underlying bulk properties of the material. A steel disk cleaned with acetone and cyclohexane using an ultrasonic bath was put in the chamber of the plasma cleaner and plasma-cleaned with an argon gas for one minute. The plasma-cleaned disk was immediately transferred to the XPS chamber using a plastic cell and characterized.

A survey spectrum of the plasma-cleaned steel surface is illustrated in Fig.6.2.8. The
figure reveals that small strong signals of oxygen and iron were detected, while carbon signal was quite small, implying that the strongly bound hydrocarbon layers was almost removed. The C1s, O1s and Fe2p3/2 high-resolution spectra of the plasma-cleaned steel surface and their curve fitting results are shown in Fig.6.2.9. The C1s spectrum (A) gives the best fit with three peaks, where the lowest peak of 285.0eV is assigned to hydrocarbon, the peak of 286.7eV is –C-OH or –COC- from the organic contamination layer, and the peak of 289.1eV is –C=O from the organic contamination layer. The O1s spectrum (B) gives the best fit with three peaks, where the lowest peak of 530.0eV is assigned to oxide, the peak of 531.7eV is assigned to oxyhydroxide and the peak of 532.9eV is attributable to –C-OH or –C=O from the contamination layer. The Fe2p3/2 spectrum (C) gives the best fit with three peaks, where the peak of 706.7eV is assigned to metal iron, the peak of 710.3eV is assigned to iron (III) oxide and the peak of 711.8eV is assigned to oxyhydroxide.

Fig.6.2.8 A survey spectrum of the plasma-cleaned steel surface

Fig.6.2.9 High-resolution spectra of the plasma-cleaned steel surface
6. Characterization of adsorbed films on steel surfaces

6.2.4 As-received steel surface

The as-received disk was mechanically polished with the procedure described in “3. Experimental, 3.2.4 Materials” by the supplier and then washed with acetone and cyclohexane using ultrasonic bath as described in “3.5 Adsorption test”.

In Fig. 6.2.10, a survey spectrum of the as-received steel disk surface is shown. Carbon, oxygen and iron signals were detected, whereas the carbon signal was much stronger than that of the re-oxidized surface or the plasma-cleaned surface, implying that quite a thick organic layer covered the surface. C1s, O1s and Fe2p3/2 high-resolution spectra of the as-received steel surface and their curve fitting results are shown in Fig. 6.2.11. The C1s spectrum (A) gives the best fit with three peaks, where the lowest peak 285.0 eV is assigned to hydrocarbon, the peak of 286.7 eV is assigned to –C-OH or –COC- from the organic contamination layer and the peak of 288.6 eV is assigned to –C=O from the organic contamination layer, too. The O1s spectrum (B) gives the best fit with three peaks, where the peak of 530.0 eV is assigned to oxide, the peak of 531.6 eV is assigned to oxyhydroxide and the peak of 532.8 eV is attributable to –C-OH, –C=O and adsorbed water from the contamination layer. The Fe2p3/2 spectrum (C) gives the best fit with three peaks, where the peak at 706.9 eV is assigned to metallic iron, the peak at 710.3 eV to iron (III) oxide and that one at 711.8 eV to oxy-hydroxide. The peak due to the photoelectrons emitted in the substrate, metallic iron, was barely detected due to the presence of the organic layer (contamination) and of the oxy-hydroxide layer in the outermost part of the surface.
6. Characterization of adsorbed films on steel surfaces

Fig. 6.2.10 A survey spectrum of the as-received steel surface

(A) C1s

(B) O1s

(C) Fe2p3/2

Fig. 6.2.11 High-resolution spectra of the as-received steel surface
6. Characterization of adsorbed films on steel surfaces

6.2.5 Summary of steel surfaces

Steel surfaces with the various surface pre-treatments were characterized with XPS in the previous sections (6.2.1-6.2.4). In this section, the obtained spectra will be compared in order to grasp how the surfaces differ from each other. In Fig.6.2.12 (A), survey spectra of the various conditions of steel surfaces, (1) the sputtered, (2) sputtered and exposed to nitrogen gas in the glove box, (3) sputtered and re-oxidized in air, (4) plasma cleaned, (5) no treatment (as-received) are shown. Each spectrum is normalized in such a way that the maximum value =1.0. The figure shows that the sputtered surface has only iron peaks, whereas the surface exposed to nitrogen gas in the glove box following sputtering shows a slight oxygen peak and carbon peak which are considered to be due to oxidation, and due to adsorption of organic contamination, respectively. Oxidation of the re-oxidized surface is much higher than the surface sputtered and transferred to the glove box. The re-oxidized surface shows relatively intense oxygen peak, while its carbon peak stays at low level. The plasma cleaned surface and the as-received surface seem to be fully oxidized. However contamination levels of the surfaces are not at the same level. The plasma-cleaned surface has very little carbon contamination.

(A) survey spectra  
(B) Fe2p3/2 high-resolution spectra

Fig.6.2.12 Spectra of steel surfaces following various mechanical treatments
6. Characterization of adsorbed films on steel surfaces

High-resolution spectra of the surfaces will support the aforementioned overview. In Fig.6.2.12 (B), Fe2p3/2 spectra with curve fitting results of the surfaces are shown. The spectra are normalized in the same way as the survey spectra, consequently quantitative matters cannot be discussed here. (The quantitative matters will appear later) The figure reveals that the sputtered surface has no oxide layer, and the surface sputtered and transferred to the glove box is slightly oxidized. The re-oxidized surface is considerably oxidized and the plasma-cleaned surface and the as-received surface seem to be fully oxidized.

6.3 Adsorbed film of amine phosphate

6.3.1 Adsorption on sputtered surface

A sample sputtered with an argon ion gun was transferred to the nitrogen atmospheric glove box using the vacuum transfer cell and then immersed in pure amine phosphate for 24 hours in the glove box. The disk was then cleaned with cyclohexane using the ultrasonic bath in the glove box in order to eliminate the excess additive on the surface. The washed sample was transferred to the XPS chamber in the nitrogen atmospheric transfer cell followed by characterization with XPS.

A survey spectrum of the adsorbed film on the sputtered surface is shown in Fig.6.3.1, where carbon, oxygen, iron, nitrogen, phosphorus and small amount of argon signal were detected. It is presumed that the argon signal is attributable to embedded argon ion when sputtered. C1s, O1s, P2p, N1s and Fe2p3/2 high-resolution spectra of the adsorbed film on the sputtered surface and their curve fitting results are shown in Fig.6.3.2. The C1s spectrum (A) gives the best fit with four peaks, where the peak of 283.3eV is assigned to carbide from the substrate, the peak of 285.0eV is assigned to hydrocarbon, the peak of 286.6eV is assigned to –C-OH, –COC- and –COP-, and the peak of 288.2eV is assigned to –C=O. The O1s spectrum (B) gives the best fit with three peaks, where the peak of 530.1eV is assigned to oxide, the peak of 531.5eV is assigned to P=O bond of the phosphate and FeOOH, the peak of 533.1eV is assigned to –COP-bond of phosphate and H2O. However, it is not distinguishable only from the O1s spectrum weather this phosphate is an organic one or an inorganic. The P2p high-resolution spectrum (C) gives the best fit with one pair of 2p3/2 peak and 2p1/2 peak. The binding energy of the 2p3/2 peak, 133.5eV, is presumed to be assigned to phosphate. There is a difference of the binding energy value in 0.5eV between the adsorbed film and pure amine phosphate, which is considered to be a significant difference. This phosphate is surmised to be ferric phosphate rather than organic phosphate judging from the reference value where the P2p3/2 binding energy value of FePO4 is 133.8eV and that of
Fe₃(PO₄)₂ is 133.5eV. The Fe2p3/2 spectrum (D) gives the best fit with three peaks, where the peak of 707.0eV is assigned to metal iron from the substrate, the peak of 710.2eV is assigned to iron (III) oxide, the peak of 712.4eV is assigned to (oxy-) hydroxide and iron phosphate. Therefore, on the basis of Fe2p, O1s and P2p signals, it might be suggested the formation of ferric phosphate. It is noteworthy that the iron oxide peak of the adsorbed steel surface is fairly strong and its position is around 710.2eV. The iron oxide peak of the sputtered steel surface just before the adsorption test, was quite small as shown in Fig.6.2.4 and Fig.6.2.5, and its peak position was that of FeO. This fact indicates that by contacting with amine phosphate, the surface was oxidized to iron (III) oxide while forming the ferric phosphate. The N1s spectrum (E) showed a poor signal to noise ratio but it gave the best fit with three peaks. The peak of 397.2eV, which was also detected on the surface before the adsorption test, would be assigned to adsorbed nitrogen gas, and the peak of 399.8eV would be assigned to an organic amine, >NH, and the peak of 401.8eV would be assigned to an ionized organic amine, >NH₂⁺. In any case, the nitrogen signal was very weak, and thereby implying, that there was only little nitrogen related to amine phosphate part of amine phosphate on the surface.

Fig.6.3.1 A survey spectrum of the adsorbed film of amine phosphate on the sputtered steel surface
Fig. 6.3.2 High-resolution spectra of the adsorbed film of amine phosphate on the sputtered steel surface
6.3.2 Adsorption on re-oxidized surface

A steel disk washed with acetone and cyclohexane using the ultrasonic bath, followed by sputtering with argon ion gun, was immersed in pure amine phosphate for 24 hours. The disk was then washed with cyclohexane using the ultrasonic bath again in order to eliminate the excess of the amine phosphate, followed by XPS analysis.

A survey spectrum of the adsorbed film on the re-oxidized steel surface was shown in Fig.6.3.3, where carbon, oxygen, phosphorus, iron and small amount of argon signals were detected, whereas nitrogen signal was barely observed. It is presumed that the argon signal is attributable to embedded argon ion when sputtered. C1s, O1s, P2p and Fe2p3/2 high-resolution spectra of the adsorbed film on the re-oxidized surface and their curve fitting results are shown in Fig.6.3.4. The C1s spectrum (A) gives the best fit with two peaks, where the peak of 285.0eV is assigned to hydrocarbon and the peak of 286.7eV is assigned to –C-OH, –COC- and –COP-. The peak around 288.5eV, which was observed with the adsorbed film on the sputtered surface, was not detected in this case. The O1s spectrum (B) gives the best fit with three peaks, where the peak of 530.2eV is assigned to oxide, the peak of 531.6eV is assigned to –COP- bond of the phosphate and FeOOH, the peak of 533.1eV is assigned to P=O bond of phosphate and adsorbed H2O. The P2p high-resolution spectrum (C) gives the best fit with one pair of 2p3/2 peak and 2p1/2 peak. The binding energy of the 2p3/2 peak, 133.5eV, is presumed to be assigned to phosphate. There is a difference of the binding energy value in 0.4eV between and the adsorbed film and pure amine phosphate, which is considered to be a significant difference. This phosphate is surmised to be ferric phosphate rather than organic phosphate judging from the reference value where the P2p3/2 binding energy value of FePO4 is 133.8eV and that of Fe3(PO4)2 is 133.5eV. The Fe2p3/2 spectrum (D) gives the best fit with three peaks, where the peak of 707.0eV is assigned to metal iron from the substrate, the peak of 710.2eV is assigned to iron (III) oxide, the peak of 712.4eV is assigned to the superimposition of oxy-hydroxide and iron phosphate contributions. Therefore, on the basis of Fe2p, O1s and P2p signals, it might be suggested the formation of ferric phosphate.
6. Characterization of adsorbed films on steel surfaces

![Survey spectrum of the adsorbed film on the re-oxidized steel surface](image)

Fig. 6.3.3 A survey spectrum of the adsorbed film on the re-oxidized steel surface

(A) C1s  
(B) O1s  
(C) P2p  
(D) Fe2p3/2

![High-resolution spectra of the adsorbed film on the re-oxidized steel surface](image)

Fig. 6.3.4 High-resolution spectra of the adsorbed film on the re-oxidized steel surface
6. Characterization of adsorbed films on steel surfaces

6.3.3 Adsorption on plasma-cleaned surface

A washed and plasma-cleaned steel disk was immersed in pure amine phosphate for 24 hours and washed with cyclohexane using an ultrasonic bath again in order to eliminate the excess of the amine phosphate. The steel disk after the adsorption test was then measured by XPS.

A survey spectrum of the adsorbed film on the plasma-cleaned surface is shown in Fig.6.3.5, where carbon, oxygen, phosphorus, iron and small amount of nitrogen signal were detected. C1s, O1s, P2p, Fe2p3/2 and N1s high-resolution spectra of the adsorbed film on the re-oxidized surface and their curve fitting results are shown in Fig.6.3.6. The C1s spectrum (A) gives the best fit with three peaks, where the peak of 285.0eV is assigned to hydrocarbon, the peak of 286.8eV is assigned to –C-OH, –COC- and –COP-, the peak of 288.9eV is assigned to –C=O. The O1s spectrum (B) gives the best fit with three peaks, where the peak of 530.1eV is assigned to oxide, the peak of 531.4eV is assigned to –COP- bond of the phosphate and FeOOH, the peak of 532.9eV is assigned to P=O bond of the phosphate and adsorbed H2O. The P2p high spectrum (C) gives the best fit with one pair of 2p3/2 peak and 2p1/2 peak. The binding energy of the 2p3/2 peak, 133.5eV, is presumed to be assigned to ferric phosphate. The Fe2p3/2 spectrum (D) gives the best fit with three peaks, where the peak of 706.9eV is assigned to metal iron from the substrate, the peak of 710.3eV is assigned to iron (III) oxide, the peak of 712.4eV is assigned to (oxy-) hydroxide and iron phosphate. The N1s spectrum (E) showed a poor signal to noise ratio but it could give the best fit with two peaks, where the peak of 399.7eV would be assigned to an organic amine, >NH, and the peak of 401.6eV would be assigned to an ionized organic amine, >NH$_2^+$. In any case, the nitrogen signal was very weak and thereby implying, that there was only little nitrogen related to alkyl amine part of amine phosphate on the surface.

![Fig.6.3.5 A survey spectrum of the adsorbed film of amine phosphate on the plasma-cleaned steel surface](image-url)
6. Characterization of adsorbed films on steel surfaces

Fig. 6.3.6 High-resolution spectra of the adsorbed film of amine phosphate on the plasma-cleaned steel surface
6. Characterization of adsorbed films on steel surfaces

6.3.4 Adsorption on as-received surface

A steel disk washed with the usual procedure was immersed in pure amine phosphate for 24 hours and washed with cyclohexane using an ultrasonic bath again in order to eliminate the excess of the amine phosphate. The disk after the adsorption test was then measured by XPS.

A survey spectrum of the adsorbed film on the as-received steel surface is shown in Fig.6.3.7, where carbon, oxygen and iron signals were detected, whereas phosphorus and nitrogen signals were barely observed. This implies that the adsorption film of amine phosphate was fairly thin or barely formed on the as-received surface. C1s, O1s, P2p, Fe2p3/2 and N1s high-resolution spectra of the adsorbed film on the as-received surface and their curve fitting results are shown in Fig.6.3.8. The C1s spectrum (A) gives the best fit with three peaks, where the peak of 285.0eV is assigned to hydrocarbon, the peak of 286.6eV is assigned to –C-OH, –COC- and –COP-, the peak of 288.7eV is assigned to –C=O. The O1s spectrum (B) gives the best fit with three peaks, where the peak of 530.0eV is assigned to oxide, the peak of 531.6eV is assigned to –COP-bond of the phosphate and FeOOH and the peak of 532.8eV is assigned to P=O bond of the phosphate and adsorbed H2O. The P2p high spectrum (C) gives the best fit with one pair of 2p3/2 peak and 2p1/2 peak. The binding energy of the 2p3/2 peak, 133.4eV, is presumed to be assigned to ferric phosphate. The Fe2p3/2 spectrum (D) gives the best fit with three peaks, where the peak of 707.0eV is assigned to metal iron from the substrate, the peak of 710.1eV is assigned to iron (III) oxide, the peak of 712.4eV is assigned to (oxy-)- hydroxide and iron phosphate. Therefore, the phosphate related peaks of C1s O1s and P2p are concluded to be ferric phosphate. The N1s spectrum (E) showed a poor signal to noise ratio but it gave the best fit with two peaks, where the peak of 399.8eV would be assigned to an organic amine, >NH, and the peak of 401.7eV would be assigned to an ionized organic amine, >NH2+. In any case, the nitrogen signal was very weak, and thereby implying, that there was only little nitrogen related to alkyl amine part of amine phosphate on the surface.

![Fig.6.3.7 A survey spectrum of the adsorbed film of amine phosphate on the as-received steel surface](image-url)
Fig. 6.3.8 High-resolution spectra of the adsorbed film of amine phosphate on the as-received steel surface
6. Characterization of adsorbed films on steel surfaces

6.3.5 Summary of adsorption of amine phosphate

Adsorption films of amine phosphate formed on steel surfaces following aforementioned various surface treatments have been characterized with XPS in the previous several sections (6.3.1- 6.3.4). In this section, the obtained spectra will be compared in order to grasp how the surfaces differ from each other. In Fig.6.3.9 (A), survey spectra of adsorption films of amine phosphate formed on the various conditions of steel surfaces, (1) sputtered, (2) sputtered and re-oxidized in air, (3) plasma cleaned, (4) no treatment (as-received) are shown. Each spectrum is normalized in such a way that the maximum value =1.0. The figure reveals that the adsorption film on the sputtered surface shows an intense peak of phosphorus compared with the other surfaces, whereas all surfaces show more or less the same intensities concerning the other peaks such as iron, oxygen and carbon peak. This indicates that the phosphorus compound exists on the sputtered surface more than the other surfaces.

High-resolution spectra of the surfaces will support the aforementioned overview. In Fig.6.3.9 (B), O1s spectra with curve fitting results of the surfaces are shown. The spectra are normalized in the same way as the survey spectra, consequently quantitative matter cannot be discussed here (The quantitative matter will be discussed later). The figure reveals that on the as-received surface, the peak of oxide is high compared with the peak of oxyhydroxide or phosphate. On the re-oxidized and the plasma-cleaned surface, both the oxide peak and the hydroxide/phosphate peak are the same level, and on the sputtered surface, the peak of oxyhydroxide/phosphate is high compared with the oxide peak. Next, as to Fe2p3/2 spectra, phosphate peaks of sputtered surface and re-oxidized surface are high compared with that of plasma-cleaned surface or as-received surface. These facts imply that amine phosphate has a high reactivity over a metal surface and then forms iron phosphate film. On the other hand, when the surface is covered with an oxide layer or an organic layer of contamination, iron phosphate is barely formed. However, as a matter of fact, iron phosphate is detected on the surface covered with oxide layer such as the re-oxidized surface, the plasma-cleaned surface, the as-received surface, accordingly amine phosphate react with the oxide to some extent.
6. Characterization of adsorbed films on steel surfaces

Fig. 6.3.12 Spectra of adsorbed films of amine phosphate formed on steel surfaces following various surface treatments

(A) Survey spectra

(B) O1s high-resolution spectra

(C) Fe2p3/2 high-resolution spectra
6. Characterization of adsorbed films on steel surfaces

6.4 Adsorbed film of phosphoric acid ester

6.4.1 Adsorption on sputtered surface

Next, adsorbed film on a sputtered steel surface of one of the two constituent molecules of amine phosphate, phosphoric acid ester, was investigated with the same experimental procedure. That is, a sample sputtered with an argon ion gun was transferred to the nitrogen atmospheric glove box using the vacuum transfer cell and then immersed in pure phosphoric acid ester for 24 hours in the glove box. The disk was then cleaned with cyclohexane using an ultrasonic bath in the glove box in order to eliminate the excess of additive on the surface. The washed sample was transferred to the XPS chamber in the nitrogen atmospheric transfer cell followed by measurement by XPS.

A survey spectrum of the adsorbed film on the sputtered surface is shown in Fig.6.4.1, where carbon, oxygen, phosphorus, iron and silicon were detected, whereas the argon signal, observed with the adsorbed film of amine phosphate, were not detected in this case. Another remarkable point is that the iron signal is fairly small, implying that a thick film covers the surface. C1s, O1s, P2p and Fe2p3/2 high-resolution spectra of the adsorbed film on the sputtered surface and their curve fitting results are shown in Fig.6.4.2. The C1s spectrum (A) gives the best fit with three peaks, where the peak of 285.0eV is assigned to hydrocarbon, the peak of 286.5eV is assigned to –C-OH, –COC- and –COP-, and the peak of 288.1eV is assigned to –C=O. The peak attributable to carbide from the substrate was not seen in this sample. The O1s spectrum (B) gives the best fit with four peaks, where the peak of 530.1eV is assigned to oxide, the peak of 531.6eV is assigned to –COP- bond of the phosphate and FeOOH, the peak of 532.8eV is assigned to P=O bond of phosphate and H2O, and the peak of 533.7eV is attributable to SiO2 contamination in the additive. The P2p high spectrum (C) gives the best fit with a pair of 2p3/2 peak and 2p1/2 peak. The binding energy of 2p3/2, 133.9eV, is presumed to be assigned to phosphate. The Fe2p3/2 spectrum (D) gives the best fit with three peaks, where the peak of 706.8eV is assigned to metal iron from the substrate, the peak of 710.4eV is assigned to iron (III) oxide and the peak of 712.4eV is assigned to (oxy-) hydroxide and iron phosphate. It is also noticeable that the fairly strong iron oxide peak of the steel surface appeared around 710.4eV although the iron oxide peak of the sputtered steel surface just before the adsorption test was quite small. This fact indicates that in the case of phosphoric acid ester too, the surface was oxidized to iron (III) oxide while forming the ferric phosphate. It is still not clear that these two reactions take place simultaneously or step by step.
6. Characterization of adsorbed films on steel surfaces

Fig. 6.4.1 A survey spectrum of the adsorbed film of phosphoric acid ester on the sputtered steel surface

Fig. 6.4.2 High-resolution spectra of the adsorbed film of phosphoric acid ester on the sputtered steel surface
6. Characterization of adsorbed films on steel surfaces

6.4.2 Adsorption on re-oxidized surface

Adsorbed film of phosphoric acid ester on a re-oxidized surface was investigated with the same procedure. A steel disk washed with the same procedure, followed by sputtering with argon ion gun, was immersed in pure phosphoric acid ester for 24 hours in air. The disk was then washed with cyclohexane using the ultrasonic bath again in order to eliminate the excess additive, followed by XPS analysis. A survey spectrum of the adsorbed film on the sputtered surface is shown in Fig.6.4.3, where carbon, oxygen, phosphorus and iron signals were detected. C1s, O1s, P2p and Fe2p3/2 high-resolution spectra of the adsorbed film on the sputtered surface and their curve fitting results are shown in Fig.6.4.4. The C1s spectrum (A) gives the best fit with four peaks, where the peak of 285.0eV is assigned to hydrocarbon, the peak of 286.8eV is assigned to –C=OH or –COC- and the peak of 288.8eV is assigned to –C=O. The O1s spectrum (B) gives the best fit with three peaks, where the peak of 530.3eV is assigned to oxide, the peak of 531.8eV is assigned to –COP- bond of the phosphate and FeOOH, the peak of 533.2eV is assigned to P=O bond of phosphate and H2O, and the peak of 534.0eV is attributable to SiO2 contamination involved in the additive. The P2p high spectrum (C) gives the best fit with one pair of 2p3/2 peak and 2p1/2 peak. The binding energy of the 2p3/2 peak, 133.9eV, is presumed to be assigned to phosphate. The Fe2p3/2 spectrum (D) gives the best fit with three peaks, where the peak of 706.9eV is assigned to metal iron from the substrate, the peak of 710.3eV is assigned to oxide and the peak of 712.4eV is assigned to (oxy-) hydroxide and iron phosphate.

![Fig.6.4.3](image_url)  
A survey spectrum of the adsorbed film of phosphoric acid ester on the re-oxidized steel surface
6. Characterization of adsorbed films on steel surfaces

6.4.3 Adsorption on as-received surface

Next, adsorbed film of one of phosphoric acid ester on an as-received steel surface was investigated with the same experimental procedure. That is, a steel disk washed with the usual procedure was immersed in pure phosphoric acid ester for 24 hours and washed with cyclohexane using an ultrasonic bath again in order to eliminate excess additive, where the aforementioned procedure was done in the air. The disk after the adsorption test was then measured by XPS.

A survey spectrum of the adsorbed film on the sputtered surface is shown in Fig.6.4.5, where carbon, oxygen, phosphorus and iron signals were detected. C1s, O1s, P2p and Fe2p3/2 high-resolution spectra of the adsorbed film on the sputtered surface and their curve fitting results are shown in Fig.6.4.6. The C1s spectrum (A) gives the best fit with three peaks,
6. Characterization of adsorbed films on steel surfaces

where the peak of 285.0eV is assigned to hydrocarbon, the peak of 286.8eV is assigned to –C-OH, –COC- and –COP-, and the peak of 288.8eV is assigned to –C=O. The peak attributable to carbide from the substrate was not seen in this sample. The O1s spectrum (B) gives the best fit with three peaks, where the peak of 531.8eV is assigned to –COP- bond of the phosphate and FeOOH, the peak of 533.0eV is assigned to P=O bond of phosphate and H2O, the peak of 533.9eV is attributable to SiO2 contamination involved in the additive. The P2p high spectrum (C) gives the best fit with one pairs of 2p3/2 peak and 2p1/2 peak, where the binding energy of the 2p3/2 peak, 134.3eV, is assigned to phosphate. As far as the Fe2p3/2 spectrum (D) is concerned, it is found to be composed of four Gaussian-lorentzian peaks: the one at the lowest binding energy is attributed to the metallic iron resulting from the substrate whereas the signals found at 710.2eV, 712.6eV and 715.1eV are due to the overlayer which is constituted of iron oxy-hydroxide and iron phosphate.

Fig.6.4.5 A survey spectrum of the adsorbed film of phosphoric acid ester on as-received steel surface

Fig.6.4.6 High-resolution spectra of the adsorbed film of phosphoric acid ester on as-received steel surface
6. Characterization of adsorbed films on steel surfaces

Fig. 6.4.6 High-resolution spectra of the adsorbed film of phosphoric acid ester on as-received steel surface

6.4.4 Summary of adsorption of phosphoric acid ester

Adsorption films of phosphoric acid ester formed on steel surfaces following aforementioned various surface pre-treatments were characterized with XPS in the previous several sections (6.4.1-6.4.3). In this section, the obtained spectra will be compared in order to grasp how the surfaces differ from each other. In Fig. 6.4.7 (A), survey spectra of adsorption films of phosphoric acid ester formed on various conditions of steel surfaces, (1) sputtered, (2) sputtered and re-oxidized in air, (3) no treatment (as-received) are shown. Each spectrum is normalized in such a way that the maximum value = 1.0. The figure reveals that the adsorption film on the as-received surface has high intensity of oxygen and phosphorus peaks compared with the sputtered surface or the re-oxidized surface.

Fe2p3/2 spectra with curve fitting results of the surfaces are shown in Fig. 6.4.7 (C). The spectra are normalized in the same way as the survey spectra, consequently quantitative matter cannot be discussed here. (The quantitative matter will be discussed later) The figure shows that the adsorption films on the sputtered surface and the re-oxidized surface have more or less the same spectrum shape, whereas the as-received surface has high intensity of phosphate peak (712.4eV) compared with the other two surfaces. The same tendency can be seen also on O1s spectra shown in Fig. 6.4.7 (B). That is, the phosphate related peaks (bridging: 531.5eV and non-bridging: 533.0eV) of the adsorption film on as-received surface are high compared with the other two surfaces, sputtered surface and re-oxidized surface. These facts imply that phosphoric acid ester has a high reactivity or adsorbability over an oxidized surface rather than a metal surface. This tendency is different from the case of amine phosphate, in which phosphoric acid ester is neutralized with alkyl amine. The mechanism of reaction will be discussed in the chapter of "8. General discussion".
6. Characterization of adsorbed films on steel surfaces

Fig. 6.4.7 Spectra of adsorption films of phosphoric acid ester formed on steel surfaces following various surface treatments

- **A** Survey spectra
- **B** O1s high-resolution spectra
- **C** Fe2p3/2 high-resolution spectra
6. Characterization of adsorbed films on steel surfaces

6. 5 Adsorbed film of alkyl amine

6.5.1 Adsorption on sputtered surface

Next, adsorbed film on a sputtered steel surface of the other constituent of amine phosphate, alkyl amine, was investigated with the same experimental procedure. A sample sputtered with an argon ion gun was transferred to the nitrogen atmospheric glove box using a vacuum transfer cell and then immersed in pure alkyl amine for 24 hours in the glove box. The disk was then cleaned with cyclohexane using an ultrasonic bath in the glove box in order to eliminate the excess of additive on the surface. The washed sample was transferred to the XPS chamber in the nitrogen atmospheric transfer cell followed by measurement by XPS.

A survey spectrum of the adsorbed film on the sputtered surface is shown in Fig.6.5.1, where carbon, oxygen, iron, nitrogen and small amount of argon signal were detected. It is thought that the argon signal is attributable to embedded argon ion when sputtered. C1s, O1s, N1s and Fe2p3/2 high-resolution spectra of the adsorbed film on the sputtered surface and their curve fitting results are shown in Fig.6.5.2. The C1s spectrum (A) gives the best fit with three peaks, where the peak of 285.0 eV is assigned to the alkyl chain; the less intense signal at 286.5 eV can be assigned to the C-N bond together with a contribution of contamination and the third one to adsorbed C=O containing-species. The O1s spectrum (B) results to be fitted with three model curve: the first one found at 529.9 eV is assigned to oxide, the second one to iron hydroxide, the peak at 532.8 eV is due to the adsorbed water. The Fe2p3/2 spectrum (C) gives the best fit with three peaks, where the peak of 706.7 eV is assigned to metal iron from the substrate and the peak of 710.2 eV is assigned to iron (III) oxide and the peak of 711.9 eV is assigned to oxyhydroxide. The N1s spectrum (D) gives the best fit with two peaks, where the peak, 399.9 eV, is assigned to an organic amine, >NH and the peak of 397.4 eV is considered to be adsorbed nitrogen gas.

![Fig.6.5.1 A survey spectrum of the adsorbed film of alkyl amine on the sputtered steel surface](image-url)
6. Characterization of adsorbed films on steel surfaces

Next, adsorbed film of alkyl amine on an as-received steel surface was investigated with the same experimental procedure. A steel disk washed with the usual procedure was immersed in pure alkyl amine for 24 hours and washed with cyclohexane using an ultrasonic bath again in order to eliminate the excess of additive, where the aforementioned procedure was done in the air. The disk after the adsorption test was then measured by XPS.

A survey spectrum of the adsorbed film on the as-received surface is shown in Fig.6.5.3, where carbon, oxygen, iron and nitrogen signals were detected. C1s, O1s, N1s and Fe2p3/2 high-resolution spectra of the adsorbed film on the sputtered surface and their curve fitting results are shown in Fig.6.5.4. The C1s spectrum (A) gives the best fit with three peaks, where the peak of 285.0eV is assigned to hydrocarbon, the peak of 286.7eV is assigned to –C-O, –COC- and –CN-, and the peak of 288.6eV is assigned to –C=O. The O1s spectrum

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Fig.6.5.2 High-resolution spectra of the adsorbed film of alkyl amine on the sputtered steel surface

6.5.2 Adsorption on as-received surface

Next, adsorbed film of alkyl amine on an as-received steel surface was investigated with the same experimental procedure. A steel disk washed with the usual procedure was immersed in pure alkyl amine for 24 hours and washed with cyclohexane using an ultrasonic bath again in order to eliminate the excess of additive, where the aforementioned procedure was done in the air. The disk after the adsorption test was then measured by XPS.

A survey spectrum of the adsorbed film on the as-received surface is shown in Fig.6.5.3, where carbon, oxygen, iron and nitrogen signals were detected. C1s, O1s, N1s and Fe2p3/2 high-resolution spectra of the adsorbed film on the sputtered surface and their curve fitting results are shown in Fig.6.5.4. The C1s spectrum (A) gives the best fit with three peaks, where the peak of 285.0eV is assigned to hydrocarbon, the peak of 286.7eV is assigned to –C-O, –COC- and –CN-, and the peak of 288.6eV is assigned to –C=O. The O1s spectrum
6. Characterization of adsorbed films on steel surfaces

(B) gives the best fit with three peaks, where the peak of 529.9eV is assigned to oxide, the peak of 531.5eV is assigned to FeOOH, the peak of 532.8eV is assigned to the adsorbed water. The Fe2p3/2 spectrum (C) gives the best fit with three peaks, where the peak of 706.9eV is assigned to metal iron from the substrate, the peak of 710.1eV is assigned to iron (III) oxide and the peak of 711.9eV is assigned to oxyhydroxide. The N1s spectrum (D) gives the best fit with one peak, where the peak of 399.9eV is assigned to an organic amine, >NH

![Survey spectrum of the adsorbed film of alkyl amine on the as-received steel surface](image1)

![High-resolution spectra of the adsorbed film of alkyl amine on the as-received steel surface](image2)

Fig.6.5.3 A survey spectrum of the adsorbed film of alkyl amine on the as-received steel surface

Fig.6.5.4 High-resolution spectra of the adsorbed film of alkyl amine on the as-received steel surface
6. Characterization of adsorbed films on steel surfaces

![Graphs of Fe2p3/2 and N1s spectra.](image)

(C) Fe2p3/2

(D) N1s

Fig. 6.5.4 High-resolution spectra of the adsorbed film of alkyl amine on the as-received steel surface

### 6.5.3 Summary of adsorption of alkyl amine

Adsorption films of alkyl amine formed on steel surfaces following aforementioned various surface treatments were characterized with XPS in the previous two sections (6.5.1-6.5.2). In this section, the obtained spectra will be compared in order to grasp how the surfaces differ from each other. In Fig. 6.5.5 (A), survey spectra of adsorption films of alkyl amine formed on two different conditions of steel surfaces, (1) sputtered, (2) no treatment (as-received) are shown. Each spectrum is normalized in such a way that the maximum value =1.0. As can be seen from the figure, the two spectra show more or less the same intensities for Fe2p, O1s and C1s whereas N1s signal is less intense, which might indicate that the alkyl amine is barely adsorbed.

Next, high-resolution spectra of Fe2p3/2 and O1s of the surfaces with curve fitting results are shown in Fig. 6.5.7 (B) and (C), respectively. The spectra are normalized in the same way as the survey spectra. The figure shows that the sputtered surface is fairly oxidized but there seems to be no nitrogen related peak on both Fe2p3/2 and O1s spectra of the sputtered surface. Since non-changes are observed on the iron and oxygen signal, a chemical reaction with formation of new Fe-N or N-O bonds has to be excluded, thus its main function is to work as a neutralizer of phosphoric acid ester. Nevertheless, judging from the fact that amine phosphate and phosphoric acid ester have different preferences of surface in terms of adsorption, it is obvious that alkyl amine play an important role of adsorption of amine phosphate. The detail of the adsorption mechanism will be discussed in the chapter "8. General discussion".

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6. Characterization of adsorbed films on steel surfaces

Fig. 6.5.7 Spectra of adsorption films of phosphoric acid ester formed on steel surfaces following various surface treatments

(A) Survey spectra

(B) O1s high-resolution spectra

(C) Fe2p3/2 high-resolution spectra
6. Characterization of adsorbed films on steel surfaces

6.6 Quantitative analysis

6.6.1 Analytical methods

The surface compositions of solid are not always the same as their bulk compositions. It is, therefore, necessary to adopt an appropriate method for quantitative analysis of the compositions of material surfaces less than several nanometers in thickness. There have been some reports regarding the quantitative analysis of surface compositions of steel by combining AES and/or XPS with ion sputtering [2-5]. However the ion sputtering occasionally causes a change in compositions on the surface. Therefore, it would be better to determine the composition of both the surface film and substrate surface without applying the ion sputtering technique. Here, a non-destructive quantification of the steel surface with various treatments was conducted using a simple model of three layer structure first proposed by Asami et. al [6-8] and then modified by Rossi et. al [9-11]. In this model, it is assumed that for a normal steel surface, the substrate is covered with a homogeneous middle layer of oxide and a homogeneous topmost layer of contaminant, as illustrated in Fig.6.6.1.

![Fig.6.6.1 A structural model for coverage of the steel substrate with ion oxide layer (middle layer) and organic contamination layer (topmost layer)](image)

In this model, the surface structure has a step function-like interface and no concentration gradient within each layer. Under this assumption, a fundamental equation for photo-electron intensity of $i$ element in the middle layer, $j$ element in the substrate and $k$ element in the contaminant layer can be conventionally given as follows [12-14]:

$$I_{i}^{ox} = \left[ (g_i \sigma_i^{ox} C_i^{ox} \rho_i \Lambda_i^{ox})/A_i \right] \times [1-\exp(-t/\Lambda_i^{ox})]\exp(-l/\Lambda_i^{con}) \quad (6.6.1)$$

$$I_{j}^{m} = \left[ (g_j \sigma_j^{m} C_j^{m} \rho_m \Lambda_j)/A_j \right] \times \exp(-t/\Lambda_j^{ox})\exp(-l/\Lambda_j^{con}) \quad (6.6.2)$$
6. Characterization of adsorbed films on steel surfaces

\[ I_k^{\text{con}} = \left[ (g_k \sigma_k^{\text{con}} C_k^{\text{con}} \rho_k^{\text{con}} \Lambda_k^{\text{con}})/A_k \right] \times \left[ 1 - \exp(-l / \Lambda_k^{\text{con}}) \right] \]  \hspace{1cm} (6.6.3)

where

- \( I \) = integrated intensity (counts x eVs\(^{-1}\))
- \( A \) = atomic weight,
- \( g \) = instrumental factor,
- \( t \) = oxide/hydroxide layer thickness,
- \( l \) = contaminant layer thickness
- \( \rho \) = density (gcm\(^{-3}\)),
- \( \sigma \) = photo-ionization cross-section value
- \( \Lambda \) = mean free-path value
- \( C \) = molar fraction

The superscripts \( \text{m} \), \( \text{ox} \) and \( \text{con} \) correspond to metal (substrate), oxide (middle layer) and contaminant (topmost layer), respectively. The photo-ionization cross-section values \( \{ \sigma(h\gamma, \gamma, i) \} \) were taken from Ref. 15 except for that of oxygen in the oxide layer. For the photo-ionization cross-section value for oxygen in the middle layer was take from Ref. 7 where \( \sigma_{\text{Fe(ox)}} / \sigma_{\text{O(ox)}} = 1.45 \). No asymmetry function are required in this case because in the case of the instrument used, ESCA PHI5700, the angle of the detected electrons with respect to the X-ray source is 54 deg, consequently asymmetry function can be canceled. The instrumental factor values \( g \) for this experimental condition was calculated as \( g = \left[ a^2/(a^2 + (KE/Ep)^2) \right]^b \) with KE= kinetic energy, Ep = 23.5eV, \( a = 13.32 \) and \( b = 0.08 \). The mean free-path values \( \Lambda(E_{\text{kin}}) \) of the electrons were calculated as \( \Lambda_i = B / E_{\text{kin}} \), with \( B = 0.054 \) for elements in their formal oxidation state of zero; \( B = 0.096 \) for the oxidized forms; \( B = 0.087 \) when taking into account the attenuation due to the contamination layer [17]. The emission angle of the detected electrons to normal of a sample surface was \( \theta = 45 \) deg.

The attenuation terms in the above equations contain the mean free path \( \Lambda_i \) for the oxide whereas the pre-exponential terms of \( \Lambda_j \) depend on the origin of the electrons (metal or oxide). The densities of steel substrate \( \rho^m \) and oxide layer \( \rho^{\text{ox}} \) used in the calculation were 7.93 gcm\(^{-3}\) and 5 gcm\(^{-3}\), respectively.

Taking the ratio of each intensity to \( I_o^{\text{ox}} \), the following equations can be obtained,

\[ \frac{I_i^{\text{ox}}}{I_o^{\text{ox}}} = \frac{g_i \cdot \sigma_i^{\text{ox}} \cdot \Lambda_i^{\text{ox}} \cdot A_i}{g_o \cdot \sigma_o^{\text{ox}} \cdot \Lambda_o \cdot A_o} \cdot \frac{C_i^{\text{ox}}}{C_o^{\text{ox}}} \cdot \frac{1 - \exp(-l / \Lambda_i^{\text{ox}})}{1 - \exp(-l / \Lambda_o^{\text{ox}})} \cdot \exp(l / \Lambda_o^{\text{ox}} - l / \Lambda_i^{\text{ox}}) \]  \hspace{1cm} (6.6.4)

\[ \frac{I_j^{\text{ox}}}{I_o^{\text{ox}}} = \frac{g_j \cdot \sigma_j^{\text{ox}} \cdot \Lambda_j^{\text{ox}} \cdot A_j}{g_o \cdot \sigma_o^{\text{ox}} \cdot \Lambda_o \cdot A_o} \cdot \frac{C_j}{C_o} \cdot \rho_j^{\text{ox}} \cdot \rho^m \cdot \frac{1 - \exp(-l / \Lambda_j^{\text{ox}})}{1 - \exp(-l / \Lambda_o^{\text{ox}})} \cdot \exp(l / \Lambda_o^{\text{ox}} - l / \Lambda_j^{\text{ox}}) \]  \hspace{1cm} (6.6.5)
6. Characterization of adsorbed films on steel surfaces

\[ I_{k}^{\text{con}} / I_{0}^{\text{ox}} = \frac{g_{k} \cdot \sigma_{k}^{\text{ox}} \cdot \Lambda_{k}^{\text{ox}} \cdot A_{k}}{g_{o} \cdot \sigma_{o}^{\text{ox}} \cdot \Lambda_{o}^{\text{ox}} \cdot A_{o}} \cdot \frac{C_{k}^{\text{con}} \cdot \rho_{k}^{\text{ox}} \cdot \left[1 - \exp(-l / \Lambda_{k}^{\text{ox}})\right]}{\left[1 - \exp(-t / \Lambda_{k}^{\text{con}})\right]} \exp(l / \Lambda_{o}^{\text{con}}) \]  

(6.6.6)

Consideration of \( \sum_{i} C_{i}^{\text{ox}} = 1 \) and \( \sum_{j} C_{j}^{m} = 1 \) leads to

\[ (\rho_{\text{ox}}^{\text{ox}} / \rho_{\text{ox}}^{\text{con}}) \sum_{j} k_{j}^{m} \exp(t/\Lambda_{j}^{\text{ox}} + l/\Lambda_{j}^{\text{con}}) = \sum_{i} k_{i}^{\text{ox}} \exp(l/\Lambda_{i}^{\text{con}}) / [1 - \exp(-l/\Lambda_{i}^{\text{ox}})] \]  

(6.6.7)

\[ (\rho_{\text{ox}}^{\text{ox}} / \rho_{\text{con}}^{\text{con}}) \sum_{k} k_{k}^{\text{con}} / [1 - \exp(-l/\Lambda_{k}^{\text{con}})] = \sum_{i} k_{i}^{\text{ox}} \exp(l/\Lambda_{i}^{\text{con}}) / [1 - \exp(-l/\Lambda_{i}^{\text{ox}})] \]  

(6.6.8)

Where

\[ k_{j}^{m} = g_{o} \sigma_{o}^{\text{ox}} \Lambda_{o}^{\text{ox}} A_{j} / g_{o} \sigma_{o}^{\text{ox}} A_{j}^{m} A_{o}, \]

\[ k_{j}^{\text{ox}} = g_{o} \sigma_{o}^{\text{ox}} \Lambda_{o}^{\text{ox}} A_{j} / g_{o} \sigma_{o}^{\text{ox}} A_{j}^{\text{ox}} A_{o}, \]

\[ k_{k}^{\text{con}} = g_{o} \sigma_{o}^{\text{ox}} \Lambda_{k}^{\text{con}} A_{k} / g_{k} \sigma_{k}^{\text{con}} A_{k}^{\text{con}} A_{o}, \]

with subscript ‘O’ indicating oxygen.

\( g_{\text{Fe}} = 0.80, g_{\text{O}} = 0.83, g_{\text{C}} = 0.85, \)

\( \sigma_{\text{Fe}}^{\text{ox}} = 10.82, \sigma_{\text{O}}^{\text{ox}} = 7.46, \sigma_{\text{C}}^{\text{ox}} = 1.00, \)

\( \Lambda_{\text{Fe}}^{m} = 1.2, \Lambda_{\text{Fe}}^{\text{ox}} = 1.9, \Lambda_{\text{Fe}}^{\text{con}} = 1.7, \Lambda_{\text{O}}^{\text{ox}} = 2.1, \Lambda_{\text{O}}^{\text{con}} = 1.9, \Lambda_{\text{C}}^{\text{con}} = 2.1, \)

Values for \( t \) and \( l \) were obtained by solving the equations (6.6.7) and (6.6.8) using three-dimensional parametric plots. Numerical methods based on versions of Newton’s method were used to find numerical approximations to the solutions of the equations. In trying to find a solution, the program starts at the start point and then progressively tries to get closer and closer to a solution.

Next, the composition of the topmost layer, the middle layer and the substrate were calculated simultaneously. First, using equation (6.6.4) and \( \sum_{i} C_{i}^{\text{ox}} = 1 \), \( C_{i}^{\text{ox}} \) can be obtained as follows:

\[ C_{i}^{\text{ox}} = \frac{I_{i}^{\text{ox}} \cdot k_{i}^{\text{ox}} \cdot \exp(l/\Lambda_{i}^{\text{con}}) / [1 - \exp(-t/\Lambda_{i}^{\text{ox}})]}{\sum_{i} I_{i}^{\text{ox}} \cdot k_{i}^{\text{ox}} \cdot \exp(l/\Lambda_{i}^{\text{con}}) / [1 - \exp(-t/\Lambda_{i}^{\text{ox}})]} \]  

(6.6.9)

and from equation (6.6.5) and \( \sum_{j} C_{j}^{m} = 1 \),

\[ C_{j}^{m} = \frac{I_{j}^{m} \cdot k_{j}^{m} \cdot \exp(l/\Lambda_{j}^{\text{con}} + t/\Lambda_{j}^{\text{ox}})}{\sum_{j} I_{j}^{m} \cdot k_{j}^{m} \cdot \exp(l/\Lambda_{j}^{\text{con}} + t/\Lambda_{j}^{\text{ox}})} \]  

(6.6.10)

and in the same way, from equation (6.6.6) and \( \sum_{k} C_{k}^{\text{con}} = 1 \),

\[ C_{k}^{\text{con}} = \frac{I_{k}^{\text{con}} \cdot k_{k}^{\text{con}} / [1 - \exp(-l/\Lambda_{k}^{\text{con}})]}{\sum_{k} I_{k}^{\text{con}} \cdot k_{k}^{\text{con}} / [1 - \exp(-l/\Lambda_{k}^{\text{con}})]} \]  

(6.6.11)
6. Characterization of adsorbed films on steel surfaces

The system of equations (Eqns (6.6.1) and (6.6.2)) written for each species present in the surface film and in the substrate was treated according to Reference 7 and put in a parametric form for the unknowns, \( t \) and \( l \)

### 6.6.2 Quantification of the steel disk surfaces

In this section, quantification of surface layer thickness and composition of steel disks with the various treatments will be discussed in accordance with the three layer model. In this quantification, it is assumed that the substrate consists of Fe element only, the oxide layer consists of Fe and O element, and the contaminant layer consists of C element from the hydrocarbon only. Moreover, it is assumed that \( \rho^{\text{con}} C^{\text{con}} = 1 \).

The oxide and the contaminant layer thickness of a sputtered, reoxidized, plasma-cleaned and as-received steel surface based on the three layer model with the abovementioned assumptions are listed in the Table 6.6.1. The as-received surface has an oxide layer of approximately 5.4nm in thickness and a contaminant layer of approximately 3.1nm in thickness. The plasma-cleaned surface has an oxide layer of more or less the same thickness and a thinner contaminant layer. This shows that the plasma cleaning technique can eliminate or decrease the contaminant on the surface, however, it does not affect the oxide layer existing underneath. Next, the reoxidized surface has relatively thin oxide and contaminant layers (2.4nm and 1.2nm, respectively) compared to the as received surface, indicating that in this experimental condition (1min re-oxidation in air), the oxide is not fully formed yet. The sputtered surface has an oxide layer of 0.3nm in thickness and a contaminant layer of 1.2nm in thickness. This reveals that the surface sputtered and then transferred to the glove box once is oxidized and also contaminated slightly in the glove box or during the transportation. The sputtered surface without moving to the glove box (the data is not shown in the table) showed no oxide and contaminant layer as expected. Next, weight fraction ratio \([\text{O}] / [\text{Fe}]\) of the surfaces are also listed in the table, where the as-received surface has the ratio of 0.31/0.69, the plasma cleaned surface is 0.30/0.70 and the reoxidized is 0.28/ 0.72, which are assigned to \( \text{Fe}_2\text{O}_3 \), while the sputtered surface have slightly lower ratio, 0.25/0.75. These result shows good agreement with the spectrum analysis described before.

<table>
<thead>
<tr>
<th></th>
<th>( t ) (nm)</th>
<th>([\text{O}]) (%)</th>
<th>([\text{Fe}]) (%)</th>
<th>( l_c ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received</td>
<td>5.4</td>
<td>31</td>
<td>69</td>
<td>3.1</td>
</tr>
<tr>
<td>Plasma cleaned</td>
<td>5.9</td>
<td>30</td>
<td>70</td>
<td>1.2</td>
</tr>
<tr>
<td>Reoxidized</td>
<td>2.4</td>
<td>28</td>
<td>72</td>
<td>1.2</td>
</tr>
<tr>
<td>Sputtered</td>
<td>0.3</td>
<td>25</td>
<td>75</td>
<td>1.2</td>
</tr>
</tbody>
</table>
6.6.3 Quantification of the adsorbed films

In this section, quantification of the adsorbed films on the various conditions of steel surface will be discussed. According to the qualitative analysis of the adsorbed surfaces, iron phosphate and organic phosphate were detected besides metal iron from the substrate, iron oxide and (oxy-) hydroxide. Therefore, for the quantification by the three layer model, it is necessary to know in which layer these compounds are involved. This can be clarified by looking at the relationship between the intensity of a key element of the compound. Now, considering the three layer model described in Fig.6.6.1, $k$ element from the topmost layer, $i$ element from the middle layer and the $j$ element from the substrate should show behaviors illustrated in Fig.6.6.2. Therefore, the plot of intensity of each element for the adsorbed surface against the take-off angle $\theta$ will indicate in which layer these compounds are involved.

![Diagram showing intensity behavior of elements in substrate, middle layer, and topmost layer against take-off angle θ.](image)

Fig.6.6.2 The intensity behavior of elements in the substrate, the middle layer and the topmost layer against take-off angle

The intensity behaviors of carbon, phosphorus, oxygen, iron and nitrogen element in the adsorbed film on sputtered surface with five different angles are shown in Fig.6.6.3. The figure shows that the phosphorus intensity decreases as $\theta$ increases, which indicates that the phosphorus is involved mainly in the topmost layer. Next, the oxygen signal also increases as $\theta$ increases and then slightly drops around $\theta = 90$ degree, which is typical behavior of an element in the middle layer. Thus oxygen mainly exists in the middle layer although oxygen should exist in the topmost layer as phosphate. The carbon signal decreases as $\theta$ increases, indicating that it is involved mainly in the topmost layer, where this carbon is probably from hydrocarbon contaminant and the organic phosphate adsorbed on the topmost of the surface without reaction.
Fig.6.6.3 The angle resolved XPS results of the steel surface adsorbed with amine phosphate

In conclusion, the layer structure of the adsorbed surface can be illustrated in Fig.6.6.4, where the substrate consists of metal state of iron, the middle layer consists of iron and oxygen from iron oxide and (oxy-) hydroxide, and the topmost layer consists of carbon element from hydrocarbon contaminant or un-reacted organic phosphate, phosphorus and oxygen element from iron phosphate or the organic phosphate, iron element from iron phosphate and nitrogen element from the un-reacted organic phosphate.

Contaminant: C
Organic phosphate: C, P, O, N
Iron phosphate: Fe, P, O
Iron oxide
Iron (oxy-) hydroxide: Fe, O
Metal iron: Fe

Fig.6.6.4 Schematic diagram of surface structure of the steel surface adsorbed with additives
One of the major problems in this quantification is the distinction between the phosphate and the (oxy-) hydroxide, since they have very close peak positions for both O1s and Fe2p spectra. Here the distinction was done by the following calculation process. First, from the curve fitting results of oxygen spectrum, the peak around 531.5 eV is assigned to P-O-C bond oxygen of phosphate and (oxy-) hydroxide, and the peak around the 533 eV is assigned to P=O bond oxygen of phosphate. Thus the intensity of the peak around 533 eV (I_{O=533}) was assigned to the topmost layer, and then three times of I_{O=533} in I_{O=531.5} was also assigned to phosphate of the topmost layer and the rest (I_{O=531.5} - 3*I_{O=533}) was assigned to (oxy-) hydroxide of the middle layer, since phosphate has three P-O-C bonds and one P=O bond. Next, from the curve fitting of the iron spectrum, the peak around 710.2 eV was assigned to oxide of the middle layer, and the peak around 712.4 eV, which contains phosphate and (oxy-) hydroxide, is divided into the phosphate and the (oxy-) hydroxide with the ratio of (I_{O=533}) : (I_{O=531.5} - 3*I_{O=533}) in accordance with the abovementioned consideration of oxygen spectrum.

Table 6.6.2 The quantitative analysis results of the various states of steel surface adsorbed with the additives

<table>
<thead>
<tr>
<th>Additive</th>
<th>Surface state before adsorption</th>
<th>Middle layer</th>
<th>Topmost layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>t (nm)</td>
<td>[O] (%)</td>
<td>[Fe] (%)</td>
</tr>
<tr>
<td>Amine phosphate</td>
<td>As-received</td>
<td>4.9</td>
<td>29.7</td>
</tr>
<tr>
<td></td>
<td>Plasma cleaned</td>
<td>5.3</td>
<td>32.5</td>
</tr>
<tr>
<td></td>
<td>Reoxidized</td>
<td>3.0</td>
<td>30.1</td>
</tr>
<tr>
<td></td>
<td>Sputtered</td>
<td>3.1</td>
<td>29.9</td>
</tr>
<tr>
<td>Phosphoric acid ester</td>
<td>As-received</td>
<td>4.6</td>
<td>32.6</td>
</tr>
<tr>
<td></td>
<td>Reoxidized</td>
<td>2.0</td>
<td>27.0</td>
</tr>
<tr>
<td></td>
<td>Sputtered</td>
<td>2.7</td>
<td>29.5</td>
</tr>
<tr>
<td>Alkyl amine</td>
<td>As-received</td>
<td>6.2</td>
<td>28.5</td>
</tr>
<tr>
<td></td>
<td>Sputtered</td>
<td>4.1</td>
<td>28.3</td>
</tr>
</tbody>
</table>

Table 6.6.2 shows the results of the quantification based on the abovementioned structure of the layers, where the thickness and the molar fraction of each element for the middle layer and the topmost layer are listed. First, adsorption of amine phosphate will be discussed here. In the adsorption of amine phosphate on the as-received or plasma-cleaned surface, the oxide layer became thinner in thickness but did not change in composition by the adsorption, whereas the topmost layer changed in composition by the adsorption, where iron phosphate was enriched in the topmost layer of the adsorbed surface. This may imply that the additive reacts with upper part of the oxide layer and formed the iron phosphate by considering the fact that the composition of the oxide did not change but iron phosphate was formed slightly on the topmost layer. Next, in the adsorption on the reoxidized surface, the oxide layer became slightly thicker in thickness and changed toward higher oxygen rate in composition by the adsorption, whereas the topmost layer became higher in thickness and
6. Characterization of adsorbed films on steel surfaces

changed to that with high rate of iron phosphate in composition.

Next, in the adsorption on the sputtered surface, the oxide layer became fairly thicker, and changed to higher rate of oxygen in composition by the adsorption, whereas the topmost layer became thicker and changed toward a higher rate of iron phosphate in composition. Now considering the topmost layers of the four different surfaces, the topmost layer on the surface that originally had a thick oxide layer (ex. as-received or plasma-cleaned surface) had relatively high rate of carbon, and low rate of phosphorus and iron, whereas the topmost layers of the surface that originally had a thin oxide layer (ex. reoxidized or sputtered surface) showed relatively low rate of carbon and high rate of phosphorus and iron. This indicates that amine phosphate tends to react more on the surface with less oxide layer.

Next, the adsorption by phosphoric acid ester will be discussed. The adsorption of phosphoric acid ester on the as-received surface caused the oxide layer to become slightly thinner and also caused its composition to change toward higher oxygen rate. By the adsorption, the topmost layer became thicker and changed to that with low carbon, but high phosphorus rate in composition. The adsorption onto the reoxidized surface caused the composition to change toward higher oxygen rate, whereas the topmost layer became thicker to 4.4nm and also became the composition with the higher oxygen rate. In the adsorption onto the sputtered surface, the oxide layer became thicker to 2.7nm and also the composition has a higher rate of oxygen like the adsorption of the as-received or reoxidized surface, whereas the topmost layer had higher rate of carbon and lower rate of phosphorus than that of the as-received surface after adsorption. These results revealed that in the adsorption of phosphoric acid ester, the additive tends to react more onto the surface with oxide layers. However, the reaction layer had relatively low rate of iron, thus, the layer appeared not to have much iron phosphate. The layer can be just physisorbed film by phosphoric acid ester.

The adsorption of alkyl amine will be discussed here. In the adsorption onto the as-received surface, the oxide layer did not change in thickness and composition and the topmost layer did not change in thickness and composition, neither. In the adsorption onto the sputtered surface, the oxide layer became thicker, however, did not change in composition, whereas no change in the topmost layer due to the adsorption was observed. This indicates that alkyl amine reacts neither on the as-received nor sputtered surface.

It is summarized that the each additive seems to have different preference of the surface state to react or adsorb. Amine phosphate reacts more with the surface which has less oxide layer, while phosphoric acid ester reacts more with the surface which has more oxide layer. The reaction products in the case of amine phosphate comprised of mainly iron phosphate, however, in the case of phosphoric acid ester comprised of physisorption film of phosphoric acid ester. As for alkyl amine, it appeared not to react or adsorb with any states of surface.
6.7 Conclusion

The adsorption films on the various state of steel surfaces were qualitatively and quantitatively characterized with XPS and the results obtained are summarized as follows.

1) The XPS characterization of steel surface after various treatment showed that the sputtered surface has just metal iron and no oxide, the sputtered and reoxidized surface has a slight oxide layer on the metal substrate and neither has organic contaminant on the top, whereas the plasma-cleaned surface is fully oxidized but very little organic contaminant and the as received surface is fully oxidized and covered with thick organic contaminant so that the metal substrate can not be detected.

2) The adsorption films of amine phosphate consist of more or less the same composition regardless of state of the steel surface. Amine phosphate can form a thicker adsorption film on an oxide surface than a metal surface.

3) Phosphoric acid ester, one component of amine phosphate, can form a thicker adsorption film on a metal surface than an oxide surface.

4) Alkyl amine can barely adsorb on any state of surface.

5) The quantitative analysis of the adsorption films using three layer model agree with abovementioned summary. The adsorption films are 4 to 6 nm in thickness.

References

6. Characterization of adsorbed films on steel surfaces

7. Characterization of tribo-films

7.1 Introduction

The macro tribological performances of the additives were discussed in chapter 5. These tests give valuable results for practical purposes, however, they alone are not enough to understand action mechanism of a lubricant additive taking place on a rubbed surface. A precise study of rubbed surfaces, and then correlating with the tribological information, is necessary for it. Highly sensitive surface analysis tools employing UHV conditions, for instance XPS, AES and SIMS, have been applied to studies of such rubbed surfaces [1], since the methods allow analysis of the chemical composition of surface layers with high depth resolution. Among them, XPS is the best suited at present for application to tribological studies since it is capable of qualitative and quantitative (or semi-quantitative) analysis of the uppermost surface layers with good sensitivity [2-11]. In this chapter a surface after the tribotests will be characterized by means of small area and imaging XPS analysis. Amine phosphate will be mainly focused on here since it was found that amine phosphate reduces friction even at room temperature by most likely forming some kind of tribo-films, and consequently only the tribo-reaction can be investigated with this additive apart from thermo-chemical reaction. Phosphoric acid ester and alkyl amine, which are constituents of amine phosphate, will also be examined in order to grasp how each constituent functions.

7.2 Small area and imaging XPS analysis of tribo-films

The conditions of tribological tests was basically the same as that in chapter 5, where the load was kept at 10N while the velocity was varied stepwise from 1.0 to 10,000mm/min, resulting in a Striebeck-like curve. In this series of pin-on-disk type tribotest, the flat chip with the size of 3.5x3.5mm surface was adopted as the geometry of the pin head so that a wide and homogeneous contact area was obtained, which is quite important for the XPS analysis that has relatively low spatial resolution (about 100µm). The lubricants used in the tribotests were not the pure additives but 3.04 x 10^{-3} atomic % of phosphorus in PAO. The condition of XPS analysis on a rubbed surface was same as that in chapter 6, where the disk after the tribotests were washed in the air using organic solvent and then introduced to the XPS chamber, assuming that no modification or oxidation occurred during the washing process.

A microscope image of a disk surface after the tribotests is shown in Fig.7.2.1. Several deep scar tracks are clearly observed in the contact area, these tracks, however, are not as severe as a scratch, the so called seizure or galling. Although both a disk and a chip for the
7. Characterization of tribo-films

tribotests were mechanically polished down to the roughness of nano-order as described in chapter 3, it seemed that some partial high-pressure points existed, and this caused these scar tracks during the running-in process as the scars were observed even at the beginning of the running-in.

Fig. 7.2.1 Microscope images of a disk surface after the tribotesting
XPS characterization of a disk surface after the tribotesting was conducted paying attention to differences among the scar track, the contact area except for the scar tracks and the non-contact area, since film formed on each area can be different. However, there is one thing that must be kept in mind for the series of analysis, that is, the small area analysis of the scar contains information from the contact area, and the analysis of the contact area may also contain information from the scar tracks since the spatial resolution of the XPS analysis in this work is relatively low (the aperture size of the XPS analyzer was of 0.400mm), as described in a schematic diagram of a disk surface after tribotesting (Fig.7.2.2).

Fig.7.2.2 Schematic diagram of the disk surface after the tribotesting
1) analysis area of the scar track, 2) analysis area of the contact area, 3) analysis area of the non-contact area

### 7.2.1 Tribo-films formed by amine phosphate

XPS mapping images of a disk surface after tribotesting using the additivated lubricant containing amine phosphate is shown in Fig.7.2.3. The elemental distribution around the contact area is clearly recognized from the figure. The figure also shows that oxygen and phosphorus signal inside the contact area is higher than the non-contact area, while carbon and iron signal is lower than the non-contact area. No significant difference between the contact area and the non-contact area is recognized with the nitrogen-mapping image. These results indicate that some film is formed on the contact area by tribological stress.

Next, small area XPS analysis on the contact area and the non-contact area are carried out. A survey spectrum of the contact area is shown in Fig.7.2.4 (A). Elements from the additive: carbon, oxygen, phosphorus and nitrogen, and element from the substrate: iron, are
detected, indicating the film formed is in the nano-meter range. High-resolution spectra of the contact area and their curve fitting results are shown in Fig.7.2.4 too. C1s spectrum, Fig.7.2.4 (B), shows that the spectrum can be fitted with only one peak for the contact area (a hydrocarbon peak of 285.0eV) and two peaks for non-contact area (a hydrocarbon peak of 285.0eV and a -COP- and -CN- peak of 286.6eV). O1s spectrum of the contact area, Fig. 7.2.4 (C), gives the best fitting with three peaks: an oxide peak of 530.4eV, an (oxy-) hydroxide and phosphate (non-bridging oxygen) peak of 531.8eV and a -CO- and phosphate (bridging) peak of 533.4eV. The peak positions of the contact area are slightly higher than those of pure amine phosphate or the adsorbed film. P2p high-resolution spectrum on the contact area, Fig.7.2.4 (D), shows the multiple splitting and gives the best fit with one pair of 2p3/2 and 2p1/2. The peak position of the P2p3/2, 133.8eV, is assigned to phosphate. Fe2p3/2 high-resolution spectrum of the contact area, Fig.7.2.4 (E), gives the best fit with three peaks; a metal peak of 706.8eV, an oxide peak of 710.2eV, an (oxy-) hydroxide and phosphate peak around 712.4eV. These results indicate that iron phosphate is generated also on the tribo-stressed surface. As to N1s high-resolution spectrum shown in Fig.7.2.4 (F), the spectrum has poor signal-to-noise ratio, implying that the nitrogen related component barely existed on the surface. Therefore, it is surmised that alkyl amine part of amine phosphate gives almost no contribution to formation of the tribo-film during friction. This can be presumed from the fact that N1s mapping image shows almost no intensity distribution around the contact area. In conclusion, the analyzed contact area consists of metal iron, iron oxide, iron (oxy-) hydroxide and phosphate compound including both iron phosphate and organic phosphate. It is also concluded that almost no nitrogen products originated from alkyl amine exists under these tribotest conditions.
Characterization of tribo-films

Fig. 7.2.3 XPS mapping images of a disk surface after tribotesting using the additivated lubricant containing amine phosphate

The size of each map is 8.0mm (horizontal) x 11.2mm (vertical).
The brighter points are correspondent of the higher intensity of the element.
7. Characterization of tribo-films

Fig. 7.2.4 Small area XPS analysis on the contact area and the non-contact area

Next, small area XPS analysis of the non-contact area is carried out with the same analysis condition as the contact area. The non-contact area was not rubbed with the counter surface, however, the area is exposed to the additivated lubricant containing 2% of amine...
phosphate. The survey spectrum of the non-contact area is shown in Fig.7.2.4 (A) too. Elements from the additive: carbon, oxygen, phosphorus and nitrogen, and element from the substrate: iron, are detected on this area as well as the contact area. High-resolution spectra of C1s, O1s, P2p, Fe2p3/2 and N1s on the non-contact area and their curve fitting results are shown in Fig.7.2.4 too. All the spectra including survey and high-resolution spectra on both the contact area and the non-contact area are normalized where the maximum values =1.0. The C1s spectrum on the non-contact area, Fig.7.2.4 (B), gives the best fit with two peaks: a hydrocarbon peak of 285.0eV and a –CO or –CN- peak of 286.6eV as well as the contact area. Concerning the intensity ratio of these two peaks, the hydrocarbon peak ratio on the non-contact area seems to be higher than that of the contact area. The O1s spectrum on the non-contact area, Fig.7.2.4 (C), gives the best fit with three peaks: an oxide peak of 530.4eV, an (oxy-) hydroxide and phosphate (non-bridging oxygen) peak of 531.8eV and a –CO and phosphate (bridging oxygen) peak of 533.4eV, as well as the contact area. As to the intensity ratio of these three peaks, there is significant difference between the spectrum on the contact area and the non-contact area. That is, the intensity ratio of the phosphate and (oxy-) hydroxide peak on the non-contact area is much lower than on the contact area. The Fe2p3/2 high-resolution spectrum on the non-contact area, Fig.7.2.4 (D), shows more or less the same curve fitting results as the contact area in regard to peak position. There is a difference in the intensity ratio of the phosphate peak, where the phosphate peak on the non-contact area is slightly lower than that of the contact area. The aforementioned results indicate that the compounds existing on the analyzed surface of the non-contact area are more or less the same as those of the contact area, whereas the ratios are different. It is considered that the analyzed surface of the non-contact area consists of metal iron, iron oxide, iron (oxy-) hydroxide and some phosphate including iron phosphate and organic phosphate. The fact that there is a significant difference in the intensity ratio between the contact and the non-contact area reveals that the tribo-film generated on the contact area is different from the film generated on the non-contact area.

This can be confirmed by observing the mapping images around the contact area more carefully. The mapping image and the small area analysis results of C1s reveal that organic compound attributable to amine phosphate does not exist a lot on the contact area. The O1s mapping image and small area analysis also lead to the conclusion that the (oxy-) hydroxide and phosphate are predominant on the contact area, while (oxy-) hydroxide is predominant on the non-contact area. The P2p results reveal that phosphate exists more on the contact area than non-contact area. Although it is not distinguishable the difference between the iron phosphate and the organic phosphate only from the P2p peak position, it is surmised that the phosphate on the contact area is mostly iron phosphate, while that on the non-contact area is mainly the adsorbed organic phosphate.
Next, a detailed chemical mapping technique can bring about more information about the oxidation state around the contact area. In Fig.7.2.5, O1s mapping images with different binding energy ranges are shown. Fig.7.2.5 (A) shows the O1s image with the whole O1s binding energy range (527.3 eV-535.9 eV), which is the same as the O1s image in Fig.7.2.3. Fig.7.2.5 (B) shows the O1s image with the binding energy range of oxide (529.0 eV-531.0 eV) and Fig.7.2.5 (C) shows the O1s with the binding energy range of phosphate (531.0 eV-534.0 eV). It is confirmed from these images that the contact area consists mostly of phosphate, while the non-contact area consists mostly of oxide in terms with the oxygen element.

![Chemical Mapping Images](image)

(A) Whole region (527.3 eV - 535.9 eV)  
(B) Oxide region (529.0 eV - 531.0 eV)  
(C) Phosphate region (531.0 eV - 534.0 eV)

Fig.7.2.5 O1s chemical mapping images of the disk surface following the tribotesting. The size of each map is 2.0 mm (horizontal) x 2.8 mm (vertical). The brighter points are correspondent of the higher intensity of the element.
Looking into the contact area by the imaging XPS with much higher spatial resolution, the elemental distribution around the wear scar track can be clearly observed. The high-resolution imaging XPS shows that oxygen and phosphorus signals are more intensive on the scar tracks compared to the outside of the scar track, while iron signal is less intensive on the scar tracks.

Fig. 7.2.6 XPS mapping images of a disk surface after tribotesting using the additivated lubricant containing amine phosphate

The size of each map is 2.0mm (horizontal) x 2.8mm (vertical). The brighter points are correspondent of the higher intensity of the element.
The small area XPS analysis of the tribo-stressed surface was carried out. Fig.7.2.7 shows the high-resolution spectrum of O1s and P2p on the scar track, comparing with the scar track, the just contact area and the non-contact area. O1s spectra show that on the scar tracks, the phosphate-related oxygen peak is higher than the other area, and P2p spectra also show that the phosphate peak of the scar track is higher than the other area. These results indicate that phosphate, most likely iron phosphate, was formed more intensively on the scar than the mere contact area. It is considered that the scar track was generated at the beginning of the running-in process due to the local high-pressure, and the tribo reaction of the additive was likely to occur on the local high-pressure area. The mechanism of this intensive reaction on the local high-pressure is not clear, but temperature rise at the area possibly enhance the tribo reaction although it was concluded that temperature rise at a contacting asperity is not large in chapter 5.

Fig.7.2.7 High-resolution spectra of the disk surface after tribotesting using the additivated lubricant containing amine phosphate

(A) O1s
(B) P2p

(1) on one of the scar tracks, (2) on the contact area, (3) on the non-contact area

Now, in order to investigate the influence of temperature on the tribo reaction, tribological test at high temperature, 150 degree centigrade using additivated lubricant with amine phosphate was carried out. Fig.7.2.8 shows XPS mapping images of a disk surface following the tribotesting at 150 degrees centigrade. The figure reveals that the images with high temperature tribotests is more contrasty and shows distinct border between the contact area and the non-contact area. The figure also shows that the contact area has lower intensity of carbon and iron and higher intensity of oxygen and phosphorus, while no elemental
distribution is recognized in the N1s mapping image. As to Fe2p mapping, overall, both contact and non-contact show rather low intensity, however, the contact area shows slightly lower intensity than the non-contact area. These results agree with the results of room temperature tribotesting. In the case of the test at room temperature tribotesting, the contact area shows lower intensity for iron signal compared to the non-contact area.

Next, small area XPS analysis was carried out on both the contact area and the non-contact area of the disk following the high temperature tribotesting. Fig. 7.2.9 shows the high-resolution spectra of C1s, O1s, Fe2p, P2p and N1s on the two areas with their curve fitting results. Overall, the number of peaks and their peak positions for both spectra show quite good agreement, indicating that the constituent of the film formed on the two surfaces are the same, while their compositions (the ratio of the constituent) can be different. Precise quantitative analysis will be discussed in section 7.3, thus qualitative matter will be mainly discussed here. Looking at each spectrum one by one, the curve fitting results of C1s spectra for both the contact and the non-contact area show more or less the same peak positions; hydrocarbon peak of 285.0eV and the -COH, -COP- and -CN- peak of 286.6eV. The O1s spectra for both the contact and the non-contact area give best fit with two peaks and their peak position area more or less the same; bridging phosphate or (oxy-) hydroxide of 531.7eV and the non-bridging phosphate or -CO or -COH of 533.2eV, where the intensity ratio of phosphate on the contact area is higher than the non-contact area. The oxide peak was not observed in the case of high temperature. The P2p spectra show more or less the same peak position each other; phosphate of 134.0eV. The Fe2p3/2 of the both contact and non-contact areas show similar results each other. The aforementioned results regarding XPS analysis data of the surface following the high temperature tribotesting indicate that almost same chemistries take place on the two areas, however the formation of reaction film takes place slightly more on the contact area than the non-contact area.
7. Characterization of tribo-films

Fig. 7.2.8 XPS mapping images of a disk surface after tribotesting at 150 deg. using the additivated lubricant containing amine phosphate. The size of each map is 2.0mm (horizontal) x 2.8mm (vertical). The brighter pints are correspondent of the higher intensity of the element.
7. Characterization of tribo-films

Fig. 7.2.9 Small area XPS analysis on the contact and the non-contact area of a disk surface after tribotesting at 150 deg. using the additivated lubricant containing amine phosphate.
7.2.2 Tribo-films formed by phosphoric acid ester

The tribological test results described in chapter 5 show that phosphoric acid ester, one constituent of amine phosphate, particularly reduces friction in the boundary lubrication region compared to amine phosphate or alkyl amine, which implies that this very component forms effective tribo-film on the surface during the friction. The adsorption test results described in chapter 6 show that phosphoric acid ester reacts with the steel surface and forms the adsorption film most likely of iron phosphate. Therefore, in this section, a disk surface following the tribotesting with the additivated lubricant with only phosphoric acid ester were characterized with the small area and imaging XPS, in order to grasp the action mechanism of phosphoric acid ester generating the tribo-films.

XPS mapping images of a disk surface after the tribotesting are shown in Fig. 7.2.10. The figure shows the elemental distribution around the contact area, where carbon, oxygen and phosphorus intensities on the contact area are higher than those of the non-contact area. The carbon mapping result does not agree with the case of amine phosphate, where the carbon intensity on the contact area in the case of amine phosphate is lower than the non-contact area.

Next, the small area XPS analysis on both the contact and the non-contact area are shown in Fig. 7.2.11. As to C1s spectra, both spectra give the best fit with two peaks; hydrocarbon of 285.0eV and -COH or -COC- of 286.6eV, and have more or less the same intensity ratio. The O1s spectra of both the contact and non-contact area show close peak positions each other; oxide of 530.4eV, (oxy-) hydroxide or phosphate (non-bridging oxygen) of 531.8eV and -COH or phosphate (bridging oxygen) of 533.0eV, and also show close intensity ratios. The P2p spectra of the two areas also show more or less the same peak position that is assigned to phosphate. As to Fe2p3/2 spectra, the spectra of both areas give the best fit with four peaks and show close intensity ratios. However, the disk surface after tribotesting with phosphoric acid ester shows lower intensity of the phosphate peak than that with amine phosphate and higher intensity of metal peak than that with amine phosphate. This tendency was observed also in the adsorption tests. From the quantitative point of view, these results indicate that the film covering the substrate surely differ from each other. (The detail of the quantitative analysis will appear in the next section). This also implies that the reactivity of the reaction component, phosphoric acid ester in this case, quantitatively affects the formation of the film.
7. Characterization of tribo-films

Fig. 7.2.10 XPS mapping images of a disk surface after tribotesting using the additivated lubricant containing phosphoric acid ester

The size of each map is 2.0mm (horizontal) x 2.8mm (vertical). The brighter points are correspondent of the higher intensity of the element.
Fig. 7.2.11 Small area XPS analysis on the contact and the non-contact area of a disk surface after tribotesting using the additivated lubricant containing phosphoric acid ester

Next, high temperature tribotesting at 150 degree centigrade using the additivated lubricant with only phosphoric acid ester were carried out in order to investigate influence of temperature on the formation of tribo-film in the case of phosphoric acid ester. Fig. 7.2.12 shows the XPS mapping images of the disk surface. As can be seen from the figure, in the
case of high temperature, carbon intensity is lower on the contact area than the non-contact area, which is the opposite tendency from the test at room temperature, whereas the oxygen and phosphorus intensities on the contact area are higher than the non-contact area as well as the test at room temperature. As to Fe2p3/2 image, the difference of the intensity between the contact and the non-contact area is relatively small, however, iron intensity on the scar is lower than the other area.

The small area XPS analysis on both the contact and non-contact area was carried out and their results are shown in Fig. 7.2.13. The curve fitting results revealed that both areas can fit with the same number of peaks and have close peak positions for all the elements measured. As to the difference distinguishable, the contact area showed higher intensity for O1s and P2p and lower intensity for C1s than the non-contact area. Also the contact area has a bit higher intensity ratio of phosphate peak than the non-contact area.

![XPS mapping images of a disk surface after tribotesting at 150 deg. using the additivated lubricant containing phosphoric acid ester](image)

Fig. 7.2.12 XPS mapping images of a disk surface after tribotesting at 150 deg. using the additivated lubricant containing phosphoric acid ester.

- The size of each map is 2.0mm (horizontal) x 2.8mm (vertical). The brighter points are correspondent of the higher intensity of the element.
Fig. 7.2.13 Small area XPS analysis on the contact and the non-contact area of a disk surface after tribotesting at 150 deg. using the additivated lubricant containing phosphoric acid ester.
7. Characterization of tribo-films

7.2.3 Tribo-films formed by alkyl amine

Next, small area and imaging XPS analysis of a disk surface following the tribotesting using the additivated lubricant with only alkyl amine, the other constituent of amine phosphate, were carried out, in order to confirm the tribological results and the adsorption test, where the tribological test revealed that alkyl amine hardly reduces friction at all, and the adsorption test revealed that alkyl amine barely forms the reaction or adsorption film on the steel surface. In short, alkyl amine does not work as a lubricant additive, but just a neutralizer of phosphoric acid ester.

Fig.7.2.14 shows the XPS mapping images of the disk surface after the tribotesting using the additivated lubricant with only alkyl amine, where elemental distribution around the contact area can be observed, showing that there is some difference in the surface layers between the contact and non-contact area. Looking at the spectra, the contact area has a higher intensity for C1s, O1s and N1s, and lower intensity for Fe2p, which indicates the film originated from alkyl amine was formed on the contact area.

Next, small area XPS analysis was carried out on both the contact and the non-contact area. The survey and high-resolution spectra on the both surfaces and their curve fitting results are shown in Fig.7.2.15. First, the survey spectra show that only carbon, nitrogen and iron elements are detected and the contact area has a slightly higher intensity for N1s than the non-contact area. As to the high-resolution spectra, the contact area shows higher total intensity for C1s, lower intensity for metal peak of Fe2p3/2, higher intensity of >NH2+ related peak of N1s, and also higher (oxy-) hydroxide peak of O1s. These results indicate that the surface of the contact area comprised of oxide and (oxy-) hydroxide layer and the adsorbed film originated from alkyl amine. The mechanism of the (oxy-) hydroxide formation is yet to be clarified, however, it is possible that the O2 gas or H2O solved in the lubricant caused the oxidation. In the case of amine phosphate or phosphoric acid ester, these additives preferentially react or adsorb to the surface, thus the influence of the O2 gas or H2O may be small, whereas in the case of alkyl amine, the additive has relatively low reactivity thus O2 gas or H2O could attach the surface.

The tribological test at 150 degrees centigrade using the additivated lubricant with only alkyl amine were also carried out in order to understand the influence of temperature on the adsorption or reaction of alkyl amine with the surface. Overall, the same tendency as the test at room temperature was observed also in these tests, thus the detail of the result is omitted here.
Fig. 7.2.14 XPS mapping images of a disk surface after tribotesting using the additivated lubricant containing alkyl amine

The size of each map is 2.0mm (horizontal) x 2.8mm (vertical). The brighter pints are correspondent of the higher intensity of the element.
7. Characterization of tribo-films

Fig. 7.2.15 Small area XPS analysis on the contact and the non-contact area of a disk surface after tribotesting using the additivated lubricant containing alkyl amine.
7.3 Quantitative analysis of tribo-films

In this section, quantitative analysis of the tribo-stressed surface will be discussed in accordance with the three-layer model as described in the quantification of the adsorbed surfaces [12-27]. The quantification was performed under the assumption that the tribo-stressed surfaces have the same structure as the adsorbed surfaces, where the topmost layer consists of contaminant hydrocarbon, un-reacted additive and reaction products of the additives with the surfaces, and the middle layer consists of iron oxide and (oxy-) hydroxide, and the substrate consists of metal state of iron. Results of the quantification of the surfaces tribo-stressed using amine phosphate, phosphoric acid ester and alkyl amine are listed in Table 7.3.1. Quantification results of the surface after high temperature tribo-testing are also listed in the table.

Looking at the quantification of the surface rubbed with amine phosphate, there are slight differences in thickness of the topmost layers and the oxide layers between the contact area and the non-contact area, where the contact area has an oxide layer of 4.8nm and the topmost layer of 4.0nm, while the non-contact area has an oxide layer of 5.4nm and the topmost layer of 3.8nm. As to their composition, they both have more or less the same composition for the oxide layer, whereas the contact area has a higher rate of phosphorus and lower rate of carbon for the topmost layer than the non-contact area. This implies that the alkyl chain of amine phosphate can be eliminated dissociatively from the molecule due to the tribo-stress.

Next, in the quantification of the surface rubbed with phosphoric acid ester, there is almost no difference in thickness between the contact area and the non-contact area, where the contact area has an oxide layer of 3.4nm and a reaction layer of 4.9nm, while the non-contact area has an oxide layer of 3.3nm and a topmost layer of 4.8nm. Their compositions also show more or less the same values. Now as to comparison between the phosphoric acid ester and amine phosphate, the surface rubbed with phosphoric acid ester has a higher rate of phosphorus and oxygen and lower rate of carbon and iron compared to the topmost layer rubbed with amine phosphate, implying that a different reaction may take place between amine phosphate and phosphoric acid ester.

Next, in the quantification of the surface tribo-stressed with alkyl amine, there is no difference in thickness between the contact and the non-contact area, where the contact area has an oxide layer of 4.3nm and a topmost layer of 2.0nm, while the non-contact area has an oxide layer of 4.6nm and a topmost layer of 1.8nm. Their compositions also show no difference between them, where the both oxide layers have similar composition consisting of a high rate of carbon and some nitrogen. These results indicate that there is no change due to tribo-stress with alkyl amine.
Looking at the quantification of the surface tribo-stressed with amine phosphate at high temperature, the contact area has a topmost layer of 6.7 nm and with such thick oxide layers that the substrate metal is not detected. Thus, the thickness of the oxide layer can not be calculated with the three layer model. The non-contact area has more or less the same composition and thickness of topmost layer and also composition of oxide layer. Regarding the compositions, both the contact and the non-contact area have an oxide layer with extremely high oxygen rate and a topmost layer with higher phosphorus rate and lower carbon and iron rate, compared to those at room temperature. The reaction is considered to be mainly thermo-chemical reaction judging from the fact that there is no difference for the topmost layer in thickness and composition between the contact area and the non-contact area. As to the surface tribo-stressed using phosphoric acid ester at high temperature, the thickness and the composition shows the same tendency as amine phosphate. In conclusion, the oxide layer and the topmost layer of the surfaces tribo-stressed using amine phosphate, phosphoric acid ester and alkyl amine differ widely from each other in thickness and composition. It is particularly of interest that amine phosphate and phosphoric acid ester differ in extent of reaction with steel surface, although they have same key compound for the reaction, phosphoric acid ester. As far as the high temperature tests are concerned, the three layer model with the substrate of metal iron, the middle layer of oxide and the topmost layer of reaction film and contaminant might not be appropriate, since in case of high temperature tests, it might have formation of polyphosphates which are together with the oxide in the middle layer. Therefore probably the model need to be modified for taking into account the presence of oxygen and phosphorus in them middle layer.

Table 7.3.1 The quantitative analysis results of the steel surfaces rubbed with the various additives

<table>
<thead>
<tr>
<th>Temp</th>
<th>Additive</th>
<th>Analytical point</th>
<th>Middle layer</th>
<th>Topmost layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$t$ (nm)</td>
<td>[O] (%)</td>
</tr>
<tr>
<td>Room temp.</td>
<td>Amine phosphate</td>
<td>Contact</td>
<td>4.8</td>
<td>26.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Non-contact</td>
<td>5.4</td>
<td>25.3</td>
</tr>
<tr>
<td></td>
<td>Phosphoric acid ester</td>
<td>Contact</td>
<td>3.4</td>
<td>27.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Non-contact</td>
<td>3.3</td>
<td>28.5</td>
</tr>
<tr>
<td></td>
<td>Alkyl amine</td>
<td>Contact</td>
<td>4.3</td>
<td>34.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Non-contact</td>
<td>4.6</td>
<td>28.7</td>
</tr>
<tr>
<td>High temp.</td>
<td>Amine phosphate</td>
<td>Contact</td>
<td>56.8</td>
<td>43.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Non-contact</td>
<td>56.9</td>
<td>43.1</td>
</tr>
<tr>
<td></td>
<td>Phosphoric acid ester</td>
<td>Contact</td>
<td>74.3</td>
<td>25.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Non-contact</td>
<td>71.5</td>
<td>28.5</td>
</tr>
</tbody>
</table>
7. Characterization of tribo-films

7.4 Influence of load on formation of tribo-films

The characterization of the surface after tribotesting at various loads using the additivated lubricant containing amine phosphate were carried out in order to investigate the influence of load, on the formation of the tribo-films. In a series of tests, the ball-on-disk type was adapted as the contact geometry to obtain high contact pressure. The average contact width is approximately 0.45mm. The load varied in the tests were 20N, 15N, 10N, 5N, 2N, 1N and 0.5N, which corresponds to approximately 120MPa, 90MPa, 60MPa, 30MPa, 12MPa, 6MPa and 3MPa in pressure, respectively. The analytical condition of XPS for the series of experiments is same as the other experiments. It should be noted that the small area analysis data on contact area at each load is an average information of a tribo-film formed under uneven contact pressure determined by the applied load and also may contain some information from a non-contact area since the contact area is not wide enough compared to the analysis area of the XPS. The tests were carried out at room temperature and the lubricant used was 2% amine phosphate in PAO. The detail of the tribotest condition is described in chapter 3.

Fig.7.4.1 shows the XPS mapping images of the disk surface following tribotesting at various loads using the additivated lubricant with amine phosphate. The elemental distribution around the contact area is clearly observed from the figures. Each curved line corresponds to each contact line with a certain value of load, where the leftmost line corresponds to the lowest load, 0.5N and the rightmost line corresponds to the highest load, 20N. (The load increases as the line goes right.) The figures show that the contact area has higher intensities of O1s and P2p, and lower intensity of Fe2p3/2 than the non-contact areas, whereas the C1s image showed almost no difference in intensity between the contact and the non-contact area. On the other hand, the opposite tendency is observed in the Fe2p3/2 image, where higher load gives lower intensity. These results imply that higher load gives the thicker tribo film of iron phosphate.

Next, small area XPS analysis of each contact line and the non-contact area were carried out. As can be seen from the Fig.7.4.2, overall, the curve fitting results agree with the results obtained from the tribotest with flat-on-flat contact geometry. The difference distinguishable is only the difference of the intensity among the each contact line. For example, O1s spectra show that a higher load gives higher intensity of phosphate related oxygen, and the P2p spectra show that a higher load gives the higher intensity of P2p which are assigned to the phosphate. Fe2p3/2 spectra also show that a higher load gives lower intensity of metal peak and slightly higher intensity of phosphate peak.
7. Characterization of tribo-films

Fig. 7.4.1 XPS mapping images of a disk surface following the tribotesting with ball on disk type at various loads using the additivated lubricant containing amine phosphate. The size of each map is 2.0mm (horizontal) x 2.8mm (vertical). The brighter points are correspondent of the higher intensity of the element.
Fig.7.4.1 XPS mapping images of a disk surface following the tribotesting with ball on disk type at various loads using the additivated lubricant containing amine phosphate. The size of each map is 2.0mm (horizontal) x 2.8mm (vertical). The brighter points are correspondent of the higher intensity of the element.
7. Characterization of tribo-films

Fig. 7.4.2 Small area XPS analysis of the disk surface following the tribotesting at various loads using the additivated lubricant containing amine phosphate.

The quantitative analysis was not conducted in this series of tests as it does not make much sense, thus influence of load on formation of the tribo-film was semi-quantitatively studied, as follows. The relationship between the load and the intensity of P2p spectrum are shown in Fig. 7.4.3. The figure shows that the intensity increases as the load increases, however, the intensity saturate over 5N, which is probably due to the saturation of maximum contact pressure, which is about 2.8 times as much as the yield stress of the softer material [28-29].
7. Characterization of tribo-films

![Graph showing the relationship between load and P2p intensities](image)

Fig. 7.4.3 The relationship between the load and the P2p intensities

### 7.5 Conclusion

Surfaces after tribo-stressed with amine phosphate, which showed most pronounced reduction of friction in a boundary lubrication region at room temperature, and its constituents were characterized by means of small area and imaging XPS analysis. The results obtained are summarized as follows.

1) Spatially resolved analysis of the tribo-stressed surface showed that the elemental distribution around the wear scar can be clearly observed.

2) Spectral analysis of the various regions around the wear scar showed that the inside of the scar consisted of high concentrations of iron phosphate with some iron oxide. Outside the wear scar, the adsorbed organic phosphate ester and iron (oxy-) hydroxide are indicated. The concentration of phosphate in the wear scar can be easily recognized.

3) A more detailed spatially resolved representation of the oxygen XPS spectra shows the distribution of the different species more precisely. The iron-oxide-related oxygen is clearly predominant outside the contact area, whereas the contact region consists mostly of oxygen characteristic of phosphate.
References

8. General discussion

8.1 Introduction

The pure additives, the adsorbed films and the tribo-films were characterized with XPS individually in chapter 4, 6 and 8, respectively. Their tribological performance was also evaluated in chapter 5. In this chapter, their tribo-reaction mechanism will be discussed from both the nano-level information of XPS analysis and macro information of tribo-tests. First, the difference between the adsorption films and the tribo-films will be discussed by comparing them, and then a reasonable mechanism of tribo-reaction with the selected additives will be discussed.

8.2 Comparison between tribo-films and adsorbed films

In Fig.8.2.1, O1s and P2p spectra of an as-received steel surface, the adsorbed films of amine phosphate on an as-received surface and on a sputtered surface, the tribo-stressed surface with amine phosphate, and pure frozen amine phosphate are shown. Looking at the O1s spectra, all the spectra have a peak of oxide around 530.2eV and a peak of (oxy-) hydroxide and/or phosphate around 531.5eV. Pure amine phosphate also has a phosphate-related oxygen peak, however this peak is shifted to higher binding energy values in respect of the adsorbed or the tribological films, which implies some chemical change in phosphorus state of the additive occurs due to adsorption or tribo-stress. Now the adsorbed film on the sputtered surface has the higher peak ratio of phosphate/oxide than the adsorbed film on the sputtered surface and the tribo film has even higher ratio than any other surfaces. Thus it is thought that phosphate present the most on the tribo-stressed surface and secondary on the adsorbed film on the sputtered surface and the least on the adsorbed film on the as-received surface.

Looking at the quantitative data illustrated in Fig.8.2.2, the adsorbed film on the as-received and that on the sputtered surface have more or less the same thickness of topmost layers, the reaction films, whereas their compositions differ from each other. The adsorbed film on the sputtered surface has much lower carbon rate than that on as-received surface, indicating that adsorption on the sputtered surface causes considerable dissociative adsorption resulting in elimination of carbon and then enrichment of phosphorus, while adsorption on the as-received surface seems to cause little dissociation. As to the tribo-stressed surface, the contact area has a slightly thinner oxide layer and a thicker topmost layer than the non-contact area, and also the topmost layer of the contact area has lower
8. General discussion

carbon rate and higher phosphorus rate than that of the non-contact area, which implies that
dissociative reaction of the additive on the surface occurs more intensively on the contact area.

![Figure 8.2.1](attachment:O1s_and_P2p_spectra.png)

**Fig. 8.2.1** O1s and P2p spectra of amine phosphate and surface films formed from amine phosphate

(1) Amine phosphate, (2) Tribo-film, (3) Adsorbed film on a sputtered surface,
(4) Adsorbed film on an as-received surface, (5) As-received steel surface

In addition, another remarkable point is that the adsorbed surface on sputtered steel has a considerably thick oxide layer, thus, the oxidation of the surface can possibly take place during the tribo-stress or the adsorption with amine phosphate as well as the main chemistry described above. This is probably due to oxygen atom of phosphate part of the additive, or dissolved oxygen gas or $\text{H}_2\text{O}$ in the additive.
Next, as to phosphoric acid ester, O1s spectra in Fig.8.2.3 show that adsorbed film of phosphoric acid ester on an as-received surface, that on a sputtered surface and the tribo-stressed surface of both the contact area and the non-contact area have very intensive phosphate-related oxygen peak around 531.5eV. As to their compositions, the adsorbed film on the as-received surface has lower carbon rate and higher phosphorus rate than that on sputtered surface. The tribo-stressed surface has the intermediate value of carbon and phosphorus rate between the adsorbed-film on as-received surface and the sputtered surface. These results imply that dissociative adsorption occurs more intensively on an as-received surface than a sputtered surface in the case of phosphoric acid ester, which is opposite to the case of amine phosphate, however, there is no sign showing that dissociative reaction occurs more aggressively by tribo-stress in the case of phosphoric acid ester.
Fig. 8.2.3  O1s and P2p spectra of phosphoric acid ester and surface films formed from phosphoric acid ester
(1) Phosphoric acid ester, (2) Tribo-film, (3) Adsorbed film on a sputtered surface,  (4) Adsorbed film on an as-received surface, (5) As-received steel surface
8. General discussion

As a summary, considering extent of dissociative reaction from carbon and phosphorus rate of the their topmost layer and also from their thicknesses, the two additives surely have different preference of surface state for dissociative reaction, where amine phosphate is likely to react with a metal surface and phosphoric acid ester is likely to react with an oxide surface. Roughly speaking, phosphoric acid ester tends to react more dissociatively than amine phosphate judging from the thickness of the topmost layers.

8.3 Chemical state information

It is still under question how the structure of the adsorbed or tribo film is like, and whether the decrease of carbon rate and increase of phosphorus rate mean change from organic phosphate to iron phosphate or not. Another question is whether the phosphorus compound of the adsorbed films and the tribo-stressed films differ from each other or not. However, it is difficult to distinguish the difference between iron phosphate and organic phosphate from O1s or P2p spectrum and then iron phosphate peak around 712.4eV of Fe2p spectrum is the only data to indicate presence of iron phosphate. Consequently it is difficult to
understand the mechanism of tribo-reaction or adsorption with the additives from those information.

Now, it is well known that chemical shifts occur with Auger lines as well as with photoelectron lines and the chemical shifts are different from those of the photoelectron lines, but they are often more pronounced. This can be very useful for identifying chemical states, especially in combination with photoelectron chemical shift data. If data for the various chemical states of an element are plotted with the binding energy of the photoelectron line on the abscissa and the kinetic energy of the Auger line on the ordinate, a two-dimensional chemical state plot can be obtained [1].

With this chemical state plot, the Auger parameter method becomes more powerful as a tool for identifying the chemical components than using photoelectron chemical shifts alone. In this method, the kinetic energy of the Auger line is plotted against the binding energy of the photoelectron line, with the latter plotted in the –x direction (kinetic energy is still, implicitly, +x). The kinetic energy of the Auger electron, referred to the Fermi level, is easily calculated by subtracting from the photo energy the position of the Auger line on the binding energy scale.

With this arrangement, each diagonal line represents all values of equal sums of Auger kinetic energy and photoelectron binding energy. The Auger parameter, $\alpha$, is defined as,

$$\alpha = KE_A - KE_P = BE_P - BE_A \tag{8.3.1}$$

or as the difference in binding energy between the photoelectron and Auger lines. This difference can be accurately determined because static charge corrections cancel. With all kinetic and binding energies referenced to the Fermi level, and recalling that:

$$KE = h\nu - BE \tag{8.3.2}$$

then,

$$KE_A + BE_P = h\nu + \alpha \tag{8.3.3}$$

or the sum of the kinetic energy of the Auger line and the binding energy of the photoelectric line equals the Auger parameter plus the photon energy. A plot showing Auger kinetic energy versus photoelectron binding energy then becomes independent of the photon energy. In general, polarizable materials, especially conductive materials, have a high Auger parameter, while insulating compounds have a lower Auger parameter. The chemical state plot of phosphorus has been successfully used for the chemical identification of its chemical state in the case of amorphous alloys [2].

In Fig.8.3.1, phosphorus chemical state plots of the tribo-stressed surfaces, the adsorbed surfaces, the frozen pure additives and some standard chemicals that can have similar structure to them are shown. The data points seem to differ from each other in the plots. Looking at their Auger parameters one by one, first as to the standard chemicals, iron phosphate has Auger parameter of 1984.0-odd eV (FePO$_4$: 1984.3eV, Fe$_4$(P$_2$O$_7$)$_3$: 1984.1eV),
iron phosphite is approximately 1987.8eV and phosphorus red is approximately 1987.0eV. Then, as to the frozen additives, both amine phosphate and phosphoric acid ester have more or less the same Auger parameter around 1983.5eV. Next regarding the adsorbed and the tribo-stressed surfaces, they can be divided into several categories, where amine phosphate has Auger parameter of around 1984.5eV for both the adsorbed and the tribo-stressed surface, which is shifted upper by 1.0eV from frozen amine phosphate, and phosphoric acid ester has Auger parameter of around 1983.8eV for both the adsorbed and the tribo-stressed surface, which are shifted upper by only 0.3eV from the frozen pure phosphoric acid ester.

Next, regarding the high temperature tests, the surfaces adsorbed or tribo-stressed with amine phosphate have Auger parameter around 1984.0eV, which is shifted up by 0.5eV from pure amine phosphate, and the surfaces adsorbed or tribo-stressed phosphoric acid ester have Auger parameter around 1983.5eV, which is more or less the same as pure phosphoric acid ester. Now, as mentioned above, it seems that the state of adsorbed or tribo-stressed surfaces differ from the pure additive, whereas difference between the adsorbed and tribo-stressed surface are not distinguishable even from the phosphorus chemical state information.

The organic phosphate has the lowest Auger parameter and the standard chemical of iron phosphate has the highest value, then the adsorbed or tribo-stressed surfaces are between them. It would be natural to think that the adsorbed or the tribo-stressed surface have intermediate structure of iron phosphate and the organic phosphate, or mixture of them, rather than to think that they are completely independent substances. Also it is thought that the more the dissociative reaction progress, the more the additives (about 1983.5eV) become closely to inorganic iron phosphate (about 1984.5eV), and the more dissociative reaction take place by the adsorption or tribo-stress, the higher the Auger parameter value shows.

Next, the adsorbed or the tribo-stressed films at high temperature has lower Auger parameter value than those at room temperature, showing that the high temperature does not enhance dissociative reaction in the case of these particular additives, which is probably opposite to major understanding that high temperature causes dissociative reaction. However, these results agree with the quantitative results, that is, the topmost layer of the adsorbed or the tribo-stressed surface at room temperature has higher rate of iron and lower rate of carbon than those at high temperature. This shows that the dissociative reaction progress more at room temperature than at thigh temperature.

In conclusion, an adsorbed or a tribo-stressed surface with amine phosphate has a structure close to iron phosphate by dissociative reaction, while that with phosphoric acid ester has a structure rather close to organic phosphate by less dissociative reaction. It is also concluded that the adsorption or tribo-reaction with these particular additives is not necessarily simple irreversible reaction that progress as temperature rise.
8.4 A consideration of the reaction mechanism

Lubrication mechanism of lubricant additive in boundary lubrication is one of the most complex aspects of tribology. The chemistry of friction surface and their state determine the interaction of those surfaces with the additives. Chemical reaction of a lubricant additive occurring during friction involves the formation of a film on a contact surface to alter its character and so protect it during friction. Lubrication mechanism of phosphate ester, e.g., TCP, has been proposed in numerous papers as mentioned in chapter 2, where iron phosphide or iron phosphate including that with hydrate are formed by thermo-chemical reaction. In this work, the reaction film is also concluded to be iron phosphate or that with hydrate with XPS characterization. In this section, feasible reaction mechanism of the selected additives on
8. General discussion

steel surface will be discussed based on the results.

All the tribo reactions start with adsorption of additive molecules on a steel surface. In the selected additives, amine phosphate and phosphoric acid ester seem to adsorb and then react with a surface at room temperature, whereas alkyl amine may adsorb but do not react with it at room temperature. States of amine phosphate and phosphoric acid ester in lubricant are illustrated in Fig.8.4.1 as discussed in chapter 4. Phosphoric acid ester exist as the formula illustrated in Fig.8.4.1 (a), whereas amine phosphate exists in the different state from the formula normally described, that is, the hydrogen atom of the phosphoric acid ester part is attracted to the alkyl amine part and consequently the phosphoric acid ester part has the two equivalent state of oxygen as illustrated in Fig.8.4.1 (b). When these additives adsorb on a steel surface, it is considered that phosphoric acid ester adsorb mainly at the double-bonded oxygen atom as Fig.8.4.1 (c) and adsorption at oxygen atoms of P-O-C or P-OH is considered to be minor because of geometric problems, while amine phosphate (the phosphoric acid ester part of amine phosphate) adsorb at the two equivalent state of oxygen atoms as Fig.8.4.1 (d).

![Diagram of adsorption of phosphoric acid ester and amine phosphate](image)

Fig.8.4.1 Adsorption of phosphoric acid ester and amine phosphate on a steel surface.
Next, chemical reaction forming inorganic iron phosphate takes place by elimination of alkyl chains from the molecules. This chemical reaction differs with whether the surface is a metal or a metal oxide. When the surface is metal, the reaction described in equation 8.4.1 should mainly take place. If influence of $\text{H}_2\text{O}$ or $\text{O}_2$ dissolved in the lubricant is taken into account, oxidation of the surface should also take place as described in equation 8.4.2 and then reaction between the oxidized metal surface and the additive would take place as equation 8.4.3. (It is considered that the reason that a sputtered steel surface, a metal surface, is fairly oxidized during adsorption of the additives (see chapter 6) is due to this oxidation reaction as described in equation 8.4.2.) On the other hand, when the surface is metal oxide, the reaction as equation 8.4.4 should mainly take place.

**[Metal surface]**
\[
\begin{align*}
\text{Fe} + R_x\text{HPO}_4 & \rightarrow \text{FePo}_4 + 2R \quad \text{(major)} \quad (8.4.1) \\
\text{Fe} + (H_2O, O_2) & \rightarrow \text{Fe}_xO_y \\
\text{Fe}_xO_y + R_x\text{HPO}_4 & \rightarrow \text{FePo}_4 \cdot zH_2O + 2R \quad \text{(minor)} \quad (8.4.3)
\end{align*}
\]

**[Oxide surface]**
\[
\begin{align*}
\text{Fe}_xO_y + R_x\text{HPO}_4 & \rightarrow \text{FePo}_4 \cdot zH_2O + 2R \quad (8.4.4)
\end{align*}
\]

Small area analysis described in chapter 6 and 7 showed that some $\text{H}_2\text{O}$ related oxygen peak was detected on an adsorbed or tribo-stressed surface with phosphoric acid ester, while it was barely detected on an adsorbed or tribo-stressed surface with amine phosphate. This means that a reaction with a metal oxide surface as equation 8.4.4 occurs mainly in adsorption or tribo-stress with phosphoric acid ester, whereas a reaction with a metal surface as equation 8.4.1 occurs mainly in adsorption or tribo-stress with amine phosphate. This tendency agrees with the result of quantitative analysis summarized in 8.1.

Now, the phenomena that amine phosphate prefers metal surface, while phosphoric acid ester prefers oxide surface can be explained reasonably by considering Lewis acids-bases principle. The acids-bases reaction can be described as follows,
\[
A + B \rightarrow A:B \quad (8.4.5)
\]
where $A$ is a Lewis acid, which accept electrons from $B$, and $B$ is a Lewis base, which donate the electrons to $A$. Chemisorption can be considered as a kind of acid-base reaction, and generally speaking an adsorbate is a base while a metal surface is an acid. Now there is one important principle in acids-bases reaction called "hard and soft acids and bases (HSAB) principle" [3]. This principle has been validated for many organic and inorganic reactions [4]. The hardness and softness as acids or bases for some metals, metal oxides and inorganic or organic compounds are listed in table 8.4.1, where a metal is categorized as a soft acid,
8. General discussion

whereas a metal oxide is categorized as a hard acid. Bases that prefer soft acids correspond to soft bases which possess movable electrons, i.e. compounds that have $\pi$ electrons as olefin and aromatic compounds, and also compounds that have movable unpaired electron as sulfur compounds. On the other hand, acids that prefer hard acids correspond to hard bases which have usually polar group as carboxyl acid ester, amine, phosphate and so on. Therefore, in general phosphoric acid ester and amine phosphate should be categorized as hard bases, which prefer a metal oxide surface, a hard acid. However, since the phosphoric acid ester part of amine phosphate exists having two equivalent oxygen atoms, whose electron are relatively movable, amine phosphate can behave as relatively soft base and consequently tends to react with a metal surface rather than a metal oxide surface.
### Table 8.4.1 Classification of Hard and Soft Acids and Bases [5]

<table>
<thead>
<tr>
<th>Acids</th>
<th>Hard acids</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H⁺, Li⁺, Na⁺, K⁺(Rb⁺, Cs⁺)</td>
</tr>
<tr>
<td></td>
<td>Be²⁺, Be(CH₃)₂, Mg²⁺, Ca²⁺, Sr²⁺(Ba²⁺)</td>
</tr>
<tr>
<td></td>
<td>Sc³⁺, La³⁺, Ce⁴⁺, Gd³⁺, Lu³⁺, Th⁴⁺, U⁴⁺, UO₂²⁺, Pu⁴⁺</td>
</tr>
<tr>
<td></td>
<td>Ti⁴⁺, Zr⁴⁺, Hf⁴⁺, VO²⁺, Cr³⁺, Cr⁶⁺, MoO³⁺, WO⁴⁺, Mn²⁺, Mn⁷⁺, Fe³⁺, Co³⁺</td>
</tr>
<tr>
<td></td>
<td>BF₃, BCl₃, B(OR)₃, Al³⁺, Al(CH₃)₃, AlCl₃, AlH₃, Ga³⁺, In³⁺</td>
</tr>
<tr>
<td></td>
<td>CO₂, RCO⁺, NC⁺, Si⁴⁺, Sn⁴⁺, CH₃Sn⁺, (CH₃)₂Sn²⁺</td>
</tr>
<tr>
<td></td>
<td>N³⁺, RPO²⁺, RSO²⁺, ROSO²⁺</td>
</tr>
<tr>
<td></td>
<td>Cl⁻, Br⁻, I⁻, I⁻²</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Borderline acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺</td>
</tr>
<tr>
<td>Rh³⁺, Ir³⁺, Ru³⁺, Os³⁺</td>
</tr>
<tr>
<td>B(CH₃)₃, GAH₃</td>
</tr>
<tr>
<td>R₃C⁺, C₆H₅⁺, Sn²⁺, Pb²⁺</td>
</tr>
<tr>
<td>NO⁺, Sb³⁺, Bi³⁺</td>
</tr>
<tr>
<td>SO₂</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Soft acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(CN)₅³⁻, Pd²⁺, Pt²⁺, Pt⁴⁺</td>
</tr>
<tr>
<td>Cu⁺, Ag⁺, Au⁺, Cd²⁺, Hg⁺, Hg²⁺, CH₃Hg⁺</td>
</tr>
<tr>
<td>BH₃, Ca(CH₃)₂, GaCl₃, GaBr₃, GaI₃, Ti⁺, Ti(CH₃)₃</td>
</tr>
<tr>
<td>CH₂, carbenes</td>
</tr>
<tr>
<td>π acceptors: trinitrobenzene, chloroanil, quinones, tetracyanoethylene, etc.</td>
</tr>
<tr>
<td>HO⁺, RO⁺, RS⁺, RSe⁺, Te⁴⁺, RTE⁺</td>
</tr>
<tr>
<td>Br₂, Br⁺, I⁺, I⁺², ICN, etc.</td>
</tr>
<tr>
<td>O, Cl, Br, I, N, RO⁻, RO₂⁻</td>
</tr>
<tr>
<td>M⁰ (metal atoms) and bulk metals</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bases</th>
<th>Hard bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃, RNH₂, N₂H₄</td>
<td></td>
</tr>
<tr>
<td>H₂O, OH⁻, O₂⁻, ROH, RO⁻, RO⁻</td>
<td></td>
</tr>
<tr>
<td>CH₃COO⁻, CO₂⁻, NO₃⁻, PO₄³⁻, SO₄²⁻, Cl⁺</td>
<td></td>
</tr>
<tr>
<td>F⁻(Cl⁻)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Borderline bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅NH₂, C₆H₆N, N₃⁻, N₂</td>
</tr>
<tr>
<td>NO₂⁻, SO₃²⁻</td>
</tr>
<tr>
<td>Br⁻</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Soft bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁻</td>
</tr>
<tr>
<td>R⁻, C₂H₄, C₆H₅, CN⁻, RNC, CO</td>
</tr>
<tr>
<td>SCN⁻, R₃P, (RO)₃P, R₃As</td>
</tr>
<tr>
<td>R₂S, RSH, RS⁻, S₂O₃⁻</td>
</tr>
<tr>
<td>I⁻</td>
</tr>
</tbody>
</table>
8. General discussion

References


9. Conclusion

9.1 Major accomplishment of the present work

The mechanism of tribo-reaction of lubricant additives in boundary lubrication condition was studied by correlating macro tribo-test information and nano surface analysis of the boundary lubrication layer, where a few lubricant additives with phosphate or thiophosphate function group were selected and examined their tribo performance as well as the additives themselves (frozen), their adsorption films on various conditions of steel surface and tribo-stressed films were characterized with XPS.

First, the technique of measuring liquid samples with XPS by freezing with liquid nitrogen enables characterization of liquid state of the selected additives. The qualitative and quantitative analysis of the additives confirmed their detailed structures, and revealed remarkably that amine phosphate exist in different state from the constitutional formula usually described.

In tribological tests, tribological performance of the selected additives was evaluated at room temperature and high temperature paying attention to influence of running-in, roughness of contacting surfaces, and temperature. It was found that amine phosphate reduces friction in a boundary lubrication condition even at room temperature, and the phosphoric acid ester part of amine phosphate particularly contributes for reducing friction.

The adsorption films of the selected additives on various states of steel surfaces were precisely investigated with XPS. The results revealed that the adsorption film mainly consists of organic/inorganic phosphate. The quantitative analysis based on three layer model (topmost layer, middle layer and substrate) revealed that thickness of surface layers, adsorption film layer and iron oxide layer, are few nano meters each.

The tribo-reaction film formed on the tribo-stressed surface was precisely investigated by imaging and small area XPS analysis. From imaging XPS, elemental distribution is clearly observed around the rubbed area. Small area analysis revealed that the contact area mainly consists of inorganic (iron) / organic phosphate, while the non-contact area consists of organic phosphate and oxide.

Finally, two dimensional phosphorus chemical state plot enables distinction among tribo-film, adsorption film and additives. The chemical state plot revealed that the tribo-film formed from amine phosphate is more polarized (closer to inorganic phosphate) than that formed from phosphoric acid ester. Furthermore, the difference of adsorbability or reactivity between amine phosphate and phosphoric acid ester was understood reasonably by considering hard and soft acids and bases (HSAB) theory.
9. Conclusion

9.2 Future work

First of all, tribological tests varying load, velocity and temperature with further more preciseness need to be carried out in order to grasp lubrication properties of the selected additives in each lubrication condition. Then, imaging and small area XPS analysis of these tribo-stressed surfaces is required for understanding better how load, velocity and temperature affect formation of tribo-films.

As far as XPS analysis is concerned, first, the accuracy of curve fitting on a Fe2p3/2 spectrum need to be improved and particularly peak identification among iron oxides and iron phosphate need to be improved. Using monochromated X-ray source is one possibility for it. There is some room for improvement in the accuracy of the quantification by means of the three layer model. The more precise estimation of the physical property parameters of each layer, such as density, is desired.

In the present work, amine phosphate and its two constituents are mainly focused, but the other selected additives also need to be investigated in the same way. Also, XPS is used as a surface analytical tool for characterizing the tribo-films and adsorbed films qualitatively and quantitatively in this work, however, use of other technique with higher surface sensitivity and higher spatial resolution, such as ToF-SIMS or AES can be helpful for understanding the mechanism of tribo-film formation. Furthermore, an in-situ study combining a tribological test and some surface analysis is desired.
Curriculum vitae

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Award received
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