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The impact of viscosity of naphthenic oils and extreme-pressure additives on lubricating greases

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Abstract:
The behaviour of lubricating grease in different tribological contacts has been discussed intensively for many decades. It is also known that there are a vast number of material related parameters that may have significant impact on the tribological behaviour of grease, such as type of thickener and amount, the viscosity and oil type, the concentration and type of additives. The above parameters are directly related to the cost of the formulation, however there are additional parameters that are directly related to the operational cost and conditions such as the contact pressure and the operating temperature is preferable that test equipment used for the development and optimisation of new grease formulations is limited.

The aim of this study is to investigate, step by step, how the formulation of lithium and lithium complex greases may be optimised using tribological tests. The thickeners chosen are lithium and lithium complex since more than 75 percent of global grease production is based on these two thickener systems. Furthermore, three straight cuts of mineral base oils with various viscosities (150, 375 and 600 mm2/s) and two additive packages: I) an additive package that consists of anti-oxidant, anti-wear and extreme pressure components and II) additive package I + an extra dosage of the same extreme pressure additive used in package I. All the greases have been produced in a laboratory pilot plant at atmospheric pressure. Besides the state of the art characteristics of the greases, the tribological properties of all formulated greases were studied by using the new generation tribometer, SRV®5. In the first stage, the tribological tests were run with respect to various ASTM methods such as D5706 B, D5707, D 2266 and D2596.

The outcome suggests that by running different tribological tests under conditions very close to relevant application fields, the formulation of the grease can be optimised further resulting in a more cost-efficient solution.

1. Introduction

Lubricating greases can be used in a wide range of applications and conditions. Various lubricating greases, depending on the type and amount of thickener, additives and viscosities of the base oils, provide the main parameters for complexity.

Complexity in the tribology of greases has been discussed for decades, in which the effect of thickeners on tribological performance has been at the core of many technical papers and publications.

The film formation of greases in rolling/sliding can be influenced by a number of the parameters such as temperature and roughness of material. However, in a tribological context, it is much more complicated than that. The aim of this work was to evaluate the impact of the characteristics of the base oils, thickener type and additive concentration tribologically, by using various SRV® methods as well as four-ball methods.

2. Experimental work

The experimental work that has been carried out in this study can be divided into the following parts: charactertistics of the selected base oils, manufacturing and charactertistics of the lubricating greases as well as tribological evaluation of the lubricating greases.

2.1. The base oils

Three hydrotreated naphthenic base oils (BO 150, BO 400 and BO 600) have been chosen for this study. Some of the characteristics of these base oils are illustrated in Table 1.

Characteristics	Unit	Method / ASTM	BO 150	BO 400	BO 600
Density @ 15°C	kg/dm^3	D 4052	0.919	0.923	0.932
Viscosity @ 40°C	mm^2/s	D 445	150	375	600
Viscosity @ 100°C	mm^2/s	D 445	10.5	20.0	21.5
Flash Point, PM	°C	D 93	222	246	250
Pour Point	°C	D 97	-24	-15	-12
Aniline Point (AP)	°C	D 611	86	98	89
Copper Corrosion	rating	D 130	1	1	1
Sulphur Content	wt. %	D 2622	0.130	0.120	0.300
Color	rating	D 1500	<2.5	<2.5	<2.5
Total Acid Number	mgKOH/g	D 974	<0.01	<0.01	<0.01

Table 1: *Typical characteristics of the naphthenic oils*

Some comments regarding the selected base oils shown in Table 1;

a) Typically, for the choice of base oils in multipurpose greases, a very important factor is viscosity, with higher viscosity being used for heavy loaded and low speed applications. Hence, theoretically speaking, BO 600 followed by BO 400 should be the most suitable products for this kind of application compared to BO 150.

b) These three naphthenic oils are all wax free and subsequently the viscosity is the dominating parameter that controls the pour point.

2.2. The greases

In total, six greases (A, B, C, D, E and F) have been produced in a pilot plant at atmospheric pressure. Grease A, B and C are conventional lithium (Li) and Grease D, E and F are lithium complex greases (Li X).

The acids that have been used are 12-hydroxystearate acid (12-HSA) and azelaic acid. In addition, two additive packages have been used;
Package I consists of antioxidant (1 wt.%), anti-wear (0.50 wt.%) and extreme pressure (1.5 wt.%) components and
Package II consists of Package I + an extra dosage (2.0 wt. %) of the same extreme pressure agent.

Properties	Grease A	Grease B	Grease C	Grease D	Grease E	Grease F
Base Oil (naphthenic)	BO 150	BO 400	BO 600	BO 150	BO 400	BO 600
Thickener Type	Li	Li	Li	Li X	Li X	Li X
Thickener Content [wt. %]	7.45	5.02	4.57	10.55	9,70	8.55
Dropping Pont [°C]	197.0	200.3	197.5	> 280	>280	> 280
Penetration after 60 str. [mm^{-1}]	258	274	276	265	281	269
Diff after 10^5 strokes [mm^{-1}]	+42	+26	+30	+40	+41	+50
Cu-Corrosion [rating]	1b	1b	1b	1b	1b	1b
Flow Pressure@-20°C [mbar]	320	370	645	345	320	720

Table 2: *Some of the characteristics of the neat greases*

A review of Table 2 suggests:

a) Low thickener content for all greases, however, BO 600 results in the lowest thickener content followed by BO 400. This can be attributed to a combination of better solvency and the higher kinematic viscosity of BO 600.

b) Dropping point was measured according to IP396. Dropping points for the lithium and lithium complex greases fulfil expectations.

c) The shear stability of the greases after 100,000 strokes has been measured according to ASTM D217 which exhibited good results for both lithium and lithium complex greases despite the low thickener contents that were used. However, it is notable that the repeatability of the worked penetration test is seven unites.

d) 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, 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, we can eliminate parameters such as wax content and polymers so the main parameters that can affect the low temperature mobility of the greases are the thickener content, the viscosity and the pour point of the oils. Hence, good low temperature mobility for all greases at -20 °C has been noted. Nevertheless, the higher pressure needed for the BO 600 based greases should be attributed to the higher pour point.

2.3. Tribological study

The tribological study is based on four different methods; two oscillatory tests by using SRV instrument; ASTM D5707 (friction coefficient and wear test) and ASTM D7506B (step load test), and two rotational tests by using four-ball machine; wear scar test (ASTM D2266) and weld load test (ASTM D2596). The standard methods and the evaluation of lubricating greases on the SRV oscillation tribometer is described in literature [1] in detail.

2.3.1. SRV Apparatus & Measurements

Modern tribometric test systems like SRV® (Schwing Reib Verschleiß) provide both suitable tools and test methods to get a deeper understanding of tribological and lubricity behaviour of the greases. In a previous study, some of the tribological aspects of neat lithium and neat lithium complex greases based on two of the oils that are used in this study (BO 400 and BO 600) were determined by using SRV® [2]. However, the frame of this work has been extended further by focusing on the additivated greases as well.

The focus of the investigation in this study was on the following issues:

1) What will be the response of the additive package in various types of greases?
2) Can lower soap content (the greases contain different soap content but same consistency) create better opportunity for the additives to perform (since soap typically competes with additives on the available positions on the metal surfaces)?
3) Is the additive package going to perform equally on various grease formulations?

The following standards have been achieved by SRV® for the investigation of different tribological performances of greases for decades:

1) Friction and wear performance - ISO 19291 / ASTM D5707
2) Load-carrying capacity (EP load) - ISO 19291 / ASTM D5706B

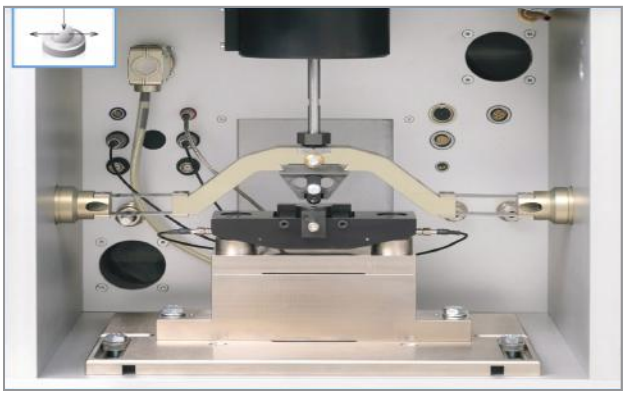

Figure 1: *SRV® oscillation chamber*

Wear values are estimated according to ASTM D5705 "Standard Practice for Determining the Wear Volume on Standard Test Pieces Used by High-Frequency, Linear-Oscillation (SRV®) Test Machine". Figure 1 shows the oscillation test chamber.

Test specimen for SRV®:

Lower specimen:

Disk 24 x 7.9 mm, both surfaces lapped, according to DIN 51834, surface roughness 0.50-0.65 µm Rz, material: 100Cr6, hardened

Upper specimen:
Steel ball 10 mm, polished, DIN 51834, material: 100Cr6

The greases will be applied onto the surface using a special grease caliber, so the quantity of the grease is fixed for all tests.

2.3.2. Test matrix for the tribological investigation

The first two standard methods (determination of friction and wear properties of lubricating greases) have been run for all tests. In Table 3 the most important test parameters of the standard tests are summarised, and in Table 4 the complete test matrix for all SRV® tests can be found.

Parameters	ASTM D5707 (determination of friction and wear properties of lubricating grease)	ASTM D5706B (determination of extreme pressure properties of lubricating grease)
Temperature [°C]	80	80 & 120
Stroke [mm]	1.0	1.5
Frequency [Hz]	50	50
Load during running-in [N]	50	50, 100
Running-in Time [s]	30	0.5 to 15 min
Normal Force [N]	200	Increasing stepwise by 100 N
Test Time [min]	120	Max 55

Table 3: *Test parameters for the chosen SRV® standards*

Greases	ASTM D5707 @ 80 °C	ASTM D5706B @ 80 °C	ASTM D5706B @ 120 °C
Grease A*, B*, C*, D*, E*, F*	X		
Grease A, B, C, D, E, F,	X	X	X
Grease C**, F**	X	X	X

Table 4: *Test matrix for SRV® tests*

3. Results of friction and wear measurements

The following part of the study was conducted using the SRV rig according to ASTM D5707 under the following test parameters:

- Temperature: 80 °C
- Load: 200 N
- Stroke: 1 mm
- Frequency: 50 Hz
- Time: 2 hours

With 200 N normal load the calculated Hertzian pressures are:

Mean contact pressure P_m = 1.84 Gpa &
Maximum contact pressure P_{max} = 2.76 Gpa

Figure 2 shows exemplary a COF (coefficient of friction) progression for Grease F.

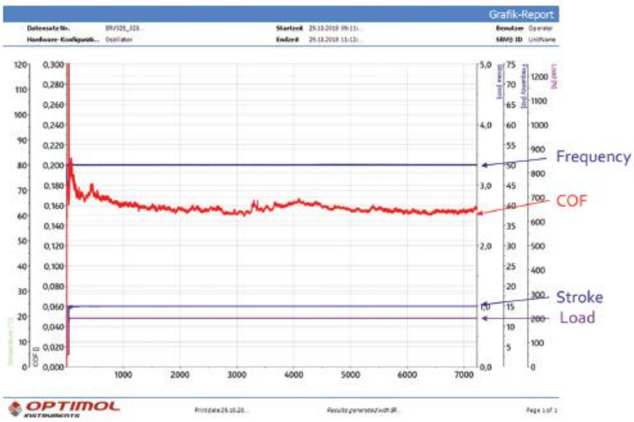

Figure 2: *Demonstrates the behavior of the friction coefficient of Grease F*

Figure 3 illustrates the wear scar on the disk and ball at the end of the test for Grease F made by a microscope. The measured wear values according to ASTM D7755 can be carried out by tip stylus profilometer or laser scanning microscope.

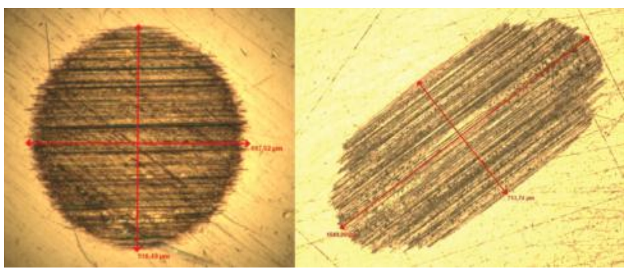

Figure 3: *Wear scar on the ball (left), wear scar on the disk (right)*

After measuring the diameter of wear scar on the ball as well as the width and length of the wear scar on the disk (Figure 3), the planimetric perpendicular surface area (Figure 4) and using the formula written in standard ASTM D7755, the wear volume can be calculated.

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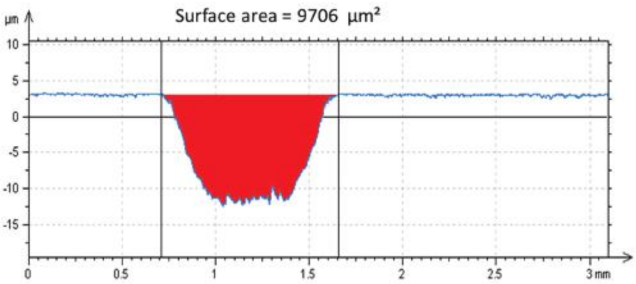

Figure 4: *Profilogram displayed on a screen and taken perpendicularly in the centre of the wear track on a SRV® test disk*

It can be noted that the higher values of COF do not always result in an increased wear volume value. This is more pronounced in case of greases where many phenomena such as structure or depletion of thickener molecules, characteristic of the base oil, contribute to the complexity of the tribo-system.

To interpret the measured data for the six greases, the following aspects were considered:

A) Impact of viscosity at the applied temperature
B) Impact of the thickener system
C) Impact of the concentration of the additives (only for BO 600 based greases; Grease C and F)

3.1 SRV tests on the greases based on BO 150

Figure 5 shows the COF values of four different formulated greases based on BO 150 (Grease A and Grease D).

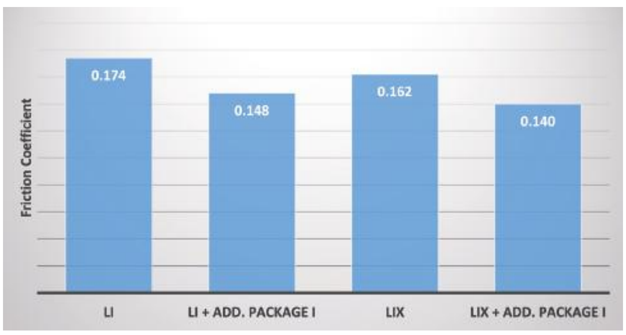

Figure 5: *Friction Coefficient for the Greases based on BO 150*

Figure 5 suggests that a) the friction coefficient is lower for the additivated greases when comparing different thickener systems (lithium vs lithium complex), and b) the Lithium complex grease runs at a lower COF than the lithium grease.

Furthermore, when considering the wear volume on the disk and the ball and finally the total wear, the differences between the formulations are significant, Figure 6.

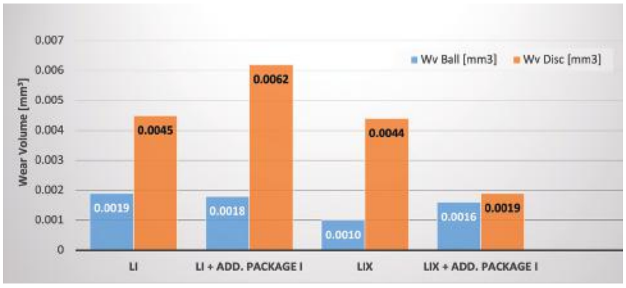

Figure 6: *Wear volumes of different formulated greases based on BO 150*

However, Figure 6 suggests that in the case of additivated lithium grease, the wear scar diameter remains unchanged, but the wear volume on disc shows a significant increase which cannot be explained. Hence, a separate investigation is required in order to find a possible reason.

3.2 Tribological tests on the greases based on BO 400

Figure 7 presents the COF results for four different formulated greases based on BO 400 (Grease B and Grease E).

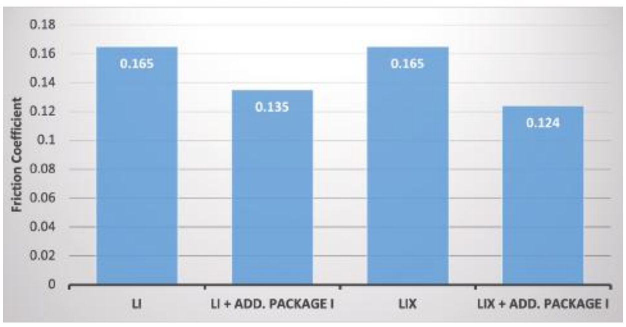

Figure 7: *Friction Coefficient for the Greases based on BO 400*

Figure 7 demonstrates the positive effect of the additive on COF for both thickener systems.

Comparing the wear values, the results are not the same as for BO 150. Regarding lithium complex as thickener the additive can reduce the wear volume especially on disk and, consequently, the total wear volume is lower. In this case the additive was, most probably, able to build-up a supporting layer on the disk.

Figure 8 shows significantly higher wear volume on disk for the lithium thickener, despite the fact that this test was repeated twice. Hence, it is speculated that the differences in polarity between the additive molecules and this thickener may, at least to some extent, cause some antagonistic effects.

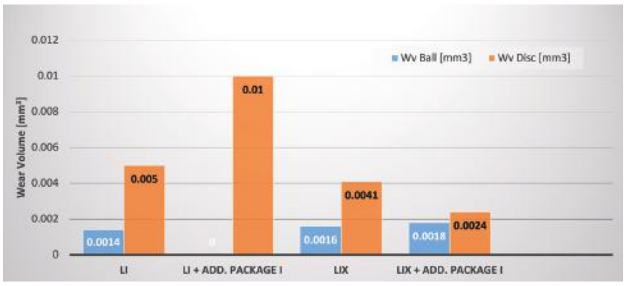

Figure 8: *Wear volumes of different formulated greases based on BO 400*

3.3 Tribological tests on the greases based on BO 600

In Figure 9, the friction coefficients for the six greases based on BO 600 are presented.

A positive effect of the additive package I on COF values is obtained for both thickener systems (lithium and lithium complex) in line with the previously reported data related to greases based on BO 150 and BO 400. However, the new finding is that the increased concentration of the extreme-pressure additive (Additive package II) has no effect on greases with either thickener system which lead us to the conclusion that more additive does not necessarily result in better performance, at least in this type of tribological contact.

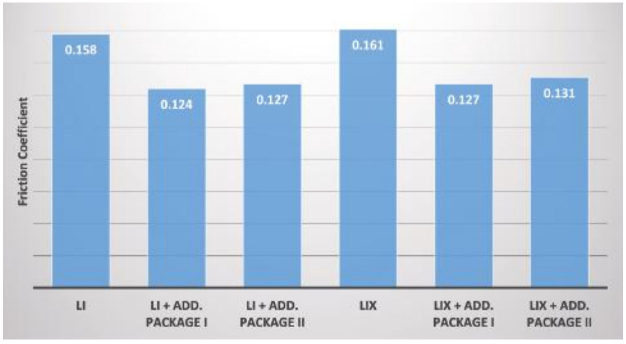

Figure 9: *Friction Coefficient for the Greases based on BO 600*

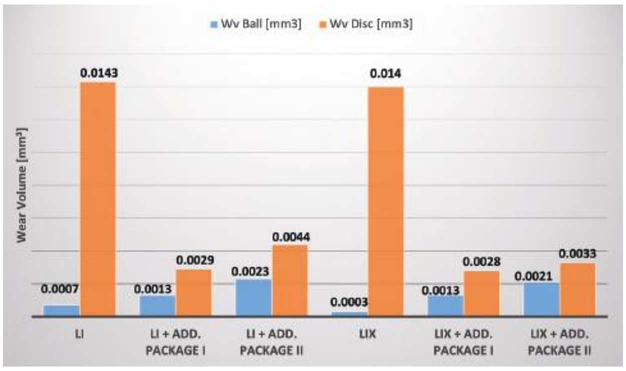

Figure 10: *Wear volumes of different greases based on BO 600 after running SRV® tests*

In Figure 10, it is interesting that for both thickener systems the extra dosage of extreme-pressure additive (Additive package II) has a negative impact on this tribological system. One possible explanation could be that active sulphur content in the extreme pressure additive interferes with the anti-wear additive when the dosage is increased.

Comparison of the tribological behaviour of the two thickener systems recorded by SRV

Within the frame of our SRV measurements, it has been found that the wear volume for additivated greases are not following expectations. For example, Figure 11 which shows the wear values of three non-additivated greases with different base oil viscosity and the corresponding ones with lithium and lithium complex thickener confirm that the greases based on highest base oil viscosity (BO 600) contribute to highest wear volume while the wear on the ball remains the lowest.

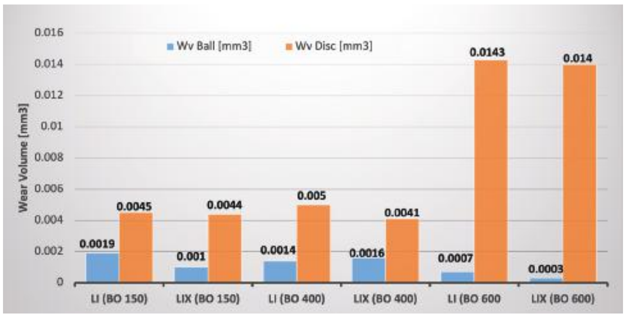

Figure 11: *The Wear Volumes for non-additivated greases*

In order to get a better understanding of the achieved results, the tests are run with the base oils (without additive), Figure 12 compares the COF values of the three base oils.

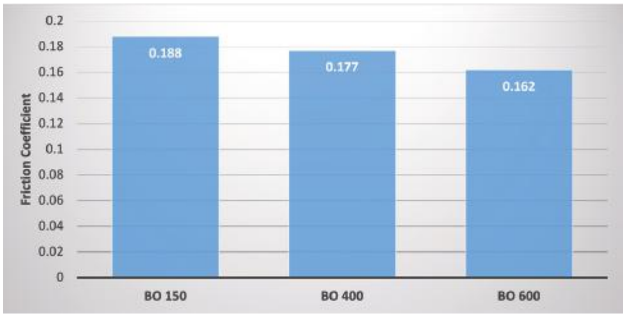

Figure 12: *COF values of the three base oils*

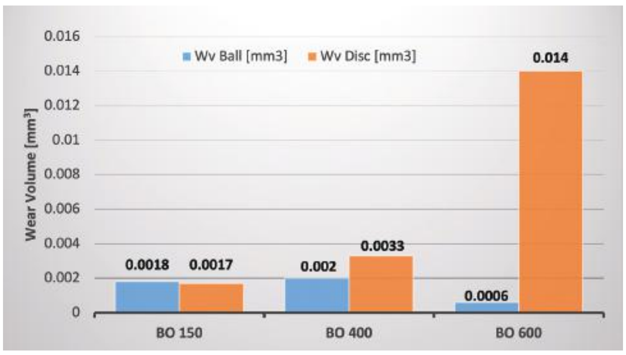

Figure 13: *The Wear Volumes for the three base oils*

Figure 12 suggests that there might be a relationship between the viscosity of the oil and the friction coefficient; the higher viscosity the lower COF. This trend can also be found on the wear scar diameter on the ball at least for the most viscous oil (BO 600), Figure 13. However, in the same figure it is obvious that the wear volume on the disk moves in the opposite direction which is more pronounced for the BO 600.

3.4 SRV test according to standard ASTM D5706 B

The load carrying capacities of additivated greases using the SRV® standard method ASTM D5706 B were determined at 80 °C as described in the procedure. The results of these tests do not show any significant differences. By increasing the test temperature to 120 °C, we can differentiate between the greases and these results are shown and discussed here. It is assumed that at higher temperatures, the extreme pressure additive adheres more easily to the metal surface and is subsequently be activated resulting in the formation of a supporting film on the contact point as expected.

The test parameters were as follows:

- Temperature: 120°C
- Stroke: 1.5 mm
- Frequency: 50 Hz
- Time: max. 55 min
- Load: 50 N / 30 s, 100 N / 15 min
- Load step: 100 N every 2 min

Figure 15 illustrates exemplarily the progression of the values during this test for one of the greases. This grease achieved a maximal load of 1200 N.

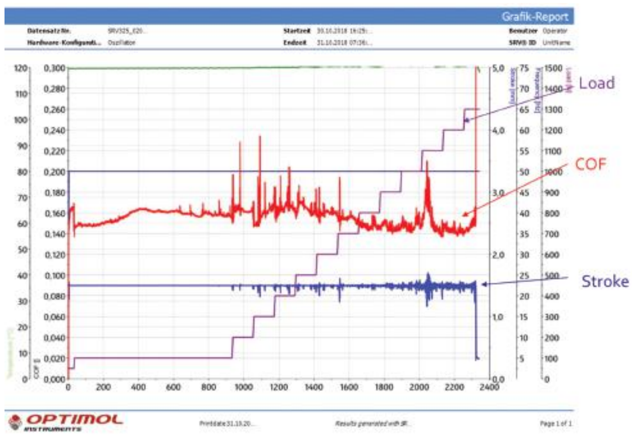

Figure 13: *Standard test ASTM D7506B for Grease E + additive package I*

The cut-off criteria of (the moment that seizure occurred) is defined in this standard ASTM D5706 B (COF > 0.0,2 for 20 s).

Based on the result obtained from this test, there is a tendency that the greases with lower viscosity and subsequently higher thickener content, show a better response to additive package I. Greases C and F, with the higher concentration of the extreme pressure agent (additive package II), do not show any increase in the load carrying capacity as expected.

Remarks	Max load carrying capacity [N]
Grease A + Additive Package I	1400
Grease B + Additive Package I	1200
Grease C + Additive Package I	1200
Grease D + Additive Package I	1200
Grease E + Additive Package I	1000
Grease F + Additive Package I	1000
Grease C + Additive Package II	1300
Grease F + Additive Package II	1000

Table 5: *Results of load carrying capacity tests measured by SRV®5*

3.5 Four-ball tests according to ASTM D 2266 and ASTM D 2596

Beside linear oscillating movement of ball on disk with SRV®, four-ball tests according to ASTM D 2266 (wear scar test) and ASTM D 2596 (weld load test) have been conducted on all greases. It is inviable to highlight the major differences between the four ball tests and SRV tests; for example in the case of four-ball tests we have point contact and rotational condition while in the case of the SRV tests, used in this study, ball on plain surface and oscillatory movement.

The obtained results are summerised in Table 7.

a) Comparing two neat lithium greases (Sample # 1 & 6); an increase of the weld load by 25 percent probably has to be attributed to the viscosity of the base oil (BO 600). The difference in wear scar diameters for the two greases is within the repeatability of the test. Furthermore, the significantly lower thickener content in Grease D has no negative impact on the wear scar or on the weld load.

b) The additive package I performs differently in lithium and lithium greases;
   i. In lithium complex greases significantly higher weld load is obtained.
   ii. In the case of wear scar diameter, the additive package performs worst in Lithium complex grease based on BO 150 (Sample # 7) and best in lithium grease based on the same base oil (Sample # 2), an increase by almost 38 percent.

c) The impact of additive package II in lithium and lithium complex greases based on BO 600 (Sample # 5 & 10); in the case of lithium greases (sample # 4 & 5), significantly higher load and lower wear scare diameter are measured which is in line with the expectations, however this could not be found in the case of lithium complex greases (sample # 9 and 10). Regardless of the reason behind this, it can be concluded that a higher concentration of the extreme pressure additive that is involved in package II, contributes to a more expensive formulation. This finding verifies the earlier observation that was found by SRV measurements, Table 5.

Sample No.	Specifications	Wear scar (mm); ASTM D 2266	Weld load (kg f); ASTM D 2596
1	Grease A	1.58	160
2	Grease A + Additive Package I	0.53	620
3	Grease B + Additive Package I	0.63	620
4	Grease C + Additive Package I	0.69	620
5	Grease C + Additive Package II	0.52	800
6	Grease D	1.51	200
7	Grease D + Additive Package I	0.85	800
8	Grease E + Additive Package I	0.65	800
9	Grease F + Additive Package I	0.54	800
10	Grease F + Additive Package II	0.56	>800

Table 7: *Results of load carrying capacity and wear tests measured by four-ball machine.*

4 Summary

Within the frame of this study, three lithium and three lithium complex greases were produced based on various naphthenic base oils. The use of naphthenic base oils has kept the thickener content low, however, a direct correlation between the viscosity of these naphthenic base oils and the thickener content was found; the higher the viscosity the lower thickener content.

The tribological investigations have proven to be crucial when optimising the grease formulation for specific tribological contacts. However, the most interesting differences between the two different thickener systems have been observed in additivated greases;

a) The additivated lithium greases based on BO 150 and BO 400 showed higher wear values than the non-additivated greases. While same package reduced significantly the wear values of disk when used in lithium complex greases, Figure 6 and 8.

b) The "Additive package II" (which contains an extra dosage of extreme pressure additive) performed differently in different test rigs;
   - SRV tests; an increase of the wear values regardless the thickener type for the greases based on BO 600 has been observed, Figure 10.
   - Four-ball tests; positive impacts (both on the wear scar diameter and load carry capacity) have been observed for the lithium grease. In the case of the lithium complex grease (Sample # 10) this positive effect was only monitored on the load carrying capacity in Table 7.

c) The thickener content of a grease seems to affect the tribological performance which, in turn, is dominated by the characteristics of the base oil, e.g. its polarity, degree of solvency and viscosity.

d) The conditions in SRV and four-ball rigs are different which can explain the different outputs. This also emphasises the necessity of selection of relevant test methods that may supposed to simulate the actual conditions of applications in the fields, otherwise the obtained data may lead to the wrong conclusions.

In complex systems, such as lithium and lithium complex greases, the components involved may sometimes interfere with each other, hence, in order to formulate a high-performance grease, the use of tribological tests, as demonstrated in this study, could be of valuable assistance.

Acknowledgment

The authors would like to thank Dr. George Dodos at Eldon's for the four-ball measurements.

Reference:

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[2] M. Fathi-Najafi et.al, The impact of high viscous naphthenic oils in various thickener systems, Eurogrease 3, July-August-September 2018

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