TRIBOLOGICAL TESTING OF THERMALLY AGED GREASES

David Gonçalves¹(†), Armando Campos³, Beatriz Graça¹, Jorge Seabra²

¹INEGI, Universidade do Porto, Faculdade de Engenharia, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal
²FEUP, Universidade do Porto, Faculdade de Engenharia, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal
³ISEP-IIP, Instituto Superior de Engenharia do Instituto Politécnico do Porto, Portugal

(*)Email: degoncalves@inegi.up.pt

ABSTRACT

Non-additized batches of lubricating greases were subjected to an artificial thermal aging procedure. The fresh and aged samples were then tribologically characterized through film thickness measurements and Stribeck curves, over a large range of entrainment speeds on a ball-on-disc test rig at different operating temperatures, ensuring fully flooded conditions. The results were analysed at the light of the physical and chemical changes regarding the fresh greases.

The film thickness increased for all greases after the thermal aging. The film thickness plateau at low speeds also changed and for certain greases it disappeared under the same range of entrainment speeds. The friction behaviour also changed considerably.

Keywords: Lubricating greases, thermal aging, film thickness, friction behaviour.

INTRODUCTION

The grease aging in rolling bearings is characterized by permanent changes in its properties. According to Cann et al. [Cann, 2001], these changes depend mostly on the grease formulation (base oil viscosity and nature, thickener type), on the bearing geometry, material and type, on the bearing house and also on the rolling bearing operating conditions (mainly speed and temperature) and running time. Wear debris and water contamination have also been reported to promote grease aging [Hurley, 2001; Hurley, 2000a; Booser, 1953; Cann, 2007].

Different aging mechanisms are known to occur with grease when lubricating a rolling bearing, depending on the operating conditions. The aging can generally be grouped in mechanical and chemical changes. It is known that during operation at high temperatures the grease is continuously stressed thermally and mechanically, leading to chemical and physical changes. However, the way these changes affect the lubricity and the capacity to maintain a lubricating film are still unknown. Nonetheless, it is frequent for rolling bearings to fail primarily due to lubrication problems than by surface fatigue [Lugt, 2013].

The chemical/thermal aging of greases is still poorly studied. The oxidation of both thickener and oil can happen (as shown in a previous work [Gonçalves, 2015a] and it was found that this type of aging can also lead to grease softening or hardening depending on the grease formulation (thickener nature, base oil viscosity/nature) [Cousseau2015]. The oxidation is known to promote reaction/consumption of additives, acid formation, thermo-oxidative degradation of thickeners, polymerization of base oils, thermo-oxidative degradation of the base oils and also to promote the formation of varnish and sludge [Lugt, 2013; Cousseau,
However, the ways these changes modify the tribological behavior are unknown.

**METHODS AND MATERIALS**

**Tested Greases**

Four lubricating greases were tested in this work: M2, M5, MLi and MLiM, specifically manufactured for this work by Axel Christiernsson. The greases' main properties are shown in Table 1.

The polymer greases M2 and M5 were formulated with the same poly-alpha-olefin (PAO) base oil. Grease MLi was formulated with a mixture of two different grades of PAO and 5% ester (PAO+5%E), added to facilitate the saponification reaction. Finally, grease MLiM was formulated with a base oil of mineral (MIN) nature.

Regarding the thickener, greases M2 and M5 were formulated with polypropylene (PP). Greases MLi and MLiM were formulated with Lithium Complex (LiX) soap thickener. None of these greases is additized. However, grease M5 and MLiM where formulated with an elastomer (as co-thickener), which works as a viscosity improver of the oil bled by the grease under work [Goncalves, 2015b].

<table>
<thead>
<tr>
<th>Grease reference</th>
<th>M2</th>
<th>M5</th>
<th>MLi</th>
<th>MLiM</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thicker type</td>
<td>PP</td>
<td>PP</td>
<td>LiX</td>
<td>LiX</td>
<td>–</td>
</tr>
<tr>
<td>Base oil nature</td>
<td>PAO</td>
<td>PAO</td>
<td>PAO+5%E</td>
<td>MIN</td>
<td>–</td>
</tr>
<tr>
<td>Thicker content</td>
<td>13</td>
<td>13</td>
<td>17.5</td>
<td>10.6</td>
<td>%</td>
</tr>
<tr>
<td>Elastomer content</td>
<td>0</td>
<td>2.6</td>
<td>0</td>
<td>0</td>
<td>%</td>
</tr>
<tr>
<td>Worked penetration (ISO 2137)</td>
<td>269</td>
<td>249</td>
<td>276</td>
<td>279</td>
<td>10^{-1} mm</td>
</tr>
<tr>
<td>NLGI</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>–</td>
</tr>
<tr>
<td>Storage modulus</td>
<td>80 ºC</td>
<td>21</td>
<td>29.810</td>
<td>22.285</td>
<td>15.820</td>
</tr>
<tr>
<td>Loss modulus</td>
<td>4596</td>
<td>6209</td>
<td>7102</td>
<td>1861</td>
<td>Pa</td>
</tr>
<tr>
<td>Base oil viscosity (ASTM D445)</td>
<td>40 ºC</td>
<td>48.0</td>
<td>178.7</td>
<td>153.3</td>
<td>mm²/s</td>
</tr>
<tr>
<td>Bleed oil viscosity (ISO 12058)</td>
<td>100 ºC</td>
<td>8.0</td>
<td>21.4</td>
<td>15.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40 ºC</td>
<td>49.3</td>
<td>779.1</td>
<td>135.2</td>
<td>159.9</td>
</tr>
<tr>
<td></td>
<td>100 ºC</td>
<td>8.3</td>
<td>93.3</td>
<td>18.9</td>
<td>16.6</td>
</tr>
</tbody>
</table>

\(^a\) values measured at the LVE region, under a frequency of \(\omega = 1\) rad/s.

**Aging Process and evaluation methods**

The aging process was performed on a sample of each fresh grease. The sample was manually spread over a steel disk forming a layer thickness of approximately 1 mm. The process was intended to replicate the aging in grease lubricated rolling bearings and the grease interaction with the steel surface. Despite the layer thickness could have a considerable influence on the overall aging of the grease sample, it was found that for this aging time and temperature, 1 mm was enough to obtain an homogeneous sample of aged grease. Similar aging methods have been used by other authors [Hurley, 1998; Hurley, 2000a; Couronne, 2000], using grease layers of different thickness.

Both the polymer and the LiX thickened greases were thermally aged in the oven for ten consecutive days (240 h) at 120 ºC which is the maximum working temperature of the
polymer greases, indicated by the manufacturer for continuous use (the corresponding temperature for the LiX thickened greases is 150 ºC). The temperature of the oven was adjusted manually through a potentiometer, using a thermometer for the atmosphere temperature evaluation. Although there was no forced convection mechanism, the oven had a breathing hole on the top, allowing the chamber atmosphere to be refreshed. Care was taken to keep the temperature constant at all times.

After the aging process, the disc was removed from the oven to the room temperature and the grease was immediately collected in a container to avoid further aging.

The aged samples will be referred to with the suffix `a" for aged. These samples were evaluated through FTIR and rheology measurements. The FTIR spectra were obtained on an Agilent Cary 630 FTIR device, using an ATR (Attenuated total reflectance) accessory. The full wavelength range (650 to 4000 cm\(^{-1}\)) available for this device was tested. The samples were analyzed through direct comparison of height of the characteristic oxidation peaks between the samples spectra. All the spectra shown in this work were taken directly from the device's software without smoothing and a very good reproducibility was achieved. All spectra were normalized to the same peak's height at 1460 cm\(^{-1}\) [Hurley, 1998], allowing the comparison between samples.

The rheology measurements were performed on a Physica MCR 301 rheometer, using a smooth plate-plate geometry PP50 (ϕ= 49.998 mm). No rough of sand-blasted plates were available. The storage and loss moduli were measured in the linear visco-elastic region, under a frequency of 1 rad/s and at 80 ºC, one of the temperatures at which the film thickness and friction tests were conducted. A gap of 1 mm between plates was chosen and a pre-shear procedure was applied to each sample before the main test.

On the other hand, the dynamic viscosity of the bleed-oils was measured using the same plate-plate geometry but with a 0.1 mm gap. The rotational speed for these measurements ranged from 10\(^4\) up to 3300 rpm. Please refer to [Goncalves, 2015a] for more information regarding the rheology measurements.

**Film Thickness measurement procedure**

The EHD2 is an equipment produced by PCS Instruments which allows the measurement of the lubricant film thickness in ball-on-disc or roller-on-disc configuration, over different ranges of temperature, speed, load and slide-to-roll ratio (SRR).

The device uses the space layer interferometry method which allows the measurement of thin-films using the setup shown in Figure 1. Light is shone into the contact between the ball and the disc. Part of this light is reflected from the underside of the glass disc and some passes through any lubricant film and is then reflected back from the steel ball. Since the two beams of light have travelled different distances they interfere, resulting in an interference image from which the central film thickness can be computed. The test conditions are shown in Table 2. Before each test a heat period of 30 minutes was applied to ensure the temperature stabilization. After this period, the space layer thickness was measured at the disc track radius, without any lubricant between the ball and the disc. The entrainment speed was then ramped up 3 times ranging from ≈0.01 to 2 m/s and a combined curve of the three measurements was created. The fully flooded condition was ensured using a grease scoop which forced the grease back into the track. The temperature deviation at each ramp up was lower than ≈2 ºC from the average.
At the end of each ramp up, a zero speed film thickness was also measured, allowing to identify if the disc track has been damaged in the process (measuring a negative film thickness) and at the same time, measuring the residual film thickness between ball and disc. The zero speed film thickness is measured after unloading the ball and without entrainment speed. The full load (50 N) is then re-applied and the static film thickness is measured only after 5 secs, allowing the squeezed film to spread. An average of three measurements for each grease was calculated.

**Table 2**

<table>
<thead>
<tr>
<th>EHD2 - Ball-on-disc film thickness test conditions.</th>
<th>Steel ball</th>
<th>Disc</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius – ( R_{x,y} )</td>
<td>9.525</td>
<td>—</td>
<td>mm</td>
</tr>
<tr>
<td>Roughness – ( R_a )</td>
<td>( \leq 20 )</td>
<td>( \approx 5 )</td>
<td>nm</td>
</tr>
<tr>
<td>Material</td>
<td>AISI 52100</td>
<td>Glass</td>
<td>—</td>
</tr>
<tr>
<td>Elastic modulus – ( E )</td>
<td>207</td>
<td>64</td>
<td>GPa</td>
</tr>
<tr>
<td>Poisson coefficient - ( \nu )</td>
<td>0.29</td>
<td>0.20</td>
<td>GPa</td>
</tr>
<tr>
<td>Load – ( L )</td>
<td>50</td>
<td></td>
<td>N</td>
</tr>
<tr>
<td>Hertzian pressure – ( p_0 )</td>
<td>( \approx 0.7 )</td>
<td></td>
<td>GPa</td>
</tr>
<tr>
<td>Entrainment speed – ( U_0 )</td>
<td>0.01–2</td>
<td></td>
<td>m/s</td>
</tr>
<tr>
<td>Slide-to-roll ratio – SRR</td>
<td>3</td>
<td></td>
<td>%</td>
</tr>
<tr>
<td>Temperature – ( T )</td>
<td>60, 80, 110</td>
<td></td>
<td>ºC</td>
</tr>
</tbody>
</table>

**Stribeck curves measurement procedure**

The Stribeck curves curves are generally measured at controlled temperature, constant load and constant SRR, while varying the entrainment speed. The entrainment speed and SRR are defined according to the equations below:

\[
U = \frac{u_{\text{disc}} + u_{\text{ball}}}{2}
\]

\[
SRR = 2 \cdot \frac{|u_{\text{disc}} - u_{\text{ball}}|}{u_{\text{disc}} + u_{\text{ball}}}
\]
The Hertzian contact pressure of these tests was ≈1.09 GPa, for a load of 50 N. The geometry, surface roughness and load involved in the Stribeck curve tests are shown in Table 3. A rough disc was used (Ra≈ 300 nm).

The curves were obtained at constant SRR of 5 or 50 %, at different operating temperatures, according to the procedure shown in Table 4.

Fully flooded conditions were assured by using a grease scoop.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Steel ball</th>
<th>Steel rough disc</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{xy}$ (mm)</td>
<td>9.525</td>
<td>–</td>
</tr>
<tr>
<td>$Ra$ (nm)</td>
<td>≤ 20</td>
<td>≈ 300</td>
</tr>
<tr>
<td>Material</td>
<td>AISI 52100</td>
<td></td>
</tr>
<tr>
<td>$E$ (GPa)</td>
<td>207</td>
<td></td>
</tr>
<tr>
<td>$\nu$ (–)</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>Load (N)</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>$P_{max}$ (CPa)</td>
<td>≈ 1.09</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4**

EHD Stribeck curves measurement procedure.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>40, 80</td>
</tr>
<tr>
<td>Entrainment speed (m/s)</td>
<td>0.04→2</td>
</tr>
<tr>
<td>SRR (%)</td>
<td>5, 50</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

**Infra-Red Spectroscopy**

In Figure 2, the FTIR spectra of both the fresh and aged samples of each lubricating grease are shown. It is possible to observe that all aged samples show different spectrum from its fresh grease. As previously analyzed in [Goncalves, 2015a; Goncalves, 2015b], the differences observed are related to oxidation and to the formation of certain compounds (esters, ketones, etc.) which lead to an increase in the viscosity of the greases' bleed-oil.

The rise of the peaks at around 1700 and 1150 cm$^{-1}$ is very often associated with oxidation and a clear indication of the different oxidation resistance of the PP thickened greases regarding the LiX thickened greases (see Figure 3 for the comparison of aged greases' spectra at the fingerprint region). Furthermore, the thermal aging is also responsible for the loss of oil through evaporation, which is very relevant for grease M2 and M5 through the reduction of the peaks at 2920 and 2850 cm$^{-1}$ and also the relative increase of the peak at 1376 cm$^{-1}$ regarding the peak at 1460 cm$^{-1}$. 

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Regarding the peaks' height at 1700 and 1150 cm\(^{-1}\), the following relationship can be established:

\[
M5a > M2a > MLia > MLiMa.
\]

According to the FTIR results, the spectra of all the aged samples showed signs of oxidation. However, depending on the grease formulation, this oxidation was more or less severe. The aged PP thickened greases M2a and M5a showed higher oxidation peaks, followed by grease MLia and then by MLiMa. The reason behind this is related to the fact that the maximum working temperature of the PP thickener is 120 °C while the LiX thickener can
work up to 150 °C. Moreover, greases M2 and M5 were formulated with a base oil of lower viscosity and therefore, more prone to be released from the grease and to evaporate. Grease MLiM was formulated with mineral base oil which is known to withstand high operating temperatures without changes in its properties and therefore, combined with the LiX thickener, it was the grease showing less degradation.

Rheology measurements

The rheological properties of the aged grease samples are shown in Table 5, as well as the viscosity of the bleed-oils obtained from these aged samples.

<table>
<thead>
<tr>
<th>Grease reference</th>
<th>M2a</th>
<th>M5a</th>
<th>MLia</th>
<th>MLiMa</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage modulus $G'$</td>
<td>80 °C</td>
<td>1942</td>
<td>573</td>
<td>27830</td>
<td>48825</td>
</tr>
<tr>
<td>Loss modulus $G''$</td>
<td>382</td>
<td>256</td>
<td>8262</td>
<td>10618</td>
<td>Pa</td>
</tr>
<tr>
<td>$\Delta = 100 \cdot \frac{aged - fresh}{fresh}$</td>
<td>$\Delta G'$</td>
<td>-90.9</td>
<td>-98.1</td>
<td>24.9</td>
<td>208.6</td>
</tr>
<tr>
<td>$\Delta G''$</td>
<td>-91.2</td>
<td>-95.7</td>
<td>16.3</td>
<td>470.6</td>
<td>%</td>
</tr>
<tr>
<td>Bleed oil viscosity (ISO 12058)</td>
<td>40 °C</td>
<td>n.a.</td>
<td>n.a.</td>
<td>395.7</td>
<td>295.7</td>
</tr>
<tr>
<td>100 °C</td>
<td>n.a.</td>
<td></td>
<td>42.0</td>
<td>23.9</td>
<td></td>
</tr>
<tr>
<td>$\Delta = 100 \cdot \frac{aged - fresh}{fresh}$</td>
<td>40 °C</td>
<td>-</td>
<td>-</td>
<td>192.3</td>
<td>84.9</td>
</tr>
<tr>
<td>100 °C</td>
<td>-</td>
<td>-</td>
<td>122.2</td>
<td>44.0</td>
<td>%</td>
</tr>
</tbody>
</table>

Analysing the values of the storage and loss moduli and comparing them to the values of the fresh samples, two behaviours can be observed:

- decrease of the moduli for the PP thickened greases - grease softening;
- increase of the moduli for the Li thickened greases - grease stiffening.

Similar results had already been reported in other works but for smaller aging times [Goncalves, 2015a; Goncalves, 2015b; Cousseau, 2013].

Following the storage and loss moduli values at 80 °C, the following relationship can be established:

$$G'_{MLiMa} > G'_{MLia} > G'_{M2a} > G'_{M5a};$$
$$G''_{MLiMa} > G''_{MLia} > G''_{M2a} > G''_{M5a}.$$

The oxidation observed on the FTIR spectra contributes to the changes in the rheological properties. The fact that grease M2a and M5a showed much smaller storage and loss moduli indicates loss of mechanical stability - softening. On the other hand, the LiX thickened greases got stiffer resulting into reduced mobility.

Regarding the viscosity of the bleed oils, it was not possible to obtain bleed-oil from greases M2a and M5a using the method described in [Goncalves, 2015a] for the same temperature and centrifuge speed. In the case of greases MLia and MLiMa, their bleed-oils showed an increased viscosity regarding the fresh samples (see Table 5) which is a result of the oxidative
process observed on the FTIR spectra, caused by the formation of oxidation products like esters, ketones and carbonyl compounds. Despite it was not possible to obtain oil from the aged greases M2a and M5a, the viscosity of their bleed-oils is expected to have greatly increased [Goncalves, 2015a]. The higher viscosity should be responsible for the more difficult oil release, retarding the bleed-rate [Baart, 2010a; Goncalves, 2015a].

The following relationship should be expected, regarding the bleed-oil viscosity:

\[ M5a > M2a > MLia > MLiMa. \]

**Film thickness results**

The film thickness variation with the entrainment speed for the fresh and aged greases, is shown in Figure 4, at the operating temperatures of 60, 80 and 110 °C. For fresh greases it is possible to observe that the film thickness increases at a rate of \( U^{0.67} \), under moderate to high speeds. This behavior is due to more a pronounced hydrodynamic effect, as the entrainment speed increases [Reynolds, 1886].

Under this regime, the following relationship can be found, for the curves at any operating temperature:

\[ MLi > MLiM > M5 > M2 \]

showing that the film thickness is higher for the greases formulated with base oils of also higher viscosity. With the decrease of the entrainment speed, the hydrodynamic effect is reduced and the film thickness also decreases, up to the point where this tendency ends. At this point, two behaviors could be identified, depending on the thickener type:

- **PP thickener:** the film thickness quickly rises at a very high rate as the entrainment speed continues to decrease, until it finally reaches a plateau at a very high film thickness value;
- **LiX thickener:** the decrease of film thickness ends and a plateau is reached but at much lower film thickness, than the PP greases.

At low entrainment speeds, the film thickness plateau of the fresh greases, shows this relationship:

\[ M2 > M5 > MLiM > MLi. \]

It is interesting to notice that, as the temperature increases and the lubricant's viscosity decreases, the film thickness also decreases but only under moderate to high entrainment speeds. Under low entrainment speeds, the film thickness seems to be fairly insensible to the temperature variation. However, the speed at which the transition between the two different behaviors occurs is not. This transition speed is higher when the operating temperature is also higher. This phenomenon was verified for all the tested greases and should be related to the decrease of the greases' consistency with temperature and the way it affects the replenishment.

After the thermal aging and following the chemical and physical changes of the greases, several differences were found. First, all aged samples produced higher film thickness, particularly greases M2a and M5a which showed a much higher film thickness regarding the fresh greases. On the other hand however, the film thickness plateau could not be found, under the same range of entrainment speed.
In the case of the aged LiX thickened greases MLia and MLiMa, the film thickness increased not only under moderate to high speeds but also at low speeds where the plateau was found. After the aging, the film thickness under fully flooded condition and $U \geq 0.2$ m/s, follows the order:

$$M5a > M2a > MLia > MLiMa.$$ 

The film thickness increased for all the tested greases but such increase was much smaller for the LiX thickened greases which were also less oxidized. On the other hand, grease M5a and M2a, highly oxidized, showed much higher film thickness than the fresh samples, which supports the theory that the active lubricant inside the contact is now of much higher viscosity. It is also interesting to notice that the film thickness plateau at low to moderate speeds was not found for greases M2a and M5a. In the case of grease MLia and MLiMa, the
plateau was found but the transition now occurs at higher speeds and at higher film thickness values than for the fresh samples.

The fact that the film thickness increased under fully flooded conditions indicates that the lubrication regime might also have changed, for the same fully flooded conditions.

**Striebeck curves**

The friction behavior of each grease was studied at two different temperatures and also different SRR values, through the measurement of Striebeck curves. In order to better understand the behavior of the coefficient of friction (COF) curves, it is necessary to plot each curve with its own abscissa.

For this purpose, a parameter similar to one originally used to represent Striebeck curves [Streibk, 1903] was developed, as represented in the equation below:

$$S_n = \frac{\eta^{0.67} \cdot U^{0.67} \cdot \alpha^{0.53}}{R_x^{0.39} \cdot F^{0.14}}$$

This dimensionless parameter “normalizes” the abscissa of the curves, allowing a better comparison of the COF of different lubricants, when tested with the same surface’s geometry ($R_x$), roughness and material. It takes into account the operating conditions ($U, F$) and the lubricant properties ($\eta, \alpha$) at the average operating temperature of the test. The inclusion of the pressure-viscosity coefficient (\(\alpha\)) is the way to account for the different natures of the lubricants, if their viscosity at the operating temperature is the same. Furthermore, the combination of the viscosity and pressure-viscosity ensures that the film thickness influence is taken into account, which is not the case with the original Striebeck parameter given by $\eta \cdot U_0 \cdot F^{-1}$ [Streibek, 1903]. The modified parameter allows plotting the COF as function of different lubrication regimes zones based on the behavior of a typical Striebeck curve [Brandao, 2011; Streibek, 1903].

This $S_n$ parameter was based on another dimensionless parameter developed by Brandao et al. [Brandao, 2011], shown here in the following equation:

$$S_p = \frac{\eta \cdot U \cdot \alpha^{0.5}}{F^{0.5}}$$

In the equations for $S_n$ and $S_p$, the values of ($\eta, \alpha$) are generally attributed to the base oil properties of the greases. However, the properties of the greases changed considerably with the aging process. Furthermore, their aged bleed-oils are significantly different from the original base oils and it was not possible to obtain them for some of the greases.

Therefore, a different method had to be used in order to calculate the Striebeck modified parameter. Using the measured values of film thickness at moderate to high speeds ($H_{exp}$) shown in Figure 4 and the Hamrock and Downson formula [Hamrock, 1977] to predict the film thickness in this region ($H_{0c}$), it is possible to quickly estimate the product $\eta^{0.67} \cdot \alpha^{0.53}$:

$$H_{0c} = H_{exp} \rightarrow H_{0c} = f(\eta, \alpha) = K \cdot \eta^{0.67} \cdot \alpha^{0.53}$$

Obtained from each film thickness curve at different operating temperatures, the product $\eta^{0.67} \cdot \alpha^{0.53}$ allows calculating the $S_n$ parameter for any temperature. A similar approach had already been developed by Van Leeuwen et al. [Leeuwen2009, VanLeeuwen2011] to calculate...
the pressure-viscosity coefficient from film thickness measurements, method which was contested by other authors [Kudish2008, Krupka2009a], claiming that it provides very inaccurate predictions of the pressure-viscosity value when compared to high-pressure rheology measurements.

Knowing the value the \( \eta^{0.67} \cdot \alpha^{0.53} \) product previously calculated from the film thickness measurements, it is now possible calculate the specific film thickness for the operating conditions of the Stribeck curves, according to equation:

\[
\Lambda = \frac{H_{0C}}{\sigma}
\]

The composite roughness of the surfaces \( \sigma \) was calculated through equation:

\[
\sigma = \sqrt{\sigma_1^2 + \sigma_2^2}
\]

The results for each grease at different operating conditions are shown in Figure 5. These curves are not representative of the real grease behavior since they do not contemplate the film thickness plateau at low speeds. However, it is possible to define the \( S_p \) numbers which correspond to the transitions between lubrication regimes, according to Spikes [Spikes, 1997]:

- **EHD**: \( \Lambda \geq 3 \Rightarrow S_n \geq 9.8 \times 10^{-5} \);
- **Mixed film**: \( 0.5 \leq \Lambda \leq 3 \Rightarrow 1.6 \times 10^{-5} \leq S_n \leq 9.8 \times 10^{-5} \);
- **Boundary film**: \( \Lambda \leq 0.5 \Rightarrow S_n \leq 1.6 \times 10^{-5} \).

In Figure 6, the measured Striebeck curves of fresh and aged greases are shown plotted against \( S_n \). The previously stated lubrication regime transitions are also represented. The same curve behavior is obtained if \( S_p \) [Brandão, 2011] is used instead.

According to this figure, it is possible to verify the different behavior of the fresh greases depending on the thickener type. Starting from high \( S_n \) numbers (and therefore, high rolling speeds), the fresh polymer greases start from mixed lubrication, while greases MLI and MLIM start from full film lubrication at 40 °C. As the rolling speed decreases, the COF increases until boundary lubrication is reached. At this point, two different behaviors are observed depending on the thickener type. The COF curve of greases M2 and M5 reaches a maximum value upon entering boundary lubrication and then, the COF starts decreasing again.

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Fig. 5 - Specific film thickness curves of the tested greases, calculated for different operating conditions.
On the other hand, the COF curves of the LiX thickened greases MLi and MLiM keep rising but at a smaller slope, reaching a plateau at very low $S_n$ numbers. The described behavior is more pronounced as the temperature increases, and the curves move to the left, towards boundary lubrication. The same behavior was observed for higher SRR ratio, even though the COF values are much higher, as expected.

An overall relationship can be established regarding the fresh greases' results under mixed lubrication:

$$\text{MLiM} > \text{MLi} > \text{M2} > \text{M5}$$

![Fig. 6 - Striebeck curves of the fresh and thermally aged greases at different operating conditions](image)

After the aging, the greases show a very different behavior. Given the previously shown film thickness increase, it is expected that the $(\eta, \alpha)$ values also increased and therefore, the COF curves of all greases now start at $S_n$ numbers which should refer to full film lubrication.
While the curve's behavior of greases MLia and MLiM a did not show much difference besides starting at higher $S_n$ numbers, in the case of greases M2a and M5a, the curve behavior is now much different. The COF of grease M2, measured under the same operating conditions, increases with the decrease of the entrainment speed as it goes from full film up to almost mixed film lubrication. The inflection previously observed for the fresh grease was not found.

On the other hand, grease M5 shows an even more different behavior. The COF decreases with the increase of the entrainment speed under full film lubrication until it reaches a minimum value. However, at 40 °C and for a SRR of 5 or 50 %, the COF starts to increase again at a very high rate up to the point where it suddenly drops. As the lubricant film builds up, given the combination of high $(\eta, \alpha)$ and high speeds, the coefficient of friction quickly rises by the increase of viscous friction. With the increasing speed, the contact should starve under high speeds leading to a quick decrease the COF explaining the inflexion on the curve. At 80 °C, the consistency of the grease is smaller and this phenomenon was not observed.

As it happened with the film thickness curves, the Strubeck curves of grease MLi and MLiM did not change considerably after the thermal aging procedure. The curves moved down and to the right (towards higher $S_n$ numbers), following the increase of the film thickness, but the COF behaviour is very similar, supporting the results which showed that the thermal aging at 120 °C was not very effective in quickly degrading these greases. Once again, the largest differences were found for samples M2a and M5a. These aged samples, for the same operating conditions, now do not reach boundary lubrication and therefore, the inflexion observed on the COF curve of the fresh greases M2 and M5 was not found for the aged samples. These greases, under fully flooded conditions now seem to run mainly under full film lubrication, only reaching mixed film lubrication at higher temperatures.

CONCLUSION

Following a previous work on the physical and chemical changes promoted by the thermal aging [Goncalves, 2015a], this work focused in analyzing the effect of thermal aging in the tribological behavior of differently formulated lubricating greases, in terms of film thickness and friction behavior. Four greases were tested, formulated with base oils of different nature, different thickener type and co-thickener content. The tests were performed with fresh and artificially aged samples and the results compared.

The following conclusion can be drawn:

- The thermal aging is responsible for the formation of oxidation products as ketones, esters and carbonyl compounds, easily identified through FTIR measurements;
- It is also responsible for the changes in the grease's rheology. The polymer thickened greases became softer and the lithium thickened greases became stiffer;
- The oxidation products highly contribute to the increase of the bleed-oil's viscosity. The micro-structural changes, coupled with the rheological changes and the increased bleed-oil viscosity, retard the bleed-rate and therefore it was not possible to obtain bleed-oil of the highly oxidized samples of aged polymer thickened greases;
- The film thickness of all aged samples increased, independently of the thickener type, base oil nature or viscosity. However, this increase was particularly important in the case of the severely oxidized samples of the polymer thickened greases whose film thickness highly increased;
• The typical film thickness plateau at low speeds was not found for the aged polymer thickened greases, while for the lithium thickened greases, the plateau was almost unchanged;

• Strubeck curves of fresh and aged samples were also performed. Plotted against a dimensionless parameter which reflects the measured film thickness behavior, the Strubeck curves showed good correlation with the specific film thickness predictions and therefore, it is possible to easily define the lubrication regime of each test;

• The aged polymer thickened samples show very different COF behavior, clearly operating under a different lubrication regime since the COF values are also much different. Once again, the lithium thickened greases follow all the previously stated results and did not show very different behavior prior and after the aging.

The results shown in this work indicate that the thermal aging leads to a higher film thickness however, it should be noticed that these are not grease life tests or any representation of it. Moreover, these test were all conducted under fully flooded conditions, which are known to happen only in the first phase of grease lubrication of rolling bearings, which is generally very short [Lugt, 2013]. The ability to effectively separate the surfaces under starved conditions or how the oxidation reduces the grease life upon failure are unknown, and should be studied more thoroughly. The way oxidation affects the replenishment or even the protection of the surfaces against wear and oxidation were not studied but should also be very important.

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