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MOLYVAN® 3000 Friction Reducer is an exceptional oil soluble MoDTC friction modifier containing 10% molybdenum with antiwear and antioxidant properties. Its unique molecular branching provides superior fluid compatibility/stability at low temperature and enhanced robustness for improved retention of friction reduction in aged oil.
Grease Production, CO2 emission...a New Relationship!
Mehdi Fathi Najafi, Andreas Dodos, George Dodos, John Kay

Back to the Basics -
The ABC's of Grease Additive Performance
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Measuring and Modeling Effects of Shearing on Grease
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NLGI Interviews Ms. Melissa J. Quinn
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Water Washout Remedies
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Awards Committee Update

Joe Kaperick
Afton Chemical
NLGI President 2018-2020

Recognition

noun rec·og·ni·tion | re-kig-'ni-shən, -kəg-

Definition
1 : the action of recognizing : the state of being recognized: such as
a : acknowledgment especially : formal acknowledgment of the political existence of a government or nation
b : knowledge or feeling that someone or something present has been encountered before
2 : special notice or attention

Above is the definition of the word Recognition. This year the word RECOGNITION can take on added meaning, for you can play a key role in having an NLGI colleague recognized at the NLGI Annual Meeting in Miami, FL.

Each year, at the NLGI Annual Meeting, distinguished individuals are recognized for their efforts in advancing knowledge and understanding in the grease industry. The NLGI strives to recognize and honor those who have furthered themselves, their company and this industry. Most likely you know of an individual who is deserving of special recognition. Make this the year that you spring into action by nominating someone for one of the following NLGI Awards:

- **NLGI Award for Achievement** – The Institute’s highest award honors the achievement of those who have made exceptional contributions to the growth and development of the Institute.
- **NLGI Fellows Award** – Acknowledges valuable work within the Institute, in the technical development of greases, grease tests, or the promotion of grease usage.
- **John A. Bellanti Sr. Memorial Award** – Acknowledges meritorious service on the NLGI Board, or on Technical Committee projects or to the industry.
- **NLGI Honorary Membership** – Entitles lifetime honorary membership to those who, over a period of years, have served the Institute in some outstanding capacity and are not now with a member company.
- **Award for Educational Excellence** – For outstanding instruction as exemplified by subject knowledge and presentation skills in NLGI educational courses.
- **NLGI Author Award (Development)** – For the best paper presented at our Annual Meeting that focuses on formulation, development, and manufacture of finished greases.
- **NLGI Author Award (Application)** – For the best paper presented at our Annual Meeting that focuses on testing, selection, application or use of greases
- **Clarence E. Earle Memorial Award** – For an outstanding contribution to the technical literature relating to lubricating greases during the year.

If you have thought about nominating someone in the past, then now is the time to act! The next NLGI Annual Meeting will be held June 14-17, 2020 at the fabulous JW Marriott Miami Turnberry Resort & Spa in Miami, FL. Imagine the pride you will feel should your nominee be recognized, among their peers, with an NLGI Award. Thank you in advance for your participation. We hope to welcome you to the JW Marriott Miami Turnberry Resort & Spa in June!

The 2020 deadline for nomination is March 1, 2020. NLGI will also accept nominations for 2021. Click here for awards nomination form. Click here.

Patrick Walsh, Chair
Chuck Coe, Joe Kaperick, Anoop Kumar, David Turner
### Warm Welcome to our New NLGI Members

<table>
<thead>
<tr>
<th>Year</th>
<th>Company</th>
<th>Type</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>2019</td>
<td>Gulf Western Oil</td>
<td>Manufacturer</td>
<td>Australia</td>
</tr>
<tr>
<td></td>
<td>Blumenthal Brands Intergrated</td>
<td>Manufacturer</td>
<td>USA</td>
</tr>
<tr>
<td>2020</td>
<td>Colonial Chemical Inc.</td>
<td>Technical</td>
<td>USA</td>
</tr>
</tbody>
</table>

### Industry Calendar of Events

Please contact Denise if there are meetings/conventions you'd like to add to our Industry Calendar, denise@nlgi.org

(Your company does not have to be an NLGI member to post calendar items.)

<table>
<thead>
<tr>
<th>Date</th>
<th>Event Description</th>
</tr>
</thead>
</table>
| Feb 1 - 3, 2020 | NLGI India Chapter 22nd Lubricating Grease Conference  
Marriott Hotel, Indore, India |
| March 9 - 11, 2020 | ALMU – Annual Meeting & Global Leadership Summit  
Bangkok, Thailand |
| April 2 - 4, 2020 | ILMA – Engage Spring Conference  
Omni Grove Park Inn, Asheville, NC |
| April 25 - 28, 2020 | ELGI – 32nd Annual General Meeting  
Grand Elysee Hotel Hamburg, Germany |
| May 3 - 7, 2020 | STLE – 75th Annual Meeting & Exhibition  
Hyatt Regency Chicago, Chicago, IL |
| June 14 - 17, 2020 | NLGI – 87th Annual Meeting  
JW Marriott Miami Turnberry Resort & Spa, Miami, FL |
| Oct 24 - 27, 2020 | ILMA – 2020 Annual Meeting  
Boca Raton Resort & Club, Boca Raton, FL |

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- Lubes’n” Greases, page 68
- Patterson Industries Canada – a Division of All-Weld Company Limited, page 69
- Petro-Lubricant Testing Laboratories Inc., page 70
- ProSys Servo Filling Systems, page 72
- Vanderbilt Chemicals, LLC, IFC
Abstract
Manufacturing conventional (simple) lithium grease is a very energy intensive operation and, surprisingly, to the knowledge of these authors, no one prior to a recent technical paper \cite{1} has studied the relationship between energy consumption, possible environmental impact of the grease manufacturing process and the choice of base oil. It is well known that carbon dioxide (CO2) is the major contributor to greenhouse gas (GHG) emissions. Global warming can be related directly to man-made GHG emissions, especially from industrial activities. Furthermore, emissions of CO2 depend directly on the energy efficiency of manufacturing processes and indirectly on their requirements for electric power generation.

The aims of this paper are to report the results of measurements of energy consumption for industrial-scale production of conventional lithium greases and compare the use of a pressurized reactor versus a traditional open kettle. All process parameters were kept constant. The selected based oils were naphthenic and paraffinic Group I (VG ISO 100 and VG ISO 220) that are used typically in the preparation of lubricating greases.

Energy consumption, electrical for mechanical operations such as pumping, mixing and homogenizing, and fuel for heating, was recorded for all production stages: vessel charging, cooking, cooling/diluting and homogenizing. The measured energy consumption for each batch was then converted to normalized CO2 emissions and savings in utilities. In order to make this comparative study more accurate, the finished greases were characterized according to the specifications required by the end-users.

In total, eight full-scale lithium-based NLGI grade 2 greases were manufactured, 8000 kg per batch, using two different base oil viscosities. For a standard NGLI Grade 2 simple lithium grease, an overall reduction in CO2 emissions of 34 percent per metric ton of grease was found when a pressurized Contactor reactor with ISO VG 220 oil (a blend of paraffinic and naphthenic oils) was employed instead of an open kettle with ISO VG 100 paraffinic oil. The outcome of this study could be a milestone in assessing grease production in terms of significant reduction of CO2 emissions and greater awareness of the impact of the grease industry on the global environment.

Keywords
Lubricating grease, Manufacture, Energy, CO2 emissions, Carbon footprint, Paraffinic oil, Naphthenic oil, Pressurized reactor, Open kettle
1. Introduction
The basic technology for production of soap-type greases has been essentially unchanged for the last fifty or more years. This is certainly true for the type of lubricating grease that is most commonly used in the global market, namely lithium-based greases, which typically represent 75 percent of global grease production [2]. In contrast, grease products are becoming ever more sophisticated and suitable for high-end and extremely demanding applications, often thanks to the use of more effective additives.

Grease manufacturers are witnessing a number of challenges, such as a rapid increase in the price of lithium hydroxide due to the extremely fast growth of the lithium-based battery industry. Some recent publications (e.g., Fathi-Najafi and Kay [3]) suggest that by using high viscosity naphthenic oils, the percent thickener content could be reduced to approximately 4.6 (wt.%) in the case of conventional lithium grease with NLGI grade 2 consistency.

Another challenge that grease makers will face, sooner or later, is how to optimize manufacturing of lubricating greases from an energy consumption point of view. The reduction of the energy required for grease production by using base oils of different solvencies has been studied [1] on a small scale, where it was demonstrated that using naphthenic versus paraffinic base oils provided a reduction of approximately 12 percent in energy consumption. The findings from that pilot plant project were then transferred to this full-scale production study. Hence, the aim of this paper is to discuss results from this full-scale production study and demonstrate means to measure total energy consumption and obtain CO2 emission per unit mass of fully formulated conventional grease.

2. Manufacturing process of lithium-based greases
Conventional lithium grease is manufactured in a two-stage process. The first stage consists of the reaction or cooking process, and the latter one being the finishing stage. Typically, two separate vessels are used. The cooking stage is carried out in either an open kettle under atmospheric pressure or a closed vessel (Figure 1). In the closed process, the reaction occurs under pressure, either in an autoclave or a pressurized reactor such as a STRATCO® ContactorTM reactor (Figure 2). The Contactor was designed to increase heat and mass transfer rates versus a kettle, thus enhancing dispersion and reducing production time as demonstrated in other studies [4].

Typically, for the finishing stage, scraped-wall vessels with cooling (and sometimes heating) capabilities are used typically in conjunction with various mixing geometries that depend on factors such as the vessel’s overall size, width-to-height ratio and type of grease product. The finishing vessel is connected to auxiliary equipment such as mills, homogenizers, filters, deaerators, etc. In some cases, “hot milling” is done during the cooking stage.
Figure 1. Typical grease production process with a kettle.

Figure 2. Typical grease production process with a pressurized reactor such as a Contactor™.
Despite advances in the equipment used to finish the product, such as high-pressure homogenizers, self-cleaning filters and inline measuring/monitoring devices, very little has changed in the way the fatty acid and alkali are reacted or in the way that the grease is handled inside the finishing kettle. Some attempts have been made to produce grease in a continuous process, but only a few facilities worldwide have the facilities and capacities to produce grease using a continuous mode of operation.

3. Energy requirements for lubricating grease manufacturing

Lubricating grease will become increasingly important for transportation applications such as electrically powered commercial and passenger vehicles. Numerous studies are being carried out to evaluate the energy efficiency of modern soap-type lubricating greases for electrical motor applications. According to one study [5] the energy dissipated in large electric motors can be reduced by 60 percent at lower speeds; 6x10^4 Hz (1000 rpm) and up to 90 percent at higher speeds, 1.5x10^5 Hz (2500 rpm) when the correct grease is being used. Comparing this to modern energy conserving engine oils, such as API SN RC, we can see that the aim is a reduction of 0.9 percent in energy consumption of the internal combustion engine [6].

The energy saving potential can be significant with the use of optimized greases. How much energy can be conserved in the production stage of lubricating grease? In comparison to other lubrication products for commercial and industrial applications, lubricating greases are significantly more energy intensive to manufacture.

To produce lubricating oil products, typically between 2.5 and 4 (kWh/MT) are required to mix and pump the product and provide low-intensity heating to, usually, below 70 degree Celsius, Figure 3. Comparing this to lithium grease where, in the reaction stage, the temperature needs to approach 200 degree Celsius and the mixing and pumping require significantly more energy due to the highly viscous nature of the product. As a matter of fact, the energy requirements for heating during grease production – including the heat of reaction – are considerably greater due to the additional heating, mixing and pumping energy associated with the much more viscous product than the same base oil in formulating a liquid lubricant.

Figure 3. Typical oil blending production process.
In principle, making process improvements could provide a seven-fold greater energy benefit on grease production compared to oil blending. The biggest portion of potential savings can be seen for the heating that accounts for almost 80 percent of the energy used in a typical grease production process. When looking at ways to optimize energy usage at a lubricant manufacturing facility, grease production can have a substantial impact on economic and environmental terms.

The largest proportion of energy used today is linked to fossil fuel. The heating oil or gas consumed for grease production process can be directly correlated to CO₂ emissions. The electricity consumed for mixing, pumping and auxiliary uses is related indirectly to fossil fuel, as the source of power generation is most often linked to fuels ranging from coal to oil, natural gas and renewable sources. The fuel mix is often variable and may be verified by the utility supplier.

Any process optimization that decreases energy consumption will lead to a reduction in CO₂ emissions and, thus, the carbon footprint linked with the product, even before it is put to use. A prior study demonstrated that base oil solvency affects energy requirements for grease production \cite{1}; using naphthenic versus paraffinic base oils provided a reduction of approximately 12 percent in energy consumption, Table 1. Based on that pilot-scale project, this full-scale production study was launched to investigate whether a reduction of the total energy consumption, and subsequently CO₂ emission per unit mass of fully formulated conventional grease, could be obtained on an industrial scale.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Method</th>
<th>Grease A</th>
<th>Grease B</th>
<th>Grease C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base oil</td>
<td>-</td>
<td>T110</td>
<td>SN525</td>
<td>T110:SN525 (1:1)</td>
</tr>
<tr>
<td>Base oil Type</td>
<td>-</td>
<td>Naphthenic</td>
<td>Paraffinic</td>
<td>Naphthenic + Paraffinic</td>
</tr>
<tr>
<td>Thickener content, [wt.%]</td>
<td>-</td>
<td>7.92</td>
<td>9.02</td>
<td>7.82</td>
</tr>
<tr>
<td>Penetration after 60 str., [mm²]</td>
<td>ASTM D217</td>
<td>239</td>
<td>258</td>
<td>272</td>
</tr>
<tr>
<td>Dropping Point, °C</td>
<td>ASTM D2265</td>
<td>206</td>
<td>207</td>
<td>209</td>
</tr>
<tr>
<td>Energy consumption, [kWh]</td>
<td>15</td>
<td>17</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>

**Table 1.** Energy consumption and thickener content for conventional lithium-based greases \cite{1}.

4. Grease Production

In this study, batches were produced on an industrial scale under closely monitored conditions. A total of eight batches were evaluated. The selected base oil viscosity grades (VG ISO 100 and VG ISO 220) were typical grades for multipurpose lithium greases. The production stage, time, temperature, electricity and liquified petroleum gas (LPG) consumption were recorded throughout each batch. Temperature inside the vessel was recorded continually during the cooking stage and measured by contact and infrared thermometers during the finishing stages.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Cooking Vessel</th>
<th>Base Oil</th>
<th>Base Oil ISO VG</th>
</tr>
</thead>
<tbody>
<tr>
<td>TB 01</td>
<td>Pressurized</td>
<td>Naphthenic</td>
<td>100</td>
</tr>
<tr>
<td>TB 02</td>
<td>Pressurized</td>
<td>Naphthenic</td>
<td>220</td>
</tr>
<tr>
<td>TB 03</td>
<td>Pressurized</td>
<td>Paraffinic</td>
<td>220</td>
</tr>
<tr>
<td>TB 04</td>
<td>Pressurized</td>
<td>Naphthenic + Paraffinic</td>
<td>220</td>
</tr>
<tr>
<td>TB 05</td>
<td>Atmospheric</td>
<td>Paraffinic</td>
<td>100</td>
</tr>
<tr>
<td>TB 06</td>
<td>Pressurized</td>
<td>Paraffinic</td>
<td>100</td>
</tr>
<tr>
<td>TB 07</td>
<td>Atmospheric</td>
<td>Naphthenic + Paraffinic</td>
<td>220</td>
</tr>
<tr>
<td>TB 08</td>
<td>Pressurized</td>
<td>Naphthenic + Paraffinic</td>
<td>100</td>
</tr>
</tbody>
</table>

**Table 2.** Batch base oil profile data.

The base oil profiles of the eight batches are presented in Table 2, and selected characteristics of the base oils used in this study are shown in Table 3.
In order for an unbiased comparison of produced batches to be made, a target of grease consistency of NLGI grade 2 with worked penetration of 270 (in units of 0.1 mm) was set. Also, based on prior knowledge of the art, the thickener base was adjusted accordingly between batches in order to produce similar quantities of finished grease. This approach was chosen as similar batch sizes in the finishing stage meant that variations in energy required for the finishing stage (mixing, cooling, homogenizing, etc.) were affected only by the thickener content and the viscosity of the base oil.

The final greases were enriched with a commercial antioxidant and anti-wear additive package at a typical treat rate recommended by the supplier. The nature of these additives did not affect the rheology of the grease products and were necessary to convert the base grease into a formulated commercial product, as required in the scope of this study.

During the production phase of these test batches, several biases were observed, namely, the ambient temperature and the time between production batches. Ambient temperature affected the energy requirement of the production process in the following two ways: a) energy required to pump the oil from the storage tank to the cooking and finishing vessels, and b) energy required to heat the base oil from ambient to reaction temperature. During the test period, the ambient temperature varied with 17 degree Celsius, which affected the viscosity up to 220 percent, depending on the base oil type. Also, with an average specific heat capacity of 1.67 (kJ/(kg K))[^8], approximately 15 (kWh) of heating energy variation can be attributed to ambient temperature differences.

Time between production batches affects the residual heat in the production system, particularly in a Contactor pressurized reactor where an energy consumption variation of up to 12.2 percent was observed between starting a batch in a cold vessel and back-to-back batch production. In order to compensate for this variability, a starting point of 70 degree Celsius was selected for the energy measurements.

### 5. Performance characteristics of the produced greases

Throughout this study, it was critical to demonstrate that the produced greases not only met the production parameters specified above, but also met the required performance characteristics of a commercial grease as required in full-scale production.

The grease test parameters provide the required evidence that each of the full-scale batches was representative of a fully formulated commercial grease. A number of parameters, such as oxidation stability, were enhanced using commercial additives to further demonstrate that these properties can also be affected and even enhanced by manipulating the appropriate manufacturing parameters and/or grease formulation. All the process parameters were kept the same when these batches were produced in this study.

---

[^8]: Specific heat capacity

---

### Table 3. Typical characteristics of the base oils.

<table>
<thead>
<tr>
<th>Remarks</th>
<th>Visc. @40 °C, [mm²/s]</th>
<th>Visc. @100 °C, [mm²/s]</th>
<th>Viscosity Index</th>
<th>Aniline Point, [°C]</th>
<th>Pour Point, [°C]</th>
<th>S-content, [wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffinic 1</td>
<td>103</td>
<td>11.1</td>
<td>92</td>
<td>108</td>
<td>-9</td>
<td>0.44</td>
</tr>
<tr>
<td>Paraffinic 2</td>
<td>218</td>
<td>18.7</td>
<td>95</td>
<td>105</td>
<td>-8</td>
<td>0.52</td>
</tr>
<tr>
<td>Naphthenic 1</td>
<td>22.3</td>
<td>3.7</td>
<td>-3</td>
<td>75</td>
<td>-45</td>
<td>0.06</td>
</tr>
<tr>
<td>Naphthenic 2</td>
<td>150</td>
<td>10.2</td>
<td>8</td>
<td>89</td>
<td>-27</td>
<td>0.13</td>
</tr>
<tr>
<td>Naphthenic 3</td>
<td>600</td>
<td>21.5</td>
<td>-12</td>
<td>89</td>
<td>-12</td>
<td>0.30</td>
</tr>
</tbody>
</table>
One parameter that was kept outside typical commercial specifications was the worked penetration of the test batches. Typically, NLGI grade 2 greases are marketed with a worked penetration between 280 and 285. However, the test batches were further treated with performance enhancing additives that brought the penetration to the required value. Tables 4 and 5 show some of the measured characteristics of the greases.

### Table 4. Characteristics of the greases (VG ISO 100).

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Test Method</th>
<th>TB 01</th>
<th>TB 05</th>
<th>TB 06</th>
<th>TB 08</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickener content (wt%), [wt %]</td>
<td></td>
<td>7.2</td>
<td>8.9</td>
<td>8.2</td>
<td>7.1</td>
</tr>
<tr>
<td>Base Oil - type</td>
<td></td>
<td>Naphthenic</td>
<td>Paraffinic</td>
<td>Paraffinic</td>
<td>Naph. + Paraf.</td>
</tr>
<tr>
<td>Cooking Vessel - type</td>
<td></td>
<td>Pressurized</td>
<td>Atmospheric</td>
<td>Pressurized</td>
<td>Pressurized</td>
</tr>
<tr>
<td>Penetration after 60 str., [mm³]</td>
<td>ASTM D 217</td>
<td>264</td>
<td>274</td>
<td>270</td>
<td>266</td>
</tr>
<tr>
<td>Dropping point, [°C]</td>
<td>IP 396-02</td>
<td>200</td>
<td>203</td>
<td>201</td>
<td>202</td>
</tr>
<tr>
<td>Oil separation, [wt%]</td>
<td>ASTM D 1742</td>
<td>&lt; 0.5</td>
<td>3.61</td>
<td>2.84</td>
<td>2.12</td>
</tr>
<tr>
<td>Water washout, [wt%]</td>
<td>ASTM D 1264-18</td>
<td>5.3</td>
<td>4.3</td>
<td>2.7</td>
<td>5.9</td>
</tr>
<tr>
<td>Diff in Pen. after 10⁵ str., [mm³]</td>
<td>ASTM D 217</td>
<td>± 31</td>
<td>± 27</td>
<td>± 35</td>
<td>+ 46</td>
</tr>
<tr>
<td>4-Ball wear scar, [mm]</td>
<td>ASTM D 2266</td>
<td>0.95</td>
<td>0.82</td>
<td>0.64</td>
<td>0.88</td>
</tr>
<tr>
<td>Copper corrosion, [rating]</td>
<td>ASTM D 4048</td>
<td>1a</td>
<td>1a</td>
<td>1a</td>
<td>1a</td>
</tr>
<tr>
<td>Oxidation stability@140°C, [min]</td>
<td>ASTM D 7575</td>
<td>510</td>
<td>769</td>
<td>1042</td>
<td>762</td>
</tr>
</tbody>
</table>

As shown in Table 4, lower thickener content can be obtained by using naphthenic (TB 01) in lieu of paraffinic (TB 05) oil. In fact, TB 08, which is a blend of naphthenic and paraffinic oils, confirmed that lower soap content can be used, even if some of the paraffinic is replaced with naphthenic oil. Batch TB 08 was cooked in naphthenic oil and then cooled by adding paraffinic oil.

Some of the performance characteristics of these batches differed. For example, oil separation increased when paraffinic oil was used, but on the other hand, oxidation stability was improved. Water washout performance followed soap content.

Manufacturing grease in an open kettle compared with a pressurized reactor for the two batches based on paraffinic oils (TB 05 versus TB 06) showed that the use of the pressurized reactor contributed to reduction of the soap content and lower risk for grease oxidation during the cooking stage. This can be attributed to the fact that the reaction time was briefer and the base oil was subjected to higher temperatures for a shorter period of time in the reactor versus the kettle. Furthermore, the pressurization process using steam generated by the chemical reaction limited the ingress of atmospheric oxygen to the system.

Surprisingly, when the average viscosity of the base oil was increased from 100 to 220 (mm²/s), several grease characteristics improved, Table 5.

### Table 5. Characteristics of the greases (VG ISO 220).

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Test Method</th>
<th>TB 02</th>
<th>TB 03</th>
<th>TB 04</th>
<th>TB 07</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickener content (wt%), [wt %]</td>
<td></td>
<td>4.8</td>
<td>7.5</td>
<td>5.4</td>
<td>7.6</td>
</tr>
<tr>
<td>Cooking Vessel - type</td>
<td></td>
<td>Pressurized</td>
<td>Pressurized</td>
<td>Pressurized</td>
<td>Atmospheric</td>
</tr>
<tr>
<td>Penetration after 60 str., [mm³]</td>
<td>ASTM D 217</td>
<td>269</td>
<td>273</td>
<td>278</td>
<td>273</td>
</tr>
<tr>
<td>Dropping point, [°C]</td>
<td>IP 396-02</td>
<td>205</td>
<td>207</td>
<td>208</td>
<td>204</td>
</tr>
<tr>
<td>Oil separation, [wt%]</td>
<td>ASTM D 1742</td>
<td>&lt; 0.5</td>
<td>1.96</td>
<td>2.85</td>
<td>3.74</td>
</tr>
<tr>
<td>Water washout, [wt %]</td>
<td>ASTM D 1264-18</td>
<td>4.7</td>
<td>4.7</td>
<td>3.6</td>
<td>4.5</td>
</tr>
<tr>
<td>Diff in Pen. after 10⁵ str., [mm³]</td>
<td>ASTM D 217</td>
<td>± 46</td>
<td>± 33</td>
<td>± 44</td>
<td>± 31</td>
</tr>
<tr>
<td>4-Ball wear scar, [mm]</td>
<td>ASTM D 2266</td>
<td>0.68</td>
<td>0.61</td>
<td>0.65</td>
<td>0.61</td>
</tr>
<tr>
<td>Copper corrosion, [rating]</td>
<td>ASTM D 4048</td>
<td>1a</td>
<td>1a</td>
<td>1a</td>
<td>1a</td>
</tr>
<tr>
<td>Oxidation stability@140°C, [min]</td>
<td>ASTM D 7575</td>
<td>750</td>
<td>1082</td>
<td>1099</td>
<td>861</td>
</tr>
<tr>
<td>Flow pressure @ -25°C, [Pa]</td>
<td>DIN 51805</td>
<td>620</td>
<td>1320</td>
<td>695</td>
<td>N/A</td>
</tr>
<tr>
<td>Flow pressure @ -30°C, [Pa]</td>
<td>DIN 51805</td>
<td>1020</td>
<td>1595</td>
<td>1145</td>
<td>N/A</td>
</tr>
</tbody>
</table>
When greases were cooked in the pressurized reactor (TB 02, TB 03 and TB 04), the significantly lower thickener content of TB 02 and TB 04 was related to the use of naphthenic oils with higher degree of solvency and viscosity. The measured characteristics of the greases also indicate the following:

a) Oil separation increased with the use of paraffinic oil, regardless of the type of cooking vessel.

b) Oxidation stability for greases formulated with paraffinic oil and cooked in the pressurized reactor (TB 03 and TB 04) was better than the other batches. However, a result of 750 minutes or more can still be regarded as good to excellent.

c) Lower flow pressure, a good indication of the degree of the pumpability of a grease, was better for greases that contained naphthenic oils.

d) All other characteristics were consistent and within the specification for this type of grease.

6. Test batch energy requirements

Two parameters were investigated with regard to energy requirements of grease production: 1) atmospheric versus pressurized production vessels, and 2) paraffinic versus naphthenic base oils. Furthermore, the effect of viscosity was considered by comparing a series of ISO VG 100 and ISO VG 220 base oil blends.

6.1 Impact of manufacturing processes on energy consumption

For each of the stages, detailed measurements of time, system temperature and energy requirements (electricity and LPG consumption) were made. As discussed in section 4, in order to minimize any bias attributed to environmental or process conditions, the energy requirements used for test batch comparison are limited to the electricity and LPG values recorded when the base oil for the cooking stage was charged and the temperature in the cooking vessel reached 70 degree Celsius. This meant that the energy measurements were biased only by any inefficiencies of the facility installation.

The fuel used for heating purposes was LPG which, based on supplier information, was an 80/20 mixture of butane/propane and provided an equivalent energy output of 31.13 (kWh/m3). LPG measurements were made in (m3) supplied to the burner and converted to the equivalent (kWh) for reporting consistency. During the production of these batches, approximately 84 percent of the energy was generated from fossil fuel and 16 percent came from renewable sources, based on the information provided by the utility provider.

To ensure the validity of the fuel measurements for this study, no other heating operations took place in the production facility during the execution of these test batches. It was expected that there would be fewer losses for the test batches made in the pressurized vessel compared to the open kettle based on the distances the heating oil has to travel through piping in the plant.

In general, the efficiency of an installation significantly affects the actual amount of energy consumed (amount of fuel used). Based on the theoretical heating energy requirements [Appendix A], 133 (kWh/MT) of heating energy are required to heat and react the raw materials and heat the base oil and water of the process. The production schedule (Table 6) for atmospheric versus pressurized production showed a significant difference in the amount of time required for the cooking stage. According to the information in Table 6, there was a difference of 220 minutes – almost 4 hours in total production time – between TB 04 and TB 07.
Table 6. Batch production schedule with P (paraffinic) and N (naphthenic) oils.

The major difference in production time occurred in the cooking stage, which required 220 additional minutes when production was carried out in the open kettle versus the pressurized Contactor reactor. It is well known that one of the main benefits of using a pressurized vessel is the shorter time required to complete the cooking stage. In the finishing stage, there was 15 minutes difference on average, which possibly depended on optimization of the finishing step.

These results are not surprising – or new to the industry - as one of the main benefits of using a pressurized vessel is the time required to complete the cooking stage. Focusing on the cooking stage, Figure 4 presents the product temperature as a function of time for all evaluated batches. There was good repeatability for both the Contactor reactor and kettle processes, as is also shown in Figure 4.

The temperature ramp was flatter for the atmospheric process in the kettle versus the pressurized Contactor reactor. One reason for this difference was that a larger amount of water was required to assist in the saponification reaction, which absorbed more energy. When comparing identical base oil compositions, Table 7 shows the heating energy used in the atmospheric process was approximately 38 to 42 percent greater than was used in the pressurized Contactor vessel. Also, significantly more energy was lost to the environment from the open kettle than the pressurized vessel.

Another reason for the flatter ramp profile was that heat transfer in the kettle was limited by surface area and lower heat transfer rates due to lower product flow rates within the vessel. These conditions explain the results in Table 7.
Looking at the electrical energy for production, it can be seen that there were no significant variations in the amount of electricity per metric ton (MT) of product, particularly in the finishing stages of the grease. This was expected, as energy required was proportional to the amount of product processed in this stage. For the cooking stage, there were notable variations, as with the heating energy.

To accurately evaluate these results, it is important to consider variations in heating energy between batches and variations in electricity energy during different stages of production, Table 8. All energy values were normalized per metric ton (MT) of grease produced. This means that, in general, batches that produce a higher yield, or have lower thickener content, will benefit more from lower energy consumption during the cooking stage and, in particular, the heating energy that accounts for approximately 85 percent of all energy required (based on this study).

Considering the average values in Figure 5 for pressurized reactor (33.76 kWh/MT) versus atmospheric kettle (40.53 kWh/MT), there was a reduction of approximately 16.7 percent in the electrical energy requirement by using the pressurized reaction process. There was more than 25 percent difference between batches with the greatest and the least efficient use of electrical energy, TB 01, pressurized reactor, and TB 07, kettle, respectively. These advantages take into account the shorter processing time with the pressurized reactor. Without taking processing time into consideration, the power requirement for the pressurized vessel is much higher than for an open kettle in order to provide the desired mixing rate.
Table 9. Energy ranking of 5 batches from pressurized process, from 1 (lowest) to 5 (highest).

<table>
<thead>
<tr>
<th>Remarks</th>
<th>Base Oil</th>
<th>Energy kWh per MT</th>
<th>Normalized Energy</th>
<th>Ranking</th>
</tr>
</thead>
<tbody>
<tr>
<td>TB 04</td>
<td>N/P (ISO 220)</td>
<td>204.06</td>
<td>1.00</td>
<td>1</td>
</tr>
<tr>
<td>TB 08</td>
<td>N/P (ISO 100)</td>
<td>214.90</td>
<td>1.05</td>
<td>2</td>
</tr>
<tr>
<td>TB 02</td>
<td>N (ISO 220)</td>
<td>222.94</td>
<td>1.09</td>
<td>3</td>
</tr>
<tr>
<td>TB 06</td>
<td>P (ISO 100)</td>
<td>225.02</td>
<td>1.10</td>
<td>4</td>
</tr>
<tr>
<td>TB 03</td>
<td>P (ISO 220)</td>
<td>233.99</td>
<td>1.15</td>
<td>5</td>
</tr>
</tbody>
</table>

With regards to the heating, all measurements were taken with a hot oil pan as a starting point. But after the first production batch, the gas supply was turned off before the cooking stage was completed to take advantage of the residual heat in the furnace and minimize the energy requirements. This explains the reduced LPG consumption in batches that followed TB 01. This methodology was applied to atmospheric and pressurized batches.

With regards to the electricity consumed, variations were observed between the recorded production stages and in the finishing stage. This can be attributed to the attempts needed to adjust the test batch to the desired consistency. Care was taken to make sure that the test batch target properties were prioritized; for some batches, many minor adjustments were made in the first or the second stage. Nevertheless, for each test batch, these two stages included the electrical energy required to mix, pump, homogenize and package the grease.

Comparing the two processes, significantly more heating energy was required to cook grease in the open kettle than in the pressurized reactor. This was in line with previous findings using pilot scale data and the lower efficiency of a traditional open kettle in terms of both heat and mass transfer compared to a pressurized Contactor reactor.

For both processes, approximately 85 percent of the total energy usage was used for heating the system. The measured fuel usage can be converted to CO2 emissions. Any improvement in this production parameter will significantly reduce the required energy for the production process with an open or a closed production system.

6.2 The impact of the base oils on the energy consumption

The essential part of the reduction in energy requirement, when it comes to the paraffinic/naphthenic based grease, came from the reduction of the thickener content. A higher yield clearly means reduced energy requirement per unit product. Also, the overall energy requirement for purely naphthenic batches (such as TB 02) compared with purely paraffinic batches (such as TB 03) was lower by about 5 percent.

![Figure 6. Total Energy requirement per MT of produced grease for TB 01 – TB 08.](image-url)
Looking at the results, there was significantly more total energy required for the test batches produced in the open kettle process versus the pressurized Contactor reactor. The difference was as high as 35.6 percent for the ISO VG 220 greases (TB 07 vs. TB 04), and 45.0 percent for the ISO VG 100 greases (TB 05 vs. TB 08) produced in the open kettle compared to the pressurized Contactor vessel.

Also, there was a small advantage when formulating grease with a higher viscosity base oil, as for three out of four comparisons, the energy required was lower, Table 10. This was mainly due to the yield benefit, Table 10, where the energy savings was between 5 and 11 percent. For TB 07, a naphthenic/paraffinic blend was used instead of a paraffinic as for TB 05. If a fully naphthenic base oil blend was chosen, a bigger difference would probably have been observed based on the other data. One additional factor to consider is that heating energy losses for the open kettle process were significantly higher than those of the pressurized vessel and, also, the time required is much longer (on average 107 versus 288 minutes). Consequently, the energy required for mixing also increased – on average, 16.7 (kWh/MT) in the pressurized Contactor vessel versus 21.71 (kWh/MT) in the open kettle, as shown in Table 7 for the cooking stage.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>TB 01 (Pressurized Contactor) Naphthenic ISO 100</td>
<td>244.53</td>
<td>TB 02 (Pressurized Contactor) Naphthenic ISO 220</td>
<td>222.94</td>
<td>TB 06 (Pressurized Contactor) Paraffinic ISO 100</td>
<td>229.02</td>
</tr>
<tr>
<td>TB 06 (Pressurized Contactor) Paraffinic ISO 100</td>
<td>214.9</td>
<td>TB 03 (Pressurized Contactor) Paraffinic ISO 220</td>
<td>233.99</td>
<td>TB 08 (Pressurized Contactor) Naphthenic - Paraffinic ISO 100</td>
<td>214.9</td>
</tr>
<tr>
<td>TB 05 (Atmospheric Kettle) Paraffinic ISO 100</td>
<td>311.65</td>
<td>TB 04 (Pressurized Contactor) Naphthenic - Paraffinic ISO 220</td>
<td>204.06</td>
<td>TB 07 (Atmospheric Kettle) Naphthenic - Paraffinic ISO 220</td>
<td>276.7</td>
</tr>
</tbody>
</table>

| Energy saving, [%] ISO 220 vs. ISO 100 | 8.8 | -2.2 | 5.0 | 11.2 |

Table 10. Energy requirement versus base oil type.

Looking at the obtained results, it should be noted that all grease batches produced with an ISO VG 220 base oil blend started with a high viscosity naphthenic base oil in the cooking stage, and then finished with a lighter naphthenic or paraffinic base oil, showed an improved yield. This in turn meant that the energy requirement on a (kWh/kg) basis was lower irrespective of the manufacturing procedure and was observed for both atmospheric and pressurized batches.

7. Carbon Footprint
The reduction of greenhouse gas (GHG) emissions is seen as a corporate responsibility, with many large and small corporations setting targets of becoming carbon neutral. The first step towards this goal is usually taken by applying a standardized reporting system such as the GHG Protocol [9], which allows the organization to uniformly account for and manage CO2 and other emissions. This forms part of a greater requirement for sustainability by managing all resources, including material, finances and people.

The most commonly considered GHGs are hydrofluorocarbon (HFC) gases, methane, oxides of nitrogen (NOx), and CO2, with the latter accounting for approximately 80 percent of global emissions.
Figures provided by the US EPA [15] show that over the past two decades, CO2 emissions have been relatively constant (Figure 7) despite numerous attempts through UN initiatives such as the Paris Agreement in 2015 and the more recent COP24 climate summit in Poland, as well as the work done by NGOs.

![Historic CO2 Emissions by Region](image)

**Figure 7.** Major contributors to CO2 global emissions.

In the present study, there are two elements to consider in the case of grease production: energy usage in the form of electricity, and energy usage in the form of heating.

Various tools are available to evaluate the carbon footprint of electricity from local utility companies. Today, some utility companies provide energy that is produced using exclusively renewable sources. Nonetheless, in various global regions, the energy source can vary from coal to nuclear and renewable sources such as water, wind and solar. Where renewable sources are used, the overall resulting CO2 emissions from a given operation can theoretically be zero.

As seen from the results of this study, the electricity consumed during grease production only represents a small amount of the total system energy, ranging from 12 to 16 percent. The majority of the energy used in grease production is needed for heating. Currently, apart from small-scale operations where the circulating medium can be electrically heated (pilot scale), only a few novel processes use electricity as a means of heating, with the most discussed method being microwave heating for grease production [10]. The supply of high pressure steam as a utility, where available, presents a unique form of energy, but the source of steam generation also needs to be evaluated.

For fuel fired systems, CO2 emissions can easily be accounted for by applying a GHG model [9] applicable for the energy source used by the local utility supplier, Table 11. For most of the grease plants, fuel for the heating source is some sort of fossil fuel such as natural gas, LPG, diesel, a heavier distillate, etc. Depending on the geographic region and electricity supplier, these sources can incorporate a sustainability factor, such as biofuel for diesel.

Table 11. CO2 emissions per kWh, Source: Fachbuch Regenerative Energiesysteme and UBA.

In this study, different test batches were compared in order to evaluate the overall carbon footprint of the production stages, Table 12. Production in the pressurized reactor using a blended naphthenic/paraffinic ISO 220 base stock (TB 04) was used as a bench mark, as it had the overall lowest energy demands in this study, Table 13.
For LPG, the fuel used for heating in this study, the CO2 emissions per kWh are given in Table 11. Electricity was generated from a fuel mix (43 percent lignite, 37 percent diesel, 12 percent LNG and 8 percent renewable), and the average CO2 emission values were calculated, Table 14.

**Table 12.** CO2 emissions for production batches in kg eCO2 per kWh.

<table>
<thead>
<tr>
<th>Energy source</th>
<th>CO2 emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating</td>
<td>0.23</td>
</tr>
<tr>
<td>Electricity</td>
<td>0.28</td>
</tr>
</tbody>
</table>

**Table 13.** Normalized CO2 emissions from production batches.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Base oil Type</th>
<th>Viscosity @ 40°C, [mm²/s]</th>
<th>Thickener content, [wt.%]</th>
<th>Cooking Vessel</th>
<th>Kg eCO2 emissions per MT</th>
<th>Normalized CO2 emissions per MT</th>
</tr>
</thead>
<tbody>
<tr>
<td>TB 04</td>
<td>Naphthenic +Paraffinic</td>
<td>220</td>
<td>5.4</td>
<td>Pressurized</td>
<td>48.62</td>
<td>1</td>
</tr>
<tr>
<td>TB 02</td>
<td>Naphthenic</td>
<td>220</td>
<td>4.8</td>
<td>Pressurized</td>
<td>53.04</td>
<td>1.09</td>
</tr>
<tr>
<td>TB 08</td>
<td>Naphthenic +Paraffinic</td>
<td>100</td>
<td>7.1</td>
<td>Pressurized</td>
<td>53.38</td>
<td>1.10</td>
</tr>
<tr>
<td>TB 06</td>
<td>Paraffinic</td>
<td>100</td>
<td>8.2</td>
<td>Pressurized</td>
<td>53.44</td>
<td>1.10</td>
</tr>
<tr>
<td>TB 03</td>
<td>Paraffinic</td>
<td>220</td>
<td>7.5</td>
<td>Pressurized</td>
<td>55.58</td>
<td>1.14</td>
</tr>
<tr>
<td>TB 01</td>
<td>Naphthenic</td>
<td>100</td>
<td>7.2</td>
<td>Pressurized</td>
<td>57.81</td>
<td>1.19</td>
</tr>
<tr>
<td>TB 07</td>
<td>Naphthenic +Paraffinic</td>
<td>220</td>
<td>7.6</td>
<td>Atmospheric</td>
<td>65.75</td>
<td>1.35</td>
</tr>
<tr>
<td>TB 05</td>
<td>Paraffinic</td>
<td>100</td>
<td>8.9</td>
<td>Atmospheric</td>
<td>73.62</td>
<td>1.51</td>
</tr>
</tbody>
</table>

**Figure 8.** Kg CO2 emitted per MT of grease produced.
Comparing grease batches formulated with the same base oil viscosity, ISO VG 220, a 26.1 percent overall reduction in CO2 emissions was achieved by switching from a paraffinic/naphthenic base oil blend in an open kettle (TB 07, 65.75 kg/MT), Table 13) to a paraffinic/naphthenic base oil mixture in a pressurized Contactor reactor (TB 04, 48.63 (kg/MT)). Similarly, for greases prepared with ISO VG 100 paraffinic/naphthenic base oil blend, CO2 emissions were 27.5 percent lower for the pressurized Contactor reactor (TB 08, 53.38 kg/MT) versus the open kettle process (TB 05, 73.62 kg/MT).

Looking at the absolute per metric ton values for every 1000 (MT) per year production, the annual reduction of CO2 emissions between open and closed kettle process is estimated at 20 (MT) for paraffinic base oil with up to an additional 5 (MT) savings if the base oil used is naphthenic. Some CO2 emission equivalents are shown in Table 15.

According to data published by a lubricants manufacturer that produces both lubricating oils and greases [11], average energy consumption was approximately 232 (kW/MT) of product. This value included all activities at a given production location. Noting that the average energy consumption of the grease batches measured in this study was 245.5 (kWh/MT) only considering the production processes, it can be deduced that any optimization in energy efficiency of grease production can have a significant impact on a company’s sustainability rating. Grease production is indisputably the most energy intensive production activity within the lubricants industry.

<table>
<thead>
<tr>
<th>Batch</th>
<th>MT CO₂ emissions per 1000 MT (Heating energy)</th>
<th>MT CO₂ emissions per 1000 MT (Electrical energy)</th>
<th>MT CO₂ emissions per 1000 MT (Heating + Electrical)</th>
<th>Total MT CO₂ emission reduction potential per 1000 MT grease (TB 04 basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TB 04</td>
<td>39.15</td>
<td>9.48</td>
<td>48.63</td>
<td>0</td>
</tr>
<tr>
<td>TB 02</td>
<td>43.18</td>
<td>9.85</td>
<td>53.03</td>
<td>4.4</td>
</tr>
<tr>
<td>TB 08</td>
<td>44.10</td>
<td>9.28</td>
<td>53.38</td>
<td>4.8</td>
</tr>
<tr>
<td>TB 06</td>
<td>44.02</td>
<td>9.41</td>
<td>53.43</td>
<td>4.8</td>
</tr>
<tr>
<td>TB 03</td>
<td>45.69</td>
<td>9.89</td>
<td>55.58</td>
<td>7.0</td>
</tr>
<tr>
<td>TB 01</td>
<td>49.02</td>
<td>8.80</td>
<td>57.82</td>
<td>9.2</td>
</tr>
<tr>
<td>TB 07</td>
<td>53.94</td>
<td>11.82</td>
<td>65.76</td>
<td>17.1</td>
</tr>
<tr>
<td>TB 05</td>
<td>62.74</td>
<td>10.88</td>
<td>73.62</td>
<td>25.0</td>
</tr>
</tbody>
</table>

**Table 14.** Emission reduction potential of using each batch process by energy stream.

**Table 15.** Emission savings and offsets.
8. Summary
In this study, the production of lithium grease on an industrial scale was carried out to evaluate the impact of key parameters (nature and viscosity of base oils, production technologies) on energy consumption and CO2 emission per unit mass of finished grease.

In total, eight batches (8000 kg each) of lithium-based grease were manufactured. The base oils were two paraffinic group I oils, three hydrotreated naphthenic oils and blends of paraffinic and naphthenic oils. Their viscosities at 40 degree Celsius were 100 and 220 (mm2/s), typical grades used in multipurpose lithium greases.

Based on results obtained in this study, the following conclusions can be made:

• For greases prepared with ISO VG 220 oil, CO2 emissions per metric ton of grease were 26.1 percent lower for grease formulated with a paraffinic/naphthenic base oil mixture and manufactured in a pressurized Contactor reactor (TB 04) versus grease made with the same base oil blend in an open kettle (TB 07).
• The reduction in energy requirement observed for greases formulated with paraffinic/naphthenic blends was related to lower thickener content. A higher yield clearly means reduced energy requirement per unit product. Nonetheless, the overall energy consumption in absolute terms was 5 percent lower to make purely naphthenic batches (such as TB 02) versus purely paraffinic batches (such as TB 03). Significantly more total energy was required for test batches produced in the open kettle process compared to the pressurized Contactor reactor. This difference was high as 35.6 percent for the ISO VG 220 greases and 45.0 percent for the ISO VG 100 greases produced in the open kettle compared to the pressurized vessel as evidenced in Table 7.
• Production of lithium-based grease could be optimized by cooking the grease in a pressurized condition (e.g., STRATCO® Contactor™ reactor) in lieu of a traditional open kettle at atmospheric pressure. The yield can be further improved by increasing base oil viscosity from 100 to 220 (mm2/s) and using naphthenic instead of paraffinic oils.
• Heating energy losses were significantly higher from the open kettle than from the pressurized vessel, and the time required was much longer (on average 107 versus 288 min). Primarily as a result of the reduced residence time in the cooking stage, the electrical energy was reduced by 4.19 (kWh/MT) and 5.71 (kWh/MT) for ISO VG 100 and ISO VG 220 base oils, respectively, by using the pressurized Contactor reactor instead of the open kettle.

References
Calculation of theoretical Energy requirements:

i. **Heating Energy**

Heating Energy required to heat the mixture/reaction components is calculated using equation (1)

\[ \sum Q = \sum_{i=1}^{n} \left( \frac{M_i}{M_T} C_{p_i} \Delta T \right) + H_S + E_A \quad [J] \]

where

- \( n \) are the components of the mixture
- \( M_i \) is the mass of each component
- \( M_T \) is the total mass of the system
- \( C_{p_i} \) is the average specific heat capacity of each component over the mixing/reaction temperature range
- \( \Delta T \) is the temperature difference between \( T_0 \) at the beginning of the mixing and \( T_{\text{max}} \), peak temperature
- \( E \) is the enthalpy of steam which includes the: \( H_s \), the latent heat of vaporisation at \( T_s \) (the temperature of saturation) and \( H \), the enthalpy of superheated steam at the operating temperature.
- \( E_A \) is the reaction activation energy.

For simple oil mixing, assuming the specific heat capacities of the oil and the additives are the same, equation (1) is reduced to

\[ Q = \frac{M_1}{M_T} C p \Delta T \quad [kJ] \]
Calculation of theoretical Energy requirements:

i. Heating Energy

Heating Energy required to heat the mixture/reaction components is calculated using equation (1)

\[
\sum Q = \sum (M_n \cdot C_{pn} \cdot \Delta T) + H_1 + E_A \ [\text{J}]
\]

where

- \(M_1 = M_T\) and
- \(\Delta T = (T_{\text{max}} - T_0) = 70 - 20 = 50\)

So,

\[
Q = 1 \times 1.67 \times 50 = 83.5 \ \text{kJ/kg} \ or \ 0.023 \ \text{kWh/kg}
\]

Similarly, for grease production making the following production assumptions.

a) A thickener base with 15.5 (wt.%) thickener content

b) Production in a pressurized vessel with an operating pressure of 400 (kN m\(^{-2}\)) = (4 bar)

The mixture will consist of the components listed in the table below

<table>
<thead>
<tr>
<th>Component</th>
<th>Base oil (SN 500)</th>
<th>Fatty acid (12-HSA)(^{[13]})</th>
<th>Alkali LiOH·H(_2)O</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{p,\text{average}} \ [\text{kJ kg}^{-1} \ K^{-1}])</td>
<td>1.67</td>
<td>2.74</td>
<td>2.07</td>
<td>4.18</td>
</tr>
<tr>
<td>(M_n/M_T)</td>
<td>0.821</td>
<td>0.136</td>
<td>0.012</td>
<td>0.031</td>
</tr>
</tbody>
</table>

The water mass fraction is derived from the following parameters

- the water contained in the alkali, typically 40 (wt.%) of the added alkali,
- the water released during the saponification reaction, approximately 6 (wt.%) of the Fatty acid added for 12-HSA, and
- the water added to the system to promote the reaction.

Considering an operating pressure of 4 (bar), the saturation temperature of steam is 143.63 (oC)\(^{[8]}\) assuming equilibrium conditions, water is heated to the above temperature, steam is generated and then it is superheated to the maximum operating temperature of \(T_{\text{max}}=200\)°C, when it is vented.

Hence, the heating energy can now be calculated as shown below:

for the thickener components:

<table>
<thead>
<tr>
<th>Component</th>
<th>Base oil (SN 500)</th>
<th>Fatty acid (12-HSA)(^{[13]})</th>
<th>Alkali LiOH·H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{p,\text{average}} \ [\text{kJ kg}^{-1} \ K^{-1}])</td>
<td>1670</td>
<td>2740</td>
<td>2070</td>
</tr>
<tr>
<td>(M_n/M_T)</td>
<td>0.821</td>
<td>0.136</td>
<td>0.012</td>
</tr>
<tr>
<td>(\Delta T \ K)</td>
<td>180</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>(Q_n \ [\text{J kg}^{-1} \ K^{-1}])</td>
<td>246,991.45</td>
<td>67,018.11</td>
<td>4,521.62</td>
</tr>
<tr>
<td>(Q_n \ [\text{kWh kg}^{-1}])</td>
<td>0.0686</td>
<td>0.0186</td>
<td>0.0013</td>
</tr>
</tbody>
</table>
The mixture will consist of the components listed in the table below:

<table>
<thead>
<tr>
<th>Component</th>
<th>Energy to heat the water to evaporation</th>
<th>Latent heat of Evaporation $H_s$</th>
<th>Enthalpy of superheated steam $H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_p$ average</td>
<td>4180</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_l/M_T$</td>
<td>0.029</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta T$ K</td>
<td>123.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_n$ J kg$^{-1}$</td>
<td>15,151.68</td>
<td>62,536.14</td>
<td>83,737.27</td>
</tr>
<tr>
<td>$Q_H$ J kg$^{-1}$</td>
<td>0.0042</td>
<td>0.0173</td>
<td>0.0233</td>
</tr>
</tbody>
</table>

From published data [7] the $E_A$ for lithium thickened grease in a non-polar (paraffinic) oil is approximately $2.2 \times 10^4$ (J mol$^{-1}$). This can be converted to (kWh/kg) by using the mass fraction of thickener in the base since the saponification reaction is a 1:1 mole ratio.

$$E_A = 2.2 \times 10^4 \text{ [J mol}^{-1}] \text{ or } 2.2 \times 10^4 \text{ [kJ kmol}^{-1}] \times \frac{1}{306.42} \text{ [kmol kg}^{-1}] \times \frac{1}{3600 \text{ s}} = 0.02 \text{ [kWh kg}^{-1}]$$ [14]

So, adding all the above we see that:

$$\Sigma_i Q = 0.1328 \text{ [kWh kg}^{-1}]$$
SAVE THE DATE
NLGI 2020 ANNUAL MEETING
SUN. JUNE 14 – WED. JUNE 17, 2020
*Schedule shifts forward by a day

JW Marriott Miami Turnberry Resort & Spa
Miami, Florida

SCHEDULE OF MAIN EVENTS:

SUNDAY, JUNE 14, 2020
• Tribology Course
• Opening Reception

MONDAY, JUNE 15, 2020
• Golf Tournament
• Working Group Meetings
• Basic & Advanced Courses
• Opening General Session
• Welcome Reception

TUESDAY, JUNE 16, 2020
• Fun Run
• Networking Breakfast
• Industry Speaker
• Basic & Advanced Courses
  *Note: the courses will be completed in time to see most of the technical presentations on Tuesday.
• Technical Presentations 1 & 2
• Spouse Tour
• Networking Lunch

WEDNESDAY, JUNE 17, 2020
• Networking Breakfast
• Technical Presentations 3 & 4
• Networking Lunch
• CLGS Exam
• Closing Night Celebration
Course Description:
As technology progresses, the design of advanced mechanical systems will rely on a greater understanding of tribological systems. This course seeks to educate students about the mechanisms of lubrication, friction and wear at a microscopic level. Topics include surface contact mechanics, lubrication regimes and the Strubeck curve, differences between abrasive wear modes and rolling contact fatigue, introduction to tribological testing, safe/not-safe sliding, and common industrial applications for tribological design considerations.

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Appropriate for students new to the lubricants industry…such as those preparing to take the NLGI Basic Grease course or reviewing for the CLGS exam, and anyone seeking a great understanding of advanced engineering design.

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Back to the Basics -
The ABC’s of Grease Additive Performance

Joseph P. Kaperick
Afton Chemical Corporation
Richmond, VA, USA

Abstract
Examining basic assumptions about additives for lubricating greases can confirm or upend conventional thinking about these materials. This paper reports results from an extensive study of individual additives, additive blends, and packages, all formulated in lithium-thickened base grease.

Research in the arena of grease chemistry can reach from the mundane to the esoteric, but sometimes it’s good to step back and examine the basic assumptions and “common wisdom” upon which those studies are often based. This paper examines in depth some of the foundational aspects of grease performance using test data to support or refute some commonly held “facts” about grease additives. The main focus will be on the role of additives in providing the essential performance characteristics typically required by bearing greases and other fully formulated lubricating greases. These focal areas include:

- Comparison of primary and secondary zinc dithiodiphosphates (ZDDPs)
- Sulfur and extreme pressure (EP) performance
- Antioxidant (AO) combinations and high temperature performance
- Additive package response

Background Work
Much work has been done to evaluate different additive components using a variety of grease bench and rig tests. Some of this work has been published in the literature on this subject. Many authors used the Four-Ball Weld test to measure the effectiveness of novel EP agents or in studies of synergies or tribochemical interactions that improve boundary lubrication protection \[^{1-9}\].

Pressurized Scanning Differential Calorimetry (PDSC) was used by Reyes-Gavilan \[^{10}\] to evaluate different antioxidants in polyurea and lithium-thickened greases by a standard test method (ASTM D5483). Senthivel et al. \[^{11}\] looked at PDSC as well as a variety of other techniques including spectroscopic analysis and thermal aging to investigate the high temperature behaviour of greases. Samman \[^{12}\] discussed relative characteristics of different components in greases and their relation to high temperature performance and utilized case studies of greases in high temperature applications.

Rheological techniques have become more common in evaluating performance of high temperature greases in recent years. Nolan and Sivik \[^{13,14}\] used rheology to compare the high temperature performance of a variety of different thickeners and compared those results to data obtained with a dropping point apparatus. Coe \[^{15}\] looked at high temperature applications of grease formulations and examined performance in dropping point as well as a variety of other high temperature bench tests. Kaperick \[^{16}\] studied the effect of boron additives in lithium greases on performance in the dropping point test.
Rhee [17] used PDSC and a Thermal Gravimetric Analysis (TGA) procedure to build a “decomposition kinetic model”, which he then correlated to the high temperature wheel bearing rig test (ASTM D3527). Ward and Fish [18] also used PDSC and the D3527 wheel bearing test as a guide and evaluated several finished greases in the FAG FE8 and FE9 rig tests. Additionally, Kaperick [19] investigated tribolayer formation and the effectiveness of different additive systems in various high temperature tests including the FAG FE9 rig test.

Recent papers that looked at the use of the Fafnir fretting rig to evaluate additive response with ASTM D4170 include those by Fish [20], Shiller [21], and Kaperick [22,23].

Methods and Materials
For this study, commonly used greases tests were applied to examine the basic responses of a core slate of additives and interactions that might occur in grease formulations. Additionally, several additive packages were included in the study to show performance differences that could be experienced by formulators. These components and packages are shown in Table 1 where some of the physical characteristics (elemental concentrations) are given along with the “ID” used in various tables and graphs to illustrate the results of the study. Different colors are also used for various components for better differentiation in graphs used in this paper.

<table>
<thead>
<tr>
<th>ID</th>
<th>Description</th>
<th>%Zn</th>
<th>%P</th>
<th>%S</th>
<th>%N</th>
<th>%B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st ZDDP</td>
<td>Primary ZDDP</td>
<td>9</td>
<td>8</td>
<td>16.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2nd ZDDP</td>
<td>Secondary ZDDP</td>
<td>9</td>
<td>8.2</td>
<td>17.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1st/2nd ZDDP</td>
<td>Mixed ZDDPs</td>
<td>9.2</td>
<td>8.35</td>
<td>17.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SIB</td>
<td>Sulfurized Isobutylene</td>
<td>-</td>
<td>-</td>
<td>46</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SO</td>
<td>Sulfurized Olefin</td>
<td>-</td>
<td>-</td>
<td>12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AO</td>
<td>Phenolic/Aminic AO Mix</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.17</td>
<td>-</td>
</tr>
<tr>
<td>BPD</td>
<td>Boron-Phosphate Dispersant</td>
<td>-</td>
<td>0.7</td>
<td>-</td>
<td>1.7</td>
<td>1.0</td>
</tr>
<tr>
<td>ZDDP Pack 1</td>
<td>Core ZDDP/Sulfur</td>
<td>4</td>
<td>3.5</td>
<td>22.9</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>ZDDP Pack 2</td>
<td>ZDDP/Sulfur + AO/RI (rust inhibitor)</td>
<td>2</td>
<td>1.8</td>
<td>12.1</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>S/P Pack 1</td>
<td>Core Sulfur/Phosphorous (S/P)</td>
<td>-</td>
<td>1.2</td>
<td>36.1</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>S/P Pack 2</td>
<td>Core S/P + AO</td>
<td>-</td>
<td>0.8</td>
<td>25.6</td>
<td>0.9</td>
<td>-</td>
</tr>
<tr>
<td>S/P Pack 3</td>
<td>Core S/P</td>
<td>-</td>
<td>1.3</td>
<td>29.6</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>S/P Pack 4</td>
<td>Core S/P</td>
<td>-</td>
<td>1.2</td>
<td>32.5</td>
<td>1.1</td>
<td>-</td>
</tr>
</tbody>
</table>

The specific types of zinc dithiodiphenyls (ZDDPs) used in the study are shown in Table 2 along with the carbon chain lengths of the primary and secondary alcohols used to make them.
Two types of sulfur compounds were used in the study – a sulfurized isobutylene with high active sulfur content and a sulfurized olefin with a low active sulfur content. Details of these two components are shown in Table 3.

To examine the effect of high temperature componentry on grease formulations, an antioxidant (AO) mixture and a borated dispersant (BPD) were included as detailed in Table 1. These types of components are often used to provide oxidative stability to the oil component (AO) and stability to the thickener at higher temperatures (BPD).

Finally, the packages used were of two basic types – those based on ZDDP chemistry and those based on ashless sulfur/phosphorous (S/P) componentry. Some of the packages included a primary antioxidant, while some benefited from the secondary antioxidant impact of ZDDP. Details of each of the packages is included in Table 1.

Grease Samples
The base greases used in this study were made in the Author’s facility using a lab-scale, covered and jacketed 5-gallon kettle operated at atmospheric pressure with a single-motion, anchor-style agitator with scraper blades and fixed vertical baffle attached to the bottom of the lid cover. Heating and cooling were achieved by the circulation of heat transfer oil through the kettle’s jacket using a loop consisting of an oil reservoir, pump, heater, and heat exchanger. The kettle was connected to a second pump that circulated the contents of the kettle through a colloid mill, to provide additional agitation, and discharged the final product. The operation of the entire unit was computer controlled.

All greases were lithium 12-hydroxy stearate greases prepared with a blend of ISO 150 paraffinic Group I oils. The alkalinitities are reported in %LiOH (not LiOH•H2O) as calculated by ASTM D128, Section 21 – Free Alkali [23a].

Test Methods
The following test methods were employed with variations from standard ASTM methodology noted:
• ASTM D1403 “Standard Test Methods for Cone Penetration of Lubricating Grease Using One-Quarter and One-Half Scale Cone Equipment” [24]

• The half-scale cone method was employed, with each of the samples being worked 60 times prior to analysis.


• ASTM D2266 “Standard Test Method for Wear Preventive Characteristics of Lubricating Grease (Four-Ball Method)” [26].

• ASTM D2596 “Standard Test Method for Measurement of Extreme-Pressure Properties of Lubricating Grease (Four-Ball Method)” [27]

This testing was carried out with the modification of using test loads at 10-kg intervals to more accurately monitor the incremental performance of the greases under extreme pressure.


This test was also run using a 67-hour duration to increase the severity of the test.

According to ASTM D1743, a bearing with no rust spots larger than 1.0 mm in diameter is considered to pass, and two out of three bearings must pass for the grease to be considered acceptable. In the present study, a modified system of rating bearings from D1743 tests was employed in order to better estimate the impact of each variable on the level of corrosion present. The raceway on the inside of each bearing cup was rated on the basis of a visual estimate (without the use of magnification) of the percent surface area covered by rust. This rating method was described in more detail in previous work [29]. To minimize variability in this modification, a single technician did all the evaluations used in this study.


• Distilled water and 100% Synthetic Sea Water (SSW) were used in this study.

• ASTM D 4048 “Standard Test Method for Detection of Copper Corrosion from Lubricating Grease” [31]

Copper strips were immersed in grease samples at test temperature and pulled at the standard 24 h then rated against the ASTM standard template. The test was also run at 80 and 120°C in addition to the standard temperature of 100°C.


A High Frequency Reciprocating Rig (HFRR) was used to generate HFRR Coefficient of Friction (COF) data. The HFRR test measures the ability of a lubricant to affect friction between the contacting parts and the wear of surfaces in sliding motion under load. A 6 mm diameter ANSI 52100 steel ball oscillates in contact with an ANSI 52100 steel flat surface under standard test conditions. The COF is measured by the HFRR tool. In this study, the test was run with a 400 g load, while the ball oscillated through a 1 mm path at 20 Hz. Test temperatures of 30, 50, 70, 90, 110, and 130⁰C were employed sequentially, with data taken every 5 s for 3 min at each test temperature (once the temperature had stabilized).
An Anton-Paar oscillatory rheometer (MCR301) was used to measure the rheological properties of the grease. The grease was compressed between a bottom plate and a parallel top plate. Both plates were 25 mm in diameter and sand-blasted. A hood that contained a temperature-controlled Peltier device was placed over the test grease and bottom plate. A temperature sweep (2°C/min) was performed on the test greases in the rheometer ranging from 40 up to 250°C with a constant oscillating shear strain of 0.05%. Both storage modulus ($G'$) and loss modulus ($G''$) measurements were taken, and the ratio of the two was plotted as “Tan Delta” ($G''/G'$). A typical interpretation of this ratio is that as the value moves from less than one to more than one, the internal structure of the grease shifts from a more solid-like material ($G'$) to a more liquid-like material ($G''$).

Thermal Gravimetric Analysis (TGA) was completed using a Perking Elmer Pyris 1 instrument. The principle behind TGA involves the measurement of sample weight loss as a function of temperature. Grease samples were heated from 50 to 900°C under a nitrogen atmosphere (60 ml/min) using a constant ramp of 20°C/min. The first derivative was plotted and showed the rate of weight loss, which correlated with % weight loss as a function of temperature.


Samples were run by the standard test method at 155°C under 500 psi (3447 kPa) oxygen atmosphere. The extrapolated onset time was measured and reported as the oxidation induction time (OIT) for each sample.

- ASTM D942 “Standard Test Method for Oxidation Stability of Lubricating Greases by the Oxygen Pressure Vessel Method”[34]

Samples of grease were oxidized in a pressure vessel heated to 99°C and filled with oxygen at 110 psi (758 kPa) for 100 h. At the end of the test period, the loss of pressure (in psi) was recorded.

**Results and Discussion**

**ZDDP Testing**

To study differences between types of ZDDP components, six greases were formulated as shown in Table 4. Due to slight differences in elemental makeup of the different additives, a constant level of phosphorus (640 ppm P) was targeted. A “typical” treat rate of 0.6 wt% of SIB was used to assess the impact of this component on performance of the ZDDPs under various test conditions.

<table>
<thead>
<tr>
<th>Component</th>
<th>Base Grease</th>
<th>1º ZDDP</th>
<th>2º ZDDP</th>
<th>1º/2º ZDDP</th>
<th>1º ZDDP + SIB</th>
<th>2º ZDDP + SIB</th>
<th>1º/2º ZDDP + SIB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium base</td>
<td>100</td>
<td>99.20</td>
<td>99.22</td>
<td>99.23</td>
<td>98.60</td>
<td>98.62</td>
<td>98.63</td>
</tr>
<tr>
<td>1º ZDDP</td>
<td>-</td>
<td>0.80</td>
<td>-</td>
<td>-</td>
<td>0.80</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2º ZDDP</td>
<td>-</td>
<td>-</td>
<td>0.78</td>
<td>-</td>
<td>-</td>
<td>0.78</td>
<td>-</td>
</tr>
<tr>
<td>1º/2º ZDDP</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.77</td>
<td>-</td>
<td>-</td>
<td>0.77</td>
</tr>
<tr>
<td>SIB</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Table 4 - ZDDP formulations
No significant differences were seen in standard tests (penetration and dropping point) that might show impacts on grease structure (Table 5).

<table>
<thead>
<tr>
<th>Test</th>
<th>ASTM</th>
<th>Base Grease</th>
<th>1° ZDDP</th>
<th>2° ZDDP</th>
<th>1°/2° ZDDP</th>
<th>1° ZDDP + SIB</th>
<th>2° ZDDP + SIB</th>
<th>1°/2° ZDDP + SIB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration (60x, 1/2 work), mm/10</td>
<td>D1403</td>
<td>233</td>
<td>239</td>
<td>239</td>
<td>240</td>
<td>241</td>
<td>241</td>
<td>240</td>
</tr>
<tr>
<td>Dropping Point, °C</td>
<td>D 2265</td>
<td>205</td>
<td>205</td>
<td>201</td>
<td>201</td>
<td>200</td>
<td>209</td>
<td>209</td>
</tr>
</tbody>
</table>

Corrosion testing shows some differentiation between different formulations as seen in Table 6.

<table>
<thead>
<tr>
<th>Test</th>
<th>ASTM</th>
<th>Base Grease</th>
<th>1° ZDDP</th>
<th>2° ZDDP</th>
<th>1°/2° ZDDP</th>
<th>1° ZDDP + SIB</th>
<th>2° ZDDP + SIB</th>
<th>1°/2° ZDDP + SIB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard bearing corrosion, DI, % Rust</td>
<td>D1743</td>
<td>5/15/15</td>
<td>0/0/0</td>
<td>-</td>
<td>0.5/1/15</td>
<td>-</td>
<td>-</td>
<td>0/5/15</td>
</tr>
<tr>
<td>Ave % rust</td>
<td>-</td>
<td>11.7</td>
<td>0</td>
<td>-</td>
<td>5.5</td>
<td>-</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>Standard bearing corrosion, DI, 67 h, % Rust</td>
<td>D1743 mod</td>
<td>-</td>
<td>0.5/0.5/0.5</td>
<td>-</td>
<td>-</td>
<td>25/5/15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ave % rust</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>15.0</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>EMCOR (DI Water), Rating</td>
<td>D6138</td>
<td>5/5</td>
<td>2/2</td>
<td>2/2</td>
<td>2/2</td>
<td>2/2</td>
<td>2/2</td>
<td>2/2</td>
</tr>
</tbody>
</table>

In all steel corrosion testing, the presence of ZDDP improved the result compared to base grease. Of interest is the fact that the addition of SIB negatively affected the ability of ZDDP to prevent rust in the standard bearing test under both standard and extended length conditions. However, this same phenomenon was not seen in the more dynamic EMCOR corrosion test. The higher temperature of the D1743 test may have activated ZDDP to form a protective layer, and the presence of SIB interfered with this activation, either by going to the surface itself or by interacting with the ZDDP. Copper corrosion testing also showed some differences between formulations, Table 7.

<table>
<thead>
<tr>
<th>Test</th>
<th>ASTM</th>
<th>Base Grease</th>
<th>1° ZDDP</th>
<th>2° ZDDP</th>
<th>1°/2° ZDDP</th>
<th>1° ZDDP + SIB</th>
<th>2° ZDDP + SIB</th>
<th>1°/2° ZDDP + SIB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu corrosion, 80°C, 24 h</td>
<td>D4048</td>
<td>3a</td>
<td>2a</td>
<td>1b</td>
<td>1b</td>
<td>1b</td>
<td>1b</td>
<td>1b</td>
</tr>
<tr>
<td>Cu corrosion, 100°C, 24 h</td>
<td>D4048</td>
<td>3a</td>
<td>2a</td>
<td>1b</td>
<td>1b</td>
<td>1b</td>
<td>2a</td>
<td>2a</td>
</tr>
<tr>
<td>Cu corrosion, 120°C, 24 h</td>
<td>D4048</td>
<td>3a</td>
<td>2a</td>
<td>1b</td>
<td>1b</td>
<td>2b</td>
<td>2b</td>
<td>2a</td>
</tr>
</tbody>
</table>
Again, the addition of ZDDP improved the results in all cases, although the primary ZDDP was less effective by itself than the secondary or mixed ZDDP components. The addition of SIB had the opposite effect with the secondary ZDDP and mixed ZDDP being less effective in the presence of SIB. This pointed to either interactions with the ZDDP or competition for the surface with the SIB causing copper corrosion (as the active sulfur it contains is well known to do). This might explain the temperature-related severity seen with the secondary ZDDP/SIB mixture while the activity of the sulfur may have been suppressed by interaction with the ZDDP in the other two cases.

The properties of ZDDP as a secondary antioxidant through its role as a peroxide decomposer are well known. As can be seen in Table 8, all the formulations containing ZDDP had a positive impact on D942 results, and the secondary and mixed ZDDPs showed the biggest impact, while SIB appeared to have a slightly negative effect. However, none of the results for ZDDP-containing greases were statistically different from one other, so additional testing would be needed to confirm any differences.

<table>
<thead>
<tr>
<th>Test</th>
<th>ASTM</th>
<th>Base Grease</th>
<th>1° ZDDP</th>
<th>2° ZDDP</th>
<th>1°/2° ZDDP</th>
<th>1° ZDDP + SIB</th>
<th>2° ZDDP + SIB</th>
<th>1°/2° ZDDP + SIB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bomb oxidation (100 h), psi loss</td>
<td>D942</td>
<td>6.1</td>
<td>3.6</td>
<td>2.7</td>
<td>2.5</td>
<td>3.1</td>
<td>3.8</td>
<td>3.9</td>
</tr>
</tbody>
</table>

To further examine the impact of ZDDP on the thermal stability of grease formulations, TGA testing was used. Since the technique is commonly used one for analysis of greases, in this study the base grease was run followed by repeat testing of the same grease to evaluate repeatability. As seen in Figure 1, the base grease had two main components, which were separated by their thermal stability under the conditions of the test. The majority of the grease sample (the base oil component) burned off between 200 and 430°C, while the thickener itself, which was more thermally stable, was eliminated between 440 and 600°C. The repeatability of the technique was seen with duplicate runs of a representative sample “B”.

![Figure 1 - Base grease response and repeatability of TGA](image-url)
The effects of the addition of ZDDPs to the base grease stability are seen in Figure 2. While the primary ZDDP showed a distinct difference around 350⁰C, it seems that all three ZDDPs increased the thermal stability of the thickener structure, as shown by the increase in peak size between 400 and 500⁰C. It seems that the addition of SIB to the secondary ZDDP particularly affected the thermal stability of the grease structure and caused the loss of base oil at a significantly lower temperature, Figure 3. However, the impact on the primary and mixed ZDDPs was not as pronounced and may even have shown some positive benefits in the grease thickener stability as seen around 450⁰C. Additional study is needed to better understand how these data relates to grease structure and the impact of additives.

High temperature rheology, another way to look at thermal stability of the grease structure, has been used more in recent research. By monitoring the ratio of G” and G’ while gradually raising the temperature, the impact of temperature on grease behavior can be more closely observed. This ratio
is typically referred to as "Tan Delta". The shift of the grease sample from more solid-like behavior at low Tan Delta values to more liquid-like behavior at higher values is commonly seen with the increase in temperature. The sudden rise in Tan Delta can be roughly correlated to dropping point, but can also provide significantly more information about high temperature performance of greases.

As seen in Figure 4, the rise in temperature led to an initial slight "solidification" of the grease structure starting at around 60° C, followed by a gradual change to a more liquid-like phase from 100 to approximately 190° C.

![Figure 4 - Base grease response in high temperature rheology](image)

This was followed by a sharp increase in Tan Delta that correlated roughly to the 205° C dropping point seen with this base grease. As the temperature continued to increase, the signal deteriorated rapidly as the oil ran out of the grease and consistent contact between the plates was lost. The repeatability of the method was quite good.

The effect of ZDDP addition on grease structure at high temperature can be seen in Figure 5.

![Figure 5 - ZDDP response in high temperature rheology](image)
The obvious impact of the ZDDP was to maintain some structural stability of the grease above 240°C. The same characteristic rise in liquid-like nature was seen around 200°C (at the dropping point), but the grease maintained its stability past that point. It is interesting to note that the dropping points measured for these greases were very similar to the dropping point of the base grease, but the high temperature behavior of the ZDDP-containing greases obviously differed significantly.

It seems that the addition of SIB, Figure 6, also impacted the high temperature stability of the grease by lessening the sharp increase in liquid-like nature that occurred around the dropping point of each grease. Again, the dropping point itself showed no significant increase with addition of either ZDDP or SIB, but the high temperature characteristic as measured by rheology obviously changed. Additionally, there appeared to be no significant differences between ZDDP type and response in high temperature rheology testing.

![Figure 6 - Impact of SIB on ZDDP response in high temperature rheology](image)

ZDDP is often used as a primary antiwear component in grease formulations, so the impact on the commonly used Four-Ball weld and wear tests was evaluated. As seen in Figure 7, ZDDP not only lowered wear significantly as compared to the base grease, but it also added EP protection, as seen in the boost in Four-Ball weld results for each formulation. Interestingly, while the primary and secondary ZDDPs boosted the EP by 20 kg, the mixed ZDDP gave a response that was 30 kg higher than that. This same directional response was seen in the presence of SIB, which provided a 60-kg boost in combination with the primary and secondary ZDDPs, but an additional 30 kg (for a total of 90 kg) weld load when added to the mixed ZDDP. This may have been due to the ability of the mixed ZDDP to decompose (and thus form a protective tribolayer) over a wider temperature range than either of the two individual ZDDPs. While ZDDPs provided significant wear protection, both with and without SIB present, no significant differences were seen between ZDDP types.
The Fafnir Fretting Wear test is a commonly used test for oscillating wear and therefore of interest in evaluating wear protection provided by ZDDP. As seen in Table 9, the fretting wear response of different ZDDPs showed that the mixed ZDDP provided some measure of fretting protection over the base grease, while neither of the other ZDDP components significantly improved fretting. The addition of SIB negatively impacted the ability of the mixed ZDDP to protect against fretting, while there was no apparent effect on the primary and secondary ZDDPs, possibly due to a lack of any initial protection by those components.

The coefficient of friction (COF) of the greases containing different ZDDP types was evaluated by HFRR at different temperatures from 30 to 130°C. The data in Figure 8 represent 3 min of COF measurements after the temperature stabilized after each increment. At the initial temperature of 30°C, the addition of ZDDP made very little difference compared to the base grease by itself. As the samples approached 70°C, the degradation of ZDDP began, and the change in COF was seen as a tribofilm formed. The region from 70 to 110°C showed widely variable COF data as the tribolayer formed and grew with increasing temperature. By the time the samples reached 130°C, the tribolayer somewhat stabilized, although there was still some variability in the measurements. Higher temperatures might give more consistent results, but the instrument used in this study could not be used safely above 130°C. The tribolayer formed by ZDDP was typically a thicker film, but still provided some reduction in friction compared to the base grease. Some evidence was seen for the
formation of a thinner, smoother tribolayer (with a lower COF) by the primary ZDDP, and slightly thicker tribolayers (with correspondingly higher COF measurements at 130°C) for the mixed and secondary ZDDPs.

When SIB was added to the ZDDP-containing greases, Figure 9, more variability was seen in the mid-temperature range as the tribolayers formed, possibly because the surface active SIB interfered with formation of the ZDDP film. At 130°C, the variability was less with both the primary and secondary ZDDPs at around the same level as the samples without SIB, although the mixed ZDDP still showed some wide variation. Longer intervals or higher temperatures might show better consistency in the signal as the tribolayer becomes better established.

**Figure 8** - ZDDP Friction data

**Figure 9** - ZDDP friction data with SIB added

**Sulfur Testing**

The two sulfur sources were blended into four formulations to investigate the impact alone and in the presence of the primary ZDDP, Table 10. Due to the wide disparity in sulfur content, the level of each sulfur component was calculated to target an equivalent level of sulfur (2780 ppm S) in each formulation. The level of ZDDP was kept the same as in the study of ZDDP components above.
Table 10 - Formulations for sulfur study

<table>
<thead>
<tr>
<th></th>
<th>Base Grease</th>
<th>SIB</th>
<th>SO</th>
<th>SIB + 1° ZDDP</th>
<th>SO + 1° ZDDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium base</td>
<td>100</td>
<td>99.20</td>
<td>99.22</td>
<td>99.23</td>
<td>98.60</td>
</tr>
<tr>
<td>SIB</td>
<td>-</td>
<td>0.60</td>
<td>-</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>SO</td>
<td>-</td>
<td>-</td>
<td>2.19</td>
<td>-</td>
<td>2.19</td>
</tr>
<tr>
<td>1° ZDDP</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.80</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Again, no significant differences were seen in standard tests (penetration and dropping point) that might otherwise reveal impacts on grease structure (Table 11).

Table 11 - Sulfur structural test results

<table>
<thead>
<tr>
<th>Test</th>
<th>ASTM</th>
<th>Base Grease</th>
<th>SIB</th>
<th>SO</th>
<th>SIB + 1° ZDDP</th>
<th>SO + 1° ZDDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration (60x, 1/2 worker), mm/10</td>
<td>D1403</td>
<td>233</td>
<td>239</td>
<td>242</td>
<td>241</td>
<td>241</td>
</tr>
<tr>
<td>Dropping Point, °C</td>
<td>D 2265</td>
<td>205</td>
<td>200</td>
<td>209</td>
<td>200</td>
<td>200</td>
</tr>
</tbody>
</table>

In all steel corrosion testing, the presence of sulfur improved the result compared to base grease. The results obtained above with the primary ZDDP by itself were included in Table 12 for comparison. As seen in the ZDDP testing, the combination of ZDDP with either sulfur source showed a negative impact on the ability of either ZDDP or sulfur alone to prevent corrosion. While still within the repeatability of the method, the EMCOR results indicated the same phenomena. It seems that this, again, indicated the formation of a protective layer by either sulfur or ZDDP individually, and adding both components interfered with this protection.

Table 12 - Sulfur steel corrosion results

<table>
<thead>
<tr>
<th>Test</th>
<th>ASTM</th>
<th>Base Grease</th>
<th>SIB</th>
<th>SO</th>
<th>SIB + 1° ZDDP</th>
<th>SO + 1° ZDDP</th>
<th>1° ZDDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard bearing corrosion, DI, % Rust</td>
<td>D1743</td>
<td>5/15/15</td>
<td>0/0/0</td>
<td>0/0/0</td>
<td>0.5/1/15</td>
<td>0.5/1/5</td>
<td>0/0/0</td>
</tr>
<tr>
<td>Ave % rust</td>
<td>-</td>
<td>11.7</td>
<td>0</td>
<td>0</td>
<td>5.5</td>
<td>2.2</td>
<td>0</td>
</tr>
<tr>
<td>Standard bearing corrosion, DI, 67 h, % Rust</td>
<td>D1743 mod</td>
<td>-</td>
<td>15/15/15</td>
<td>0/5/5</td>
<td>5/15/25</td>
<td>15/15/25</td>
<td>0.5/0.5/0.5</td>
</tr>
<tr>
<td>Ave % rust</td>
<td>-</td>
<td>-</td>
<td>15.0</td>
<td>3.3</td>
<td>15.0</td>
<td>21.7</td>
<td>0.5</td>
</tr>
<tr>
<td>EMCOR (DI Water), Rating</td>
<td>D6138</td>
<td>5/5</td>
<td>1/2</td>
<td>1/2</td>
<td>2/2</td>
<td>2/3</td>
<td>2/2</td>
</tr>
</tbody>
</table>

Interestingly, the addition of SIB to the base grease caused a decrease in copper corrosion compared to the base grease, Table 13. The addition of sulfurized olefin by itself, or ZDDP in combination with either sulfur source, resulted in high levels of protection against copper corrosion. While it was not surprising that the higher level of active sulfur in SIB caused more copper corrosion than sulfurized olefin, it was surprising that it lowered the amount of copper corrosion seen in the base grease alone. This might have been due to the interaction of the active SIB sulfur with “bad actors” in the base grease, but further study would be recommended to investigate these results.
Sulfurized olefin is used as an antioxidant in engine oil and other formulations, so it was not surprising to see that it provided oxidative stability compared to the unadditized base grease, Table 14. The addition of ZDDP did not appear to provide any synergy, but the low levels of oxidation in this particular base grease did not provide much opportunity to differentiate. SIB did not appear to provide any improvement in oxidative stability, but the combination of SIB and ZDDP reduced oxidation, probably due to the role of ZDDP as a secondary antioxidant.

**Table 14 - Sulfur oxidation results**

<table>
<thead>
<tr>
<th>Test</th>
<th>Base Grease</th>
<th>SIB</th>
<th>SO</th>
<th>SIB + 1° ZDDP</th>
<th>SO + 1° ZDDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper corrosion, 80C, 24 h</td>
<td>6.1</td>
<td>5.3</td>
<td>2.4</td>
<td>3.1</td>
<td>3.3</td>
</tr>
<tr>
<td>Copper corrosion, 100C, 24 h</td>
<td>5.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper corrosion, 120C, 24 h</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It seems that the TGA results in Figure 10 indicated that SIB provided much more thermal stability than sulfurized olefin when used as individual components. This may have been due to the higher activity of the SIB providing more crosslinking and, therefore, more structural stability to the grease thickener at higher temperatures. Additionally, it seems that the addition of ZDDP improved the thermal stability of both sulfur components to about the same level. Overall, it seems that the combination of sulfur and ZDDP provided additional thermal stability versus either of the components by themselves.

**Figure 10 - Sulfur TGA results**

The high temperature rheology testing showed no signs of improvement of the grease structure by either of the individual sulfur sources, Figure 11. As seen in the TGA study, however, the addition of
ZDDP did significantly improve the structure at high temperatures, as the grease maintained a signal and showed relatively low Tan Delta values. However, no differentiation was seen between the sulfur types.

![Figure 81 - Sulfur high temperature rheology results](image)

Since sulfur is often used primarily for extreme pressure protection, testing was done for both Four-Ball weld and Four-Ball wear, Figure 12. Perhaps not surprisingly, the more active sulfur in SIB led to a higher Four-Ball weld result even though both were treated at equal levels of sulfur. Both additives still provided a significant boost over the base grease; both also contributed roughly equal levels of increased wear. The addition of ZDDP not only reduced the wear (as expected), but also provided a small boost in EP protection, which seemed to level out the differences seen for the individual sulfur compounds.

<table>
<thead>
<tr>
<th>Test</th>
<th>ASTM</th>
<th>Base Grease</th>
<th>SIB</th>
<th>SO</th>
<th>SIB + 1° ZDDP</th>
<th>SO + 1° ZDDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 Ball EP Weld Point</td>
<td>D 2596</td>
<td>180</td>
<td>230</td>
<td>210</td>
<td>240</td>
<td>230</td>
</tr>
<tr>
<td>4 Ball Wear (40kg, 75°C, 1200 rpm, 1 hr), mm</td>
<td>D 2266</td>
<td>0.67</td>
<td>0.91</td>
<td>0.97</td>
<td>0.49</td>
<td>0.50</td>
</tr>
</tbody>
</table>

![Figure 92 - Sulfur extreme pressure and antiwear results](image)

As expected, neither sulfur source had a positive impact on fretting wear, Table 15. Even the addition of ZDDP did not improve the performance of either component.
In friction testing by HFRR, Figure 13, the sulfur components brought a little improvement in overall COF by the time the sample reached 130⁰C. Prior to that, the sulfurized olefin increased the friction, sometimes even above the base grease. It appeared that ZDDP helped improve the overall friction by the end of the test, but more study will be needed to confirm the behavior and possible interactions seen here.

**Table 15 - Sulfur fretting wear results**

<table>
<thead>
<tr>
<th>Test</th>
<th>ASTM</th>
<th>Base Grease</th>
<th>SIB</th>
<th>SO</th>
<th>SIB + 1° ZDDP</th>
<th>SO + 1° ZDDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fretting wear, mg</td>
<td>D4710</td>
<td>27.8</td>
<td>25.2</td>
<td>41.2</td>
<td>25.3</td>
<td>26.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>33.6</td>
<td>29.2</td>
<td>24.0</td>
<td>31.2</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 103 - Sulfur friction testing results**

**Antioxidant/Borate Testing**

A third category of additives was tested because of the importance of high temperature performance for many greases. Antioxidants are considered useful for enhancing the oxidative stability of the base oil (the major component of grease formulations) under high temperature or other conditions of thermal-oxidative stress. Borated components are also considered useful for high temperature performance due to their ability to strengthen the grease thickener structure at high temperatures.

For comparison, ZDDP was included with the antioxidant mixture, and borate was added sequentially. Two levels of the borate were examined in combination with the ZDDP and the AO mixture, Table 16.
Although no significant differences were seen in the penetrations of the grease formulations, the effect of the borate in raising dropping point was obvious from the data in Table 17. This is seen commonly with borates, especially in combination with ZDDP, and in this study, it was likely due to some kind of cross-linking structural stabilization of the grease thickener that allowed it to hold on to the oil at higher temperatures.

### Table 17 - AO/Borate physical structure results

<table>
<thead>
<tr>
<th>Testing</th>
<th>ASTM</th>
<th>Base Grease</th>
<th>1° ZDDP</th>
<th>1° ZDDP + AO</th>
<th>1° ZDDP + AO + BPD (1.5%)</th>
<th>1° ZDDP + AO + BPD (3%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Worked 60 Penetration - 1/2 worker (mm/10)</td>
<td>D1403</td>
<td>233</td>
<td>239</td>
<td>239</td>
<td>238</td>
<td>237</td>
</tr>
<tr>
<td>Dropping Point</td>
<td>D2265</td>
<td>205</td>
<td>205</td>
<td>209</td>
<td>239</td>
<td>288</td>
</tr>
</tbody>
</table>

Minimal testing was done with copper or steel corrosion due to the expectation that these components were unlikely to affect performance significantly. However, the results of EMCOR corrosion testing in Table 18 showed a surprising impact from the boronated dispersant. It was possible that this was due to the reaction of the borated species with the water, which kept it away from the surface, or it may have provided a tribofilm that protected against corrosion. Further study would be needed to confirm the mechanism.

### Table 18 - AO/Borate steel corrosion results

<table>
<thead>
<tr>
<th>Testing</th>
<th>ASTM</th>
<th>Base Grease</th>
<th>1° ZDDP</th>
<th>1° ZDDP + AO</th>
<th>1° ZDDP + AO + BPD (1.5%)</th>
<th>1° ZDDP + AO + BPD (3%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMCOR (DI Water), Rating</td>
<td>D6138</td>
<td>5/5</td>
<td>2/2</td>
<td>1/0</td>
<td>0/0</td>
<td></td>
</tr>
</tbody>
</table>

As expected in the pressurized vessel oxidation testing, the addition of the AO mixture had an incremental benefit when used in combination with the ZDDP, which provided some oxidation stability itself, Table 19. The addition of the borate had no significant impact under the conditions of this test.
Table 19 - AO/Borate oxidation results

<table>
<thead>
<tr>
<th></th>
<th>ASTM</th>
<th>Base Grease</th>
<th>1° ZDDP</th>
<th>1° ZDDP + AO</th>
<th>1° ZDDP + AO + BPD (1.5%)</th>
<th>1° ZDDP + AO + BPD (3%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bomb oxidation (100 h), psi loss</td>
<td>D942</td>
<td>6.1 5.6</td>
<td>3.6</td>
<td>2.5</td>
<td>2.2</td>
<td>x</td>
</tr>
</tbody>
</table>

Testing by TGA showed definite evidence of increased thermal stability of the grease in Figure 14. As expected from the dropping point results, borate-containing greases held on to the oil in its matrix at a significantly higher temperature than those without borate. Interestingly, the grease that contained only ZDDP and AO showed a lower thermal stability, and its oil came off at a significantly lower temperature. This did not appear to affect the stability of the grease thickener, as seen by the peak at around 500°C. This may indicate that oil itself was thermally less stable with the AO present, but further testing would be needed to confirm this.

![Figure 114 - AO/Borate TGA results](image)

High temperature rheology of these greases also highlighted the ability of the borate to help maintain a consistent grease structure at higher temperatures, Figure 15. The impact of the ZDDP by itself and in combination with the AO mixture provided some continuous structure through the temperature at which the dropping point was measured, which showed that some benefit was provided here. However, the borate almost eliminated the sharp increase in liquid-like nature seen around 200°C, and the grease appeared to keep a more solid-like nature through that entire temperature zone. This sample was tested up to 300°C, and the slow increase in liquid-like nature was seen through this higher temperature range. Further work at these higher temperatures with some of the other greases studied would be of interest as well.
While the AO would not be expected to have an impact on EP performance, a slight boost was seen in all three greases that contained the AO mixture, Table 20. Surprisingly, it seems that the AO mixture in combination with the ZDDP decreased wear as well. This may indicate some interaction with ZDDP that allowed the ZDDP to provide more EP and AW protection, but the repeatability of the tests would require additional testing to confirm this. On the other hand, the borate degraded the antiwear protection of the ZDDP and gave wear scars that were comparable to the base grease. This may have been due to the formation of a thinner borate film that was not as good at protecting against wear. As discussed further in this study, HFRR testing showed significant decrease in friction with the borated dispersant, and this is usually indicative of thinner films that provide less protection from wear.

<table>
<thead>
<tr>
<th>Test</th>
<th>ASTM</th>
<th>Base Grease</th>
<th>1º ZDDP</th>
<th>1º ZDDP + AO</th>
<th>1º ZDDP + AO + BPD (1.5%)</th>
<th>1º ZDDP + AO + BPD (3%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 Ball EP, Weld Point</td>
<td>D 2596</td>
<td>180</td>
<td>200</td>
<td>220</td>
<td>210</td>
<td>220</td>
</tr>
<tr>
<td>4 Ball Wear (40 kg, 75°C, 1,200 rpm, 1 h), mm</td>
<td>D 2266</td>
<td>0.67</td>
<td>0.53</td>
<td>0.42</td>
<td>0.70</td>
<td>0.72</td>
</tr>
</tbody>
</table>

In the case of fretting wear, Table 21, there was no statistically significant indication of improvement from the ZDDP, the AO or the borated dispersant.

<table>
<thead>
<tr>
<th>Test</th>
<th>ASTM</th>
<th>Base Grease</th>
<th>1º ZDDP</th>
<th>1º ZDDP + AO</th>
<th>1º ZDDP + AO + BPD (1.5%)</th>
<th>1º ZDDP + AO + BPD (3%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fretting wear, mg</td>
<td>D4710</td>
<td>27.8</td>
<td>33.5</td>
<td>28.3</td>
<td>31.9</td>
<td>32.3</td>
</tr>
</tbody>
</table>
Finally, as mentioned above, the HFRR test results showed a clear reduction in friction at the 1.5% treat level of the borate as seen from the duplicate runs in Figure 16. It seems that raising the borate level increased the friction, possibly due to formation of a thicker film with the higher level of boron and phosphorus present. Of additional interest was the higher friction seen with the addition of AO to the ZDDP. This may have been due to an increase in film formation and could be linked to the reduction in wear seen with that formulation.

Figure 136 - AO/Borate HFRR friction results

**Package Testing**
While understanding the behavior of different components individually or in binary combinations with other commonly used additives is important, a finished grease formulation often includes some combination of all these components. While additive packages have some shortcomings in terms of flexibility of use, they are often used to help meet clear performance goals in higher volume greases. In this study, six packages were blended in the same lithium base grease with treat rates calculated to deliver an equivalent amount of sulfur (~5400 ppm S) in each finished formulation, Table 22.

**Table 22 - Package grease formulations**

<table>
<thead>
<tr>
<th></th>
<th>Base Grease</th>
<th>ZDDP Pack 1</th>
<th>ZDDP Pack 2</th>
<th>S/P Pack 1</th>
<th>S/P Pack 2</th>
<th>S/P Pack 3</th>
<th>S/P Pack 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium base, % wt</td>
<td>100</td>
<td>97.64</td>
<td>95.54</td>
<td>98.50</td>
<td>97.89</td>
<td>98.18</td>
<td>98.34</td>
</tr>
<tr>
<td>Package Treat, % wt</td>
<td>2.36</td>
<td>4.46</td>
<td>1.50</td>
<td>2.11</td>
<td>1.82</td>
<td>1.66</td>
<td></td>
</tr>
<tr>
<td>Calculated S, ppm</td>
<td>5404</td>
<td>5397</td>
<td>5415</td>
<td>5402</td>
<td>5387</td>
<td>5395</td>
<td></td>
</tr>
<tr>
<td>Calculated P, ppm</td>
<td>826</td>
<td>803</td>
<td>180</td>
<td>169</td>
<td>237</td>
<td>199</td>
<td></td>
</tr>
<tr>
<td>Calculated Zn, ppm</td>
<td>944</td>
<td>892</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Calculated N, ppm</td>
<td>24</td>
<td>268</td>
<td>120</td>
<td>190</td>
<td>146</td>
<td>183</td>
<td></td>
</tr>
</tbody>
</table>
No significant differences were seen in standard tests (penetration and dropping point) that might otherwise show some weakening of grease structure due to interaction with additive components, Table 23.

### Table 23 - Packages physical testing results

<table>
<thead>
<tr>
<th>Test</th>
<th>ASTM</th>
<th>Base Grease</th>
<th>ZDDP Pack 1</th>
<th>ZDDP Pack 2</th>
<th>S/P Pack 1</th>
<th>S/P Pack 2</th>
<th>S/P Pack 3</th>
<th>S/P Pack 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration (60x, 1/2 worker), mm/10</td>
<td>D1403</td>
<td>264</td>
<td>267</td>
<td>275</td>
<td>269</td>
<td>279</td>
<td>277</td>
<td>273</td>
</tr>
<tr>
<td>Dropping Point, °C</td>
<td>D 2265</td>
<td>197</td>
<td>197</td>
<td>204</td>
<td>204</td>
<td>211</td>
<td>204</td>
<td>207</td>
</tr>
</tbody>
</table>

Each of the packages showed varying degrees of rust protection, with S/P Packs 1 and 4 the least effective in the D1743 bearing corrosion test, Table 24. In the dynamic corrosion (EMCOR) test, ZDDP Pack 1 was the least effective, and ZDDP Pack 1 and S/P Pack 2 showed slight corrosion in one bearing. This not only showed the variation in rust protection systems of various packages, but also the differences in the severity of different corrosion tests and the response of additives.

### Table 24 - Packages steel corrosion results

<table>
<thead>
<tr>
<th>Test</th>
<th>ASTM</th>
<th>Base Grease</th>
<th>ZDDP Pack 1</th>
<th>ZDDP Pack 2</th>
<th>S/P Pack 1</th>
<th>S/P Pack 2</th>
<th>S/P Pack 3</th>
<th>S/P Pack 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Std bearing corrosion, D1, % Rust</td>
<td>D1743</td>
<td>-</td>
<td>0/0/0</td>
<td>0/0/0</td>
<td>0/0/0</td>
<td>0/0/0</td>
<td>0/0/0</td>
<td>0/0/0</td>
</tr>
<tr>
<td>Ave % rust</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Std bearing corrosion, D1, 67 h, % Rust</td>
<td>D1743</td>
<td>-</td>
<td>0/0/0</td>
<td>0/0/0/0.5</td>
<td>1/5/10</td>
<td>-</td>
<td>-</td>
<td>5/1/10</td>
</tr>
<tr>
<td>Ave % rust</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>0.2</td>
<td>5.3</td>
<td>-</td>
<td>-</td>
<td>5.3</td>
</tr>
<tr>
<td>EMCOR (D1 Water), Rating</td>
<td>D6138</td>
<td>2/2</td>
<td>1/1</td>
<td>0/1</td>
<td>0/0</td>
<td>0/1</td>
<td>0/0</td>
<td>0/0</td>
</tr>
</tbody>
</table>

In this particular base grease, all of the S/P Packs showed less protection against copper corrosion than the ZDDP-containing packages, Table 25. This was not surprising in light of the positive impact seen above with ZDDP and the negative impact due to the more active sulfur found in the S/P packages. It was interesting to note that the only S/P package that contained AO showed more protection than the other S/P packages, which did not contain AO.

### Table 25 - Packages copper corrosion results

<table>
<thead>
<tr>
<th>Test</th>
<th>ASTM</th>
<th>Base Grease</th>
<th>ZDDP Pack 1</th>
<th>ZDDP Pack 2</th>
<th>S/P Pack 1</th>
<th>S/P Pack 2</th>
<th>S/P Pack 3</th>
<th>S/P Pack 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper corrosion, 100°C, 24 h</td>
<td>D4048</td>
<td>3a</td>
<td>1b</td>
<td>1b</td>
<td>3a</td>
<td>2e</td>
<td>3a</td>
<td>3b</td>
</tr>
</tbody>
</table>

Unfortunately, the unadditized base grease used for testing the packages had a very low pressure loss result in the D942 testing, and no significant differences were seen between packages in this test, Table 26. More severe conditions would be needed to be able to differentiate the response.
As seen in Figure 17, both ZDDP packages showed a significant increase in thermal stability of the grease compared to the base grease. In Figure 18, it seems that the S/P packages also had an impact on the grease thickener, although it was less distinct, with the region of the thermogram associated with base oil almost unchanged. How this would impact the performance of the grease, especially at high temperatures, is unknown at this time.

**Table 26 - Packages oxidation results**

<table>
<thead>
<tr>
<th>Test</th>
<th>ASTM</th>
<th>Base Grease</th>
<th>ZDDP Pack 1</th>
<th>ZDDP Pack 2</th>
<th>S/P Pack 1</th>
<th>S/P Pack 2</th>
<th>S/P Pack 3</th>
<th>S/P Pack 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bomb oxidation (100 h), psi loss</td>
<td>D942</td>
<td>4.3</td>
<td>2.9</td>
<td>3.4</td>
<td>3.5</td>
<td>2.8</td>
<td>4.5</td>
<td>2.8</td>
</tr>
</tbody>
</table>

![Figure 147 – ZDDP packages TGA results](image1)

![Figure 158 - S/P Packages TGA results](image2)
High temperature rheology showed similar results with differentiation between ZDDP and S/P packages. There were some small differences between ZDDP Packs 1 and 2 (Figure 19) that may have been due to the inclusion of a high level of AO in ZDDP Pack 2, but both showed good consistency and stability through the dropping point range and maintained a signal up to the end of the test. This was different than what was seen in Figure 20, where results for all four S/P packages were similar with a loss of signal corresponding to the approximate temperature at which the dropping point was measured (~200°C). Interestingly, the AO-containing S/P package shows a similar trend toward a more liquid-like nature in the lower temperature range (140 to 190°C) as the AO-containing ZDDP package.
It was interesting to see the differences in response to extreme pressure protection between packages that contained the same nominal amount of sulfur, Table 27. This highlighted differences between activities of sulfur and the interaction of ZDDP and other components of the packages. In general, the higher activity S/P packages gave better EP but worse AW protection, whereas the ZDDP-containing packages sacrifice a little EP protection for better AW. The exception was S/P Pack 3, which showed high EP while maintaining a small wear scar.

**Table 27 - Packages EP & AW results**

<table>
<thead>
<tr>
<th>Test</th>
<th>ASTM</th>
<th>Base Grease</th>
<th>ZDDP Pack 1</th>
<th>ZDDP Pack 2</th>
<th>S/P Pack 1</th>
<th>S/P Pack 2</th>
<th>S/P Pack 3</th>
<th>S/P Pack 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 Ball EP, Weld Point</td>
<td>D2596</td>
<td>180</td>
<td>240</td>
<td>230</td>
<td>280</td>
<td>270</td>
<td>270</td>
<td>270</td>
</tr>
<tr>
<td>4 Ball Wear (40 kg, 75°C, 1200 rpm, 1 h), mm</td>
<td>D2266</td>
<td>0.67</td>
<td>0.53</td>
<td>0.45</td>
<td>0.68</td>
<td>0.58</td>
<td>0.52</td>
<td>1.06</td>
</tr>
</tbody>
</table>

The results for fretting wear, Table 28, were somewhat surprising in view of the relative lack of significant impact from the individual components studied above. Each pack showed a significant improvement on the fretting wear of the base grease. The increased treat rate of individual components, as well as the presence of some phosphate antiwear additives not studied above, may account for the improvement. ZDDP Pack 2 showed the best results, with an average of 14 mg wear, while each of the S/P packages were roughly equal at 19 to 24 mg wear.

**Table 28 - Packages fretting wear results**

<table>
<thead>
<tr>
<th>Test</th>
<th>ASTM</th>
<th>Base Grease</th>
<th>ZDDP Pack 1</th>
<th>ZDDP Pack 2</th>
<th>S/P Pack 1</th>
<th>S/P Pack 2</th>
<th>S/P Pack 3</th>
<th>S/P Pack 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fretting wear, mg</td>
<td>D4710</td>
<td>36.7</td>
<td>25.7</td>
<td>15.1/13.0</td>
<td>20.0</td>
<td>21.8</td>
<td>19.3</td>
<td>23.7</td>
</tr>
</tbody>
</table>

The friction testing by HFRR, Figure 21, showed a wide spread of results, with the two ZDDP-containing packages showing the same fluctuations in the mid-temperature range representative of the tribofilm formation in that region. Both ended up with relatively high COF values (near the base grease), probably due to the formation of thick films by the relatively high concentrations of ZDDP in both formulations. The S/P packages showed a split; S/P Packs 1 and 4 ended up with friction levels higher than the base grease, while S/P Packs 2 and 3 ended up with relatively low COF values (below 0.12). This was likely due to the different phosphorus films formed and the interactions with the active sulfur sources present in each formulation. Interestingly, this roughly correlated with the wear scar data shown above and indicated that the type of films formed with the S/P packages were more likely smooth films associated with polyphosphates that appeared to protect from wear while also reducing friction. The tribofilms associated with ZDDP were typically thicker, rougher films which, while protecting against wear, also tended to raise friction.
Summary and Conclusions

**ZDDP** – ZDDP is typically used in grease as an antiwear agent that can also bring some benefits as a secondary antioxidant through its role as peroxide decomposer. Testing in this study of lithium-thickened grease confirmed these benefits in Four-Ball wear and oxidation testing, with no significant differences seen between types of ZDDP. It seemed that thicker tribolayers formed by ZDDP also contributed to improvements in Four-Ball EP testing, and to a lesser extent, in the fretting wear test. The mixed ZDDP showed significantly better performance Four-Ball EP and fretting tests. Protection was also seen in both steel and copper corrosion tests. The thicker tribolayer also contributed to higher friction by HFRR. Finally, evidence was seen of stabilization of the grease thickener structure at higher temperatures in both TGA and high temperature rheology measurements.

**Sulfur** – As expected, the role of sulfur in protecting surfaces under extreme pressure was confirmed with an accompanying detriment in wear protection. Surprisingly, it seemed that both sulfur sources provided some protection against steel and copper corrosion over the lithium-thickened base grease. The sulfurized olefin also provided the expected oxidation benefits in the pressure vessel oxidation test, but both sulfur sources showed minimal improvement to the grease structure at high temperatures unless used in combination with ZDDP. Interactions with ZDDP had an impact on performance due to apparent competition for the surface. These interactions need to be taken into account when formulating with both component types.

**AO/Borate** – While the expected benefits in oxidative and thermal stability were observed in dropping point, TGA, high temperature rheology and oxidation testing, the borated dispersant also improved steel corrosion and possibly impacted the wear protection negatively.

**Packages** – The packages tested in this study overall illustrated some of the benefits that well-formulated packages can bring, such as additional protection, over the use of individual components. This testing also emphasized the point that packages need to be chosen with overall performance of the finished grease in mind. There is no “one-size-fits-all” package because each package can have strengths and weaknesses in a particular grease. Overall, the packages that contained ZDDP showed good EP/AW balance and improved copper corrosion, oxidation, and high temperature performance.
In this study of lithium-thickened grease, the S/P-based packages gave improved EP performance but sometimes sacrificed antiwear protection, showed better steel corrosion protection in some cases, overall lacked copper passivation, and in general did not perform as well at higher temperatures.

**Future** – It seems that additional work is needed in many areas that were examined in this study of lithium-thickened grease. Some performance areas seemed to show a benefit (or detriment), but the results were not statistically significant. Additional testing in those areas would be beneficial to confirm initial findings and hypotheses. The high temperature work with TGA and rheology showed interesting differences that can be linked to additive componentry, but this area needs further study to correlate these findings to bearing response at high temperatures. Finally, it would be of interest to compare some of the key findings from this study of lithium-thickened grease to responses in a lithium complex grease, and to look at the effect of slight differences in straight lithium bases by changing alkalinity, base oil, or manufacturing process.

**References**


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Abstract
Shearing can cause irreversible changes to the thickener structure of greases. This mechanical degradation can affect oil bleed and grease performance in all applications. There is significant interest in establishing laboratory tests to measure the effects of long-term shear on grease, developing models to describe mechanical degradation, and predicting grease service life. This paper reviews recent progress on these subjects and provides suggestions for future research.

1. Introduction
The unique properties of grease make it an ideal lubricant in many situations, such as rolling element bearings, slider bearings, gears, and flexible couplings [1]. Lubricating grease is composed of a base lubricating oil contained in a thickener structure, with additives often added to improve performance in particular applications. The complex interactions of the two main components allow grease to flow like a liquid at high shear rates while resisting flow at low shear rates. As a grease experiences shear stress, the thickener structure can break down, releasing oil and allowing it to flow to the mechanical components that need it. When the shear stress is discontinued, the grease can relax; its thickener may partially (but not completely) recover its structure [2]. This means that there has been some irreversible damage done to the grease, and it has undergone mechanical degradation.

Degradation is an irreversible process that tends to accumulate with time, concomitantly reducing the system’s free energy and lowering its performance quality. Thus, a measure of irreversibility can be used to quantify deterioration. For this purpose, the concept of entropy as defined by the second law of thermodynamics provides a path forward.

Every real process is irreversible at a fundamental level, meaning that entropy is always generated. Recent theoretical developments [10] have implemented the use of entropy in modeling degradation, allowing degradation models that are based on thermodynamics, rather than empirical formulations.
This idea has been used with success in modeling processes such as wear \cite{11-13}, fatigue \cite{14-17}, battery degradation \cite{18-20}, and grease degradation \cite{21-26}. An entropic model of mechanical grease degradation \cite{27} has been established and validated by researchers, and their use in predicting grease life is discussed in Section 4 after an introduction to the relevant measurements and experimentation techniques.

2. Measuring Degradation

For grease, the effects of degradation can be measured in a variety of ways such as response to applied shear stress, apparent viscosity, and consistency \cite{18}. Other techniques, such as Fourier Transform Infrared Spectroscopy (FTIR) provide useful information, but this information can be difficult to quantify for use in a life model.

2.1 Shear Stress

The response of grease to applied shear depends on shear rate and time, known as shear thinning and thixotropic behavior, respectively \cite{28}. This is displayed in Figure 1 \cite{21,25}. This means that shear stress can be a description of a grease’s degradation at a given time. However, the shear-thinning behavior of a grease must be understood in order to evaluate degradation from shear stress data. For devices operating at a constant shear rate, this concern is mostly alleviated. The only additional major uncertainty is the grease’s tendency to relax and partially recover its structure after shearing \cite{2}.

![Shear Stress vs Shear Rate](image1.png)

![Shear Stress vs Time](image2.png)

**Figure 1:** Grease’s (a) shear thinning \cite{21} and (b) thixotropic \cite{25} nature

2.2 Viscosity

The viscosity of a fluid is a measure of its resistance to motion, defined as shear stress divided by shear rate. In other words, it is the slope of the shear stress-shear rate plot (Figure 1). Viscosity is a constant value for Newtonian fluids, but the viscosity of a non-Newtonian fluid, such as grease, depends on the shear rate. Because the shear stress (at a fixed shear rate) declines over time as a grease is sheared, the viscosity declines as well. Similar to shear stress, the viscosity is dependent on shear rate and time spent shearing, meaning that it has similar advantages and disadvantages to shear stress as a measure of degradation.
2.3 Consistency
Consistency is often considered to be the most important property about a grease, and it changes as a grease degrades. Consistency depends heavily on thickener type and concentration, base oil viscosity, and temperature \[^1\]. As a fibrous grease degrades, its thickener structure becomes fragmented, thinning its consistency. Thus, measuring a grease’s consistency can be a useful method for assessing its mechanical degradation.

The most widely accepted standard for measuring grease consistency is ASTM D217 \[^29\]. Consistency grades defined by NLGI range from 000 (similar to oil) to 6 (similar to cheddar cheese). Grease consistency is measured by working (shearing) grease in a standard cup and allowing a cone-shaped tool to drop and penetrate the grease sample. The depth of penetration defines the consistency grade of the grease.

Another way of quantifying the consistency of a grease involves using oscillatory strain sweep measurements to monitor the changes to the crossover point or the yield stress. These are covered in Section 3.2.

2.4 FTIR
An important tool in observing the degradation of grease is FTIR. An FTIR spectrum (Figure 2) reveals information about the chemical composition of the sample, so it is an excellent means to evaluate the extent of chemical degradation. However, FTIR is impractical for modeling mechanical degradation in cases where chemical changes are negligible.

![FTIR spectrum](image)

**Figure 2:** FTIR for a grease at different stages of mechanical degradation \[^23\]

3. Experimental Studies of Mechanical Degradation
In an effort to test changes to a grease’s structure due exclusively to mechanical degradation, experiments were carefully designed to minimize the influence of additional degradation mechanisms.

3.1 Equipment for Mechanical Degradation Tests
Researchers have developed laboratory equipment that can apply shear to samples of grease for prescribed periods of time to “mechanically age” them. Some researchers have mechanically aged
grease samples for short periods of time in rheometers, while others \cite{23, 24} fabricated custom rigs, shown in Figure 3 \cite{30} and Figure 4 \cite{8, 23}, for extended periods of mechanical aging. Many researchers \cite{21-24} also used a grease worker. All aging procedures were conducted near room temperature, which is appropriate for isolating mechanical degradation. That is, high temperatures may lead to oxidation and chemical degradation, while excessively low temperatures may lead to condensation of moisture from the ambient air.

In rheometers and custom rigs, grease was aged by the rotation of a wall or plate. For rheometer aging, a grease sample is spread on a base plate and the top plate is lowered onto the sample to a prescribed gap distance above the base plate. Excess grease is removed from around the plates, and the top plate is set to rotate for the desired time. For the custom test rigs, the gap distance is fixed based on the chosen geometry. Throughout all tests, the shear stress and shear rate are monitored.

**Figure 3:** Rotating-bob aging machine used by Lijesh and Khonsari \cite{30}

**Figure 4:** Couette aging test rig used by Zhou et al. \cite{8}
3.2 Degradation Measurements

A rheometer can be used to measure shear stress and viscosity. The rheometer applies a varying rotational speed (shear rate) and measures the resistance to rotation at each shear rate, giving a “flow curve” as output. A flow curve shows viscosity as a function of shear rate and shear stress as a function of shear rate. Effects of shearing on mechanical degradation of grease can be evaluated by comparing flow curve data, such as the zero-shear viscosity. Figure 5 \cite{23} shows the change in zero shear viscosity as a function of entropy related to mechanical degradation generated by shearing (discussed below).

![Figure 5: Zero-shear viscosity decrease as entropy is generated\cite{23}](image)

A rheometer can be used to measure grease consistency through the use of fixed-load compression testing or oscillatory strain sweep testing. These tests can be easily performed with less than 5 g of grease and can still yield sufficiently repeatable results.\cite{31}

Fixed-load compression testing \cite{21-24} uses a rheometer to perform a modified version of a cone penetration test. Rezasoltani and Khonsari \cite{21}, and Lijesh and Khonsari \cite{24}, used a-plate rheometer setting to provide a constant compressive force to a grease sample. A grease sample was placed on the base plate of the rheometer, and the top plate was lowered to the predetermined gap. The rheometer then applied a constant force for a prescribed period of time, and the resulting distance traveled by the top plate was recorded and used as an indicator of consistency.

Kuhn \cite{22} and Zhou et al. \cite{23} used a rheometer to find yield stress or crossover stress, and used these values to measure consistency. These tests were done through oscillatory strain sweep mode in a rheometer, where a grease sample was placed between rheometer plates and the top plate oscillated at a fixed frequency with an increasing amplitude. The crossover point was the first point at which the storage modulus ($G'$) and loss modulus ($G''$) reached the same value, marked in Figure 6 \cite{32}.

Cyriac et al. \cite{33} defined the yield stress as the first point at which the stress-strain plot deviates from a line by a prescribed amount, shown in Figure 7 \cite{34}. The stress needed to reach the crossover stress or the yield stress is indicative of a grease’s consistency and the two can be related by empirical curve fits such as those proposed by Speigel et al. \cite{35}.
Another method of monitoring degradation is through the use of a torque meter or ammeter to provide instantaneous data about the shear stress and/or viscosity of grease in operating machinery. This method, used by Lijesh and Khonsari \cite{24,30}, requires careful calibration of the equipment under unloaded conditions in order to monitor the changes to these conditions over time. Assuming proper lubrication is maintained, the torque over time and power drawn over time are proportional to the grease's shear stress, which decreases over time.
3.3 Models and Experimental Results

Rezasoltani and Khonsari \cite{21} analyzed their experimental rheometer data for penetration by applying the Degradation Entropy Generation (DEG) theorem \cite{10}. They interpreted the mechanical degradation of grease in terms of the breakdown of the thickener into fragments and related this change to an increase in disorder or entropy. Rezasoltani et al. reported a linear trend between penetration and entropy generated per unit volume of grease, shown in Figure 8.

Similar results were obtained by aging grease in a rheometer, in a journal bearing, and in a grease worker. This line was approximately the same across all tests performed. Thus, this line is a “characteristic line” for the particular grease being tested.

Assuming that other degradation mechanisms were not present during aging, the slope of this characteristic line represents the coefficient of proportionality between entropy generated and degradation of that grease. They proposed extrapolating this line to estimate the service life of that grease in applications where mechanical degradation is the dominant mechanism.

Kuhn \cite{22} and Zhou et al. \cite{23} sought to verify the results and approach of Rezasoltani et al. They used different ranges of values, and they observed additional behavior: transient and steady state grease degradation. The transient region was categorized by rapid structural degradation, while the steady state region served as a grease’s working life, where degradation happened at a slower rate. Figure 9 shows both regions as observed by different researchers.
Lijesh and Khonsari \cite{24} additionally found that this transient region depended on shear rate, and the degradation took a longer time and to reach a steady state when grease was sheared at a higher shear rate.

Since the shear rates used during the initial experiments of Rezasoltani and Khonsari can be considered relatively low, this is an additional justification for it making up a negligible portion of the obtained results. Because the most rapid degradation happens within this transient region, it is important to understand how a grease changes throughout this time to ensure that it properly lubricates throughout this period and afterward.

4. Applications
These experimental results (in conjunction with the principles of modern degradation theory\cite{10}) are the foundation for recent development of grease life models. Mechanical degradation of grease under shearing is modeled as a function of the change in entropy. With this approach, the life of a grease can be predicted (in the absence of other degradation mechanisms). This model can be adapted to account for changes in operating conditions such as shaft speed.

4.1 Predicting Grease Life
Rezasoltani and Khonsari \cite{25} used changes in grease consistency measurements from rheometer compression tests to determine a failure criterion. For an NLGI grade 2 grease, the failure criterion was established as a consistency drop to NLGI grade 1. Lijesh and Khonsari \cite{24} used the same idea of a drop in NLGI grade but used the entropy generation rate as the measurement tool. Assuming that the grease is sheared at constant shear rate and temperature, the entropy generation rate is proportional to the instantaneous shear stress.

Since Rezasoltani and Khonsari sheared a grade 2 grease until it degraded to grade 1, the consistency of a grade 1 grease had to be established as a basis for comparison. Rezasoltani and Khonsari used fixed-load compression testing in a rheometer to measure the consistency of a grade 1 grease in terms of penetration. Therefore, when the grade 2 grease was tested in the rheometer and had the same penetration as the grade 1 grease, it was considered fully degraded. This is shown in Figure 10 \cite{25}.
Figure 10: XHP 222 penetration vs with failure criterion [25]

Figure 10 shows the characteristic line given by a linear curve fit to Figure 8. This life estimation method determined that, in order to reach the penetration given by a grade 1 grease, the grade 2 grease must have an entropy input of 0.224. Therefore, if an equation relating the entropy generation to time is developed for a particular application, it can be used to estimate the grease life.

An alternative technique for estimating grease life uses the change in entropy generation rate over time instead of the change in penetration depth over time. If the same failure criterion - a consistency drop by one NLGI grade - is used, then the initial entropy generation rate of the lower grade must be measured in order to establish when the higher grade grease has degraded to that point. Figure 11 [24] shows how the entropy generation rate of a grade 2.5 grease (solid black line) and a grade 1 grease (dashed blue line) change as they are sheared over a long period of time.

The entropy generation rate from shearing the grade 2.5 grease eventually reaches the starting entropy generation rate of the grade 1 grease (shown by the dashed black line). At this point, the grease is considered failed, and the time it takes to reach this state is considered the grease’s life. This method used a torque meter to provide constant, online information about the state of degradation. If this method is used in practice, a machine could be re-lubricated when the entropy generation rate reaches a particular value.

Figure 11: Entropy generation rate over time for three grades [24]
4.2 Monitoring the Condition of In-Service Machinery
Taking machinery out of service has undesirable repercussions, so stopping a machine to remove a grease sample for quality analysis should be performed as infrequently as possible. In addition, some quality monitoring techniques such as microscopy give data which cannot be easily applied to predicting the remaining life of grease. Therefore, an online method for monitoring grease degradation is highly desirable.

The online monitoring of grease performed by Lijesh and Khonsari [24] proved to be an effective method for monitoring the status of a grease. This method has application for industrial machinery for which it is practical to dedicate a torque sensor. Using such a monitoring technique has the potential to drastically reduce machine failure since the grease’s condition can be monitored without significantly affecting the machine’s operation. Nevertheless, these preliminary results should be viewed as a proof of concept. Much more research is needed to generalize and apply this method in the field.

5. Conclusions
Mechanical degradation of a grease subjected exclusively to long-term shearing has been studied experimentally and modeled on the basis of entropy related to thickener fragmentation. Nevertheless, other sources of physical degradation are commonly present, including evaporation, oil-thickener separation, and contamination. In addition, chemical degradation, especially oxidation, can degrade the grease in many applications. Since the entropic model has the ability to combine the effects of multiple degradation mechanisms, it shows promise for providing a more accurate grease life estimation in situations where many of these act simultaneously.

Existing grease life prediction models are sufficient for a general approximation of the grease life in a device, but the actual flow of grease throughout the bearing or other device is a complicated topic. In reality, grease does not degrade uniformly, and a superior model would describe grease degradation with a dependence on location in equipment.

In addition, a model for grease life should include all possible degradation mechanisms. Future research is needed on the significance of other degradation mechanisms in addition to mechanical shearing. Applicable thickener types, the temperature range within which the mechanical degradation model provides acceptable results, and effects such as contamination and oil leakage should be included to refine the current model.

Acknowledgments
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References

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Start of a Career

NLGI: Why Sydney?

MQ: I was born in Wagga Wagga, Australia, which is an inland city located about a five-hour drive southwest of Sydney, the capital of the state of New South Wales. While over five million citizens live in Sydney, a fortunate 56,000-plus Australians call Wagga Wagga their home. The name Wagga Wagga originated with the Wiradjuri people who originally settled there on the banks of the Murrumbidgee River and means 'the place of many crows'.

When I was about 7 years old, my family moved to Sydney, and that’s where I’ve lived for most of my life.

NLGI: Why chemistry?

MQ: After graduating high school, I studied at The University of Sydney and earnt a Bachelor of Science Honours Class 1 degree in chemistry. When I was in high school, I didn’t know what I wanted to do career wise, but I enjoyed studying the sciences, particularly chemistry. I think it was the practical side of chemistry more than anything that appealed to me, and I always enjoyed doing experiments in class.

I was also very interested in the Japanese language because I spent a month in Japan as an exchange student and fell in love with the language and the culture. So, I applied to the University of Sydney because it provided the unusual opportunity to study chemistry and the Japanese language, and combine both subjects in a single degree.

After my first year of studying at the University of Sydney, I realised that chemistry was my true passion; learning the Japanese language became more of a hobby. I focused on chemistry and completed my degree. Then, I was keen to enter the workforce and apply everything I’d learnt in my studies.

NLGI: How did your chemistry degree lead to your career in the lubricant industry? Was this by chance or by plan?

MQ: It was quite by chance that I ended up working in the lubricant industry. While studying at University, I was convinced that I would go into the pharmaceutical industry – the topic of my honours thesis was looking for a cure for gingivitis!

After graduation, I started applying for various jobs and managed to get two offers at the same time. One offer was with a pharmaceutical company where I would collate clinical trial data, and the other was working in the lab at Chevron International Technical Center in Sydney. I decided that my first proper job should be working in a lab, so I ended up in the lubricants industry, and I haven’t looked back.

During my career in the lubricants industry, I have been lucky enough to have roles
in different areas - product development, supply chain, quality control, product management, product marketing, technical sales, technical support and OEM liaison.

**NLGI: What was your first role at Chevron?**

**MQ:** At Chevron, I worked as a Grease Chemist and a member of the global grease team. This team was involved in evaluating new formulations and troubleshooting grease performance issues in the Asia-Pacific region.

I thoroughly enjoy working in global teams. I learned that even though my colleagues and I may work for the same Company, we work on projects where each country could have different requirements. For example, Australia is usually grouped geographically with China, Japan and other countries located in Asia. However, in terms of lubricant requirements and technologies, Australia is more closely aligned with North America and Europe.

Working on global teams, I also learned that there can also be issues with language barriers. Even for teammates from different countries where English is spoken as a native language, colloquialisms can sometimes make communication more complicated, but also interesting at the same time. Australians have unique 'slang' and abbreviations, which can be hard for others to understand at times.

But even though I lived in a great country, the distance between Australia and my teammates meant many early morning or late night telephone calls with them, which can sometimes be a challenge.

**Grease Industry Insights**

**NLGI: Is there anything you can highlight about lubricants that is unique or optimized for the Asia-Pacific region and perhaps dissimilar from products for North American and European markets?**

**MQ:** Temperatures in the Asia-Pacific region differ from those in other parts of the world, and lubricant specifications reflect these differences. In the Pacific and Southeast Asia areas, customers don’t experience the extreme cold conditions faced by end-users in North America and Europe. As a result, cold temperature properties of lubricants aren’t much of an issue. However, lubricants must be able to handle heat and high temperature conditions present in the Asia-Pacific region.

In terms of grease types, Asia-Pacific is similar to the rest of the world. In Australia, lithium and lithium complex greases still dominate the market. Calcium sulfonates are present and slowly moving in smaller volumes into the mining segment. I see growing opportunities for polyurea greases in Australia. However, there can be issues with registration and import of their ingredients, and that can making things challenging for polyureas.
In the Asia-Pacific region, one of the big differences I found was the large motorcycle market, it’s something you don’t see anywhere else. This means that there has to be a big focus on these products and also other services that can be provided to the customers at motorcycle workshops [repair shops].

Automotive lubricant products in Australia are closely aligned with those for North American and European markets. This has a lot to do with the low sulfur level in our fuel [gasoline] and also our automotive carpark [parking lot] – there are a lot of European cars in Australia. This differs from Asia, where their domestic vehicles dominate.

**NLGI:** When it comes to doing business and building business relationships in Asia-Pacific, is there anything you might highlight?

**MQ:** Doing business in the Asia-Pacific region, I learned that there can be cultural differences, and it is important for colleagues to respect one other. In some cultures, it is more typical to be forthcoming and to say what is on your mind, while in other cultures, there is a greater tendency to be more reserved and not voice your opinion. Getting to know people and learning to understand what is important to them and how they work can help build mutual respect and make doing business smoother.

**NLGI:** You moved to Caltex Australia Petroleum Pty. Ltd. Was this for a new role?

**MQ:** Caltex Australia is a refiner, importer and marketer of transportation fuels and lubricants. Caltex is a petroleum marketing brand of Chevron and operates in over 60 countries in the Asia-Pacific region, the Middle East and Southern Africa.
At Caltex, I assumed management responsibilities for marketing lubricants, sales and technical support for mining and industrial lubricant products.

It was a new experience for me to switch to a marketing role from the technical side of the lubricant business. Having a technical background definitely helped me when I moved into a marketing-type of role. Being able to understand in detail the benefits of the products made it easier for me to go out and market them. At times, I found it challenging to learn to take a step back from the technical side and clearly explain things to nontechnical colleagues and customers.

**NLGI:** What are some priorities, lubricant products and technical considerations that are unique to the mining industry?

**MQ:** One of the key priorities in mining centers around equipment availability. Unscheduled downtime can be costly, so ensuring that you have the right product in the right place is key for mining applications.

When it comes to grease, the biggest customer requirement is for a heavy duty EP-type of grease, formulated with solids such as molybdenum disulfide, for lubricating the large excavators, draglines and haul trucks. Technical considerations for these heavy duty greases include pumpability along with good EP properties (generally with a 4-Ball weld point of 500 to 620 kgf, depending on the equipment) and good shear stability properties, particularly in hot operating conditions.

**Career Development**

**NLGI:** What do you think about working for major multinational companies versus smaller, privately-held companies?

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VOLUME 84, NUMBER 2
MQ: I have been lucky to have experienced working for multinational companies as well as small, privately-owned companies. I’ve had good experiences at both types of organizations, and I wouldn’t say that one is better than the other. They are different experiences.

One of the advantages of working for a major multinational is the access to resources, such as a global network of people you can call on for support with various projects. At multinationals, there can also be great opportunities for career development, sometimes even career paths you didn’t think of beforehand.

However, there can be some disadvantages. For example, sometimes it can take longer to get some things done at a multinational. A small, private company often has the ability to react quickly and think outside the box to get things done and ensure the customer is satisfied.

NLGI: Could you describe your new position and responsibilities at BP?

MQ: In late 2018, I joined BP Australia as a Senior Technical Support Technologist responsible for the General Industrial portfolio, which includes grease, hydraulic oils, industrial gear oil, turbines oils and the like for Australia and New Zealand (ANZ). As part of the Technology Deployment team, I was involved in rolling out new product technology into ANZ. I also provided technical advice to sales and marketing and supported product manufacturing with new production introductions and material substitutions.
In January 2020, I made the move the UK to join the Product Development team for grease based in Pangbourne. As part of my role as a Senior Technologist, I’m responsible for the development and delivery of a pipeline of new product offers while keeping up to date with the latest developments in the field of grease, including formulations and applications.

**NLGI: What have been some ‘tipping points’ and major decisions in your career?**

**MQ:** I would have to say that the major tipping point in my career is the phase I’m entering right now in my new role at Pangbourne. It’s been a huge decision to leave my family and friends behind and move to the other side of the world. I’ve definitely had the support of my family, who have been amazing in helping me navigate the changes and been a sounding board for all my thoughts about my decision to relocate.

Moving to Pangbourne is an exciting opportunity for me not only career wise, but personally, too. I’m stepping out of my comfort zone, and I think it will really make me grow.

Taking a leap of faith with your career and believing in yourself isn’t always easy, but sometimes you just need to trust your gut and go for it when an opportunity comes along. It definitely helps to work for a great company and work in a field that you enjoy and are passionate about!

**Role of NLGI**

**NLGI: Which NLGI meetings have you attended? How did you benefit?**

**MQ:** I attended my first NLGI Annual Meeting back in 2004 at Dana Point, California. I’d been involved working with greases for a bit over a year. At the 2004 Meeting, I completed the Advanced Grease Course, which I recommend to anyone starting out in the grease industry – I still have the course notes folder in my home office.

Then, a few years passed until I was able to attend another NLGI meeting. In 2010, I went to the Annual Meeting in Florida. This marked my first year playing in the NLGI Annual Golf Tournament, which was (and is always) a lot of fun! I also attended NLGI Annual Meetings in 2012, 2013, and 2016 through 2019.

I get a lot of benefits out of attending NLGI Annual Meetings. When I was working for an additive distributor, NLGI Meetings were a great opportunity to meet all the suppliers I represented in one place and find potential new business. Now that I’m working for a manufacturer and marketer of grease, I find the technical presentations extremely useful. I’ve never come home from an NLGI Meeting without obtaining information that is relevant to something I am working on or an idea for something new.

Networking opportunities are another benefit of attending NLGI Meetings. You get to meet...
a great bunch of people at these Meetings, and I’m sure I wouldn’t be where I am with my career if I hadn’t made some of those contacts at NLGI.

NLGI: Is there a chapter of NLGI in Australia?

MQ: Unfortunately not. Although there is a considerable amount of grease being sold in Australia, there are only three grease manufacturers in the entire country. A few of us who work in the grease industry agree that it would be great to have an Australian chapter of NLGI. However, we are too few in number to organize and support a chapter. Most lubricant professionals in Australia travel to meetings of global organisations such as NLGI, ELGI, STLE or ALMU (Asian Lubricant Manufacturers Union).

NLGI: How do you see NLGI supporting or adding value to the grease industry?

MQ: NLGI is a great organisation for educating people about grease, especially through Education Courses at their Annual Meetings and the recent inaugural Hands-On Education Course. NLGI also provides opportunities for people to share their knowledge through technical articles in The NLGI Spokesman, presentations at the annual meetings, and participation in working groups.

Spare Time?

NLGI: Do you have time to be involved in volunteer activities or hobbies?

MQ: I consider myself bit of a ‘foodie’ and always research restaurants before heading to visit a new city. Earlier this year, I volunteered at the OzHarvest CEO Cook Off. OzHarvest is Australia’s leading food rescue organisation, which collects quality excess food from commercial outlets and delivers it directly to charities that support people in need across the country. BP fuels
OzHarvest’s truck fleet and provides quality surplus food from BP stores for donation across Australia.

The CEO Cook Off event brings together CEOs, business leaders, corporate teams and some of Australia’s top chefs to create a gourmet dinner in Sydney for more than 1,400 vulnerable Australians. In 2019, over A$2.7 million was raised from this event. It was a highlight for me to see how happy and appreciative the attendees were, and realize how lucky we are to be able to have a hot meal every night.

I also love to bake. My colleagues at BP have come to expect and enjoy my baked goods in the office. I recently participated in a ‘Bake Club Challenge’ where celebrity chefs provided a new recipe each month. It was a lot of fun, and I learnt a lot of new skills such as tempering chocolate, which is a method to melt chocolate for making a smooth, shiny, tasty coating on candies.

Travel

NLGI: When you are not working, where is your favorite place to travel?

MQ: That’s a tough question. I love to travel, and it’s hard to pick a favourite. As soon as I return from a holiday, I’m usually busy booking the next one.

The Galapagos Islands, near Ecuador, and Easter Island, off the coast of Chile, are two of my favourites. In 2016, I did a trip there with my Dad, and they are both fascinating places. The wildlife in the Galapagos - giant tortoises, blue footed boobies and flamingoes - is amazing and unlike creatures at any other place I’ve visited.

Easter Island is also very unique with an interesting history. I still can’t wrap my head around how the Rapa Nui people managed to carve and move their Moai stone statues, human figures up to 10 m (33 ft.) in height and 82 tonnes (90.4 short tons) in weight, onto platforms across the Island, between the years 1250 and 1500.

I have also loved exploring volcanoes and marine life on The Big Island (officially named Hawaii), where swimming with manna rays was an unforgettable experience. Most recently, I visited the tulip fields outside of Amsterdam. The amazing colour and quantity of flowers inspired me to attempt to grow tulips at home which, I am happy to report, was a great success.

When I’m looking for a place to relax, Fiji is where I generally head. The islands are beautiful, the water crystal clear and the locals friendly.

NLGI: Do you have any suggestions for NLGI members who might visit Australia?

MQ: Australia is known for its ‘great outdoors’, and there is definitely plenty to see and do.

Being from Sydney, I would suggest you start there - take a swim at Bondi Beach, followed by some fresh prawns at Bondi Icebergs Swim Club overlooking the Beach. Make your way into Circular Quay and, if you’re feeling adventurous, you can walk up the Sydney Harbour Bridge and take in a view of the City like no other. Finish the day with a glass of wine at the Opera Bar, next to the Opera House, while watching the sun set over the Harbour.
Melbourne is ‘foodie central’, and there is a huge selection of trendy restaurants and cocktail bars on offer. A few of my favourites include Chin Chin, Tonka, Supernormal and Eau de Vie.

There is no shortage of great wine regions in Australia. The Hunter Valley, Yarra Valley, Barossa Valley and Margaret River are all good starting points. These regions are also great locations to spot a kangaroo or three in the wild, particularly at dawn and dusk.

Finally, no trip to Australia would be complete without seeing the Great Barrier Reef - sprawling 2,300 km of coastline in far north Queensland, where the blue of the water and variety of sea life have to be seen to be believed. On a recent trip there, my family spotted green sea turtles, white tip reef sharks and a wide variety of brightly coloured fish including Nemo [the Ocellaris Clownfish that played a starring role in the Disney film, Finding Nemo]. Just be careful of swimming during ‘stinger season’ (November through March), when there are many of the smallest (1 cm3) and most venomous varieties of jellyfish in the world. But if you just don a ‘stinger suit’ [similar to a wetsuit], you’ll be sweet. Come to think of it, we have quite a few deadly creatures in Australia...

This interview series, started in 2019 by Dr. Moon and Dr. Shah, gives NLGI members a bit of insight into the professional and personal lives of their colleagues, developments in the grease industry and the role of NLGI worldwide. If you would like to suggest the name of a colleague for an interview (or volunteer to be considered as a candidate), please kindly email Mary at mmmoon@ix.netcom.com or Raj at rshah@koehlerinstrument.com.

Dr. Mary Moon is Technical Editor of The NLGI Spokesman. She writes scientific and marketing features published in Lubes’n’Greases and Tribology & Lubrication Technology magazines, book chapters, and other works. Her experience in the lubricant and specialty chemicals industries includes R&D, project management, and applications of tribology and electrochemistry. She served as Section Chair of the Philadelphia Section of STLE.

Dr. Raj Shah is currently a Director at Koehler Instrument Company and was an NLGI board member from 2000 to 2017. He is an elected fellow of NLGI, STLE, INSTMC, AIC, Energy Institute and the Royal Society of Chemistry. A Chartered Petroleum Engineer from EI and a Chartered Chemical Engineer from IChemE, he is currently active on the board of STLE and on the advisory boards of the Engineering Departments at SUNY Stony Brook, Auburn University and Pennsylvania State University. More information on Raj can be found at https://www.astm.org/DIGITAL_LIBRARY/MNL/SOURCE_PAGES/MNL37-2ND_foreword.pdf
Abstract
In steel mills and other applications where water spray is common, the service lives of greases and bearings depend critically on the ability of lubricants to repel water and metalworking fluids. This study focused on measuring the response of four types of commonly used greases to water spray: simple lithium soap, lithium complex soap, lithium calcium mixed soap, and overbased calcium sulfonate. Grease consistency, base oil viscosity, two types of polymer additives, and total base number (in the case of overbased calcium sulfonate greases) were varied in this study. All greases were tested for water washout under the same conditions according to ASTM D1264. Grease water repellency was improved by a high molecular weight polymer additive and by using a higher total base number calcium sulfonate to make overbased calcium sulfonate grease. Increasing the kinematic viscosity of the base oil from 150 to 320 mm²/s (cSt) was also beneficial in the formulations tested.
**Introduction**

Water intrusion into the grease is a challenge for applications in cold rolling steel mills. Water can form an emulsion with base oils, and there can be loss of grease structure and consistency. The softened grease becomes more susceptible to washing out of the bearings as its consistency drops. Operators use frequent or continuous bearing re-lubrication strategies to compensate, but bearing failures are common. Production losses from bearing failures and maintenance lead to higher production costs. An optimal choice of grease becomes an important technical decision that can reduce these risks.

In steel mills, the service requirement is for grease to maintain its structure, resist water intrusion through adequate water repellency, and maintain its lubrication properties. Cold rolling steel mills have traditionally used greases formulated with simple lithium soap, lithium calcium mixed soaps, and lithium complex thickeners. In the experience of these Authors, overbased calcium sulfonate greases are gaining favor as lubricants for the bearings that support the rollers in steel mills.

It is hypothesized that the service life of the grease and bearings can be substantially improved by increasing the grease’s water repellency and raising its water tolerance and resistance. This study focuses on the water washout performance of four commonly used soap-based greases by examining their water resistance when the grease consistency and formulation are altered.

Formulating greases for steel mill applications must balance many considerations. The grease must withstand the force of sprays of water and metalworking fluid emulsions. As centralized grease systems commonly are employed to supply grease to the roller bearings, greases with NLGI 3 consistency are problematic as they can plug supply pipes. Experience dictates that the ideal consistency range for this application is between NLGI grade 1 and NLGI grade 2 (e.g., NLGI grade 1.5).

In this study, the properties of grease consistency, base oil viscosity, and the total base number (TBN) of the calcium sulfonate used to make overbased calcium sulfonate grease were varied to examine their effects on grease performance. Customary units of for kinematic viscosity, centistokes or cSt, were used throughout this paper.

![Water washout test device (Courtesy of Koehler Instrument Company)](image-url)
**Design and Execution of Experiments**

**Effects of NLGI Grade and Base Oil Viscosity**

In the first phase of this study, four candidate greases were compared: simple lithium soap, complex lithium soap, lithium calcium mixed soap, and overbased calcium sulfonate. All greases were formulated with Group I base oil. The soap greases were formulated with 150 cSt base oil, and the overbased calcium sulfonate grease was prepared from a slightly higher base oil viscosity of 180 cSt. Each of these greases was thickened to NLGI grade 3 consistency. The soap greases were blended by hand with appropriate heating and milling, and the overbased calcium sulfonate grease was manufactured on a commercial scale.

These greases were tested to ASTM D1264 water washout test conditions. In D1264, a bearing is packed with grease and mounted in a shielded, unsealed housing. Water at a temperature of 79°C (100°F) impinges on the bearing as it rotates (600 rpm). The percent weight loss of grease is measured and reported. (1-3)

The loss of measured grease ranged from 3.6 to 6% by mass (Table 1).

<table>
<thead>
<tr>
<th>Grease Type</th>
<th>ASTM D217 Grease Consistency (mm/10)</th>
<th>ASTM D445 Base Oil Viscosity 40°C (cSt)</th>
<th>Water Washout ASTM D1264 79°C (% loss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple lithium soap</td>
<td>245</td>
<td>150</td>
<td>6</td>
</tr>
<tr>
<td>Lithium calcium soap mixture</td>
<td>244</td>
<td>150</td>
<td>5</td>
</tr>
<tr>
<td>Lithium complex</td>
<td>246</td>
<td>150</td>
<td>5</td>
</tr>
<tr>
<td>Calcium sulfonate</td>
<td>245</td>
<td>180</td>
<td>3.6</td>
</tr>
</tbody>
</table>

In the second experiment, the same group of thickeners and base oils were used to formulate NLGI grade 2 greases. In water washout tests, these greases lost from 6.8 to 12% by mass (Table 2).
Table 2. Candidate greases with NLGI 2 consistency and tested for water washout

<table>
<thead>
<tr>
<th>Grease Type</th>
<th>ASTM D217 Grease Consistency (mm/10)</th>
<th>ASTM D445 Base oil Viscosity 40°C (cSt)</th>
<th>Water Washout ASTM D1264 79°C (% loss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple lithium soap</td>
<td>274</td>
<td>150</td>
<td>12</td>
</tr>
<tr>
<td>Lithium calcium soap mixture</td>
<td>276</td>
<td>150</td>
<td>10</td>
</tr>
<tr>
<td>Lithium complex</td>
<td>275</td>
<td>150</td>
<td>10</td>
</tr>
<tr>
<td>Calcium sulfonate</td>
<td>276</td>
<td>180</td>
<td>6.8</td>
</tr>
</tbody>
</table>

In the next experiment, these thickeners were blended with heavier Group I base oil (220 cSt) to make NLGI grade 2 greases. The ASTM D1264 test results ranged from 5.1 to 9.5% by mass (Table 3).

Table 3. Candidate greases with NLGI 2 consistency prepared from 220 cSt base oil, water washout results.

<table>
<thead>
<tr>
<th>Grease Type</th>
<th>ASTM D217 Grease Consistency (mm/10)</th>
<th>ASTM D445 Base Oil Viscosity 40°C (cSt)</th>
<th>Water Washout ASTM D1264 79°C (% loss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple lithium soap</td>
<td>274</td>
<td>220</td>
<td>9.5</td>
</tr>
<tr>
<td>Lithium calcium soap mixture</td>
<td>276</td>
<td>220</td>
<td>8</td>
</tr>
<tr>
<td>Lithium complex</td>
<td>275</td>
<td>220</td>
<td>8</td>
</tr>
<tr>
<td>Calcium sulfonate</td>
<td>276</td>
<td>220</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Next, NLGI grade 2 greases were prepared from these thickeners and 320 cSt Group I base oil. The loss of grease volume ranged from 4.29 to 8% (Table 4).
Table 4. Candidate greases with NLGI 2 consistency and ISO 320 base oil

<table>
<thead>
<tr>
<th>Grease Type</th>
<th>ASTM D217 Grease consistency (mm/10)</th>
<th>ASTM D445 Base Oil Viscosity 40°C (cSt)</th>
<th>Water Washout ASTM D1264 79°C (% loss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple lithium soap</td>
<td>274</td>
<td>320</td>
<td>8</td>
</tr>
<tr>
<td>Lithium calcium</td>
<td>276</td>
<td>320</td>
<td>6.4</td>
</tr>
<tr>
<td>soap mixture</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lithium complex</td>
<td>275</td>
<td>320</td>
<td>6.5</td>
</tr>
<tr>
<td>Calcium sulfonate</td>
<td>276</td>
<td>320</td>
<td>4.29</td>
</tr>
</tbody>
</table>

Effect of Calcium Sulfonate TBN

The total base number (TBN) of overbased calcium sulfonate thickened grease is believed to be an indicator of the water resistance and spray-off resistance properties. Calcium sulfonate grease is typically manufactured from a 300 TBN and 400 TBN overbased calcium sulfonate. It is expected that raising the TBN will increase the grease’s beneficial structure retaining properties. Conversely, a TBN less than 300 is expected to reduce the tolerance of grease to water. This hypothesis was tested using calcium sulfonates with TBN values of 300 and 400 in the fifth experiment (Table 5).

Table 5. Calcium Sulfonate greases with two thickener TBNs

<table>
<thead>
<tr>
<th>Grease Type</th>
<th>Grease Consistency</th>
<th>ASTM D445 Base Oil Viscosity 40°C (cSt)</th>
<th>Water Washout, ASTM D1264 79°C % loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium sulfonate</td>
<td>275</td>
<td>320</td>
<td>5.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.28</td>
</tr>
</tbody>
</table>

Effect of Polymer Additives

In the sixth and final experiment, two different types of polymer additives were evaluated to determine if they would further enhance water washout of greases. The first polymer (P1), was a high molecular weight polyisobutylene, and the second polymer (P2) was a specially designed hydrocarbon resin polymer known to be highly hydrophobic and very shear stable.
Each polymer was added at the same treat level (2%) to four candidate greases prepared with Group I 320 cSt base oils and thickened to NLGI grade 2 consistency. The treat levels of other additives – antiwear (AW), antioxidant, rust and corrosion inhibitors – were the same as those used as in other experiments described above.

Without the addition of either polymer, grease losses ranged from 1.97 to 5% by mass. Both polymers significantly reduced percent loss for all greases tested (Table 6). Of the four thickener chemistries, the overbased calcium sulfonate gave the best performance with and without polymer additives.

While these two polymers were tested only in greases formulated with 320 cSt base oil, similar performance is expected in greases prepared with 150 or 220 cSt viscosity oils.

Table 6. Addition of polymers to greases prepared with 320 cSt base oil

<table>
<thead>
<tr>
<th>Grease Type</th>
<th>Grease Consistency</th>
<th>Water Washout, ASTM D1264 79°C (% loss)</th>
<th>Water Washout, ASTM D1264 79°C % loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple lithium soap</td>
<td>274</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>Lithium calcium mixed soap</td>
<td>276</td>
<td>6.4</td>
<td>2</td>
</tr>
<tr>
<td>Lithium complex</td>
<td>275</td>
<td>6.5</td>
<td>4.4</td>
</tr>
<tr>
<td>Calcium sulfonate</td>
<td>278</td>
<td>4.29</td>
<td>1.97</td>
</tr>
</tbody>
</table>

P1 - High molecular weight polymer, P2 - Hydrocarbon resin polymer

Results

These experimental data clearly confirmed the hypothesis that using a higher viscosity base oil reduces the loss of grease mass from water washout as measured by ASTM D1294 (Table 7). This was true for all grease types tested, and the pattern held regardless of the base oil viscosity. Increasing the base oil viscosity from 150 to 320 cSt reduced the loss of grease during water washout testing by 4% for the simple lithium soap, 3.6% for the lithium calcium soap mixture, 3.5% for the lithium complex soap, and 2.3% for the overbased calcium sulfonate.

Overbased calcium sulfonate grease had lower percent mass loss than the other three candidate greases for each consistency or viscosity tested. This result supports the move of the steel industry towards calcium sulfonate grease for hot rolling steel roller bearing lubrication. It should be noted that successful field installation has been employed, and positive feedback has been received. (4,5)

While increasing the viscosity had clear benefit in reducing water wash out for all greases tested
in this study, the viscosity choice is of fundamental importance in applications in the field. Base oil viscosity affects film thickness at the point of lubrication of the rolling elements within the bearing. An improper viscosity choice may adversely affect the bearing lubrication film thickness and cause premature bearing failure. Operators and technical support staff should use caution to choose grease with appropriate base oil viscosity that meets the bearing load and speed requirements and provides optimum resistance to water washout.

**Table 7. Summary data table**

<table>
<thead>
<tr>
<th>Grease Type</th>
<th>ASTM D217 Grease Consistency (mm/10)</th>
<th>ASTM D445 Base Oil Viscosity 40°C (cSt)</th>
<th>Water Washout ASTM D1264 79°C (% loss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple lithium soap</td>
<td>274</td>
<td>150</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>274</td>
<td>220</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>274</td>
<td>320</td>
<td>8</td>
</tr>
<tr>
<td>Lithium calcium soap mixture</td>
<td>276</td>
<td>150</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>276</td>
<td>220</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>276</td>
<td>320</td>
<td>6.4</td>
</tr>
<tr>
<td>Lithium complex</td>
<td>275</td>
<td>150</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>220</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>320</td>
<td>6.5</td>
</tr>
<tr>
<td>Calcium sulfonate</td>
<td>276</td>
<td>180</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>276</td>
<td>220</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>276</td>
<td>320</td>
<td>4.29</td>
</tr>
</tbody>
</table>

As discussed above, both polymers significantly reduced percent loss for all greases tested, as discussed above. The use of polymer additives could potentially balance the use of lower viscosity base oil needed to meet the bearing lubrication requirements. Likewise, using higher TBN calcium sulfonate to formulate overbased calcium sulfonate grease reduced water washout loss.
Conclusions

Increasing the grease consistency from NLGI grade 2 to 3 improved (lessened) water washout for all four greases in this study of simple lithium soap, lithium complex soap, lithium calcium mixed soap, and overbased calcium sulfonate greases formulated with Group I base oil. However, this approach is expected to lead to clogging of the grease supply lines and is a poor remedy to improve water washout performance.

Increasing the base oil viscosity had a clear benefit in all grease types tested. However, this remedy should be employed only after a determination is made that the correct base oil viscosity supports the bearing lubrication function.

Overbased calcium sulfonate showed best overall results in this study. Increasing the TBN of the calcium sulfonate raw material and adding polymers gave the best overall results. These are good remedies to improve water washout performance and thereby extend the service life of grease while lubricating and protecting bearings.

Field testing is recommended to evaluate overbased calcium sulfonate greases with polymer additives in roller bearings for steel mill hot rolling applications.

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References

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2020 ELGI AGM Information

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NLGI currently licenses grease through their Certification Mark program which includes the well-known GC-LB Performance Classification. This certification program has provided an internationally-recognized grease specification for grease and bearing manufacturers, users and consumers since 1989. Although originally conceived as an automotive chassis and wheel bearing specification, GC-LB is recognized as a mark of quality for grease specifiers. Due to advancements in materials, technologies and applications, NLGI recognizes that current applications may be better served by updated specifications.

Because NLGI’s working groups are made up of volunteers from the industry, NLGI has contracted with The Center for Quality Assurance to interview and survey members of the grease industry with a goal of defining these new specifications and ensuring that they meet the needs of today’s grease-lubricated applications. The initial focus will be on updated specifications for a premium grease that could be used in a variety of bearings and applications which require similar lubricating properties. Additional specifications will be defined for high load, water resistance, corrosion resistance, low temperature and long-life applications. Future specification work may include grease for gear boxes, electric motors and other applications.

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*Please note the GC-LB is not being replaced. The new specifications will be in parallel to GC-LB. NLGI will continue to support GC-LB certification and the use of the mark on finished products. The new specifications, certification and marks will be used in applications as appropriate and useful to the industry. NLGI will continue to support the use of the current GC-LB marks as long as there is a market for them.