Modeling of the Effects of Lubricant Chemistry on Engine Component Wear and Parametric Analysis

by

Kai Liao

B.S.E., Jet Propulsion, Beijing University of Aeronautics and Astronautics, 2007

Submitted to the Department of Aeronautics and Astronautics in Partial Fulfillment of the Requirements of the Degree of Master of Science in Aeronautics and Astronautics Engineering at the Massachusetts Institute of Technology

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Abstract

Recently, due to the strengthened regulations on diesel engine emissions, the dynamic understanding of engines’ antiwear processes has drawn renewed attention. Oil additives can help engines resist wear by forming a thin solid layer of antiwear film, and zinc dialkyldithiophosphate (ZDDP) is the most commonly used oil additive. There has been sufficient experimental effort in trying to understand the dynamics of ZDDP antiwear film formation and its effect on wear between engine components, but the effort of predicting antiwear film formation and the effect of lubricant chemistry on engine wear through modeling has just begun to emerge.

The purpose of this research is going to improve such a model modeling ZDDP antiwear processes so that it can be used to understand the dynamics of antiwear film formation at different operating conditions, and use this model to gain insight into the antiwear film formation processes.

The effect of different processes on antiwear film formation and the sensitivity of the film formation to different parameters have been demonstrated and analyzed.

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- Chevron
- Ciba Specialty Chemicals
- Cummins, Inc
- Department of Energy
- Komatsu
- Lutek
- Sud-Chemie
- Valvoline

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1. Introduction

Component wear is one of the major factors that limit the life of an automotive engine. Zinc dialkyldithiophosphate (ZDDP) is an oil additive that can help engine components resist wear by forming a thin layer of solid antiwear film on each contacting surface. It has been used since the late 1930s [Spikes, 2004]. Since then, ZDDP has been the most widely used engine oil additive.

ZDDP can reduce engine component wear in three major ways: 1. by leading to the generation of a thin layer of antiwear film that acts as a physical barrier, 2. by reducing the oxidation of engine components, and 3. by softening the abrasive particles in the engines [Spikes, 2004]. It is believed that the generation of antiwear film is the most significant way that ZDDP can help resist wear.

Recently, due to strengthened emission regulations on diesel engines, studies on ZDDP and its effects on the resisting of engine components wear have drawn more attention from different research groups and companies. ZDDP may increase emissions because a small portion of the engine oil will be burnt by the combustion inside the engine, and the burning products from ZDDP will clog the engine aftertreatment system.

Despite sufficient theoretical and experimental research on ZDDP, approaches using computer modeling are rare. Ben Thomas built a computer model that includes the framework of ZDDP antiwear theory. It assumes that the antiwear film formation is a three-step process including 1. ZDDP decomposition in the oil, 2. the adsorption of decomposed products onto the contacting surfaces, and 3. an adsorbed products oxidation process on the surfaces. It also calculates the removal of antiwear film and the wear of sliding surfaces using a modified Greenwood function [Thomas, 2007]. However, the dynamics of each antiwear film formation steps are not demonstrated and the question of how this model can be used to predict real engine wear remains unanswered. Therefore, it is necessary to conduct a parametric analysis on this model to understand the effects of different parameters and processes on antiwear film formation and make the effort to utilize the model on real engines.
Theoretically, the antiwear film formation and removal processes are affected by different parameters, including temperature, contact pressure, ZDDP concentration and sliding speed. Different combinations of the parameters can represent the working conditions of different engine components. Higher contact pressures can predict the working conditions of a valve train, while lower contact pressures usually correspond to those of the piston rings. By changing these parameters according to the measurements from real engines, component wear can be predicted with the model.

Due to the strengthened regulation of ZDDP concentrations within lubricant oil, many oil companies have shown great interest in a model that can predict whether lubricant oil with certain compositions can effectively protect an engine. This will require a detailed model simulating the effects of various oil additives, including ZDDP, detergents and dispersants. The current research provides insights into how should these factors be included.

**Contributions**

This work has demonstrated the processes to analyze the ZDDP antiwear film formation and its protection of engine components using a fundamental lubricant-chemistry model. It has also conducted sensitive analysis on the antiwear film formation processes. The dynamics of ZDDP antiwear film formation has been shown and the effect of flash temperature on ZDDP tribo-film formation has been discussed.
2. Lubricant Chemistry Model

2.1 Model Structure and Governing Equations

A wear model considering lubricant chemistry has been previously introduced [Thomas, 2007]. It simulates both the antiwear film formation processes and the wear process under boundary lubrication regime, in which direct surface contact will occur and the effect from hydraulic force can be neglected. For the antiwear film formation process, it has divided the entire process into three sub-steps. First, ZDDP molecules will undergo a decomposition process in the oil solution to become decomposition product; thereafter, the decomposition product will be adsorbed to the contacting surfaces and become the adsorbed product; finally, the adsorbed product will undergo an oxidation process on the surface to become the antiwear film.

For the decomposition process, ZDDP is known to be able to decompose through different pathways [Spikes, 2004]. In this model, ZDDP thermal decomposition, autocatalytic decomposition and decomposition proceeded by ligand exchange have been considered. In the ZDDP thermal decomposition process, the reactions are mainly driven by thermal energy. In the autocatalytic decomposition process, the previously formed decomposition products will act as catalyst to facilitate ZDDP decomposition. In the ZDDP decomposition proceeded by ligand exchange process, ZDDP molecule will first react with iron cations to form the less stable MDDP before further decomposition. The three decomposition pathways are assumed to be parallel to each other.

The rates of the three decomposition pathways can be calculated as follow [Missen et al, 1999]:

Thermal decomposition [Thomas, 2007]:

\[ r_T = k_T C_Z^{\alpha_1} \]  (1)
where \( r_T \) is the thermal decomposition rate, \( k_T \) is the proportionality term of the thermal decomposition process, \( c_z \) is the concentration of ZDDP, and \( a_1 \) is a constant power denoting the reaction order.

Autocatalytic decomposition [Thomas, 2007]:

\[
r_A = k_A \frac{c_z^{a_2} c_p^{a_3}}{c_z^{a_2} + c_p^{a_3}} \tag{2}
\]

where \( r_A \) is the autocatalytic decomposition rate, \( k_A \) is the proportionality term of the autocatalytic decomposition process, \( c_z \) is the concentration of ZDDP, \( c_p \) is the concentration of decomposition product, the order of the reaction is denoted by the sum of \( a_2 \) and \( a_3 \).

Decomposition proceeded by ligand exchange [Thomas, 2007]:

\[
r_{lg} = k_{lg} \frac{c_z^{a_4} c_{Fe}^{a_5}}{c_z^{a_4} + c_{Fe}^{a_5}} \tag{3}
\]

where \( r_{lg} \) is the rate of decomposition proceeded by ligand exchange, \( k_{lg} \) is the proportionality term of the decomposition proceeded by ligand exchange process, \( c_z \) is the concentration of ZDDP, \( c_{Fe} \) is the concentration of iron cations, the order of the reaction is denoted by the sum of \( a_4 \) and \( a_5 \).

It is known that the antiwear film formation processes are sensitive to the temperature. Therefore, the proportionality terms in different processes can be described by the Arrhenius equation [Missen et al, 1999]:

\[
k = A e^{-\frac{E}{RT}} \tag{4}
\]
where $A$ is the pre-exponential constant of the reaction, $E$ is the activation energy of the reaction, $R$ is the ideal gas constant, and $T$ is the local temperature.

The adsorption rate is given by:

$$ r_{Ad} = c_p \sum k_i \theta_i \quad \sum \theta_i = 1 $$

(5)

where $c_p$ is the concentration of decomposition product, $k_i$ is a proportionality term that corresponding to different surface coverage material, and $\theta_i$ is the fractional coverage of surface material. The surface can be covered by newly adsorbed product, antiwear film, a thin layer of iron oxide or still be bare metal surface.

The adsorbed product oxidation rate is given by:

$$ r_{Oxd} = k_{Oxd} \theta_p c_{Ox}^\alpha $$

(6)

where $k_{Oxd}$ is the proportionality term, $\theta_p$ is the fractional coverage of adsorbed product, representing the reactant material, $c_{Ox}$ is the concentration of the oxidant, and $\alpha$ is the order of the reaction.

The steps and processes considered in the antiwear film formation process can be summarized by the figure below.
For the antiwear film removal and wear processes, a modified general wear equation is used.

$$U_w = K \frac{P U_s \eta_c}{H} \tag{7}$$

Where $U_w$ is wear speed, $K$ is wear coefficient, $P$ is real contact pressure, $U_s$ is sliding speed, $\eta_c$ is the ratio of real to nominal contact area, and $H$ is hardness.

Whether the antiwear film can effectively protect the contacting surfaces depends on the relationship between antiwear film formation rate and antiwear film removal rate. If the antiwear film formation rate exceeds the antiwear film removal rate, in a long run, ZDDP antiwear film will accumulate on the contacting surfaces. Otherwise, direct substrate contact will occur and wear will happen.
2.2 Reactor Volume

Since the antiwear film formation processes are mainly driven by chemical reactions, the previously introduced model has concentrated on a “reactor volume” that is able to describe the reactants and products between the contacting surfaces. The “reactor volume” is defined as “the volume above a macroscopically homogeneous element of surface area” [Thomas, 2007]. In such a reactor volume, macroscopic conditions, including macroscopic temperatures, pressures, sliding speeds, etc are constant during one calculation time step.

In addition, within the reactor volume, each of the contacting surfaces has been divided into two sub-partitions, the peak partition and the valley partition. The peak partition is defined as the area that will be in real contact when it meets with the peak partition of the opposite surface, and the valley partition is defined as the area that will never be in real contact with the opposite surface. Follow the definition of the surface partitions, when two surfaces are sliding against each other, only part of the peak partition will be in real contact, and bear the contact pressure. The part of peak partition that is in real contact is defined as the “real contact area”. The macroscopic contacting area is sometimes referred as “nominal contact area” or “apparent contact area”.

From the definition above, wear can only happen between the real contacting areas. Under the same load and before the surface profile undergoes significant changes due to severe wear, the ratio of real contact area to nominal contact area may stay the same, but the actual contacting region may be different.

On the peak partition, ZDDP film is formed under the real contact pressure and abrasive wear. The local temperature at the peak partition may be higher due to the heat generated from the friction. This higher temperature at the peak partition is also referred to as “flash temperature”. Flash temperature is considered in the calculation of the decomposition, adsorption and oxidation processes. This is a good representation of the formation conditions of the ZDDP tribo-film.

On the valley partition, no real contact will happen and film is formed under the bulk temperature. The film formed on the valley partition should be more similar to the ZDDP thermal film.
2.3 Dynamics of Antiwear Film Formation

In order to analysis the dynamics of the antiwear formation process, a simplified baseline simulation is used.

The baseline simulation is targeting at the friction between the top piston ring and the cylinder in an internal combustion engine. The region that is looked into has a total nominal contact area of 10mm². The peak partition is assumed to be 10% of the total nominal contact area; and the valley partition is assumed to be 90% of the total nominal contact area.

To simplify the calculation and concentrate on the film formation processes, the replenishing process and wear process are neglected from the first baseline calculation. The physical parameters include bulk temperature, 403K, mean separation between two contacting surfaces, 500nm, sliding speed, 0.1m/s, initial ZDDP concentration, 0.1wt%P, or 14.19mol/m³, real contact pressure, 0.5GPa. The reactor volume, which is assumed to be a rectangular with a bottom surface equal to the nominal contact area and a height equal to half of the mean separation, has a volume of 2.5x10⁻³ mm³, and the total amount ZDDP within the reactor volume is originally 3.55x10¹¹ mol.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Mean Separation</th>
<th>Sliding Speed</th>
<th>Initial ZDDP concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>403 (K)</td>
<td>500 (nm)</td>
<td>0.1m/s</td>
<td>0.1wt%P or 14.19mol/m³</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Real Contact Pressure</th>
<th>Reactor Volume</th>
<th>Total ZDDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5GPa</td>
<td>2.5x10⁻³ mm³</td>
<td>3.55x10¹¹ mol</td>
</tr>
</tbody>
</table>

Table 1: Physical parameters used in the baseline calculation

This baseline case represents the following scenario: the total mole of ZDDP is fixed in the reactor volume. It will only undergo different reactions and change in forms. One mole of ZDDP can lead to the production of one mole of decomposition product, one mole of adsorbed product or one mole of antiwear film. No material will flow in or out of the reactor volume.
Based on the assumption above, neglecting the effect of replenishment, the total amount of ZDDP, decomposition product, adsorbed product and antiwear film in terms of mole should be constant in the entire film formation process.

Table 2 shows in the first 0.0010s, the transformation of ZDDP into different forms. The amounts of different materials in mole at different times are recorded in terms of percentage of original ZDDP. Initially, all ZDDP is in the original form. Once the reaction starts, it will react to become decomposition product (prod), adsorption product (AP), or antiwear film (film). The concentrations of ZDDP and its decomposition products are assumed to be uniform at each time step in the reactor volume. However, it should be noticed that the contacting surfaces have been separated into peak partition and valley partition, and the adsorbed product and antiwear film on each of the partitions are calculated and kept track of separately.

Since the total number of mole of material should not change before and after the reactions, the sums of each row in table 2 are all equal to 100%.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Step</th>
<th>ZDDP</th>
<th>prod</th>
<th>AP_valley</th>
<th>AP_peak</th>
<th>film_valley</th>
<th>film_peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>0</td>
<td>100.00%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.00%</td>
</tr>
<tr>
<td>0.0001</td>
<td>1</td>
<td>88.92%</td>
<td>11.08%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.00%</td>
</tr>
<tr>
<td>0.0002</td>
<td>2</td>
<td>77.98%</td>
<td>17.93%</td>
<td>3.63%</td>
<td>0.46%</td>
<td>0.00%</td>
<td>0.00%</td>
</tr>
<tr>
<td>0.0003</td>
<td>3</td>
<td>67.73%</td>
<td>21.59%</td>
<td>9.47%</td>
<td>1.20%</td>
<td>0.00%</td>
<td>0.00%</td>
</tr>
<tr>
<td>0.0004</td>
<td>4</td>
<td>58.42%</td>
<td>23.04%</td>
<td>16.45%</td>
<td>2.09%</td>
<td>0.01%</td>
<td>0.00%</td>
</tr>
<tr>
<td>0.0005</td>
<td>5</td>
<td>50.12%</td>
<td>23.03%</td>
<td>23.80%</td>
<td>3.02%</td>
<td>0.02%</td>
<td>0.00%</td>
</tr>
<tr>
<td>0.0006</td>
<td>6</td>
<td>42.83%</td>
<td>22.12%</td>
<td>31.07%</td>
<td>3.93%</td>
<td>0.04%</td>
<td>0.01%</td>
</tr>
<tr>
<td>0.0007</td>
<td>7</td>
<td>36.48%</td>
<td>20.68%</td>
<td>37.96%</td>
<td>4.80%</td>
<td>0.07%</td>
<td>0.01%</td>
</tr>
<tr>
<td>0.0008</td>
<td>8</td>
<td>30.99%</td>
<td>18.96%</td>
<td>44.33%</td>
<td>5.60%</td>
<td>0.10%</td>
<td>0.01%</td>
</tr>
<tr>
<td>0.0009</td>
<td>9</td>
<td>26.27%</td>
<td>17.15%</td>
<td>50.11%</td>
<td>6.33%</td>
<td>0.13%</td>
<td>0.02%</td>
</tr>
<tr>
<td>0.0010</td>
<td>10</td>
<td>22.22%</td>
<td>15.34%</td>
<td>55.27%</td>
<td>6.97%</td>
<td>0.17%</td>
<td>0.03%</td>
</tr>
</tbody>
</table>

Table 2: The transformation of ZDDP in the first 0.001s
The trends of the changes of ZDDP into different forms are plotted in figure 2.

![Graph showing the trends of ZDDP into different forms](image)

**Figure 2:** The trends of the changes of ZDDP into different forms in the first 0.001s

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>0.0001</th>
<th>0.0002</th>
<th>0.0003</th>
<th>0.0004</th>
<th>0.0005</th>
</tr>
</thead>
<tbody>
<tr>
<td>det(ZDDP)</td>
<td>11.08%</td>
<td>10.94%</td>
<td>10.25%</td>
<td>9.31%</td>
<td>8.29%</td>
</tr>
</tbody>
</table>

**Table 3:** The trend of ZDDP decomposition

The time interval between two time steps is selected to be 0.0001s. In the first 0.0001s, 11.08% of the total ZDDP is decomposed to become the decomposition product. Due to the lack of decomposition product in the original oil, no adsorbed product is found after the first time step. From 0.0001s to 0.0002s, another 10.94% of ZDDP is decomposed. At the same time, part of the previously formed decomposition product is adsorbed onto the surface to become adsorbed product. Since no adsorbed product presents after the first 0.0001s, no antiwear film is formed after 0.0002s. Thereafter, the decomposition and adsorption process continue. In the third time step, although adsorbed product presents on the surface, no observable antiwear film is formed after 0.0003s. This is largely due to the limitation of the oxidation rate. As the oxidation process continues, the antiwear film becomes observable on both peak partition and valley partition after a few more time steps.
The limitation of adsorbed product oxidation rate can be seen from figure 3. The figure compares the ZDDP decomposition rate, total adsorption rate (decomposition product is adsorbed to both peak and valley partition) and total oxidation rate (adsorbed product is oxidized on both peak and valley partition) in the initial 0.001s. It shows that at the beginning of the antiwear film formation process, adsorbed product oxidation rate is much lower than that of the ZDDP decomposition rate and decomposed product adsorption rate.

At the same time, a decreased trend of ZDDP decomposition rate is observed. This is due to the decrease in the total amount of available reactant, ZDDP. As reaction proceeds, ZDDP continuously decomposes to become decomposition product and undergoes further reactions. Under the condition that no oil replenishment is provided, the remaining amount of ZDDP, or the ZDDP concentration in the reactor volume will decrease.

In addition, the first increasing then decreasing trend of decomposition product adsorption rate also follows the change of the amount of total available reactant, or decomposition product as shown in figure 2.
At any given time, the contacting surfaces may be covered by adsorbed product, antiwear film, iron oxide, or still be bare metal. When the concentration of decomposition product is the same in the oil solution, the adsorption rate of decomposition product to different kind of surfaces are different. The decomposition product is more easily to be adsorbed onto the bare metal or iron oxide, while the adsorption of decomposition product onto antiwear film or adsorbed product is much slower.

The adsorption rate is affected by both the concentration of the available reactant and the surface conditions. At the initial stage of the baseline calculation, when the major part of the contacting surfaces is still bare metal, the surface condition is not the major factor influencing the adsorption process. Therefore, decomposition product adsorption is mostly affected by the concentration of decomposition product, \( C_p \), which is directly proportional to the adsorption rate.

![Figure 4: The trend of adsorbed product oxidation rate at the initial stage of the antiwear film formation process](image)

The rate of oxidation of the adsorbed product is much slower than that of the ZDDP decomposition rate and the decomposed product adsorption rate. But a closer look at the adsorbed product oxidation rate shows that it is increasing over time at the initial stage. This trend is shown in figure 4.
The adsorbed product oxidation rate is directly proportional to the availability of the adsorbed product, or $\theta_p$. At the initial stage of the antiwear film formation process, the decomposition product adsorption rate exceeds the adsorbed product oxidation rate, resulting in the accumulation of adsorbed product on the contacting surfaces. As a result, the adsorbed product oxidation rate increases, accelerating the consumption of the adsorbed product on the contacting surfaces.

3. Wear Simulation

3.1. Physical System

The simulation is targeted at the wear between engine components under working conditions. The nominal contact area is selected based on the length scale of specific engine components. The typical cam-lobe width is at the order of 15mm [Paranjpe et. al., 1992] and the contact is closed to line contact. Therefore, the nominal contact area is selected to be 10mm$^2$. The total area of peak partition is set to be 1mm$^2$. In order to simplify the calculation and facilitate the results comparison between the calculations under different contact conditions, the contact areas have been normalized. Since the antiwear film thickness and wear depth are average values over the entire partition, the absolute values of these length scales are not affected by the normalization. However, the decomposition rates, adsorption rates and oxidation rates are all calculated based on the normalized surface area, in terms of the mass of reacted species per unit time. Therefore, when estimating the mass of reactants in a specific reactor volume, the reaction rates should be rescaled based on the surface area under the case in concern.
The mean separation between the two surfaces together with the bottom surface area determines the size of the reactor volume. The previously introduced model is targeting at the contact under boundary lubrication regime, in which the mean separation of the two surfaces is at the order of the composite surface roughness. After run-in period, the surface roughness of the contacting surfaces in an internal combustion engine is at the order of a few hundred nanometers. Therefore, the mean separation is generally less than one micro meter. In this simulation, the mean separation between the two contacting surfaces is 500nm.

The material of the contacting surfaces is assumed to be cast iron. The hardness, thermal conductivity, heat capacity are all selected based on this assumption. For this simulation, the contacting surfaces have been assumed to be the same material. The model also allows the simulation of wear between surfaces of different material.

3.2. Kinetic Constants

The major kinetic constants in the previously introduced model include the ones from the calculations using Arrhenius equations, namely the pre-exponential constants (A) and the activation energies (E) of decomposition, adsorption and oxidation processes. Many researches have been done to understand the mechanism of the film formation and wear processes. However, these numbers are still not precisely known.

The values of Arrhenius constants along ZDDP antiwear film formation processes can be obtained through direct or indirect methods.

For direct methods, a quantum chemical method has been successfully used to determine the energies barriers of the reactions involved in the ZDDP decomposition process. [Mosey and Woo. 2004] The mechanism of decomposition of ZDDP with different alkyl groups have been studied as well.

For indirect methods, efforts have been devoted to identify the relationship between the reaction rate and the corresponding temperature.
Since the Arrhenius equation can be written as:

\[ \ln k = \ln A - \left( \frac{E}{R} \right) \frac{1}{T} \]  \hspace{1cm} (8)

Based on the form of Arrhenius equation, if the reaction rate of the processes in concern can be measured at different temperatures, an Arrhenius plot of the reaction rate can be generated and the activation energy and the pre-exponential constant can be solved numerically. However, the detailed mechanism of antiwear film formation is still not well known and different formation processes have been proposed. Therefore, not all the Arrhenius parameters used in the model are precisely known.

### 3.2.1. Sensitivity Analysis

To determine the proper Arrhenius parameters for each of the sub-steps has become the major concern. However, a parametric analysis has shown that the antiwear film formation process is not sensitive to every Arrhenius parameter. A series of simulations have been conducted to identify the sensitivity of antiwear film formation to the Arrhenius parameters of different steps. The pre-exponential constant and activation energy of the decomposition process, adsorption process and oxidation process are changed from 30% below to 30% over the original values; the corresponding antiwear film thicknesses after the 1000s simulations are used as the criteria to judge the sensitivity of antiwear film formation the Arrhenius parameters.

The first group of simulations is run under a temperature of 375K, a sliding speed of 1m/s, a ZDDP concentration of 0.56wt%P and a real contact pressure of 0.5GPa. All the processes including the ZDDP decomposition process, the decomposed product adsorption process and the adsorbed product oxidation process are considered in the simulation. This is closed to a scenario where the replenishing oil is fresh oil, without decomposition product.
The following figures show the Arrhenius parameters that are observed to have effects on the antiwear film formation processes. The Arrhenius parameters that have little effect on the film thickness are not shown.

Figure 5: The sensitivity of film thickness to the pre-exponential constant $A_{\text{therm}}$ and activation energy $E_{\text{therm}}$ of the thermal decomposition process

Figure 5 indicates that under the conditions stated, ZDDP antiwear film is highly sensitive to the activation energy of the thermal decomposition process. A 30% decrease in the activation energy of the process may lead to a 4 time increase in the antiwear film thickness. A 20% to 30% increase in the activation energy may lead to the failure of antiwear film formation. In addition, the film formation process is more sensitive to the initial variation of the activation energy. A further change beyond a critical value may have limited effect on the antiwear film formation process. At the same time, the pre-exponential constant of the thermal decomposition process also has observable effect on the antiwear film thickness.
Figure 6: The sensitivity of film thickness to the pre-exponential constant $A_{lg}$ and activation energy $E_{lg}$ of the decomposition proceeded by ligand exchange process.

Figure 6 shows that the activation energy of the decomposition proceeded by ligand exchange process has medium effect on the antiwear film thickness. A 30% decrease in the activation energy value may lead to more than 40% increase in the antiwear film thickness. However, when the activation energy of the decomposition proceeded by ligand exchange process increases, no obvious change in antiwear film thickness is observed. In addition, the pre-exponential constant of the decomposition proceeded by ligand exchange process has little effect on the antiwear film thickness.
Figure 7: The sensitivity of film thickness to the activation energy of the adsorbed product oxidation process, $E_{\text{ox\_prod}}$

Figure 7 indicates that under the conditions considered, the activation energy of the adsorbed product oxidation process has medium effect on the antiwear film formation process. A 30% increase in the activation energy may lead to an about 20% decrease in the antiwear film thickness. However, the decrease in the activation energy up to 30% has little effect on the antiwear film formation process.

From the results shown above, it is indicated that when all the processes involved in the antiwear film formation are considered, the antiwear film formation processes are most sensitive to the activation energy of thermal decomposition process. Little effect is observed from the Arrhenius parameters of autocatalytic decomposition process and adsorption process.

In the case of aged oil, some ZDDP molecules have been decomposed in the oil solution before entering the reactor volume between the two contacting surfaces. In most of the cases, lubricant in an internal combustion engine is aged to a certain degree. The ZDDP decomposition that happens in the oil sink should mainly be thermal driven.

In order to investigate the sensitivity of antiwear film formation to Arrhenius parameters in different processes when oil is aged, the effect of decomposition process is isolated by setting the concentration of decomposition product to be 1mol/m$^3$. This can be understand as a case where
the majority of ZDDP modules have been decomposed, or the concentration of ZDDP decomposition product is high enough so that the decomposition process is not rate limiting. Under the conditions stated, the effects of the Arrhenius parameters in adsorption and oxidation processes are compared.

**Figure 8:** The sensitivity of film thickness to the pre-exponential constant $A_{\text{ox\_prod}}$ and activation energy $E_{\text{ox\_prod}}$ of the adsorbed product oxidation process

Figure 8 indicates that when the decomposition process is not rate limiting, the antiwear film formation process is highly sensitive to the activation energy of the adsorbed product oxidation process. A 30% decrease in the activation energy lead to more than four times increase in the antiwear film thickness, and a 20% increase in activation energy may stop the antiwear film formation process. Meanwhile, the pre-exponential constant of the adsorbed product oxidation process also has moderate effect on the antiwear film formation process. However, the effectiveness is limited compared to that of the activation energy.
Figure 9 indicates that under the condition that the decomposition process is not rate limiting, the antiwear film formation is also sensitive to the Arrhenius parameters of the adsorption process, which the decomposed products are adsorbed onto the film. When the activation energy is decreased by 10%, an increase to 20% in film thickness is observed. Further decrease in activation energy has little effect on the film formation process. When the activation energy is decreased by 10%, the film thickness decreases almost 80%. A further 20% increase in activation energy may lead to the failure of film formation. Meanwhile, the effect of pre-exponential constant of the adsorption process is limited.

This group of simulations indicates that when decomposition product is sufficient in the oil, or the decomposition process is not rate limiting, the antiwear film formation process becomes most sensitive to the activation energy of the adsorbed product oxidation process.

Comparing the two cases considered, it is indicated that the antiwear film formation process is most sensitive to the activation energy of the rate limiting step. In each sub-step, the corresponding activation energy is always of more significance than that of the pre-exponential constant. In addition, the sensitivity ranges for different reactions are different.
Therefore, in order to increase the accuracy of the previously introduced model, it is important to identify the most appropriate values for the activation energies of the thermal decomposition process, the decomposed product adsorption process and the adsorbed product oxidation process.

### 3.2.2. Decomposition

Decomposition has been identified as the major processes that lead to the formation of antiwear film precursors. Thermal decomposition, oxidative decomposition, autocatalytic decomposition and decomposition proceeded by ligand exchange have been identified as some of the ZDDP decomposition pathways. A ZDDP molecule isomerization process has also been identified before the decomposition process. [Mosey, 2004] ZDDP isomers of different types, olefins, dialkyl sulfides, trithiophosphates, tetrathiophosphates and alkyl mercaptan are the major products formed through the isomerization and decomposition process. [Coy and Jones, 1981] Since the reactions that lead to the imperative precursors of ZDDP antiwear film are always accompanied by olefin elimination or dialkyl sulfide formation [Mosey and Woo, 2004], the formation rates of olefin or dialkyl sulfide from ZDDP or ZDDP isomers have been used to derive the ZDDP decomposition rate.

An experiment has shown that the activation energy of thermal decomposition is about 31 kcal/mole, which is about 130 KJ/mol. [Dickert and Rowe, 1966] In this experiment, it has been reported that the key steps in thermal decomposition scheme include an isomerization followed by an intramolecular elimination process, in which olefin is eliminated from the thiolosulfur. The rate of olefin formation has been used to calculate the activation energy of thermal decomposition. In addition, an autocatalytic decomposition process has been identified to be in parallel with the thermal decomposition process in the same experiment. Therefore, it is reasonable to assume the Arrhenius parameters of the autocatalytic decomposition process have similar values with the thermal decomposition process.

In addition, in both experiments and parametric analysis through the previously introduced model, the autocatalytic decomposition and decomposition proceeded by ligand exchange
processes are not recognized as the major decomposition pathways. Therefore, the values of the Arrhenius parameters of these two processes do not require to be known in a high accuracy. Some people believe that the ligand exchange process takes place before the thermal decomposition process [Mosey and Woo, 2004]. In the introduced lubricant chemistry model, route of ZDDP decomposition proceeded by ligand exchange has been treated as a parallel process with the thermal decomposition and autocatalytic decomposition. Therefore, the decomposition proceeded by ligand exchange process can be seen as a decomposition process which is preceded by ligand exchange. Estimations of the activation energies of the autocatalytic decomposition and decomposition proceeded by ligand exchange processes have been based on the available thermal decomposition information, together with simulations and analysis, until the calculation results, especially the film thicknesses are comparable to the available data.

A quantum chemical method has also been employed to calculate the energies barriers of the decomposition processes of ZDDP molecule with different alkyl groups, aimed at examining the reaction kinetic differences between straight-chained primary, secondary and branched primary alkyl ZDDPs. [Mosey and Woo, 2004] The straight-chained primary, secondary and branch primary alkyl ZDDPs are represented by ZDDPs with alkyl groups of ethyl, isopropyl and isobutyl. It is found that the energies barriers for the isomerization processes of different ZDDP molecules are neglectable, while the olefin and dialkyl sulfide elimination steps have much higher energy barriers. ZMTP has been identified a major precursor for film formation that is formed through the elimination processes. The energy barriers for the ZMPT formation process of straight-chained primary, secondary and branched primary alkyl ZDDPs molecules are about 17.6 kcal/mol, 34.3 kcal/mol and 27.7 kcal/mol, which are 73.7 kJ/mol, 143.6 kJ/mol and 116.0 kJ/mol respectively. The big difference in energy barriers between the first one and the last two systems is due to the first one mainly decompose through an intramolecular alkyl group transfer process while the last two mainly decompose through an olefin elimination process. In commercial lubricant, the mixed ZDDP usually contains 85% of secondary ZDDP. Therefore, the activation energy for the thermal decomposition process should be near to but less than 143.6kJ/mol.

From the experiment and calculation results shown above, an activation energy value of 130kJ/mol is representative for the thermal decomposition process. The values of other
Arrhenius parameters in other decomposition pathways can be set with initial values close to that of the thermal decomposition process and evaluated numerically until a reasonable range is achieved.

3.2.3. Adsorption

Different researches have shown that antiwear film is a thin layer of polyphosphate glass. Before the antiwear film is formed on the contacting surfaces, the adsorption of phosphorous containing material onto the surfaces is a necessary process. ZDDP decomposition products can be adsorbed on to contacting surfaces via physisorption or chemisorption. It has been reported that ZDDP molecules adsorb on iron via the sulphur atom of P=S bond [Yamaguchi, et.al, 1993]. Above 60°C, the adsorption is generally chemisorption and irreversible. [Spikes, 2004] The working temperature in an automotive engine is higher than this value. Therefore, it is justified to neglect the desorption process in the introduced lubricant chemistry model.

A study of the adsorption and desorption behaviors of ZDDP has shown that the rate constant of adsorption is $1 \text{ L mol}^{-1} \text{s}^{-1}$, between 40°C and 80°C, $3 \text{ L mol}^{-1} \text{s}^{-1}$, between 80°C and 145°C. [Wu and Dacre, 1997] It has suggested that the variation of rate constants is due to different adsorption mechanisms at high and low temperature. At higher temperature, which is the regime the model mainly concerns, the activation energy of adsorption is reported to be 68KJ/mol. The test conditions used in the experiment above are close to those can be observed under engine operation conditions. Therefore, the results reported in the first experiment are used in the model.

In addition, Gao et al have shown the activation energy of the desorption of tributyl phosphate onto iron oxide, $\text{Fe}_3\text{O}_4$, ranges from 109 to 115 kJ/mol at a temperature of about 200K. [Gao et. al., 2004] This result indicates that the activation energy required for desorption process is much higher than that for the adsorption process. Therefore, the desorption reaction is much slower than the adsorption reaction, and should not be the major process in concern.
3.2.4. Oxidation

Three types of oxidation reactions are related to the ZDDP film formation process. ZDDP molecule can react with the oxidant in the oil, playing as an anti-oxidant that resists lubricant degradation. However, the product from the reaction can no longer be used to form ZDDP antiwear film. In addition, the adsorbed ZDDP decomposition products will undergo a decomposition process before the antiwear film is formed. Third, paralleling with the ZDDP antiwear film formation process, the metal substrate may also be oxidized to form a thin layer of iron oxide, which is at the order of 5nm. In the current simulation, the anti-oxidant reactions of ZDDP is not included.

ZDDP is first introduced as an anti-oxidant, and many studies have been concentrating on the anti-oxidation properties of ZDDP. Adhvaryu et al. have introduced a method to calculate activation energy based on peak temperature (K) and program rate (β) relationship. [Adhvaryu and Perez, 1999] The kinetic parameters can be calculated from the plot of log program rate (β) versus the inverse peak temperature of the base oil, from the equation:

\[ E = 2.19R \frac{\beta \log \beta}{\delta (1/T)} \]  

(9)

Where R is the gas constant (1.987 cal/mol K) and β is the program rate (°C/min). In this experiment, the system was heated at three program rates of 5, 15, and 20 °C/min.

Four types of oil have been tested and the activation energies are reported from 13.00 Kcal/mol to 83.9 Kcal/mol [Adhvaryu and Perez, 1999]. One of the oil used, labeled BO-10, when tested alone, an activation energy of 83.90 Kcal/mol, and a rate of oxidative degradation of k=1.17 min⁻¹ are obtained, while after adding ZDDP in the same oil (0.13% Zn in total oil formulation), an activation energy of 51.50Kcal/mol, or 215.27 KJ/mol, and a rate of oxidative degradation of k=0.75 min⁻¹ are obtained.
It is proposed that zinc polyphosphates are formed by the oxidative reaction between adsorbed ZDDP decomposition products and O₂ or ROOH, which is related to the anti-oxidation reactions of ZDDP. [Nicholls, 2005] However, data on direct measurement of the activation energy and pre-exponent constant of the adsorbed product oxidation process are limited. Numerical analysis and estimation is necessary in order to identify a proper value for the Arrhenius parameters.

For the oxidation of substrate, the activation energy of iron oxidation process has been suggested by Grosvenor et al. [Grosvenor, et al, 2005]. The activation energy for the reaction of Fe with O₂ was determined to be 32±6 kJ/mol for exposure times of 20-2000s and 28±3kJ/mol for the reaction of Fe with water vapor for exposure times of 100-2000s. The previously introduced model used 28 kJ for the substrate oxidation process. In addition, Quinn has reported the activation energy of tribological oxidation activation energy at a similar range. [Quinn, 1998]

### 3.2.5. Summary of Arrhenius Parameters

Based on the calculation and analysis, the significance of the quantitative set of input Arrhenius parameters can be summarized as follow:

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbols</th>
<th>Values</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(thermal)</td>
<td>A&lt;sub&gt;Therm&lt;/sub&gt;</td>
<td>1*10&lt;sup&gt;13&lt;/sup&gt; mol/m&lt;sup&gt;2&lt;/sup&gt;s</td>
<td>Medium</td>
</tr>
<tr>
<td>E(thermal)</td>
<td>E&lt;sub&gt;Therm&lt;/sub&gt;</td>
<td>130KJ/mol</td>
<td>High</td>
</tr>
<tr>
<td>A(auto)</td>
<td>A&lt;sub&gt;auto&lt;/sub&gt;</td>
<td>1*10&lt;sup&gt;13&lt;/sup&gt; mol/m&lt;sup&gt;2&lt;/sup&gt;s</td>
<td>Low</td>
</tr>
<tr>
<td>E(auto)</td>
<td>E&lt;sub&gt;auto&lt;/sub&gt;</td>
<td>130KJ/mol</td>
<td>Low</td>
</tr>
<tr>
<td>A(ligand)</td>
<td>A&lt;sub&gt;ig&lt;/sub&gt;</td>
<td>1*10&lt;sup&gt;13&lt;/sup&gt; mol/m&lt;sup&gt;2&lt;/sup&gt;s</td>
<td>Low</td>
</tr>
<tr>
<td>E(ligand)</td>
<td>E&lt;sub&gt;ig&lt;/sub&gt;</td>
<td>125KJ/mol</td>
<td>Low</td>
</tr>
<tr>
<td>A(adsorb)</td>
<td>A&lt;sub&gt;adsorb&lt;/sub&gt;</td>
<td>6.6*10&lt;sup&gt;5&lt;/sup&gt; mol/m&lt;sup&gt;2&lt;/sup&gt;s</td>
<td>Medium</td>
</tr>
<tr>
<td>E(adsorb)</td>
<td>E&lt;sub&gt;adsorb&lt;/sub&gt;</td>
<td>68KJ/mol</td>
<td>High</td>
</tr>
<tr>
<td>A(oxidation) of Product</td>
<td>A&lt;sub&gt;ox Prod&lt;/sub&gt;</td>
<td>6.6*10&lt;sup&gt;5&lt;/sup&gt; mol/m&lt;sup&gt;2&lt;/sup&gt;s</td>
<td>Medium</td>
</tr>
<tr>
<td>E(oxidation) of Product</td>
<td>E&lt;sub&gt;ox Prod&lt;/sub&gt;</td>
<td>80KJ/mol</td>
<td>High</td>
</tr>
<tr>
<td>A(oxidation) of Substrate</td>
<td>A&lt;sub&gt;ox Prod&lt;/sub&gt;</td>
<td>1.5*10&lt;sup&gt;6&lt;/sup&gt; mol/m&lt;sup&gt;2&lt;/sup&gt;s</td>
<td>Low</td>
</tr>
<tr>
<td>E(oxidation) of Substrate</td>
<td>E&lt;sub&gt;ox Prod&lt;/sub&gt;</td>
<td>28KJ/mol</td>
<td>Low</td>
</tr>
</tbody>
</table>

Table 4: Arrhenius parameters and their significance
3.3. Physical and Chemical Parameters

3.3.1. Concentrations

The concentrations of four species are recorded in the introduced lubricant chemistry model: the concentrations of ZDDP, ZDDP decomposition products, oxidant and iron cations.

The concentration of ZDDP is one of the most important parameters in the model. It can greatly affect the antiwear film formation rate since the different ZDDP decomposition routes are all first order reactions that are directly related to the concentration of ZDDP in the oil solution. [Thomas, 2007] Three types of ZDDP are usually observed in the commercial lubricant, primary ZDDP, secondary ZDDP and aryl ZDDP, with secondary ZDDP as the major type of ZDDP in present. The model is not explicitly calculating the decomposition rates of each type of the ZDDPs. But when there are differences in chemical properties between different ZDDPs, corresponding values used are weighted towards those of the secondary ZDDPs. The decomposition process is also the first step that leads to the antiwear film formation, which is limiting the following adsorption process through the amount of available ZDDP decomposition products that can be adsorbed on to the contacting surface.

In this simulation, the concentration of ZDDP in the replenishing oil is set to be 0.1wt%P. This is closed to the ZDDP concentration limit of CJ-4 commercial oil. Compared to the volume of the oil sink, the amount of oil consumed in the reactor volume is limited. Therefore, it is assumed that the concentration of ZDDP in the replenishing oil stays constant.

The concentration of ZDDP decomposition products are recorded in the introduced model. The ZDDP decomposition products include ZDDP isomers, olefin, sulfides and gas phase products. The decomposition products kept track of in the model refer to those products that can be adsorbed onto the surface and form zinc polyphosphate. ZDDP isomers and ZMTP are the major products of this type. [Nicholas et. al., 2004] Since one mole of ZDDP molecule can decompose to one mole of ZDDP isomers or one mole of ZMTP, the concentrations of these two materials can be recorded together as the decomposition products. It is assumed that the replenishing oil is fresh oil and does not contain decomposition product.
The oxidants in lubricant are mainly oxygen or peroxides. The concentrations of oxidant are assumed to be constant at a given temperature and pressure. In this simulation, the concentration of the oxidant is set to be 9 mol/m$^3$.

Iron cations can facilitate the ZDDP decomposition process because they can react with ZDDP to form the more easily decomposed MDDP. The iron cations usually come from the wear of the metal substrate or iron oxide [Thomas, 2007]. Part of the worn metal or iron oxide will generate iron cations, leads to the increase in iron cation concentration increase in the reactor volume. The concentration of iron cations will be updated based on the ion exchange reaction and the oil replenishing rate. It is assumed that the replenishing oil does not contain iron cations.

3.3.2. Flow Rates

The flow rate affects the antiwear film formation in that it will decide the concentration changes within the control volume.

It is assumed that the rate of change of ZDDP composition in the reactor volume equals to the new ZDDP brought in by the inflow minus the ZDDP brought away by the outflow minus the change due to ZDDP decomposition.

$$\frac{dC_z}{dt} = \frac{V_{in}C_{z0} - V_{out}C_z - r_{decomp}}{Vol}$$  \hspace{1cm} (10)

Where $C_{z0}$ is the ZDDP concentration in the replenishing oil, $C_z$ is the concentration of ZDDP in the original oil in the control volume, $V_{in}$ is the inflow rate, $V_{out}$ is the outflow rate, $r_{decomp}$ is the decomposition rate, $Vol$ is the volume. The values of $V_{in}$ and $V_{out}$ decide the percentage of original oil that is going to be replaced by the replenishing oil during each replenishing period. This percentage of oil replaced can also be expressed in terms of residence time, [Thomas, 2007]
\[ m = \frac{\Delta t}{t_r + \Delta t} \]  

(11)

where \( m \) is the percentage of fluid replaced, \( \Delta t \) is the mixing time and \( t_r \) is residence time.

In this simulation, mixing time is 0.2s and residence time is 0.1s. In another word, 66.7% of the oil in the reactor volume is going to be replaced by the replenishing oil in each mixing step.

### 3.3.3. Pressure, Temperatures and Sliding Speed

The previously introduced lubricant chemistry model has divided the contacting surfaces into two partitions, peak and valley. It is assumed that the peak partition includes the asperities that bear the contact load, while there is no direct contact between valley partitions. Therefore, the pressure acted on the peak partition should be the real contact pressure. Under the working conditions of a typical internal combustion engine, the value of real contact pressure is at the order of 0.5 GPa. This simulation sets the real contact pressure to be 0.5 GPa.

Two types of temperatures are used in this model, one is bulk temperature, which refers to the temperature of the oil between the contacting surfaces; the other is flash temperature, which takes into account the heat generate from the friction between the peak partitions of the two surfaces. It has been reported that in the oil gallery, the oil temperature ranges from 75°C to 149°C, or 348K to 422K, under different load. [McGeehan et. al, 1990] The bulk temperature used in the calculation is selected to be 403K. The flash temperature can be calculated from the given bulk temperature, sliding speed, contact pressure and the physical properties of the contacting surfaces.

Engine wear often happens at low relative sliding speed when lubricant oil film breaks down and direct surface contact happens. This model is a boundary lubrication model targeting at the regime when lubricant oil film cannot fully develop between the contacting surfaces. Based on this consideration, a sliding speed of 0.1 m/s is selected in this simulation.
3.4. Summary of Input Parameters

A list of important input parameters are given in table 5 below:

<table>
<thead>
<tr>
<th>Nominal Contact Area</th>
<th>Peak Partition Area</th>
<th>ZDDP Concentration</th>
<th>Decomp. Prod. Concentration</th>
<th>Iron Cations Concentration</th>
<th>Oxidant Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>10mm²</td>
<td>1mm²</td>
<td>0.1wt%P</td>
<td>0</td>
<td>0</td>
<td>9mol/m³</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mixing Time</th>
<th>Residence Time</th>
<th>Real Contact Pressure</th>
<th>Bulk Temperature</th>
<th>Sliding Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2s</td>
<td>0.1s</td>
<td>0.5GPa</td>
<td>403K</td>
<td>0.1m/s</td>
</tr>
</tbody>
</table>

Table 5: Table Summary of input parameters

(The concentrations refer to the concentrations of the material in the replenishing oil)

3.5. Results Analysis

The wear process simulation includes the calculation of the removal of the adsorbed decomposition product, the removal of antiwear film, the wear of iron oxide or the wear of metal substrate. If exists, the sequence of the four layers of material, from bottom up, will be metal substrate, iron oxide, antiwear film and adsorbed decomposition product. The surface coverage of the four types of material and the layer thicknesses of antiwear film and iron oxide will be recorded. The adsorbed decomposition product can only be of a monolayer thickness, since the newly adsorbed products can no longer adsorb decomposition products. The thickness of the metal substrate is not recorded and can be treated as constant. Since when there exists oxidant in the oil solution, metal substrate is usually oxidized first and then worn, the wear of iron oxide
can also be seen as the lost of material from the metal substrate. Initially the surface is assumed to be bare metal.

![Figure 10: The accumulated wear volume of each species](image_url)

The simulation result for material wear is shown in Figure 10. It indicates that at the initial antiwear film formation stage, metal substrate has not been entirely covered by the antiwear film. The adsorbed product, antiwear film, iron oxide and metal substrate share the coverage of the entire surface. When abrasive wear takes place, each of the material is going to be removed from the surface. Since the antiwear film formation rate exceeds the antiwear film removal rate, antiwear film will first gain in coverage of the surface, and then increases in average thickness. After antiwear film has covered the entire surface and accumulated in average thickness, further wear will result in antiwear film removal. Metal substrate wear is avoided.

Therefore, under the conditions stated, at a long run, antiwear film can be well formed on the peak partitions of the contacting surfaces. When direct contact between two surfaces takes place,
the adsorbed decomposition product and antiwear film will be removed from the surface and the substrate will be protected.

4. Flash Temperatures

Thermal energy is a major driving force for ZDDP film formation. ZDDP thermal film is formed when immersing certain metals in ZDDP solution at a temperature above of about 100°C. While ZDDP tribo-film can form at a much lower temperature. In addition, tribo-film formation rate and thickness both exceed that of the thermal film.

The reason why tribo-film can form under low temperature is still under debate. One of the major beliefs is that flash temperature plays an effective role in the ZDDP tribo-film formation process [Rounds, 1966]. Flash temperature refers to the transient high temperature generated due to the heat from the friction of contacting surfaces. Flash temperature is a local phenomenon mainly affects the area where real contacts between asperities take place.

Flash temperature can be calculated by [Thomas, 2007]:

\[ T_f = T_s + \frac{p\mu U_s}{\pi^{3/2}r_a K_{eff}} \tan^{-1}\left(\frac{4a_{eff} t}{r_a^2}\right)^{1/2} \] (12)

where \( T_s \) is the bulk temperature of the metal surface, \( K_{eff} \) is the effective thermal conductivity, \( a_{eff} \) is the effective thermal diffusivity, and \( p \) is a partition function that assigns the appropriate fraction of total heat to the asperity, \( L \) is the load, \( U_s \) is the sliding speed, \( r_a \) is the average asperity radius.

In order to understand the effectiveness and sensitivity of flash temperature, a group of simulations are run at a bulk temperature of 403K, ZDDP concentration of 0.1wt%P, residence time of 0.1s. The flash temperature under different contact pressure and sliding speed are
considered. The sliding speeds are selected to be 0.1m/s, 1m/s and 10m/s. Under each sliding speed, the contact pressures are changed from 0.25GPa, 0.375GPa, 0.5GPa, 0.625GPa to 0.75GPa. The corresponding flash temperatures under each of the conditions are reported.

![Graph showing the effect of contact pressure and sliding speed on flash temperature](image)

**Figure 11: The effect of contact pressure and sliding speed on flash temperature**

Figure 11 indicates that at a sliding speed lower than 1m/s, and when the contact pressure is below 0.75GPa, the difference in flash temperature and bulk temperature is not obvious. Under the conditions considered, antiwear film is observed to be formed on the contacting surfaces. The antiwear film has a much lower friction coefficient than that of the metal. The friction coefficient of antiwear film is about 0.12, and the friction coefficient of bare steel surface is about 0.8. In addition, heat generated is also directly related to contact pressure and sliding speed. Under a low sliding speed, and mild contact, the heat generated from friction is limited.

When the sliding speed is increased to 10m/s, under the same pressures considered before, the flash temperatures are about 20K to 70K higher than the bulk temperature. Under the conditions considered, antiwear film cannot be formed on the contacting surface. Bare metal surfaces are in direct contact with each other. Therefore, a higher friction coefficient in addition to a high sliding speed make the effect of heat generated from friction more obvious.
However, when oil exists between the contacting surfaces, real contact of the asperities only takes place when the oil film breaks down. When the sliding speed of the two surfaces is high, it will be usually in a hydrodynamic lubrication regime, where oil film is isolating the two surfaces. Only when the sliding speed is low and the oil film breaks down will it enter a boundary lubrication regime, and direct surface contact may happen.

![Figure 12: Wear constant under different lubrication regime (Gangopadhyay, 2000)](image)

Therefore, under the boundary lubrication regime when the sliding speed is relatively low, flash temperature may be only less than 10K higher than the bulk temperature.

Since ZDDP thermal film will only form when immerse the metal piece in ZDDP solution above about 100°C, and ZDDP tribo-film can be formed at as low as 50°C [Spikes, 2004], the incremental in temperature due to the heat generated from the friction is not high enough to be account for the only reason that lead to the tribo-film formation under low temperature.

In addition, for a certain area, real contact only happens intermittently. Usually, the duration of the flash temperature is very short. Therefore, the effect of flash temperature on tribo-film formation is limited.
5. Surface Coverage and Film Development Processes

5.1. Surface Coverage

The dynamics of ZDDP surface coverage and surface competition mechanisms are of great interest since they are highly related to the antiwear property of ZDDP. However, the details of the mechanisms are still not well known. A study using the model has shown a possible mechanism of lubricant additive surface coverage and surface competition.

Once ZDDP molecules finish the decomposition process in the oil solution, the products will be adsorbed onto the contacting surfaces. In a system with ZDDP as the only lubricant additive under consideration, four major types of surfaces with different material coverage serve as the candidate of adsorption sites: the surface could be covered by newly adsorbed decomposition products, by antiwear film, by iron oxide, or still be fresh substrate such as cast iron. The simulations show that decomposition products are most easily to be adsorbed onto metal substrate or iron oxide while can hardly be adsorbed onto newly adsorbed products.

Therefore, when ZDDP is sufficient in the replenishing oil, a monolayer of the ZDDP decomposition products will soon cover the entire substrate. At the same time, some of the adsorbed products will be oxidized to form antiwear film; result in antiwear film’s gaining surface coverage, until the entire contacting surface has been covered by a monolayer of antiwear film. Thereafter, if the antiwear film formation rate exceeds the removal rate, decomposition products will continue to adsorb onto the surface covered by antiwear film and oxidized to form new film, so that antiwear film will increase in thickness.
To demonstrate the surface coverage process by ZDDP decomposition product, a simulation is done at the bulk temperature of 475K, sliding speed of 0.5m/s, mean separation of 500nm, nominal contact area of 1cm². In order to concentrate on the adsorption process of ZDDP film formation, the wear process and iron oxide formation process have been isolated from the simulation. The decomposition product concentration has been set to be 1 mol/m³.

Under mild wear conditions, when antiwear film can be formed on the entire contacting surface and gain in thickness, it is found that decomposition products and antiwear film are competing for surface coverage. Figure 13 shows the competition for surface coverage between decomposition products and antiwear film. Adsorbed product (AP) will always be on top of all layers. After the adsorption process, part of AP will be oxidized and become film, and the rest stay on top the antiwear film, gaining surface coverage ratio. AP will only be in a monolayer form, it cannot accumulate in thickness. Whereas, for antiwear film, it will first gain surface coverage on metal substrate, and then covered by AP, losing surface coverage. Even when antiwear film has entirely been covered by AP, the oxidation of AP will lead to the formation of new antiwear film, and the lost of surface coverage by AP. Therefore, the mass and thickness of film will continue to grow even after it has been totally covered by AP.
5.2. Effect of Surface Coverage Condition on Adsorption

Figure 14: The amount of decomposition product that is adsorbed to each type of the surface.

Figure 14 shows the accumulative amount of ZDDP decomposition products that have been adsorbed to different area of the surface. The decomposition product may be adsorbed to adsorbed decomposition product on valley partition (product_valley), ZDDP film on valley partition (film_valley), iron oxide on valley partition (oxide_valley), metal substrate of the valley partition (substrate_valley), adsorbed decomposition product on peak partition (product_peak), ZDDP film on peak partition (film_peak), iron oxide on peak partition (oxide_peak), or metal substrate of the peak partition (substrate_peak).

It indicates that in the initial a few seconds, for valley and peak partition, most decomposition products have been adsorbed to the substrate. The amount of product that is adsorbed to iron oxide also exceeds that adsorbed to the film. Thereafter, when the substrate and iron oxide have been covered by film, most of the decomposition products have been adsorbed on the film covering each partition. Since on the contacting surfaces, the area of the valley partition is
usually much larger than that of the peak partition, over the time, the film formed on the valley partition of the surface has become the main site for the adsorption of decomposition product.

6. Parametric Analysis

6.1. Baseline Case

ZDDP antiwear film formation will mainly undergo a decomposition process, an adsorption process and an oxidation process. Each of the sub-processes may have different effects on the entire process of antiwear film formation.

In order to understand how each individual process can affect the total ZDDP antiwear film formation, the three major processes leading to the formation of ZDDP antiwear film, the decomposition process, the adsorption process and the oxidation process should be studied first.

6.1.1. Decomposition

Figure 15: Effects of decomposition rate on antiwear film formation
In order to understand the effect of decomposition process to the antiwear film formation, a group of simulations are run under the conditions of bulk temperature of 403K, sliding speed of 0.1m/s, contact pressure of 0.5Gpa, residence time of 0.1s, and ZDDP concentration of 0.1wt%P. The antiwear film thicknesses at 1000s are compared. The original decomposition rate and the corresponding antiwear film thickness are recorded as 100% in the figure. Thereafter, only the decomposition rate is lowered to a certain percentage of the original value. The calculated antiwear film thicknesses at 1000s are reported and compared.

Under the conditions above, no obvious change in antiwear film thickness is observed when increasing the decomposition rate. When decreasing the decomposition rate, antiwear film thickness only starts to decrease obviously after the decomposition rate has been lowered to 5% of the original value. From the results, it can be concluded that the decomposition process is not limiting the growth of the antiwear film under the conditions. The reason may be that under the original decomposition rate, the rate is high enough to decompose all the available ZDDP in the reacting volume before the replenishment. Only when the decomposition rate decreased to 5% or under can the ZDDP be left between each replenishing interval.

Since under the conditions provided, ZDDP antiwear film formation is not sensitive to the variation of decomposition process, other additives that interfere with the ZDDP antiwear film formation through affecting the decomposition of ZDDP may not have strong effects. Detergent belongs to such an example that can affect ZDDP antiwear film formation but not strongly.
6.1.2. Adsorption and Oxidation

A similar simulation is done to analyze the sensitivity of antiwear film formation to the adsorption and oxidation processes under the same conditions. The rates of each process are changed individually and the resulted antiwear film thicknesses are plotted together. Figure 16 shows that the antiwear film thickness starts to decrease as soon as the adsorption rate and oxidation rate decreases. Under the given conditions, the adsorption and oxidation processes directly affect the antiwear film formation process even when only small changes take place.

Since ZDDP antiwear film is very sensitive to the adsorption process, the other lubricant additives that affecting the ZDDP antiwear film formation through interfering with the adsorption process are expected to have strong influence on the entire ZDDP antiwear film formation. One of such examples is dispersant which compete with ZDDP decomposition products for surface coverage. Since dispersant is limiting the available surface area the ZDDP decomposition products can be adsorbed onto, directly affecting the adsorption process, it is reported to have strong influence on antiwear film formation process.
6.1.3. Comparison

A comparison of the sensitivity of antiwear film formation to the three individual processes shows, under the given conditions ZDDP antiwear film formation is more sensitive to the adsorption and oxidation processes.

This also implies that a higher ZDDP concentration in the oil does not necessarily lead to a high ZDDP antiwear film formation rate. Since ZDDP molecules in the solution provide reactant for the decomposition process, once sufficient decomposition products exist in the oil, adsorption process and the following oxidation process are the limiting steps. A further increase in the rate of the initial step does not necessarily have effect on the entire antiwear film formation.
Figure 18: The effect of oxidation rate on film thickness under different adsorption rate

Figure 19: The effects of oxidation rate under different adsorption rate
The previous simulations show that ZDDP antiwear film formation is more sensitive to the adsorption process and oxidation process. In addition, adsorption process comes before the oxidation process, limiting the amount of available adsorbed products to be oxidized. Therefore, it is interesting to know how the adsorption process will affect the oxidation process.

A group of simulations are run under the same conditions as before, at a bulk temperature of 403K, sliding speed of 0.1m/s, contact pressure of 0.5Gpa, residence time of 0.1s, and ZDDP concentration of 0.1wt%P. The adsorption rate is first lowered to 10% of the original value and kept constant, and gradually lower the oxidation rate from 100% to 80%, 50%, 30%, 10% and 1% of the original value. The resulted antiwear film thickness and change of film thickness in percentage of the value at 100% of oxidation rate are reported.

The above figures indicate that when changing the oxidation rate under different adsorption rate conditions, although the absolute antiwear film thickness is lower under lower adsorption rate, the percentage change of antiwear film thickness due to the change of oxidation rates are similar.

![Graph showing the comparison of decomposition, adsorption and oxidation rate on antiwear film formation at lower temperature](image)

**Figure 20:** The comparison of the effect of decomposition, adsorption and oxidation rate on antiwear film formation at lower temperature
Repeat the same simulation, while decrease the bulk temperature to 353K. Under the conditions of bulk temperature of 353K, sliding speed of 0.1m/s, contact pressure of 0.5Gpa, residence time of 0.1s, ZDDP concentration of 0.1wt%, the film thicknesses, in terms of the percentage of original values, at 100%, 80%, 50%, 30%, 10% and 1% of the original rates are reported.

Figure 20 indicates that at a lower temperature, the antiwear film formation process is more sensitive to the decomposition and adsorption process. Under a temperature of 353K, or 80°C, ZDDP decomposition process has been greatly slowed down, and started to have strong effect on the entire antiwear film formation process. While at a higher temperature, the available ZDDP in the solution will be rapidly decomposed to decomposition products.

6.1.4. Decomposition Pathways

![Graph showing decomposition pathways](image)

**Figure 21: The weights of different decomposition pathways under different temperature**

It is known that ZDDP can be decomposed to decomposition products mainly through three pathways: the thermal decomposition, the autocatalytic decomposition and decomposition
proceeded by ligand exchange [Thomas, 2007]. However, the significance of each pathway under different conditions is not well known. In order to understand the significance of different pathways under different temperature, a group of simulations are run at temperature from 303K to 453K at a 25K interval, and a sliding speed of 0.1m/s, contact pressure of 0.5GPa, residence time of 0.1s, and ZDDP concentration of 0.1wt%. The temperature is the only parameter that is changed in these simulations. The percentage of ZDDP that decomposed through different pathways is presented and the antiwear film thicknesses at different temperature are also shown.

Figure 21 shows that ZDDP decompose mainly through thermal decomposition under the range of temperature simulated. Autocatalytic decomposition contributes more than 20% of the total decomposition products at a temperature higher that 353K. However, under mild contact pressure when antiwear film can fully develop on the sliding surface, preventing direct metal surface contact, decomposition proceeded by ligand exchange is not an effective way for ZDDP decomposition. This is because in order for the ligand exchange to take place, iron cations are necessary to present in the oil to substitute Zinc cations and form MDDP. When the metal substrates are protected by antiwear film, no direct contact will take place between the metal surfaces. Therefore, iron cations will not be generated. Assuming that iron cations does not present in the replenishing oil, the reactor volume will be free from iron cations.

When bulk temperature is lowered to 303K, when antiwear film cannot fully develop, direct metal contact happens. Under such condition, ZDDP may decompose via ligand exchange. But even when it takes place, this pathway only has limited effect on the entire decomposition process.
6.2. Macroscopic operating variable

6.2.1. Bulk Temperature

It has been reported that operating conditions may have significant effect on antiwear film formation. [Norton, 2007] The macroscopic conditions will come to affect the antiwear film formation process by changing the reaction rates of each sub-process.

The major reactions involved in the antiwear film formation processes are thermally driven. Therefore, temperature is expected to have great impact on the antiwear film formation. In order to understand the significance of temperature to antiwear film formation and its sub-processes, a group of simulations are run with initial conditions of a bulk temperature of 403K, a sliding speed of 0.1m/s, contact pressure of 0.5Gpa, residence time of 0.1s, and a ZDDP concentration of 0.1wt%P. Then the bulk temperature is increased to 428K and 453K, and reduced to 378K, 353K and 303K. The rates of decomposition, adsorption and oxidation are reported at each temperature.

![Graph showing the effect of bulk temperature on decomposition, adsorption, and oxidation](image)

**Figure 22:** The effect of bulk temperature on decomposition, adsorption and oxidation process
The results shown in figure 22 indicate that when increasing the bulk temperature from 403K to 453K, the changes of decomposition rate, adsorption rate and oxidation rate are not obvious. When decreasing the temperature from 403K to 303K, the decomposition rate starts to decrease as the temperature lowered fewer than 373K. The adsorption rate and oxidation rate start to decrease right after the temperature is lowered from 403K. In addition, the sensitivities of adsorption and oxidation processes to temperature are identical under the temperature range considered.

The figure also indicates that the decomposition rate is more sensitive to temperature between 353K and 378K. The adsorption and oxidation process are more sensitive to temperature at the range of 353K to 403K. Due to the difference in temperature sensitivity range of different reaction processes, the antiwear film formation is sensitive to different sub-process at different temperatures.

ZDDP film can be formed on either the peak partition or valley partition of the contacting surfaces. The major difference between the films formed on the two partitions is that the peak partition will undergo intermittent contact with the opposite surface while the valley partition is
assumed to be not able to be in contact with the opposite surface. As a result, the local temperature of the peak partition and the valley partition can be different due to the heat generated during friction. In addition, the film formed on the peak partition will undergo a removal process which will not affect the film formed on the valley partition.

Under the same conditions as stated before, the film formed on the peak partition and the valley partition of the surface under the temperature from 303K to 403K are compared. The film formed at 403K is selected to be the ‘original thickness’. The films formed at other temperatures are compared with that value. The results in figure 23 indicate that films formed on peak and valley partition have similar sensitivity to the bulk temperature. In addition, the films formed on both types of surfaces are more sensitive to the bulk temperature between the range of 353K and 403K.

6.2.2. ZDDP Concentration

Due to the regulation on heavy duty diesel engines emissions, the limitation on the concentration of ZDDP in lubricant has been strengthened. The effect of ZDDP concentration on film formation process is of great interest.

In order understand the effect of ZDDP concentration on the sub-processes and antiwear film formation mechanism, a group of simulations are run at a bulk temperature of 403K, a sliding speed of 0.1m/s, contact pressure of 0.5GPa, and residence time of 0.1s. The ZDDP concentration is originally 0.1wt%P. The ZDDP concentration is changed to 50%, 75%, 125% and 150% of the original value individually and the corresponding reaction rates and antiwear film thicknesses are reported.
The results shown in figure 24 indicate that ZDDP decomposition rate, decomposed product adsorption rate and adsorbed product oxidation rate are positively related to ZDDP concentration. The sensitivity of the reactions under consideration to ZDDP concentration is similar. ZDDP decomposition process is more sensitive to ZDDP concentration at higher concentration ranges.

ZDDP decomposition process is directly related to the ZDDP concentration, which describes the available reactant for the decomposition reaction. The products of the decomposition reaction provide reactant for the adsorption process, and the adsorbed products will undergo an oxidation process before the antiwear film is formed.
Figure 25: The effect of ZDDP concentration on film thicknesses on peak and valley partition

Figure 25 shows the sensitivity of antiwear film formed on peak and valley partition to ZDDP concentration in the solution. The results indicate that film formed on both peak and in valley partition are positively related to ZDDP concentration. The sensitivity of film formation to ZDDP concentration is similar on both types of surfaces. The major difference between the two partitions is the surface conditions, the contact pressure, and the local temperature. The oil properties, including additive concentrations, are homogeneous above different types of surfaces. Therefore, the effects of ZDDP concentrations on film formed on different surface partitions are similar.

6.2.3. Contact Pressure

In order to understand the effect of contact pressure on ZDDP antiwear film formation, a group of simulations are run at a bulk temperature of 403K, sliding speed of 0.1m/s, residence time of 0.1s, and ZDDP concentration of 0.1wt%P. The original contact pressure is 0.5GPa. Thereafter, contact pressure is changed to 50%, 75%, 125% and 150% of the original value. The resulted
The pressure considered in the model is the real contact pressure between the contacting asperities. It is assumed that only the peak partition that in contacting state will take the load acting on the surfaces. The contact pressure may have both positive and negative effect on the film formed on the peak partition. Antiwear film growth is related to the antiwear film formation process and the antiwear film removal process. A higher contact pressure will increase the antiwear film removal rate, negatively affecting the antiwear film growth. At the same time, the local temperature will increase due to the heat generated from friction. Since the antiwear film formation rate, including decomposition rate, adsorption rate and oxidation rate, are positively related to temperature, the contact pressure may lead to an increase in certain reaction rates.

Figure 26: The effect of contact pressure on ZDDP decomposition rate, decomposition product adsorption rate and adsorbed product oxidation rate

Figure 26 shows the effect of contact pressure to the ZDDP decomposition rate, decomposed product adsorption rate and adsorbed product oxidation rate. Under the conditions stated, the
ZDDP decomposition rate is positively related to the contact pressure. The heat generated from the friction may be the major reason for this trend. However, the effect of contact pressure on adsorption process is neglectable, and when the real contact pressure increases from the original value to 125% of the original value, a decrease trend is observed.

Figure 27: The effect of contact pressure on the ZDDP film formed on peak and valley partition

Figure 27 shows the effect of contact pressure on ZDDP film formed on both peak and valley partition. Since no direct contact take place between valley partitions of the surfaces, contact pressure does not have influence on the film formed on the valley partition. The conditions for the film formed on the valley partition are more closed to that for the thermal film formation.

The thickness of antiwear film formed on peak partition is observed to decrease slightly as the contact pressure increase to 125% of its original value. This trend coincides with the trend of the adsorbed product oxidation rate. This can be understood in that antiwear film formation is directly decided by the adsorbed product oxidation rate.
Figure 28: The effect of contact pressure on antiwear film removal rate

Figure 28 shows that antiwear film removal rate is proportional to the contact pressure. But the entire antiwear film formation trend does not follow the trend of the antiwear film removal rate. The conditions considered, a high temperature and a mild contact pressure, is favorable for antiwear film formation.

From figures 26 and 27, it is indicated that under the situation considered, antiwear film is insensitive to contact pressure. One possible reason is that the low sliding speed limited the effect of abrasive wear on antiwear film formation. In order to verify the assumption, a group of comparison simulations are run under the same conditions with only a higher sliding speed of 1 m/s.
The results from figure 29 show that under a higher constant sliding speed of 1m/s, the effect of contact pressure on antiwear film formation is more obvious. The antiwear film formed on the peak partition is more sensitive to the contact pressure, while the effect of contact pressure on the film formed on the valley partition is limited.

The reason for the observation is that the antiwear film removal rate is proportional to the product of contact pressure and relative sliding speed. The value of the sliding speed is scaling the effect of contact pressure.
7. Summary and Conclusion

The lubricant chemistry model introduced by Thomas [Thomas, 2007] and developed in this thesis can be used to predict the wear of different surface material in a tribological system. It can be also used to study and analysis the dynamics of ZDDP antiwear film formation and the wear under boundary lubrication regime with the consideration of the protection from antiwear additives.

The sensitivity of the antiwear film formation to the considered sub-processes including the decomposition process, adsorption process and oxidation process in addition to input parameters has been analyzed and demonstrated. The analysis of the dynamics of antiwear film formation using the model has been discussed.

Through the analysis of the antiwear film formation processes, it is found that:

1. The significance of the ZDDP decomposition process, the decomposition product adsorption process and the adsorbed product oxidation process to ZDDP antiwear film formation is different at different temperature. At a temperature of 403K or higher, the antiwear film formation is more sensitive to the adsorption and oxidation processes; while at a temperature of 353K or lower, the antiwear film formation is more sensitive to the decomposition and adsorption processes.
2. For the ZDDP decomposition process, thermal decomposition is the most significant pathway.
3. Among the chemical properties, the activation energy of the rate limiting step in the film formation process has the greatest effects on the dynamics of film formation.
4. Surface coverage conditions have great effect on the decomposed product adsorption process.
5. Under a typical engine operation condition, the temperature increase due to the heat generated from friction is only at the order of 10K. Therefore, flash temperature should not be the major reason that leads to the different behavior of the ZDDP antiwear film (tribo film) and ZDDP thermal film formation. The contacting surface should have played a catalyst role to facilitate the tribo film formation at low temperature. [Hsu & Gates, 2005]
References


Paranjpe, R. S., Gecim, B. A., 1992, “Comparative Friction Assessment of Different Valve-Train Types Using the FLARE (Friction and Lubrication Analysis) Code,” SAE, 920491


Nomenclature

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