DE-LUBRICATION DURING SINTERING OF P/M COMPACTS: OPERATIVE MECHANISM AND PROCESS CONTROL STRATEGY

Report No. 2001# 1

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PROJECT STATEMENT

Objectives

- Determine various parameters and optimum conditions for complete de-lubrication.
- Identify various gases and byproducts released during the de-lubrication of EBS.
  - Develop a mathematical model to control and predict the completion of de-lubrication.
  - Extend the mathematical model for other lubricants other than EBS.
  - Develop a simple excel worksheet to predict the completion of de-lubrication for various lubricants.

The project was subdivided into 3 major phases.

Phase 1: Ascertain the most important parameters that affect the kinetics of de-lubrication.
Phase 2: Investigate the type of gases and by-products released during de-lubrication. This was required to gain an understanding of the
fundamental reactions during the degradation of EBS (Acrawax). This is required to control the process.

Phase 3: Determine a control strategy for de-lubrication. Extend the mathematical model to other lubricants.

**ACHIEVEMENTS THIS QUARTER**

**Phase 3**

The mathematical formulation to predict de-lubrication was put forth in the previous report (2000-2). The process of de-lubrication can be described by the following equation:

\[
\alpha = \frac{1}{1 + \left(\frac{t}{t_{\text{max}}}ight)^b}
\]

Where, \(\alpha\) = weight fraction of the lubricant in the part at any time \(t\) \(t_{\text{max}}\) and \(b\) are constants dependent on the heating rate

The model was used for the prediction of de-lubrication of Acrawax and was verified in an industrial furnace. The overwhelming success of the model prompted the focus group to extend the model to other lubricants. In the last quarter, experiments were performed at WPI, extending mathematical model to other lubricants (Kenolube, Polywax, Zinc Stearate and Acrawax). The Table I lists the constants derived for the above lubricants at various different densities. The experiments for Zinc Stearate (all densities) and Polywax (Density 7.30 gm/cc) are underway at WPI.

**Table I: Theoretical and Empirical model constants for the various lubricants at various green densities**

<table>
<thead>
<tr>
<th>Density</th>
<th>Lubricant</th>
<th>(E) (kJ)</th>
<th>(A_0) (1/min)</th>
<th>(T_{\text{max}}) (K^{-1}) Vs Rate of Heating (R) (0^\circ)C/sec</th>
<th>(b') Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.05</td>
<td>Kenolube</td>
<td>42.01314</td>
<td>0.06340989</td>
<td>-5053.3 / (ln(R) - 5.2743)</td>
<td>18 - 24</td>
</tr>
<tr>
<td></td>
<td>Polywax</td>
<td>38.74989</td>
<td>0.184151513</td>
<td>-4660.8 / (ln(R) - 4.8698)</td>
<td>25 - 37</td>
</tr>
<tr>
<td></td>
<td>Acrawax</td>
<td>45.98224</td>
<td>1.0067</td>
<td>-5530.7 / (ln(R) - 6.165)</td>
<td>20 - 35</td>
</tr>
<tr>
<td>7.20</td>
<td>Kenolube</td>
<td>41.75</td>
<td>0.042156905</td>
<td>-5021.6 / (ln(R) - 5.1371)</td>
<td>16 - 24</td>
</tr>
<tr>
<td></td>
<td>Polywax</td>
<td>50.668</td>
<td>0.110526076</td>
<td>-6094.3 / (ln(R) - 6.2638)</td>
<td>18 - 32</td>
</tr>
<tr>
<td></td>
<td>Acrawax</td>
<td>41.227</td>
<td>0.076889769</td>
<td>-4958.7 / (ln(R) - 5.2297)</td>
<td>22 - 33</td>
</tr>
<tr>
<td>7.30</td>
<td>Polywax</td>
<td>49.079</td>
<td>0.001189263</td>
<td>-5903.2 / (ln(R) - 5.9879)</td>
<td>18 - 36</td>
</tr>
<tr>
<td></td>
<td>Acrawax</td>
<td>45.451</td>
<td>0.001261249</td>
<td>-5466.8 / (ln(R) - 5.6747)</td>
<td>24 - 36</td>
</tr>
</tbody>
</table>
*Attachment I* is a summary of all the work to date emphasizing the foundations of the de-lubrication process. *Attachment II* gives the detailed results of the control model applied to a variety of different lubricants other than Arcawax.
DE-LUBRICATION DURING SINTERING OF P/M COMPACTS: OPERATIVE MECHANISM AND PROCESS CONTROL STRATEGY

- Summary Report
1.0 **INTRODUCTION:**

A typical sintering furnace is divided into three zones. The first zone of a sintering furnace is solely used for the removal of lubricants from the compacted part. This is achieved by heating the part to temperatures in the range of 500-600°C at a controlled rate and atmospheric conditions. The de-lubricated part then enters the hot zone where it is heated to higher temperatures (close to its melting point) for sintering. The third zone or the cooling zone cools the sintered part at a desired rate to get the requisite micro structural properties. Proper de-lubrication is an important issue for the following reasons:

1. The end temperature of the first zone is normally 550-600 °C. The primary function of the first zone, also called the De-lube zone, is to remove the lubricants from the green parts. As the part enters the hot zone (temperatures of 1200-1300 °C), it experiences a temperature gradient in a very short time, which causes the left over lubricant to expand rapidly and introduce cracks on the surface (blistering).
2. Improper gas flows and belt speeds can lead to the deposition carbon on the part. This is called sooting.
3. Most lubricants are hydrocarbons and improper removal can lead to carbon segregation at the grain boundaries.

Micro-cracks, carbon segregated grain boundaries and sooting are strong quality detractors of sintered parts. Very little knowledge base in the various parameters and kinetics of the reactions during de-lubrication has has stymied the development of effective control systems for this process. Manufacturers follow different strategies to alleviate this problem. These vary from longer de-lubrication zones to increased amount of moisture in the furnace.

The literature review and the plant visits we carried out have confirmed that the physics of de-lubrication are not well established and the reason why there exists so many approaches. The objective of this work is to understand the physics of de-lubrication, and based on this knowledge, to recommend a control strategy.

2.0 **ORGANIZATION OF WORK**

According to this objective, i.e., to understand the de-lubrication process and to develop control systems for effective de-lubrication we subdivided the project in three phases.

Phase 1: Ascertain the most important parameters that affect the kinetics of de-lubrication.

Phase 2: Investigate the type of gases released during de-lubrication. This is required to control the process.
Phase 3: Recommend a control strategy.

The following sections outline the experiments and results performed at WPI in the last quarters.

3.0 PHASE 1

In Phase 1, our goal was to determine the most important parameter affecting the kinetics of de-lubrication. Previous researchers have shown that the parameters affecting the process of de-lubrication are the rate of heating, molecular structure, green density, atmospheric composition and the flow rate of gases. In accordance to the above stated objective, experiments were designed using Taguchi analysis, to identify their effect on the kinetics of de-lubrication. Sets of 3 experiments (for three different densities 6.80, 6.95 and 7.04 gm/cc) were performed. The various parameters and various levels are shown in Table 1. The Taguchi matrix is shown in Table II.

Table I. Experimental variables and levels

<table>
<thead>
<tr>
<th>VARIABLE</th>
<th>LEVEL # 1</th>
<th>LEVEL # 2</th>
<th>LEVEL # 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating Rate (°C/min)</td>
<td>10</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>% Hydrogen</td>
<td>5</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>Moisture</td>
<td>-</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Flow Rate (ml/cc)</td>
<td>40</td>
<td>60</td>
<td>80</td>
</tr>
</tbody>
</table>

Table II. Taguchi Matrix to determine the effect of various parameters on the rate of de-lube

<table>
<thead>
<tr>
<th>Run Trial</th>
<th>Factors</th>
<th>Heating rate (°C/min)</th>
<th>% H₂</th>
<th>Moisture</th>
<th>Flow rate (ml/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>10</td>
<td>5</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>10</td>
<td>15</td>
<td>Low</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>10</td>
<td>30</td>
<td>High</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>20</td>
<td>5</td>
<td>Low</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>20</td>
<td>15</td>
<td>High</td>
<td>40</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>20</td>
<td>30</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>30</td>
<td>5</td>
<td>High</td>
<td>60</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>30</td>
<td>15</td>
<td>-</td>
<td>80</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>30</td>
<td>30</td>
<td>Low</td>
<td>40</td>
</tr>
</tbody>
</table>

TGA (Thermo gravimetric analysis) was used to determine the rate of de-lube. The TGA allows one to heat a sample and progressively measure the change in
weight of the sample. Most TGA samples are in the 1 — 2 gm range; however the surface to volume ratio in such samples does not simulate industrial conditions. Accordingly, we used larger samples; 35 — 37 gm. TRS bars of dimensions _ square base and height 1 _ were used. This allowed us to have weights ranging from 35-37 gm per sample (depending on the green density). Using this apparatus, samples of _ square base and 1 _ height were put in the atmosphere dictated by the L9 Taguchi matrix. All the samples have the same composition Fe-0.8% C with 1% lubricant (EBS). The onset of de-lubrication, end of de-lubrication and the slope of the weight loss curve were obtained from the data analysis software provide by the TGA. The data obtained from these experiments are profiled by curves similar to the one shown in Figure 1. The critical information obtained from the TGA data are: Start temperature, Onset temperature, Slope (dW/dt), Final temperature, End temperature; these are shown pictorially in the same figure.

3.1 Results and Conclusions

The data collected were mathematically interpreted using ANOVA (Analysis of variance). ANOVA reveals the contribution of the process parameters on the variance of the process output. Table III shows the data for the ANOVA analysis for all three densities. The percentage contribution of each parameter on the kinetics of de-lubrication is shown in Table IV.
Table III. Taguchi L9 matrix and data for three different densities

<table>
<thead>
<tr>
<th>Trial Run</th>
<th>Rate of heating (°C/min)</th>
<th>% H2</th>
<th>Moisture</th>
<th>Gas Flow (ml/min)</th>
<th>Slope (mgs/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.80 gm/cc 6.95 gm/cc 7.04 gm/cc</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>5</td>
<td>-</td>
<td>40</td>
<td>-38.3</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>15</td>
<td>Low</td>
<td>60</td>
<td>-46.4</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>30</td>
<td>High</td>
<td>80</td>
<td>-51</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>5</td>
<td>Low</td>
<td>80</td>
<td>-88.6</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>15</td>
<td>High</td>
<td>40</td>
<td>-91.2</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>30</td>
<td>-</td>
<td>60</td>
<td>-60.2</td>
</tr>
<tr>
<td>7</td>
<td>30</td>
<td>5</td>
<td>High</td>
<td>60</td>
<td>-121.8</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>15</td>
<td>-</td>
<td>80</td>
<td>-72.1</td>
</tr>
<tr>
<td>9</td>
<td>30</td>
<td>30</td>
<td>Low</td>
<td>40</td>
<td>-119.9</td>
</tr>
</tbody>
</table>

Table IV: Percentage Contribution of Parameters on the kinetics of De-lubrication

<table>
<thead>
<tr>
<th>FACTORS</th>
<th>Percentage Contribution to variance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.80 gm/cc 6.95 gm/cc 7.04 gm/cc</td>
</tr>
<tr>
<td>Rate of Heating</td>
<td>70.25 71.62 65.06</td>
</tr>
<tr>
<td>% Hydrogen</td>
<td>3.35 4.38 5.88</td>
</tr>
<tr>
<td>Moisture</td>
<td>23.27 21.19 24.57</td>
</tr>
<tr>
<td>Gas Flow</td>
<td>3.13 2.81 4.48</td>
</tr>
</tbody>
</table>

Taguchi analysis has clearly shown that the kinetics of decomposition is essentially a thermal event and that the rate of heating determines the decomposition kinetics. For a control system to evolve and to ensure effective de-lubrication, the rate of heating has to be controlled. The moisture has shown to have an effect on the de-lubrication kinetics, but controlling the moisture in a control system is not desired as it oxidizes the surface of iron samples, and requires a reducing gas, and hydrogen, to maintain the balance. Moisture and the flow of gases may be required, on the other hand to prevent sooting and the build up of a stagnant layer on the part. Taguchi analysis has also revealed that moisture plays a significant role in the decomposition of EBS. Though higher heating rates remove lubricants faster from the part, the faster the better approach might be deleterious to the resultant part quality.
4.0 PHASE 2

One of the challenges for a sintering furnace operator is to ensure that, the lubricant in the green part is removed completely before the part enters the sintering zone. Various companies have adapted different techniques to ensure complete lubricant removal. Some manufacturers have longer de-lubrication zones while others have introduced moisture into their furnaces. Though, these de-lube solutions have partly solved the problems, most industries have numerous questions unanswered; what gases are released during de-lubrication? Does moisture play a role in the decomposition of lubricants? Is there the possibility to control the process? These questions were partly answered by Harb Nayar and George White in 1995. Their study however, did not lay down the mechanism of de-lubrication and failed to conclusively identify the various gases and by-products released during de-lubrication. The effect of moisture on de-lubrication was left untouched. Understanding the fundamental reactions and identifying the gaseous by-products formed during de-lubrication is the key to sensor development. The primary motivation for this phase is to identify various gases released during de-lubrication and to identify the mechanism of de-lubrication. Identification of gases was performed using the FTIR (Fourier transform infrared spectroscopy) and DUV (Deep ultraviolet spectroscopy). The results of this study will aid in the development of future sensors for de-lubrication.

4.1 Experimental setup and design

Samples (square base and height 1) containing 1% EBS (Acrawax) as the lubricant were heated in a specially designed furnace. The atmosphere used in all the experiments had a composition of 95 % Nitrogen + 5% Hydrogen. To add moisture to the atmosphere, the mixture of nitrogen and hydrogen was passed through a bubbler. The flow rate of the gases was 2 liters/min. The temperature of the bubbler was maintained to the required temperature by heating coils around the bubbler. Check valve A and B prevented the outflow of moisture laden gas back through the flow meter in case of pressure build up. The gas direction valve ensured either moisture or no moisture into the furnace. The pipes were heated to prevent moisture condensation. The temperature was maintained by self-heating coils. A schematic of the entire setup is shown in Figure 2.
The actual experimental setup is shown in Figure 3. The following steps were followed in all the experiments:

- The entire system was purged with dry nitrogen for 15 minutes.
- Background spectrums were collected at random during this initial process to ensure minimum atmospheric contamination.
- The atmosphere for the experiment (N$_2$/H$_2$ mixture + moisture/no moisture) was then passed for a period of 15 min and allowed to stabilize.
- The furnace temperature with the sample was maintained and equilibrated at 1000°C during the entire process of atmospheric control.
- The temperature of the gas tubes was maintained by self-heating coils to temperature above that of the water bath (in wet conditions) to ensure that the moisture content remains constant during the collection of spectrums.
- The FTIR cell and the DUV cells were insulated and heated to 120°C to prevent condensation of moisture on the cell windows.
- Once the background spectrums showed minimum contamination, the sample was heated at 10°C/min to 600°C.
- The optical path lengths were maintained at 5m for the FTIR and 0.5 m for the DUV.
- FTIR and DUV spectrums were collected every 2.5 minutes.
- The flow rate of the gases was maintained at 2 liters/min.
Flow Controller

Nitrogen + 4 – 5% Hydrogen Cylinder

T-junction, for wet and dry gas.

Bubbler for wet atmosphere

FTIR cell

Temperature controller of the furnace

Furnace

Junction splitting the volume of by-products to DUV and FTIR cells

DUV cell

Figure 13: Experimental Setup
4.2 Results and conclusions

The primary by-products identified were:
- A long chain hydrocarbon (due to -CH3, -CH2-)
- Carbon Dioxide
- Ammonia (from the DUV unit)
- Carbon Mono-oxide

To identify the hydrocarbon released during the decomposition of EBS, a sample of the solid phase was collected on a KBr disc and observed in the FTIR. The hydrocarbon was identified as Heptadecane. Figure 4 — 7 show the concentration profile with time for the various identified gaseous phases.

The effect of moisture in the decomposition of EBS is a simple hydrolysis reaction. The reaction probably occurs on the P/M part surface. This explains the effect of moisture observed in the Phase I of our experiments. The primary gases identified during the decomposition of EBS are carbon dioxide, carbon monoxide, ammonia and a heavy hydrocarbon (hepta-decane). The experiments involved are from a part containing 1% lubricant (EBS) in them. The maximum concentration detected for the various identified gases are listed as follows:

- Carbon Monoxide - 19 ppm
- Carbon dioxide - 350 ppm
- Ammonia - 22 ppm
- Hepta-decane - 850 ppm

Development of sensor to detect the changes in concentration would require the detection of CO₂ and hepta-decane. A typical furnace has a load varying from 150 lb/hr — 1000 lb/hr. The concentrations listed above are for a single part of weight 35 gm. The concentration of gases under industrial conditions should be an order of magnitude higher.
Figure 4: CO concentration with time (min)
Figure 5: CO$_2$ concentration with time (min)
Figure 6: Hydrocarbon concentration (as propane) vs time (min)
Figure 7: Ammonia concentration with time (min)
5.0 **PHASE III**

To control the de-lubrication process a quantitative (not qualitative) understanding and a functional relationship of the process parameters. Such knowledge enables are to predict and control the process on-line. De-lubrication is a combination of two processes:

1. The thermal degradation of the polymer to smaller hydrocarbons.
2. The transfer of the polymer/degraded molecules from the part to the atmosphere.

The kinetics of degradation of any polymer is given by the following equation:

\[
\frac{d\alpha}{dt} = A(1-\alpha)^n \exp\left(-\frac{E}{RT}\right)
\]  

(1)

Where:

- \( \alpha \) = Weight fraction of polymer
- \( A \) = Pre-exponential factor (1/min)
- \( E \) = Activation energy (J/mol)
- \( R \) = Gas Constant \( (8.314 \text{ J/mol K}) \)
- \( T \) = Temperature (K)
- \( n \) = reaction order

The values of \( n \), \( A \) and \( E \) vary with the amount of energy supplied. The energy supplied is directly dependent on the applicable heating rate. If the constants \( n \), \( A \) and \( E \) are known for a heating rate, the process is fully described. However, the additional variables in powder metallurgical applications such as green density, % hydrogen and moisture, make the exact mapping of \( n \), \( A \) and \( E \) with temperature quite complex. To describe the process mathematically with the objective of having a workable model for de-lubrication, we have taken two parallel approaches:

1. Evaluate the average activation energies (E), A and n as described in equation or various conditions during de-lubrication.
2. Formulate an empirical predictive model for the process of de-lubrication, which is empirically based.

5.1 **Theoretical Model Of De-Lubrication**

Experiments on polymers are performed on a Thermo-gravimetric analysis machine (TGA), which determines the weight loss of the lubricant as a function of time / temperature. Thermo-gravimetric analysis can be used to provide information regarding the activation energy and the overall reaction order order [1 - 4]. A typical TGA curve is shown in Figure 1. However, deducing precise
Information on the kinetics of polymer breakdown cannot be obtained from TGA data because the reaction order (n) is not known. Most researchers assumed a first order reaction (n = 1), which remains a good approximation. Mathematical analysis of Equation 1 performed by Kyong Ok Yoo et al. has shown that the plot of \( \ln(\text{Rate of heating}) \) and \( 1/T_{\text{max}} \) should be a straight line. \( T_{\text{max}} \) is the temperature on the curve where the rate of weight loss is the maximum (point of inflection on the TG-curve / \( f^2 \alpha \over f t^2 = 0 \)). The following data can be inferred from the curve of \( 1/T_{\text{max}} \) and \( \ln(\text{Rate of Heating}) \):

\[
\text{Slope} = -\frac{E}{R} \\
\text{Intercept} = \ln(A_0) + \left( \frac{3}{2} \right) \ln(T_{\text{max}}) - \ln \left( \frac{E}{RT} + \frac{1}{2} \right)
\]

### 5.1.1 Experimental Design

To determine the kinetic parameters of de-lubrication during the process of sintering, TGA was performed with samples containing 1% acrawax (EBS). All the samples were compacted to densities ranging from 6.80 — 7.04 gm/cc. Only Fe-0.8%C compacted powders were considered for analysis. Historically, equation (1) has been used in the study for the degradation of pure polymers. The activation energies would vary in a compacted part, compared to that of a pure lubricant, as the presence of metal can alter the reaction kinetics. To have a model, that predicts the breakdown of lubricant in a furnace, necessitates the use of metallic compacts. The compacts had the following dimensions: 1/2 square base and 11/4 height. Experiments were conducted in the presence and absence of moisture.

### 5.1.2 Results and conclusions

The values of \( A_0 \) and \( E \) calculated from the data generated are shown in Table V.

**Table V. \( 'A_0' \) and \( 'E' \) for EBS at the point of inflection**

<table>
<thead>
<tr>
<th>Rate of Heating (^{\circ}\text{C/min})</th>
<th>No Moisture (Nitrogen)</th>
<th>Moisture</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_0 ) (1/min)</td>
<td>( E ) (kJ/mol)</td>
<td>( A_0 ) (1/min)</td>
</tr>
<tr>
<td>10</td>
<td>1.0067</td>
<td>41.229</td>
</tr>
<tr>
<td>20</td>
<td>1.0577</td>
<td>0.9610</td>
</tr>
<tr>
<td>30</td>
<td>1.0929</td>
<td>39.743</td>
</tr>
</tbody>
</table>

Table V clearly shows that there is a slight decrease in the activation energy of
de-lubrication when moisture is added to the system. However, these values of $E$ and $A$ are at the point of inflection ($\frac{f^2 \alpha}{ft^2} = 0$). The drawback of this analysis is the determination of $n$ during degradation. Though the average value of $n$ can be considered equal to unity, the value of $n$ changes as the decomposition changes from the scission of $-\text{CH}_2$ to $-\text{CH}_3$ monomer units to other random units. Moreover, the activation energy determined from this model is the energy at the point of inflection. Realistically, the value of $E$ changes as the mode of scission changes from one monomer unit to another. The change in the values of $n$ and $E$ with time only complicates the mathematical model, as more approximations are made to mathematically solve the problem.

5.2 Empirical Model Of De-Lubrication

The kinetic model explained in the earlier section clearly explains the underlying thermal kinetics. In this section we determine an empirical model for de-lubrication by curve fitting techniques. De-lubrication curves obtained from the experiments in the previous section were analyzed to determine a mathematical function. The de-lubrication curve can be described as shown in equation 14.

$$\alpha = \frac{1}{1 + \left(\frac{t}{t_{\text{max}}}\right)^b}$$

Where,

$\alpha = \frac{W_t}{W_0}$ (Weight fraction at any time $t$)

$W_0$ = Initial weight of the lubricant

$W_t$ = Weight of the lubricant at any time $t$

$t$ = Time

$t_{\text{max}}$ = Time at the point of inflection (Max. slope of the curve)

$b$ = Constant depending on the conditions

The boundary conditions governing the equation are: $t = 0, \alpha = 1$ and $t = \text{infinite}, \alpha = 0$. Table VI summarizes the values of $b$ and $t_{\text{max}}$ for all the experiments.
Table VI. 'b' and 'tmax' for the predicted curves

<table>
<thead>
<tr>
<th>Rate of Heating (°C/min)</th>
<th>No Moisture</th>
<th>Moisture (Low)</th>
<th>Moisture (High)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>b</td>
<td>tmax (secs)</td>
<td>b</td>
</tr>
<tr>
<td>10</td>
<td>20.4</td>
<td>2467</td>
<td>23.6</td>
</tr>
<tr>
<td></td>
<td>20.4</td>
<td>2652</td>
<td>22.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23.5</td>
<td>2705</td>
</tr>
<tr>
<td>20</td>
<td>18.2</td>
<td>1484</td>
<td>29.7</td>
</tr>
<tr>
<td></td>
<td>18.7</td>
<td>1540</td>
<td>31.7</td>
</tr>
<tr>
<td></td>
<td>15.1</td>
<td>1473</td>
<td>32.7</td>
</tr>
<tr>
<td>30</td>
<td>18.6</td>
<td>1123</td>
<td>34.8</td>
</tr>
<tr>
<td></td>
<td>18.7</td>
<td>1161</td>
<td>30.9</td>
</tr>
</tbody>
</table>

The empirical model has only two parameters (b and tmax) and it completely describes the process of de-lubrication. Unlike the theoretical model, where the values of E and n are the average values of the entire process, the parameters in the empirical model can be classified as follows:

- tmax is an intrinsic property of a polymer (equal to the point of inflection in a TGA curve) and is independent on external conditions.
- b is an extrinsic property, which varies on external conditions (Green density, Moisture, Gas flow rate, Alloying elements, Hydrogen, thermal conductivity etc).

This model can be utilized directly in the development of control systems for its simplicity. Once the system conditions are gauged and the value of b determined, the model easily predicts the time required for complete de-lubrication.

5.2.1 Industrial validation of the empirical model

The proposed mathematical model was applied in furnace to see if there was an anomaly in the model. Ten compacts (Figure 7) of different weights were put in a furnace.

Figure 7: Compacts used for the validation of model
All the compacts had 0.5 % lubricant in them. The largest of the sample had a weight of 35 gm and the smallest 24 gm. The furnace conditions are tabulated in Table VII.

**Table VII. Sintering furnace condition**

<table>
<thead>
<tr>
<th>ZONE</th>
<th>TEMP. SET POINT (°F)</th>
<th>FLOW RATE OF GASES (SCFH)</th>
<th>Length (ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Nitrogen</td>
<td>Moisture</td>
</tr>
<tr>
<td><strong>PREHEAT ZONE</strong></td>
<td>Zone 1</td>
<td>950</td>
<td>300</td>
</tr>
<tr>
<td><strong>HIGH HEAT ZONE</strong></td>
<td>Zone 2</td>
<td>1250</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zone 3</td>
<td>1675</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zone 4</td>
<td>2020</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zone 5</td>
<td>2020</td>
<td></td>
</tr>
<tr>
<td><strong>COOLING ZONE</strong></td>
<td>Room temp.</td>
<td>350</td>
<td></td>
</tr>
</tbody>
</table>

The following calculations were performed to estimate the time required for de-lubrication the sample.

Rate of Heating (from the slope of the thermal profile) = 0.30 °F/sec

\[
t_{\text{max}} = 2731.7 \text{ sec}
\]

\[
b = 22 \text{ (From nitrogen through water at room temp.)}
\]

\[
\text{Part1} = 24 \text{ gm (0.5 % lubricant (EBS))}
\]

\[
\text{Part2} = 36 \text{ gm (0.5 % lubricant (EBS))}
\]

\[W_t\] as a function of time was plotted (Figure 8) using equation 2. Ideally the value of \[W_t = 0\] at infinite time (t); the value is however, negligible after 3500 sec.

![Figure 8: Predicted weight of the lubricant Vs time](image)
The model predicted that the parts be put in the furnace for 3500 sec (58.33 min) for complete de-lubrication. The belt speed was determined using the following calculations:

- Length of the Pre-heat zone = 16 ft
- Time required for de-lubrication = 58 min
- Belt speed = 0.27 ft/min
  \[= \text{3.24 inch/min}\]

The parts were put on a plate and heated in the furnace at the required belt speed for a period of 53 min. 5 min were taken to pull the parts from the furnace and for them to cool down. The samples were then re-heated to 600 °C in a TGA machine to study the amount of residual lubricant.

**Results**

The samples from the furnace were put in a TGA machine and reheated at 10 °C/min to 600 °C. The atmosphere was 100 % Nitrogen. Figure 9 shows a close up of the parts. The parts have no stains on them; implying clean burnout.

![Figure 9: Parts after de-lubrication in the furnace; absence of 'C' stains](image)

Figure 10 and Figure 11 are the representative curves for parts with weight 24 gram and 34 gram respectively. The curves clearly show the absence of remnant lubricant in the part.
Part # 1

Rate of Heating: 10 °C/min
Final Temperature: 600 °C

Figure 10: Larger parts re-heated to 600 °C

Part # 4

Figure 11: Smaller parts re-heated to 600 °C
Figure 12 shows the mathematical model in relation to the FTIR analysis performed in section 4. The top graph is a concentration plot with time for all the identified gases, the bottom graph is a weight loss plot of a similar sample (weight and %EBS) predicted by the mathematical model. The value of $b$ used in the model is an average of the all the $b$ values in Table VI. Figure 12 clearly shows that the point of inflection predicted by the model (in this case $\frac{f^2}{ft^2} = 0$ at 2637 sec = 712.5 K). Referring to the FTIR graph, the decomposition of the hydrocarbon (which is the heavier molecule in the system) is maximum at 748 K. The error calculated between predicted and actual observed maxima is 36.

![Experiment E (moisture)](image)

Figure 2: Comparison of the FTIR data and the mathematical model
MATHEMATICAL MODEL APPLIED TO COMMON LUBRICANTS USED IN THE P/M INDUSTRY
OBJECTIVES:

The mathematical model described in Attachment I provided a simple tool to evaluate the time required for the complete de-lubrication. In the meeting held at WPI 12/01/2000, the focus group members expressed the desire to extend the model to other lubricants. It was also decided to test the model for green densities higher than 7.05 gm/cc (max. density used in the previous study). The following lubricants were studied in the last quarter:

Density of the compact: 7.05 gm/cc

Kenolube — 0.8% Asbury 3203 Graphite, 1 %Lubricant
Zinc Sterate — 0.8 % Asbury 3203 Graphite, 1 % Lubricant
Poywax — 0.8% Asbury 3203 Graphite, 1 % Lubricant

Density of the compact: 7.20 gm/cc

Kenolube — 0.5% Asbury 3203 Graphite, 0.5 %Lubricant
Zinc Sterate — 0.5 % Asbury 3203 Graphite, 0.5 % Lubricant
Poywax — 0.5% Asbury 3203 Graphite, 0.5 % Lubricant
Acrawax C — 0.5 % Asbury Graphite, 0.5 % Lubricant

Density of the compact: 7.30 gm/cc

Kenolube — 0.5% Asbury 3203 Graphite, 0.5 %Lubricant
Zinc Sterate — 0.5 % Asbury 3203 Graphite, 0.5 % Lubricant
Poywax — 0.5% Asbury 3203 Graphite, 0.5 % Lubricant
Acrawax C — 0.5 % Asbury Graphite, 0.5 % Lubricant

Experimental Procedure

TGA analysis was performed on the samples at various heating rates. The atmosphere was 100 % Nitrogen. The data collected was analyzed for the values of $T_{max}$ and $b$ for the empirical model and $A_o$ and $E$ for the theoretical model.

Results

Table I lists the values of $A_o$, $E$, $T_{max}$ and $b$ for the various lubricants. Figure 1 - 3 shows the value of $T_{max}$ as a function of heating rate for various lubricants (Same density). Figure 4 - 6 shows the same values for a particular lubricant with increasing green density. These graphs could be utilized to study the variations in $T_{max}$ values (half lubricant burn off ) and their relationship to green density.
Table I. Constants for various different lubricants at green densities

<table>
<thead>
<tr>
<th>Density</th>
<th>E (kJ)</th>
<th>A₀ (1/min)</th>
<th>$T_{\text{max}}$ (K⁻¹) Vs Rate of Heating ($R , ^{0}\text{C/sec}$)</th>
<th>b' Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.05</td>
<td>Kenolube</td>
<td>42.01314</td>
<td>0.06340989</td>
<td>-5053.3 / (ln(R) - 5.2743)</td>
</tr>
<tr>
<td></td>
<td>Polywax</td>
<td>38.74989</td>
<td>0.184151513</td>
<td>-4660.8 / (ln(R) - 4.8698)</td>
</tr>
<tr>
<td></td>
<td>Acrawax</td>
<td>45.98224</td>
<td>1.0067</td>
<td>-5530.7 / (ln(R) - 6.165)</td>
</tr>
<tr>
<td>7.20</td>
<td>Kenolube</td>
<td>41.75</td>
<td>0.042156905</td>
<td>-5021.6 / (ln(R) - 5.1371)</td>
</tr>
<tr>
<td></td>
<td>Polywax</td>
<td>50.668</td>
<td>0.110526076</td>
<td>-6094.3 / (ln(R) - 6.2638)</td>
</tr>
<tr>
<td></td>
<td>Acrawax</td>
<td>41.227</td>
<td>0.076889769</td>
<td>-4958.7 / (ln(R) - 5.2297)</td>
</tr>
<tr>
<td>7.30</td>
<td>Polywax</td>
<td>49.079</td>
<td>0.001189263</td>
<td>-5903.2 / (ln(R) - 5.9879)</td>
</tr>
<tr>
<td></td>
<td>Acrawax</td>
<td>45.451</td>
<td>0.001261249</td>
<td>-5466.8 / (ln(R) - 5.6747)</td>
</tr>
</tbody>
</table>
**Figure 1:** Variation of $T_{\text{max}}$ for different lubricants at green density 7.05 gm/cc

**Figure 2:** Variation of $T_{\text{max}}$ for different lubricants at green density 7.20 gm/cc
**Figure 3:** Variation of $T_{\text{max}}$ for different lubricants at green density 7.30 gm/cc

**Figure 4:** Variation in $T_{\text{max}}$ of Kenolube at various green densities
**Figure 5:** Variation in $T_{\text{max}}$ Polywax at various green densities

**Figure 6:** Variation in $T_{\text{max}}$ of Acrawax at various green densities
CONCLUSIONS:

The empirical model has been shown to work for P/M parts at green densities as high as 7.30 gm/cc. The simplicity of the empirical model is that it consists of only two parameters: $T_{\text{max}}$ and $b$ which, completely describe the process of de-lubrication. Figures 4 — 6 depict the change in $T_{\text{max}}$ (or the delay in the lubricant burn off) at higher green densities. Figure 7 graphically depicts the importance of delay in lubricant burn off with heating rate.

![Graph showing the relationship between Green density, $T_{\text{max}}$ and Rate of heating](image)

Figure 7: The relationship between Green density, $T_{\text{max}}$ and Rate of heating
The value of $T_{\text{max}}$ determines the point where the lubricant has decomposed by half its original weight. This can be clearly seen as follows:

\[ \alpha = \frac{1}{1 + \left( \frac{T}{T_{\text{max}}} \right)^b} \]

In the equation

\[ T = T_{\text{max}} \quad \text{at} \quad \alpha = 0.5 \]

This simple relationship makes it easier to determine the values of $T_{\text{max}}$ for other lubricants and conditions. The value of $b$ on the other hand does not shift the position of the de-lube curve, it only changes the slope of the curve. Figure 8 illustrates this graphically.

**Figure 8:** Variation of $b$ from 10 to 50, variation changes the slope of the curve.

For practical purposes, the value of $b$ can be assumed from 22 — 35, the higher values for higher rates of heating. Ideally, one would require a lubricant with a low value of $b$ (for slow and continuous degradation) and a low value of $T_{\text{max}}$ (so that the lubricant is removed early). Table I quantifies the relationship of $T_{\text{max}}$ with the rate of heating for various green densities. These relationships clearly provide the necessary tool to predict de-lubrication.