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An experimental and analytical study of the effect of water and its 
tribochemistry on the tribocorrosive wear of boundary lubricated systems 
with ZDDP-containing oil

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Abstract

Water has long been recognised as a contaminant in lubricants. It can affect wear performance, especially in bearing systems, in complex ways. Water can also induce corrosion, which in turn can enhance wear. The individual parts of any tribocorrosion system are related to a complex mix of system parameters such as lubricant and additives, relative humidity and temperature. The effect of different water concentrations and different temperatures has been studied experimentally in this work. A modification to Archard’s wear coefficient was applied with respect to the experimental measurements. The new wear model considering the effect of water was implemented into the previously-reported numerical model to develop a new semi-deterministic numerical wear model adapted to the tribo-corrosion system in this work.

1 Introduction

Water in lubricants has been known to be a contaminant for many systems [1-3]. It is shown to affect the wear performance, especially in bearing systems, in different ways [4-10]. The presence of water in lubricated tribosystems, particularly in bearing applications, can cause corrosion and hydrogen embrittlement, which can increase wear and friction [8]. In addition, even small amount of water in parts per million (ppm) may accelerate the oxidation of oil [11].

To investigate the effect of water contamination on the performance of lubricated systems, it is essential to know the form that water exists in the oil [12]. Water can be present in oil in
two different forms which are dissolved water and free water \[13\]. Dissolved water occurs when the amount of water in oil is less than the saturation point \[1\]. Free water occurs when the amount of water in oil exceeds the saturation level. In this case, droplets of water will be formed in oil resulting in emulsion formation \[11\].

The factors determining the water absorption properties of lubricants are oil composition, physiochemical properties, concentration of additives, contaminants and local environment, e.g. temperature and pressure \[13\].

1.1 Oil oxidation

Ciruna and Szieleit \[8\] suggested that the main sources of atomic hydrogen are water and lubricant decomposition. The interaction of heat, pressure and air in the lubricated system can result in oil oxidation. The oil oxidation can be enhanced by water contamination by orders of magnitude. The by-products of oil oxidation are always acids, which can make the environment more corrosive. This corrosive environment in oil can accelerate the wear rate \[2\].

Interacting surfaces can be affected directly by water or they can be affected indirectly when the water oxidises the lubricants and additives or generates atomic hydrogen that leads to hydrogen embrittlement.

1.2 Effect of water on the lubricant performance

A review of the effect of water on friction and wear of lubricated systems is made by Lancaster et al. \[14\] and more recently by Cen et al. \[11\]. Firstly, water may affect the formation and removal of the tribofilm by altering the capability of long chain molecules to adhere to the surface. Secondly, it may modify the chemical composition of the tribofilm. Thirdly, water can increase pitting especially in rolling elements. These effects are manifested in altering the bearing performance by modifying friction and wear. Sheiretov et al. \[15\] investigated the effect of dissolved water on the tribological properties of three oils, i.e. Polyalkylene Glycol (PAG) with water content from 200 to 17000 ppm and two Polyolester (PE1 and PE2) oils with water content from 70 to 1600 ppm. In all the measurements conducted in an air atmosphere, the wear of cast iron plates shows a decrease with increasing the water content. Different additives can be added to lubricants to achieve certain properties. These additives can be viscosity-index improvers, anti-wear, friction modifier and extreme pressure additives \[11\].
It has been widely reported that ZDDP acts as an antiwear additive in the boundary lubrication regime by forming a relatively thick tribofilm on the contacting asperities. This solid-like tribofilm increases the load carrying capacity of the surfaces and protects the surfaces by being partially removed and preventing the direct solid-solid contact of substrates. Chemical, physical and mechanical properties of this tribofilm control the wear behaviour of the system (16).

Rounds (17) studied the effect of free water on the decomposition of ZDDP and the results showed that water seems to accelerate the rate of ZDDP decomposition and the formation of tribofilm. Therefore, they suggested that the decomposition of ZDDP is due to not only thermal decomposition but also hydrolysis. In contrast, Faut and Wheeler (18) found that for another type of phosphate additives, i.e. Tricresyl Phosphate (TCP), water inhibits the tribofilm formation.

Nedelcu et al. (19) studied the effect of water concentration in lubricated sliding and rolling contacts with PAO and ZDDP additive. They showed that water affects the decomposition of ZDDP and inhibits the growth of the ZDDP tribofilm. These results are obviously in contrast with the results reported by Rounds et al. (17). The difference might arise from the two different concepts. Rounds showed that adding water to ZDDP results in reducing the induction time for formation of the tribofilm on the surfaces (17). While, Nedelcu showed that the presence of water might interfere with additive adsorption on the steel surface, changing the tribochemical reactions and reducing the evolution of the rate of formation of tribological film with time. This effect manifests itself in the formation of shorter polyphosphate chains. This was attributed to the depolymerisation reactions of the long polyphosphate chains and to the increased surface distress in the presence of water. Cen et al. (11, 20) studied the effect of relative humidity, i.e. 20, 60 and 100%, on ZDDP anti-wear performance in lubricated steel/steel contacts under extreme pressure and pure sliding conditions. Similar to the findings of Nedelcu et al. (19) they found that the water in the oil inhibits the formation of the protective ZDDP tribofilm.

While recent research has increased the understanding on ZDDP tribofilm, the effect of water in oil on tribological performance is still not fully understood. In addition, wear prediction in these systems is still very limited. The current study aims to experimentally assess the impact of water in oil on tribofilm growth rates with the purpose of developing models capable to predict wear.
1.3 Wear prediction

Predicting wear is one of the greatest challenges in the tribology. There have been many attempts to predict wear in lubricated systems for different tribological configurations. Evaluating wear in boundary lubrication has been extensively the subject of many studies. There are almost 300 equations for wear/friction in the literature which are for different conditions and material pairs but none of them can fully predict the wear based on first principles including the whole physics of the problem. Some examples of these models are Suh delamination theory of wear, Rabinowicz model for abrasive wear and the Archard’s wear equation. Wear occurs by different interfacial mechanisms and all these mechanisms can contribute in changes in the topography. It has been widely reported that 3rd body abrasive particles play an important role in the wear of the surfaces. The model proposed by Archard was investigated in a wide range of studies, different contact configurations and also different scales. Archard’s model was initially developed for sliding in dry conditions and no effect of lubricant or chemistry was involved in the model. By the current understanding of the wear problem and the development of advanced surface analytical techniques, it is clear that the chemical and mechanical properties of the tribofilms play a very important role in the wear behaviour of the tribosystems and should be considered when developing wear models for lubricated contacts. There is therefore a need to see the chemical effects incorporated into any new wear models growing forward.

Some researchers have suggested modifications to the Archard’s model. A mathematical model developed by Sullivan describes oxidational wear in boundary lubrication contacts. The model is based on different parameters that together can be assumed as Archard’s wear coefficient. Another attempt to investigate the wear in micro contacts is made by Zhang et al. They used classical wear models to calculate the probability of contact to be covered by physically and chemically adsorbed layers. Flash temperatures, real area of contact and friction force were also calculated by the model. The model suggests that higher lubricant/surface reactivity or substrate hardness enhance the micro-contact behaviour therefore affecting the wear of the system.

In work by Andersson et al., a mathematical and chemical model was developed to capture the growth of the tribofilm at a local scale which changes the geometry of contacting surfaces. Archard’s wear equation was then used to calculate wear at the asperity scale. They
predicted the growth of the tribofilm on the contacting asperities for different surface roughnesses. The same coefficient of wear was considered for tribofilm and substrate which was one of the drawbacks of the model. Another model developed by Bosman et al. [30] proposes a numerical formulation for mild wear prediction under boundary lubrication systems. They suggest that chemically-reacted layers are the main mechanisms responsible for protecting boundary lubricating systems and when these layers are worn off, the system will restore the balance and the substrate will react with the oil to produce a tribofilm. The effect of tribofilm was then considered in the model and the amount of substrate atoms in the depth of the tribofilm was reported to be the reason for the wear of the system in the presence of the tribofilm.

Recently a wear model was proposed by Ghanbarzadeh et al. [31] which considers the growth of ZDDP tribofilm on the contact asperities in boundary lubrication systems. The model takes into account the effect of ZDDP tribofilm in changing Archard’s wear coefficient. The analytical results were validated with experiments in rolling-sliding conditions reported in another work [32]. The model considers the partial removal of the tribofilm and relates it to the wear of the substrate in the case of ZDDP on steel surfaces. The tribochemistry model was an important part of the whole semi-deterministic model because it defines the behaviour of tribofilm growth on the contacting asperities.

In the current study an investigation into the effect of temperature and water concentration in oil on the growth of the film in tribocorrosion conditions is carried out. A set of experiments for different concentrations of water in oil was designed and carried out to study the effect on wear and growth of the tribofilm. The effect of water on the growth of the ZDDP tribofilm obtained by experimental results is then inputted into the wear model reported in [31] and briefly explained in the following section.

2 Numerical approach

The deterministic approach used in this work is based upon the model developed to simulate a boundary lubricated contact reported in. In the current study, a new part is added to the original model to include the effect of water concentration by using two approaches explained bellow. Although the model components are explained briefly in this section, the
details of the contact model and the wear mechanism can be found in Ref. [31] and [32] respectively.

The model consists of the following main parts:

- A deterministic contact model for rough surfaces using elastic-perfectly plastic theory
- A semi-analytical tribofilm growth model based on thermodynamics of interfaces
- Tribofilm mechanical properties which includes the values reported previously in the literature
- A new proposed modification of Archard’s wear model considering the effect of ZDDP tribofilm

In this model, digitized surfaces have been used as the inputs. This method is explained in detail by Tonder et al. [33] and in the author’s previous work [31]. The contact mechanics model is a plastic-perfectly plastic approach using the complementary potential energy formulation [31].

In order to consider tribochemistry, this model contains the tribofilm formation part which is based on kinetics of tribochemical reactions and is combined with a phenomenological term that accounts for dynamics removal of the tribofilm [31] and is shown by Equation 1.

\[
h = h_{\text{max}} \left(1 - e^{-k_{T}T_{\text{tribo}}t}\right) - C_3(1 - e^{-C_4t})
\]

(1)

in which \(k_3\) and \(h'\) are the Boltzmann and the Plank’s constant, \(T\) is the flash temperature and \(C_3\) and \(C_4\) are removal constants. The term \(x_{\text{tribo}}\) was interpreted as the mechanoactivation in inducing the tribochemical reactions. A detailed discussion can be found in the previous work [31].

The wear model used in the numerical approach is a modified version of Archard’s wear equation that accounts for the growth of the ZDDP tribofilm on the surface. The wear model is local and is space and time-dependant. Assuming that the coefficient of wear is at its
maximum for steel-steel contact and at its minimum when the tribofilm has its maximum thickness, the equation for calculating coefficient of wear is as follows:

\[ K_{tr} = K_{steel} - (K_{steel} - K_{min}) \cdot \frac{h}{h_{max}} \]  

(2)

where \( K_{tr} \) is the coefficient of wear for a tribofilm with thickness \( h \). \( K_{steel} \), \( K_{min} \) and \( h_{max} \) are coefficients of wear for steel and the maximum ZDDP tribofilm thickness and maximum film thickness respectively. It was reported that wear can occur due to the removal of the tribofilm from the surface. There is limited number of the substrate atoms in the bulk of the tribofilm due to different surface phenomena [34-36]. Therefore the dynamic process of the formation and removal of the tribofilm on the contacting asperities will lead to the removal of the substrate atoms [32]. This is a simple mathematical formulation for studying the effect of ZDDP tribofilm on reducing wear on steel surfaces. This wear model is explained in detail in [32] and is validated against experimental results.

3 Experimental procedure

3.1 Test rig

A Mini Traction Machine (MTM, PCS Instruments UK) [Figure 1] is used to assess the effect of water on wear under rolling and sliding conditions. One of the key points in using MTM is that slide-to-roll ratio (SRR) can be changed in the experiments and it is possible to run the experiment in the wide range of slide to roll ratio (0 < SRR < 5) [37]. SRR is defined as the following:

\[ SRR = \frac{U_A - U_B}{U_A + U_B \cdot \frac{2}{2}} \]  

(3)

In which \( U_A \) and \( U_B \) are the speed of surfaces A and B respectively. The SRR is the ratio of the sliding and the entrainment speeds.

In the standard configuration the test specimens are a 19.05 mm (3/4 inch) steel ball and a 46 mm diameter steel disc. The ball is loaded against the face of the disc and the ball and disc are driven independently to create a mixed rolling and sliding contact. The frictional force between the ball and disc is monitored by a force transducer. The applied load and the lubricant temperature are monitored by sensors.
3.2 Spacer Layer Interferometry

Spacer Layer Interferometry Method (SLIM) was used to measure tribofilm thickness in-situ while experiment is running [38]. Figure 1 shows the Spacer Layer Interferometry schematically. Ball is loaded against the disc to carry out the test and depends on the program defined to the MTM, test is stopped periodically and the ball loaded in reverse against the glass disc. The glass disc is coated with a thin layer of silicon oxide which has a semi-reflective layer of chromium on top. The contact of the ball is illuminated by white light through the microscope and the coated glass. Part of the light is returned back from the semi-reflective chromium layer on top of the coated glass and other part goes through the silicon oxide layer and tribofilm formed on the surface and is reflected back from the steel ball. These light paths are captured by RGB colour camera and it can be analysed by the software to evaluate the tribofilm thickness during the experiments. This method is capable of measuring the film thickness of any reaction layer as they formed on the surface.

![Figure 1 MTM and the Spacer Layer Interferometry configuration](image)

3.3 Material and test conditions

In this study the balls and disc used were both of AISI 52100 steel with hardness of 6 GPa. New balls and discs were used for each experiment. They were cleaned up before each test by immersing in isopropanol and petroleum ether in an ultrasonic bath for 20 minutes. All the experiments were conducted at an applied load of 60 N. According to the diameter of the ball
which is 19 mm, the maximum Hertzian contact pressure of 1.2 GPa was calculated. The material properties are shown in the Table 1. Experiments were carefully designed to study wear in boundary-lubricated contacts at different temperatures, water concentration. A small entrainment speed was chosen for this purpose. The working conditions and the corresponding λ ratios are reported in Table 2. Water and oil were mixed at four different levels of water concentration in the ultrasonic bath for 5 minutes.

<table>
<thead>
<tr>
<th>Table 1 Material properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material properties</td>
</tr>
<tr>
<td>Hardness (Ball/Disc) (GPa)</td>
</tr>
<tr>
<td>Elastic modulus (Ball/Disc) (GPa)</td>
</tr>
<tr>
<td>Ball surface roughness (Rₐ)</td>
</tr>
<tr>
<td>Disc surface roughness (Rₐ)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2 Experimental working conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters</td>
</tr>
<tr>
<td>Maximum contact pressure (GPa)</td>
</tr>
<tr>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>Water contents (Wt%)</td>
</tr>
<tr>
<td>Entrainment speed (m/s)</td>
</tr>
<tr>
<td>SRR</td>
</tr>
<tr>
<td>Test duration (min)</td>
</tr>
<tr>
<td>λ ratio</td>
</tr>
<tr>
<td>Oil used</td>
</tr>
<tr>
<td>Dimensions (mm)</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
3.4 Lubricating oil

In this study, PAO+ZDDP and PAO+ZDDP+water were used. Water and oil were mixed in ultrasonic bath for 5 minutes to have four different concentrations of water as mentioned in Table 3. PAO+ZDDP+water shows an emulsion state (free water) at room temperature but at 80°C and 100°C the water seems to be dissolved. It is in agreement with this concept that higher temperature leads to the higher saturation point and likewise, there is no free water after each tribological test.

Table 3 Lubricants

<table>
<thead>
<tr>
<th>Details</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAO+ZDDP (0.08 mass% phosphorus)</td>
<td>PAO+ZDDP</td>
</tr>
<tr>
<td>PAO+ZDDP (0.08 mass% phosphorus) + (0.5 mass %) Distilled water</td>
<td>PAO+ZDDP+water (0.5)</td>
</tr>
<tr>
<td>PAO+ZDDP (0.08 mass% phosphorus) + (1.5 mass %) Distilled water</td>
<td>PAO+ZDDP+water (1.5)</td>
</tr>
<tr>
<td>PAO+ZDDP (0.08 mass% phosphorus) + (3 mass %) Distilled water</td>
<td>PAO+ZDDP+water (3)</td>
</tr>
</tbody>
</table>

3.5 Experimental approach

The experimental part of this study can be split into two. All tribological experiments were carried out by MTM to simulate rolling/sliding conditions in boundary lubrication with four different water concentration values. The tribofilm thickness was measured using Spacer Layer Interferometry to evaluate the tribofilm formation in-situ. Finally the tribofilm was removed from the samples and wear was measured using White Light Interferometry. The sub-sets of tribological experiments are:

I. Experiments at 80°C for different levels of water concentration to investigate the effect of water on tribofilm formation and removal and tribological performance

II. Experiments at 100°C for different water concentration values to study the effect of water on tribological performance and tribofilm formation and removal
4 Results and discussion - Experimental

4.1 The effect of water on wear

The effect of water on wear performance is shown in Figure 2. According to the results, it can be seen that higher water concentration leads to higher wear. It could be concluded that water in oil accelerates wear. These results are in agreement with the works published by Lancaster [14] and Cen [11]. They proposed that water plays more significant role in increasing wear compared to the effect on friction. In both cases, higher water concentration results in higher wear. The comparison between two temperatures suggests that the lower temperature results in higher wear. It can be attributed to the lower water contents at higher temperature due to the evaporation of water. There is also less wear observed for 100°C compared to 80°C at zero percent water content. This can be related to the thicker tribofilm formed at higher temperatures. The results are in qualitative agreements with the recent studies [20, 32].

It is interesting to see that water concentration in oil for the case of 100°C is less than 80°C. It should be noted that the effect of temperature in changing the viscosity of the oil and therefore changing the severity of the contact is negligible in this case as the lambda ratio for both temperatures was calculated to be around 0.04. The water concentrations have been measured by Karl Fischer Titration Method before and after each experiment and the results are reported in Table 4.
Figure 2 Effect of water on average wear depth at two different temperatures of 80°C and 100°C

Table 4 Water concentration measurements before and after tribological test

<table>
<thead>
<tr>
<th>Lubricants</th>
<th>Water content before test (ppm)</th>
<th>Water content after 2hr test (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>80°C</td>
</tr>
<tr>
<td>PAO+ZDDP</td>
<td>71</td>
<td>11</td>
</tr>
<tr>
<td>PAO+ZDDP+water (0.5)</td>
<td>4736</td>
<td>62</td>
</tr>
<tr>
<td>PAO+ZDDP+water (1.5)</td>
<td>16540</td>
<td>121</td>
</tr>
<tr>
<td>PAO+ZDDP+water (3)</td>
<td>38920</td>
<td>274</td>
</tr>
</tbody>
</table>
4.2 Effect of water on tribofilm growth and wear

The lower tribofilm growth was observed for higher water concentration (Figure 3 and Figure 4) and this effect is more significant at lower temperature. This decrease significantly affects the tribofilm growth in the running-in period. It can affect the wear process due to the fact that the running-in period plays a significant role in the wear of the system. The results show that increasing the water concentration accelerates wear and it can be related to the effect of water on tribofilm growth at the beginning of the experiment. Steady state tribofilm thickness is also affected by water concentration in the oil; the more water concentration the less the tribofilm thickness. The results are in line with the previous research by Nedelcu et al. (19) and Cen et al. (11). It can be linked to the formation of shorter chain polyphosphates due to the depolymerisation of the longer chain polyphosphates by water molecules (11).

The same pattern was observed at 80°C and 100°C in terms of tribofilm growth rate (Figure 3 and Figure 4). The only difference is that the effect of water on tribofilm growth is clearly distinguishable at lower temperature indicating that the effect of water on the growth of the tribofilm in the running-in period at 80°C is more significant compared to 100°C. The steady state tribofilm thickness follows the same pattern for both temperatures indicating the lower tribofilm thickness for higher water concentration (Figure 5). It is also reported in Figure 5 that higher temperature leads to the higher tribofilm thickness and it is in line with the results Fujita et al. (39) published previously regarding ZDDP antiwear formation and removal. They proposed that both the tribofilm growth and steady state tribofilm thickness increase with temperature. For comparison purposes, the steady-state tribofilm thickness is plotted against the measured wear depth for both temperatures in Figure 6. It can be seen while the steady-state tribofilm thickness is higher, less wear occurs. However, tribofilm thickness in steady-state does not give a full picture of the wear behaviour in boundary lubricated systems. There are more physical, chemical and mechanical parameters responsible for the wear. In fact, the whole growth behaviour of the tribofilm on the surfaces is important for capturing the wear behaviour. It is important how the tribofilm was formed during the running-in process. A detail discussion on this can be found in Ref (32). Comparisons made between the effect of water on steady state tribofilm thickness and the average wear depth for 80°C and 100°C are plotted in Figure 7 and Figure 8 for 100°C and 80°C respectively. The trends indicate that increasing the water content in the oil affects wear by decreasing the steady state tribofilm thickness.
Figure 3 Tribofilm thickness measurement results for 100°C at different water concentrations

Figure 4 Tribofilm thickness measurement results for 80°C at different water concentrations
Figure 5 Steady state tribofilm thickness results for different water concentrations

Figure 6 Steady state tribofilm thickness results vs measured wear depth
Figure 7 Comparison between average wear depth and tribofilm thickness at different water concentration at 100°C

Figure 8 Comparison between average wear depth and tribofilm thickness at different water concentration at 80°C
5 Numerical analysis

The experimental results reported in Section 4 are used in this section in two different approaches to predict wear of the boundary-lubricated contact with the oil containing ZDDP additive.

5.1 First approach: semi-deterministic coefficient of wear

In this approach it is assumed that the tribofilm thickness is following the same behaviour for all levels of water concentration. It means that the growth of tribofilm is the same for all water concentration experiments and the same amount of tribofilm is formed on the surfaces for all different experiments. This is not accurate in reality and experimental results reported in Section 4 show otherwise. But this approach is used to see if the same tribofilm growth behaviour is modelled for all experiments, a modification to Archard’s wear equation can predict the wear of the system. The only parameter that can be affected by water is assumed to be the initial coefficient of wear. The calibration procedure for the initial coefficient of wear is reported in Ref [32]. This approach is applied to semi-deterministically find the true coefficient of wear corresponding to the different levels of water concentration. The value of the average wear depth measured experimentally and reported in Section 4.1 was used to match the average wear depth results from the simulations for every level of water concentration. The procedure for determining the initial wear coefficient involves conducting simulations with different initial coefficients of wear to identify the coefficient value that exactly matches the wear behaviour observed in the experiment. The difference between the value of the calculated wear and the wear measured experimentally in Section 4.1 was set to be less than 0.1 nm in order to get the best match. The initial wear coefficients calculated from the simulations are reported in Table 5 for different water concentrations for 80°C and 100°C.

A factor $\psi$ is added to the proposed wear model of Equation 2 that is responsible for the effect of water on tribocorrosive wear of the system. Equation 2 is then converted to Equation 4.

$$K_{tr} = \psi K_{steel} - (\psi K_{steel} - K_{min}) \cdot \frac{h}{h_{max}}$$

$\psi$ is calculated between 1 and 2.5 in all ranges of water concentrations and is more for higher concentrations. These simulation results show that the coefficient of wear can be modelled.
for different levels of water concentration to predict wear. If the appropriate Ψ value is assigned in the simulation of wear in the presence of water, wear values can be successfully predicted by Equation 4. Ψ is then reported in Table 6 for different levels of water concentration.

Table 5 Wear coefficients used in the numerical simulations (Dimensionless)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>0%</th>
<th>0.5%</th>
<th>1.5%</th>
<th>3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>100°C</td>
<td>$10^{-8}$</td>
<td>1.64*10^{-8}</td>
<td>1.65*10^{-8}</td>
<td>2.3*10^{-8}</td>
</tr>
<tr>
<td>80°C</td>
<td>2*10^{-8}</td>
<td>2.7*10^{-8}</td>
<td>3.1*10^{-8}</td>
<td>3.5*10^{-8}</td>
</tr>
</tbody>
</table>

Table 6 Ψ for different water concentrations at different temperatures (Dimensionless)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>0%</th>
<th>0.5%</th>
<th>1.5%</th>
<th>3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>100°C</td>
<td>1</td>
<td>1.35</td>
<td>1.55</td>
<td>1.75</td>
</tr>
<tr>
<td>80°C</td>
<td>1</td>
<td>1.64</td>
<td>1.65</td>
<td>2.30</td>
</tr>
</tbody>
</table>

5.2 Second approach: effect of tribochemistry

To study the effect of tribochemistry, unlike the first approach, the starting coefficient of wear is assumed to be the same in the numerical model for different levels of water concentration. Following that, the effect of water in changing the growth behaviour of the tribofilm observed experimentally in Figure 3 and Figure 4 has been used to capture the behaviour in the model. As discussed in section 2.2, the changes in growth behaviour of the tribofilm will change the wear coefficient locally at the asperity scale. For the tribofilm growth part of the model, the four parameters $x_{tribo}$, $h_{max}$, $C_1$ and $C_2$ need to be determined for each set of experimental conditions in order to capture the tribofilm behaviour, which is different in each case. This is achieved by fitting Equation 1 to experimental measurements of tribofilm thickness of Section 4.2. These parameters are reported in Table 7 for different water contents. The wear is then calculated with respect to this growth behaviour and the results have been compared to the experimental wear depth results obtained experimentally.

Table 7 Simulation inputs and calibration parameters

<table>
<thead>
<tr>
<th>Water Concentration (wt %)</th>
<th>T=100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>$x_{tribo}$</td>
<td>1.66*10^{-16}</td>
</tr>
</tbody>
</table>
The tribofilm growth simulation results are plotted in Figure 9. The simulation wear results corresponding to the different levels of water concentrations for 100°C and 80°C are also shown in Figure 10 and are compared with the experimental results of section 4.1. It can be seen that tribofilm affects the wear of the system. In the higher concentrations of water a lower rate of formation of the tribofilm is being observed. This lower rate of formation results in higher coefficient of wear according to Equation 2. It is important to notice that once the tribofilm behaviour is captured (Figure 9), the model is able to predict the wear behaviour for the case of ZDDP on steel surfaces (Figure 10). So far in this research, capturing the tribofilm behaviour was dependent on the experimental results due to the lack of comprehensive mechanistic understanding of tribofilm formation and removal. Despite all the complexities, such simplified semi-analytical models for tribofilm growth can be good starting points for the problem. This is therefore a good approach for modelling wear in boundary lubricated contacts which can include the effect of water in the tribological behaviour of the system.
Discussion - Numerical

Tribocorrosive wear of the boundary lubricated system by oil containing a ZDDP antiwear additive has been modelled in this work considering the tribochemistry of the antiwear additive. It is shown that considering growth behaviour of the tribofilm for ZDDP on steel surfaces is a reasonable approach for modelling wear in tribocorrosive tribological systems. Experiments were designed to monitor the tribofilm growth in addition to the measurement of wear to be able to make a link between them. Two numerical approaches were tested in this work in order to study the effect of water in tribocorrosive wear of the boundary lubrication contacts and the results were shown in the previous section. For the first approach, coefficients of wear were semi-deterministically obtained from the simulations to satisfy the wear measurements. This approach suggests that for different water concentrations wear of the system is different and Archard’s wear equation needs to be modified accordingly. It was reported in Section 5.1 of the numerical results that a modification parameter can be used to modify the Archard’s wear coefficient in the previously reported tribochemistry wear model. This parameter (ψ) is calculated from the simulations and the range was between 1 and 2.5 for all water concentrations used in this study. It is shown that, without changing the growth
behaviour of the tribofilm (tribochemistry), simulations can predict the wear of tribocorrosion systems by changing the Archard’s wear coefficient. In the second approach, unlike the first one, the effect of water on the growth of the ZDDP tribofilm was considered. The growth model was calibrated for all different tribofilm growth cases and the simulations were carried out using those growth behaviours. The coefficient of wear was assumed to be constant for all the simulations in this approach unlike the first approach and the only parameter changing the coefficient of wear was the difference in tribofilm thickness of the different cases. Wear results in this case were shown in the previous section and good agreement can be seen with experimental results.

As shown in Table 7 the rate of formation of tribofilm is different for different levels of water concentration at the same temperature. The term $x_{tribo}$ which is responsible for the effect of mechanical rubbing on the initiation of tribochemical reactions \[31\] is reported in Table 7. It is clear both from experimental and numerical results that the formation rate decreases when water concentration increases. The term $x_{tribo}$ for different levels of water concentration is plotted in Figure 11.

![Figure 11](image_url)

**Figure 11** $x_{tribo}$ calibrated for different temperatures at different water concentrations at (a) 100° C and (b) 80° C
The simulation results based on the second approach show that if a good prediction in the
growth behaviour of the tribofilm is calculated, it can lead to a good prediction in the wear of
the system. In previous work by the authors [32], the wear model and the effect of tribofilm
in reducing wear have been studied and the numerical model showed good predictive
capabilities for wear. The term $x_{tribo}$ that is a major part in the growth behaviour of the
tribofilm will be the subject of future work of the authors with a focus being on how different
oils and tribological parameters affect the value. Understanding and being able to quantify
this term for tribocorrosion conditions will help to obtain a more robust predictive tribofilm
growth model. Tribofilm growth prediction then impacts the prediction of wear according to
Equations 2 and 3. In this stage of the work, only the predictive capability of the model in
tribocorrosive conditions was tested and the results are promising. More results and
development of this model will be reported in the future.

7 Conclusions

The effect of water on wear behaviour of boundary lubricated tribosystem in a rolling/sliding
contact has been studied experimentally and analytically in this work. It is concluded that:

- Water affects the tribochemistry of the zinc polyphosphates tribofilm on the surfaces.
  Water influences the growth behaviour of the tribofilm on the surfaces and more
  water in the oil results in lower rate of the growth on contacting surfaces.
- Water in oil can delay the growth of the tribofilm in the running-in period and it can
  significantly affect tribocorrosive wear in boundary lubricated system. This effect is
  more significant for the tests at 80$^\circ$C in comparison with tests at 100$^\circ$C due to more
  water in the oil.
- Higher water concentration leads to a reduction in growth rate of the tribofilm which
  in nature results in an increase in the wear of the system. This reduction in growth rate
  might be because of the difficulty that ZDDP molecules have in reacting with the
  substrate in the presence of the water.
- It was shown that tribofilm thickness in steady-state condition is not a good
  representative of the wear behaviour of the system. However other important
  physical, chemical and mechanical parameters are involved. The whole growth
behaviour of the tribofilm can be significantly important to characterize wear. This means that running-in period is also important in determining the wear of boundary lubricated systems.

- Two different numerical approaches were used to test the model and also represent the effect of water in wear of the system. With respect to the first approach, tribocorrosive wear can be predicted by modifying the Archard’s wear coefficient. The modification parameter (Ψ) increases by increasing the water concentration. The simulation wear results show good agreement with the experimental wear measurements.

- It is concluded in this work that once the characteristics of the tribofilm growth are captured, the model is capable of predicting tribocorrosive wear in boundary lubrication regime.

8 Acknowledgement

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9 References

An experimental and analytical study of the effect of water and its tribochemistry on the tribocorrosive wear of boundary lubricated systems with ZDDP-containing oil

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Abstract

Water has long been recognised as a contaminant in lubricants. It can affect wear performance, especially in bearing systems, in complex ways. Water can also induce corrosion, which in turn can enhance wear. The individual parts of any tribocorrosion system are related to a complex mix of system parameters such as lubricant and additives, relative humidity and temperature. The effect of different water concentrations and different temperatures has been studied experimentally in this work. A modification to Archard’s wear coefficient was applied with respect to the experimental measurements. The new wear model considering the effect of water was implemented into the previously-reported numerical model to develop a new semi-deterministic numerical wear model adapted to the tribo-corrosion system in this work.

1 Introduction

Water in lubricants has been known to be a contaminant for many systems [1-3]. It is shown to affect the wear performance, especially in bearing systems, in different ways [4-10]. The presence of water in lubricated tribosystems, particularly in bearing applications, can cause corrosion and hydrogen embrittlement, which can increase wear and friction [8]. In addition, even small amount of water in parts per million (ppm) may accelerate the oxidation of oil [11].

To investigate the effect of water contamination on the performance of lubricated systems, it is essential to know the form that water exists in the oil [12]. Water can be present in oil in...
two different forms which are dissolved water and free water. Dissolved water occurs when the amount of water in oil is less than the saturation point. Free water occurs when the amount of water in oil exceeds the saturation level. In this case, droplets of water will be formed in oil resulting in emulsion formation.

The factors determining the water absorption properties of lubricants are oil composition, physiochemical properties, concentration of additives, contaminants and local environment, e.g. temperature and pressure.

1.1 Oil oxidation

Ciruna and Szieleit suggested that the main sources of atomic hydrogen are water and lubricant decomposition. The interaction of heat, pressure and air in the lubricated system can result in oil oxidation. The oil oxidation can be enhanced by water contamination by orders of magnitude. The by-products of oil oxidation are always acids, which can make the environment more corrosive. This corrosive environment in oil can accelerate the wear rate.

Interacting surfaces can be affected directly by water or they can be affected indirectly when the water oxidises the lubricants and additives or generates atomic hydrogen that leads to hydrogen embrittlement.

1.2 Effect of water on the lubricant performance

A review of the effect of water on friction and wear of lubricated systems is made by Lancaster et al. and more recently by Cen et al. Firstly, water may affect the formation and removal of the tribofilm by altering the capability of long chain molecules to adhere to the surface. Secondly, it may modify the chemical composition of the tribofilm. Thirdly, water can increase pitting especially in rolling elements. These effects are manifested in altering the bearing performance by modifying friction and wear. Sheiretov et al. investigated the effect of dissolved water on the tribological properties of three oils, i.e. Polyalkylene Glycol (PAG) with water content from 200 to 17000 ppm and two Polyolester (PE1 and PE2) oils with water content from 70 to 1600 ppm. In all the measurements conducted in an air atmosphere, the wear of cast iron plates shows a decrease with increasing the water content. Different additives can be added to lubricants to achieve certain properties. These additives can be viscosity-index improvers, anti-wear, friction modifier and extreme pressure additives.
It has been widely reported that ZDDP acts as an antiwear additive in the boundary lubrication regime by forming a relatively thick tribofilm on the contacting asperities. This solid-like tribofilm increases the load carrying capacity of the surfaces and protects the surfaces by being partially removed and preventing the direct solid-solid contact of substrates. Chemical, physical and mechanical properties of this tribofilm control the wear behaviour of the system (16).

Rounds (17) studied the effect of free water on the decomposition of ZDDP and the results showed that water seems to accelerate the rate of ZDDP decomposition and the formation of tribofilm. Therefore, they suggested that the decomposition of ZDDP is due to not only thermal decomposition but also hydrolysis. In contrast, Faut and Wheeler (18) found that for another type of phosphate additives, i.e. Tricresyl Phosphate (TCP), water inhibits the tribofilm formation.

Nedelcu et al. (19) studied the effect of water concentration in lubricated sliding and rolling contacts with PAO and ZDDP additive. They showed that water affects the decomposition of ZDDP and inhibits the growth of the ZDDP tribofilm. These results are obviously in contrast with the results reported by Rounds et al. (17). The difference might arise from the two different concepts. Rounds showed that adding water to ZDDP results in reducing the induction time for formation of the tribofilm on the surfaces (17). While, Nedelcu showed that the presence of water might interfere with additive adsorption on the steel surface, changing the tribochemical reactions and reducing the evolution of the rate of formation of tribological film with time. This effect manifests itself in the formation of shorter polyphosphate chains. This was attributed to the depolymerisation reactions of the long polyphosphate chains and to the increased surface distress in the presence of water. Cen et al. (11, 20) studied the effect of relative humidity, i.e. 20, 60 and 100%, on ZDDP anti-wear performance in lubricated steel/steel contacts under extreme pressure and pure sliding conditions. Similar to the findings of Nedelcu et al. (19) they found that the water in the oil inhibits the formation of the protective ZDDP tribofilm.

While recent research has increased the understanding on ZDDP tribofilm, the effect of water in oil on tribological performance is still not fully understood. In addition, wear prediction in these systems is still very limited. The current study aims to experimentally assess the impact of water in oil on tribofilm growth rates with the purpose of developing models capable to predict wear.
1.3 Wear prediction

Predicting wear is one of the greatest challenges in the tribology. There have been many attempts to predict wear in lubricated systems for different tribological configurations. Evaluating wear in boundary lubrication has been extensively the subject of many studies. There are almost 300 equations for wear/friction in the literature which are for different conditions and material pairs but none of them can fully predict the wear based on first principles including the whole physics of the problem \(^{(21, 22)}\). Some examples of these models are Suh delamination theory of wear \(^{(23)}\), Rabinowicz model for abrasive wear \(^{(24)}\) and the Archard’s wear equation \(^{(25, 26)}\). Wear occurs by different interfacial mechanisms and all these mechanisms can contribute in changes in the topography. It has been widely reported that 3\(^{rd}\) body abrasive particles play an important role in the wear of the surfaces. The model proposed by Archard \(^{(25)}\) was investigated in a wide range of studies, different contact configurations and also different scales. Archard’s model was initially developed for sliding in dry conditions and no effect of lubricant or chemistry was involved in the model. By the current understanding of the wear problem and the development of advanced surface analytical techniques, it is clear that the chemical and mechanical properties of the tribofilms play a very important role in the wear behaviour of the tribosystems and should be considered when developing wear models for lubricated contacts. There is therefore a need to see the chemical effects incorporated into any new wear models growing forward.

Some researchers have suggested modifications to the Archard’s model. A mathematical model developed by Sullivan \(^{(27)}\) describes oxidational wear in boundary lubrication contacts. The model is based on different parameters that together can be assumed as Archard’s wear coefficient. Another attempt to investigate the wear in micro contacts is made by Zhang et al \(^{(28)}\). They used classical wear models to calculate the probability of contact to be covered by physically and chemically adsorbed layers. Flash temperatures, real area of contact and friction force were also calculated by the model. The model suggests that higher lubricant/surface reactivity or substrate hardness enhance the micro-contact behaviour therefore affecting the wear of the system.

In work by Andersson et al. \(^{(29)}\), a mathematical and chemical model was developed to capture the growth of the tribofilm at a local scale which changes the geometry of contacting surfaces. Archard’s wear equation was then used to calculate wear at the asperity scale. They
predicted the growth of the tribofilm on the contacting asperities for different surface roughnesses. The same coefficient of wear was considered for tribofilm and substrate which was one of the drawbacks of the model. Another model developed by Bosman et al. [30] proposes a numerical formulation for mild wear prediction under boundary lubrication systems. They suggest that chemically-reacted layers are the main mechanisms responsible for protecting boundary lubricating systems and when these layers are worn off, the system will restore the balance and the substrate will react with the oil to produce a tribofilm. The effect of tribofilm was then considered in the model and the amount of substrate atoms in the depth of the tribofilm was reported to be the reason for the wear of the system in the presence of the tribofilm.

Recently a wear model was proposed by Ghanbarzadeh et al. [31] which considers the growth of ZDDP tribofilm on the contact asperities in boundary lubrication systems. The model takes into account the effect of ZDDP tribofilm in changing Archard’s wear coefficient. The analytical results were validated with experiments in rolling-sliding conditions reported in another work [32]. The model considers the partial removal of the tribofilm and relates it to the wear of the substrate in the case of ZDDP on steel surfaces. The tribochemistry model was an important part of the whole semi-deterministic model because it defines the behaviour of tribofilm growth on the contacting asperities.

[31]In the current study an investigation into the effect of temperature and water concentration in oil on the growth of the film in tribocorrosion conditions is carried out. A set of experiments for different concentrations of water in oil was designed and carried out to study the effect on wear and growth of the tribofilm. The effect of water on the growth of the ZDDP tribofilm obtained by experimental results is then inputted into the wear model reported in [31] and briefly explained in the following section.

2 Numerical approach

The deterministic approach used in this work is based upon the model developed to simulate a boundary lubricated contact reported in. In the current study, a new part is added to the original model to include the effect of water concentration by using two approaches explained bellow. Although the model components are explained briefly in this section, the
details of the contact model and the wear mechanism can be found in Ref. [31] and [32] respectively.

The model consists of the following main parts:

- A deterministic contact model for rough surfaces using elastic-perfectly plastic theory
- A semi-analytical tribofilm growth model based on thermodynamics of interfaces
- Tribofilm mechanical properties which includes the values reported previously in the literature
- A new proposed modification of Archard’s wear model considering the effect of ZDDP tribofilm

In this model, digitized surfaces have been used as the inputs. This method is explained in detail by Tonder et al. [33] and in the author’s previous work [31]. The contact mechanics model is a plastic-perfectly plastic approach using the complementary potential energy formulation [31].

In order to consider tribochemistry, this model contains the tribofilm formation part which is based on kinetics of tribochemical reactions and is combined with a phenomenological term that accounts for dynamics removal of the tribofilm [31] and is shown by Equation 1.

\[
h = h_{max}\left(1 - e^{-\frac{k_1 T}{h'}x_{tribo}}\right) - C_3\left(1 - e^{-C_4 t}\right) \tag{1}
\]

in which \(k_1\) and \(h'\) are the Boltzmann and the Plank’s constant, \(T\) is the flash temperature and \(C_3\) and \(C_4\) are removal constants. The term \(x_{tribo}\) was interpreted as the mechanoactivation in inducing the tribochemical reactions. A detailed discussion can be found in the previous work [31].

The wear model used in the numerical approach is a modified version of Archard’s wear equation that accounts for the growth of the ZDDP tribofilm on the surface. The wear model is local and is space and time-dependant. Assuming that the coefficient of wear is at its maximum for steel-steel contact and at its minimum when the tribofilm has its maximum thickness, the equation for calculating coefficient of wear is as follows:
where $K_{tr}$ is the coefficient of wear for a tribofilm with thickness $h$. $K_{steel}$, $K_{min}$ and $h_{max}$ are coefficients of wear for steel and the maximum ZDDP tribofilm thickness and maximum film thickness respectively. It was reported that wear can occur due to the removal of the tribofilm from the surface. There is limited number of the substrate atoms in the bulk of the tribofilm due to different surface phenomena [34-36]. Therefore the dynamic process of the formation and removal of the tribofilm on the contacting asperities will lead to the removal of the substrate atoms [32]. This is a simple mathematical formulation for studying the effect of ZDDP tribofilm on reducing wear on steel surfaces. This wear model is explained in detail in [32] and is validated against experimental results.

3 Experimental procedure

3.1 Test rig

A Mini Traction Machine (MTM, PCS Instruments UK) [Figure 1] is used to assess the effect of water on wear under rolling and sliding conditions. One of the key points in using MTM is that slide-to-roll ratio (SRR) can be changed in the experiments and it is possible to run the experiment in the wide range of slide to roll ratio (0 < SRR < 5) [37]. SRR is defined as the following:

$$SRR = \frac{U_A - U_B}{U_A + U_B}$$  \hspace{1cm} (3)

In which $U_A$ and $U_B$ are the speed of surfaces A and B respectively. The SRR is the ratio of the sliding and the entrainment speeds.

In the standard configuration the test specimens are a 19.05 mm (3/4 inch) steel ball and a 46 mm diameter steel disc. The ball is loaded against the face of the disc and the ball and disc are driven independently to create a mixed rolling and sliding contact. The frictional force between the ball and disc is monitored by a force transducer. The applied load and the lubricant temperature are monitored by sensors.
3.2 Spacer Layer Interferometry

Spacer Layer Interferometry Method (SLIM) was used to measure tribofilm thickness in-situ while experiment is running [38]. Figure 1 shows the Spacer Layer Interferometry schematically. Ball is loaded against the disc to carry out the test and depends on the program defined to the MTM, test is stopped periodically and the ball loaded in reverse against the glass disc. The glass disc is coated with a thin layer of silicon oxide which has a semi-reflective layer of chromium on top. The contact of the ball is illuminated by white light through the microscope and the coated glass. Part of the light is returned back from the semi-reflective chromium layer on top of the coated glass and other part goes through the silicon oxide layer and tribofilm formed on the surface and is reflected back from the steel ball. These light paths are captured by RGB colour camera and it can be analysed by the software to evaluate the tribofilm thickness during the experiments. This method is capable of measuring the film thickness of any reaction layer as they formed on the surface.

![Figure 1 MTM and the Spacer Layer Interferometry configuration](image)

3.3 Material and test conditions

In this study the balls and disc used were both of AISI 52100 steel with hardness of 6 GPa. New balls and discs were used for each experiment. They were cleaned up before each test by immersing in isopropanol and petroleum ether in an ultrasonic bath for 20 minutes. All the experiments were conducted at an applied load of 60 N. According to the diameter of the ball
which is 19 mm, the maximum Hertzian contact pressure of 1.2 GPa was calculated. The material properties are shown in the Table 1. Experiments were carefully designed to study wear in boundary-lubricated contacts at different temperatures, water concentration. A small entrainment speed was chosen for this purpose. The working conditions and the corresponding λ ratios are reported in Table 2. Water and oil were mixed at four different levels of water concentration in the ultrasonic bath for 5 minutes.

**Table 1 Material properties**

<table>
<thead>
<tr>
<th>Material properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness (Ball/Disc) (GPa)</td>
<td>6</td>
</tr>
<tr>
<td>Elastic modulus (Ball/Disc) (GPa)</td>
<td>210</td>
</tr>
<tr>
<td>Ball surface roughness (Rₐ)</td>
<td>20 nm</td>
</tr>
<tr>
<td>Disc surface roughness (Rₐ)</td>
<td>130 nm</td>
</tr>
</tbody>
</table>

**Table 2 Experimental working conditions**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum contact pressure (GPa)</td>
<td>1.2</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>80,100</td>
</tr>
<tr>
<td>Water contents (Wt%)</td>
<td>0%, 0.5%, 1.5%, 3%</td>
</tr>
<tr>
<td>Entrainment speed (m/s)</td>
<td>0.1</td>
</tr>
<tr>
<td>SRR</td>
<td>5%</td>
</tr>
<tr>
<td>Test duration (min)</td>
<td>120</td>
</tr>
<tr>
<td>λ ratio</td>
<td>0.04</td>
</tr>
<tr>
<td>Oil used</td>
<td>PAO+ZDDP</td>
</tr>
</tbody>
</table>
| Dimensions (mm)                 | Ball = 19.05  
                              | Disc = 46   |
3.4 Lubricating oil

In this study, PAO+ZDDP and PAO+ZDDP+water were used. Water and oil were mixed in ultrasonic bath for 5 minutes to have four different concentrations of water as mentioned in Table 3. PAO+ZDDP+water shows an emulsion state (free water) at room temperature but at 80°C and 100°C the water seems to be dissolved. It is in agreement with this concept that higher temperature leads to the higher saturation point and likewise, there is no free water after each tribological test.

<table>
<thead>
<tr>
<th>Details</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAO+ZDDP(0.08 mass% phosphorus)</td>
<td>PAO+ZDDP</td>
</tr>
<tr>
<td>PAO+ZDDP (0.08 mass% phosphorus) + (0.5 mass %) Distilled water</td>
<td>PAO+ZDDP+water (0.5)</td>
</tr>
<tr>
<td>PAO+ZDDP (0.08 mass% phosphorus) + (1.5 mass %) Distilled water</td>
<td>PAO+ZDDP+water (1.5)</td>
</tr>
<tr>
<td>PAO+ZDDP (0.08 mass% phosphorus) + (3 mass %) Distilled water</td>
<td>PAO+ZDDP+water (3)</td>
</tr>
</tbody>
</table>

3.5 Experimental approach

The experimental part of this study can be split into two. All tribological experiments were carried out by MTM to simulate rolling/sliding conditions in boundary lubrication with four different water concentration values. The tribofilm thickness was measured using Spacer Layer Interferometry to evaluate the tribofilm formation in-situ. Finally the tribofilm was removed from the samples and wear was measured using White Light Interferometry. The sub-sets of tribological experiments are:

I. Experiments at 80°C for different levels of water concentration to investigate the effect of water on tribofilm formation and removal and tribological performance

II. Experiments at 100°C for different water concentration values to study the effect of water on tribological performance and tribofilm formation and removal
4 Results and discussion- Experimental

4.1 The effect of water on wear

The effect of water on wear performance is shown in Figure 2. According to the results, it can be seen that higher water concentration leads to higher wear. It could be concluded that water in oil accelerates wear. These results are in agreement with the works published by Lancaster and Cen. They proposed that water plays more significant role in increasing wear compared to the effect on friction. In both cases, higher water concentration results in higher wear. The comparison between two temperatures suggests that the lower temperature results in higher wear. It can be attributed to the lower water contents at higher temperature due to the evaporation of water. There is also less wear observed for 100°C compared to 80°C at zero percent water content. This can be related to the thicker tribofilm formed at higher temperatures. The results are in qualitative agreements with the recent studies.

It is interesting to see that water concentration in oil for the case of 100°C is less than 80°C. It should be noted that the effect of temperature in changing the viscosity of the oil and therefore changing the severity of the contact is negligible in this case as the lambda ratio for both temperatures was calculated to be around 0.04. The water concentrations have been measured by Karl Fischer Titration Method before and after each experiment and the results are reported in Table 4.
Figure 2 Effect of water on average wear depth at two different temperatures of 80°C and 100°C

Table 4 Water concentration measurements before and after tribological test

<table>
<thead>
<tr>
<th>Lubricants</th>
<th>Water content before test (ppm)</th>
<th>Water content after 2hr test (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>80°C</td>
</tr>
<tr>
<td>PAO+ZDDP</td>
<td>71</td>
<td>11</td>
</tr>
<tr>
<td>PAO+ZDDP+water (0.5)</td>
<td>4736</td>
<td>62</td>
</tr>
<tr>
<td>PAO+ZDDP+water (1.5)</td>
<td>16540</td>
<td>121</td>
</tr>
<tr>
<td>PAO+ZDDP+water (3)</td>
<td>38920</td>
<td>274</td>
</tr>
</tbody>
</table>

4.2 Effect of water on tribofilm growth and wear

The lower tribofilm growth was observed for higher water concentration [Figure 3 and Figure 4] and this effect is more significant at lower temperature. This decrease significantly affects
the tribofilm growth in the running-in period. It can affect the wear process due to the fact that the running-in period plays a significant role in the wear of the system. The results show that increasing the water concentration accelerates wear and it can be related to the effect of water on tribofilm growth at the beginning of the experiment. Steady state tribofilm thickness is also affected by water concentration in the oil; the more water concentration the less the tribofilm thickness. The results are in line with the previous research by Nedelcu et al. \cite{19} and Cen et al. \cite{11}. It can be linked to the formation of shorter chain polyphosphates due to the depolymerisation of the longer chain polyphosphates by water molecules \cite{11}.

The same pattern was observed at 80°C and 100°C in terms of tribofilm growth rate \cite{Figure 3} and \cite{Figure 4}. The only difference is that the effect of water on tribofilm growth is clearly distinguishable at lower temperature indicating that the effect of water on the growth of the tribofilm in the running-in period at 80°C is more significant compared to 100°C. The steady state tribofilm thickness follows the same pattern for both temperatures indicating the lower tribofilm thickness for higher water concentration \cite{Figure 5}. It is also reported in \cite{Figure 5} that higher temperature leads to the higher tribofilm thickness and it is in line with the results Fujita et al. \cite{39} published previously regarding ZDDP antiwear formation and removal. They proposed that both the tribofilm growth and steady state tribofilm thickness increase with temperature. For comparison purposes, the steady-state tribofilm thickness is plotted against the measured wear depth for both temperatures in \cite{Figure 6}. It can be seen while the steady-state tribofilm thickness is higher, less wear occurs. However, tribofilm thickness in steady-state does not give a full picture of the wear behaviour in boundary lubricated systems. There are more physical, chemical and mechanical parameters responsible for the wear. In fact, the whole growth behaviour of the tribofilm on the surfaces is important for capturing the wear behaviour. It is important how the tribofilm was formed during the running-in process. A detail discussion on this can be found in Ref \cite{32}. Comparisons made between the effect of water on steady state tribofilm thickness and the average wear depth for 80°C and 100°C are plotted in \cite{Figure 7} and \cite{Figure 8} for 100°C and 80°C respectively. The trends indicate that increasing the water content in the oil affects wear by decreasing the steady state tribofilm thickness.
Figure 3 Tribofilm thickness measurement results for 100°C at different water concentrations

Figure 4 Tribofilm thickness measurement results for 80°C at different water concentrations
Figure 5 Steady state tribofilm thickness results for different water concentrations

Figure 6 Steady state tribofilm thickness results vs measured wear depth
Figure 7 Comparison between average wear depth and tribofilm thickness at different water concentration at 100°C

Figure 8 Comparison between average wear depth and tribofilm thickness at different water concentration at 80°C
5 Numerical analysis

The experimental results reported in Section 4 are used in this section in two different approaches to predict wear of the boundary-lubricated contact with the oil containing ZDDP additive.

5.1 First approach: semi-deterministic coefficient of wear

In this approach it is assumed that the tribofilm thickness is following the same behaviour for all levels of water concentration. It means that the growth of tribofilm is the same for all water concentration experiments and the same amount of tribofilm is formed on the surfaces for all different experiments. This is not accurate in reality and experimental results reported in Section 4 show otherwise. But this approach is used to see if the same tribofilm growth behaviour is modelled for all experiments, a modification to Archard’s wear equation can predict the wear of the system. The only parameter that can be affected by water is assumed to be the initial coefficient of wear. The calibration procedure for the initial coefficient of wear is reported in Ref [32]. This approach is applied to semi-deterministically find the true coefficient of wear corresponding to the different levels of water concentration. The value of the average wear depth measured experimentally and reported in Section 4.1 was used to match the average wear depth results from the simulations for every level of water concentration. The procedure for determining the initial wear coefficient involves conducting simulations with different initial coefficients of wear to identify the coefficient value that exactly matches the wear behaviour observed in the experiment. The difference between the value of the calculated wear and the wear measured experimentally in Section 4.1 was set to be less than 0.1 nm in order to get the best match. The initial wear coefficients calculated from the simulations are reported in Table 5 for different water concentrations for 80°C and 100°C.

A factor $\psi$ is added to the proposed wear model of Equation 2 that is responsible for the effect of water on tribocorrosive wear of the system. Equation 2 is then converted to Equation 4.

$$K_{tr} = \psi K_{steel} - (\psi K_{steel} - K_{min}) \frac{h}{h_{max}} \quad (4)$$

$\psi$ is calculated between 1 and 2.5 in all ranges of water concentrations and is more for higher concentrations. These simulation results show that the coefficient of wear can be modelled
for different levels of water concentration to predict wear. If the appropriate \( \Psi \) value is assigned in the simulation of wear in the presence of water, wear values can be successfully predicted by Equation 4. \( \Psi \) is then reported in Table 6 for different levels of water concentration.

### Table 5 Wear coefficients used in the numerical simulations (Dimensionless)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>0%</th>
<th>0.5%</th>
<th>1.5%</th>
<th>3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>100°C</td>
<td>(10^{-8})</td>
<td>1.64*10^{-8}</td>
<td>1.65*10^{-8}</td>
<td>2.3*10^{-8}</td>
</tr>
<tr>
<td>80°C</td>
<td>2*10^{-8}</td>
<td>2.7*10^{-8}</td>
<td>3.1*10^{-8}</td>
<td>3.5*10^{-8}</td>
</tr>
</tbody>
</table>

Table 6 \( \Psi \) for different water concentrations at different temperatures (Dimensionless)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>0%</th>
<th>0.5%</th>
<th>1.5%</th>
<th>3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>100°C</td>
<td>1</td>
<td>1.35</td>
<td>1.55</td>
<td>1.75</td>
</tr>
<tr>
<td>80°C</td>
<td>1</td>
<td>1.64</td>
<td>1.65</td>
<td>2.30</td>
</tr>
</tbody>
</table>

### 5.2 Second approach: effect of tribochemistry

To study the effect of tribochemistry, unlike the first approach, the starting coefficient of wear is assumed to be the same in the numerical model for different levels of water concentration. Following that, the effect of water in changing the growth behaviour of the tribofilm observed experimentally in Figure 3 and Figure 4 has been used to capture the behaviour in the model. As discussed in section 2.2, the changes in growth behaviour of the tribofilm will change the wear coefficient locally at the asperity scale. For the tribofilm growth part of the model, the four parameters \( x_{tribo}, h_{max}, C_1 \) and \( C_2 \) need to be determined for each set of experimental conditions in order to capture the tribofilm behaviour, which is different in each case. This is achieved by fitting Equation 1 to experimental measurements of tribofilm thickness of Section 4.2. These parameters are reported in Table 7 for different water contents. The wear is then calculated with respect to this growth behaviour and the results have been compared to the experimental wear depth results obtained experimentally.

### Table 7 Simulation inputs and calibration parameters

<table>
<thead>
<tr>
<th>Water Concentration</th>
<th>0</th>
<th>0.5</th>
<th>1.5</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>T=100°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The tribofilm growth simulation results are plotted in [Figure 9](#). The simulation wear results corresponding to the different levels of water concentrations for 100°C and 80°C are also shown in [Figure 10](#) and are compared with the experimental results of section 4.1. It can be seen that tribofilm affects the wear of the system. In the higher concentrations of water a lower rate of formation of the tribofilm is being observed. This lower rate of formation results in higher coefficient of wear according to Equation 2. It is important to notice that once the tribofilm behaviour is captured [Figure 9](#), the model is able to predict the wear behaviour for the case of ZDDP on steel surfaces [Figure 10](#). So far in this research, capturing the tribofilm behaviour was dependent on the experimental results due to the lack of comprehensive mechanistic understanding of tribofilm formation and removal. Despite all the complexities, such simplified semi-analytical models for tribofilm growth can be good starting points for the problem. This is therefore a good approach for modelling wear in boundary lubricated contacts which can include the effect of water in the tribological behaviour of the system.
Discussion - Numerical

Tribocorrosive wear of the boundary lubricated system by oil containing a ZDDP antiwear additive has been modelled in this work considering the tribochemistry of the antiwear additive. It is shown that considering growth behaviour of the tribofilm for ZDDP on steel surfaces is a reasonable approach for modelling wear in tribocorrosive tribological systems. Experiments were designed to monitor the tribofilm growth in addition to the measurement of wear to be able to make a link between them. Two numerical approaches were tested in this work in order to study the effect of water in tribocorrosive wear of the boundary lubrication contacts and the results were shown in the previous section. For the first approach, coefficients of wear were semi-deterministically obtained from the simulations to satisfy the wear measurements. This approach suggests that for different water concentrations wear of the system is different and Archard’s wear equation needs to be modified accordingly. It was reported in Section 5.1 of the numerical results that a modification parameter can be used to...
modify the Archard’s wear coefficient in the previously reported tribochemistry wear model. This parameter ($\psi$) is calculated from the simulations and the range was between 1 and 2.5 for all water concentrations used in this study. It is shown that, without changing the growth behaviour of the tribofilm (tribochemistry), simulations can predict the wear of tribocorrosion systems by changing the Archard’s wear coefficient. In the second approach, unlike the first one, the effect of water on the growth of the ZDDP tribofilm was considered. The growth model was calibrated for all different tribofilm growth cases and the simulations were carried out using those growth behaviours. The coefficient of wear was assumed to be constant for all the simulations in this approach unlike the first approach and the only parameter changing the coefficient of wear was the difference in tribofilm thickness of the different cases. Wear results in this case were shown in the previous section and good agreement can be seen with experimental results.

As shown in Table 7 the rate of formation of tribofilm is different for different levels of water concentration at the same temperature. The term $x_{\text{tribo}}$ which is responsible for the effect of mechanical rubbing on the initiation of tribochemical reactions [31] is reported in Table 7. It is clear both from experimental and numerical results that the formation rate decreases when water concentration increases. The term $x_{\text{tribo}}$ for different levels of water concentration is plotted in Figure 11.

![Figure 11](image)

**Figure 11** $x_{\text{tribo}}$ calibrated for different temperatures at different water concentrations at (a) 100°C and (b) 80°C
The simulation results based on the second approach show that if a good prediction in the growth behaviour of the tribofilm is calculated, it can lead to a good prediction in the wear of the system. In previous work by the authors [32], the wear model and the effect of tribofilm in reducing wear have been studied and the numerical model showed good predictive capabilities for wear. The term $x_{triб}$ that is a major part in the growth behaviour of the tribofilm will be the subject of future work of the authors with a focus being on how different oils and tribological parameters affect the value. Understanding and being able to quantify this term for tribocorrosion conditions will help to obtain a more robust predictive tribofilm growth model. Tribofilm growth prediction then impacts the prediction of wear according to Equations 2 and 3. In this stage of the work, only the predictive capability of the model in tribocorrosive conditions was tested and the results are promising. More results and development of this model will be reported in the future.

7 Conclusions

The effect of water on wear behaviour of boundary lubricated tribosystem in a rolling/sliding contact has been studied experimentally and analytically in this work. It is concluded that:

- Water affects the tribochemistry of the zinc polyphosphates tribofilm on the surfaces. Water influences the growth behaviour of the tribofilm on the surfaces and more water in the oil results in lower rate of the growth on contacting surfaces.

- Water in oil can delay the growth of the tribofilm in the running-in period and it can significantly affect tribocorrosive wear in boundary lubricated system. This effect is more significant for the tests at 80°C in comparison with tests at 100°C due to more water in the oil.

- Higher water concentration leads to a reduction in growth rate of the tribofilm which in nature results in an increase in the wear of the system. This reduction in growth rate might be because of the difficulty that ZDDP molecules have in reacting with the substrate in the presence of the water.
• It was shown that tribofilm thickness in steady-state condition is not a good representative of the wear behaviour of the system. However other important physical, chemical and mechanical parameters are involved. The whole growth behaviour of the tribofilm can be significantly important to characterize wear. This means that running-in period is also important in determining the wear of boundary lubricated systems.

• Two different numerical approaches were used to test the model and also represent the effect of water in wear of the system. With respect to the first approach, tribocorrosive wear can be predicted by modifying the Archard’s wear coefficient. The modification parameter (Ψ) increases by increasing the water concentration. The simulation wear results show good agreement with the experimental wear measurements.

• It is concluded in this work that once the characteristics of the tribofilm growth are captured, the model is capable of predicting tribocorrosive wear in boundary lubrication regime.

8 Acknowledgement

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9 References

<table>
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</tr>
</tbody>
</table>
To the editor of the Wear Journal

The effect of water and its tribochemistry on the wear of boundary lubricated contacts have been studied experimentally and numerically in this work. Experimental work focuses on the tribochemistry of the film and its effect on the wear. The experimental results have been fed into the recently developed tribochemical numerical framework [1] that was validated against experiments [2] to adapt to the tribocorrosion conditions. Two numerical approaches were used to see the effect water on the wear modelling of boundary lubricated conditions. The paper was proofread by Professor Duncan Dowson at every stage of the research.

With Regards

Pourya Parsaeian

On behalf of the authors