On the Degradation of Lubricating Grease

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ON THE DEGRADATION OF LUBRICATING GREASE

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Mechanical and Industrial Engineering

by

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August 2016
To my beloved family
ACKNOWLEDGEMENTS

I would like to express my appreciation to my advisor, Prof. Michael M. Khonsari, for his invaluable support and guidance throughout my PhD career. I would also like to thank all my colleagues at the CeRoM laboratory of Louisiana State University for their priceless help. I would also like to thank my committee members, Prof. Guoqiang Li, Prof. Shengmin Guo, Prof. Robert I. Hynes, and Dr. J Y Jang, for their time and kind assistance.
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ABSTRACT

A comprehensive literature review on physical and chemical degradation monitoring and life estimation models for lubricating greases is presented in chapter one. Degradation mechanisms for lubricating grease are categorized and described, and an extensive survey of the available empirical and analytical grease life estimation models including degradation monitoring standards and methods are presented.

In chapter two, irreversible thermodynamic theory is employed to study the mechanical degradation of lubricating grease. A correlation between the mechanical degradation and entropy generation is established and the results are verified experimentally using a rheometer, a journal bearing test rig, and a modified grease worker machine. It is shown that the degradation rate is linearly related to the entropy generation, and that it can be used for estimation of the mechanically degraded grease life.

In chapter three, a model is presented that uses the principles of irreversible thermodynamics to predict the life of a lubricating grease undergoing mechanical shearing action. Here we restrict our attention to operating temperatures far below the initial activation energy needed to initiate chemical degradation or base oil evaporation. Thus, mechanical degradation is the dominant degradation process. The predictions of the model are validated using the experimental results obtained by testing three greases subjected to different shear rates and temperatures.

In chapter four, mechanical life of grease in an elastohydrodynamic (EHL) line contact between two steel rollers is studied. Grease traction curves are measured and reported in different conditions. Three successive lubricating phases of “Fully grease covered rollers”, “Slippage and
“Grease separation” and “Formation of liquid lubricant reservoir” are observed and their behaviors are examined. The traction of the grease is monitored during a long term mechanical degradation process. Our mechanical life prediction model is applied to the lubricating grease at the contact.

In chapter five, chemical degradation is studied from an energy point of view. A theory is introduced based on acquired experimental results, and is verified using a roller tester rig. The theory is used to estimate the chemical life of a grease at different temperatures.

Summary and conclusions are given in Chapter six along with recommendations for future studies.
CHAPTER 1: OVERVIEW AND LITERATURE SURVEY

1.1 Introduction

Grease is a widely used lubricant in many machine elements. In most applications, grease lubrication is cheaper and more convenient than oil lubrication. In fact, more than 90% of all rolling element bearings are grease lubricated. While the life of the grease is shorter than the rolling element bearing’s components, the grease life has remarkable importance in reliable functionality of mechanical equipment.

The lubricating life of a grease is limited by the physical and chemical degradations caused by shear stresses, pressure, age, and low or high temperatures experienced by the grease. Physical degradation includes mechanical degradation (deterioration of thickener structure), increased base oil separation, base oil evaporation, and also increased contamination. Chemical degradation includes additive depletion (mostly antioxidant), base oil and thickener oxidation. Physical and chemical degradations can occur simultaneously. However, generally physical degradations are dominant in low operating temperatures and high speeds while chemical degradations are dominant in high operating temperatures and low speeds.

Physical and chemical characterizations of grease behavior are very complex. It is, thus, no surprise that limited studies have been reported on the degradation and life prediction of grease. The current practices are based on utilizing grease life models developed primarily by the bearing manufacturers. These procedures are obtained empirically from testing of a sufficiently large number of bearings using bearing test machines. These procedures are obtained empirically from testing of a sufficiently large number of bearings using bearing test machines. The main parameters determining the grease life in these tests are the DN (the product of mean bearing diameter in mm
by the rotational speed in rpm) and operating temperature, and the associated results are specific to the operating and geometric conditions tested and cannot be generalized.

In this dissertation, an analytical mechanical life estimation model for lubricant grease is presented that uses the concept of energy/entropy. The model is validated in different working conditions using different test rigs and grease samples. While this model accurately predicts mechanical life of a grease, we seek to develop a chemical degradation model to predict grease life when operating under higher temperatures where chemical degradation is dominant. Chemical degradation is also studied from an energy/entropy point of view.

1.2 Dissertation Outline

This dissertation is presented in six chapters. In each chapter, one aspect of grease degradation is investigated.

In chapter 1, the state of the art is discussed through a literature survey on the important contributions of leading researchers.

In chapter 2, Irreversible thermodynamic theory is employed to study the mechanical degradation of lubricating grease undergoing shearing action.

In chapter 3, the correlation acquired in chapter 2 is used to establish a model to predict the life of a lubricating grease undergoing mechanical shearing action.

In chapter 4, Mechanical life of grease in an EHL line contact between two steel rollers is studied.

In chapter 5, we study the chemical degradation and propose a grease life model for the prediction of grease chemical life.

The final chapter (Chapter 6) summarizes the results presented in the dissertation and suggests topics for the possible future studies.
1.3 Literature survey and summary

The lubricating effectiveness of a grease is limited by both physical and chemical deteriorations caused by shear stresses, pressure, and severity of the operating conditions particularly temperature. Degraded grease becomes inefficient and eventually loses its lubrication capacity such that it can adversely affect the machine performance and functionality. Proper monitoring of degradation and on-schedule replacement/replenishment of grease are important facets of machinery maintenance practices. Presently, grease replacement is performed periodically according to time schedules adapted from empirical models. Although, some empirical relationships for estimating grease life are available, they tend to be restrictive. The drawback of empirical models is associate with limited applicability when the working condition of grease is different from the operating condition of the empirical models. In applications where the bearing element is lubricated and sealed for life, there are quality control standard procedures to measure the grease resistance to different degradation processes.


This chapter presents a review of published works and the authors’ perspective on the present empirical and analytical grease life estimation models including popular grease degradation monitoring methods and a summary of the pertinent contributions on this subject matter based on the available information in the open literature.
The contribution of the published papers are categorized based on different grease degradation mechanisms as mechanical, chemical, base oil evaporation/separation, and contamination. Empirical models usually consider the degradation mechanisms together, thus they come separately. A summary table of all related literatures is presented at the end of this paper.

1.3.1 Empirical Models

Many empirical models to predict the grease life are primarily developed by bearing manufacturers [4], thus they are not readily available in the open literatures. They are normally presented in the bearing manufacturers’ catalogues using a specific bearing size, speed and working temperature. Booser [6] presented a model for estimating grease life by considering the most influential factors such as temperature, grease composition, bearing speed and load. For the effect of temperature, he reported the following empirical logarithmic-reciprocal absolute temperature relation inspired from the Arrhenius equation:

\[
\log L_0 = K_G + \frac{K_T}{273+T}
\]

(1.1)

where \( L_0 \) is the geometric mean grease life without accounting for either speed or load. \( K_T = 2450 \) is the temperature factor developed based on observations that the grease life drops by a factor of 1.5 for each 10 °C temperature rise. \( K_G \) is the life parameter, which depends on the composition of the grease. Comparing the values of \( K_G \) for different greases, Booser chose a typical value of \( K_G = -2.30 \).

To implement the effect of speed on grease life reduction, Booser included two additional terms in Equation (1.1) in terms of a half-life subtraction speed factor \( S_G \) (tabulated for different greases) and a DN factor as shown below:

\[
\log L_0 = -2.30 + \frac{2450}{273+T} - 0.301 S_G - 0.26 \frac{DN}{(DN)_{L}}
\]

(1.2)
where $D$ is the shaft diameter at bearing seat in millimeter, $N$ is speed in rpm, and $(DN)_L$ is the limiting $DN$ value for different ball bearing types (approximately 270,000 for medium cross section ball bearings). Also to account for effect of load, Booser incorporated an additional term as follows:

$$Log L_0 = -2.30 + \frac{2450}{273+T} - 0.301 S_G - 0.26 \frac{DN}{(DN)_L} - 0.18 \frac{NDW}{C^2}$$  \hspace{1cm} (1.3)

where $W$ the radial is load and $C$ is the specific dynamic capacity of the ball bearing ($W$ and $C$ are in Pounds). To simplify Equation (1.3), Booser went on to define a total half-life subtraction speed factor $S = S_G + S_N + S_W$ where $S_N = 0.864 \frac{DN}{(DN)_L}$ and $S_W = 0.61 \frac{NDW}{C^2}$.

This simplified the Equation (1.3) to:

$$Log L_0 = -2.30 + \frac{2450}{273+T} - 0.301$$  \hspace{1cm} (1.4)

Similarly, by considering the effect of temperature, speed, and load on the life of grease, Kawamura et al. [7] also presented two grease life formulas for Urea and lithium soap greases.

Emphasizing the effect of temperature, Booser and Khonsari [8] studied the grease life in different temperature zones. In their model, the life of grease in different temperatures is extrapolated from stable conditions. In high temperatures (above 160°C) where the grease life is limited by oxidation, they suggested using an Arrhenius equation in the form of:

$$Log L = A + \frac{B}{273+T}$$  \hspace{1cm} (1.5)

where $A$ and $B$ are constants. Assuming that the grease life drops in half for 10°C rise in this temperature zone, $B$ is calculated to be 6000 and $A = 10.75$. 

For lower temperatures between 70 to 160°C (warm zone), they assumed that the grease life drops by a factor of 1.5 per 10 °C temperature rise because of base oil evaporation. Their presented formula for predicting the life of grease in the warm zone is very close to Equation (1.1) presented earlier by Booser, where $E=2450$ and $D = -2.6$.

$$\log L = D + \frac{E}{273+T}$$  \hspace{1cm} (1.6)

For normal industrial temperature zone, they suggest using the bearing manufacturer relubrication life period of 40,000 hours. In low temperatures (below 40 °C), considering the effects of grease hardening and high oil viscosity, they estimated the grease life from its life at 40 °C using the change in its base oil viscosity $\nu$:

$$L = L_{40°C} \times \left(\nu/\nu_{40}\right)^2$$  \hspace{1cm} (1.7)

The calculated grease life from Equations (1.5-1.7) needs to be modified by adding correction factors for demanding conditions of high DN operation, centrifugal grease throw-off and outer ring rotation and cage effect as it is described in their paper. Figure 1.1 shows guidelines for bearing re-greasing intervals with mild operating conditions adapted from [9].

1.3.2 Lubricant degradation processes

Grease degradation is categorized into physical and chemical. Physical degradation covers all the physical changes in the grease during usage [5, 10]. This degradation category includes the integral parts of mechanical degradation (breaking of grease thickener’s structure), increased base oil separation, base oil evaporation, and also increased contamination. Chemical degradation covers all the chemical reactions inside the grease that affect grease lubricating life including additive depletion (mostly antioxidant), base oil oxidation and thickener oxidation. Physical
degradation is more sensitive to applied force (shear stress) and velocity (shear rate), and chemical degradation is more sensitive to operating temperature.

Figure 1.1  Guidelines for bearing re-greasing intervals with mild operating conditions [10]

1.3.3  Mechanical degradation

Lubricating grease consists of a lubricant base oil (liquid) and a thickener agent (semi-solid) that keeps the base oil. There are different types of base oil and thickeners, but normally the thickener is a structure of long molecules. Figure 1.2 shows a SEM image of the thickener structure of a fresh lithium-complex grease. The image is obtained after washing out the base oil using a volatile solvent.
Figure 1.2  Soap network of a fresh lithium-complex grease after washing out the base oil

When a grease experiences mechanical shear/force, the structure of its thickener breaks down mechanically. This is a gradual process and is called grease mechanical degradation. Mechanical degradation is the most dominant degradation process in low and medium operating temperatures (between 40°C to 70°C). This range of operating temperature covers many bearings in electro-motors as well as a wide variety of other industrial applications. In addition, at lower temperatures (below 40°C), the grease degradation can be considered to be mechanically dominated [8]. Figure 1.3 shows the broken structure (with shorter and thinner fibers) of the same grease after 15 hours of shearing in a rheometer with a shear rate of 5000 1/s in 25°C.
After breaking the thickener structure, the grease loses its consistency and becomes softer. However, since the broken structure is not able to retain the base oil, the bleeding rate of the grease increases, and as a result the grease becomes dry and hard. Increasing the load and speed accelerates the mechanical degradation. Similarly, low operating temperature can also make the grease harder and more prone to mechanical breakdown. Khonsari and Booser [8] showed empirically that grease experiences a distinctive drop in life in lower temperatures than 40°C which is proportional to the square of the base oil viscosity changes.
1.3.3.1 Mechanical degradation monitoring

There are several methods to monitor mechanical degradation. Scanning electron microscopy can be used to examine the structure of a grease before and after degradation, but it is difficult to measure the degradation quantitatively by this method. The grease sample also should be prepared by washing the base oil with a solvent.

Standard Test Methods for Cone Penetration of Lubricating Grease (ASTM D217) is a popular method to measure grease consistency and can be used as a measure of the grease mechanical degradation. Based on the standard method, a fresh grease should be worked by a grease worker before penetration test. The penetration measured by a rheometer has been also used in [11] as mechanical degradation monitoring parameter.

An important parameter for characterizing the behavior of a grease is the shear stress. Monitoring the variation of shear stress as a function of time in a constant shear rates reveals how a grease softens. Figure 1.4 shows a typical shear stress curve of a grease when it is sheared in a rheometer with a constant shear rate of 2500 1/s and at a constant temperature of 35 °C.

![Shear stress decrease vs. time for a grease during a constant shear rate of 25001/s and at a constant temperature of 35 °C](image)

Figure 1.4 Shear stress decrease vs. time for a grease during a constant shear rate of 25001/s and at a constant temperature of 35 °C
The shear stress decreases until it reaches to its minimum value at $\tau(\infty)$. Different empirical shear stress functions have been presented by researchers [12-14]. In a recent paper [15], the correlation between mechanical degradation and entropy generation introduced in [11] was used to generate an analytical shear stress function. Some of these models are presented in the sections that follow.

1.3.3.2 Mechanical life estimation models

Mechanical degradation is an irreversible process. The mechanical energy is dissipated inside the grease, breaks the structure of the thickener, and generates heat. Since the whole process involves energy transfer and entropy generation, it can be studied from an energy/entropy point of view.

Kuhn developed a model for characterizing the grease mechanical degradation from an energy point of view. By analogy to the solid body wear, he defined an apparent rheological energy density $e_{rheo}^*$ which is the sustainable energy level per volume unit of grease for a certain level of structural degradation. This energy is dissipated by frictional force between the layers of the grease during a shearing process [16]. In a viscometric flow with a controlled shear stress of $\tau = \tau_c = \text{constant}$, he calculated the energy density simply from the product of the shear stress and the strain rate as follows [17]:

$$e_{rheo}(t) = \tau_c \int_0^t \dot{\gamma}(\xi) \, d\xi$$

(1.8)

And in a controlled shear strain (rate) test with the shear rate of $\dot{\gamma} = \dot{\gamma}_c = \text{constant}$, Kuhn calculated the energy density as follows:

$$e_{rheo}(t) = \dot{\gamma}_c \int_0^t \tau(\xi) \, d\xi$$

(1.9)

He used Equations (1.8) and (1.9) to calculate $e_{rheo}^*$. 

11
Kuhn then introduced the following empirical model for shear stress as a function of time [12, 18]:

\[
\tau(t) = \tau_{lim} \cdot \left(\frac{t}{t_{lim}}\right)^{-n} \quad [\text{Pa}]
\]

(1.10)

where \(\tau_{lim}\) is defined as the final nearly constant value of shear stress versus stress time. Since at \(t = 0\) this equation returns a zero value for initial shear stress, he stated that the equation is not defined at \(t = 0\). Using Equation (1.9), Kahn then estimated the energy which is necessary to obtain a limiting shear stress [12, 18]:

\[
e(t) = \tau_{lim} \cdot \left(\frac{1}{1-n+1}\right) \cdot \left(\frac{t}{t_{lim}}\right)^{-n+1} \quad \left[\frac{1}{\text{mm}^2}\right]
\]

(1.11)

Utilizing this concept, he defined a mechanical dissipation function to characterize the structural degradation of grease. Further, considering the irreversibility of the mechanical degradation, Kuhn suggested the application of thermodynamic entropy in the study of mechanical degradation of lubricating grease [19, 20].

Applying the thermodynamic entropy concept, Rezasoltani and Khonsari [11] developed a correlation between mechanical degradation and energy accumulation/entropy generation inside the grease. The correlation was validated experimentally using three different test rigs. They monitored grease consistency as a measure of mechanical degradation during prolonged shear processes at different shear rates and temperatures (up to 45°C) and showed that in the normal industrial temperatures where the mechanical degradation is the dominant degrading process, mechanical degradation depends only on the generated irreversible entropy inside the grease regardless of test conditions (shear rate and temperature). The correlation was used to establish a grease mechanical life prediction model published in their recent paper [15].

1.3.3.3 Shear stress empirical functions
There are several empirical models for modeling the shear stress of grease as a function of time. Some of them are reported here as Kuhn model [12], Czarny model [14], and Bauer model [13] by equations 12, 13, and 14, respectively.

\[
\tau(t) = \tau_\infty \left(\frac{L}{L_{lim}}\right)^{-n} \quad \text{(1.12)}
\]

\[
\tau(t) = \tau_\infty + c \cdot t^m \quad \text{(1.13)}
\]

\[
\tau(t) = [k_1 \cdot (m - 1) \cdot t \cdot \tau_0^{1-m} + (\tau_0 - \tau_\infty)^{1-m}] \cdot \frac{1}{1-m} + \tau_\infty \quad \text{(1.14)}
\]

In above models, \(\tau_0\) is the initial shear stress value at time zero, and \(\tau_\infty\) is the final constant shear stress reached at \(t_\infty\) or \(t_{lim}\). Other parameters \((n, m, \ldots)\) are constants unique to the grease and must be determined experimentally.

1.3.3.4 Shear stress analytical functions:

Spiegel et al. [21] studied the grease softening analytically. They assumed that grease consists of large particles that upon applying a shearing action they tend to break down into smaller spherical particles. They assumed that during revolution each particle is subjected to surface shear twice by its neighboring particles (once in the direction of rotation and once in the opposite direction. see Figure 1.5).

Figure 1.5   Spiegel et al. model [21]
They further assumed that the particle size decreases gradually as a result of the shearing action and that the reduction in particle size will continue until reaching a final value. They concluded that since it is easier to roll the smaller size particles, the grease becomes softer (loses consistency) by particles size reduction. They went on to define \( Z \) as the number of load cycle (rotation of the particles). They related the angular velocity \( \omega \) and frequency of rotation \( f \) of the particles to the shear rate in a shearing action:

\[
\dot{\gamma} = \frac{\omega}{2} = (\pi, f)
\]  \hspace{1cm} (1.15)

Based on their definition for \( Z \), the frequency of rotation \( f \) is equal to the number of load cycle \( Z \). Then for a shearing action with the shear rate of \( \dot{\gamma}(t) \) from \( t = t_b \) to \( t = t_e \) they wrote:

\[
Z = \frac{1}{\pi} \int_{t_b}^{t_e} \dot{\gamma}(t)dt
\]  \hspace{1cm} (1.16)

For a constant shear rate

\[
Z = \frac{\dot{\gamma}(t_e-t_b)}{\pi}
\]  \hspace{1cm} (1.17)

They also assumed a Wohler curve between shear stress and \( Z \):

\[
\ln \tau(t) = f(\ln(Z))
\]  \hspace{1cm} (1.18)

And finally came up with the following equation for calculating the decrease in shear stress:

\[
\tau(t) = \tau_\infty + (\tau_0 - \tau_\infty), e^{\frac{Z}{Z_0}}
\]  \hspace{1cm} (1.19)

where \( Z_0 \) is a reference number of load cycles, \( \tau_\infty \) is the yield stress when \( Z \to \infty \) and \( \tau_0 \) is the yield stress for \( Z = 0 \). The number of load cycles \( Z \) is calculated differently from shear rate for each application. For example, for the standard grease worker (DIN ISO 2137) it is defined as:

\[
Z = \frac{8 \cdot \phi \cdot (\frac{D_m}{d})^2 \cdot H}{\pi \cdot d \cdot i}
\]  \hspace{1cm} (1.20)
where $D_m$ is the diameter of the grease worker plunger disc (0.075 m), $d$ is the diameter of the holes on the disc (0.00635 m), $H$ is the height of the chamber (0.0635 m), $i$ is the number of holes on the disc (51 holes), and $\varnothing$ is a number that defines the non-Newtonian behavior (for Newtonian behavior $\varnothing = 1$).

For the grease flow inside a pipe with length $L$ and diameter $D$ they defined:

$$Z = \frac{8L}{\pi D}$$ (1.21)

Their model can be used for comparing grease mechanical life in different applications such as flow in a pipe versus grease worker, but cannot be used as a general model for grease mechanical life prediction.

A more comprehensive shear stress function was derived by Rezasoltani and Khonsari [15]. Considering a shear process with the shear rate of $\dot{\gamma}(t)$, they defined $\tau^*(t) = \tau(t) - \tau(\infty)$, where $\tau^*(t)$ denotes the shear stress at time $t$. Then, they express the shear stress at time $t+dt$ as:

$$\tau^*(t + dt) = \tau^*(t) - \alpha \frac{\tau^*(t) \dot{\gamma}(t)}{\tau(t)} dt$$ (1.22)

where $dS_g = \frac{\tau^*(t) \dot{\gamma}(t)}{\tau(t)} dt$ is the generated entropy during the small time increment of $dt$, and $\alpha$ was assumed to be a unique parameter for a grease at the testing conditions.

$$\tau^*(t + dt) = \tau^*(t) - \alpha \frac{\tau^*(t) \dot{\gamma}(t)}{\tau(t)} dt$$ (1.23)

After replacing $\frac{\tau^*(t + dt) - \tau^*(t)}{dt}$ by $\dot{\tau}(t)$ which is equal to $\dot{\tau}(t)$, one arrives at the following

$$\dot{\tau}(t) + \frac{\alpha \dot{\gamma}(t)}{\tau(t)} \tau^*(t) = 0$$ (1.24)

$$\dot{\tau}(t) + \frac{\alpha \dot{\gamma}(t)}{\tau(t)} \tau(t) = \frac{\alpha \dot{\gamma}(t)}{\tau(t)} \tau(\infty)$$ (1.25)

$$\dot{\tau}(t) + \frac{\alpha \dot{\gamma}(t)}{\tau(t)} \tau(t) = \beta(t)$$ (1.26)
where \( \beta(t) = \frac{\alpha \dot{\gamma}(t)}{\tau(t)} \cdot \tau(\infty) \).

Equation (1.26) (a first-order, linear ordinary differential equation (ODE)) has a solution in the form of:

\[
\tau(t) = e^{-\int \frac{\alpha \dot{\gamma}(t)}{\tau(t)} \, dt} \left( \int \beta(t) \cdot e^{\int \frac{\alpha \dot{\gamma}(t)}{\tau(t)} \, dt} \, dt + C \right)
\]

where \( \tau(t) \), \( \dot{\gamma}(t) \), and \( T(t) \) are shear stress, shear rate, and temperature as functions of time, respectively. \( \dot{\gamma}(t) \) and \( T(t) \) must be determined experimentally or predicted analytically.

\[
\beta(t) = \frac{\alpha \dot{\gamma}(t)}{\tau(t)} \cdot \tau(\infty)
\]

where \( \tau(\infty) \) is the final constant shear stress and \( \alpha \) and \( C \) are constants. For shearing a grease in constant shear rate and temperature, the equation was simplified to:

\[
\tau(t) = \tau_{\infty} + (\tau_0 - \tau_{\infty}) \cdot e^{-\frac{\alpha \dot{\gamma} t}{\tau}}
\]

which is similar to Equation (1.19) (developed by Spiegel et al. [21]).

1.3.4 Chemical degradation

Chemical degradation of grease is primarily a result of oxidation reactions. Despite the complexity and variations that exist in different types of grease, the process of chemical degradation involves several distinct phases as described next.

- Phase 1: Initiation (Formation of free radicals)
In the first step, the breaking of C-C and H-C bonds, results in the formation of carbon radicals that react with the present oxygen to form oxy-radicals and peroxides. Some of the produced radicals are Peroxy radicals ROO', Alkoxy radicals RO, and the radicals that are produced at higher temperatures when Hydroperoxides (ROOH) is not stable. A complete description of the
radical formation process can be found in [22]. Formation of free radicals happens regardless of the presence of antioxidants. Antioxidant agents do not play any role in this phase [23].

Radical formation:

\[ R'-R'' \rightarrow R'^* + R''^* \]  \quad (1.29)  
\[ R'-H' \rightarrow R'^* + H'^* \]  \quad (1.30)

where the symbols \( R' \) and \( R'' \) denote hydrocarbon side chains of any length and \( H' \) is an attached hydrogen. \( R'^* \) and \( R''^* \) represent free produced hydrocarbon radicals after breaking chemical bonds. \( H'^* \) denotes a free hydrogen radical.

- Phase 2: Antioxidant sacrifice and depletion

Antioxidant agents react to form free radicals according to the following hemolytic cleavage equation. In organic chemistry, a hemolytic cleavage is breaking of the chemical bonds in which the bonding electron pair is split evenly between the products and often produces radicals [24].

After a certain period of time the hydrocarbon radicals in the lubricant consume all the antioxidants according to the following scavenging equations [23]. The symbol \( AO \) denotes any kind of antioxidant agent and \( H \) is an attached hydrogen.

Cleavage of antioxidants \( AO-H \) to form antioxidant radicals:

\[ AO-H \rightarrow AO^* + H^* \]  \quad (1.31)

Scavenging (vanishing) of hydrocarbon radicals after reacting with antioxidant radicals \( AO^* \) and \( H^* \):

\[ AO^* + R'^* \rightarrow AO-R' \]  \quad (1.32)  
\[ H^* + R'^* \rightarrow R'-H \]  \quad (1.33)
The above-mentioned steps (one and two) are normally referred to as the grease primary oxidation phase [23] or induction period [25]. Oxidation inhibitors protect the grease base oil and thickener against radicals. Ito [26] showed that the base oil oxidation, which is accompanied by acidic product formation, begins after antioxidant depletion, and that the acid number increases after antioxidant depletion. The induction period time depends on the initial antioxidant content, and it is a major portion of the whole grease oxidation life. After the induction period, when the base oil oxidation starts, the grease’s chemical composition will start to change gradually.

Although the grease can still lubricate the contact to some extent, its useful chemical life is practically governed by this induction period time. The base oil viscosity will increase because of polymerization reactions, and oxidation insoluble products decrease the lubrication ability. It will be shown in the next section that the induction time is considered as a milestone for grease life estimation. This can be quantitatively measured by different oxidation monitoring methods to estimate the grease chemical stability in high temperatures.

Steps 3 and 4 comprise of a secondary oxidation phase. They include the base oil and thickener oxidation and finally varnish and sludge formation.

- Phase 3: Chain propagation and degenerate chain-branching

Chain propagation involves the interaction of free radicals with molecules of hydrocarbons, and degenerate chain-branching is a process of new radical formation from intermediate products accumulating during the oxidation process [22].

Chain-initiation:

\[ RH + O_2 \rightarrow R^* + HO_2^* \]  \hspace{1cm} (1.34)

\[ 2RH + O_2 \rightarrow 2R^* + H_2O_2 \]  \hspace{1cm} (1.35)
Chain-propagation:

\[ R^* + O_2 \rightarrow RO_2^* \]  \hspace{1cm} (1.36)

\[ RO_2^* + RH \rightarrow ROOH + R^* \]  \hspace{1cm} (1.37)

Degenerate chain-branching:

\[ ROOH \rightarrow RO^* + OH^* \]  \hspace{1cm} (1.38)

- Phase 4: Chain-termination

Chain-termination is the final step of oxidation process. In this step, because of high free radicals’ concentration, they react together based on the following reactions and turn to the following products [22]:

Chain-termination:

\[ R^* + R^* \rightarrow R - R \]  \hspace{1cm} (1.39)

\[ R^* + RO_2^* \rightarrow ROOR \]  \hspace{1cm} (1.40)

\[ RO_2^* + RO_2^* \rightarrow ROH + ROOR + O_2 \]  \hspace{1cm} (1.41)

Low molecular weight (LMW) products and high molecular weight (HMW) products are produced during the secondary oxidation phase. Naldu et al. [27] modeled the process of chemical degradation of a lubricant on a hot metallic surface. They consider the chain of chemical processes which starts with primary oxidation of lubricant and results in production of liquid LMW products. While some of these LMW products as well as the original lubricant evaporate, a portion of them polymerize into liquid HMV products. After a period of time, these HMW products become insoluble and form sludge and varnish type deposits. Varnish and sludge formation is the last step of chemical degradation.
Chemical degradation secondary phases accompany with significant changes in the lubricant properties as it changes the chemical composition of the lubricant and produces some liquid or solid deposits inside the rolling elements. It decreases the volume and lubricating ability of the oil or grease and damage the equipment, often with catastrophic consequences. The chemical degradation process is accelerated by the heat and high temperature caused by decreased lubricating ability and poor lubrication. This is why chemical degradation monitoring of lubricants is quite important in all mechanical equipment.

1.3.4.1 Chemical degradation monitoring methods

Several methods are available for monitoring chemical degradation of grease. Some of the popular methods are PDSC/SDSC calorimetry, Fourier transform infrared spectroscopy (FTIR), Acid number (AN) or Total Acid Number (TAN), and RULER (Linear sweep voltammetry).

- DSC/PDSC/SDSC calorimetry

Differential Scanning Calorimetry (DSC) was developed for comparing the oxidation stabilities of materials that contain oxidation inhibitors such as lubricating oils, edible oils, greases and polymers for quality control and research purposes. The instrument measures the differences between the thermal fluxes through the test sample and a reference sample (typically an empty sample pan) when the two samples are heated or cooled according to a specified procedure. The temperature differences between the test and the reference samples —caused by endothermal or exothermal reactions occurring in the test sample— are proportional to the heat fluxes. DSC is used to measure two types of data: induction times when temperature is constant or induction temperature when temperature is rising.

The induction time can be predicted from induction temperatures by applying the Arrhenius equation and assuming an activation energy of 140 kJ/mol, for a variety of materials
with ±15% error [28]. Pressurized Differential Scanning Calorimetry (PDSC) is a modified version of DSC machine including a high pressure cell. In the PDSC cell, lubricants are exposed to high temperature and oxygen under high pressure. The high gas pressure has two main benefits. First, high-pressure elevates the boiling points and decreases the sample volatility, and second it increases the concentration of the reacting gases. This decreases the test time at the same temperatures and allows the use of lower test temperatures [29]. It also avoids the interaction of the oxygen with the lubricant being controlled by diffusion [23].

Sealed capsule Differential Scanning Calorimetry (SDSC) uses the standard DSC machine with sealed sample pans. A special press is used to seal a lid on the pans after inserting the sample. The benefit of SDSC is the capability of avoiding lubricant evaporation, but the oxidation process can suffer from limited content of oxygen inside the sealed pan. This is why normally a small sample is used in this method. Some researchers use an oxygen purged glove bag during preparation and pressing the sample pans to increase the oxygen content of the capsules. The bag is kept slightly inflated during the sealing process by regulating the oxygen flow rate [30].

Among all the mentioned DSC methods, the PDSC is the most popular approach for testing the thermal stability of lubricating grease. A new oxidation stability test method based on PDSC was tested and presented in 1990 by Rhee [31]. The method was tested in a round robin program with five cooperators using eleven grease samples (six military greases, three commercial greases, one federal specification grease and one NLGI Reference grease). The test was designed to measure an induction time between 10 to 120 minutes in a constant temperature. Three test temperatures of 210°C, 180°C, and 155°C were specified for the test. Depending on the type and thermal stability of the grease, one of the specified test temperatures was selected to keep the induction time between 10 to 120 minutes for all types of grease. Oxygen was purged at the
pressure of 500±25 psig with the rate of 100±10 ml/min during the test. By plotting the induction times in a natural logarithmic vertical axis versus reciprocal related test different temperatures in the horizontal axis Rhee showed that the data points fall on straight lines with almost identical slopes (Figure 1.12). This means that the grease oxidation follows a first order kinetic model (Arrhenius equation). The kinetic model was used to estimate a grease induction time in a different temperature rather than the test temperature [31]. This model was further improved by Rhee in his later papers [32, 33]. The presented method was published as ASTM D5483 [34] in 1993. Since then, updated editions of the standard have been published. The standard is used for research and quality control purposes, but, as stated in the standard, it should not be used to estimate grease life.

- Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy is used to monitor the additive depletion, contaminant build up and base stock degradation in oil lubricants. The lubricant’s components at a molecular level is evaluated by this method. ASTM Practice E 2412-04 describes the standard methodology for the test. To minimize the sample handling issues associated with the high viscosity of in-service oils, an alternative method for the ASTM practice is also presented by Van de voort and Sedman [35] for condition monitoring of in-service lubricants. FTIR method is performed on lubricating grease as well as its extracted base oil or its separated thickener to monitor the changes in the level of the components or additives (antioxidant agents for example) of the grease during chemical degradation. The changes in infrared spectra of the extracted base oil of a grease subjected to chemical oxidation is shown in Figure 1.6 [36]. The horizontal axis in the picture shows different wave numbers each corresponding to a component. The vertical axis shows the “transmittance” stated in percent (%). Formation or depletion of any chemical component is monitored comparing the transmittance level at the component’s associated wave
number. For example, Zone 960 cm\(^{-1}\) to 1020 cm\(^{-1}\), and Zone 650 cm\(^{-1}\) to 690 cm\(^{-1}\) (circumscribed by rectangles denoted by number 3 in Figure 1.6) correspond to ZDDP antioxidant additive. The change in transmittance in these zones shows a decrease in ZDDP antioxidant’s level during the chemical degradation. Zone 1780 cm\(^{-1}\) to 1700 cm\(^{-1}\) (circumscribed by rectangle denoted by number 1 in Figure 1.6) correspond to the EP (extreme pressure) additive which is not affected during the laboratory oxidation test [36].

Figure 1.6  IR spectra of extracted base oil of a grease during chemical degradation [36]

- Acid number (AN) or Total Acid Number (TAN)

Since, as described before, grease oxidation process is accompanied by the acidic product formation, the acidic content measurement can also be used to monitor the chemical degradation of a grease. A titration process is performed to measure the Acid Number (AN) or the total acid number (TAN) based on two available standards methods of ASTM D974 (colorimetric) [37] or
ASTM D 664 (potentiometric) [38] titration. During the titration, the acidic contents available in 15 grams of lubricant’s sample is naturalized by adding potassium hydroxide. The milligrams of required potassium hydroxide is expressed as acid number.

- **RULER (Linear sweep voltammetry)**

  Anti-oxidants are scarified and finally depleted during the chemical degradation. RULER (Linear sweep voltammetry) is a method to measure the anti-oxidants level present in the lubricant. The anti-oxidants are extracted from the lubricant sample by using a solvent, and the extract is subjected to an increasing potential. Since anti-oxidants are electrically conductive, the percentage of them is measured comparing the change in the electrical current to a baseline [39].

  Chemical degradation monitoring is routinely performed in sensitive equipment such as gas turbines. However, in some equipment such as vehicle engines, a time schedule is used for lubricant replacement instead of monitoring the lubricant due to the cost and inconveniences associated with monitoring methods. Thus, a chemical life estimating model can be very helpful in decreasing the cost and time of equipment’s maintenance.

  **1.3.4.2 Kinetic models**

  Kinetic models are used to estimate the induction times for a grease in different temperatures. Induction time is used to compare the oxidation stability of different greases in any temperature, but cannot predict the oxidation life of a grease. Almost all the kinetic models are first order where the reaction rate coefficient is calculated from the Arrhenius law. In a first order reaction, the reaction rate depends on the concentration of only one reactant. Mathematically, this is expressed as:

  \[
  \frac{dc}{dt} = -kc
  \]  

  Solving the above differential equation, we get
\[ C = C_i e^{-kt} \]  

(1.43)

where \( k \) is calculated from Arrhenius equation,

\[ k = k_0 e^{\frac{-E_a}{RT}} \]  

(1.44)

A zero order reaction is also a reaction that its rate does not depend on the concentration of reactants.

The rate equation has been solved for oxidation and evaporation of lubricating oil. Although the equation has not been solved for grease (because of the complexity of grease), examination at the oil models can provide a good insight at least for the oxidation and evaporation of the base oil of grease.

Naidu et al. [27] presented a kinetic model for high-temperature oxidative degradation of lubricant oil operating under the boundary lubrication condition. They used a microoxidation test to study the oxidation of a thin layer of polyolester, trimethylolpropane triheptanoate (TMPTH) oil as a simple reaction. A schematic of the apparatus is shown in Figure 1.7. It consists of a glass tube with a flat bottom and gas inlet and outlet on the top. A small metal cup which is placed at the bottom of the test tube is filled by the sample oil, and the entire unit is immersed in a constant-temperature bath operating in the range between 150°C to 245°C. When the tube is purged by air both the oxidation and evaporation occurs, but the effect of evaporation is studied separately when only nitrogen gas is purged.

The products are then diluted with tetrahydrofuran and analyzed by gel permeation chromatography (GPC). The GPC analysis provides information on the molecular weight/size distribution of the products.
Figure 1.7 Microoxidation test apparatus [27]

Figure 1.8 shows their oxidation model, where “A” represents the original oil, “E” the evaporated original oil (A) in the vapor phase, “B” the LMW (Low Molecular Weight) liquid-phase oxidation products, “F” the evaporated LMW products (B) in the vapor phase, “P” the HMW (High Molecular Weight) liquid-phase condensation polymerization products, and “D” sludge and varnish deposits. The constants $k_1$, $k_2$ and $k_5$ are first order reaction rate constants. The constants $k_3$ and $k_4$ are composite evaporation rate constants. A diagram of the reaction scheme is shown in Figure 1.9.

$$ k_1 \quad k_2 \quad k_3 \quad k_4 \quad k_5 $$

Figure 1.8 Naidu et al. oxidation model [27]
They showed that the rate of evaporations can be assumed to be constant for their experiments. Therefore, according to [27]:

\[
\text{Rate of formation of } B = k_1 M_A \\
\text{Rate of reaction of } B = -k_2 M_B \\
\text{Rate of formation of } P = k_2 M_B \\
\text{Rate of formation of } D = \text{negligible under the test condition (as sludge formation is a very slow process)}
\]

\[
\text{Rate of evaporation of } A = -k_3 \\
\text{Rate of evaporation of } B = -k_4
\]

where \( M_A \) is the mass of the original oil A at any time \( t \) in the liquid form and \( M_B \) is the mass of LMW product B. By defining \( M_{A_0} \) as the mass fraction of the original oil present initially at the start of the test, and dividing all the mass fractions and evaporations rates by \( M_{A_0} \) (\( \bar{M} = \frac{M}{M_{A_0}} \), \( k^* = \frac{k}{M_{A_0}} \)), these following equations are derived based on their oxidation model [27]:

\[
\frac{d\bar{M}_A}{dt} = -k_3^* - k_1 \bar{M}_A
\]

(1.45)
\[
\frac{d\bar{M}_B}{dt} = k_1 \bar{M}_A - k_2 \bar{M}_B - k_4^* 
\]  
(1.46)

\[
\frac{d\bar{M}_P}{dt} = k_2 \bar{M}_B 
\]  
(1.47)

\[
\frac{d\bar{M}_E}{dt} = k_3^* 
\]  
(1.48)

\[
\frac{d\bar{M}_F}{dt} = k_4^* 
\]  
(1.49)

Naidu et al. solved above equations with the initial conditions of:

\[
\bar{M}_B = \bar{M}_P = \bar{M}_E = \bar{M}_F = 0 
\]  
(1.50)

\[
\bar{M}_A = 1 
\]  
(1.51)

And the solutions are:

\[
\bar{M}_A = \left[\frac{k_3^* + 1}{k_1}\right] e^{-k_1 t} - \frac{k_3}{k_1} 
\]  
(1.52)

\[
\bar{M}_B = \left[\frac{k_3^* + k_4^*}{k_2}\right] \left[ e^{-k_2 t} - 1 \right] + \left[\frac{k_3^* + k_4^*}{k_2 - k_1}\right] \left[ e^{-k_1 t} - e^{-k_2 t} \right] 
\]  
(1.53)

\[
\bar{M}_P = \left[ k_3^* + k_4^* \right] \left[ \frac{1-e^{-k_2 t}}{k_2} - t \right] + \left[ \frac{k_2(k_3^* + k_4^*)}{k_2 - k_1}\right] \left[ \frac{1-e^{-k_1 t}}{k_1} - \frac{1-e^{-k_2 t}}{k_2} \right] 
\]  
(1.54)

\[
\bar{M}_E = k_3^* t 
\]  
(1.55)

\[
\bar{M}_F = k_4^* t 
\]  
(1.56)

The mass fraction of original oil remaining (\(M_A\)) and the mass fraction of HMW products (\(\bar{M}_P\)) are determined from GPC analysis of the oxidation products. \(\bar{M}_E\) and \(k_3^*\) are measured from evaporation test. \(\bar{M}_F\) is calculated from mass balance equation. It was shown that in all cases \(k_2\) was at least 100 times larger than \(k_1\) which means the rate of polymerization (HMW production from LMW products) is much higher than the rate of LMW products formation. Therefore, \(\bar{M}_B\) approximately is equal to zero, and Equation (1.54) can be simplified as:
\[ \bar{M}_p = [k_3^* + k_4^*](-t) + \left[ \frac{(k_3^* + k_1)}{k_1} \right] (1 - \exp(k_1 t)) \] (1.57)

Oxidation and evaporation tests were conducted at 150, 185, 200, 225, and 245 °C. Arrhenius plots for \( k_1, k_3^*, \) and \( k_4^* \) are shown in Figure 1.10.

![Arrhenius plots for \( k_1, k_3^*, \) and \( k_4^* \) [27]](image)

where \( k_1 \) is constant for all the temperatures, \( k_3^* \), and \( k_4^* \) change slightly with the temperature.

Comparison between the model prediction and the experimental data is shown in Figure 1.11 for 185 °C [27].

It appears that for the most part, the data expected by the model agrees reasonably well with the experimental data.
The following conclusions can be drawn from Naidu et al. [27] work:

- The first order kinetic model seems to fit well on the oxidation of the lubricant.
- The zero order kinetic model seems to fit well on the evaporation of the base oil and LMW products.
- The mass fraction of the original oil ($M_A$) decreases almost linearly with time from the first moment of the process.
- The mass fraction of evaporated oil ($M_E$) and evaporated LMW products ($M_F$) increase linearly with time from the first moment of the process.
- The mass fraction of HMW products ($M_P$) increases exponentially with time. There is not any HMW product formation for a while at the beginning of the process. It can be
concluded that the oxidation inhibitors’ scarification prevents the polymerization of the radicals in this induction phase.

- Because of the small size of oil sample, the model neglect the effect of oxygen diffusion. However, the oxidation rate can be limited by the oxygen diffusion mechanism in real applications. Therefore, the model underestimates the life of the lubricant in larger size samples.

Gimzewski [28] also used a first order kinetic model (by considering a constant mass fraction for oxygen) to derive an equation that relates induction times and induction temperatures in two different DSC tests (isothermal mode to measure induction times at a constant temperature and scanning mode to measure induction temperatures when temperature is rising with a rate of $\beta = \frac{dT}{dt}$). He considered fully formulated products which include primary oxidation inhibitors — such as hindered phenols or aromatic amines, which remove peroxyl radicals (ROO*)— and secondary oxidation inhibitors — such as zinc dialkyl dithiophosphate, which decompose the autocatalytic hydroperoxides (ROOH)— and assumed that the oxidation rate of a thin film of oil in a DSC experiment is limited by the chain initiation reaction (Equation (1.58)) rate when either type of inhibitor reaches a critically low value.

$$RH + O_2 \rightarrow R^* + HO_2^*$$  \hspace{1cm} (1.58)

The corresponding rate equation for Equation (1.58) is:

$$-\frac{d[RH]}{dt} = [RH][O_2]Aexp\left(-\frac{E_a}{RT}\right)$$  \hspace{1cm} (1.59)

Gimzewski [28] wrote the rate equation for both types of DSC test modes, and by separating the variables and assuming an equal $[RH]_{\text{induction}}$ in both cases, he derived the following
relation to estimate an oxidation induction time for an isothermal run at $T_{iso}$ to the oxidation induction temperature for a scanning run at a heating rate of $\beta$:

$$t_{ind} = \frac{1}{[\exp\left(-\frac{E_a}{RT_{iso}}\right)\beta]} \int_0^{T_{ind}} \exp\left(-\frac{E_a}{RT}\right) dT$$  \hspace{1cm} (1.60)

He assumed an activation energy $E_a$ of 140 kJ/mol and performed tests on 16 lubricating oils, two gasolines and one grease. His analytical results showed agreement with experimental results with less than 15% error. He also measured the activation energy by performing DSC tests in different temperature and using Arrhenius equation for four different oils. All the activation energies fell in the range of 140±30 kJ/mol. Equation (1.60) is used to select the optimum test temperature for a DSC isothermal oxidation test by performing a scanning DSC test. The lubricant will oxidize in a reasonable induction time when the test is performed at the optimum test temperature. Gimzewski’s work is not a life estimation model, but showed that considering an activation energy of 140kJ/mol is a good assumption for most of lubricants.

Rhee [31] also used a first order kinetic model for grease oxidation. He used PDSC to measure the induction time in different temperatures for four different greases and showed an Arrhenius plot of the results (plotting induction times in a natural logarithmic vertical axis versus reciprocal related test temperatures in the horizontal axis). He showed that the results are linear with almost the same slop for all the greases. He showed that the results are linear with almost the same slop for all the greases He showed that the results are linear with almost the same slop for all the greases. He showed that the results are linear with almost the same slop for all the greases. He showed that the results are linear with almost the same slop for all the greases. He showed that the results are linear with almost the same slop for all the greases. He showed that the results are linear with almost the same slop for all the greases. He showed that the results are linear with almost the same slop for all the greases. He showed that the results are linear with almost the same slop for all the greases. He showed that the results are linear with almost the same slop for all the greases. He showed that the results are linear with almost the same slop for all the greases. He showed that the results are linear with almost the same slop for all the greases (Figure 1.12). He concluded that a first order kinetic model fits well on the grease oxidation—because of the linearity—and the activation energy (slope of the lines in Arrhenius plot) is almost independent of the greases type and it is almost 146 kJ/mol.
From Figure 1.12 the induction time can be expressed as:

\[ \ln(t) = \ln(A) + \frac{E}{RT} \] (1.61)

where \(T\) is temperature, \(E\) is the activation energy, \(R\) is gas constant, 8.314 J/mol K, and \(A\) is the oxidation coefficient of grease which is constant and different for any grease. Assuming a value of 146 kJ/mol for activation energy, Equation (1.61) can be simplified to:

\[ t = A \exp\left(\frac{17500}{T}\right) \] (1.62)

The oxidation coefficient for a grease may be calculated by solving the Equation (1.62) for \(A\), using a known induction time.

1.3.4.3 Chemical life estimating models

Despite the existence of rich volumes of published works on the chemical degradation monitoring and kinetic models, a practical chemical life estimating model is still unavailable.

Rhee attempted to utilize his kinetic model to develop a grease life prediction model. In his later work [32], he addressed two limitations of his kinetic model pertaining to limited capability
to predict the induction time due to its inaccurate activation energy determination, and addressing
the need for the capability to estimate the oxidation life of grease in a PDSC test.

To address the first limitation, he suggested measuring two induction times ($t_1$ and $t_2$)
measured at two different temperatures ($T_1$ and $T_2$) and finding the activation energy for any grease
from Equation (1.62):

$$E = R \frac{T_1 T_2}{T_1 - T_2} \ln \left( \frac{t_1}{t_2} \right)$$  (1.63)

To address the second limitation, he developed an empirical relation between the
experimentally-measured, high-temperature grease life and induction time by curve fitting. The
experimental grease life were obtained from testing the grease in an automotive wheel bearing test
drig at 160 °C based on ASTM D 3527 standard test method [40]. The empirical relation is:

Grease High Temperature Life(hr) = 177$t^{0.31}$  (1.64)

Equation (1.64) was tested for ten grease samples. The results are shown in Table 1.1.

Three grease samples’ life (F, H, and I) show a significant difference with the predicted
life by Equation (1.64). It was concluded that these greases have thermal stability problem at tested
temperature which causes excessive oil separation and evaporation, and also because ASTM
D3527 test is a dynamic test, the excessive oil does not remain in the bearing where in PDSC
which is a static test the separated oil is still present. Therefore, Rhee suggested using the model
for the greases with less than 30% oil separation at 180 °C. However, the predicted life for grease
A with 25.9% oil separation still shows a good agreement with ASTM D3527 experimental results.
Note that this model neglects the physical degradation (such as evaporation and mechanical grease
degradation) of grease in a dynamic application such as ASTM D 3527 test. This may explain the
discrepancy since a greases with good chemical stability may still suffer from physical degradation.

Table 1.1 Comparison between actual and predicted grease life using Equation (1.64) [32]

<table>
<thead>
<tr>
<th>Sample</th>
<th>ASTM D 3527 (hr)</th>
<th>Predicted Grease Life (hr)</th>
<th>Oil Separation @ 180 °C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>151</td>
<td>150</td>
<td>25.9</td>
</tr>
<tr>
<td>B</td>
<td>340</td>
<td>368</td>
<td>2.9</td>
</tr>
<tr>
<td>C</td>
<td>400</td>
<td>395</td>
<td>4.4</td>
</tr>
<tr>
<td>D</td>
<td>240</td>
<td>228</td>
<td>13.2</td>
</tr>
<tr>
<td>E</td>
<td>171</td>
<td>191</td>
<td>12.0</td>
</tr>
<tr>
<td>F</td>
<td>100</td>
<td>313</td>
<td>82.3</td>
</tr>
<tr>
<td>G</td>
<td>192</td>
<td>186</td>
<td>12.7</td>
</tr>
<tr>
<td>H</td>
<td>20</td>
<td>200</td>
<td>31.8</td>
</tr>
<tr>
<td>I</td>
<td>40</td>
<td>158</td>
<td>52.9</td>
</tr>
<tr>
<td>J</td>
<td>287</td>
<td>266</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Rhee addressed the oil separation and evaporation in his later work [33] by adding a decomposition model to his kinetic model. He measured the grease weight decrease from base oil evaporation and separation using a modified Thermogravimetric Analyzer (TGA). TGA is normally used to measure the evaporative weight decrease of materials in high temperatures. By punching pinholes on the TGA pan to collect the separated oil, he successfully measured the total evaporative and oil separation weight losses. Rhee considered a first order kinetic model for grease
evaporation and oil separation and, similar to his derivation of the kinetic model, he derived an
equation based on the Arrhenius law. Then, he combined the decomposition model which was
based on TGA with the kinetic model which was based on PDSC imperially and came up with the
following decomposition kinetic model:

\[ t \text{ (hr)} = \left( \frac{E}{k_0 T_0} \ln \frac{1}{120} \right)^{1/6} \alpha \]  \hspace{1cm} (1.65)

where \( \alpha = \frac{t_i}{120} \) and \( t_i \): Induction time in PDSC at test temperature. If \( t_i > 120 \), then \( \alpha = 1 \).

The parameters \( k_0 \) and \( E \) are calculated based on TGA results in two different temperatures.
Rhee subsequently derived the following empirical relation by comparing the new decomposition
kinetic model by ASTM D 3527 results.

Grease High Temperature Life (hr) = 65 \( t^{0.32} \)  \hspace{1cm} (1.66)

Equation (1.66) was also tested for ten grease samples. The results are shown in Table 1.2.
With this new relation, the results are more promising for F, H, and I greases. However, for grease
A the model overestimated life. This new model is empirically-derived and still ignores the
mechanical grease degradation. The linear curve fit to the TGA results based on the assumption of
a first order kinetic model is shown in Figure 1.13. Since the trend of the curve is not completely
linear, the assumption of a first order kinetic model for base oil separation and evaporation may
not very accurate. Since the trend of the curve is not completely linear, the assumption of a first
order kinetic model for base oil separation and evaporation may not very accurate. Naidu et al.
[27] used a zero-order kinetic model for the base oil evaporation. Oil separation/bleeding has been
related to the base oil/thickener combination and kinematic viscosity of the base oil [41] or to the
viscous flow of the base oil through the porous microstructure of the thickener [42].
### Table 1.2 Comparison between Actual Grease Life (ASTM D3527) and Predicted Grease Life using Equation (1.66) [33]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Kinetic life @180°C (hr)</th>
<th>ASTM D3527 (hr)</th>
<th>Predicted grease life (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>19.1</td>
<td>150</td>
<td>167</td>
</tr>
<tr>
<td>B</td>
<td>59</td>
<td>240</td>
<td>240</td>
</tr>
<tr>
<td>C</td>
<td>21.2</td>
<td>170</td>
<td>174</td>
</tr>
<tr>
<td>D</td>
<td>0.02</td>
<td>20</td>
<td>18.6</td>
</tr>
<tr>
<td>E</td>
<td>20.7</td>
<td>196</td>
<td>171</td>
</tr>
<tr>
<td>F</td>
<td>4.6</td>
<td>100</td>
<td>106</td>
</tr>
<tr>
<td>G</td>
<td>30</td>
<td>192</td>
<td>194</td>
</tr>
<tr>
<td>H</td>
<td>7.29</td>
<td>120</td>
<td>123</td>
</tr>
<tr>
<td>I</td>
<td>0.25</td>
<td>40</td>
<td>41</td>
</tr>
<tr>
<td>J</td>
<td>108</td>
<td>275</td>
<td>290</td>
</tr>
</tbody>
</table>

**Figure 1.13**  
linear curve fit to the TGA results based on the assumption of a first order kinetic model [33]
1.3.5 Summary and Conclusions

Figure 1.14 provides a summary of grease life degradation and life prediction. Although this section is a summary of the literatures on grease degradation and life prediction, some papers on grease flow that may include useful related information to the topic of this research are also listed in Figure 1.14.

<table>
<thead>
<tr>
<th>Empirical models</th>
<th>[43], [6], [7], [8], [9], [40], [44], [45]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical Degradation</td>
<td>Mechanical degradation</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Base oil evaporation [50], [48], [41]</td>
</tr>
<tr>
<td></td>
<td>Base oil separation/ Grease leakage [26], [41],[42]</td>
</tr>
<tr>
<td></td>
<td>Contamination [54]</td>
</tr>
<tr>
<td>Chemical Degradation</td>
<td>Monitoring</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kinetic models [23], [27], [28], [31], [62], [33]</td>
</tr>
<tr>
<td></td>
<td>Chemical stability [31, 34]</td>
</tr>
<tr>
<td></td>
<td>Life predicting models [32], [62], [33]</td>
</tr>
<tr>
<td>Grease Flow</td>
<td>Monitoring</td>
</tr>
<tr>
<td></td>
<td>Starvation[54], [63], [64], [65]</td>
</tr>
</tbody>
</table>

Figure 1.14 Summary on the literatures on grease degradation and life prediction

The following conclusions are drawn from the literature review:

- Mechanical and Chemical degradations are important grease degradation mechanisms.
- Mechanical and Chemical degradations are irreversible processes.
- Mechanical degradation can be addressed from an energy/entropy point of view.
- Chemical degradation has been studied applying a first order kinetic model.
• Arrhenius law has been used to calculate the activation energy and reaction rate in the applied first order kinetic model.

• Chemical degradation is controlled by the activation energy provided to grease, and it can be studied from an energy/entropy point of view.

• Mechanical and Chemical degradation occur simultaneously in real applications.

1.4 References


CHAPTER 2: ON THE CORRELATION BETWEEN MECHANICAL DEGRADATION OF LUBRICATING GREASE AND ENTROPY

2.1 Introduction

Lubricating greases are used in daily operation of many vital mechanical components. In fact, more than 90% of all rolling element bearings are grease lubricated. While some greased-lubricated components are sealed for life, many require periodic grease replacement, a process that is expensive and often requires shutting down or disassembling the machine. Therefore, determination of the grease life is an important factor in assessment of the component’s reliable functionality [1]. The current practices are based on utilizing grease life models developed by the bearing manufacturers. These procedures are obtained empirically from testing of a sufficiently large number of bearings using R0F, R2F [2] or FE9 [3] machines. The main parameters determining the grease life in these tests are DN (the product of mean bearing diameter in mm by the rotational speed in rpm) and temperature [1], and the associated results are specific to the operating and geometric conditions tested and cannot be generalized. This research attempts to develop a systematic life model for assessment of grease degradation. As a first step toward this objective, we confine our attention to mechanical degradation only.

Greases experience both chemical and physical degradation during their normal use. Chemical degradation typically occurs because of the oxidation reactions that take place at high temperatures with associated oil evaporation and bleeding [4]. Physical (mechanical) degradation is primarily due to the loss of the base oil or destruction of the thickener structure. The loss of the base oil is either due to the evaporation of the oil at high temperatures or because of the increase in the bleeding rate and oil leakage [5]. Destruction of the thickener structure, on the other hand,
is either due to long-term use of the grease (mechanical breakdown) or chemical breakdown [6]. When operating at normal temperatures, the most important factor for reduction of life is the destruction of thickener structure due to mechanical working of the grease as it is sheared.

Mechanical degradation of grease is an irreversible dissipative process. During the shearing action, the accumulated energy dissipates inside the grease and breaks down the structure of the thickener. To quantify this degradation we refer to the work of Bryant et al. [7], according to which any irreversible degradation can be related to the production of thermodynamic entropy associated with the dissipative processes. This concept has been successfully applied to different degradation processes such as wear and fatigue [8-13].

Presented in this research are experimental methods to quantify the level of mechanical degradation due to structural damages inside the grease, and also to measure the accumulated energy as well as entropy generation. Based on the results of a series of experiments, a correlation between the mechanical degradation of the grease and entropy generation is established.

2.2 Theoretical

2.2.1 Dissipation energy and entropy calculation

Based on the second law of thermodynamics, entropy is generated during an irreversible process. The amount of the generated entropy is calculated by dividing the amount of the produced heat during the irreversible process to the common temperature of the system and surroundings. Since the common temperature may change during the process, the formulation can be written in an infinitesimal form as follow:

\[ dS = \frac{\delta Q}{T} \]  

(2.1)

Also based on the first law of thermodynamics, the change in the internal energy is considered due to a combination of heat added to the system and work done by the system.
\[-W + Q = \Delta U \quad (2.2)\]

Assuming the temperature of a grease sample is maintained constant, the change of internal energy is zero if the grease sample undergoing shear action is considered to be a closed system. Therefore, based on the first law of thermodynamics:

\[-W + Q = 0 \Rightarrow W = Q \quad (2.3)\]

where \(W\) is the work done on the grease sample during the shear process and \(Q\) is the heat transferred from the grease sample to surroundings to maintain the temperature constant. \(W\) is also equal to the accumulated energy that dissipated in the grease sample. Therefore equation (2.1) can be rewritten as:

\[dS = \frac{\delta W}{T} \quad (2.4)\]

\(W\) can be calculated from:

\[W = \int \tau(t) \cdot \dot{\gamma}(t) \cdot dt \quad (2.5)\]

where \(\tau(t)\) is the shear stress, and \(\dot{\gamma}(t)\) is the shear rate. The shear rate is calculated by dividing the linear velocity by the gap between the surfaces. Thus the entropy generated inside the grease, \(S_g\), during the shear process is:

\[S_g = \frac{\int \tau(t) \dot{\gamma}(t) \cdot dt}{T} \quad (2.6)\]

If the shear rate \(\dot{\gamma}(t)\) is constant during the mechanical degradation testing, then Equation (2.6) simplifies to:

\[S_g = \dot{\gamma}(t) \cdot \frac{\int \tau(t) \cdot dt}{T} \quad (2.7)\]

The entropy generation can also be calculated from equation of entropy balance as described in [14].

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2.2.2 Degradation monitoring

Grease penetration value was monitored to measure the amount of degradation. Penetration test is generally done to measure the grease rating using a nine-level grading system established by the National Lubricating Grease Institute (NLGI). The grade of the grease is a measure of its consistency and softness.

The penetration values and specification of different grades are presented in Table 2.1. During prolong shearing process a grease sample tends to degrade to a lower grade. For example, according to these results after 96 hours of shearing in a rheometer with a constant temperature of 25°C and a constant shear rate of 174 1/s, Grease B (Grade 2) degrades to Grease A, which can be classified as Grade 1. This change of the penetration after a shearing process can be considered as a measure of the grease’s structural damage. Penetration test procedure and apparatus will be described in the experimental Section 3.2.2.

Table 2.1 NLGI standard grease grades, and penetration values [15]

<table>
<thead>
<tr>
<th>NLGI Grade</th>
<th>Worked penetration after 60 strokes at 25 °C (0.1 mm)</th>
<th>Appearance</th>
<th>Consistency food analog</th>
</tr>
</thead>
<tbody>
<tr>
<td>000</td>
<td>445-475</td>
<td>fluid</td>
<td>cooking oil</td>
</tr>
<tr>
<td>00</td>
<td>400-430</td>
<td>semi-fluid</td>
<td>applesauce</td>
</tr>
<tr>
<td>0</td>
<td>355-385</td>
<td>very soft</td>
<td>brown mustard</td>
</tr>
<tr>
<td>1</td>
<td>310-340</td>
<td>soft</td>
<td>tomato paste</td>
</tr>
<tr>
<td>2</td>
<td>265-295</td>
<td>&quot;normal&quot; grease</td>
<td>peanut butter</td>
</tr>
<tr>
<td>3</td>
<td>220-250</td>
<td>firm</td>
<td>vegetable shortening</td>
</tr>
<tr>
<td>4</td>
<td>175-205</td>
<td>very firm</td>
<td>frozen yogurt</td>
</tr>
<tr>
<td>5</td>
<td>130-160</td>
<td>hard</td>
<td>smooth pate</td>
</tr>
<tr>
<td>6</td>
<td>85-115</td>
<td>very hard</td>
<td>cheddar cheese</td>
</tr>
</tbody>
</table>
2.3  Experimental

2.3.1  Materials

All the tests were conducted with Grease B whose properties are listed in Table 2.2. Also shown is Grease A, which has the same base oil, but is classified as NLGI Grade 1.

Table 2.2 Properties of the studied materials

<table>
<thead>
<tr>
<th></th>
<th>Mobil grease A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>NLGI Grade</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Thickener Type</td>
<td>Li-Complex</td>
<td>Li-Complex</td>
</tr>
<tr>
<td>Color, Visual</td>
<td>Dark Blue</td>
<td>Dark Blue</td>
</tr>
<tr>
<td>Penetration, Worked, 25º C, ASTM D 217</td>
<td>325</td>
<td>280</td>
</tr>
<tr>
<td>Dropping Point, ºC, ASTM D 2265</td>
<td>280</td>
<td>280</td>
</tr>
<tr>
<td>Viscosity of Oil, ASTM D 445 cSt @ 40º C</td>
<td>220</td>
<td>220</td>
</tr>
</tbody>
</table>

Grease B is a shear-thinning fluid. The measured flow curves of the grease are shown in Figure 2.1.

![Flow curves of Grease B measured in the lab using rheometer](image)

Figure 2.1  Flow curves of Grease B measured in the lab using rheometer
2.3.2 Rheometer

An Anton Paar MCR 301 rheometer was used for shearing the grease as well as the penetration tests. The instrument has the following measurement range: torque 0.1 μN.m to 200 mN.m with 0.001 μN.m resolution and 0.2 μNm accuracy; normal load 0.005 N to 50 N with 0.002 N resolution and ±0.03 N accuracy; and rotational speed of 10⁻⁶ rpm to 3000 rpm. Temperature can be controlled by the Peltier temperature control system that can operate in the range of -40°C up to +200°C with an error of ±0.1°C. The rheometer is equipped with different flat or cone rotating upper plates. The flat Upper plate with the diameter of 24.955 mm was used for all the tests. Two types of experiment were done with the rheometer: long-term shear tests, and penetration tests.

2.3.2.1 Long-term shear test procedure

In the long-term shear tests, the grease sample was sheared in the gap between the rheometer plates. The gap and the temperature were kept constant during the tests. The tests were performed at temperatures varying from 25°C to 45 °C. The temperature range chosen was to avoid condensation of the air humidity in lower temperatures and unfavorable chemical degradation of grease in higher temperatures. The gap was kept constant at 1.5 mm for all the tests. Having the shear stress vs. time curve from the rheometer after the test, the entropy generation is calculated. Since the shear rate was constant in all the shear tests, Equation (2.7) applies.

2.3.2.2 Penetration test procedure

ASTM D217 standard test methods for cone penetration of lubricating grease is the accepted and popular test procedure to perform a penetration test [16]. The penetration tests also can be performed using the same rheometer. This is advantageous because it provides the ability
of conducting the penetration test immediately after finishing the shear test at the same temperature and condition. According to the pre-defined penetration test procedure of the rheometer, the grease sample was squeezed between the plates of the rheometer with a normal force, and the upper plate vertical displacement was plotted versus time. All the penetration tests were done with a normal force of 50 N, a gap of 1.5 mm, and the test time of 60 seconds. The net penetration of the grease was calculated by subtracting the displacement of the upper plate from the initial gap (1.5 mm). In all the penetration tests, the temperature was kept constant at 25°C.

2.4 Correlation between entropy generation and grease degradation

Figure 2.2 shows the net penetration plotted versus accumulated energy and the entropy generation for Grease B subjected to different shear rates and temperatures. The graphs are obtained using experimental data from shear and penetration tests performed by the rheometer. Figure 2.3 shows the lines fitted to the results with a goodness value of approximately $R^2 = 0.94$. Based on the results, the net penetration—which is a measure of degradation of the grease—increases linearly with the energy accumulated in the grease. The same trend exists between the penetration and the generated entropy as given in the following expressions.

$$\Delta = 0.014 \varepsilon + 0.069$$  \hspace{1cm} (2.8)

$$\Delta = 4.162 S_g + 0.071$$  \hspace{1cm} (2.9)

where $\Delta$ is the net penetration, $\varepsilon$ is the accumulated energy, and $S_g$ is the generated entropy. Under the condition tested, this linear correlation remains valid regardless of the applied shear rate or the grease temperature. Thus if the rate of energy accumulation, or entropy generation is available, the expected time for the mechanical grease degradation can be calculated from the Equations (2.8) or (2.9).
Note that Equations (2.8) and (2.9) are unique for Grease B and can be considered to be the mechanical degradation characteristic lines of the grease. The slope of the characteristic lines shows the durability of a grease and can be assumed as the associated “degradation coefficient” due to shearing. A grease with a smaller degradation coefficient last longer. The y-intercept of the characteristic lines shows the initial net penetration value of fresh Grease B, and it is canceled out in the calculation of the grease life when only the change of net penetration is considered.

Figure 2.2 Accumulated energy and entropy generation vs. net penetration for Grease B in different shear rates and temperatures

Figure 2.3 Curve-fitted lines to the results of Figure 2.2
Before we proceed to validating the results, it is worthwhile to point out that degradation rate can be viewed as an essential consequence of the degradation entropy generation (DEG) theorem proposed by Bryant et al. [6]. It defines a relationship between the degradation rate and entropy generation. An application of this theorem to adhesive wear and its relationship to Archard’s law with experimental verification is described in [11,12][17].

2.5 Validation Tests

Two different rigs were used to validate the theory. They were: a journal bearing rig and a modified automatic grease worker machine.

2.5.1 First validation: Journal bearing test apparatus

Figure 2.4 shows a picture of a journal bearing test apparatus used for shearing the grease and measuring the accumulated energy. The rig consists of a rotating shaft which is supported by two roller bearings and is rotated by an electrical motor. A journal bearing with a clearance of 2 mm is attached to the end of the shaft. The gap of the journal bearing was filled with the grease sample, and the shaft was rotated in a constant angular speed. Using a feeler gauge, the journal was centered in the bearing before filling the gap to ensure that the gap is uniform around the journal, so that under no load, the grease is evenly distributed around the circumference to prevent any contact between journal and bearing. An accurate torque meter with the capacity of 15 N.m (combined error of ± 0.25% and non-repeatability of ± 0.05%) was used to measure the required torque associated with shearing the grease sample. The accumulated energy was then calculated by integrating the product of the measured torque and the rotational speed over the time. The grease temperature was measured by a thermocouple inserted very close to the grease sample in a hole drilled on the casing of the journal bearing. The rig was operated at the room temperature (23°C) and no temperature control system was used for the grease.
The test procedure is as follows. After calibrating the load cell and centering the journal in the bearing, the machine was run without the grease sample to measure the friction torque resulting from the operation of the machine. The measured operational torque is different for each rotational speed, and should be measured and subtracted from the grease test results for each rotational speed. The gap of the journal bearing was filled with the grease sample, and the extra grease was removed from the sides. Experiments were performed at different time intervals at the desired rotational speed, and the torque was measured as a function of time. A penetration test was performed after each time interval to monitor the mechanical degradation of the grease during the test. The accumulated energy imparted onto by the grease during the time testing-interval was calculated by the integrating the product of the rotational speed and the net torque during the time interval. At the end of the interval, a small sample of the grease was extracted from the machine for use in the
rheometer for the penetration test. After the penetration test, sample was inserted back into
clearance of the journal bearing, and the rig was run for the next time interval with the same
rotational speed. The process was repeated for several time intervals and at the end of each time
interval, the sum of the calculated accumulated energy for the interval and all the other calculated
accumulated energy for the previous intervals was considered to be the total accumulated energy
up to the end of the interval. Having determined the total accumulated energy and net penetration
values for each time interval, the net penetration vs. accumulated energy curve were plotted for
the selected rotational speed. The net penetration vs. entropy generation curve is also plotted by
dividing the accumulated energy values by the temperature of the grease sample.

Figure 2.5 shows the results where the triangle and square points correspond to rotational
speeds of 203 rpm and 506 rpm at 23°C, respectively. The solid lines in the pictures show the
characteristic lines of the grease. Although the results are close to the characteristic lines
(especially for the initial points), some features are noticeable about the machine. As mentioned
in the previous section, the machine had to be shut down several times during the test to extract
some grease samples for penetration tests. This requires that the gap of the journal bearing should
be large enough to include required amount of grease sample. This requires that the gap of the
journal bearing should be large enough to include required amount of grease sample. However, a
large clearance (2 mm in our test rig) causes low shear rate. As a result of having a low shear rate,
the rate of grease degradation is fairly small. Therefore, the test was run for several weeks to obtain
the results presented. The shear rate can be improved by increasing the rotational speed. However,
in this particular rig at higher speeds the grease tends to separate from the journal, and the first
layer of grease begins to slide on the journal. The same phenomenon also occurs when the grease
consistency drops to a low value due to the degradation of the grease. This explains why the last few points in Figure 2.5 have less agreement with the theory.

Figure 2.5 Results of the journal bearing test rig vs. the obtained linear correlation

2.5.2 Second validation: Modified grease worker machine

An automatic grease-worker machine was instrumented with a sensor and a computerized data acquisition system to measure the accumulated energy as the grease is “worked on” by a plunger. The modification of the grease worker rig involved retrofitting the original cups and plungers with a transparent grease cup and adding a new reciprocating mechanism that has a shorter stroke than the original to have room for installing a load cell below the grease cup. The new cup was made of plexiglass with the internal diameter of 40 mm and 50 mm depth. The plunger is a flat 5 mm-thick metal disc with the outer diameter of 38 mm that has 8 evenly-distributed, 8-mm radial holes on a 26-mm diameter around the center. The cup and the plunger are shown in Figure 2.6. When the grease worker is turned on, the plunger travels up and down in
the grease sample in the cup and forces the entire grease sample to pass through the holes in the plunger. A load cell made by Interface (type SM-50N) with the capacity of 50 N, nonlinearity of ± 0.03, hysteresis of ± 0.02, and non-repeatability of ± 0.01 was used to measure the applied force as a function of time.

The output of the load cell is force versus time which is periodic and has the same frequency as that of the reciprocating plunger. The sign of the force changes, of course, between tension and compression half cycles, and the average amplitude of the force became zero after subtracting the weight of the grease sample and the cup to calibrate the system. Note that the frictional force between the reciprocating rod and the cup’s lid seal was measured and found to be quite low in presence of grease and therefore was neglected.

Figure 2.6  Grease cup and plunger
The test procedure is as follows. The cup was filled with the grease sample, and the load cell was calibrated to measure zero force at stationery condition of the machine. The machine was turned on and the force which is a periodic curve with decreasing amplitude was measured. The accumulated energy for each half cycle of the curve is equal to the work been done on the grease in one stroke of the plunger. The work is the product of the average force and the plunger displacement or stroke length. Since the displacement of the plunger is the same for all the cycles, the total accumulated energy is the product of the plunger displacement and the summation of all the average forces. The entropy generation was also calculated by dividing the accumulated energy by the measured temperature of the grease sample. During the test, the machine was shut down several times and a small sample of the grease was extracted from the cup for use in the rheometer for penetration tests. The extracted sample was returned to the cup after each penetration test. The net penetration curves vs. accumulated energy and entropy generation were drawn based on the tests results.

Figure 2.7 shows the results of modified grease worker rig. The temperature of the grease sample was about 24°C. The grease worker worked at its nominal constant speed for all the tests. The penetration test was done for each point on the charts of Figure 2.7. The results show good agreement with the grease characteristic lines obtained from rheometer results. Figure 2.7 shows the results of modified grease worker rig. The temperature of the grease sample was about 24°C. The grease worker worked at its nominal constant speed for all the tests. The penetration test was done for each point on the charts of Figure 2.7. The results show good agreement with the grease characteristic lines obtained from rheometer results.
Figure 2.7  Results of the modified grease worker test rig vs. the obtained linear correlation

2.6 Conclusions

The following conclusions can be drawn based on the results of this investigation.

- The dissipated energy as a result of shearing of a grease breaks down the structure of the grease thickener and results in heat and entropy generation. The generated heat flows to the surrounding by heat transfer processes to keep the grease temperature constant.

- Based on the experimental results obtained for Grease B, a strong linear correlation is found to exist between the rates of entropy generation and mechanical degradation and also between the rates of energy dissipation and mechanical degradation. However, the correlation between entropy and degradation is thermodynamically and physically more consistent and lends itself to the determination of the degradation coefficient as a constant material property for the studied grease.
The application of the principle of irreversible thermodynamics provides a promising tool for analyzing mechanical degradation of grease in a shear process.

Having the degradation coefficient for a given grease in practice, one can estimate the grease mechanical life prediction by defining a threshold of consistency as the grease failure for the grease in a specific application by measuring or calculating the entropy generation rate in the application.

Further research is needed on the entropy generation rate changes vs. time to establish a scientific base for developing a reliable model for mechanical degradation of grease that affects its performance. Extension of the work to include chemical degradation is also necessary for complete understanding the nature of grease life.

2.7 References


CHAPTER 3: AN ANALYTICAL MODEL FOR LIFE PREDICTION OF LUBRICATING GREASE SUBJECT TO MECHANICAL DEGRADATION

3.1 Introduction

Estimation of grease life is essential for determining the lubricant suitability for specified operating conditions and for predicting re-lubrication intervals in a bearing. Currently, only empirically-based models—developed primarily by bearing manufacturers—are available for estimation of grease life [1]. A good summary of the state-of-the-art on the available empirical models is presented by Lugt [1]. The non-empirical models mostly pertain to chemical models that predict the thermal oxidation life of the grease based on antioxidant depletion time using different approaches such as the FTIR techniques [2, 3], application of the Arrhenius activation energy law using PDSC [4], and thermogravimetric analysis [5]. Chemical models are applicable in high temperature applications where chemical degradation is dominant. In low and moderate temperatures, however, mechanical degradation may prevail and must be properly taken into consideration.

In a grease with a low mechanical stability, the life of the grease is affected by Mechanical degradation. A summary of importance and effectiveness of different mechanical stability tests has been presented by Lundberg and Höglund [6]. Mechanical degradation of grease has been studied from an energy point of view. By analogy to the model of solid body wear, Kuhn defined an apparent rheological frictional energy density as a sustainable energy level for a certain extent of structural degradation, and used it to define a linear intensity for the structure degradation called Mechanical dissipation function [7]. Considering the irreversibility of the mechanical degradation,
Kuhn suggested the application of thermodynamic entropy in the study of mechanical degradation of lubricating grease [8, 9].

In a recent paper [10], the principle of irreversible thermodynamics [11] was successfully applied to the mechanical degradation of grease. This type of a treatment has been applied to different degradation processes such as wear and fatigue [12-17]. According to the degradation entropy generation theory [11] any irreversible degradation associated with dissipative processes can be related to the thermodynamic entropy generation. The results revealed the existence of a linear correlation between the changes in the net penetration of the grease (caused by mechanical degradation under shear stresses) and the production of thermodynamic entropy in the volume unit of the grease. This was identified as the grease characteristic line [10]. It was shown that, in the absence of high temperatures responsible for initiating chemical degradation, this linear correlation remains valid regardless of the applied shear rate. Based on [10] any grease has its own characteristic line and the slope of the characteristic line —called “degradation coefficient”— can be measured and reported as a mechanical property of the grease. A grease with smaller degradation coefficient is expected to have a longer service life under mechanical shear.

In this chapter we explore how the concept of degradation coefficient can be used to quantify the mechanical life of a grease.

3.2 Theoretical

3.2.1 Mechanical Degradation

A lubricating grease consists of a base oil for lubrication, and a thickener which is responsible for containing the base oil in the contact. A thickener possesses a microscopic mechanical structure. This structure can be seen using a Scanning Electron Microscope (SEM)
Figure 3.1 shows an SEM image of thickener’s structure of a fresh sample of Grease B with Li-Complex soap thickener.

![SEM images of Grease B soap network after washing out the base oil with a volatile solvent (Right and left pictures have taken with magnifications of 25000 X and 15000 X, respectively)](image)

Figure 3.1 SEM images of Grease B soap network after washing out the base oil with a volatile solvent (Right and left pictures have taken with magnifications of 25000 X and 15000 X, respectively)

As shown in Figure 3.1, the structure consists of many particles that take on the shape of long tangled-ropes. Similar to any other mechanical structure, the thickener’s structure is prone to gradual break down under load and stress. Figure 3.2 shows the SEM image of the same grease after 15 hours of shearing at the rate of 5000 1/s at 25° C in a rheometer.

Also described by other researchers [1, 17], mechanical degradation is a physical process that destroys the thickener structure and decreases the grease consistency. As a result, during long term applications, the grease leakage and bleeding rate tend to increase, thus reducing the lubricating effectiveness of the grease [18]. A grease can also suffer from other types of degradations such as base oil evaporation and chemical degradation which accelerate dramatically with temperature rise and become dominant in higher temperatures.
Figure 3.2 SEM images of Grease B soap network after 15 hour shearing with a shear rate of 5000 1/s in 25°C (Right and left pictures have taken with magnifications of 25000 X and 15000 X respectively)

However, in the temperature range tested in this study (between 25°C to 45°C), the greases tested are chemically stable, and mechanical degradation is considered to be the most dominant degradation mode.

3.2.2 Mechanical degradation and entropy generation

The performance of a grease tends to degrade when subjected to mechanical shearing action after a prolong length of time. Here we restrict our attention to operating temperatures far below the initial activation energy needed to initiate chemical degradations, so that the grease is assumed to be subjected to mechanical degradation only.

Research shows that mechanical degradation is related linearly to the entropy generation inside the grease during the shearing process [10]. At moderate temperatures, this linear correlation remains valid regardless of the applied shear rate and can be measured and reported as a
mechanical property of the grease. The general form of the mechanical degradation coefficient characteristic line is

\[ \Delta = m S_g + b \]  \tag{3.1} 

where \( \Delta \) is the net penetration and \( S_g \) is the generated entropy. Parameters \( m \) and \( b \) are unique for each grease. For example for Grease B, \( m=4.162 \) and \( b=0.71 \) mm (see Figure 3.3) [10]. When a grease has a smaller \( m \) value, its net penetration is less affected by the change in the entropy generated inside the grease during a shear process. Thus, the slope of the characteristic line shows the durability of the grease against mechanical degradation and can be regarded as the associated “degradation coefficient” when subjected to shearing. A grease with a smaller degradation coefficient lasts longer. The y-intercept of the characteristic line shows the initial net penetration value of fresh grease.

![Figure 3.3 Characteristic line of Grease B [10]](image)

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3.2.3 Mechanical life prediction model

The correlation described in section (3.2.2) can be used to establish a mechanical life prediction model for a grease. Figure 3.4 shows the characteristic line of Grease B with identifying points A and B on the vertical axis. According to NLGI, this grease is classified as Grade 2. Point A is the initial condition of fresh Grease B with the initial net penetration value of 0.071 mm. Let Point B designate the maximum acceptable value for the net penetration of the grease where the grease consistency reaches its minimum acceptable value for the application. The minimum acceptable consistency depends on the application (bearing size, geometry, speed,..) and needs to be defined appropriately in any application. For example in a sealed bearing application, after a NLGI 2 grease is degraded to NLGI 1, it may still stay in the contact and provides lubrication for more several years. However, in another application (for example in an unsealed larger bearing with a higher speed with higher centrifugal forces), NLGI 1 grease may leak out and terminate the lubricating life of the grease. The minimum acceptable consistency should be defined based on the safety or cost considerations. For example, where the grease failure will have severe consequences, a higher minimum acceptable consistency should be implemented.

To show the application of the model, consider an application where Grease A will leaks out when degrades by one grade level on the NLGI scale from NLGI 2 to NLGI 1 with the measured net penetration value of 1 mm. Based on the characteristic line, the total amount of entropy generated inside the grease as it degrades from point A (NLGI, Grade 2) to point B (NLGI, Grade 1) is $\Delta S_g = 0.224 \text{ J/mm}^2\text{K} \, .$

We now proceed to develop an appropriate governing relationship to determine $\Delta S_g$. The generated entropy during the grease degradation from starting the shear process at point A (time
$t_A = 0$ ) up to the grease degradation at point $B$ ( time $t_B$ ) can be determined from the following expression:

\[
\Delta S_g = \int_{t_A=0}^{t_B} \frac{\tau(t)\dot{\gamma}(t)}{T(t)} \, dt
\]

where $\tau(t)$, $\dot{\gamma}(t)$, $T(t)$ are shear stress, shear rate and temperature as functions of time, respectively. $\dot{\gamma}(t)$ and $T(t)$ must be determined experimentally or predicted analytically. $\tau(t)$ depends on the shear rate and grease viscosity which itself depends on the grease consistency and temperature. When the temperature and shear rate are constant, the shear stress decreases during the grease degradation as the grease loses its consistency. If $\tau(t)$ is available, the expected life of the grease $t_B$ can be calculated from Equation (3.2).

3.2.4 The shear stress as a function of time

If the shear rate and temperature are maintained constant, then Equation (3.2) is simplified to:
To proceed further, we need to determine how the shear stress changes with time. During the shearing process with a constant shear rate and temperature, the shear stress decreases with time as the grease mechanically degrades and loses its consistency. To illustrate, Figure 3.5 shows how the shear stress of Grease B changes versus time. These results are obtained by shearing the grease in a temperature-controlled rheometer at a shear rate of 2500 1/s and 35°C while the gap was maintained constant (see Section 3.2 for details).

![Shear stress vs time for Grease B](image)

**Figure 3.5** Shear stress vs time for Grease B, Measured by rheometer at constant shear rate of 2500 1/s at T = 35°C

The reduction in the shear stress shown in Figure 3.5 is caused by mechanical degradation. During the degradation process, the structure of the grease thickener is “damaged”. This causes a decreasing trend in shear stress and consistency (illustrated in Figure 3.2). This is an irreversible process and is a source of entropy production. The decreasing trend lasts until the maximum level
of damage occurs for the applied shear rate. Then the shear stress becomes stable and remains constant at $\tau(\infty)$.

Several empirical models were presented for shear stress as a function of time by other researchers [18-21]. Following are some of them cited and compared by Kuhn [18]:

$$\tau(t) = \tau_{lim} \cdot \left(\frac{t}{\tau_{lim}}\right)^{-n} \quad (3.4)$$

$$\tau(t) = \tau_t + c \cdot t^m \quad (3.5)$$

$$\tau_f = \tau_{f,\infty} + (\tau_{f,0} - \tau_{f,\infty}) \cdot e^{\frac{t}{\tau}} \quad (3.6)$$

$$\tau(t) = [k_1 \cdot (m - 1) \cdot t \cdot \tau_0^{1-m} + (\tau_0 - \tau_r)^{1-m}]^{\frac{1}{1-m}} + \tau_r \quad (3.7)$$

In all these models the parameters $\tau_r$, $\tau_{f,\infty}$, $\tau_t$, $\tau_{lim}$ present $\tau(\infty)$ and other parameters are empirical. Equation (3.4) is not defined at $t=0$.

Here we propose an analytical model for $\tau(t)$ using the principle of irreversible thermodynamics. Define $\tau^*(t) = \tau(t) - \tau(\infty)$, where $\tau(t)$ denotes the shear stress at time $t$. The shear stress at time $t+dt$ can be expressed as:

$$\tau^*(t + dt) = \tau^*(t) - \alpha \cdot dS_g \quad (3.8)$$

where $dS_g$ is the generated entropy during the time increment of $dt$, and $\alpha$ is assumed to be a unique parameter for a grease at the testing conditions. Figure 3.6 (is plotted using Figure 3.5 experimental data) shows a measure of shear stress plotted versus the entropy generation for Grease B. The results show that $\alpha$ does not change with time.

Substituting $dS_g$ from Equation (3.2).

$$\tau^*(t + dt) = \tau^*(t) - \alpha \cdot \frac{\tau^*(t) \cdot y(t)}{\tau(t)} dt \quad (3.9)$$

After replacing $\frac{\tau^*(t+dt)-\tau^*(t)}{dt}$ by $\tau^*(t)$ which is equal to $\dot{\tau}(t)$:
\[ \dot{t}(t) + \frac{\alpha \dot{\gamma}(t)}{T(t)} \cdot \tau(t) = 0 \]  

(3.10)

Figure 3.6  Shear stress vs generated entropy for Grease A, Plotted using Fig. 5 experimental data

\[ \dot{t}(t) + \frac{\alpha \dot{\gamma}(t)}{T(t)} \cdot \tau(t) = \frac{\alpha \dot{\gamma}(t)}{T(t)} \cdot \tau(\infty) \]  

(3.11)

\[ \dot{t}(t) + \frac{\alpha \dot{\gamma}(t)}{T(t)} \cdot \tau(t) = \beta(t) \]  

(3.12)

where \( \beta(t) = \frac{\alpha \dot{\gamma}(t)}{T(t)} \cdot \tau(\infty) \).

Equation (3.12) is a first-order, linear ordinary differential equation (ODE) and has a solution in the form of:

\[ \tau(t) = e^{-\int \frac{\alpha \dot{\gamma}(t)}{T(t)} dt} (\int \beta(t) \cdot e^{\int \frac{\alpha \dot{\gamma}(t)}{T(t)} dt} dt + C) \]  

(3.13)

Now, the shear rate as a function of time, \( \dot{\gamma}(t) \), can be calculated based on the bearing geometry and rotational speed. In the case of a constant shear rate and temperature \( \beta = \frac{\alpha \dot{\gamma}}{T} \cdot \tau(\infty) \) is constant, and the solution is:
\[ \tau(t) = \frac{\tau_0}{\alpha} + C \cdot e^{-\frac{\alpha}{\tau_0} t} = \tau_\infty + C \cdot e^{-\frac{\alpha}{\tau_0} t} \]  

(3.14)

The initial condition is:

At \( t = 0 \), \( \tau(t) = \tau_0 \)  

(3.15)

Applying the initial condition yields:

\[ C = \tau_0 - \tau_\infty \]  

(3.16)

\[ \tau(t) = \tau_\infty + (\tau_0 - \tau_\infty) \cdot e^{-\frac{\alpha}{\tau_0} t} \]  

(3.17)

Therefore, in a grease experiencing mechanical degradation, the shear stress decreases exponentially from \( \tau_0 \) to \( \tau_\infty \). Note that \( \tau_0, \tau_\infty, \) and \( \alpha \) depend on the grease type, shear rate and temperature, and should be measured experimentally.

In the following section we present experimental measurements and several tests conducted with different greases to test the validity of the approach.

### 3.3 Experimental

#### 3.3.1 Lubricants

Four different greases were used to conduct the tests. Their properties are listed in Table 3.1.

<table>
<thead>
<tr>
<th>Grease</th>
<th>Grease A</th>
<th>Grease B</th>
<th>Grease C</th>
<th>Grease D</th>
</tr>
</thead>
<tbody>
<tr>
<td>NLGI Grade</td>
<td>Multipurpose</td>
<td>Multipurpose</td>
<td>Multipurpose</td>
<td>Paper Machine</td>
</tr>
<tr>
<td>Application</td>
<td>Li-Complex</td>
<td>Li-Complex</td>
<td>Li-Complex</td>
<td>Li-Complex</td>
</tr>
<tr>
<td>Thickener type</td>
<td>Penetration, Worked, 25º C, ASTM D 217</td>
<td>325</td>
<td>280</td>
<td>280</td>
</tr>
<tr>
<td></td>
<td>Dropping Point, ASTM D 2265</td>
<td>280</td>
<td>280</td>
<td>265</td>
</tr>
<tr>
<td>Base oil type</td>
<td>Mineral</td>
<td>Mineral</td>
<td>Synthetic</td>
<td>Synthetic</td>
</tr>
<tr>
<td>Viscosity of Oil, ASTM D 445 cSt @ 40º C</td>
<td>220</td>
<td>220</td>
<td>220</td>
<td>220</td>
</tr>
</tbody>
</table>
3.3.2 Rheometer

An Anton Paar MCR 301 rheometer was used for conducting the tests. The instrument has the following measurement range: torque 0.1 μN.m to 200 mN.m with 0.001 μN.m resolution and 0.2 μN.m accuracy; normal load 0.005 N to 50 N with 0.002 N resolution and ±0.03 N accuracy; and rotational speed of $10^{-6}$ rpm to 3000 rpm. Temperature can be set by the Peltier temperature control system that can operate in the range of –40°C up to +200°C with an error of ±0.1°C. The rheometer is equipped with different flat or cone rotating upper disks. The flat upper disk with the diameter of 24.955 mm was used for all the tests.

3.3.3 Shear test procedure

In the long-term shear tests, the grease sample was sheared in the gap between two flat disks. The gap and the temperature were kept constant during the tests. The tests were performed at temperatures varying from 25 °C to 45 °C. The temperature range chosen was to avoid condensation of the air humidity in lower temperatures and chemical degradation of grease in higher temperatures.

3.4 Results and discussion

Figure 3.7 show some samples of shear stress curves plotted as a function of time for the tested greases for different shear rates and temperatures. The blue circle data points are measured by the rheometer, and the solid black lines are the best curve fits on the measured results. The following conclusion can be drawn by examination of these measurement results:

The following conclusion can be drawn by examination of these measurement results:

- The initial shear stress ($\tau_0$), and also the final stable shear stress ($\tau_{fs}$) depend on the type of the grease, as well as the shear rate and temperature of the test.
• When the shear rate is high, the mechanical degradation rate is also high and consequently the grease reaches its final shear stress ($\tau_\infty$) in a shorter time. This trend can be seen by comparing the curves of Grease B at different shear rates of 4000, 5000, and 25000 at the same temperature of 25°C.

• In some of the tests with Grease C and Grease D (the three last curves in Figure 3.7) the grease experienced a rapid slip at the beginning of the test. This occurred when the grease was completely stationery, and the upper disk started to rotate with a high speed suddenly, causing a “grease slippage”. In these situations the measured initial shear stress is considered to be accurate, but the rate of decrease in the shear stress is higher than usual. In these situations the measured initial shear stress is considered to be accurate, but the rate of decrease in the shear stress is higher than usual. Nevertheless, the shear stress eventually returns back to its normal trend when, after a while, the first layer of the grease catches up with variation the speed of the upper disk. Nevertheless, the shear stress eventually returns back to its normal trend when, after a while, the first layer of the grease catches up with variation the speed of the upper disk. This phenomenon is identified on the curves with red blocks. The measured shear stresses during the slip process are excluded from the results before curve fitting.

As shown in the figures, the best fitting model is an exponential relationship in the form of

$$\tau(t) = a \cdot e^{-bt} + c$$  \hspace{1cm} (3.18)$$

Comparing Equation (3.18) with Equation (3.17), the parameters are $a = (\tau_0 - \tau_\infty), b = \frac{a \cdot \gamma}{\tau},$ and $c = \tau_\infty$

Parameters and calculated errors are listed in Table 3.2 for all the experiments.
Figure 3.7 Shear stress vs time with the best fitted curves for different greases and conditions
Table 3.2 Parameters and calculated errors for all the experiments

<table>
<thead>
<tr>
<th>Grease Type</th>
<th>Shear Rate (1/s)</th>
<th>Temp (°C)</th>
<th>a</th>
<th>b $\times 10^{-6}$</th>
<th>C</th>
<th>$\tau_0$ (Pa)</th>
<th>$\tau_\infty$ (Pa)</th>
<th>$\alpha$</th>
<th>$R^2$</th>
<th>%Error for (a)*</th>
<th>%Error for (c)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>3000</td>
<td>25</td>
<td>5208.9</td>
<td>394</td>
<td>469.2</td>
<td>5760</td>
<td>475</td>
<td>39.16</td>
<td>0.98</td>
<td>1.44</td>
<td>1.22</td>
</tr>
<tr>
<td>B</td>
<td>4000</td>
<td>25</td>
<td>7027.9</td>
<td>732</td>
<td>471.8</td>
<td>7140</td>
<td>498</td>
<td>54.56</td>
<td>0.98</td>
<td>5.81</td>
<td>5.26</td>
</tr>
<tr>
<td>B</td>
<td>4000</td>
<td>35</td>
<td>4708.1</td>
<td>363</td>
<td>314.0</td>
<td>4620</td>
<td>302</td>
<td>27.96</td>
<td>0.98</td>
<td>9.01</td>
<td>3.97</td>
</tr>
<tr>
<td>B</td>
<td>4000</td>
<td>45</td>
<td>3271.2</td>
<td>254</td>
<td>306.3</td>
<td>3450</td>
<td>299</td>
<td>20.20</td>
<td>0.98</td>
<td>3.81</td>
<td>2.44</td>
</tr>
<tr>
<td>B</td>
<td>5000</td>
<td>25</td>
<td>8297.2</td>
<td>1041</td>
<td>550.7</td>
<td>8567</td>
<td>518</td>
<td>62.07</td>
<td>0.98</td>
<td>3.09</td>
<td>6.31</td>
</tr>
<tr>
<td>B</td>
<td>10000</td>
<td>25</td>
<td>10849.6</td>
<td>1566</td>
<td>4911.8</td>
<td>15900</td>
<td>4700</td>
<td>46.69</td>
<td>0.97</td>
<td>3.13</td>
<td>4.51</td>
</tr>
<tr>
<td>B</td>
<td>15000</td>
<td>25</td>
<td>13876.4</td>
<td>1662</td>
<td>8106.0</td>
<td>21200</td>
<td>7820</td>
<td>33.04</td>
<td>0.98</td>
<td>3.71</td>
<td>3.66</td>
</tr>
<tr>
<td>B</td>
<td>25000</td>
<td>25</td>
<td>16219.5</td>
<td>1728</td>
<td>7675.1</td>
<td>24500</td>
<td>7350</td>
<td>20.61</td>
<td>0.98</td>
<td>5.43</td>
<td>4.42</td>
</tr>
<tr>
<td>C</td>
<td>25000</td>
<td>25</td>
<td>6437.2</td>
<td>2652</td>
<td>10361.2</td>
<td>17219</td>
<td>10324</td>
<td>31.63</td>
<td>0.98</td>
<td>6.64</td>
<td>0.36</td>
</tr>
<tr>
<td>C</td>
<td>15000</td>
<td>40</td>
<td>3130.1</td>
<td>489</td>
<td>3900.7</td>
<td>7394</td>
<td>3921</td>
<td>10.21</td>
<td>0.98</td>
<td>9.87</td>
<td>0.52</td>
</tr>
<tr>
<td>D</td>
<td>15000</td>
<td>40</td>
<td>2155.0</td>
<td>324</td>
<td>4132.3</td>
<td>6609</td>
<td>4219</td>
<td>6.77</td>
<td>0.99</td>
<td>9.83</td>
<td>2.05</td>
</tr>
<tr>
<td>D</td>
<td>10000</td>
<td>25</td>
<td>4266.0</td>
<td>330</td>
<td>5082.0</td>
<td>9766</td>
<td>5070</td>
<td>9.84</td>
<td>0.95</td>
<td>9.16</td>
<td>0.24</td>
</tr>
</tbody>
</table>

* The % Error for (a) is calculated from \( \left| \frac{a-(\tau_0-\tau_\infty)}{(\tau_0-\tau_\infty)} \right| \times 100 

** The % Error for (c) is calculated from \( \left| \frac{c-\tau_\infty}{\tau_\infty} \right| \times 100 

The results show that Equation (3.17) is valid for the tested greases, with less than 10% error under the conditions tested. The parameters of Equation (3.17) can also be measured for any other grease type in a similar fashion. Once determined, the grease life subjected to mechanical degradation can be determined by substituting $\tau(t)$ from Equation (3.17) into Equation (3.3) if the shear rate and temperature remain constant. In applications where shear rate and temperature are not constant, one must use Equation (3.2) and Equation (3.13). However, parameter $\alpha$ cannot be considered constant and the change of $\alpha$ versus shear rate and temperature changes should be
estimated and taken into account. Figures 3.8 and 3.9 show changes of $\alpha$ versus temperature and shear rate respectively.

**Figure 3.8** Parameter $\alpha$ vs temperature at constant shear rate of 40001/s for Grease B

**Figure 3.9** Parameter $\alpha$ vs shear rate at constant temperature of 25°C for Grease B
The above figures are plotted based on the results of experiments reported in Table 3.2. A change in the trend of the curve is seen in Figure 3.9 which can be explained by the shear thinning behavior of grease that affects the grease viscosity in low shear rates more significantly.

It is also interesting to note that the same procedure which was presented for predicting the mechanical life of a fresh grease, can also be used for predicting the remaining life of a used grease. A penetration test has to be done on the used grease to measure the entropy level of the grease and calculating $\Delta S_g$ for using in Equation (3.3). In section 5, we present illustrative examples to show the application of the model developed in this research.

### 3.5 Illustration examples

#### 3.5.1 Estimation of fresh grease life

Determine the useful life of Grease B (Grade 2) if it is subjected to a constant shear rate of 174 1/s at 25°C assuming that its performance is unacceptable if the consistency drops to a Grade 1 level. The shear stress of the grease during the degradation time is plotted in Figure 3.10. Also shown is an exponential curve fitted to the data.

![Figure 3.10 Shear stress vs time for the fresh grease (illustrative example 1)](image)
Using Equation (3.2):

\[
S_{g_{th}} = \int_{t_A=0}^{t_B} \tau(t) \dot{\gamma}(t) \, dt = \int_0^{t_B} \frac{(721.3 e^{-0.00000069 t} + 816.2) \times 174}{298.15} \, dt \quad (3.19)
\]

According to Figure 3.2, the amount of entropy generated to degrade the consistency of Grease B from Grade 2 to Grade 1 is:

\[
S_{g_{th}} = 0.224 \, \text{J/mm}^3/\text{K} \quad (3.20)
\]

Integrating Equation (3.19) after substituting \(S_{g_{th}}\) and solving for \(t_B\) yields:

Grease degradation time = \(t_B = 329,000 \, s = 91.39 \, \text{hr}\)

Therefore, it is predicted that it takes 91.39 hours for this grease to degrade from Grade 2 to Grade 1. Experimental results show that this occurs in 96 hours.

3.5.2 Example 2: Estimation of final consistency of a used grease after a shear process

A used sample Grease B with an initial net penetration value of \(\Delta_{in} = 0.14 \, \text{mm} \) was sheared in two successive shear rates of 150 1/s for 22 hours followed by 75 1/s for 96 hours as shown in Figure 3.11. Determine the final consistency of the grease in terms of net penetration value.

![Figure 3.11 Shear stress vs time for the second Illustration example test, Grease B, Shear rate: 150 1/s(22 hours)+75 1/s(96 hours), T=25°C](image)
Figure 3.12 and Figure 3.13 show the best curve fit to the results of the first and second decreasing parts of the curve which are exponential as it was predicted by the model.

Figure 3.12  Shear stress vs time with the best fitted curve for the first step of the test, shear rate: 150 1/s

Figure 3.13  Shear stress vs time with the best fitted curve for the second step of the test, shear rate: 75 1/s
The fitted exponential equations are used to calculate theoretical entropy generation using Equation (3.2):

\[ S_{g_{th}} = \int_{t_A=0}^{t_B} \frac{\tau(t)\gamma(t)}{T(t)} \, dt \]

\[
S_{g_{th}} = \int_0^{79200} \frac{220.6 \, e^{-0.000015t+599.3} \times 150}{298.15} + \int_{79200}^{424800} \frac{458 \, e^{-0.000028t+200.7} \times 75}{298.15} \, dt
\]

\[ S_{g_{th}} = 0.02902 + 0.03789 = 0.0669 \, \text{J/mm}^2\text{K} \]

This amount of the entropy generation can also be determined directly by numerically calculating the area under the experimental shear stress curve (Figure 3.11). The result is:

\[ S_{g_{ex}} = 0.02901 + 0.03792 = 0.0670 \, \text{J/mm}^2\text{K} \]

The estimated theoretical net penetration is calculated by using the grease characteristic line slope or degradation coefficient.

\[ \Delta_{th} - \Delta_{in} = 4.162 \, S_{g_{th}} = 0.28 \, \text{mm} \]

\[ \Delta_{th} = 0.14 + 0.28 = 0.42 \, \text{mm} \]

The experimental net penetration value also was carried out using the rheometer by performing a penetration test. The result is:

\[ \Delta_{ex} = 0.39 \, \text{mm} \]

Figure 3.14 shows the grease characteristic line along with the theoretical and experimental intermediate points (between two shearing steps). The intermediate points are calculated or measured after the first step in the same method as final points.
Figure 3.14  Second illustration example results, estimation versus Experiment

3.5.3 Example 3: Remaining life of a used grease

Consider a bearing lubricated with Grease B operating at a shear rate of 150 1/s. Measurement of a sample of this grease prior to 22 hours of use yields a consistency of 0.14 mm. Assuming that the maximum acceptable consistency of 0.42 mm, determine the grease life if the shear rate is reduced by two fold. The operating temperature is 25 °C.

Solution: After 22 hours shearing at the shear rate of 150 1/s, the shear rate drops proportionally by a factor of two to 75 1/s. From the grease characteristic line we can calculate the required entropy generation for degrading the grease from initial consistency (net penetration of 0.14) to the final consistency (net penetration of 0.42 mm):

$$\Delta_2 - \Delta_1 = 4.162 \cdot \Delta S_g$$

$$\Delta S_g = \frac{(0.42 - 0.14)}{4.162} = 0.067$$
From Equation (3.2):

\[
\int_{t_A=0}^{t_B} \frac{\tau(t) \dot{y}(t)}{T(t)} \, dt = \Delta S_g
\]

Substituting \( \tau(t) \) from Example 2:

\[
\int_0^{79200} \frac{(220.6 e^{-0.000015t} + 599.3) \times 150}{298.15} \, dt \\
+ \int_{79200}^{t_B} \frac{(458 e^{-0.000028t} + 200.7) \times 75}{298.15} \, dt = 0.067
\]

and solving for \( t_B \)

\[ t_B = 424800 \text{ s} \]

the remaining life of the grease is:

\[ t_B - 79200 \text{ s} = 345600 \text{ s} = 96 \text{ hours} \]

Based on the experimental results, the grease degraded to the consistency of 0.39 mm after 96 hours and the consistency of 0.43 mm after 96.5 hours.

The result shows that the model is valid when the grease is not fresh or when the shear rate is not constant.

3.6 Conclusions

Based on the correlation between thermodynamic entropy and grease mechanical degradation, a model is presented to predict the mechanical life of a lubricating grease. The model uses shear stress, shear rate and temperature as functions of time. These parameters must be determined experimentally or predicted analytically. In this research, an ordinary differential equation (ODE) is derived for calculating shear stress as a function of time. The ODE shows that during the grease degradation the shear stress decreases exponentially. An experimental procedure
is described for shear test which is used for measuring and calculating the exponential parameters of shear stress function.

The shear stress function was validated for different grease types in different shear rates and temperature, and error study shows a maximum error of less than 10%. Examples are presented to show how this development can be applied in practice in constant and variable shear rates.

3.7 References


CHAPTER 4: MECHANICAL DEGRADATION IN EHL CONTACT

4.1 Introduction

A mechanical life prediction model for grease was introduced and experimentally verified in the last chapters. The model uses shear rate function $\gamma'(t)$, shear stress function $\tau(t)$, and temperature function $T(t)$ to calculate the predicted mechanical life of a grease. In order to establish the validity of the model, the prediction results were verified experimentally using a rheometer, an instrumented grease working machine and a journal bearing test rig.

A lubricant separating the surfaces of two bodies in relative motion experiences a shearing rate which is calculated by dividing the difference between the speeds of the surfaces by the distance (gap) between them. In many physical applications, the geometry dictates non-uniform speeds and gaps. For example, in a ball bearing the shear rate of the grease in the contact between the balls and races (high speed and very small gap) can be many orders of magnitude larger than the shear rate of the grease being sheared at the sides of the cage where the speed is moderate and the gap is large. Thus, the mechanical life of a grease employed to lubricate a rolling element could vary from very short to very long depending on the location of the grease inside the rolling element. Therefore, a good working knowledge of the rolling mechanism is necessary prior to applying the mechanical life predicting model. This concept is introduced and explored in this chapter through the study of an elastohydrodynamic (EHL) line contact between two grease-lubricated steel rollers. An EHL contact is defined as a contact between two surfaces that are separated by the hydrodynamic pressure of lubricant and that the surfaces are deformed elastically because of high pressure and load. In an EHL contact, the lubricant film thickness is larger than the surface asperity heights so that no asperity contacts take place. Such a contact is seen in ball and rolling elements.
bearings as well as gears. In this chapter we begin by presenting the description of the contact and lubrication mechanism by close observation. We, then, go on to apply the mechanical life predicting model on the grease in the EHL contact.

4.2 Test Rig

Figure 4.1 shows the test rig utilized for this study. The EHL contact is between two steel rollers installed on two separate shafts supported by bearings and driven by two independent electromotors. Since the speed of each electromotor is set separately by a Variable Frequency Drive (VFD), different shear rates and slide-to-roll ratios can be easily accommodated by the system. To apply the required contact force on the rollers, one of the shaft assemblies (roller, shaft, torque sensor and electromotor) is installed on a moving saddle which is moved toward the other shaft assembly by using a hydraulic ram. The ram has a maximum pressure of 20.7 MPa (3000 psi), provided by a hydraulic pump. Two separate torque sensors measure the torque on each shaft.

This test rig was originally designed for use with liquid lubricants pumped from a reservoir equipped with a heating unit and injected directly into the contact area via a nozzle attached to a tube. For the present experiments, the rig had to be modified to accommodate the use of grease instead of oil. For this purpose, a new grease chamber was designed that could fully enclose the rollers within it. The chamber equipped with a heating unit (Figure 4.2) with a temperature control system (Figure 4.3) to maintain the temperature at desired value. The chamber (made of aluminum) is thermally insulated by ceramic fiber insulator (not shown in the pictures). Adjusting the load and average rolling speed, the contact remains elastohydrodynamic lubricated to avoid asperity contacts. Therefore, it can be assumed that all the mechanical torque (after subtracting the torque loss due to the bearings) is applied on the grease.
Figure 4.1 Test Rig
4.3 Instrumentation

All the sensors and gages (torque sensors, pressure gauges, thermocouple and VFDs) were calibrated prior to use. A computerized data acquisition system was used for logging and recording data for future analysis. Labview software was used as the interface to collects and save the sensors’ readings.

The accuracy of the temperature sensor (a type K thermocouple) was checked by testing known minimum and maximum reference temperatures. The thermocouple tip is inserted inside the chamber on the side of the contact as close as possible to the contact (shown in Figure 4.4). It measures the average grease temperature in the chamber.

The accuracy of the temperature control system (shown in Figure 4.3) was also checked. The temperature control system has its own thermocouple (yellow wire in Figure 4.3). It turns on and off the heater elements based on its thermocouple reading. Its thermocouple should be attached to the aluminum chamber (not grease). The set temperature of the temperature control system was
adjusted accordingly based on the grease temperature measurement from Type K thermocouple. It typically takes less than 5 minutes for the temperature control system to reach the set temperature.

Figure 4.4 Thermocouple position

Two Bourdon type industrial pressure gages with the ranges of 20 MPa (3000 psi) and 4 MPa (600 psi) were utilized to measure the pressure of the hydraulic ram. The measured pressure is used to calculate the normal force produced by the ram.

VFDs speed control accuracy was checked using a portable tachometer in different testing conditions. The torque sensors are heavy duty rotary sensors with maximum capacity of 1000 in-lb (113 N-M) with linearity and hysteresis of 0.1% of full scale. The accuracy of torque sensors was checked by attachment of an arm to each shaft and hanging standard mass weights from the arms. In calibrating of the torque sensors, the friction of bearings also was measured in different testing speeds and deducted appropriately from the torque sensors reading. Traction force was calculated by multiplying each torque sensor reading by related roller radius. The traction force was plotted online in Labview software for each roller. With an appropriate calibration, traction
forces should be almost similar. The average value was also calculated and plotted online in the software and was reported as the final traction force.

### 4.4 Preparation and Alignments

Shafts parallelism should be measured and checked accurately to avoid non-uniform pressure distribution along the line of contact between the rollers. This was done by accurate measurement of shaft distances at the two ends. After alignment of the shafts, a small gap of 0.2 mm was adjusted between the rollers using a filler gauge. Then, the filler gauge was moved along the gap to ensure that identical gap exists in both edges of the rollers. Next, the rollers were pushed together using the high pressure ram (at the same pressure of testing), and consistent blockage of light through the gap was observed using a flashlight on the other side of the gap which means the contacting surfaces of the rollers are parallel.

Rollers are made of AISI 4140 carbon steels with diameters of 3 and 4 inches and width of 1 inch. The larger roller is chamfered in both edges and the contact area has a width of 10 mm rollers are hardened to 42–44 RC. The surface roughness value for the rollers is fairly close and is in the range of $Ra = 0.15–0.25 \, \mu m$.

The rollers were run in for 8 hours at the rolling speed of 0.065 m/s and slide-to-roll ratio of 0.15 under the normal force of 2930 N ($P_{\text{Hertz,Max}} = 0.7 \, \text{GPa}$). Running in process should be performed whenever a roller is replaced with a brand new roller to ensure the repeatability of the test results. The surface of the new roller is formed into a final steady state condition during the running in process. The same testing grease was used to lubricate the rollers during the running in process. Rollers’ alignment was checked afterward and the used grease was replaced with fresh grease. Grease B was used for all the experiments including the running in process. The specification of the grease is listed in Table 4.1.
Table 4.1 Grease specification

<table>
<thead>
<tr>
<th>Grease B</th>
</tr>
</thead>
<tbody>
<tr>
<td>NLGI Grade</td>
</tr>
<tr>
<td>Thickener</td>
</tr>
<tr>
<td>Penetration, Worked, 25 ºC, ASTM D 217</td>
</tr>
<tr>
<td>Dropping Point ºC, ASTM D 2265</td>
</tr>
<tr>
<td>Base oil type</td>
</tr>
<tr>
<td>Viscosity of Oil, ASTM D 445 cSt @ 40º C</td>
</tr>
</tbody>
</table>

4.5 Speed and Pressure Settings

To avoid asperity contact, it is very important to select appropriate speeds and slide-to-roll ratios. The slide-to-roll ratio is defined as the sliding velocity \((U_2 - U_1)\) divided by the rolling velocity \((U_1 + U_2)/2\). Sliding velocity is the difference in linear speed between two sliding surfaces. Rolling speed is the average of linear speeds of the surfaces. A slide-to-roll ratio of \(S=0\) is pure rolling where the traction is minimum and a slide-to-roll ratio of \(S=2\) is pure sliding where one of the surfaces is stationery. The lubricated contact becomes starved of the grease in high speeds or high slide-to-roll ratios. This results in asperity contacts which damages the roller’s surfaces and can even cause severe problems to the rig by seizure. This can be detected by a jump in the traction curve (see [1, 2]) and the rise in temperature following by a grinding noise in the machine. Table 4.2 lists the applied speed and frequency setting of each VFD and the rolling speed of each roller. The slide-to-roll ratio was varied from zero to 0.75 in our experiments.
Table 4.2 Speed Settings

<table>
<thead>
<tr>
<th>Rolling Speed (m/s)</th>
<th>Slide-to-roll ratio</th>
<th>$U_1$(m/s)</th>
<th>$U_2$(m/s)</th>
<th>RPM1</th>
<th>RPM2</th>
<th>f1(Hz)</th>
<th>f2(Hz)</th>
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<td>0.065057</td>
<td>0.065057</td>
<td>12.2</td>
<td>15.7</td>
<td>9.9</td>
<td>12.7</td>
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<td>0.065382</td>
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<td>6.51E-02</td>
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<td>0.065708</td>
<td>0.064406</td>
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<td>10.0</td>
<td>12.6</td>
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<td>0.064081</td>
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<td>0.066683</td>
<td>0.063431</td>
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<td>14.5</td>
<td>10.6</td>
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<td>11.4</td>
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<td>11.9</td>
<td>10.2</td>
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<td>0.048793</td>
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<td>13.6</td>
<td>8.0</td>
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</tbody>
</table>

Two Maximum Hertzian pressures of 0.5 and 0.7 GPa were used in the experiments. Table 4.3 lists the related normal force and the ram pressure setting for each Hertzian Pressure.

Table 4.3 Pressure Settings

<table>
<thead>
<tr>
<th>W (dimensionless load number)</th>
<th>P_Hertz_max (GPa)</th>
<th>Set Pressure on ram (PSI)</th>
<th>Normal Force (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.00E-05</td>
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<tr>
<td>6.00E-05</td>
<td>0.7</td>
<td>54</td>
<td>2927.6</td>
</tr>
</tbody>
</table>

4.6 Experimental procedure

After calibrations, preparations and alignments, the chamber was filled with fresh grease and the rig was used for three different following experiments:
• Traction curve measurement
• Grease flow observation
• Long term degradation

Each test procedure is described separately in the following sections.

4.6.1 Traction measurements

Traction between the rollers was measured in different temperatures from 25 °C to 115 °C for two different maximum Hertzian pressures of 0.5 and 0.7 GPa according to the following procedure. The grease chamber is heated to the test temperature while the rollers are rotating with the slide-to-roll ratio of 0.01 (Table 4.2) under a ram pressure setting of zero (open bypass valve). After reaching the test temperature, the ram pressure is set based on Table 4.3 for the desired maximum Hertzian pressure and the experiment is run for 15 minutes. Because of the thermal expansion of the rollers, the pressure of the ram increases and needs readjustment. Then the test is run until a steady state condition is reached by observing both the traction and grease temperature. The measured traction force at this point is reported for traction at slide-to-roll ratio of 0.01. Then the speed setting of VFDs is adjusted for the next slide-to-roll ratio using Table 4.2. The traction response to the speed change is quick and it becomes steady after almost two minutes. At that stage, traction can be recorded and the machine can be run for the next slide-to-roll ratio. After testing with the last slide-to-roll ratio (when the machine is still running with the slide-to-roll of 0.75), measurements were repeated for all the slide-to-roll ratios of Table 4.2 by decreasing the slide-to-roll ratio from 0.75 to 0.01.

The traction curve of fresh Grease B at room temperature is shown in Figure 4.5 for two different loads.
As expected, the traction is higher for higher loads. At the slide-to-roll ratios between zero and 0.1, traction increases with a high rate. The increasing trend slows down at higher slide-to-roll ratios because of thermal effects which affect the viscosity of the lubricant and finally turns to a decreasing trend. At the slide-to-roll ratios between zero and 0.1, traction increases with a high rate. The increasing trend slows down at higher slide-to-roll ratios because of thermal effects which affect the viscosity of the lubricant and finally turns to a decreasing trend. The same trend has been reported by Masjedi and Khonsari [4] for oil lubricants—using the same test rig. Unlike oil, grease is non-Newtonian and has a yield stress at zero shear rate. This is why grease traction has a non-zero value at pure rolling.

The variation of the traction curves with temperature for two different maximum Hertzian pressures of 0.7 and 0.5 GPa are shown in Figures 4.6 and 4.7 respectively.
Figure 4.6  Variation of fresh Grease B traction curve with temperature at Max Hertzian pressure of 0.7 GPa.

Figure 4.7  Variation of fresh Grease B traction curve with temperature at Max Hertzian pressure of 0.5 GPa.
It is difficult to accurately measure the traction exactly at slide-to-roll ratio of zero because the friction forces start fluctuating in a range of ±15% at the slide-to-roll ratio of zero. The best average measured results close to pure rolling condition are shown in Figure 4.8.

![Graph showing traction curves of fresh Grease B](image)

**Figure 4.8** Traction curves of fresh Grease B at very small slide-to-roll ratios and close to pure rolling condition, Max Hertzian pressure of 0.7 GPa.

### 4.6.2 Grease flow observation

To study the lubrication mechanism in the contact and visually examine the flow behavior of the grease, the upper section of the chamber was opened and several tests were videotaped. Significant changes were observed in the grease flow and lubrication mechanism. The entire process can be described in three phases. Figure 4.9 shows an illustrative sketch about different phases. These phases are described in the following sections.
Phase 1: Fully grease covered rollers

Phase 2: Slippage and grease separation

Phase 3: Formation of Liquid lubricant reservoir

Figure 4.9 An illustrative sketch about different phases of lubrication mechanism
4.6.2.1 Phase 1: Fully grease covered rollers

Figure 4.10 shows the initial grease flow immediately after running the test. Visual observation reveals that grease tends to attach itself to the rollers from the bottom of the chamber and is carried into the contact region by the rotation of the rollers. Some of the grease passes through the contact by forming a full film while the rest tends to go around the sides of the rollers, bypassing the contact area. Both the rollers’ surfaces are fully covered by grease at this stage. The moving grease tend to return to the contact repetitively and the rollers remain fully covered by thick layers of grease until the end of this phase which takes several minutes.

![Figure 4.10](image)

Figure 4.10  Phase 1: the initial grease flow immediately after running the test

4.6.2.2 Phase 2: Slippage and grease separation

In the second phase, grease is suddenly separated from the rollers’ contacting surfaces (Figure 4.11). This first occurs in the roller with larger diameter and soon extends to both rollers. Physically, the portion of the moving grease in contact with the roller surfaces begins to slide on the surface of the rollers without being carried into the contact area by the rollers’ rotation. Interestingly, the rollers’ side surfaces (away from the contact area) remain fully covered with grease. During the second phase (which lasted almost 10 minutes in our experiments), the rolling
surfaces may occasionally become partially covered by grease, but this process becomes less frequent as time passes.

Figure 4.11  Phase 2: grease separation

4.6.2.3 Phase 3: Formation of Liquid lubricant reservoir

During the final phase, no solid grease is observed on the rolling surfaces (Figure 4.12). The rolling surfaces are covered by a very thin film of liquid lubricant which is highly mechanically degraded grease. It contains a mixture of base oil and destroyed thickener particles. Since the rollers are surrounded by solid grease on either sides of the rollers, the thin liquid layer which still lubricates the contact is constrained from leaving the contact—akin to a soft seal—and thus remains in the contact for a long period of time. A liquid lubricant reservoir is generated between the solid grease and rollers’ surfaces that feeds the contact continuously. It is noteworthy that other researchers [3] also have documented the sealing effect of solid grease at the contact sides. Grease edges on the sides of the contact are shown in Figure 4.13. Note that these edges along the boundaries are continuously subjected to shearing and mechanical degradation, but the rate of their mechanical degradation is low due to small shear rate. This low speed degradation results in continuous base oil bleeding which is desirable for a better lubrication, but also it destroys the grease thickener gradually.
It is noteworthy that other researchers [3] also have documented the sealing effect of solid grease at the contact sides. Grease edges on the sides of the contact are shown in Figure 4.13. Note that these edges along the boundaries are continuously subjected to shearing and mechanical degradation, but the rate of their mechanical degradation is low due to small shear rate. This low speed degradation results in continuous base oil bleeding which is desirable for a better lubrication, but also it destroys the grease thickener gradually.

Figure 4.12 Liquid lubricant reservoir formation

Figure 4.13 Grease edges

...the described degradation phases, are also observed by Cann [4]. Figure 4.14 shows her summary of the process.

More explanation and discussion will be provided in theoretical (Section 4.7) about the flow observation.
4.6.3 Long term degradation

To study the long-term degradation effect, the apparatus was programmed to run for 6 time-increments each lasted 510 minutes (nearly almost 8.5 hours). The rolling speed and slide-to-roll ratio were 0.065 m/s and 0.15 respectively and the normal force was 2930 N (Maximum Hertzian Pressure of 0.7 Gpa). The traction force and temperature were continuously recorded during each time increment. The results are shown in Figures 4.15 and 4.16, respectively. After each time increment, the traction was also measured in the same fashion as described in Section 4.6.1. The
traction results are shown in Figure 4.17. More discussion on the results will be provided in theoretical section (Section 4.7.1) along with the physical meaning.

Figure 4.15  Variation of friction force during long term degradation

Figure 4.16  Variation of temperature during long term degradation
4.7 Theoretical

4.7.1 Grease degradation process in the contact

The three phases of grease lubrication observed in Section 4.6.2 can be described by the following theory. In the first phase, the fresh grease is carried into the EHL contact where the grease experiences very high shear rate and shear stress and mechanically degrades. The rollers act like a mill and break the structure of the thickener of the grease. As the grease degrades and loses its consistency, less torque is required to rotate the rollers. Furthermore, breaking the thickener’s structure releases base oil that flows into the contact and provides lubrication. As a result, the traction force has a decreasing trend. This is seen in the first portion of Fig 4.15. This decreasing trend also appears in Fig 4.17 comparing the traction curve of the fresh grease and the traction of grease after 2 hours shearing. This process generates entropy, but it is confined to the grease in the very small area (right at the contact) and thus its effect on the measured grease...
temperature by the thermocouple (shown in Figure 4.4) is not detected in Figure 4.16 as the thermocouple does not measure the temperature right at the contact.

The highly degraded layer of the grease (almost base oil) which is much thinner than the solid grease, covers the surface of the rollers in a short period of time and causes the solid grease to experience slippage on the surfaces in Phase 2. During this phase, the degradation continues, and traction reaches its minimum level at the end of Phase 2. The highly degraded lubricant (liquid) is sealed by the solid grease walls/edges and lubricates the contact for a long period of time. However, the film thickness of the lubricant decreases gradually with time. This phenomenon has been reported by other researchers [5, 6] under starved lubrication condition, when no attempt is made to resupply grease to the inlet. Gradual decrease of the film thickness increases the friction force over the time as seen in Figure 4.17. The same trend for traction force was also observed by Yousif et al. [1, 2].

The highly mechanically degraded lubricant stays in the contact area as long as it is sealed by the “solid grease walls”. However, the solid grease inner walls are also subject to low shear rate mechanical degradation which causes base oil bleeding and loss in grease consistency over time. The bleeding effect is desirable as some of the oil is fed to the contact to provide some lubrication, but decrease in grease consistency can break down the grease edges/walls’ sealing effect and result in liquid lubricant leakage. The liquid lubricant leakage can eventually starve the contact. As a result of depletion of lubricant, a sudden increase in the traction and temperature will eventually occur signifying failure and damage to the rollers. Figures 4.18 and 4.19 show the increase in traction and temperature at the end of the long term degradation experiment when the liquid lubricant was carefully cleaned off from the moving contacting surfaces of the rollers with a soft cloth (while the upper section of the chamber was open). In the next section we will show that the
theory predicts that under the conditions tested, the walls’ sealing effect will break down after 4 years.

![Figure 4.18](image)

Figure 4.18  Increase in friction after cleaning the liquid lubricant

![Figure 4.19](image)

Figure 4.19  Increase in temperature after cleaning the liquid lubricant
4.7.2 Applying the mechanical life model

The mechanical life model established in chapter 3 can be applied to the EHL contact. Assuming constant temperature and speed, the mechanical life of grease can be estimated using Equation (4.1):

\[ \int_{t_a=0}^{t_B} \tau(t) \, dt = T \cdot \frac{\Delta S_g}{\gamma} \]  

(4.1)

In this equation, \( \Delta S_g \) is the entropy generation and should be calculated from grease characteristic line (see Figure 3.4 and Section 3.5.1 on estimation of fresh grease life). Assuming that the limiting mechanical life of Grease B is reached after reduction in its consistency by one unit on the NLGI grade level, then:

\[ \Delta S_g = 0.224 \frac{1}{\text{mm}^3/\text{K}} \]

This model is assumed to be applicable to the grease in the contact area as well as the grease at the contact sides/edges since in these areas the grease is subjected to mechanical degradation.

4.7.2.1 Estimating the mechanical life of grease at the contact:

As observed in Section 4.6.2 and theorized in Section 4.7.1, the fresh grease at the contact is subjected to a very high shear rate and shear stress, and is thus mechanically degraded in the first few minutes of the test. The mechanical life prediction model can be used here to verify this phenomenon. To apply the model, we need to measure or estimate the grease average temperature and film thickness during this short degradation period. The average temperature of the grease exiting the contact was measured using an infrared temperature gun. While the thermocouple (shown in Figure. 4.4) reading was almost 26 °C, the infrared temperature sensor reading for the solid grease exiting from the center of the contact measured 33 °C.
To calculate the shear rate $\dot{\gamma}$, the grease film thickness at EHL contact must be estimated. This was done using the available data in the literatures since direct measurement of film thickness in our apparatus is not feasible. Typically grease film thickness in an EHL contact is measured using the interferometry technique [5, 7-9]. Cann [5] measured grease film thickness at temperatures of 20, 50, and 80 °C and rolling speeds of 0.025, 0.05, 0.1 m/s under maximum Hertzian pressure of 0.48 GPa. Based on her work, grease film thickness is dependent on the rolling speed and it decreases during disc revolutions. Her results for a lithium grease at 20 °C are shown in Figure 4.20. Based on her work, grease film thickness is dependent on the rolling speed and it decreases during disc revolutions. Her results for a lithium grease at 20 °C are shown in Figure 4.20.

In a later paper [7], Cann cites film thickness measurement of thermally aged grease in an EHL contact (shown in Figure 4.21) by Harley [8].

![Figure 4.20](image)

Figure 4.20  Film thickness measurement for a lithium grease at 20 °C under the Max Hertz Pressure of 0.48 GPa [5]
Morales-Espejel et al. [10] also used interferometry technique to measure the grease film thickness in a ball-on-disc tribometer at 40 °C under a maximum Hertzian contact pressure of 0.456 GPa in different rolling speeds. An example of their results for three lithium complex greases is shown in Figure 4.22. The solid lines in the figure are trend lines.

Figure 4.22  Film thickness versus rolling speed for three lithium complex greases under a maximum Hertzian contact pressure of 0.456 GPa in 40 °C [10]
Astrom et al. [9] also showed experimentally (using interferometry technique) that the film thickness of a grease lubricated point EHL contact in a ball-on-disc experiment with maximum Hertzian pressure of 0.38 GPa and rolling speed of 55 mm/s decreased from 600 nm to 15 nm over 100 cycles of the disc rotation.

Considering our test conditions (rolling speed of 0.065 m/s, Temperature of 33 °C, and maximum Hertzian contact pressure of 0.7 GPa) and comparing with other researchers’ results described above, a constant average film thickness of $d=100$ nm is assumed for the film thickness in the contact during the first several minutes of rollers rotation. Although this assumption may not be very accurate, it is used here to show the application of our model in the EHL contact. Although this assumption may not be very accurate, it is used here to show the application of our model in the EHL contact. The calculations will be repeated for two more film thicknesses of $d=75$ nm and $d=125$ nm also. Although this assumption may not be very accurate, it is used here to show the application of our model in the EHL contact. The calculations will be repeated for two more film thicknesses of $d=75$ nm and $d=125$ nm also. With the rolling speed of $U_r=0.065$ m/s and the slide to roll ratio of $SR=0.15$, the difference in linear speed of the rollers’ surfaces at the contact is calculated to be $\Delta U=0.15 \times 0.065 =0.001$ m/s. Therefore, the shear rate is:

$$\dot{\gamma} = \frac{\Delta U}{d} = \frac{0.001}{100 \times 10^{-9}} = 10000 \text{ 1/s}$$

As it was noted in chapter 3, the shear stress is an exponential function of time. To calculate the exponential parameters of the shear stress function, a sample of the fresh grease was subjected to the same shear rate and temperature in the rheometer. As it was noted in chapter 3, the shear stress is an exponential function of time. Figure 4.23 shows the reduction of shear stress versus time and also the best fitted curve to the results in the form of an exponential function.
Figure 4.23  Shear stress vs time for the film thickness assumption of 100 nm

From Figure 4.23:

\[ \tau(t) = (4981.2 e^{-0.00094 t} + 3532.5) \]

Substituting in Equation (4.1):

Grease degradation time = \( t_B = 1020 \) s = 17 min

For a film thickness assumption of \( d=0.75 \) nm the shear rate is recalculated to be:

\[ \dot{\gamma} = \frac{\Delta U}{d} = \frac{0.001}{75 \times 10^{-9}} = 13333 \text{ 1/s} \]

Figure 4.24 shows the reduction of shear stress versus time and also the best fitted curve to the results for this shear rate.
From Figure 4.24:

\[ \tau(t) = (8061.5 e^{-0.00168 t} + 3638.48) \]

Substituting in Equation (4.1):

Grease degradation time = \( t_B = 580 \text{ s} = 9.66 \text{ min} \)

Also for a film thickness assumption of \( d = 0.125 \text{ nm} \) the shear rate is recalculated to be:

\[ \dot{\gamma} = \frac{\Delta U}{d} = \frac{0.001}{125 \times 10^{-9}} = 8000 \text{ 1/s} \]

Figure 4.25 shows the reduction of shear stress versus time and also the best fitted curve to the results for this shear rate. During this test, the grease experienced a “grease slippage”. This phenomenon was described in Chapter 3 (Section 3.4). It occurs when the grease experiences a rapid slip. In these situations, the measured initial shear stress is considered to be accurate, but for
a portion of the curve, the rate of decrease in the shear stress is higher than usual. Nevertheless, the shear stress eventually returns back to its normal trend when, after a while, the first layer of the grease catches up with variation the speed of the upper disk. This phenomenon is identified on the curves with red blocks. The measured shear stresses during the slip process are excluded from the results before curve fitting.

![Graph showing shear stress vs time for the film thickness assumption of 125 nm](image)

**Figure 4.25**  Shear stress vs time for the film thickness assumption of 125 nm

From Figure 4.25:

\[ \tau(t) = (4213.5 \ e^{-0.00024 \ t} + 3718.9) \]

Substituting in Equation (4.1):

Grease degradation time = \( t_B = 1160 \) s = 19.33 min
Table 4.4 shows the predicted mechanical life for the grease at the contact for each assumed film thickness.

Table 4.4 grease predicted life for different film thicknesses

<table>
<thead>
<tr>
<th>Film thickness assumption (nm)</th>
<th>Predicted life (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>9.66</td>
</tr>
<tr>
<td>100</td>
<td>17</td>
</tr>
<tr>
<td>125</td>
<td>19.33</td>
</tr>
</tbody>
</table>

The predicted mechanical life of the grease is less sensitive to the film thickness in higher film thicknesses. Increasing the film thickness from 100 nm to 125 nm (25% increase) increases the predicted life by a factor of 1.14 where decreasing the film thickness from 100 nm to 75 nm (% 25 reduction) decreases the predicted life by a factor of 1.76.

Even though the film thickness assumption can affect the predicted life by large factors, it can be generally concluded that the life of the grease at the contact can vary from several seconds (in smaller film thicknesses) to several minutes (in larger film thicknesses). This conclusion is in complete agreement with the experimental observation described in Section 4.6.2 and proves the theory introduced and described in Section 4.7.1 about grease degradation phases in the EHL contact.

4.7.2.2 Estimating the mechanical life of grease walls at the contact edges

Mechanical life of the grease at the edges is calculated in the same fashion. From thermocouple reading at the edge $T = 26 \, ^\circ$C. To calculate the shear rate $\dot{\gamma}$, we need to have the linear speed difference and grease thickness. The grease thickness is calculated from the geometry of the rollers. As shown in Figure 4.26 the grease thickness and also the difference in linear speeds are not constant. However, from the geometry, we can assume an average value of 1 mm for the
grease thickness and the difference in linear speed can be assumed the same as before
\[ \Delta U = 0.15 \times 0.065 = 0.001 \text{ m/s}. \]
Therefore:
\[
\dot{\gamma} = \frac{\Delta U}{d} = \frac{0.001}{1 \times 10^{-3}} = 1 \text{ 1/s}
\]

Figure 4.26  Rollers’ geometry at the edge of the contact

To calculate the exponential parameters of the shear stress function, a sample of the fresh

grease was subjected to the same shear rate and temperature in the rheometer. Figure 4.27 shows

the reduction of shear stress versus time and also the best fitted curve to the results.

Figure 4.27  Shear stress vs time for the film thickness assumption of 1 mm
From Figure 4.27:

\[ \tau(t) = (219 \ e^{-0.0028 \ t} + 482.9) \]

Substituting in Equation (4.1):

Grease degradation time = \( t_B = 138,765,000 \ s = 4.4 \) years

Comparing 4.4 years to the several minutes predicted for the grease life at the contact (Table 4.4) shows the grease mechanical degradation at the walls is a slow process. While the part of the grease at the contact becomes soft at the several initial minutes of the lubrication process, the solid grease at walls last for several years and maintain the soft lubricant inside the contact while its gradual mechanical degradation feed the contact by releasing base oil.

4.8 Conclusions

Grease degradation in an elastohydrodynamic (EHL) line contact between two steel rollers is studied. Experimental procedure for grease traction measurement is described. Three lubrication phases are observed and their behavior are described. A mechanical life prediction model is applied to gain further insight into the grease degradation process. It is shown that grease within the contact area is highly degraded in a very short period of time (several minutes), and that this degraded grease is sealed by the solid grease walls at the sides of the contact. The highly degraded grease continues to lubricate the contact as long as the walls sealing effect persists. The mechanical life prediction model is also applied to the grease walls at the sides of the EHL contact. It is shown that the sealing effect of walls can last for a long period of time (several years).

4.9 References


CHAPTER 5: CHEMICAL DEGRADATION

5.1 Introduction

Mechanical life of grease was studied in previous chapters. The results of the study can be used for grease life prediction where the mechanical degradation is dominant. This primarily occurs at temperatures below 60 °C. However, chemical degradation initiates and becomes dominant as the operating temperature increases. In this chapter we study the chemical degradation and propose a grease life model for the prediction of grease life.

A literature review including chemical degradation was presented in the first chapter of this dissertation (Section 1.3). It was shown that no attempt has been done on the study of chemical degradation of grease from an energy point of view. In this chapter, an experimental setup is prepared and the relation between chemical degradation and energy is experimentally studied testing with two different greases. A theory is developed for chemical degradation of grease based on the experimental results.

5.2 Experimental

5.2.1 Lubricants

Two different greases were used to conduct the tests. Their properties are listed in Table 5.1.

<table>
<thead>
<tr>
<th>Grease</th>
<th>B</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>NLGI Grade</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>Thickener type</td>
<td>Li-Complex</td>
<td>Li-Complex</td>
</tr>
<tr>
<td>Penetration, Worked, 25°C, ASTM D 217</td>
<td>280</td>
<td>305</td>
</tr>
<tr>
<td>Dropping Point, ASTM D 2265</td>
<td>280</td>
<td>275</td>
</tr>
<tr>
<td>Base oil type</td>
<td>Mineral</td>
<td>Synthetic</td>
</tr>
<tr>
<td>Viscosity of Oil, ASTM D 445 cSt @ 40°C</td>
<td>220</td>
<td>220</td>
</tr>
</tbody>
</table>
5.2.2 Pressure Differential Scanning Calorimeter (PDSC)

A PDSC machine (Figure 5.1) at LSU Chemistry Department was utilized to measure the activation energy of the grease and to monitor the chemical degradation process. The machine was calibrated prior to testing according to the ASTM D5483 standard [1], and all the tests were performed according to the recommended test procedure in the standard. Based on the procedure, 0.002 gram of grease is weighted in a small standard aluminum pan (inserted inside the high pressure cell of the machine) and is oxidized under 3.5 MPa of oxygen pressure at a constant test temperature. An empty pan is also inserted inside the cell as a reference (Figure 5.2). The machine heats up both pans at the same rate to the test temperature and maintains the temperature at the desired specification. When the oxidation reaction initiates, the heater under the sample pan needs to generate less heat (since the oxidation reaction is exothermic) than the heater under the reference pan to maintain the test temperature. The difference in heat flow is recorded and is plotted as a function of time. The grease induction time (oxidation time) is defined as the instant in time when heat flow curve rises due to initiation of exothermic reactions after antioxidants depletion. It is measured on the time axis at the intersection of two tangent lines to the heat flow curve drawn before and after the rise in the heat flow. The difference in heat flow is recorded and is plotted as a function of time. The grease induction time (oxidation time) is defined as the instant in time when heat flow curve rises due to initiation of exothermic reactions after antioxidants depletion. It is measured on the time axis at the intersection of two tangent lines to the heat flow curve drawn before and after the rise in the heat flow. The activation energy is calculated using two measured induction times at two different temperatures. More details are provided in the theoretical Section 5.3.1.
5.2.3 Heater setup

An experimental setup was prepared to heat up a grease sample for several hours at high temperatures and study the relation between energy and chemical degradation. Figure 5.3 shows a schematic of the test set up. It consists of a thermally insulated heating chamber (shown in Figure 5.4) whose temperature is controlled by a temperature control unit (Figure 5.5) and a Watt-meter (Figure 5.6) that measures the electrical power consumed to heat up the chamber.
Figure 5.3  Schematic of the experimental set up

Figure 5.4  Thermally insulated heating chamber

Figure 5.5  Temperature control unit
The heating chamber is a small electric furnace with the capacity of 520 W and the maximum temperature of 1150 °C. It has an inside cylindrical empty space with heating elements all around it and a small hole on the top wall for inserting the thermocouple (yellow wire in Fig 5.4). The temperature control unit is a regular temperature controller with the maximum load capacity of 10 A. The Watt-meter is a plug in type energy meter with accuracy of ±1.5%.

5.2.3.1 Test procedure

Although the heating chamber is thermally insulated, some heat is likely to escape to the surroundings. The heat lost should be measured at each test temperature. For this purpose, the empty chamber is heated up to the test temperature and only when the temperature is stabilized, the electrical energy per hour being used to maintain the temperature is measured by the Watt-meter and recorded as the heat lost rate. This is the steady rate of heat being lost from the chamber at each testing temperature, and since it is measured after reaching to the test temperature, it does not include the electrical power used to raise the temperature of the chamber. This procedure is repeated for each test temperature.
The test procedure is as follows. The chamber is heated up to the desired test temperature and maintained long enough until steady state is attained. Next, 25 grams of the grease sample is weighted in an aluminum container (Figure 5.7) and the container is inserted into the heating chamber. The Watt-meter is reset at this time and the energy (Watt hours) measurement begins.

![Figure 5.7 Grease sample in the heating chamber](image)

The change of energy is recorded during the test time. Small samples of grease (each almost 0.1 gram) are extracted from the heating chamber frequently during the test time. The samples are used to monitor the changes in the induction time of the grease during heating process. The samples’ induction times are measured by the PDSC machine described in Section 5.2.2.

5.2.4 Roller tester rig

The roller tester rig, introduced and described in the last chapter (Section 4.2), was used in this study to validate our theory. The instrumentation, calibration and alignment of the machine are the same as described previously. The test procedure is different and will be described in the validation Section 5.4.

5.3 Theoretical

5.3.1 Activation energy calculation

The activation energy of grease is measured from PDSC induction time measurements at two different temperatures according to the procedure described in [3]. According to the
Arrhenius model, the oxidation reaction rate is related to the oxidation temperature by the following relation [4]:

\[ k = k_0 e^{-\frac{E_a}{RT}} \]  \hspace{1cm} (5.1)

where \( k \) is the rate constant, \( E_a \) is the activation energy, \( R \) represents the universal gas constant (8.314 J/mol.k), \( k_0 \) is a frequency factor, and \( T \) is temperature in Kelvin. The grease oxidation is a first order kinetic reaction (depends linearly on only one reactant concentration) and can be expressed in terms of fractional conversion \( x \) and the rate constant \( k \) [4]:

\[ t = \frac{-\ln(1-x)}{k} \]  \hspace{1cm} (5.2)

where \( t \) is the induction time and \( x \) is the fractional conversion. The fractional conversion \( x = \frac{n(t=0)-n(t)}{n(t=0)} = 1 - \frac{n(t)}{n(t=0)} \) is defined as the changes in the number of moles \( n \) of the reactant at time \( t \) divided by its initial number of moles at time zero.

Substituting \( k \) from Equation (5.1) into Equation (5.2), we arrive at the following equation.

\[ t = -\frac{1}{k_0} \ln(1-x) e^{-\frac{E_a}{RT}} \]  \hspace{1cm} (5.3)

\[ \ln(t) = \frac{E_a}{R} \left(\frac{1}{T}\right) + \ln(A) \]  \hspace{1cm} (5.4)

In an Arrhenius coordinate, which has a reciprocal scale for temperature and a natural logarithmic scale for induction time, Equation (5.4) is a line with the slope of \( \frac{E_a}{R} \).

The induction time for Grease B was measured using the PDSC machine at two temperatures of 200 and 220 °C. Figures 5.8 and 5.9 show the heat flow curves and calculated induction times (at the cross of the shown tangent lines) for the temperatures. The blue curves are the derivatives of heat flow curves. These are used to locate the tangent lines.
Figure 5.8  Induction time measurement of fresh Grease B at 200 °C

Figure 5.9  Induction time measurement of fresh Grease B 220 °C
The induction time of Grease B was also measured at the temperature of 210 °C. Table 5.2 shows the measured induction times in different temperatures.

Table 5.2 Measured Induction times

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Induction time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>473.15</td>
<td>31.59</td>
</tr>
<tr>
<td>483.15</td>
<td>13.8</td>
</tr>
<tr>
<td>493.15</td>
<td>6.24</td>
</tr>
</tbody>
</table>

Figure 5.10  Arrhenius plotting for fresh Grease B

Figure 5.10 shows that the induction time versus temperature is a line in an Arrhenius coordinate. It reveals that the oxidation of Grease B follows the first order kinetic equation. The activation energy of this grease is calculated from the slope of the line to be $E_a = 157.13 \frac{\text{kJ}}{\text{mol}}$. The induction time measurements for fresh Grease D at two test temperatures of 225 °C and 210 °C are shown in Figures 5.11 and 5.12, respectively.
Figure 5.11  Induction time measurement of fresh Grease D grease at 225 °C

Figure 5.12  Induction time measurement of fresh Grease D grease at 210 °C
Following a similar procedure, the activation energy of Grease D is calculated to be $E_a = 149.7 \text{ kJ mol}^{-1}$. Although Grease D has a smaller activation energy than Grease B, its induction times are longer, which means that this grease is more resistant to high temperatures.

5.3.2 Induction time monitoring during chemical degradation

It was shown in the first chapter (Section 1.3, literature survey and summary) that induction time of a fresh grease measured by PDSC machine indicates the level of antioxidant agents available in the grease. Since the antioxidants postpone the oxidation reactions, a fresh grease with higher induction time is considered to last longer in high temperatures. This was the main concept used in the development of an oxidation stability test method for greases using a pressure differential scanning calorimeter introduced by Rhee [3] and was later developed as ASTM D 5483 standard test method [1]. As indicated in the standard, the oxidation stability test is not capable of predicting grease life and is used to compare high temperature stability of different greases.

In his later work [4], Rhee correlated his induction time measurements to the actual grease life measured from the wheel bearing standard test method (ASTM D 3527 [5]). Figure 5.13 shows his reported empirical correlation.

Figure 5.13  Correlation between induction times and grease life from ASTM D 3527 test [4]
Although the correlation showed good agreement for most of the tested greases, it was not accurate for greases having excessive oil separation or poor thermal stability [4]. The wheel-bearing standard test method, as described in ASTM D 3527, is a dynamic test and therefore also includes mechanical degradation. Thus, it is not accurate to correlate wheel-bearing test results with a pure chemical test such as induction time measurement. Undoubtedly, a grease with low mechanical stability will fail mechanically through oil separation/bleeding and leakage before it fails chemically.

The induction times reported in Figure 5.13 are for fresh greases. We now proceed to monitor the changes in the induction time of one fresh grease (Grease B) during purely chemical degradation process when exposed to high temperature in a heating chamber. As described in the setup test procedure with heating element (Section 5.3.2), grease samples were extracted from the heater for further testing. These greases were placed in the PDSC apparatus and their induction times were measured. Figures 5.14 and 5.15 show the heat flow curves measured at 200 °C by PDSC machine for two of the samples along with calculated induction times. As the grease samples experienced preheating in the heater setup, their induction times are less than that of the fresh grease (30.59 minutes). See Figure 5.8.

Figure 5.16 shows the induction time change of Grease B during the heating process at the heater setup for two temperatures of 140 °C and 165 °C. (The first point at time zero and induction time of 30.59 min. is common between both results and shows the induction time of fresh grease). Since the antioxidants are used during the heating process, the induction time of the grease decreases versus time. This happens faster in high temperatures.
Figure 5.14  Grease induction time measurement of Grease B after 2.6 hours preheating in heater setup at 140 °C

Figure 5.15  Grease induction time measurement of Grease B after 2 hours preheating in heater setup at 165 °C
The induction time monitoring for heating processes at higher temperatures of 180 °C and 210 °C was also performed using the grease samples extracted from the heater. However, for these temperatures, no rise in the heat flow was observed for the samples preheated for more than an hour. This also happened for the grease samples preheated for more than 3 hours at 165 °C. Figure 5.17 shows one of the induction measurement curves without any rise observed in the heat flow. Physically, this implies that the antioxidants are depleted in a short period of time in high temperatures, and induction time is not a proper parameter to monitor the entire chemical
degradation process. It will be shown in the following sections that the lubricating life of a grease is not fully exhausted at the onset of antioxidants’ depletion.

![Graph showing grease induction time measurement for Grease B after one hour preheating at 210°C.](image)

**Figure 5.17**  Grease induction time measurement for Grease B after one hour preheating at 210°C

The same process for induction time monitoring was followed for the Grease D. The induction times were measured by PDSC at 210 °C. The same process for induction time monitoring was followed for the Grease D. The induction times were measured by PDSC at 210 °C. Figure 5.18 shows the induction time change of Grease D during the heating process for two temperatures of 140 °C and 180 °C. (The first point at time zero and induction time of 40.82 min. is common between both results and shows the induction time of fresh grease).
Figure 5.18  Induction time change versus time for two preheating process at temperatures of 140 °C and 180 °C for Grease D grease measured by PDSC at 210 °C

5.3.3 Thermal Energy absorption

Electrical consumption of the heater setup introduced in experimental Section 5.2.3 was measured in different temperatures. Figure 5.19 shows the energy versus time at different test temperatures for Grease B.

Figure 5.19  Electrical energy consumed to maintain the temperature of the heater chamber at different test temperatures for Grease B
A part of the consumed energy is lost from the heater and a part of it is absorbed by the grease. As described in test procedure, the lost heat was measured by running the empty chamber at each temperature. Table 5.3 shows the measured heat lost for all testing temperatures.

Table 5.3 Measured heat lost in different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Heat lost per hour (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>8.55</td>
</tr>
<tr>
<td>110</td>
<td>14.37</td>
</tr>
<tr>
<td>125</td>
<td>17.10</td>
</tr>
<tr>
<td>140</td>
<td>19.95</td>
</tr>
<tr>
<td>165</td>
<td>24.80</td>
</tr>
<tr>
<td>180</td>
<td>27.48</td>
</tr>
<tr>
<td>210</td>
<td>32.00</td>
</tr>
</tbody>
</table>

The thermal energy which is absorbed by the grease sample is calculated after deducting the lost heat from the total energy consumed. Thermal energy absorption of Grease B is shown in Figure 5.20 for all testing temperatures.

Figure 5.20 Electrical energy absorbed by grease versus time for Grease B

The following points can be concluded from Figure 5.20. First, grease absorbs more energy in higher temperatures. Second, the energy absorption trend is more linear in lower temperatures
and is more curved in higher temperatures. Third, the rate of energy absorption (slope of the curves) decreases over time. Figure 5.21 shows the best curves fitted on the lowest and highest temperature results.

![Figure 5.21 Fitted curves on Fig 5.20 results](image)

Interestingly, a power equation is the best fitted equation with a high goodness of fit ($R^2 > 0.99$) for both the curves (lowest and highest temperatures) shown in Figure 5.21. This is also valid for other temperatures. Table 5.4 shows the curve fit results for all the test temperatures.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>a</th>
<th>b</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>0.859273</td>
<td>0.976393</td>
<td>0.999885</td>
</tr>
<tr>
<td>110</td>
<td>1.000489</td>
<td>0.972834</td>
<td>0.999271</td>
</tr>
<tr>
<td>125</td>
<td>1.622851</td>
<td>0.827506</td>
<td>0.999476</td>
</tr>
<tr>
<td>140</td>
<td>2.404413</td>
<td>0.657265</td>
<td>0.999386</td>
</tr>
<tr>
<td>165</td>
<td>3.882827</td>
<td>0.572494</td>
<td>0.998856</td>
</tr>
<tr>
<td>180</td>
<td>4.751787</td>
<td>0.531342</td>
<td>0.999705</td>
</tr>
<tr>
<td>210</td>
<td>5.673466</td>
<td>0.495141</td>
<td>0.999248</td>
</tr>
</tbody>
</table>
Figure 5.22 shows the change of power equation parameters $a$ and $b$ versus temperature. Changes in parameters $a$ and $b$ are insignificant at the temperatures lower than 110 °C. Physically, this implies that the oxidation reactions are still slow in this temperature range for the tested grease (This is not surprising for Grease B as it is categorized as a high temperature performance grease). Physically, this implies that the oxidation reactions are still slow in this temperature range for the tested grease (This is not surprising for Grease B as it is categorized as a high temperature performance grease). Parameter $b$ is very close to one at low temperatures which means the energy absorption versus time is almost linear for the temperatures below 110 °C. Increasing the temperature, parameter $a$ increases almost linearly and parameter $b$ decreases exponentially. The same behavior was also observed testing Grease D. Figure 5.23 shows the energy absorbed by Grease D at three different temperatures. For this grease also a power curve is the best fitted equation with a high goodness of fit ($R^2 > 0.99$). Table 5.5 shows the curve fit results for all the test temperatures.
Figure 5.23 Electrical energy absorbed by grease versus time for Grease D

Table 5.5 Power equation \(( a \cdot t^b)\) parameters and goodness of fit for results of Figure 5.23

<table>
<thead>
<tr>
<th>Temperature</th>
<th>(a)</th>
<th>(b)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>1.40132</td>
<td>0.73909</td>
<td>0.99949</td>
</tr>
<tr>
<td>180</td>
<td>3.10642</td>
<td>0.59060</td>
<td>0.99876</td>
</tr>
<tr>
<td>210</td>
<td>4.29199</td>
<td>0.53119</td>
<td>0.99235</td>
</tr>
</tbody>
</table>

Figure 5.24 shows the change of power equation parameters \(a\) and \(b\) versus temperature for Grease D. Similar trends observed for Grease B are also seen in the change of parameters \(a\) and \(b\) for Grease D.

Figure 5.24 Power equation parameters versus temperature for Grease D
5.3.4 Relation between thermal energy absorption and induction time

The induction time monitoring during chemical degradation was described in Section 5.3.2. The reductions in the induction time of fresh Grease B during 14 hours heating at 140 °C and also during 2 hours heating at 165 °C were presented in Figure 5.16. The thermal absorbed energy by the same grease during the same heating processes was also calculated in Section 5.3.3 and was presented in Figure 5.21. We proceed here to plot the changes in induction times versus absorbed energy for the heating processes. We proceed here to plot the changes in induction times versus absorbed energy for the heating processes. This is shown in Figure 5.25.

![Figure 5.25](image-url) Induction time vs absorbed energy for two preheating processes at temperatures of 140 °C and 165 °C for Grease B measured by PDSC at 200 °C

Interestingly, the induction time changes similarly for both heating temperatures versus absorbed energy. This shows that the grease absorbs similar amount of energy to degrade to a level regardless of temperature. The energy absorption occurs in a longer time when operating at a lower temperature and in a shorter time when operating at a higher temperature. This is also valid for Grease D. Figure 5.26 shows the changes in induction times versus absorbed energy for Grease D.
Figure 5.26  Induction time change versus absorbed energy for two preheating processes at temperatures of 140 °C and 180 °C for Grease D measured by PDSC at 210 °C

The physical meaning and importance of absorbed energy is described in next section.

5.3.5 Maximum energy absorption theory

It was shown that the energy absorption follows this power equation:

\[ E(\text{energy absorption}) = a \cdot (\text{time})^b \quad (5.5) \]

It was also shown that the exponent parameter \( b \) starts from one at low temperatures and decreases as temperature increases. The derivative of energy absorption is written as:

\[ E' = a \cdot b \cdot (\text{time})^{b-1} \quad (5.6) \]

Since \( b \) is less than one, \( E' \) approaches to zero when time goes to infinity. This means that the energy absorption function approaches to a maximum value when time goes to infinity. Assuming that the maximum value of the energy absorption is the same for the grease regardless of testing temperature, then all the curves in Figure 5.21 should approach to the same value as time approaches to infinity and the difference between the curves should become nil. Having the power
equation for each curve, the difference between each two curves can be calculated at any time. Therefore, the time that the difference between the two curves becomes very small can be calculated. This is the time that energy absorption approaches to its maximum. Our assumption about having the same maximum energy absorption for all the temperatures can be verified if the same maximum value is calculated using any two combinations of the curves. For example, the maximum energy absorption of Grease B is calculated here using the power equations of 165 °C and 210°C. From Table 5.5:

\[
\begin{align*}
E_{210°C} &= 5.673466 \text{time}^{0.495141} \\
E_{165°C} &= 3.882827 \text{time}^{0.572494} \\
E_{210°C} - E_{165°C} &\leq 0.001 \text{ when time } \approx 134.65 \text{ hrs}
\end{align*}
\]

Therefore, Maximum Energy Absorption for Grease B \(\approx 64.3 \text{ Watt-hours}\)

The energy absorptions at 134.65 hours were also calculated for other temperatures and are listed in Table 5.6.

**Table 5.6 Calculated energy absorption in different temperatures**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>(a)</th>
<th>(b)</th>
<th>(E @ t=134.65 \text{ hr}) (Watt-hours)</th>
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<tr>
<td>140</td>
<td>2.404413</td>
<td>0.657265</td>
<td>64.2844</td>
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<tr>
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<td>0.572494</td>
<td>64.2974</td>
</tr>
<tr>
<td>180</td>
<td>4.751787</td>
<td>0.531342</td>
<td>64.2844</td>
</tr>
<tr>
<td>210</td>
<td>5.673466</td>
<td>0.495141</td>
<td>64.3201</td>
</tr>
</tbody>
</table>

All the calculated energy absorptions are approaching to 64.3 Watt-hour. This is the maximum energy absorption for Grease B regardless of the oxidation temperature. The grease absorbs the same maximum energy at a longer time in lower temperature and at a shorter time in high temperatures. This phenomenon is demonstrated in the schematic of Figure 5.27.
The maximum energy absorption can also be calculated for Grease D using its power equations of 180 °C and 210°C. From Table 5.3:

\[ E_{210°C} = 4.29199 \text{ time}^{0.531197} \]

\[ E_{180°C} = 3.10642 \text{ time}^{0.590602} \]

\[ E_{210°C} - E_{180°C} \leq 0.001 \text{ when time } \approx 230.9 \text{ hrs} \]

Therefore, Maximum Energy Absorption for Grease D \( \approx 77.3 \text{ Watt-hours} \)

Using the grease power equation of 140 °C, it can be shown that the energy absorptions of the grease approaches to the calculated maximum energy absorption after 230 hours degrading at 140 °C.
Physically, the maximum energy absorption can be considered as the total energy required for the grease to burn completely and degrade to its final state when all of its chemical compounds are decomposed.

5.3.6 Maximum energy absorption versus activation energy

Referring to Section 5.3.1, the calculated activation energy of Grease B is $E_a = 157.13 \text{ kJ mol}^{-1}$. To gain further insight, it is worthwhile to calculate it for the whole grease sample (25 grams), convert its units to Watt-hour and compare it with the maximum energy absorption. In order to do so, the molar mass (g/mole) of the grease is required. Since grease is a complex material and contains several chemical components and additives, it is not possible to calculate its molar mass analytically. The molar mass of Grease B can be estimated from ASTM D2502 standard [6], and it is found to be 520 g/mole using the values of the grease’s base oil viscosity of 220 cSt at 40 °C and 16 cSt at 100°C. Using the estimated molar mass, the activation energy for each gram of grease is calculated as:

$$E_a = \frac{157315 \text{ J mol}^{-1}}{520 \text{ g mol}^{-1}} = 302.53 \text{ J g}^{-1}$$

For 25 grams of grease, the total value is:

$$E_a = 7563.22 \text{ J} = 2.1 \text{ Watt.hours}$$

The calculated activation energy is very small compared to the calculated maximum energy absorption of 64.3 Watt-hours. Referring to Figure 5.20, at high temperatures, the calculated activation energy (2.1 Watt-hours) is absorbed by the grease in a short period of time. This implies that in the chemical degradation process at high temperatures, the oxidation reactions initiate very
rapidly (at least for the outer layer of grease exposed to oxygen). The rest of the maximum energy absorption is used to decompose the grease thickener and base oil by breaking down the chemical bonds of the grease component molecules. The following two interesting phenomena were observed in our experiments.

First, the grease color changes to black during the heating process in the heater setup. It happens much faster in higher temperatures and the discoloration process starts from the outer layer of the grease which is directly exposed to oxygen and penetrates to inner layers as oxygen diffuses inside the grease. This means that the oxidation process is a gradual process which depends on the availability of oxygen and the diffusion speed of the oxygen.

Second, the blackened grease is still lubricous and contains oil even after 7 hours of degrading at 180 °C. Thus, the lubricating life of the grease is not completely diminished. It will be shown in the next section that the black grease can still lubricate a highly loaded contact for at least 18 hours.

5.4 Validation

The roller tester rig (Section 5.2.4) was used to chemically degrade several grease samples (by heating them in the rollers’ chamber) for different periods of time at different temperatures, and the remaining lubricating life of each grease sample was measured using the sample to lubricate the rollers. The traction behavior of the degraded grease was monitored to investigate the effectiveness of the grease. Failure is assumed when the traction curve experiences a rapid rise, which signifies the onset of damage to the rollers if the operation is allowed to continue. The traction behavior of the degraded grease was monitored to investigate the effectiveness of the grease. Failure is assumed when the traction curve experiences a rapid rise, which signifies the
onset of damage to the rollers if the operation is allowed to continue. The results of the test are used to validate the theory.

5.4.1 Test procedure

The roller tester machine was used in the last chapter to study the mechanical degradation at EHL contact between two rollers. The rig with the same configuration is used to study chemical degradation here. The roller tester machine was used in the last chapter to study the mechanical degradation at EHL contact between two rollers. The rig with the same configuration is used to study chemical degradation here. Figure 5.28 shows the grease chamber with the heating elements. The rig is calibrated and aligned as described in Section 4.4. At the first stage of the test, the grease sample is chemically degraded inside the chamber in a high temperature for specific time (several hours) while the rollers are not touching each other and primarily serve as a “grease mixer”. During this period, the lowest possible shear rate (0.025 m/s rolling speed, zero slide-to-roll ratio and 3 mm gap between the rollers) was applied. Here, the grease sample is blended during the heating process to create oxygen exposure condition for the whole grease sample, and the shear rate is kept low to minimize the mechanical degradation inside the grease sample. After the heating process, the heating elements are turned off and enough time is provided in order for the grease to cool down to the room temperature.

Here, the grease sample is blended during the heating process to create oxygen exposure condition for the whole grease sample, and the shear rate is kept low to minimize the mechanical degradation inside the grease sample. After the heating process, the heating elements are turned off and enough time is provided in order for the grease to cool down to the room temperature.
At the second stage of the test, the degraded grease—which is still in the chamber—is used to lubricate the contact between rollers and its lubricating ability is tested to determine the grease’s remaining useful life. The rollers are loaded with a maximum Hertzian pressure of 0.7 GPa and the rollers are rotating with the rolling speed of 0.065 m/s with a slide-to roll ration of 1.3 at room temperature. The traction force between the rollers is monitored during the test. When the traction force increases dramatically, the test is terminated automatically by a built-in stopping mechanism that halts the motors to avoid damaging the rollers and the rig. When the traction force increases dramatically, the test is terminated automatically by a built-in stopping mechanism that halts the motors to avoid damaging the rollers and the rig. This test was performed on Grease B at two temperatures of 180 °C and 210 °C. The heating period was 7 hours in both tests. Figures 5.29 and 5.30 show the traction force measurements in the second stage of the tests.
Comparing Figures 5.29 and 5.30, the first noticeable point is that by 30 °C increase in the test temperature (from 180 °C to 210 °C), the lubricating life of the grease decreases by a factor of 8.3. This dramatic life reduction in high temperatures was reported by other researchers as grease
life dropping in half for each 10 °C rise in temperature [7]. The second point is that the change in
the preheating temperature, did not noticeably affect the grease traction (measured in room
temperature in similar load and SR ratio).

From visual observation, the degraded grease was black in color and dry but remained
slippery. Slight vibration was observed in the rotation of the rollers during the lubrication life test.
This vibration is reflected in Figures. 5.29 and 5.30. The traction rises several times due to poor
lubrication condition, but it returns back to its normal value. This trend continues up to the test
termination point when the traction rises to a very high value and continuing the test could damage
the rollers’ surfaces. As pointed out previously, the machine was programmed to automatically
stop at this point prior to initiation of damage.

It is worthwhile to calculate and compare the absorption energy level of the greases after
preheating process at the two temperatures tested. Using the value of power equation reported in
Table 5.4, the absorption energy for Grease B after 7 hours heating is calculated as:

\[ E_{210^\circ C} = 5.673466 \times (7)^{0.495141} = 14.87 \text{ Watt.hours} \]

\[ E_{180^\circ C} = 4.751787 \times (7)^{0.531342} = 13.36 \text{ Watt.hours} \]

The time that it takes for a grease sample to reach to the same energy absorption level of
\( E_{210^\circ C} = 14.87 \text{ Watt.hours} \) while it is being heated at 180 °C is calculated from:

\[ E_{180^\circ C} = 4.751787 \times \text{time}^{0.531342} \]

If \( E_{180^\circ C} = 14.87 \text{ Watt.hours} \) yields time \( \approx 8.5 \text{ hours} \)

Therefore, the grease sample absorbs the same amount of thermal energy (14.87 Watt-
hours) either when it is heated for 8.5 hours at 180 °C or it is heated for 7 hours at 210 °C. Figure
5.31 shows the lubricating life test result after 8.5 hours preheating the grease sample at 180 °C.
The measured lubricating life of the grease is 2.36 hours which is close to the lubricating life of the grease after 7 hours preheating at 210 °C which was 2.23 hours.

Figure 5.31  Traction measurement of Grease B after 8.5 hours preheating at 180°C, Ur=0.065 m/s, SR=1.3, temperature =26 °C, maximum Hertzian pressure=0.7 GPa

5.4.2  Grease flow observation

Grease flow between the rollers was observed for fresh grease in chapter 4 (Section 4.6.2). It was shown that the fresh grease experienced three successive phases of “Fully grease covered rollers”, “Slippage and grease separation”, and “Formation of liquid lubricant reservoir”. The same experiment was performed here with the chemically degraded grease. The grease flow between the rollers was observed and captured for the degraded grease (preheated for 8.5 hours in the grease chamber at temperature of 180°C). Following are the descriptions of each phase with comparison with the same phase for fresh grease.

5.4.2.1  Phase 1: Fully grease covered rollers

Figure 5.32 shows the first phase of grease flow for both chemically degraded grease (Left picture) and fresh grease (Right picture). From visual inspection, the degraded grease is darker, and looks dried and non-uniform. The volume of the grease has also been decreased.
As it was described for fresh grease in Section 4.6.2.1, in the first phase both the rollers are fully covered with the grease for the first several minutes of the test. Visual observation revealed that grease tends to attach itself to the rollers from the bottom of the chamber and is carried into the contact region by the rotation of the rollers. Some of the grease passes through the contact by forming a full film while the rest tends to go around the sides of the rollers, bypassing the contact area. The moving grease tend to return to the contact repetitively and the rollers remain fully covered by thick layers of grease until the end of this phase which takes several minutes.

The following differences were observed for the first phase of degraded grease flow. The rollers are not fully covered with the grease at the beginning of the test. The tendency of the grease to attach to the rollers is less. The degraded grease looks dry in the first glance, however, because of the chemically broken thickener structure, it releases a large amount of base oil under high shear rate and stress in the EHL contact. The released oil color is green, which is different from the blue color of the base oil of the fresh grease. The first phase is ended after several seconds and grease slippage and separation (Phase 2) starts very soon due to the released base oil. The grease turns almost immediately to a mixture of separated degraded base oil and very soft broken degraded thickener.

Figure 5.32  Phase 1: Fully grease covered rollers, comparison between chemically degraded grease (Left picture) and fresh grease (Right picture)
5.4.2.2 Phase 2: Slippage and grease separation

As described in chapter 4 (Section 4.6.2.2) for the fresh grease, in the second phase, grease is suddenly separated from the rollers’ contacting surfaces. This first occurs in the roller with larger diameter and soon extends to both rollers. Physically, the portion of the moving grease in contact with the roller surfaces begins to slide on the surface of the rollers without being carried into the contact area by the rollers’ rotation. During the second phase (which lasted almost 10 minutes in our experiments), the rolling surfaces may occasionally become partially covered by grease, but this process becomes less frequent as time passes.

For the chemically degraded grease, the second phase was started sooner and lasted shorter. The separation happened on both rollers almost at the same time. Figure 5.33 shows the second phase of grease flow for both chemically degraded grease (Left picture) and fresh grease (Right picture). From visual inspection, the degraded grease breaks to a very soft (with low consistency) material after passing through the contact.

![Figure 5.33](image)

Figure 5.33 Phase 2: Slippage and grease separation, comparison between chemically degraded grease (Left picture) and fresh grease (Right picture)

5.4.2.3 Phase 3: Formation of Liquid lubricant reservoir

It was described for fresh grease in chapter 4 (Section 4.6.2) that during the final phase, no solid grease is observed on the rolling surfaces. The rolling surfaces are covered by a very thin
film of liquid lubricant which is highly mechanically degraded grease. It contains a mixture of base oil and destroyed thickener particles. Since the rollers are surrounded by solid grease on either sides of the rollers, the thin liquid layer which still lubricates the contact is constrained from leaving the contact—akin to a soft seal—and thus remains in the contact for a long period of time. A liquid lubricant reservoir is generated between the solid grease and rollers’ surfaces that feeds the contact continuously.

The importance of the solid grease walls/edges at the sides of the contact (to seal and keep the liquid lubricant in the contact) was emphasized in Section 4.7.1. It was shown that the solid grease walls/edges are subjected to low shear rate mechanical degradation which brake their sealing effect after a long period of time (several years).

For the chemically degraded grease, the formation of liquid lubricant reservoir and grease walls/edges was observed (Figure 5.34).

![Figure 5.34](image)

**Figure 5.34** Phase 3: Formation of Liquid lubricant reservoir, comparison between chemically degraded grease (Left picture) and fresh grease (Right picture)

Interestingly, since the degraded grease is softer than the fresh grease, at the exit of the contact when the edges are split, the grease edges are formed taller. The difference in the edges of degraded and fresh grease is shown in figure 5.35.
Although the grease edges are taller in the degraded grease, they are unable to seal the contact. The consistency of the grease at the edges was measured using our rheometer. The net penetration was measured $\Delta = 1.01$. Referring to Figure 3.4 from chapter 3, it implies that the grease edges have already crossed the maximum acceptable level. In chapter 4 (Section 4.7.2.2), it was calculated that the grease edges are mechanically degraded to the maximum acceptable level after 4.4 years. It is interesting that high temperature caused the same amount of degradation in 8.5 hours. Since in our validation experiments (Section 5.4), the chemically degraded greases were used to lubricate the contact, the grease edges were not able to seal the lubricant oil at the contact from the beginning of the test. The base oil also was a degraded oil. Thus the contact experienced poor lubrication from the beginning of the tests. This explains the source of vibration observed in the rotation of the rollers and the resulting fluctuations in traction reflected in Figures. 5.29, 5.30 and 5.31. The contact became starved after a short period of time (2.3 hours in Figure 5.31) as a result of broken sealing effect of grease edges and poor lubrication.

5.6 Conclusions

This chapter is devoted to the determination of a correlation between chemical degradation of lubricating grease and energy. Two different greases were chemically degraded
inside the heating chamber of the experimental setup, and their energy absorption during the heating process was measured accurately. A theory was introduced based on acquired experimental results. It was shown that the level of absorbed energy can be used to determine the state of chemical degradation regardless of temperature and time. A grease absorbs the same amount of energy when is heated in a shorter time at a higher temperature or in a longer time at a lower temperature. It was shown that for the tested greases, energy absorption versus time always follows a power equation in the format of \( E(\text{energy absorption}) = a. (\text{time})^b \). The power curves are linear \((b \approx 1)\) for lower temperatures and become nonlinear for higher temperatures. All the power curves are approaching to a maximum energy absorption value when time goes to infinity. Physically, the maximum energy absorption value can be considered as the total energy is given to the grease to burn completely and degrades to its final state when all of its chemical compounds are decomposed. The maximum energy absorption value was calculated for Grease B and it was compared to the measured activation energy of the grease. The theory was verified using a roller tester rig. According to the power equations of Grease B, the grease absorbs the same amount of energy when is heated for 7 hours at 210 °C or is heated for 8.5 hours at 180 °C. The same remaining lubricating life was measured by the roller tester rig testing two grease samples were heated for 7 hours at 210 °C and for 8.5 hours at 180 °C. This concept can be used to estimate the chemical life of a grease at different temperatures.

5.7 References


CHAPTER 6: SUMMARY AND FUTURE WORK

6.1 Summary and Conclusions

The present dissertation concentrates on the different degradation mechanisms that affect the lubricating life of the grease. While more than 90% of all rolling element bearings are grease lubricated, in most of the applications the lubricating life of the grease is shorter than the life of the other bearing components. Thus, the reliable functionality of the mechanical equipment is limited by the grease life. On the other hand, a systematic life prediction model for grease is lacking. As described in the literature survey (Section 1-3), the available models are empirically obtained by bearing manufacturers and are not necessarily applicable in different working conditions. This study attempted to develop a systematic life predicting model for lubricating grease. Two major degrading processes which are mechanical and chemical degrading were addressed in this dissertation. Following is a summary of all chapters:

- A comprehensive literature review on physical and chemical degradation monitoring and life estimation models for lubricating greases was presented in chapter one. Degradation mechanisms for lubricating grease were categorized and described, and an extensive survey of the available empirical and analytical grease life estimation models including degradation monitoring standards and methods were presented. A useful summary table of the important contributions on grease degradation was presented. It was shown that the mechanical and chemical degradations are the most important degrading mechanisms that limit the life of a grease. Examination of the literatures published on the grease degradation revealed that a practical analytical model to predict the grease life in different working
conditions is still unavailable. Grease degradation is an irreversible process and can be studied from an energy/entropy point of view. It was shown that grease degradation has not been studied from an energy/entropy point of view.

- Mechanical degradation was studied from an energy/entropy point of view in chapter two. The dissipated energy as a result of shearing of a grease breaks down the structure of the grease thickener and results in mechanical degradation. The principle of irreversible thermodynamics provided a promising tool for analyzing of grease in a shear process. Grease samples were sheared in the constant gap between the rheometer plates at different constant shear rates and temperatures. Accumulated dissipation energy and entropy generation were calculated for each testing condition. Net penetration values were also measured several times during each test to monitor mechanical degradation. Based on the experimental results, a strong linear correlation is found to exist between the rates of irreversible entropy generation and mechanical degradation (Penetration change) and also between the rates of energy dissipation and mechanical degradation. The linear correlations were called grease characteristic lines. The slope of the characteristic lines shows the durability of a grease and can be assumed as the associated “degradation coefficient” due to shearing. The degradation coefficient is a constant material property. A grease with a smaller degradation coefficient last longer. The results were verified experimentally using a rheometer, a journal bearing test rig, and a modified grease worker machine. It was shown that the degradation rate is linearly related to the entropy generation, and that it can be used for estimation of the mechanically degraded grease life.
Based on the correlation between thermodynamic entropy and grease mechanical degradation, a novel mechanical life prediction model was established and introduced in chapter three. The model uses shear stress, shear rate and temperature as functions of time. These parameters must be determined experimentally or predicted analytically. In this study, an ordinary differential equation (ODE) is derived for calculating shear stress as a function of time. The ODE shows that during the grease degradation the shear stress decreases exponentially. An experimental procedure is described for shear test which is used for measuring and calculating the exponential parameters of shear stress function. The shear stress function was validated for different grease types in different shear rates and temperature. Examples were presented to show how this development can be applied in practice in constant and variable shear rates.

In chapter four, the established mechanical life model introduced in chapter three was applied on the grease in an elastohydrodynamic (EHL) line contact between two grease-lubricated steel rollers. It was shown that at the contact, grease is highly degraded in a very short period of time (several minutes), and the highly degraded grease is sealed by the solid grease walls at the sides of the contact. The highly degraded grease continues to lubricate the contact as long as the walls sealing effect persists. The mechanical life prediction model was also applied to the grease walls at the sides of the EHL contact. It was shown that the sealing effect of walls persists for a long period of time (several years). The effect of mechanical degradation on the grease lubricating ability was also studied through the grease traction.
measurement and monitoring. Experimental procedure for grease traction measurement was described. Three lubrication phases were observed during grease lubrication. A theory was established to describe the physical meaning of the observed lubrication phases.

- Chemical degradation was studied from an energy point of view in chapter five. Two different greases were chemically degraded inside a heating chamber of an experimental setup, and their energy absorption during the heating process was measured accurately. A theory was introduced based on acquired experimental results. It was shown that the level of absorbed energy can be used to determine the state of chemical degradation regardless of temperature and time. A grease absorbs the same amount of energy when is heated in a shorter time at a higher temperature or in a longer time at a lower temperature. It was shown that for the tested greases, energy absorption versus time always follows a power equation in the format of \[ E(\text{energy absorption}) = a \cdot (\text{time})^b. \] The power curves are linear (\( b \approx 1 \)) for lower temperatures and become nonlinear for higher temperatures. All the power curves are approaching to a maximum energy absorption value when time goes to infinity. Physically, the maximum energy absorption value can be considered as the total energy is given to the grease to burn completely and degrades to its final state when all of its chemical compounds are decomposed. The maximum energy absorption value was calculated for two greases and it was compared to the measured activation energy of the greases. The theory was verified using a roller tester rig. According to the power equations of the grease, the grease absorbs the same amount
of energy when is heated for 7 hours at 210 °C or is heated for 8.5 hours at 180 °C. The same remaining lubricating life was measured by the roller tester rig testing two grease samples were heated for 7 hours at 210 °C and for 8.5 hours at 180 °C. This concept can be used to estimate the chemical life of a grease at different temperatures.

6.2 Recommendations for Future Work

The following topics are suggested for possible future research:

- A considerable research has been done on the grease flow in a contact and measurement and monitoring of the grease film thickness during time in a starved grease lubricated contact. The introduced mechanical life model can be used to estimate the grease structural changes during time. It can describe the grease flow in the contact and the changes in the grease film thickness in different working conditions.

- The chemical model and the power equation’s parameters introduced in chapter five can be developed through performing more tests on different greases.

- The base oil evaporation process can be studied from an energy point of view. The evaporation of the base oil of the grease can cause grease dryness which affects the lubricating ability of the grease. The evaporation process occurs in all temperatures and its rate increases in high temperatures. In low temperatures (less than 60 °C), the speed of the evaporation process is low and the lubricating life of a grease is limited by mechanical degradation. In very high temperatures (higher than 120° C), the speed of the base oil evaporation is high, but oxidation reactions are faster and
the lubricating life of the grease is limited by chemical degradation. In the middle
temperature range (between 60 ° C and 120 ° C), especially in the applications
where grease is exposed to high air flow, the evaporation of the base oil of the
grease is the dominant grease degradation process. Since less work has been done
on the base oil evaporation, its study from an energy point of view is recommended
as a future work.

- Depending on the working conditions of a grease (temperature, speed, load, air and
contamination exposure), one of the described physical or chemical degradation
processes limits the lubricating life of a grease. By performing a study on the
importance and speed of each of the degrading processes, generating a map that
shows the most important (dominant) degrading process at each working condition
is recommended.
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