Evaluation of the impact of High Viscosity Naphthenic Oils in various thickener systems

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Abstract

Mineral oils that are used by grease manufacturers can be divided into two major groups, paraffinic oils (API Groups I, II and III) and naphthenic oils (API Group V). These categories of base oils have their own advantages and disadvantages depending on the type of applications and cost.

Right now, grease manufacturers are witnessing two major challenges: 1) a shortage of bright stock because of the ongoing rationalisation of paraffinic Group I refineries, and 2) a rapid price increase for lithium hydroxide due to market demands for lithium batteries. These challenges are pushing the grease industry to intensify their development activities in order to be able to provide new products to the market without compromising performance.

The purpose of this paper is to target these challenges, namely, by using naphthenic oils. Traditionally speaking, high viscosity naphthenic oils are only used as a minor part of the formulation of lubricating greases. However, this paper investigates the impact of using two straight cut naphthenic oils, with viscosities of 380 mm²/s and 620 mm²/s, with various thickener types.

The chosen thickeners were conventional lithium, lithium complex and organophilic clay, which together represent more than 75 percent of the thickener in global grease production.

The greases were fully characterised, including rheological measurements, and thereafter compared with each other. In addition, since high film thickness and load carrying capacity are important parameters for industrial applications, the greases were studied tribologically.

In summary, based on the results obtained, two different but pragmatic solutions were suggested targeting the issues described above. Moreover, the use of wax free naphthenic oils in these formulations resulted in greases with good low temperature mobility, despite the high viscosity of the base oils, and they can be suitable for a number of applications, e.g., in central lubrication systems.

Introduction

The base oil industry has been going through fundamental changes in the last decade. These changes have been marked by the rapid growth in production capacity of Group II and Group III base oils.
The closure of Group I refineries has brought with it a deficit on the availability of high viscosity base oils. This deficit is having a major impact on the lubricant and grease industry since neither Group II nor Group III refineries can produce bright stocks. At the same time, there is a huge demand for lithium, which is used in the production of batteries for, among other things, mobile phones and vehicles.

This demand from the battery industry created a sudden price increase for lithium hydroxide during the last few years, and it is believed that prices will continue to increase as the world moves forward rapidly into the automobile’s electrification age.

The use of highly viscous naphthenic oils in lubricating grease formulations can be one of the solutions available for grease manufacturers today. Previous publications, e.g. [1], have indicated that the use of highly viscous naphthenic oils, and its blends with other base oils (mainly with paraffinic Group I, II and III oils), results in savings on soap consumption in most of the existing thickener systems, while keep the same grease performance.

The aim of this paper is to evaluate the performance of two-high viscosity naphthenic oils in lithium, lithium complex and bentonite (clay) greases. All these thickener systems, along with high viscosity base oil, can be used successfully in many applications, e.g., in the sugar mill industry. It is notable that high viscosity naphthenic oils will work excellently in most of the existing thickener systems such as aluminum complex.

The Base Oils
Two highly viscous naphthenic base oils (BO1 and BO2), which were hydrotreated, were chosen for this study. Table 1 highlights some of the characteristics of these oils.

Table 1 shows some oil properties that directly connected to properties in greases that might be produced with these oils, mainly:

- a) the higher values of VGC and CA as well as the lower aniline point suggest that BO2 has higher solvency power than BO1.
- b) BO2 has significantly higher kinematic viscosity (> 60%) than BO1.
- c) BO1 has lower pour point due its lower viscosity.
- d) the sulfur content of BO2 is almost three times higher than BO1, which may have some positive impact on some properties, e.g., oxidation stability.

The Greases
In total, six greases (A, B, C, D, E and F) were prepared in a pilot plant using the two naphthenic oils. The thickeners were conventional lithium, lithium complex and organophilic clay. The acids were 12-hydroxystearate acid (12-HSA) and azelaic acid. It is well known that manufacturing process of Lithium, lithium complex and Bentonite greases are different. Thus, the greases have been produced according to the state of art, however, in the case of lithium and lithium complex greases 50 (wt.%) of the amount of base oil was used in the cooking stage and 50 (wt.%) during the cooling and finishing stages. For Bentonite greases, all oil was used at the beginning of the process.

Notable a) the process parameters for each type of grease were kept constant and b) no additives were added into the greases.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Unit</th>
<th>Method/ASTM</th>
<th>BO1</th>
<th>BO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density @ 25°C</td>
<td>kg/dm³</td>
<td>D4052</td>
<td>0.923</td>
<td>0.934</td>
</tr>
<tr>
<td>Viscosity @ 40°C</td>
<td>mm²/s</td>
<td>D445</td>
<td>375</td>
<td>618</td>
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<tr>
<td>Viscosity @ 100°C</td>
<td>mm²/s</td>
<td>D445</td>
<td>19</td>
<td>21.8</td>
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<tr>
<td>Flash Point, PM</td>
<td>°C</td>
<td>D93</td>
<td>264</td>
<td>255</td>
</tr>
<tr>
<td>Pour Point</td>
<td>°C</td>
<td>D97</td>
<td>-18</td>
<td>-12</td>
</tr>
<tr>
<td>Aniline Point (AP)</td>
<td>°C</td>
<td>D611</td>
<td>98</td>
<td>87</td>
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<tr>
<td>Viscosity Gravity Constant</td>
<td></td>
<td>D2001</td>
<td>0.850</td>
<td>0.818</td>
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<tr>
<td>Reflective Index @ 20°C</td>
<td></td>
<td>D1747</td>
<td>1.507</td>
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<tr>
<td>Copper Corrosion</td>
<td>rating</td>
<td>D130</td>
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<td>1</td>
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<tr>
<td>Sulfur content</td>
<td>wt.%</td>
<td>D2622</td>
<td>0.32</td>
<td>0.33</td>
</tr>
<tr>
<td>Color</td>
<td>rating</td>
<td>D1500</td>
<td>&gt;2.5</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>Total Acid Number</td>
<td>mgKOH/g</td>
<td>D074</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
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<td>Carbon Type Composition</td>
<td></td>
<td>D2140</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C14 (Aromatic content)</td>
<td>%</td>
<td>-</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>C24 (Naphthenic content)</td>
<td>%</td>
<td>-</td>
<td>55</td>
<td>51</td>
</tr>
<tr>
<td>C16 (Paraffinic content)</td>
<td>%</td>
<td>-</td>
<td>33</td>
<td>34</td>
</tr>
</tbody>
</table>

Table 1: Typical characteristics of the two naphthenic oils.
A review of Table 2 suggests:

a) Thickener content was low for all greases; however, less thickener was needed to make greases with BO2 than BO1. The reductions were about 9 percent for lithium grease, 12 percent for lithium complex grease and 22 percent for bentonite grease.

b) Dropping point was measured according to IP396. Excellent dropping points for the lithium and lithium complex greases were measured. It is well known that bentonite clay based grease is a gel and doesn’t have a dropping point.

c) The shear stability of the greases after 100,000 strokes was measured according to ASTM D217, and results were good for the lithium and lithium complex greases. It is well known that bentonite clay based grease is a gel and doesn’t have a dropping point.

d) Bentonite clay based grease is known to have poor shear stability compared with, e.g. lithium grease, due to the nature of the thickener system. However, it has been documented that the use of high viscosity napthenic oil with relatively high polarity has offset and reduced this weakness. Hence, the measured consistency after 100,000 strokes should be regarded as good for this type of grease.

e) The results for the degree of oil separation, measured according to IP 121 (40 °C/168 hrs.), for these greases are quite interesting. The higher soap content is expected to correspond to lower oil separation, of course if the manufacturing process is kept constant. However, BO2 based greases showed less oil separation despite having lower thickener content, which can be explained by the viscosity differences between BO1 and BO2 at 40 °C.

f) Pumpability of the lubricating greases can be simulated by different methods, e.g., measurement of the flow pressure according to DIN 51805. Parameters such as consistency of the grease, polymer content, kinematic viscosity of the oil and pour point, as well as the degree of the wax content in the base oil, are the main parameters that can affect the mobility of the greases. In this study, wax content and polymers were eliminated, and the low temperature mobility of the greases depended on the thickener content, the viscosity and the pour points of the oils. Good low temperature mobility for all greases at -20 °C was noted. Nevertheless, higher pressure was needed for the BO2 based greases because of the significantly higher viscosity of BO2 and its higher pour point.

g) Water wash out was measured according to ASTM D1264. The outcome was good to excellent for all greases. Better resistance to water for lithium complex greases was expected due to the significantly higher thickener content of those greases. If Grease A and Grease B (lithium greases based on BO1 and BO2, respectively) are compared, much better resistance to water can be noted for Grease B despite having lower thickener content. Most probably, this is because of the significantly higher viscosity of BO2.

h) Four ball tests were conducted according to ASTM D2266, with 40 kg load for 60 min., which is a severe test for a neat grease. In Table 2, the average wear scar diameter for each grease is shown. All the greases showed the same degree of wear, with the exception for Grease B which showed a significantly smaller wear scar.

**Oxidation stability** tests were conducted by using a small-scale oxidation test (RSSOT). By using this
method, it is possible to estimate the oxidation stability of oil and grease. According to ASTM standard method (ASTM D7575), the oxidation stability is determined via oxygen consumption. In number of publications, e.g. [3], the method has been described. The procedure of the test is as follows: a breakpoint, at which there is a pressure drop of 10 percent below maximum pressure, is recorded as the induction time (IT) at a constant temperature of 140 °C. Maximum pressure is the sum of the applied oxygen pressure (700 kPa) and the vapor pressure of the sample.

It has been reported that fully formulated mineral oil based lithium and lithium complex greases may have induction times ranging from 176 to 481 min. This means that the results for neat greases that are shown in Table 3 are good with respect to the fact that no antioxidant was used. Grease F shows a significantly longer induction time which can be explained by the fact that the oil was not exposed to high temperatures when bentonite grease was produced. In a previous study [3], it was shown that, e.g., the induction time for the fresh base oil is longer than the induction time for the same base oil that was used in the production of lithium grease.

Rheological behavior of the greases was studied by using a rotational rheometer in oscillating mode. The complex modulus of a lubricating grease is determined in a dynamic strain sweep measurement at constant temperature. The complex modulus (\(G^*\)) is calculated from the viscous modulus (\(G'\), the storage modulus) and the elastic modulus (\(G''\), the loss modulus) and characterizes the nature of the lubricating grease, which is a viscoelastic material. In an oscillatory test, such as strain sweep at constant temperature and low deformation, \(G'\) and \(G''\) are constant, which means that the grease structure is unchanged. This regime is also called the Linear Viscoelastic Region (LVR).

The longer the LVR is a function of shear stress, the more shear stable is the grease. In order to carry out a temperature sweep test, e.g., at constant shear stress, it is essential that the chosen shear stress is in the LVR. Figure 1 illustrates the viscosity modulus, elasticity modulus and the complex modulus as functions of strain for Grease D.

<table>
<thead>
<tr>
<th>Property</th>
<th>Grease A</th>
<th>Grease B</th>
<th>Grease C</th>
<th>Grease D</th>
<th>Grease E</th>
<th>Grease F</th>
</tr>
</thead>
<tbody>
<tr>
<td>IT (min) @ 140 °C</td>
<td>360</td>
<td>239</td>
<td>140</td>
<td>264</td>
<td>N/A</td>
<td>564</td>
</tr>
</tbody>
</table>

Table 3: The measured induction time (IT) for the greases.

a) In Figure 2, the calculated complex modulus for the two lithium complex greases at 0.1% strain (within the LVR) may be interpreted as follow: at 25 and 40 °C, Grease C, (based on BO1) has higher complex modulus than Grease D (based on BO2). One possible explanation could be the higher thickener content of Grease C (about 13.5 wt.% higher). While at 100 and 150 °C, the larger complex modulus of Grease D may be justified by the higher viscosity of BO2 at these temperatures. One source of the deviation here is that we are assuming that the fibrous soap structures have been formed uniformly. Nevertheless, more investigation is needed in order to understand these behaviours.
Tribological study of the performance of base oils and greases was conducted by using an SRV rig. The tests were run within the boundary lubrication region under the following conditions: an applied load of 150 N (corresponding to 2.5GPa maximum Hertzian pressure) at 40 °C, with a sliding frequency of 50 Hz and an amplitude of 1 mm. The wear of the tested balls and discs was measured with a 3D profilometer (New View 7300 3D, Middlefield, CT, USA).

Figure 4 illustrates the measured friction coefficient (COF) for BO1 and lithium and lithium complex greases. After just a few minutes of running time, the measured COF of BO1 increased by almost 20 percent, from 0.111 up to about 0.142. After an additional 20 min., the COF started to dive and reached a lower stable level of about 0.13. Grease A (lithium grease), however, showed smooth and stable COF within the entire running cycle, while the COF of Grease C (lithium complex grease) increased at the end of the running period to about 0.160.

The measured smaller wear scars on the balls and discs are consistent with the lower and more stable friction coefficients for BO2 and the greases based on BO2, especially for lithium complex grease, versus BO1 and the greases based on BO1, Table 4.

Appendix A contains the pictures of the wear scars on the discs and balls for each sample after the test run.

Summary
This multidisciplinary study showed that high viscosity naphthenic oils can be used successfully in the production of lubricating greases with various thickener systems. The characterization of the greases revealed that good to excellent properties were obtained despite low thickener content.
The low thickener content, especially in the case of lithium based greases, can bring cost savings to the grease producer in a market where rapid increase in the price of lithium hydroxide is observed due the demands for lithium to make batteries for the electrification age.

BO1, the base oil with a kinematic viscosity of about 375 (mm²/s), proved to be an excellent product for use in greases with low thickener content and excellent low temperature mobility.

BO2, the base oil with a kinematic viscosity of about 620 (mm²/s) and a high degree of solvency, greatly minimized the use of thickeners in greases with excellent water resistance. Furthermore, the low and stable friction coefficient and low degree of wear for BO2 and the greases based on BO2, in the boundary lubrication regime, indicated the potential for possible energy reduction and good lubricity in applications. The measured wear on balls and discs for Grease D (lithium complex grease based on BO2) were very low.

Furthermore, this study showed that base oils with high viscosity and good solvency such as BO1 and BO2 can be used successfully in grease formulations. There are reasons to believe that those benefits can be obtained either by using these oils on their own or in blends with paraffinic Group I, II and III base oils.

Reference
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2) Dodos, G. S. and M. Fathi-Najafi, Oxidation stability parameters as novel monitoring tools for a more robust grease production, 29th ELGI Conference, May 2017, Finland

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Appendix A

Reference
www.nynas.com/en/