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

Report No. 01-2

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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

The project has been completed. The attached Appendices A, B and C are the resultant work products.

Acknowledgements go to the wonderful support of the Focus Group of this project.
Control Strategy for the De-lubrication of P/M Compacts

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ABSTRACT

Lubricants (high molecular weight hydrocarbons) are admixed with powder particles prior to compaction. The direct benefits of lubricant addition are superior powder packing, increased die life and uniform green density. The lubricant admixed during compaction is removed while sintering, through controlled heating and atmospheric conditions. Improper de-lubrication leads to defects such as blistering, sooting, micro-porosity, carbon segregation etc in a sintered part. However, lack of appropriate sensors in the de-lube zone of a sintering furnace has stymied the development of appropriate “closed looped control” systems. The key to quality assurance during processing is to identify/predict the time required for complete lubricant removal. This paper discusses and presents a simple mathematical model to predict the time required for complete de-lubrication. EBS (N,N’-Ethylenebisstearamide or “Acrawax”) has been used as a case study in determining the efficacy of the mathematical model.

INTRODUCTION

During the process of compaction, powder used in P/M parts is subjected to enormous pressures as the powder is compacted in a die to the required green density and shape. The frictional forces during the process of compaction can be categorized as (a) friction
between the powder particles as they flow with increasing pressure, (b) friction between the die wall and the powder as the powder is compacted, (c) frictional forces generated when the compacted part is ejected from the die. The frictional forces between the powder particles deter achievable higher and uniform green density. These disadvantages are alleviated by the use of lubricants during compaction. Lubricants are usually admixed with the metal powder before compaction for better die life and lower ejection pressures. Typical concentrations of added lubricants vary between 0.5 and 1.5 % by weight. However, the lubricant added prior to compaction need to be removed from the part, and this is achieved during sintering. The first zone of a sintering furnace is dedicated to 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 microstructural properties. Proper de-lubrication is an important issue for the following reasons:

- The end temperature of the first zone is normally 550-600 °C. As the part enters the hot zone (temperatures of 1200-1300 °C), it experiences a temperature gradient in a short period of time, which causes the remaining lubricant to expand rapidly and introduce cracks in the part (blistering).
- Improper gas flows and belt speeds can lead to carbon deposition on the part. (Sooting)
- 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. Recent work performed at MPI, has identified the path for the development of ‘Future sensors’ for P/M furnaces. The need of a sensor is evident as there are many different “industry practices” being followed through the P/M industry to ensure complete lubricant removal. The question with sensors is what is (are) the key
parameters, which need to be measured? Control of the process depends on the measuring the critical process parameters.

**PARAMETERS AFFECTING LUBRICANT REMOVAL**

De-Lubrication is the process of thermal decomposition of the higher molecular weight hydrocarbon under controlled conditions. **Heating rate** affects the decomposition kinetics of lubricants. The decomposition of a large chain varies from one polymer to another. Poly-vinyl alcohol decomposes by side chain group elimination; polyacetal requires a reactive atmosphere to break up the molecule chain; paraffin wax decomposes by oxidation, etc. [3]. The differences are due to chemical bonding and the structure of the polymer [4]. DTA analyses carried out by Harb Nayar & George White [5] on EBS (‘Acrawax’) indicate that the breakdown of the lubricant occurs in successive steps of endothermic reactions, followed by an exothermic reaction. Analysis by the authors on the kinetics of decomposition showed that the decomposition of acrawax is a strong function of the heating rate [6]. The most common problem during de-lubrication due to improper **atmospheric conditions** and **gas flow rates** is ‘Sooting’. Sooting is the deposition of carbonaceous material from the lubricant on the part surface. Sooting is also associated with the migration of de-lubrication products into the sintering zone of the furnace, insufficient gas flow and down draughts in the exhaust stacks of the de-lubrication zone[7]. Analysis done by Colllen and Smrasekera has shown the linear dependence of gas velocity on the mass transfer phenomena of the lubricant. As the thermal pyrolysis of the lubricants occurs rapidly, insufficient gas flows lead to a stagnant layer of the lubricant vapor on the part which increase the localized C/H ratio to a value greater than 1. This leads to ‘sooting’ or deposition of C on the surface of the part[7]. The sequence of events that lead to lubricant removal is melting, vapor formation, vapor diffusion through the pores and finally the lubricant vapor being swept away by the gases in the furnace[8]. As the lubricant vaporizes and migrates to the part surface, the presence of oxidizing atmosphere helps in cracking the hydrocarbon molecule. Studies done by Renowden and Pountalet [8] have shown that de-lubrication is mostly unaffected by the use of moisture. Their experiments have shown that hydrogen affects the process of
lubricant breakdown. They concluded that hydrogen breaks down the hydrocarbon by diffusing into the part and at the same time reducing the oxides. However, studies done by George White, Antony Griffo and Harb Nayar [9] on the effect of atmosphere showed that the addition of water vapor with hydrogen had the greatest increase in the efficiency of de-lubrication.

One of the steps in lubricant removal is its diffusion through these internal pores to the surface. **Green density** is an indication of the level of internal porosity in a part. As the pressure for densification is increased, the number of pores on the surface shows a dramatic decrease[4]. Auborn and Joon have also shown that there was an observed delay in the start of de-lubricant at higher green densities[4].

**EMPIRICAL MODEL FOR DE-LUBRICATION**

In this section we develop an empirical model for de-lubrication using curve fitting techniques. A typical de-lubrication curve is obtained by heating a P/M compact (with admixed lubricant) in a TGA machine. TGA records the weight change as a function of Time/Temperature. A typical curve obtained is represented in Figure 1.

![Figure 1](image-url)  
*Figure 1: Typical weight / temperature curve obtained from a TGA machine.*
The loss curve of a typical de-lubrication equation is similar to a sigmoidal function (symmetrical S shaped curve extending to infinity). These curves are typically represented by equation 1 shown below:

\[
F(x) = \frac{(x-d)}{(1+(\frac{y}{c})^e)} + d
\]

Where, ‘c’, ‘d’, and ‘e’ are constants

Experiments were performed on various lubricants (Acrawax, Kenolube, polywax and Zinc Stearate). Extensive data analysis on data obtained from various experiments has showed that this equation can be modified for de-lubrication of P/M compacts by equation 2.

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

Where,

\[\alpha = \frac{W_t}{W_0}\] (Weight fraction at any temperature ‘T’)

\[W_0 = \text{Initial weight of the lubricant}\]

\[W_t = \text{Weight of the lubricant at any temperature ‘T’}\]

\[T = \text{Temperature (K)}\]

\[T_{max} = \text{Temperature (K) at the point of inflection (Maximum slope of the curve in the theoretical model)}\]

\[b = \text{Constant depending on the conditions.}\]

The boundary conditions governing the equation are: \(T = 0, \alpha = 1\) and \(T = \text{infinite}, \alpha = 0\). For practical applications, de-lubrication is assumed to be complete when \(\alpha = 0.03\) (97% of the lubricant is removed from the green part).
Significance of ‘$T_{\text{max}}$’ and ‘$b$’?

$T_{\text{max}}$ or the temperature of inflection is the point on the weight loss curve were the decomposition rate is the maximum or $\frac{\partial^2 \alpha}{\partial t^2} = 0$. In the mathematical model, it represents the point were the weight fraction of the lubricant is 0.5 or 50 % the initial weight. ‘$b$’ signifies the rate of de-lube. The values of $T_{\text{max}}$ and $b$ are illustrated in Figure 2. The values of ‘$T_{\text{max}}$’ and ‘$b$’ increase linearly with the increase in the rate of heating.

![Graph showing the relationship between $\alpha = W/W_0$ and temperature $T$ with $T_{\text{max}}$ and $b$ indicated.]

Figure 2: $T_{\text{max}}$ is represented as the point when the second derivative ($\frac{d^2 \alpha}{dT^2} = 0$) and in the model the point where the weight loss of the lubricant is 50%. ‘$b$’ is the rate of de-lubrication or the slope of the curve. The slope is determined at the point of inflection.

MODEL VERIFICATION

Experiments were performed to test validate the model with laboratory experiments. Table I lists the powder composition and the amount of lubricant used in them. The
dimension of the samples used was " square base X 1 " height. The effective weight of each P/M sample was 35 – 36 gm. The samples were then heated in a TG-131 machine and the weight loss curve determined. The values of \( T_{\text{max}} \) for each experiment was determined at \( \alpha = \frac{W_f}{W_0} = 0.5 \) or when the lubricant is 50 % degraded. The values of \( b \) were determined using the best fit to real values. The values of \( T_{\text{max}} \) and \( b \) were then superimposed on the actual curve to ascertain the deviation from actual data. The values of \( \alpha \) were then determined using the empirical model (Equation 2) by varying the temperature (\( T \) in Equation 2). Figures 3 through 5 show the predicted and actual data generated for each experiment.

Table I: Powder composition with the amount of lubricant

<table>
<thead>
<tr>
<th>Density of the compact: 7.05 gm/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kenolube</td>
</tr>
<tr>
<td>0.8% Asbury 3203 Graphite, 1 %Lubricant</td>
</tr>
<tr>
<td>Acrawax C</td>
</tr>
<tr>
<td>0.8% Asbury 3203 Graphite, 1 % Lubricant</td>
</tr>
<tr>
<td>Polywax</td>
</tr>
<tr>
<td>0.8% Asbury 3203 Graphite, 1 % Lubricant</td>
</tr>
</tbody>
</table>

<table>
<thead>
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<th>Density of the compact: 7.20 gm/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kenolube</td>
</tr>
<tr>
<td>0.5% Asbury 3203 Graphite, 0.5 %Lubricant</td>
</tr>
<tr>
<td>Polywax</td>
</tr>
<tr>
<td>0.5% Asbury 3203 Graphite, 0.5 % Lubricant</td>
</tr>
<tr>
<td>Acrawax C</td>
</tr>
<tr>
<td>0.5% Asbury Graphite, 0.5 % Lubricant</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Density of the compact: 7.30 gm/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kenolube</td>
</tr>
<tr>
<td>0.5% Asbury 3203 Graphite, 0.5 %Lubricant</td>
</tr>
<tr>
<td>Polywax</td>
</tr>
<tr>
<td>0.5% Asbury 3203 Graphite, 0.5 % Lubricant</td>
</tr>
<tr>
<td>Acrawax C</td>
</tr>
<tr>
<td>0.5% Asbury Graphite, 0.5 % Lubricant</td>
</tr>
</tbody>
</table>
Figure 3: Actual (dark) and predicted curve (cross) for Kenolube heated at 30°C/min. ($T_{max} = 537^\circ C$ and $b = 24$).

Figure 4: Actual (dark) and predicted curve (cross) for Polywax heated at 30°C/min. ($T_{max} = 570^\circ C$ and $b = 34$).
Figure 5: Actual (dark) and predicted curve (cross) for Acrawax heated at 30 °C/min. ($T_{\text{max}} = 520$ °C and $b = 34$).

**$T_{\text{max}}$ AND RATE OF HEATING:**

Numerous experiments were performed by varying the heating rate. The values of $T_{\text{max}}$ were obtained at the point were $\alpha = 0.5$. Heating rates were varied from 10 °C/min to 30 °C/min. A straight line plot was obtained between $1/T_{\text{max}}$ and the logarithmic rate of heating. Figures 6 through 8 show a very good correlation between the data considered. Figures 6 through 8 had parts with a density of 7.20 gm/cc.
Figure 6: Plot of $T_{\text{max}}$ versus rate of heating for a part containing Kenolube.

Figure 7: Plot of $T_{\text{max}}$ versus rate of heating for a part containing Acrawax.
Polywax in a part of density 7.20 gm/cc

\[ y = -5903.2x + 5.9879 \]
\[ R^2 = 0.9902 \]

Figure 8: Plot of \( T_{\text{max}} \) versus rate of heating for a part containing Polywax.

‘b’ AND RATE OF HEATING:

Figures 9 through 11 show the variation of ‘b’ with rate of heating. Figure 9 represents the variation of ‘b’ values for Kenolube, Figure 10 for Polywax and Figure 11 for Acrawax respectively.

Figure 9: ‘b’ versus the rate of heating for Kenolube
One can clearly see that there exists a correlation between the values of ‘b’ and the rate of heating, though not as robust as the correlation between the values of $T_{max}$ and the rate of heating. Figure 12 shows the significance of the variation of ‘b’ on the time required for a de-lubrication; it consists of an assumed value of $T_{max} = 570 \degree C$. The values of ‘b’ were
varied to show how it affects the overall time for de-lubrication. Though the values of ‘b’ show a linear relation with the rate of heating, it can be seen from Figure 12 that, ‘b’ greater than 15 has negligible effect in predicting the final de-lubrication temperature. In Figure 12 when \( b = 5 \), \( \alpha = 0.03 \) or 97% lubricant is removed at more than 900 °C. Values of ‘b’ greater than 15 (applicable for most commercial applications), the difference is less than 10 °C, which is well within the errors considered. It is for this reason, that more emphasis has been placed on the relation between \( T_{\text{max}} \) and the rate of heating / green density in the following sections.

![Figure 12: Plot of \( \alpha \) (weight fraction of lubricant in the part) and temperature.](image)

Each plot has a different value of ‘b’, which was varied from 5 to 40 for a fixed \( T_{\text{max}} \) (550 °C). Only very low values of ‘b’ (here \( b = 5 \)) show significant change in the temperature required for 97% removal of lubricant.

**\( T_{\text{MAX}} \) AND GREEN DENSITY:**

Similar empirical relations were obtained for parts with various green densities (7.05 and 7.30 gm/cc). Auborn and Joon have shown that there was an observed delay in the start of de-lubrication at higher green densities[4]. They explained this phenomenon by the result of decreased open porosity. A plot of \( T_{\text{max}} \) and rate of heating was then obtained...
similar to the one used in the previous section. Figures 13 through 15 show the plot of $T_{\text{max}}$ and the rate of heating for three green densities considered.

**Figure 13:** Delay in the $T_{\text{max}}$ (50 % burn-off) of Kenolube for increasing density

**Figure 14:** Delay in the $T_{\text{max}}$ (50 % burn-off) of Polywax for increasing density
MODEL VALIDATION (CASE STUDY WITH ACRAWAX)

In order to test the validity of the empirical model proposed, an independent experiment with the same parameters, powder composition and heating were performed. The authors had analyzed the gases released during the de-lubrication of Acrawax [2]. The data generated during the FTIR (Fourier transform Infrared Spectroscopy) and DUV (Deep Ultraviolet Spectroscopy) were compared to the predicted degradation of Acrawax, based on the empirical model. Figure 16 consists of two graphs, the one on the top shows the identified by-products (a heavy hydrocarbon, carbon dioxide, carbon monoxide and ammonia) on a concentration/temperature curve. The bottom curve is plotted using the empirical model. The weight of the lubricant in the part was 1 % Acrawax, heating rate was 10 °C/min. Figure 15 gives the value of $T_{\text{max}}$ (50 % weight fraction of Acrawax) as 712 K. The value of ‘b’ in the model was assumed to be 24 (From Figure 11). A variation of not more than 5 % was predicted. As can be seen, the comparison of the FTIR and DUV results of de-lubrication with the predicted model is excellent.
Figure 16: Predicted curve (for Acrawax heated at 10 °C/min) versus FTIR / DUV analysis for same experimental conditions
DISCUSSION:

In the model described by Equation 2, $T_{\text{max}}$ is the temperature when the lubricant is 50% removed. There exists a very strong relation between the $T_{\text{max}}$ value and the rate of heating as depicted in Figures 6 through 8. In an industrial furnace, the relation between $T_{\text{max}}$ and the heating rate provides a furnace operator with the knowledge regarding the processing windows for “safe operation”. Figure 17 is a hypothetical furnace profile, representative of the types of profiles observed in commercial sintering furnaces.

![Typical furnace profile](image)

**Figure 17: Typical furnace profile**

In the profile seen above it is evident that the part has been heated to 1650 F ($900^\circ$C) in 45 min at a heating rate of $20^\circ$C/min. Assuming a part having density 7.05 gm/cc containing Acrawax, using Figure 15, the $T_{\text{max}}$ was determined to be 760 K (appox.) or 404 $^\circ$C. Keeping in mind that $T_{\text{max}}$ represents 50% lubricant removal, we can then establish that 97% of the lubricant is removed at 847 K or 452 $^\circ$C by utilizing Equation 2 (using $T_{\text{max}} = 760$ K (Figure 15), $b = 28$ (Figure 11) and $\alpha = 0.03$). The model thus allows
one to determine a “safe” processing window for the temperature control in phase I of the sintering process. Specifically, for the case considered here, the processing window is:

\[
\begin{align*}
\text{Final temperature to which part heated to in de-lube zone} & \quad \rightarrow \quad \text{Temperature at which 97\% of the lubricant is removed} & \quad \rightarrow \quad \text{Temperature range for lubricant to escape from the part} \\
(900\text{ \degree C}) & \quad \rightarrow \quad (452\text{ \degree C}) & \quad \rightarrow \quad 448
\end{align*}
\]

Applying it to the case considered, yields:

\[
\begin{align*}
\text{Final temperature to which part heated to in de-lube zone} & \quad \rightarrow \quad \text{Temperature at which 97\% of the lubricant is removed} & \quad \rightarrow \quad \text{Temperature range for lubricant to escape from the part} \\
(900\text{ \degree C}) & \quad \rightarrow \quad (452\text{ \degree C}) & \quad \rightarrow \quad 448
\end{align*}
\]

If for example, in the case considered, the green part’s density is increased to 7.30 gm/cc, then the \( T_{\text{max}} \) value from Figure 15 is increased to 850 K (454 \text{ \degree C}). Thus 97\% of the lubricant is now removed at 947 K (508 \text{ \degree C}). The “safe” processing becomes narrower than when the part had a density of 7.05 gm/cc. Specifically, the processing window is 900 – 508 = 392 \text{ \degree C}. In industrial furnaces where the length of the de-lubrication zone is finite, the processing window is an important and crucial knowledge base. To highlight the impact on the processing window when the green density is increased from 7.05 to 7.30 gm/cc, it will be useful to convert the temperature difference by the applied heating rate (here 20 \text{ \degree C/min}). This yields

\[
\frac{440 – 392 \text{ \degree C}}{20 \text{ \degree C/min}} = 2.8 \text{ min}
\]

The above illustration points out the value of the model in determining the appropriate processing window for de-lubrication of the green part.

Figure 18 shows a profile of a furnace in the de-lubrication zone given in a Time-Temperature space. Four heating rates 10, 20, 30 and 50 \text{ \degree C/min} are considered.
Figure 18: Schematic of a furnace profile with the concept of $T_{\text{max}}$ and the rates of heating (Example of ‘Acrawax’). For a heating rate of 10 $^\circ$C/min, the time from 97 % lubricant removed to the high heat zone is 50 min. This ‘buffer zone’ reduces drastically to just 9 min if the heating rate is 50 $^\circ$C/min. The safe limit reduces drastically with different rates of heating. Increasing densities (Increases $T_{\text{max}}$ for same heating rate), only reduces the time in the buffer zone.
It can be seen that the time a part stays in a furnace after 97% of the lubricant is burnt reduces drastically once the heating rates are increased. For example, for the 10°C/min heating rate, the time the part resides in the furnace considered before it enters the high heat zone is 50 min, whereas for a heating rate of 50°C/min, the time is reduced to 9 min. Thus increasing the heating rate five times, reduces the time the part spends in the de-lube zone after 97% removal by five. The current example considered is for Acrawax, which degrades much faster compared to Polywax or Zinc Stearate, and the current furnace provides ample opportunity for any remaining lubricant to be removed, before it reaches the sintering zone. For a part with higher green densities, the window of safety would be reduced considerably at higher – moderate heating rates. Though the model does not predict the regimes of sooting or other defects, it provides the safe window of for a furnace operator. The model is based on a very simple geometric part and does not include the effects of surface / volume ratios or the effect of porosity (open) at still higher green densities. It lays down the foundation for further research for the development of “user-friendly-charts” for furnace operators. A chart, typically like the one shown in Figure 14 for various lubricants and green densities would equip an operator with the needed knowledge base to ensure that complete de-lubrication has occurred prior to sintering.

CONCLUSIONS:

An empirical model is developed that describes the weight loss curve of a typical de-lubrication cycle. It is based on two parameters $T_{\text{max}}$, defined as the temperature when the part loses 50% of the lubricant, and ‘b’, defined as the rate of de-lubrication. There exists a very strong correlation between $T_{\text{max}}$ and the rate of heating. The value of ‘b’ does not adversely affect the predicted curve for heating rates typically used in industry. It can be assumed to be a constant. Whereas, $T_{\text{max}}$ was found to increase with an increase in the part density, implying delay in the lubricant burnout at higher green densities. The model was verified and validated by FTIR / DUV analysis. The accuracy is within 5%. The model provides the furnace operator with a knowledge base, and specifically a “safe” operating window to ensure that de-lubrication is complete prior to sintering. The model
needs to be expanded for complex parts to take into account surface/volume ratios. The methodology and the mathematical representation developed lays the foundation for process control of de-lubrication.

To implement a closed loop control system, sensor data is needed which will detect lubricant breakdown and release. Our FTIR and DUV work [2] has enabled us to focus on the kind of sensors needed to measure and report de-lubrication in the furnace. Armed with this knowledge, and with the empirical model presented here, a complete control system for de-lubrication can be achieved.

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REFERENCES

1. Powder Metallurgy Science, Randall M. German


CONTROL OF DE-LUBRICATION UTILIZING A LOGISTIC FUNCTION BASED EMPIRICAL MODEL

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ABSTRACT

Lubricants (high molecular weight hydrocarbons) are admixed with powder particles prior to compaction. The direct benefits of lubricant addition are superior powder packing, increased die life and uniform green density. The lubricant admixed during compaction is removed while sintering through controlled heating and atmospheric conditions. However, the control of the de-lubrication product has uncertain since the appropriate “measures” have been lacking. Incomplete de-lubrication can lead to defects such as carbon segregation, sooting, etc in the finished product. The key to quality assurance during processing is to identify/predict the time required for complete lubricant removal. This paper is divided into two parts, the first part analyses the activation energies for de-lubrication as described by a theoretical model for monomer/polymer degradation. The second part of the paper presents a simple model based on a logistic function to describe lubricant degradation. The model describes the complete process of de-lubrication using two constants. The control model has been tested (verified and validated) for both laboratory and industrial conditions. This model may be incorporated into a sintering furnace control system to ensure complete de-lubrication.

INTRODUCTION

De-lubrication is the first stage in a typical sintering operation where, the lubricant in a compacted part is removed by controlled heating and atmospheric conditions. Previous researchers have shown the effect of various parameters on the kinetics of de-lubrication [1 - 4]. The important parameters, which need to be considered, are heating rate, moisture content, hydrogen and the flow rate of the gases. However, an understanding of this process is complete only when the process is well described by a mathematical function, which incorporates in it, all the parameters involved. To control the de-lubrication process a quantitative (not qualitative) understanding and a functional relationship of the process parameters are needed. Such knowledge enables one 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:
\[ \frac{d\alpha}{dt} = A(1-\alpha)^n \exp\left(-\frac{E}{RT}\right) \]

Where;
- \(\alpha\) = Weight fraction of lubricant in the compact
- \(A\) = Pre-exponential factor (min\(^{-1}\))
- \(E\) = Activation energy (J/mol)
- \(R\) = Gas Constant (8.314 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 at a specific temperature considered, the process is fully described. However, the additional variables in P/M processing 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 (1) or various conditions during de-lubrication.
2. Formulate an empirical predictive model for the process of de-lubrication, which is ‘user friendly’.

These are discussed in the following sections.

**KINETIC STUDY 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 [5 - 8]. A typical TGA curve is shown in Figure 1, where weight as a function of time is plotted. It can be noted here that de-lubrication is complete when the temperature reaches 600 °C. 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 [9]. Mathematical analysis of equation (1) performed by Kyong Ok Yoo et al [10] 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 \(/ \frac{\partial^2 \alpha}{\partial t^2} = 0 \)). Though Yoo’s work [10] was for polymers, we believe that it is applicable to the breakdown of EBS into smaller molecular weight products. The following data can be inferred from the curve of \( 1/T_{\text{max}} \) and \( \ln(\text{Rate of Heating}) \):

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

These values (\( T_{\text{max}} \) w.r.t to heating rate) can be used to determine the time required for complete de-lubrication.

**Determination of \( E, A_0 \) for EBS**

We limited our experiments to the analysis of EBS. 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 used for this study. The compacts had the following dimensions 1/2” square base and 11/4” height. Experiments were conducted in the presence and absence of moisture. Figure 2 – 3 show the plot of \( \ln(\text{Rate of Heating}) \) and \( 1/T_{\text{max}} \) for the two conditions, without moisture and with moisture.

![Graph showing Ln (Heating rate) Vs 1/Tmax for parts de-lubricated in the absence of moisture](image)

**Figure 2:** Ln (Heating rate) Vs 1/Tmax for parts de-lubricated in the absence of moisture
Results

The values of $A_0$ and $E$ calculated from the data of Figures 2 – 3 are shown in Table I.

Table I: Values of $A_0$ and Activation energy ($E$) at the point of inflexion for the de-lubrication of EBS.

<table>
<thead>
<tr>
<th>Rate of Heating ($^{\circ}$C/min)</th>
<th>No Moisture (Nitrogen)</th>
<th>Moisture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_0$ (1/min)</td>
<td>$E$ (kJ/mol)</td>
</tr>
<tr>
<td>10</td>
<td>0.073</td>
<td>56.80</td>
</tr>
<tr>
<td>20</td>
<td>0.057</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.048</td>
<td></td>
</tr>
</tbody>
</table>

Table I clearly shows that there is a slight decrease in the activation energy of de-lubrication when moisture is added to the system. The values of $E$ and $A_0$ are at the point of inflexion ($\frac{\partial^2 \alpha}{\partial t^2} = 0$). The order of reaction $(n)$ varies over the entire range of decomposition. According to Denq et al [11], thermal degradation by zero-order reaction order indicates that the molecular chain breaks by monomer scission at the chain end. Thermal degradation by first-order reaction indicates weight loss by the random scission of the main chain. A second order reaction order would indicate intermolecular transfer and random scission. A zero order reaction $(n=1)$ should be a valid assumption in the case of a monomer (EBS) as the molecular chain has to break in the weakest point in the molecule. EBS breaks down to smaller hydrocarbons, CO$_2$, CO and NH$_3$ [12].

Conclusions

The kinetic model shows that moisture reduces the activation energy required for thermal degradation. The decrease in energy is however negligible ($\cong E = 1.484$ KJ/mol). The same model can be used to determine the effect of alloying elements (Ni, Cu, etc in the compact) on de-lubrication. The drawback of this analysis is the determination of ‘$n$’ during degradation. Though the value of ‘$n$’ can be considered equal to unity, the value of ‘$n$’ changes during the entire cycle. Moreover, the activation energy determined from this model is the energy at the point of inflexion. Realistically, the value of $E$ changes as different energies are required to
break a specific bond. The change in the values of n and E with time only complicates the mathematical model, as more approximations are introduced into the model. In the next section, the value of $T_{\text{max}}$ is used one of the variables in the simple empirical model. The kinetic model work (Figures 2 –3) allows us to evaluate how various processing parameters influence $T_{\text{max}}$. The kinetic model is most valuable in mapping out a viable processing window for optimum sintering of P/M green compacts.

**EMPIRICAL MODEL FOR DE-LUBRICATION**

The kinetic model reviewed in the previous section clearly explains the underlying thermal kinetics. In this section we determine an empirical model for de-lubrication using curve fitting techniques. De-lubrication curves obtained from the experiments in the previous section were analyzed to determine a mathematical function. The data generated from the experiments were analyzed to obtain the best fitting curve. The loss curve of a typical de-lubrication equation is similar to a sigmoidal function (symmetrical S shaped curve extending to infinity). These curves are typically represented by equation 4 shown below:

$$F(x) = \frac{(x - d)}{(1 + (\frac{x}{c})^d)} + d$$  \hspace{2cm} (4)

Where, ‘c’, ‘d’, and ‘e’ are constants

Extensive data analysis on this equation has showed that this equation could be modified for de-lubrication by equation 5.

$$\alpha = \frac{1}{1 + (\frac{T}{T_{\text{max}}})^b}$$  \hspace{2cm} (5)

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’
- $T$ = Temperature (K)
- $T_{\text{max}}$= Temperature (K) at the point of inflection (Max. slope of the curve in the theoretical model)
- $b$ = Constant depending on the conditions.

The boundary conditions governing the equation are: $T = 0$, $\alpha =0$ and $T = \infty$, $\alpha = 1$. For practical applications, de-lubrication is assumed to be complete when $\alpha = 0.03$ (97% of the lubricant is removed form the green part). Figure 4 shows the fit between the predicted curve for a heating rate (here 10°C/min) and an actual TGA curve generated in the lab.
Figure 4: Predicted and actual TGA curve for P/M part admixed with 1 % EBS

The value of $T_{\text{max}}$ was determined from Figure 2. Figure 8 shows the plot of ‘b’ for various atmospheric conditions and the rate of heating.

Figure 8: Plot showing the variation of ‘b’ Vs Rate of heating for P/M parts with 1%EBS

Increasing the heating rate shifts the curve (Weight / Temperature) to the right as shown in Figure 1. Interestingly, as the heating rate is increased, the time for de-lubrication decreases. For example, at a heating rate of 10 °C/min and 30 °C/min, times for de-lubrication are 57 min and 19 min respectively. The assumption here is that the lubricant is removed completely at 600 °C. But in reality, there is a shift in the curve at higher heating rates. The $T_{\text{max}}$ value at 10 °C/min is 444 °C whereas for a heating rate of 30 °C/min it is 550 °C. The time for $\alpha = 0.03$ at 30 °C/min is 21 min, implying that the part has to be in a furnace for an extra 2 min for 97 % removal.
Industrial Validation of the Mathematical Model

The proposed mathematical model was tested in an industrial furnace to see if there was an anomaly in the model. Ten compacts (Figure 9) of different weights were put in a furnace. 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 III.

![Compacts used for the validation of the empirical model in a sintering furnace](image)

Table III: Sintering Furnace Conditions

<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>Zone 1</td>
<td>950</td>
<td>300</td>
<td>COLD</td>
</tr>
<tr>
<td>Zone 2</td>
<td>1250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zone 3</td>
<td>1675</td>
<td>800</td>
<td>-</td>
</tr>
<tr>
<td>Zone 4</td>
<td>2020</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zone 5</td>
<td>2020</td>
<td></td>
<td></td>
</tr>
<tr>
<td>COOLING ZONE</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 = 10 °C/min = 0.167 °C/sec

\[
T_{\text{max}} = 717 \text{ K (From Figure 2)}
\]

\[
b = 30 \text{ (From Figure 8 for nitrogen through water at room temp.)}
\]

\[
Part 1 = 24 \text{ gm (0.5% lubricant (EBS))}
\]

\[
Part 2 = 36 \text{ gm (0.5% lubricant (EBS))}
\]

Temperature \((\alpha = 0.03)\) = \[T_{\text{max}} \left(\frac{1}{\alpha} - 1\right)^{\frac{1}{\tau}} = 805 \text{ K} = 532 \degree C\]

Predicted Time of De-lube = \(532/10 = 53.2 \text{ min}\)

\(W_t\) as a function of time was plotted using equation 5. We terminated the value of \(\alpha\) at 0.03, decreasing the value of \(\alpha\) will lead to increased predicted times in the furnace.
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
- = 3.24 inch/min

The parts were put on a plate, which was connected through a coil. The wire was marked at the length of the de-lube zone. The plate was then put on the sintering furnace belt and heated 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 700 °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 11 shows a close up of the parts. The parts have no stains on them; implying clean burnout.

**Figure 10:** Predicted weight of the lubricant with time

Figure 11: Parts after de-lubrication, showing no stains

Figures 12 – 13 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. The increase in weight shown is due to slight oxidation of the part.
CONCLUSIONS

The empirical model has only two parameters (‘b’ and ‘T_{max}’) and it completely describes the process of de-lubrication. Unlike the kinetic 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:

- ‘T_{max}’ is an intrinsic property of a polymer (equal to the point of inflection in a TGA curve) and is independent on external conditions. T_{max} is the time required when $\alpha = 0.5$ or the time when the weight of the lubricant reduces to 50%.
‘b’ is an extrinsic property, which varies on external conditions (In our experiments moisture and heating rate). The change in the value of ‘b’ could be determined for other parameters by changing the powder composition, atmosphere 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. The variation in the values of these parameters are being determined for varying green densities at the P/M center at Metal Processing Institute at Worcester Polytechnic Institute.

ACKNOWLEDGMENT

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REFERENCES

MECHANISM OF DE-LUBRICATION DURING SINTERING: REACTION KINETICS AND DECOMPOSITION STAGES

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ABSTRACT
Lubricants are used in P/M processing to reduce inter-particle and particle/die friction. However, for complete sintering to occur, it is critical that the lubricant is removed. N,N’-Ethylenebisstearimide (Acrawax) is the most commonly used lubricant in the P/M industry because of its low burnout temperatures (~ 500 – 660 °C) and because it does not give rise to metallic residues. Acrawax is a long chain hydrocarbon with a molecular weight of 540 gm and a melting point of 143 – 150 °C. Though Acrawax is completely removed from the green compacts before 600 °C at industrial heating rates, the exact mechanism of de-lubrication, especially in the presence of moisture, is not understood. In this study, the de-lubrication degradation mechanism and kinetics were studied using high resolution FTIR (Fourier Transform Infrared) and DUV (Dispersive Ultraviolet) absorption spectroscopy. Previous work by Harb Nayar/ George White [1] using FTIR employed low resolution and without UV spectroscopy; product identification was qualitative, and a reaction mechanism for the thermal decomposition of the di-amide was not proposed. In this work, the sequence of de-lubrication is determined in the presence and in the absence of moisture, by complete, quantitative product analysis. This work with a higher resolution FTIR/DUV spectroscopy indicates a sharp increase in the concentration in CO2 above 350 – 370 °C. Aliphatic hydrocarbons were observed at 420 °C. The concentration of CO2 and the hydrocarbon decreased beyond 520 °C. Ammonia was observed at 420 °C in the UV spectra. Hydrolysis of Acrawax, leads to the formation of CO2, aliphatic hydrocarbon(s), NH3 and C2H4. The decomposition of Acrawax in the presence and in the absence of moisture is compared and reaction mechanism posulated. The results are the basis for sensor development for P/M sintering.

INTRODUCTION
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 an important role in the decomposition of lubricants? Is there the possibility to sense the gases released and then control the process? These questions were partly answered by Harb Nayar and George White [1] 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. They also investigated only the thermal decomposition of the pure lubricant, without incorporating it in a metal
compact. 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 work is to identify various gases released during de-lubrication and to identify the mechanism of de-lubrication. The results of this study will aid in the development of future sensors for de-lubrication.

When radiation interacts with gaseous molecules, it can be absorbed by inducing vibration-rotation (IR) and/or electronic (UV-vis) transitions within the molecules. The frequency of absorption band(s) is typical of chemical functionality (e.g; C=O bond in aldehydes, ketones, amides, and carboxylic acids) and, for small molecules, the fine structure can yield unique “fingerprint” information. The extent of absorption is directly proportional to the analyte concentration and the optical path length, making absorption spectroscopy a powerful, non-invasive tool to study chemical process. In this work, gas-phase IR (6000 – 650 cm\(^{-1}\)) and UV-Vis (190 – 500 nm) absorption spectroscopy were employed to fully characterize and quantify the reaction products formed when N,N’ – Ethylenebisstearimide (EBS, Acrawax) compacted with iron powder is thermolyzed under a hydrogen – nitrogen atmosphere in the presence of moisture.

**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 schematic diagram of the furnace is shown in Figure 1. The thermal well above the sample was designed to bring the thermocouple tip as close as possible to the sample. The atmosphere used in all the experiments had a composition of 95% Nitrogen + 5% Hydrogen. The flow rate of the gases was 2 liters/min. To add moisture to the atmosphere, the mixture of nitrogen and hydrogen was passed through a bubbler. The temperature of the bubbler was maintained to the required temperature by heating coils around the bubbler. A schematic of the gas connections are shown in Figure 1. Figure 2 shows the gas flow direction into the furnace.

(Dimesions: \(a = 15\) mm, \(b = 150\) mm, \(c = 6\) mm, \(d = 50\) mm, \(e = 73\) mm, \(f = 38\) mm)

![Figure 1: Schematic diagram of the heating furnace](image-url)
Figure 2: Schematic diagram showing gas flow direction

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 3.

Figure 3: Schematic diagram of the FTIR and DUV spectroscopy experimental setup
The actual experimental setup is shown in Figures 4. The following steps were followed in all the experiments:

- The entire system was purged with dry nitrogen for 15 minutes.
- Background spectra were collected during the entire process to zero the analyzers.
- The atmosphere for the experiment (N2/H2 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 zero-ing process.
- 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 spectra.
- The FTIR cell and the DUV cells were insulated and heated to 1200°C to prevent condensation of moisture on the cell windows.
- Once the background spectra were collected, the sample was heated at 10°C/min to 600°C.
- The optical path lengths were maintained at 5 m for the FTIR and 0.5 m for the DUV.
- FTIR and DUV spectra were collected every 2.5 minutes.
- The flow rate of the gases was maintained at 2 liters/min.

Three experiments were performed for a wet atmosphere and three under dry conditions. The experiments were labeled as follows:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, C and E</td>
<td>Wet</td>
</tr>
<tr>
<td>B, D and F</td>
<td>Dry</td>
</tr>
</tbody>
</table>

Each experiment consisted of 19 spectra and a background spectrum. The spectra obtained were studied to identify the by-products released during the decomposition of EBS. The spectra were analyzed, for the various peaks (product identification) and concentrations (investigation of reaction rate).
RESULTS

Qualitative spectrum analysis

Table I - II lists the wavenumbers, corresponding to expected functional groups along with theoretical values [2].

Table I. Observed wavenumbers and functional groups obtained in the absence of moisture

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Expected Functional Group</th>
<th>Theoretical Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>3085, 3015</td>
<td>Stretch of unsaturated CH</td>
<td>3080 and 3020</td>
</tr>
<tr>
<td>2965, 2863</td>
<td>Stretching of Methyl (-CH₃)</td>
<td>2960 and 2870</td>
</tr>
<tr>
<td>2932, 2855</td>
<td>Stretching of Methylene (-CH₂⁻)</td>
<td>2925 and 2850</td>
</tr>
<tr>
<td>2360</td>
<td>O = C =O</td>
<td>2349</td>
</tr>
<tr>
<td>2149</td>
<td>C = O</td>
<td>2145</td>
</tr>
<tr>
<td>1646</td>
<td>C = C stretch</td>
<td>1640</td>
</tr>
<tr>
<td></td>
<td>Terminal Methylene stretch in R/CH₂ = CH₂</td>
<td>1645</td>
</tr>
<tr>
<td></td>
<td>C = C stretch of terminal Methylene</td>
<td>1655</td>
</tr>
<tr>
<td>1470 - 1458</td>
<td>Methylene and methyl bending</td>
<td>1470 and 1460</td>
</tr>
<tr>
<td>980 - 1000</td>
<td>N-H stretch</td>
<td>1000</td>
</tr>
<tr>
<td>992, 912</td>
<td>Out of plane δCH of terminal vinyl</td>
<td>990 and 910</td>
</tr>
<tr>
<td>966</td>
<td>Out of plane δCH of trans double bond</td>
<td>965</td>
</tr>
<tr>
<td>UV</td>
<td>Ammonia</td>
<td>195 – 220 nm</td>
</tr>
</tbody>
</table>

Table II: Observed wavenumbers and functional groups obtained in the presence of moisture

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Functional Group</th>
<th>Theoretical Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>2967, 2863</td>
<td>Stretching of Methyl (-CH₃)</td>
<td>2960 and 2870</td>
</tr>
<tr>
<td>2933</td>
<td>Stretching of Methylene (=CH₂)</td>
<td>2925 and 2850</td>
</tr>
<tr>
<td>2360</td>
<td>O = C =O</td>
<td>2349</td>
</tr>
<tr>
<td>2149</td>
<td>C = O</td>
<td>2145</td>
</tr>
<tr>
<td>1646</td>
<td>Water Interference</td>
<td></td>
</tr>
<tr>
<td>1470 - 1458</td>
<td>Water Interference</td>
<td></td>
</tr>
<tr>
<td>992, 910</td>
<td>Out of plane δCH of terminal vinyl</td>
<td>990 and 910</td>
</tr>
<tr>
<td>966</td>
<td>Out of plane δCH of trans double bond</td>
<td>965</td>
</tr>
<tr>
<td>798</td>
<td>Rocking of -CH₃ = CH2</td>
<td>780</td>
</tr>
<tr>
<td>744 - 740</td>
<td>Double of (CH₃)ₙ where n &gt; 4, Higher with lower 'n'</td>
<td>725 – 720</td>
</tr>
<tr>
<td>UV</td>
<td>Ammonia</td>
<td>195 – 220 nm</td>
</tr>
</tbody>
</table>

The primary by-products can be readily inferred from Table I and II:

- A long chain hydrocarbon (due to - CH₃, -CH₂-)
- Carbon Dioxide (CO₂)
- Ammonia (NH₃)
- Carbon Mono-oxide (CO)
To identify the hydrocarbon released during the decomposition of EBS, a sample of the solid phase was collected on a potassium bromide optical window and observed by FTIR spectroscopy. The spectrum obtained is shown in Figure 6.

![Figure 6: Spectrum of the solid by-product (hydrocarbon)](image)

This spectrum was compared to the vapor phase spectra from NIST to identify the hydrocarbon. The spectrum closely matched that of heptadecane (C\textsubscript{17}H\textsubscript{36}).

**Quantitative analysis (Concentration of identified products)**

Absorption spectra can be used to determine the concentration of the measured analyte if the optical path length and molecular extinction coefficients (at that wavenumber) are known. Theoretically, the value of the molecular extinction coefficient is a unique function of the component in question, at the frequency for which it is determined. A plot of absorbance and concentration should be a straight line. However, in practice, it is dependent on the instrument imperfection, leading to non-linearity. This is remedied by calibrating the instrument with products of known concentration over the range of concentrations required. Known concentrations of gases are flowed through the instrument’s optical cell and the actual and observed values are compared. All the calibrations were performed using the same operating conditions and gas flow rates. The low concentrations of CO observed in the experiments led to a linear relation in the range of interest. As blended heptadecane gas are not available commercially, the concentration is reported as a ratio of a most readily available hydrocarbon, the concentrations is reported as propane, a more common aliphatic hydrocarbon. Thus a calibration curve using propane was generated. Figures 7 – 10 show the concentration profiles of CO\textsubscript{2}, CO, NH\textsubscript{3} and C\textsubscript{17}H\textsubscript{36} (as propane) when 1% EBS in a compacted part is heated at 10\textdegree C/min The similarity of the spectra of heptadecane and propane is shown in Figure 11.
Figure 7: CO concentration variation as a function of time (min)
Figure 8: CO$_2$ concentration variation as a function of time (min)
Figure 9: Hydrocarbon concentration (as propane) as a function of time (min)
Figure 10: Ammonia concentration as a function of time (min)
CONCLUSIONS

The primary gases identified during the decomposition of EBS are CO₂, CO, NH₃ and a heavy hydrocarbon (most probably C₁₇H₃₆). Figures 8 – 10 show the concentration profile of the various gases identified during the de-lubrication of EBS. The experiments were conducted with a part containing 1% lubricant (EBS). The maximum concentration detected for the various identified gases are listed as follows:

- CO  - 19 ppm
- CO₂ - 350 ppm
- NH₃ - 22 ppm
- HC (as propane) - 850 ppm

Based on the product characterization described above, a reaction mechanism (shown in Figure 13) can be postulated. Hydrolysis of amide group (1) affords heptadeconic acid (2), which decarboxylates to yield heptadecane (4) (b.p. 302 °C) and CO₂. The strong observed C-H stretch is probably due to the presence of (4), which eventually condenses in the sampling system as the concentration increases. Amino-acid (3) also hydrolyzes to (2) and produces another molecule of (4) upon decarboxylation. N,N’ – Ethylenediamine (5) probably constitutes an unidentified UV chromophore; this is currently researched. Ammonia is presumably formed from the diamine. Note that we never observed an amide or carboxylic acid C = O stretch in the IR, which indicates that these molecules decompose in the reactor.

Due to the elevated boiling point, it is not surprising that (4) is always after CO₂, as the hydrocarbon will undoubtedly migrate slowly out of the samples’s pores and through the sampling system to the optical cells. This further corroborates the presence of (4), as did the IR spectrum of the solid condensate on the potassium bromide disk.

Development of sensors to detect the changes in concentration will 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 weighing 35 gm. The concentration of gases under industrial conditions should be an order of magnitude higher.

Figure 13: Schematic representation of the reactions during the decomposition of EBS

REFERENCES

3. Organic Chemistry, David A. Shirley