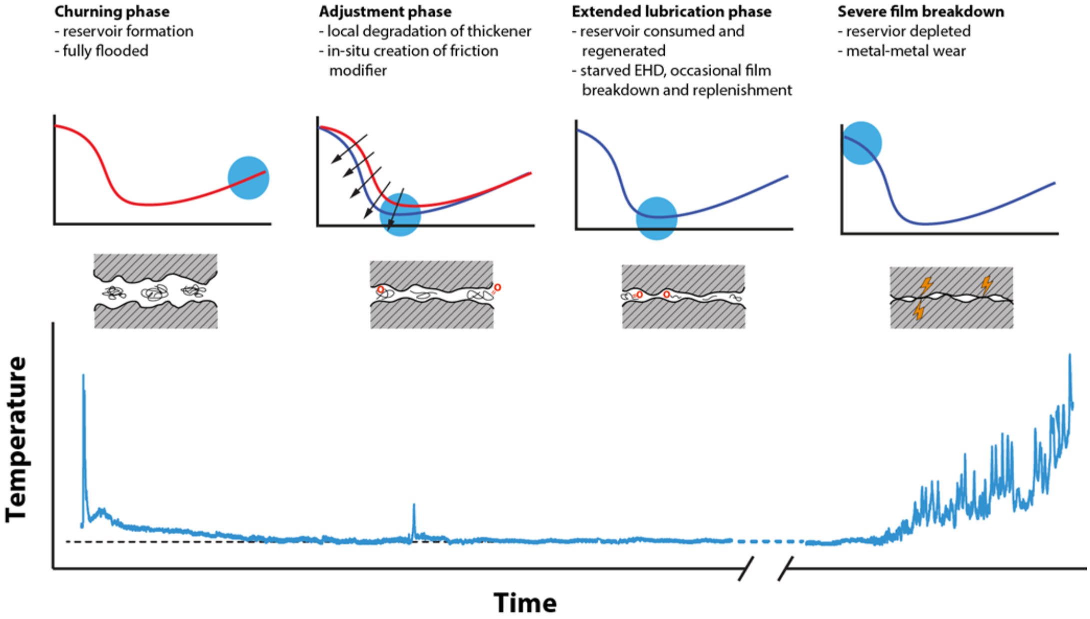
Polypropylene – A novel thickener technology with many surprises.



Johan Leckner and René Westbroek

Axel Christiernsson International AB, Nol, Sweden

Presented at the 29th ELGI AGM Helsinki - Finland
6 – 9th May 2017

ABSTRACT

In recent conference presentations we have shown that the lubricating mechanism of polypropylene thickened greases in rolling element bearings differ significantly from that of soap based greases. These differences give rise to lower self-induced running temperatures, a very effective replenishment mechanism and a seven times longer grease life.

In this paper we dive deeper into the mechanistic differences that we have already presented. Furthermore, we expand the study into showing differences in additive response, low temperature lubricity and behavior when subjected to high temperature and oxidation promoting conditions.

INTRODUCTION

We have over the years, from the early field trials with experimental batches to the greases produced today, seen very good, and often astonishingly good, results with polypropylene thickened greases. Some of these results have been presented to the public [1, 2, 3], but the vast majority has not. For a long time these results spoke for themselves - the polypropylene thickened grease resulted in lower self-induced running temperatures and significantly longer lubrication life than the corresponding soap based greases. About three years ago we set out on a quest to understand the mechanisms governing the extraordinary lubrication performance of the polypropylene grease. Since then we have been surprised many times by what we have found.

As the most common application for this type of grease is lubrication of rolling element bearing we decided to focus on this. There are a number of challenges when it comes to investigating grease lubrication of bearings. To run tests with full bearings at typical operation conditions is very time consuming as the grease life is measured on the scale of years. Therefore, bearing tests are most often stopped after a fraction of the expected grease lubricating life, long before the grease lubrication starts to deteriorate (*e.g.* SKF R2F-A and FAG FE8 at ambient temperatures are run for 480 h and 500 h respectively). Another approach is to stress the grease by running the test at harsher conditions (commonly at elevated temperatures, e.g. FAG FE9, ASTM D3336 and SKF R0F). The problem with the latter approach is that if the system is stressed too much there is a significant risk that the failure mechanism will change and that the test is evaluating the wrong thing. There is nothing wrong with assuming an Arrhenius behavior (*i.e.* that the rate constant for chemical reactions increase exponentially with temperature) as long as it can be shown that the failure mechanism remains the same. Unfortunately this is something that is very hard, if not impossible, to prove when analyzing a phenomenon like grease bearing lubrication, which itself can be described as chaotic [4]. What has to be taken into consideration is that it is not only the rate of chemical reactions that change with temperature, there are also a lot of physical changes occurring in the grease, resulting in changes in, for example, oil bleed and grease flow. Therefore, Arrhenius behavior can only safely be assumed for moderate temperature changes.

An alternative is to focus on the tribo-contact inside the bearing and to study this in detail, in order to get a more fundamental understanding. The normal strategy would be to simulate the contact pressure and the slide to roll ration of the bearing in a ball-on-disc instrument (*e.g.* a mini traction machine). An issue here is that a single ball on a disk will not simulate the successive rollovers that will occur in a bearing, furthermore the absence of a cage and a grease reservoir removes important factors for track replenishment [5]. Therefore, in this type of test, starvation of the contact occurs rather fast as the ball, in combination with centrifugal forces, will push the grease out of the contact. A way to overcome starvation is to use a so called "grease scoop", which is a small device that will push the grease back into the running track. The scoop ensures that starvation will not occur, but the lubrication situation will be a fully flooded contact which more simulates the conditions when a bearing is first stated (*i.e.* in the churning phase) than the starved electrohydrodynamic conditions that are characteristic for grease bearing lubrication. This type of test have previously been performed with polypropylene thickened greases resulting in interesting data [6, 7, 8, 9] providing insight into the behavior in fully flooded contacts.

With the aim of better understanding the performance in industrial bearing applications the authors decided to focus on full bearing tests performed at ambient temperature. Previously some bearing tests with the same type of polymer grease have been reported with thrust bearings [10, 11, 12], but here the running times have been limited to a few minutes. As the goal here was to understand performance in industrial applications longer test times was important. The choice of test to run was a modified SKF R2F-A test. To focus on the thickener system it was further decided to exclude all additives and study a system consisting only of thickener and oil. The results from this initial study was presented at the ELGI AGM in Barcelona 2015 [3]. One of the key findings in this study was that the polypropylene grease demanded very long run-in times to reach steady (in the case of the R2F-A test 7-10 days).

In the following investigation we therefore used the SKF R2F test as a grease life test, running the bearings to failure. Leaving the additives out of the greases here became essential not to have to run the tests for years. The differences noted between soap based greases and the polypropylene thickened grease leads us to the point where a modified model was needed to describe the bearing lubrication mechanism for polymer greases. Such a modified model was also presented at a number of occasions during 2016 [13, 14, 15, 16]. An alternative model for the lubrication mechanism of polypropylene grease, based on nano-fluid properties, was presented in a 2017 study [17]. This model, which contains interesting data on the micro structure of polypropylene thickened greases, fails to explain many of the observations reported by the authors here.

In this paper the authors summarize previous findings and complement it with new data. Be prepared to be surprised!

MATERIALS and METHODS

Grease manufacturing

Manufacturing lithium complex grease: The production of the lithium complex greases was done in a pilot reactor with a batch size of 8 kg. The manufacturing procedure followed a standard protocol. The soap was synthesized in around 40% of the total oil volume. The first saponification using 12-hydroxystearic acid was performed at 90°C with a hold time of 30 minutes. The temperature was then increased to around 115°C and kept there for two hours after which the second saponification using azelaic acid took place. The grease was then kept at 115°C for 30 minutes before the temperature was increased to the top temperature of 205°C. The cooling was performed using 5% portions of oil with a hold time of 15 minutes between each addition. The grease was finally milled and deaerated for 1 hour.

Manufacturing polymer grease: The first phase in the manufacturing of the polymer grease is the melting of the polypropylene in the oil. This was carried out in a round flask with a mantle heater with a batch size of 1.2 kg. The polymer/oil solution was then quench cooled to a temperature far below the melting point of the polymers. In the second phase four batches of quenched material were transferred to a mixing vessel where the material was deaerated and worked into the desired consistency

Grease composition

The polypropylene and lithium complex thickened greases produced for this study have been designed to be as similar as possible. The base oil composition of the four grease samples with pairwise identical base oil viscosities are based on straight PAO grades with an 6.3% addition of adipate ester to facilitate the saponification in the case of the lithium complex (see *Table 1*).

PAO grade	**PAO** [wt%]	**Ester** [wt%]	**BOV@40°C** [mm^2/s]	**BOV@100°C** [mm^2/s]
PAO-10	93.7	6.3	61.4	9.4
PAO-50			351.3	43.9

Table 1: *The theoretically calculated base oil viscosities (ASTM D7152-05) of the two base oil blends containing 93.7% PAO and 6.3% adipate ester.*

Standard grease tests.

In this study we evaluated the greases using a number of tests that are common to the grease industry. In *Table 2* these tests and the corresponding standards used are listed.

Test	Condition	Standard
Penetration after 60 strokes	25°C	ISO 2137
Shell roll stability	80°C for 50h	ASTM D1831 modified^A
Water washout	79°C	ISO 11009
Viscosity	40° and 100°C	ISO 12058
Emcor	distilled water	ISO 11007
Dropping point		IP 396

Table 2: *The common grease tests and the corresponding standards used in the analysis of the samples.* ^{A}*Test run at 80°C for 50 h which are non-standard conditions.*

Thermal ageing

In order to investigate the effect of thermal ageing the grease were aged statically in a pre-heated oven at 120±2°C. Five glass plates were cleaned properly with hexane. An even grease layer of 1.5 mm was spread over each glass plate, after which they were stacked on top of each other with a 2 cm spacer separating them. The top glass plate was covered with an additional glass plate without grease on it so that the air flow was as constant as possible. At regular intervals samples were removed from the oven. In this paper only the effect on the two greases based on PAO-10 (*i.e.* PP-10 and LiX-10) have been investigated.

Figure 1: *The setup with glass plates used to thermally age the greases*

In addition to the greases also the oil blend used in the PAO-10 based greases (see *Table 1*) was thermally aged in the oven. In this case, a petri dish with the amount of oil needed make a 1.5 mm thick layer was placed in the oven. Here the space between the top of the petri dish and the covering glass plate was smaller (around 1 cm) and the air flow, and subsequently the oxidation, might therefore be slightly affected.

All infra-red spectra were recorded on a Bruker Tensor 27 equipped with a Golden Gate ATR.

Oil and thickener extraction

The oil and thickener was separated by completely dissolving 3 grams grease sample in 250 ml petroleum ether with a boiling point range of 40-60°C. The solution was then filtered in a vacuum funnel with a filter paper having a 2 µm cut-off (Munktell OOH). The petroleum ether was then evaporated and the remaining fractions of thickener and oil analyzed. The total mass loss using this method was around 2%.

Grease contamination

Metal particle contamination: Metal, and metal oxides, were purchased from Sigma Aldrich (see *Table 3*). The metal powder was mixed uniformly into the grease using a DAC600 SpeedMixer with a treat rate of 0.10 wt%. The larger particle size of the brass lead to some sedimentation in the SpeedMixer and the brass was therefore further dispersed by passing the samples three times through a three-roller-mill. The same ageing and analysis procedure as for the grease without contamination was used.

Lithium hydroxide contamination: An oil-based dispersion of micro-sized anhydrous lithium hydroxide (Lubrizol 5280GR) was used to contaminate the greases with free lithium hydroxide. In the tests reported here a total amount of 4% dispersion was mixed into the grease (corresponding to approx. 1,4% lithium hydroxide) using a DAC600 SpeedMixer.

Compound	**Average size** [µm]	**Maximum size** [µm]	**Purity/composition**
Brass	n/a	250 (mesh 60)	70% Cu, 30% Zn
Copper	3	45	99.7%
Iron	n/a	44 (mesh 325)	97%
Iron trioxide	1	5	>99%
Iron tetra oxide	n/a	5	95%

Table 3: *The particle size and purity/composition for the five different contaminants used.*

SKF R2F-A bearing test

The lubricity of the greases were tested using the SKF R2F-A test. The test consists of a pair spherical roller bearings (SKF 22312) that have been run-in according to a specific protocol. The test is then performed at ambient temperature for 20 days at a 8340 N radial load and a speed of 2500 rpm. After one day a relubrication is performed and the test then continues for the remaining 19 days. During the test, the outer ring temperature profile is recorded at two positions (upper and lower) for each bearing and, after the test, roller and cage wear is measured. The ambient temperature during the test is controlled and kept at 20±0.5°C.

In this study we have mainly used the test differently. The test is started as a normal R2F-A test with a relubrication after day one. Then the test is run at 2500 rpm until one bearing of the pair fails. The test is judged to have failed if there is a large temperature increase in combination with excess vibrations from either of the two test bearings or if the test rig stops as a result of the increased friction. All tests in this paper was performed using the same test rig. For the greases LiX-10 and PP-10 the power consumption was monitored during the test with an Efergy CT Sensor.

Sliding friction and wear tests

Reciprocating ball on flat (SRV) test: The reciprocating wear test was performed on an SRV4 according to ASTM D5707 with standard specimens. The conditions for the test is found in *Table 4*. The duration of the standard test is 2 hours. Here the test time was extended to 6 hours. A running-in at 50 N for 30 seconds was performed prior to the wear test. The wear scars were analyzed using a Bruker Contour GT-K0 optical profiler.

Ball-on-disc (MTM2) sliding test: Experiments were performed with ball-on-disk geometry using Mini Traction Machine 2. The disc was rotating while the ball was kept stationary. A grease scoop was used to force grease to flow back to the track to avoid starvation of the ball-disk contact. Detailed test conditions is found in *Table 4*.

	Sliding test (MTM2)	**Reciprocating test (SRV)**
Normal load	60 N	200 N
Hertzian contact pressure	2.57 GPa	2.74 GPa
Temperature	80°C	80°C
Sliding speed	50 mm/s	Average 100 mm/s
Frequency	n/a	50 Hz
Stroke length	n/a	1 mm
Running time	6 hours	6 hours
Material	AISI 52100 bearing steel	
Ball diameter	6 mm	10 mm
Ball roughness, Ra	0.02	0.025
Disk roughness, Ra	0.06	0.046
Grease amount	0.5 g	0.2 g

Table 4: *The test conditions for the two sliding friction and wear test performed. The slinging speed given for the reciprocating test is the average speed.*

RESULTS

Grease properties

Some general properties of the four greases with pairwise identical base oil viscosities are given in *Table 5*. In most of the other tests run to evaluate the greases (see *Table 2*) the two series with identical base oil viscosity are quite comparable. Emcor, water washout and Shell roll stability was also comparable, but were only tested for the grades based on PAO-10 and are given in *Table 6*. The only, and expected, differences is the dropping point where the two lithium complex greases had a dropping point above 280°C and the polymer greases had dropping points in the range 152 to 160°C and the oil bleed. Concerning the oil bleed the polymer greases bleed significantly more oil in the IP121 test.

Sample name	**Theoretical viscosity**		**Measured viscosity**		**Thickener content** [wt%]	**Pen60** [10^{-1} mm]
	BOV@40°C [mm^2/s]	**BOV@100°C** [mm^2/s]	**BOV@40°C** [mm^2/s]	**BOV@100°C** [mm^2/s]		
PP-10	61.4	9.4	61.6	9.7	12.5	280
PP-50	351.3	43.9	351.6	44.3	10.0	282
LiX-10	61.3	9.4	63.5	9.8	18.2	275
LiX-50	350.5	43.8	349.9	43.0	18.0	270

Table 5: *The four greases in this study. The number after the identifier for the thickener gives the viscosity grade of the PAO used. The theoretically calculated base oil viscosities given in the table have been calculated using ASTM D7152-05. Bleed oil from the IP121 test (40°C/168h) has been used to measure the viscosities according to ISO 12058.*

Sample name	**Emcor dist. water**	**WWO@79°C** [wt%]	**SRS (80°C/50h)** [Δ 1/10 mm]
PP-10	0/0	2%	53
LiX-10	0/0	6%	58

Table 6: *Emcor distilled water, water washout and Shell roll stability results for PP-10 and LiX-10.*

R2F grease life test

The normal SKF R2F-A test is designed to assess the lubricating ability and wear prevention of lubricating grease [5]. The test is run for 20 days and then the condition inside the bearings are inspect (lubricating film on the rollers, discoloration/consistency of grease etc.) and the roller and cage wear is measured. The information collected, together with the temperature curve, is then used to assess the lubricity performance of the grease under the tested conditions. Here we have used this test in a different way by not stopping the test at day 20, but continuing until failure. A failure is here equal to that the equipment stops by itself due to the resistance inside the test bearings, or that strong vibrations in combination with elevated temperature occurs. The latter criteria has been implemented in order not to damage the test equipment.

The churning phase.

During the first hour, or hours, after starting a newly lubricated bearing the grease is redistributed inside the bearing giving rise to a temperature increase. During this so-called churning phase the bearing contacts will be fully flooded with lubricant and the film thicknesses will be much thicker than what is expected from the oil alone. In the PAO-50 based greases there is no observable difference between the polymer and lithium complex thickened greases in the churning phase (see *Figure 2, panel A*), both PP-50 and LiX-50 give rise to temperature spikes in the range 70-80°C. In contrast, for the two PAO-10 based greases the difference is very pronounced. The PP-10 grease cause temperature events of the same magnitude as the PP-50 and LiX-50 greases, but for the LiX-10 sample there is no observable churning events at all (*Figure 2, panel B*).

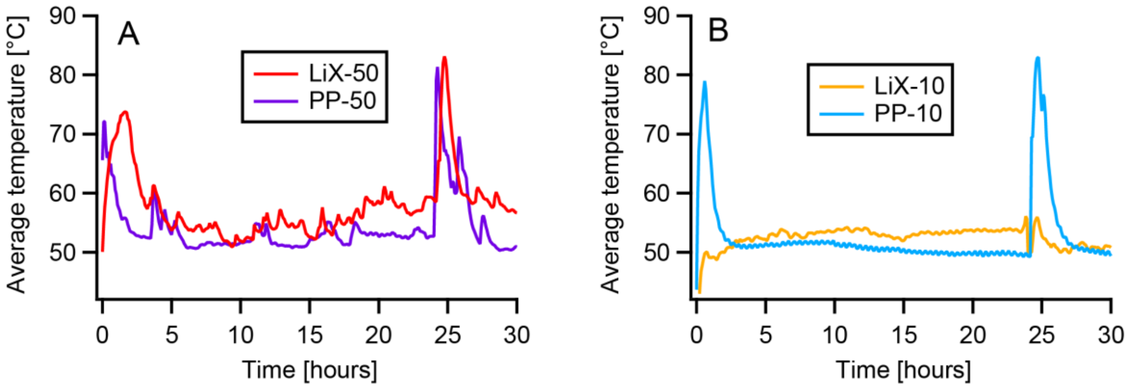


Figure 2: *The average temperature (form all four probes) for each grease during the first 30 hours of the test. The temperature spikes seen at startup and day one (relubrication) is due to grease churning.*

The first 20 days.

If we first focus on the first 20-days of the test there are a number of observations that can be made. For the two higher viscosity grades, LiX-50 and PP-50, there is an extremely large difference between the temperature curves (see *Figure 3 panel A*). Both greases start at a similar temperature level, but soon the lithium complex grease starts to increase rapidly in temperature. The gradually increasing temperature and the large number of thermal events indicates a deteriorating lubrication leading up to a total lubrication failure. There is a fairly large difference between the temperature levels of the right and left bearing lubricated with the LiX-50 grease but this is still nothing out of the ordinary. Occasionally large differences between bearings lubricated with the same grease is not surprising [4].

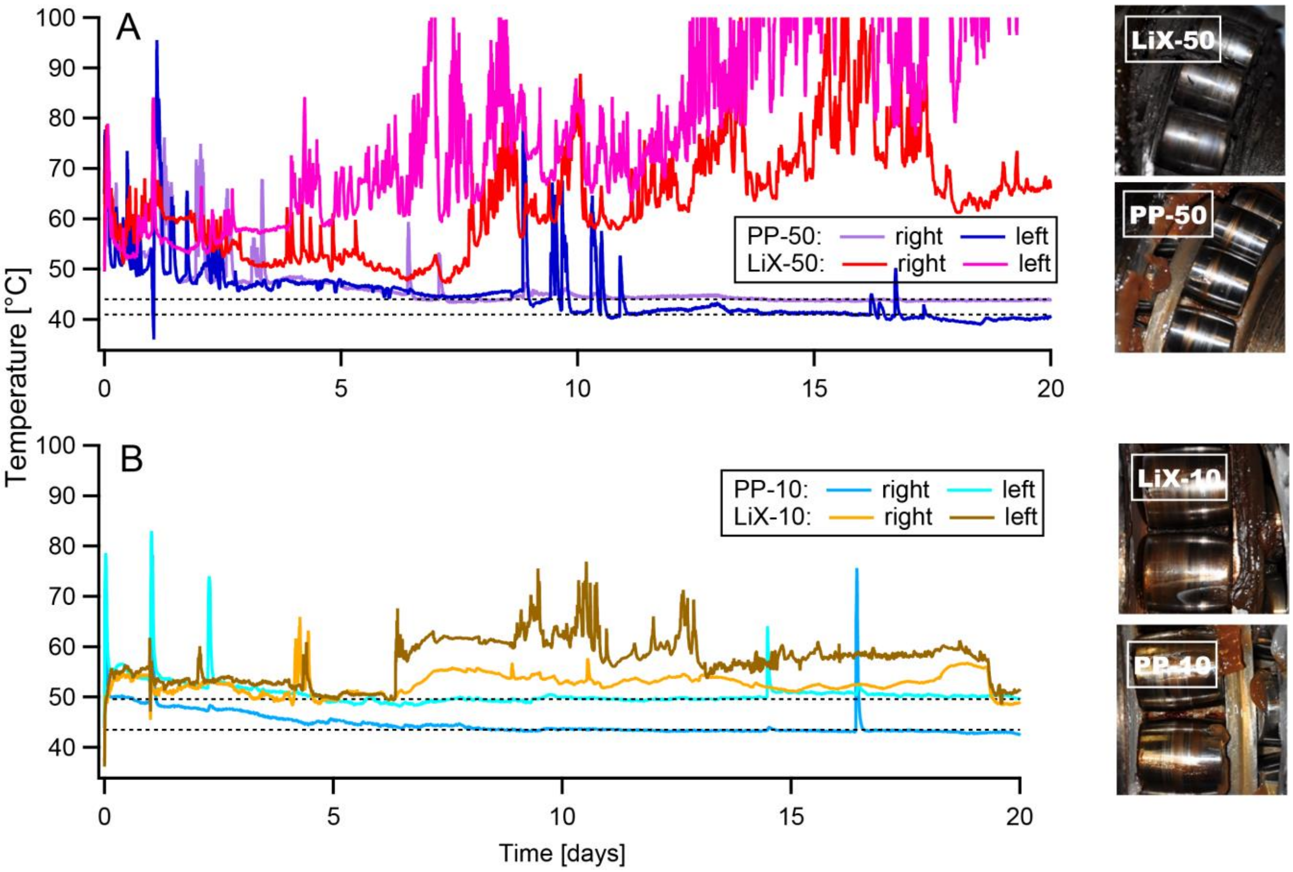


Figure 3: *The temperature curves (bottom temperature sensor) from the R2F-A for the first 20 days for all four greases. The temperature spikes at startup and day one (relubrication) is due to churning. The dotted lines indicates the steady-state temperature for the polymer greases. The images to the right show the appearance of the grease inside the bearing after running a standard (20 days) SKF R2F-A test.*

What is surprising is the very large difference in the temperature profiles when comparing the LiX-50 with the PP-50 grease. It might here be good to remember that the base oil viscosity of the oil is very high – a lot higher that what is fit for the application, with kappa-values for the oil above 20 for both samples. This does in no way explain the large difference between the greases as both are based on PAO-50 oil, but we see this difference being significantly reduced when comparing the two greases based on PAO-10 which has more normal kappa-values (*Figure 3 panel B*).

Since the samples are being run until failure we do not have the possibility to look inside the bearings to inspect the grease at the end of the 20 day period, but we have previously run standard SKF R2F-A tests for the same samples and the appearance of the grease inside these bearings can be seen in the photos in *Figure 3*. In the high viscosity samples the difference is striking. In the bearing with LiX-50 the rollers are completely dry and the grease close to the raceway is completely carbonized. The contrast to the PP-50 sample is as big as in the temperature profiles – much less oxidation and an oil film on the rollers. A similar, but not as pronounced, difference is seen between the LiX-10 and PP-10 samples. Here there still is an oil film on the rollers lubricated with the LiX-10 grease.

Considering the dissimilarity in the temperature curves the appearance between the high viscosity samples is expected to differ. For the low viscosity greases there is also a quite pronounced difference between the samples, especially when comparing the appearance of the grease between the rollers, even though the average temperature difference between the samples only is around 7°C.

There is one more important observation to be made and that is the duration it takes the polymer greases to reach a steady-state. For both the PP-50 and PP-10 samples it takes 7-10 days before the temperature stops decreasing and stabilizes, this is a much longer time than for the corresponding lithium complex grease. This behavior is not only seen in these two polymer grease samples tested here – it is a common theme in all R2F-A tests we have performed with the polymer grease [3]. The behavior is not just limited to the R2F test, the authors have seen the same pattern in tests with thrust bearings and we have similar experiences from field trials (personal communication, Roger Persson, Volvo Group).

The full test

The final result for the test is presented in *Figure 4***.** The data for each sample is presented as the average temperature of all four temperature probes (the data for each individual temperature probe can be found in *Appendix 1*). Again there is a significant difference in the running temperature between the LiX and PP greases, but the most striking difference is the lubrication life, which is seven times longer for the PP compared to LiX grades.

One issue encountered during the test is the performance of the support bearings, which are lubricated with a standard lithium EP2 grease. During the 430 day running time of the PP-10 sample we were forced to change support bearings no less than three times (indicated by the red arrows in *Figure 4*). This process involves stopping the test, unloading it and replacing the support bearings *in situ*, trying not to disturb the test bearings. What effect his has had on the test is unknown, but the final support bearing change (at around 415 days) coincides with a very strong temperature increase in the left test bearing (see *Appendix 1*, bottom panel).

Comparing the average running temperature between the high viscosity grades does not make much sense as the lubrication for LiX-50 is deteriorating too fast. For the lower viscosity grade the difference in average running temperature is around 6°C (46°C for PP-10 and 52°C for LiX-10). If we convert this difference into power losses by estimating the heat dissipated from the system [18, 19] we end up with an annual difference of 900 kWh (or 110 € electricity cost) for a system running 24/7 for one year. We also had a power consumption logging system connected to the test rig (see *Figure 5*) which indicates a power saving of around 3.5% or 330 kWh per year for the entire test rig.

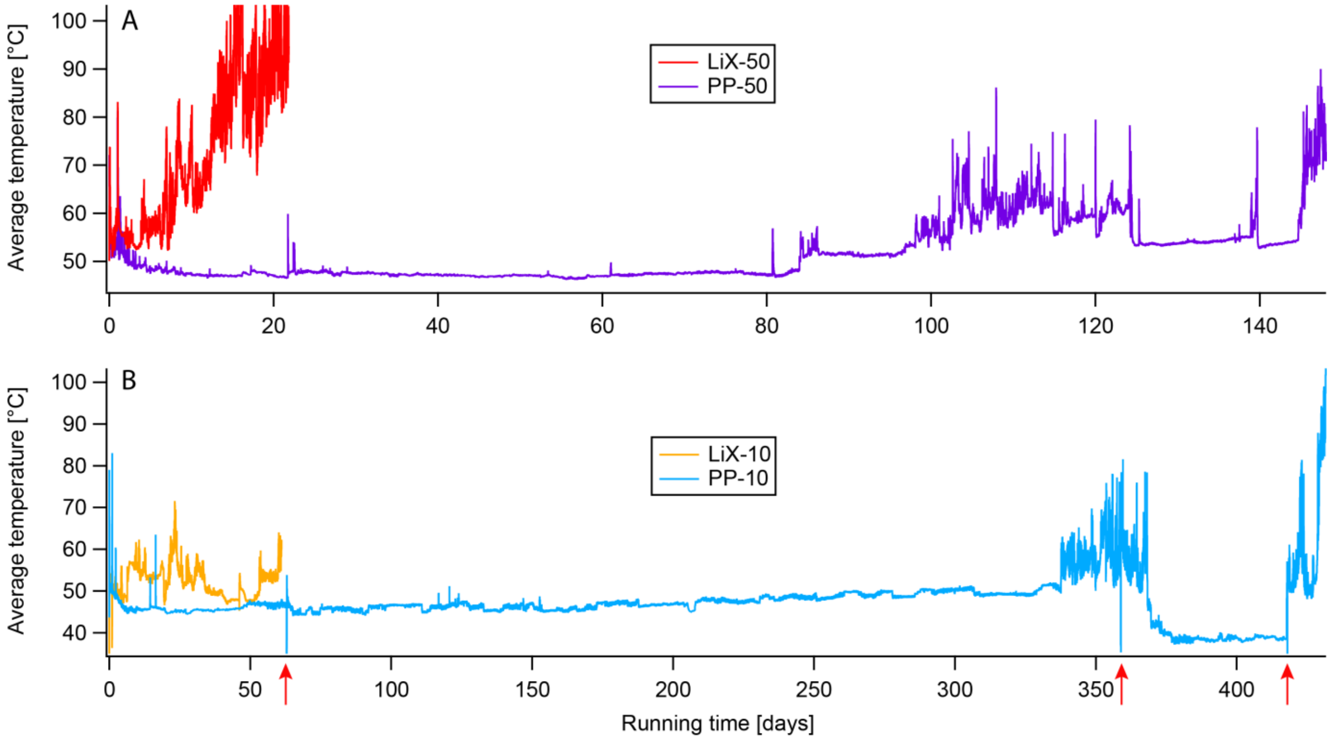


Figure 4: *The average temperature profiles from all for temperature probes for the four different greases. The top panel (A) contains the data for the PAO-50 based greases. The LiX-50 sample stopped after 21 days and the PP-50 sample was stopped after 148 days. The lower panel (B) contains data for the low viscosity grades. The LiX-10 sample was stopped after 62 days due to excessive vibration and the PP-10 sample was stopped after 430 days. The red arrows in panel B indicates the three times support bearings had to be replaced during the PP-10 test duration.*

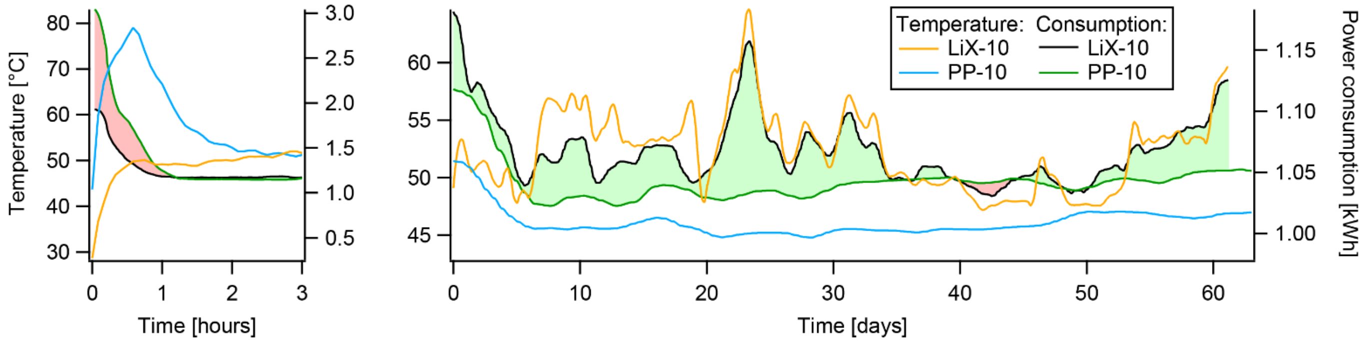


Figure 5: *The measured electrical power consumption of the test equipment and the average running temperature during the first 62 days. For ease of viewing the temperature and power consumption data has been smoothed using local weighted regression smoothing (LOESS). The red area indicates higher power consumption for PP-10 and the green higher power consumption for LiX-10. The left panel zooms in on the first 3 hours. Here the comparably high churning of the PP-10 grease also gives rise to higher power consumption as expected.*

After the completed test the wear of rollers and cages were measured in the cases where this was possible (see *Table 7*). For three of the bearings, both LiX-50 bearings and the left PP-10 bearings, the oxidation and bearing damage was too severe to be able to measure them. Looking at the wear after a test that has been run to failure is in many ways not a fair comparison, but the data can nevertheless provide some interesting information. In particular if focusing on the bearing in the pair that did not cause the failure. For the PAO50 based greases the wear was very severe, but no exact comparison is possible due to the state of the LiX-50 bearings after the test. In case of the PP-50 grease it is the left bearing, that also caused the test to stop, that has the most severe wear.

For the LiX-10 grease the cause of terminating the test were elevated vibrations from the right bearing and it is also this bearing that has the greatest wear. For the PP-10 the left bearing was too damaged to measure, but the left bearing only has a total wear of 15 mg after the 430 day test.

	Test bearing	Roller / cage wear [mg]	Wear rate [mg/day]
LiX-10	Left	402 / 226	10
	Right*	624 / 448	17
PP-10	Left*	- / -	-
	Right	9 / 6	0

	Test bearing	Roller / cage wear [mg]	Wear rate [mg/day]
LiX-50	Left*	- / -	-
	Right	- / -	-
PP-50	Left	1416 / 553	13
	Right*	4048 / 477	30

Table 7: *The roller and cage wear measured after the end of the grease life test. For the LiX-50 greased bearings and the left PP-10 bearing it was impossible to measure the wear due to too severe oxidation and too damaged bearings. The wear rate is calculated as the total wear (rollers and cage) divided by the time until failure. The asterisk (*) indicates the bearing that was the cause for stopping each test.*

Thermal ageing

In a recent paper, co-authored by the authors, the static oxidation of a 1 mm polymer grease layer on a steel plate in an oven at 120°C was compared to that of a lithium complex grease [20]. The polymer grease in this study is the same as PP-greases with the exception of being based on a PAO-8 and not containing any adipate ester. The lithium complex grease in the study is the same as the LiX in this study with the exception of being an NLGI 1.5 grade and based on a blend of PAO-8 and PAO-100.

In this paper it was found that without additives the polymer grease is more prone to oxidation, as the lithium soap, or the small excess of lithium hydroxide used in the manufacturing, seems to have antioxidative properties [21, 22]. The effect of the oxidation was also observed in the viscosity of the bleed oils of the thermally treated greases, where the increase was larger for the polymer grease than for the lithium complex. With this in mind it would be natural to expect that the consistency of the polymer grease would increase more after oxidation than the lithium complex grease, but that was not the case. Instead the lithium complex grease increased in consistency whereas the polymer grease lost consistency. Similar increase in consistency has also been observed by Couronné and Vergne for mineral oil based lithium, lithium complex and poly urea greases at 120°C [23]. For the two lithium greases Couronné and Vergne also observed a loss of consistency at 150°C due to the thermal degradation of the soap thickener.

In a similar experiment the authors aged greases PP-10 and LiX-10 in an oven at 120°C on glass plates, collecting samples every day. In addition, the oil blend used in the greases was also subjected to the same ageing procedure. The results of these experiments are matching what has been published for grease ageing on steel plates: The polymer grease displays a more rapid formation of oxidation products compared to the lithium complex grease as judged by IR-spectroscopy (see *Appendix 2*). This is, for example, clearly seen in the acidic products formed by oxidation which has their main absorption bands in the region 1740 – 1700 cm^{-1} (C=O stretch vibrations originating from formed aldehydes, ketones and carboxylic acids). The increase in these chemical species can be followed by the decrease in transmission at 1716 cm^{-1} (see *Figure 6*).

The unchanged intensity of the carboxylate resonances at 1580 and 1560 cm^{-1} originating from the lithium complex soap indicates that it is probably mainly the oil that is affected by oxidation in the LiX-10 grease as no degradation of the soap is noticed (*Appendix 2, panel A*). This is in line with what have been observed for regular lithium soaps under similar conditions [24] and the fact that no softening (*i.e.* a breakdown of the thickener structure) is observed.

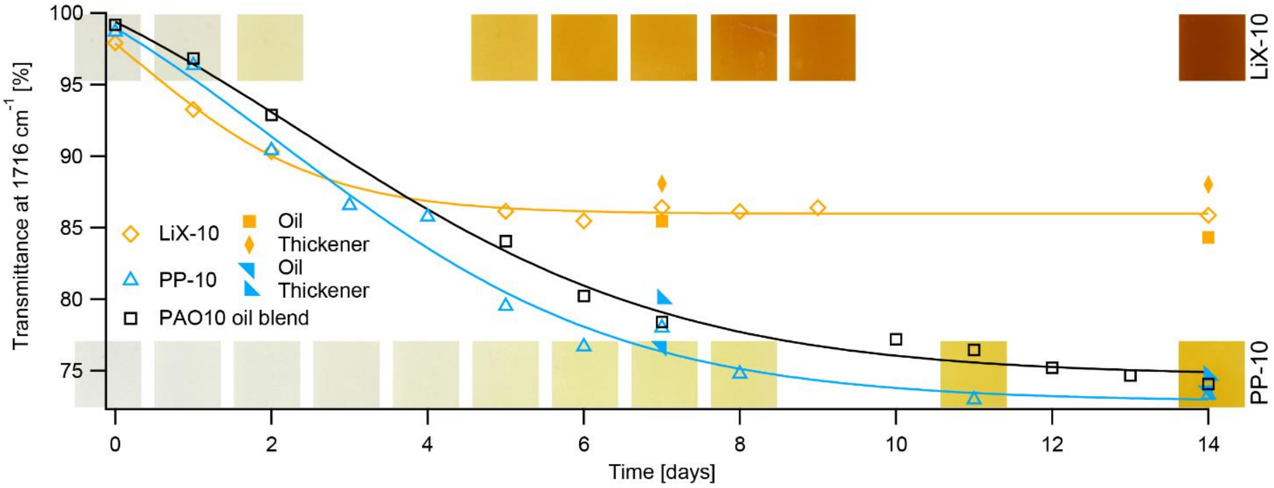


Figure 6: *The decrease in transmittance at 1716 cm^{-1} and the visual change of the LiX-10 and PP-10 when being aged at 120°C for up to 14 days. The decrease in transmittance is correlated to the increased concentration of carbonyl groups (C=O) resulting from oxidation. For 7 and 14 days the transmittance data for extracted thickener and oil is also given.*

The oxidation of the pure oil blend has an oxidation rate that is close to that of the polymer grease. This again illustrates that the small amounts of excess lithium hydroxide or the lithium soap itself has a seemingly stabilizing effect on the oil. In the oxidation test the oil was placed in a Petri dish with the same film thickness as the grease. The distance from the top of the Petri dish to the covering glass plate therefore became only half of that in the grease test. This might have influenced the air flow thereby reducing the oxidation rate somewhat. In reality the oxidation of the oil blend may therefore be even closer to the polymer grease than detected here. The difference in oxidation behavior is also seen when analyzing the 7 and 14 day aged samples where the oil has been extracted from the thickener. In *Figure 6* one can see that the oil and thickener in PP-10 oxidizes to the same extent as the PP-10 grease and the PAO-10 oil blend. The thickener and oil form the LiX-10 sample has a transmittance intensity in line with that of the LiX-10 grease.

With the higher degree of oxidation in mind one would expect also that the polymer grease would be the one that shows the largest visual signs for oxidation, but this is clearly not the case. Looking at the photo inserts in *Figure 6* it is apparent that the lithium complex grease becomes darker much faster than the polymer grease. Already after 5 days the visual appearance of the LiX-10 sample is similar to that of the 14 day old PP-10 grease. As the color change does not correlate with the oxidation products picked up by IR this must be related a chromophore originating from the lithium complex thickener. When extracting the oil from the 7 and 14 day aged samples it is noted that the color of the extracted oil from the LiX-10 sample is much darker than the oil from the PP-10 sample. Therefore we can conclude that the chromophore originating from the lithium complex thickener is soluble in oil.

Thermal ageing and boundary friction

The samples from the thermal ageing experiment was subjected to an SRV wear test at 80°C according to ASTM D5707, with the exception of being extended from 2 to 6 hours (see *Figure 7*). The data presented for each sample consists of the average of three representative runs.

For the LiX-10 grease the coefficient of friction does not change with ageing time, if anything it slightly increases for the 7 day aged samples. Again the behavior of the PP-10 grease is fundamentally different: Around day 2 the coefficient of friction starts decreasing and continues to decrease until around day 7 when it has been reduced to half. The ball wear scars are similar for all samples measured (*Figure 8, Panel A*). If anything there is a trend of increasing wear scars for the aged LiX-10 samples. For the samples aged longer time it becomes increasingly hard to get representative data sets as many of the samples seize before the end of the 6 hour period. Therefore, full data sets have only been collected until the day 7 aged samples.

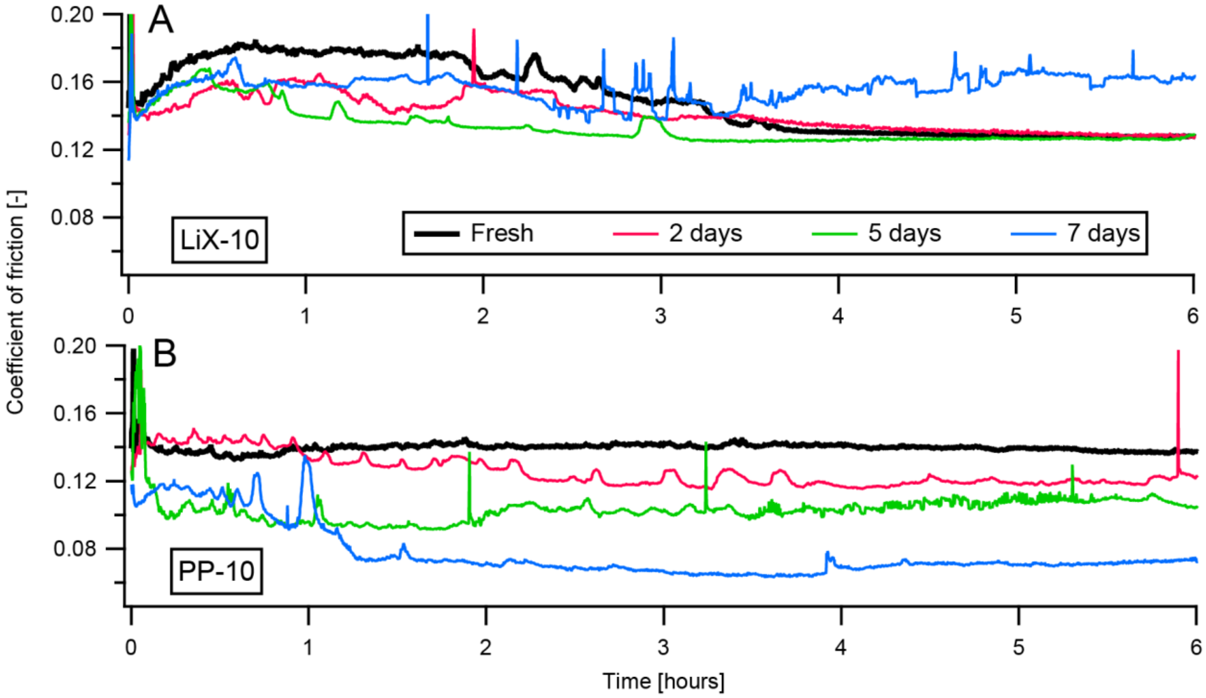


Figure 7: *The friction traces from the extended SRV wear tests at 80°C at different days of thermal ageing. Each trace is the average friction trace of three individual representative runs. The friction level for the LiX-10 grease remains unchanged for the differently aged samples. For the PP-10 grease there is a clear trend of reduction in friction with a minimum reached around 7 days.*

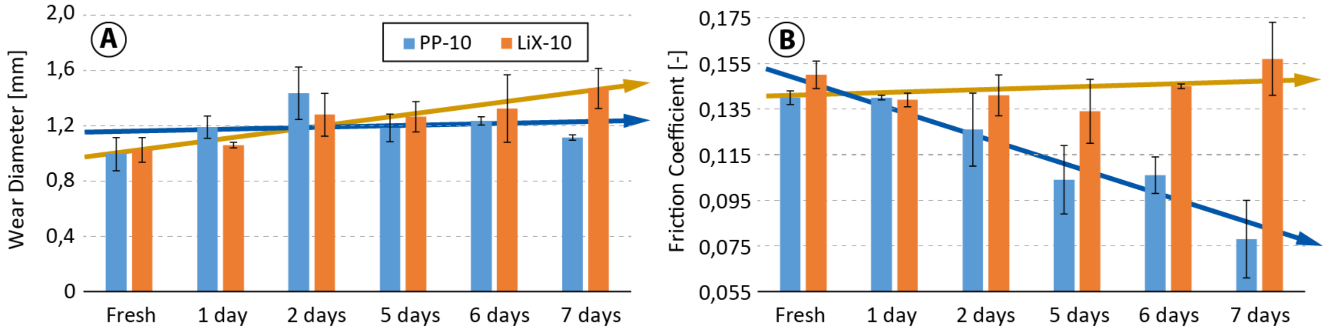


Figure 8: *Panel A shows the average ball scar diameter from the extended ASTM D5707 test at different days of ageing at 120°C. The corresponding average coefficient of friction during the 6 hour test for all three runs is shown in Panel B. The error bars indicate the standard deviation. The arrows are trend lines.*

The thermal degradation products, probably polar degradation products of polypropylene, apparently have friction modifying properties that are clearly seen in the SRV tests. To investigate the nature of the friction modifier further the authors also ran the same SRV wear test on the oil extracted from the 7-day aged samples. The friction curve from the oil extracted from PP-10 clearly illustrates reduced friction (see *Figure 9*). Therefore we can deduce that the friction modifier is extracted with the oil and that it is of lower molecular weight compared with the PP. Exactly what type of chemical species that is responsible for the reduced friction is outside the scope of this investigation, but some type of organic friction modifier or a functionalized polymer is expected [25]. This is further strengthened by the fact that the oil extracted from PP-10 has a higher viscosity than the aged oil blend (see *Table 8*) even though both samples show a similar oxidation as seen with IR-spectroscopy. The authors also tried to run the wear test with a fresh oil blend of equal viscosity to the PP-10 7 days extracted oil, but the test always seized before the end of the 6 hour test (the longest test achieved was 4 hours), therefore data for the first 2.5 hours is only shown in *Figure 9*.

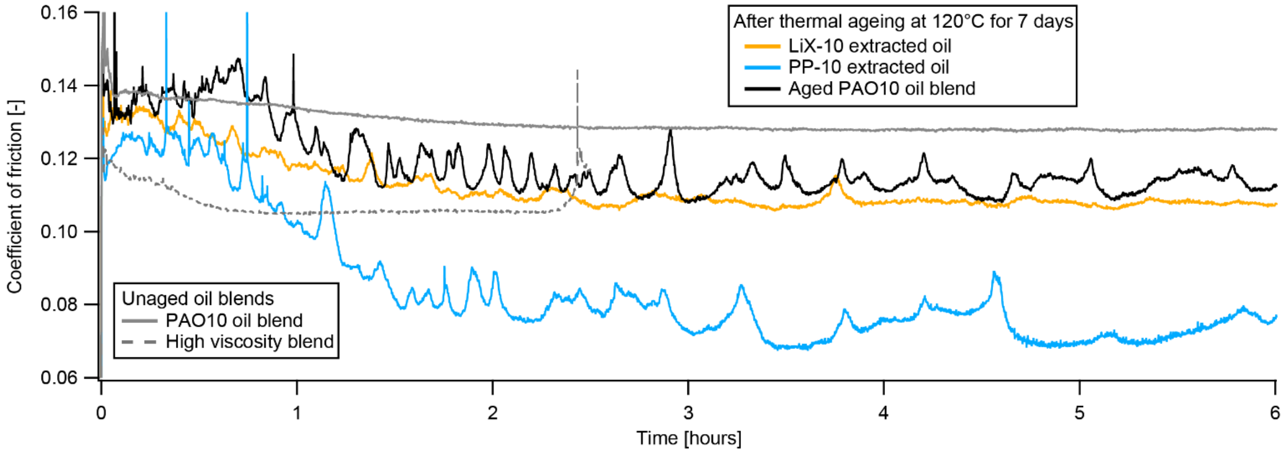


Figure 9: *The average friction curve of at individual representative runs for oil extracted from PP-10 and LiX-10 after 7 days of thermal ageing at 120 °C. As a reference the fresh and thermally aged base oil blend is also shown. The friction curve for the high viscosity blend (equal to the 7 day extracted PP-10 oil) ends after 2.5 hours as it was not possible to run the full 6 hours.*

Interestingly, for the wear tests in *Figure 9* with aged extracted oil there is also a notable difference in the wear scars. The extracted oil from LiX-10 results in much deeper disc scars than the oil extracted from PP-10 (see *Table 8*). On the other hand, the polymer grease gives rise to somewhat larger and deeper ball scars. The aged oil blend results in an even shallowed disc scar but also the largest ball scars. Fresh (unaged) oil blend also gives a shallow disc scar in addition to the smallest ball scars.

	Viscosity 25°C [mm^2/s]	**Avg COF** Last 3 h	**Disc** **Scar depth** [µm]	**Ball** **Diameter** [mm]	**Scar depth** [µm]
Extracted oil LiX-10	300	0,11	16-18	1,05-1,10	20-24
Extracted oil PP-10	1380	0,07	6-9	1,15-1,25	32-38
Aged PAO-10 blend	610	0,11	3-5	1,35-1,55	42-60
Fresh PAO-10 blend	128	0,13	5-8	0,55-0,75	8-13
High viscosity blend	1400	n/a	n/a	n/a	n/a

Table 8: *The range of the scar depths and the ball wear scar diameter from the tests performed on oil extracted from 7 day thermally aged samples of PP-10 and LiX-10. In addition, the results from the tests with the fresh and aged PAO-10 oil blend is given. The viscosity at 25°C and the average coefficient of friction during the last 3 hours of the test is also given.*

Thermal ageing – contamination

Metal powder contamination: When setting up the experiments for the thermal ageing of the greases the starting point was using a metal substrate before turning to glass plates (for ease of comparison with already published data [20]). The reason for changing substrate was that the authors noted a poor repeatability in the tests when using a metal substrate. This poor repeatability was interestingly different for the lithium complex grease and the polymer grease and it was therefore decided to investigate this further, with a focus on simulating the oxidative environment that might exist inside a bearing with wear debris. Therefore, the LiX-10 and PP-10 samples were contaminated with 0.1% of selected metal particles listed in *Table 9*.

Compound	
Brass	To simulate brass cage wear debris.
Copper	Known to catalyze oxidation. Main component in brass.
Iron	To simulate roller and raceway wear debris.
Iron trioxide	
Iron tetra oxide	

Table 9: *The metals and metal oxides chosen as contaminants to evaluate the effect on oxidation rate.*

The previously observed difference in color change also holds for the metal contaminated samples, but the change is significantly accelerated especially for the lithium complex grease and particularly for the copper and brass contaminated samples, but also for the iron contaminated sample (see *Figure 10* for two examples). Interestingly, when analyzing the IR-spectra there are only small differences between the metal free and metal contaminated samples when it comes to the increase in carbonyl signal. As can be seen in *Figure 11* the intensity of the carbonyl signal in the PP-10 greases is still much larger than for the LiX-10 greases. As observed before, the color change is in no way correlated with the appearance of oxidation products.

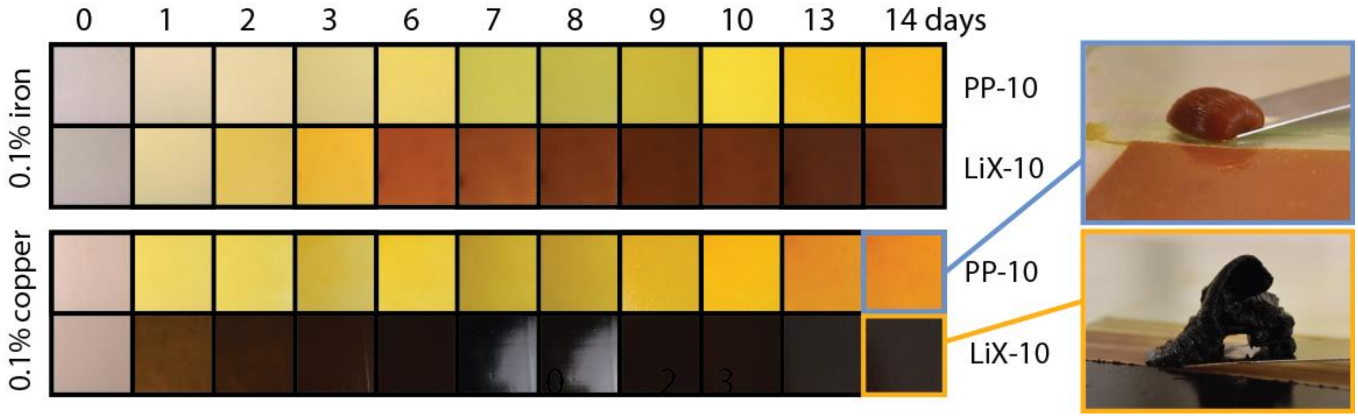


Figure 10: *The visual color change for the iron and copper contaminated samples. The inserts to the right illustrate the structural changes that occur in the greases when thermally aged. The 14 day aged polymer grease with copper contamination becomes tackier and slightly thicker. The corresponding lithium complex grease changes structurally by getting a thicker grainy structure and appearing dryer.*

Another observation that can be made are the structural changes occurring to the greases. The polymer grease first becomes softer (approximately day 2-7) and then it becomes tackier than the starting material. The lithium complex grease changes differently – becoming more grainy and drier in appearance with ageing time. In the greases aged for a longer period there is also a skin like texture on the top. The images inserted in *Figure 10* illustrates this by showing the appearance of the copper contaminated greases when being scraped off the class plate after 14 days at 120°C. Rheological measurements of the greases reveal that the polymer grease becomes more liquid like with ageing time and that the lithium complex grease becomes thicker. One issue with analyzing the structural changes in the lithium complex grease is that the structures created by thermal ageing seems quite easy to disrupt and in the transfer process from the glass plate to the rheometer a lot of structural information is lost. Currently the authors are working on investigating the structural changes further by developing a method to analyze the undisturbed aged greases. The first attempts for such a method has proven to be challenging, especially to get good enough repeatability.

Lithium hydroxide contamination: To test the effect of free lithium hydroxide on the rate of carbonyl signals in the IR measurements a sample was contaminated with 1.4% micro-sized anhydrous lithium hydroxide [26]. The effect in the IR signal for samples aged 7 and 14 days is shown in *Figure 11*. The effect of the lithium hydroxide is quite clear: The transmittance signal is identical for both greases and it is much higher than the LiX-10 signal. It should be pointed out that the level of lithium hydroxide used here is many times higher than the possible excess in a normal lithium complex grease. The high level of lithium hydroxide also seems to affect the color change of the grease. The contaminated LiX-10 sample is lighter in color than the uncontaminated, whereas the contaminated PP-10 sample is much darker than when not contaminated. Overall the color of the contaminated LiX-10 and PP-10 greases are quite similar (data not shown).

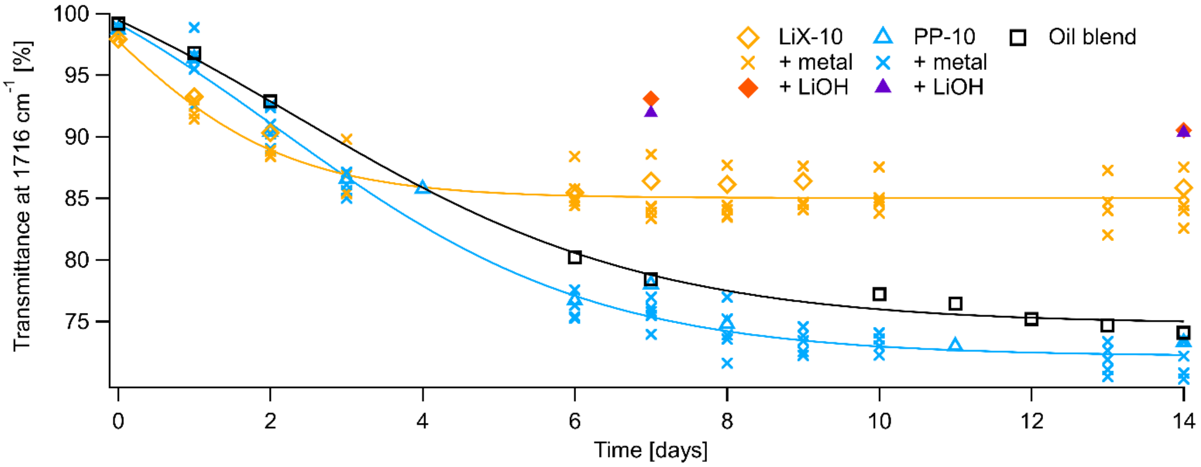


Figure 11: *The rate of transmittance change at 1716 cm^{-1} for the PP-10 and LiX-10 greases when contaminated with 0.1% of a metal (brass, iron or copper), or a metal oxide (Fe_2O_3 or Fe_3O_4). Interestingly the difference between the PP-10 and LiX-10 greases is similar to the uncontaminated greases for all the metal contaminants. For 7 and 14 days data is also given for greases contaminated with lithium hydroxide. The data given for the uncontaminated greases and the oil blend is the same as given in Figure 6.*

Additive response

Example 1 – boundary friction: To illustrate the differences in additive response resulting from using different thickener systems we selected a traditional boundary friction modifier system, consisting of a zinc dialkyldithiophosphate (ZDDP) and a molybdenum dialkyldithiocarbamate (MoDTC). This is a synergistic additive combination that has been around for decades and has thus been the subject for many academic papers [25]. The data presented below is just a preview from one of the test conditions studied in an collaboration with Professor Sergei Glavatskih and his team at the Royal Institute of Technology in Stockholm (compete study to be published soon) [27].

In the test the two PAO-10 based greases without additives is compared with the same greases containing the boundary friction reducing additive combination. The two tests were set up using quite similar conditions when it comes to substrate material, test temperature and contact pressure (see *Table 4* for more information), but using two very different motions: One unidirectional sliding ball-on-disc geometry, which is flooded by using a grease scope, and one reciprocating ball-on-flat geometry.

The results from both tests are shown in *Figure 12*. In addition, the average coefficient of friction during the last two hours of the test and the average ball wear scar from three tests is given in *Figure 13*. Both the PP-10 and LiX-10 greases without any additives result in an coefficient of friction in the range 0.12 to 0.14. Furthermore the ball wear scars are comparable between the greases but the higher loads in the reciprocating test, unsurprisingly, gives overall larger wear scars. Overall the results from the two unadditized greases give very comparable results in the two test. For the two greases with the boundary friction additive package the story is quite different. In both greases the wear diameter is reduced to around half of the wear without additives (*i.e.* the wear volume is reduced by a factor 16). The main difference is found in the friction levels. When adding the additives to the LiX-10 grease a reduction in friction of around 15-30% is measured, whereas when adding it to the PP-10 grease the friction is reduced by 60%.

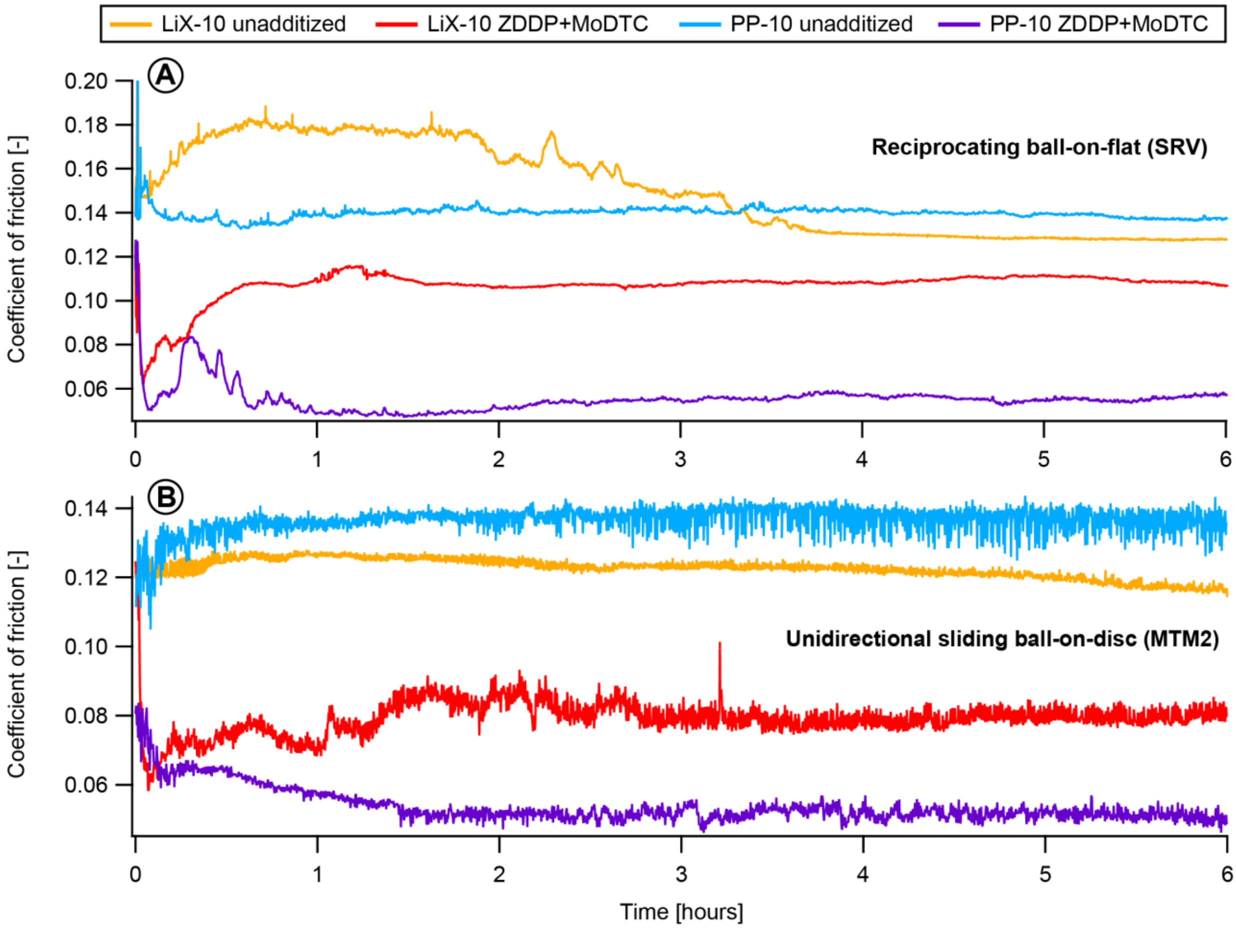


Figure 12: *The friction curves from two different tribological tests. In panel A the average friction curve from three representative runs using the reciprocating ball-on-flat test is depicted. Panel B the friction curves from one of the three the unidirectional sliding test is shown. The result from both tests have the same pattern. Both greases without additives show friction of the same magnitude, but for the greases containing additives there is a clear difference. Here the polymer grease gives much lower friction levels.*

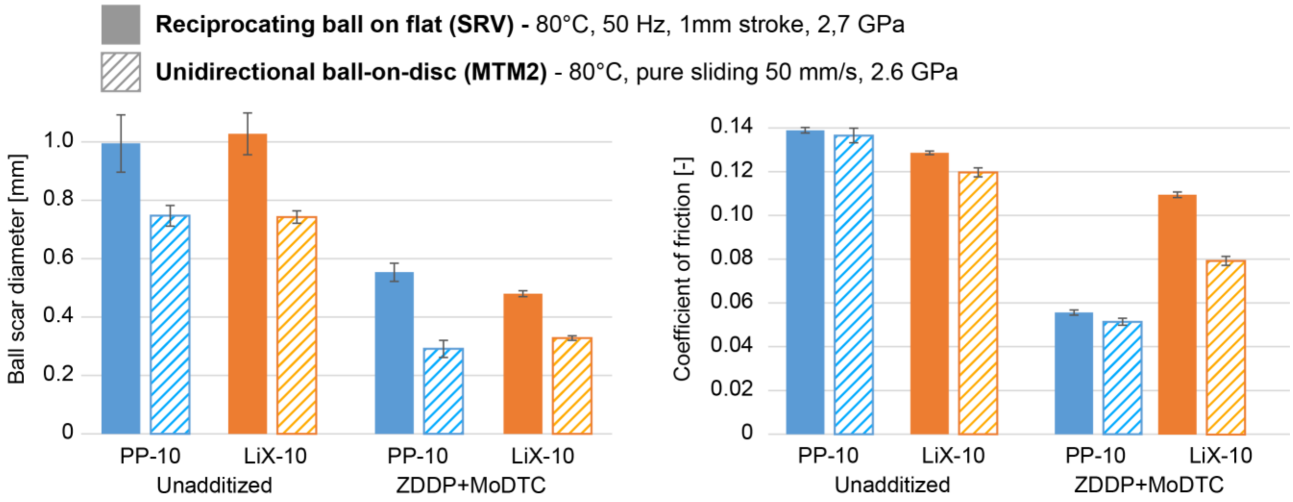
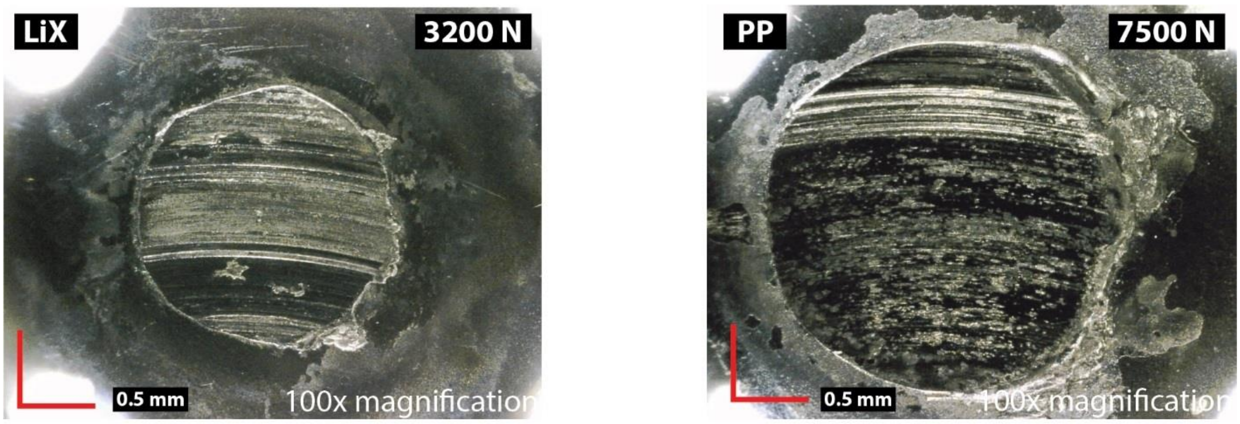


Figure 13: *Average data for ball wear scar and friction for three representative test runs. The average ball wear scar (left panel) and the average coefficient of friction (right panel) during the last two hours of the 6 hour test.*

Example 2 – Extreme pressure: The second example is based on slightly different grease formulations than in the rest of this paper. Here the consistency of both greases are NLGI 1 grade and the base oil is a blend of PAO-8 and PAO-100 resulting in a viscosity is 320 cSt at 40°C. In addition the lithium complex base oil blend also contains a smaller amount of adipate ester, but the polymer grease does not. The extreme pressure additive used in the data presented here is a material consisting of tungsten disulfide (WS_2) multi-layered nano-spheres in combination with similar ZDDP and MoDTC combination as in example 1.



Weld load 3400 N

Weld load > 7500 N

Figure 14: *Wear scars from the DIN 51350 weld load test. The left image shows the scar for the lithium complex grease from the load step before the weld point, which was 3400 N. The right image shows the wear scar at 7500 N, the maximum load of the test rig, for the polypropylene grease.*

The performance of the two greases are very different in the four ball extreme pressure test as measured by DIN 51350-4 (1 minute test duration). The lithium complex grease welds at 3400N. The wear scar at 3200 N ,the load preceding the weld, can be seen in the left picture in *Figure 14*. The polypropylene grease with the same additive package passes the maximum load of the test equipment used. The wear scar at this load, 7500 N, is shown in the right image in *Figure 14*. No further investigations of the wear scars have been made at this point in time, but just the optical appearance suggests that the tribofilms formed are quite different.

DISCUSSION

The mechanism behind grease lubrication of bearings is very complex and the different phases of grease lubrication are not fully understood [5]. What is known from literature is that thickener type, thickener content and base oil viscosity all have an influence on track replenishment [28, 29]. Characteristics of the thickener that reduce oil bleed (*e.g.* evaporation, oxidation and polymerization) or reduce surface spreading (side flow) will affect track replenishment negatively [4]. On the other hand shear degradation [30], but also moderate oxidation [31] improve track replenishment in soap based greases. At low speeds both soap and polymer thickeners have been shown to form thick surface layers [29, 32] but also at higher running speeds the thickener is found in the running track of bearings [33]. What is undisputable is that the properties of the thickener will have an effect on track replenishment thereby affecting the degree of starvation and in the long run will have an impact on grease life.

Commonly grease bearing lubrication is said to have three phases [5]: A churning phase, followed by a bleeding phase and finally we end up in a situation where the lubricant no longer is able to supply the contact and we have a film breakdown resulting in failure (see illustration in *Figure 15*). In general, this description works for most greases, but this is not the case for the polypropylene thickened grease. In the following paragraphs we will go through the behaviour of the polymer grease from startup to failure, resulting in a suggested modified lubrication mechanism for this chategory of greases.

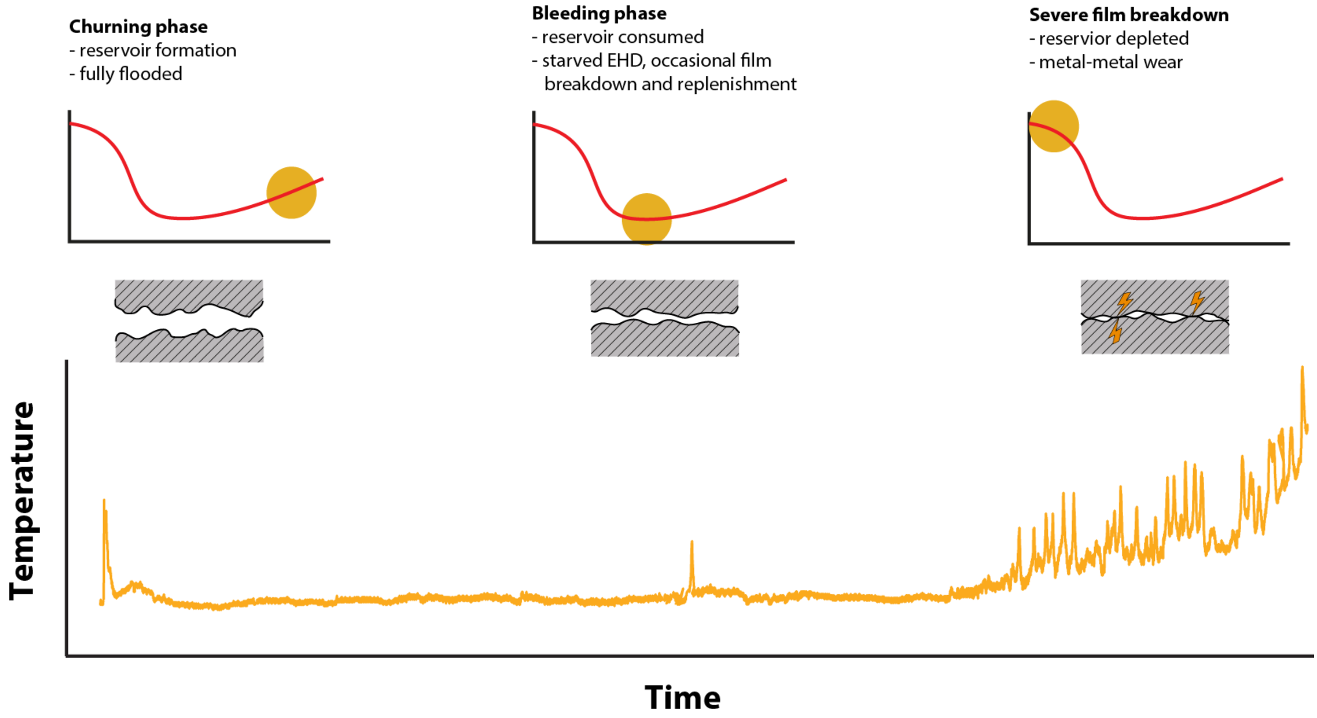


Figure 15: *Schematic figure of the phases of grease lubrication in a bearing (adapted from [5]) illustrated by a mock-up temperature curve.*

Churning

During the first hour, or hours, after starting a newly lubricated bearing the grease is redistributed inside the bearing giving rise to high film thickness and a temperature increase. This period is known as the churning phase. The churning effect for the polymer grease is known to be high from previous bearing tests and field trials. Here we have the possibility to compare two lithium complex greases with polymer greases of exactly the same base oil composition. From *panel B in Figure 2* it is really apparent that the PP-10 grease gives rise to much higher churning effect than the than the corresponding lithium complex grease. The origin of this indisputably originates from the thickener and the explanation is probably simple: That the polypropylene enters the contact to a much higher degree that the soap, giving rise to a considerably higher viscosity and film thickness. That the PP enters the contact has also been observed by Cousseau in fully flooded film thickness measurements [32] where the conclusion was that the polymer grease entered the contact more frequently than the soap based greases studied. The same result has later been verified in samples that are very similar to the polymer grease studied here [7]. A recent study also provides a possible explanation for that the polypropylene entering the contact to such high degree. It was shown that the polypropylene thickener consists of nano-size polymer particles resulting in a nano-fluid like behavior feeding the thickener into the contact [17]. More generally, Couronné et al made a similar observations in their study on VI improvers, where it was concluded that polymers always enter the contact [34].

For the higher viscosity grade, based on PAO-50 oil, the difference in churning effect is gone. The explanation for this is likely that the high base oil viscosity, in itself giving rise to a high film thickness, is cloaking the film thickness increasing effect from the polypropylene entering the contact.

After the churning phase the temperature normally stabilizes quite fast, but it is not uncommon to see temperature spikes also at a later stage that can be explained by additional churning caused by grease entering the contact [4].

Adjustment phase

The running-in time for the polymer grease is significantly longer compared to soap thickened greases, but once the system stabilizes it is generally less fluctuating than the corresponding lithium complex grease [3]. *Figure 3* illustrates this behavior quite well, but the same behavior is present in almost all bearing tests run so far.

The reason behind the long running-in time of the polymer grease, in the tests performed here around 7 days, must be directly related to the physiochemical properties of the thickener. Most likely the explanation is related to how the polypropylene that is in, or near, the contact zone is degraded. The initial thick lubricating film caused by polypropylene entering the contact during the churning phase will quickly be reduced as the high shear forces and locally high temperatures will degrade the long PP molecules into smaller molecular species resulting in a local reduction of viscosity, thereby lowering the film thickness. In the longer run the continued shear degradation of polypropylene in the interface between moving and stationary parts may lead to something resembling a low shear stress liquid film. Another plausible contribution to the adjustment phase is that it is related to the disentanglement of the nano-sized polymer particles making up the thickener [17] by degrading extended polymer chains.

The continued degradation of polypropylene inside the track will also result in the generation of compounds with boundary friction reducing properties as seen in the SRV wear measurements (*Figure 7*). The exact nature of the degradation products is unknown and outside what has been investigated in this paper. Considering the low running temperatures, indicating moderate film thicknesses, it is likely that the viscosity of the lubricant in the running track is not very high. Therefore some form of an organic friction modifier is considered likely, but something resembling a functionalized polymer is also plausible [25].

In the end is likely a combination of polymer degradation and generation of friction modifier that gradually lowers the running temperature. The time it takes to reach a steady-state temperature depends on both the shear forces to which the grease is subjected and the temperature in the contact zone. Therefore, both the duration of this phase and the nature of the degradation products will likely be different from case to case - depending on bearing geometries, bearing speed and load, base oil viscosity and so on. The authors have therefore decided to call this additional phase an adjustment phase.

Extended lubrication phase

The main phase in grease lubrication is what is commonly referred to as the “bleeding phase”, which normally accounts for close to 100% of grease life. Here the main mechanism of track replenishment is oil release from the thickener, but also thickener components entering the contact can be directly involved in the lubrication [29]. When the grease no longer is able to supply the contact with oil the lubrication will ultimately fail [35].

Soap thickened greases: During the bleeding phase it is normal to encounter shorter periods of depletion of the lubricating film leading to rapid temperature increases promoting additional oil bleed from the grease [36]. These temperature spikes, or events, are common during bearing tests (see for example *Figure 4*). Another consequence of the temperature events is that it promotes oxidation, polymerization and evaporation. In a soap based grease this in the long run leads to an increase in consistency and reduced bleed oil rate [24]. It can also lead to the formation of a so called “grease skin”, which prevents oil bleed [36]. At elevated temperatures crust formation, due to carbonization, can effectively stop oil bleed in soap based greases [5].

Another mechanism working in the other direction is the degradation of the thickener. The main mechanism is shear degradation of the thickener close to the lubricating track [30]. The severe shear forces close to the contact zone will result in a mechanical degradation of the thickener resulting in release of oil. At high temperatures chemical degradation of the thickener is also present for soap based thickeners [23], but it is counterbalanced by more severe oxidation, polymerization and evaporation.

Polypropylene thickened greases: If we examine the different behavior of the two types of grease with track replenishment in mind there are some obvious advantages in the behavior of the polymer grease. As the grease closest to the raceway is subjected to elevated temperatures it does not increase in consistency; rather it loses consistency which further increases the oil bleed, improving the track replenishment and keeping the running temperature down. When it comes to shear stability it is not expected that there are any major differences in shear stability between the two thickener systems at moderate shear forces, based on what is observed in mechanical stability tests like the Shell roll stability test (see *Table 6*). Subjected to the very high shear forces in, and close to, the running track it is very likely that the long polypropylene molecules are more heavily degraded. This is also supported by what is reported by Kompaniets *et al.* on the decrease of molecular weight of polypropylene by shear deformation under high contact pressure [37, 38, 39]. The contact pressures that were investigated (1, 2 and 5 GPa) are of the same magnitude what may occur inside rolling element bearings [40].

The feed mechanism for the polymer grease will therefore be a combination of bleed oil and degraded polymer that enters the track. For the high viscosity grades this replenishment mechanism becomes extra apparent. Starvation in grease lubrication is known to increase with base oil viscosity [28] and as this limits the availability of the lubricant in the running track. Factors that promote oil bleed reduce the risk for starvation. One important factor that releases oil is shear degradation of the thickener [30]. In the LiX-50 grease the high viscosity hampers the oil bleed to such a degree that already after a few days lubrication failure starts to occur. For the polymer grease the shear, or thermal, degradation of the polymer thickener close to the running track significantly improves the track replenishment, in effect reducing the thickener content locally in the shear zone, turning it into a liquid lubricant. This prevents the starvation seen in soap based greases of the same viscosity grade.

As the polymer thickener is sheared down it will be a mixture of oil and degraded polymer that replenishes the track. At the same time the polypropylene is *in-situ* converted to a friction modifier. The mechanism is therefore quite different compared to soap based greases where oil bleed, to some degree promoted by shear degradation, is the main source of lubrication [34]. Occasionally also fresh lumps of soap thickened grease will enter the contact and give rise to replenishment, but this will cause additional churning and temperature events [4]. In addition, soap based greases can only bleed out a certain amount of oil before they stop bleeding oil altogether [35]. For the polymer grease this is not such a big issue as the both the oil and the thickener in the shear zone will actively participate in track replenishment. The superior lubricating ability of the polymer grease is further strengthened if we compare the wear damages from rollers and cages from the bearings not causing the termination of the tests (see *Table 7*). Comparing the left LiX-10 bearing, which has a wear rate of 10 mg/day, with the right PP-10 bearing which has a total wear of 15 mg during 430 days gives a quite clear picture.

Taking into account the explanation for the lower friction levels produced by the polymer grease (demonstrated both by lower running temperatures and lower power consumption) and that the lubrication life is 7 times longer the authors feel that the description bleeding phase does not describe the replenishment process of the polymer grease well, and have therefore renamed it an extended lubrication phase – characterized by consumption and regeneration of the lubricant reservoir.

Film breakdown - Lubrication failure

At some point the reservoir will be depleted even for the polymer grease. The amount of high molecular weight compounds, due to polymerization and evaporation, have now increased to high enough amounts that the grease near the running track has become very tacky. The slow increase in the viscosity of the polymer grease is even visible in the test data generated. In *Figure 4* it can be noted that from day around day 200 and forward the running temperature is gradually increasing with one or two degrees per month. This is most likely related to the lubricant in the running track becoming thicker, due to oxidation of the oil and an increasing ratio of polypropylene degradation products. The remaining thickener is at this point not able to feed the contact any more.

A very interesting observation is that the polymer grease seems to have a superior ability to recover from starvation. This can be seen in both PP-50 greases, but especially in the left PP-10 bearing (see *Appendix 1*). During the test there is a period where the temperature increases significantly and reaches close to 120°C, indicating poor lubrication and starvation. The temperature in the plot is measured on the outer ring, the actual temperature in the loaded zone will be higher, possibly high enough to locally melt the thickener structure resulting in a partial "resetting" of lubrication. This is at least one possible interpretation of the temperature curve of the left PP-10 bearing. The temperature before the high temperature period (between days 340-370) was around 57°C, which is around 15°C higher than the initial steady state temperature after the adjustment period. Around day 370 something happens and the temperature drops by 25°C in only a few days – a quite astonishing recovery, which could be explained by a redistribution of grease inside the bearing caused by the partial melting, or softening, of the thickener structure.

If we move back in time to before the failure there are some important differences between the polymer grease and the lithium complex grease in the way oxidation occurs. The closer we get to the end of the grease life the more likely it is that we experience short events of lubrication failure, leading to temperature spikes and vibrations, that accelerates additional oil bleed or thickener entering the contact. During these events it is likely that metal-metal contact occurs, causing wear and the formation of wear debris. In a bearing the most likely type of debris are particles of iron and its oxides form the raceway and copper and zinc form the cage (in the case of a brass cages). It is common knowledge that transition metals, even at very low levels, can accelerate oxidation processes [24]. This is also something that likely occurs in a bearing, especially towards the end of life.

Interestingly enough, we don't see large differences between the metal free and the metal contaminated samples when it comes to the intensity of the IR carbonyl peak. Here the results are very similar to what we noted for the metal free samples (see *Figure 11*). The lithium complex grease shows the lowest level of oxidation and the polymer grease and the oil have a higher degree of oxidation. Contaminating the greases with high levels of lithium hydroxide results in that the intensity of the carbonyl signal becomes lower and identical for both PAO-10 based greases as shown in *Figure 11.* Possible explanations are that the free lithium hydroxide is preventing the accumulation of carbonyl species either by working as an antioxidant or by catalyzing further reactions of the formed carbonyl species. Based on the lower oil viscosity extracted from the lithium complex grease and what others have reported [21, 22] the former is likely to be the mechanism here.

Looking beyond IR there are other changes occurring to the two grease types when oxidized that are quite different, in both cases these changes are significantly accelerated by contamination of metal particles (*Figure 10*). The polymer grease initially becomes softer and then gradually turns tackier and tackier. The lithium complex grease changes rapidly and becomes darker and gets a drier more grainy appearance. On the air exposed surface of the LiX-10 grease, aged for longer times, there is a surface layer forming with even thicker consistency. The nature of this layer sounds very similar to the "grease skin" reported by others [36]. Such a layer, or skin, will have negative consequences for lubrication as it strongly reduces oil bleed.

The authors are currently investigating the structural changes in more detail, but based on currently available data the authors can see two different main mechanisms for lubrication failure in the two different grease types. In the polymer grease the slowly increasing base oil viscosity in the running track, caused by polymerization and evaporation of low molecular species in combination with an increasing content of polypropylene degradation products, leads to increasing viscosity and temperatures that in turn promotes further oxidation. At some point the lubricant in and near the contact becomes so thick that lubrication fails.

In the lithium complex grease we have a lower degree of oil oxidation as seen by IR. Furthermore, the viscosity of the extracted oils is lower. The main cause of lubrication failure here is due to structural changes in the thickener, resulting in stronger oil retention and higher consistency. The formation of a "grease skin" near the running track will further reduce the replenishment. Once lubrication failure starts to occur the metal debris formed will further strongly accelerate the deteriorating lubrication.

Modified lubrication mechanism for polypropylene thickened greases

Combining the data we have collected in this investigation with our experiences from other investigations and field trials the authors would like to suggest an alternative model, consisting of four phases, to explain the lubrication phases of polypropylene thickened greases.

- *Churning phase* - Similar to the churning phase of soap based greases with the exception that the polymer to a much larger extent enters the contact resulting in stronger churning.
- *Adjustment phase* – Additional phase for polypropylene greases. During this phase the PP entering the contact is degraded resulting in the *in-situ* formation of a friction modifier. The thickener in the interface between moving and stationary parts will be sheared down creating a low viscosity fluid film.
- *Extended lubrication phase* – To emphasize the difference in feed mechanism the name *"bleeding phase"* is changed. For the polymer grease the reservoir is not simply consumed – it is also continuously regenerated by the local shear and thermal degradation of the polypropylene – leading to a phase which is seven times longer compared to the bleeding phase in soap based greases.
- *Film breakdown* – When the grease no longer is able to feed the contact with lubricant we reach the end of lubricating life. For the polymer grease it is the increasing viscosity, as a result of oxidation and an increasing amount of degraded polypropylene, that finally prevents replenishment.

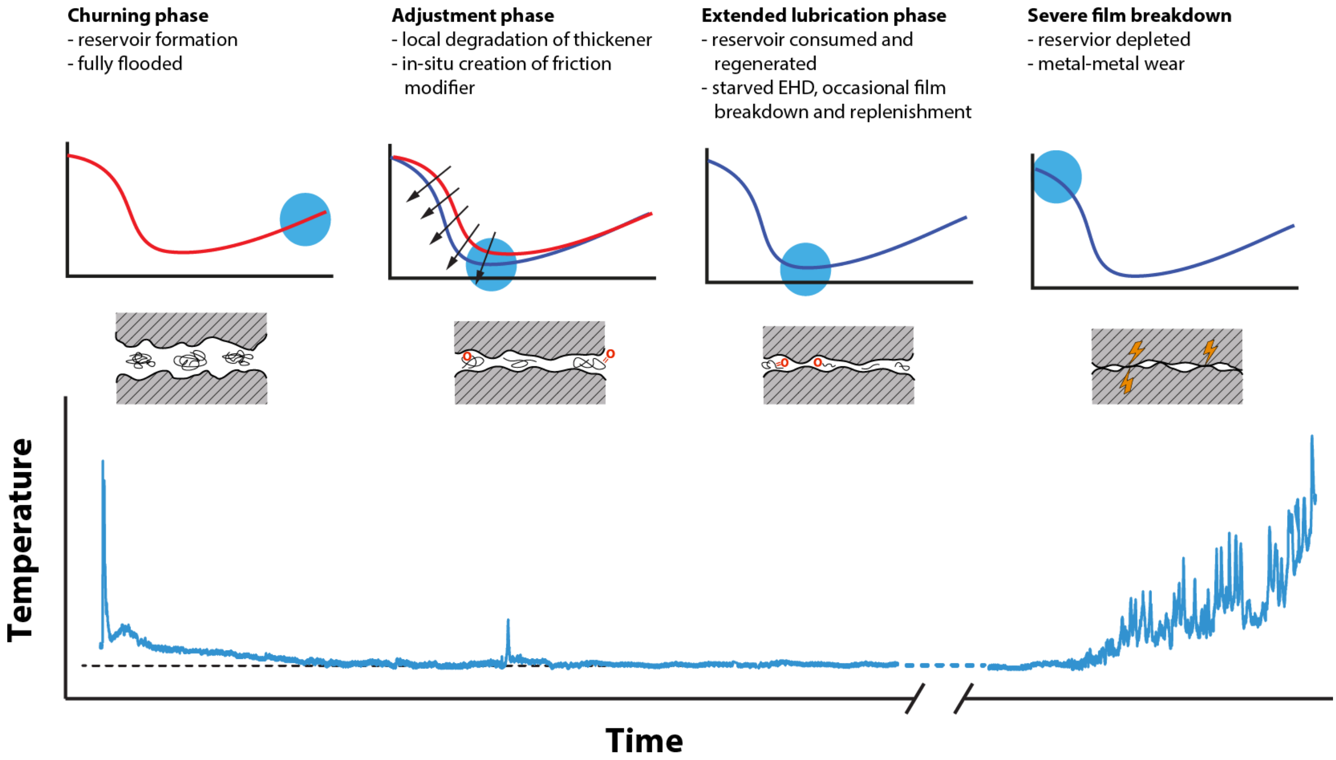


Figure 16: *The polypropylene thickened greases do not fit into the same description of lubrication phases for bearings as soap based greases. In addition we also have an adjustment phase where the degradation of the thickener close to the shear zones leads to the formation of a friction modifier originating from the PP-thickener. In addition the bleeding phase is significantly extended for the polymer greases as the combination of shear and temperature will keep the contact feed with lubricant. At some point the viscosity of the lubricant in, and near, the running track, will become so thick that it no longer can supply the contact with lubricant and subsequently lubrication will fail.*

Additive response

We often experience that the additive response is different in the polymer grease compared to soap based greases. In this paper we give two examples where we have very different additive response between polypropylene thickened grease and a lithium complex grease.

The first example is a traditional friction modifier package consisting of a combination of ZDDP and MoDTC [25]. Here we see a significant improvement in wear scar for both grease types, but when it comes to friction reduction this is much larger for the polymer grease (60%) compared to the lithium complex grease (15-30%). This result is seen in two quite different test methods: One fully flooded unidirectional sliding test and one reciprocating test where the contact commonly becomes starved. This indicates that it is not the property of the polypropylene to enter the contact that is the main difference as it would do so to a much higher degree in the fully flooded unidirectional sliding test. The high noise level of the unadditized PP-10 curve (compare with LiX-10 in *Figure 12*) is most likely due to the effect of polypropylene thickener entering the contact, in line with what has already reported by others [32, 7]. The second example is an extreme pressure additive package where the lithium complex grease welds at 3400 N and the polymer grease passes 7500 N which is the maximum load of the 4-ball machine used.

The explanation for these differences is probably quite simple: Traditional greases are thickened by an organic salt (*i.e.* soap). The soap can in some cases bring desired properties to the lubrication (commonly referred to as functional thickeners, *e.g.* lithium bismuth complex soap) but in most cases the soap will have a negative impact on the function of the additives. Either by competing for, and blocking access to the metal surface, or by being directly involved in tribochemical reactions. In addition most soap based greases contain a small excess of alkali to prevent oxidation and discoloration of the grease during manufacturing. This alkali is a reactive species that can further affect additive performance negatively [22]. The thickener in a polymer grease is very similar to the base oil in its physiochemical properties and is therefore very unlikely to interfere negatively with additive performance.

More surprises to come

The authors are, as of writing this, involved in a number of studies focusing on the characteristics if the polypropylene thickened grease. Some of these results are about to be published, like the study on additive response [27], other investigations need more effort before they are ready to be presented to the public. What we can promise is that more surprises are to come.

CONCLUSIONS

In this paper the authors have shown that grease thickened by polypropylene deviates from the most common mechanism used to describe grease bearing lubrication. Instead the authors suggest a modified mechanism (*Figure 16*) that better describes the behavior of the polypropylene thickened greases in bearings consisting of:

- ***Churning phase*** *(duration hours):* As the polypropylene has been shown to enter the contact to a high degree the observed film thickness and churning is high. The polypropylene in the contact zone is rapidly degraded, reducing the local viscosity and the film thickness.
- ***Adjustment phase*** *(duration days):* In the interface between moving and stationary parts the shear and temperature will continue to affect the polymer creating a film of low viscosity. This film will separate the grease unaffected by shear and the moving surface, creating a low shear stress liquid layer. In parallel, the degradation of polypropylene gives rise to the *in-situ* formation of a friction modifier.
- ***Extended lubrication phase*** *(duration months):* The layer of oil and degraded propylene close to the contact zone is continuously supplying the contact with lubricant. At the same time the reservoir is continuously regenerated by additional mechanical and thermal degradation, creating an extremely long lasting feed mechanism for the contact. Where a normal grease essentially is a two-phase system with a liquid-phase consisting of oil and a solid-phase consisting of the thickener, a

polymer grease is more of a quasi-one-phase system with a low-viscosity hydrocarbon dissolved in an extremely high viscosity hydrocarbon. When the polymer gets sheared down close to the contact zone we locally end up with a true one-phase system. In other words, the polymer grease turns into 100% oil, giving rise to more lubricating capacity than a soap based grease, thereby giving rise to much longer lubrication life.

- ***Lubrication failure:*** Severe film breakdown occurs when the grease no longer can feed the contact with lubricant. For the polymer grease this is caused by an increase in viscosity caused by oxidation and an increasing amount of degraded polypropylene in the contact zone. The grease simply becomes too thick and tacky to flow. For the lithium complex grease the main mechanism is not oxidation of the oil, but a change in the thickener structure causing the grease to get a higher consistency and a drier appearance at the same time as the oil retention increases. The presence of metal debris accelerates the structural change of the lithium complex grease to a higher degree than for the polymer grease.

The key findings in this paper are:

- The lubrication potential of a polymer grease is up to 7 times longer than a comparable lithium complex grease.
- The polypropylene enters the contact and is directly involved in the lubrication.
- The polypropylene is *in-situ* converted to a friction modifier.
- Low shear films separating moving parts and the lubricant reservoir reduces shear losses.
- The polymer grease finally fails due to an increasing consistency of the lubricant, the lithium complex fails due to the increased oil retention of the thickener.
- The reduced power consumption for the polymer grease seen in the tests is around 3-5%
- Where higher viscosity grades of the lithium complex thickened greases fail to lubricate – the feed mechanism of the polypropylene grease lubricate efficiently.
- The additive response in polypropylene thickened greases is often quite different due to the absence of a soap thickener.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the support from their colleagues in the R&D laboratory at Axel Christiernsson International AB.

REFERENCES

[1] G. Gow, "Ecclesiastes 3:1," in *NLGI 74th Annual Meeting*, Scottsdale, Arizona, 2007.

[2] M. Fathi-Najafi, G. Gow and M. Kruse, "REACH-Free Lubrication with A Novel Polymer Thickened Lubricant," in *ELGI AGM*, Cyprus, 2007.

[3] J. Leckner, "Energy efficiency and lubrication mechanisms of polymer thickened greases.," *Eurogrease Magazine*, no. 3, pp. 12-29, 2015.

[4] P. M. Lugt, S. Velickov and J. H. Tripp, "On the Chaotic Behavior of Grease Lubrication in Rolling Bearings," *Tribology Transactions*, vol. 52, no. 5, pp. 581-590, 2009.

[5] P. M. Lugt, Grease lubrication in rolling bearings, Wiley, Tribology Series, 2013.

[6] T. Cousseau, M. Björling, B. Graça, A. Campos and R. Larsson, "Film thickness in a ball-on-disc contact lubricated with greases, bleed oils and base oils," *Tribology International*, vol. 53, p. 53–60, 2012.

[7] D. Gonçalves, B. Graça, A. V. Campos, J. Seabra, J. Leckner and R. Westbroek, "On the film thickness behaviour of polymer greases at low and high speeds.," *Tribology International*, vol. 90, pp. 435-444, 2015.

[8] D. Gonçalves, B. Graça, A. V. Campos and J. Seabra, "On the friction behaviour of polymer greases," *Tribology International*, Vols. 93, Part A, p. 399–410, 2015.

[9] D. Gonçalves, B. Graça, A. V. Campos and J. Seabra, "Film thickness and friction behaviour of thermally aged lubricating greases," *Tribology International,* p. Available online 5 February, 2016.

[10] T. Cousseau, B. Graça, A. Campos and J. Seabra, "Friction torque in grease lubricated thrust ball bearings," *Tribology International,* vol. 44, no. 5, p. 523–531, 2011.

[11] T. Cousseau, B. Graça, A. Campos and J. Seabra, "Influence of grease rheology on thrust ball bearings friction torque," *Tribology International,* vol. 46, no. 1, pp. 106-113, 2012.

[12] D. Gonçalves, S. Pinho, B. Graça, A. V. Campos and J. H. O. Seabra, "Friction torque in thrust ball bearings lubricated with polymer greases of different thickener content," *Tribology International,* vol. 96, p. 87–96, 2016.

[13] R. Westbroek and J. Leckner, "Lubrication mechanism of polypropylene thickened grease: Improved energy effiency and grease life," in *TAE*, Esslingen, 2016.

[14] J. Leckner and R. Westbroek, "Polypropylene – a new thickener technology for energy efficient lubrication.," in *STLE presentation*, Las Vegas, 2016.

[15] J. Leckner and R. Westbroek, "Polypropylene – a new thickener technology for energy efficient lubrication.," *NLGI Spokesman,* vol. 81, no. 1, pp. 34-56, 2017.

[16] R. Westbroek and J. Leckner, "Lubricating Mechanism of Polypropylene Thickened Grease - Improved Energy Efficiency and Grease Life," in *Nordtrib presentation*, Hämeenlinna, Finland, 2016.

[17] D. Muller, C. Matta, R. Thijssen, M. bin Yusof, M. van Eijk and S. Chatra, "Novel polymer grease microstructure and its proposed lubrication mechanism in rolling/sliding contacts," *Tribiology International,* vol. accepted manuscript, 2017.

[18] T. A. Harries, Rolling Bearing Analysis. 4th edition, John Wiley and Sons, 2001.

[19] Publ. No. WL 81 115/4 EA, "Rolling bearing lubrication," FAG Kugelfischer Georg Schäfer AG, Schweinfurt, 2002.

[20] D. Gonçalves, B. Graça, A. V. Campos, J. H. Seabra, J. Leckner and R. Westbroek, "Formulation, Rheology and Thermal Aging of Polymer Greases - Part I: Influence of the thickener content," *Tribology International,* vol. 87, pp. 160-170, 2015.

[21] L. W. Sproule, J. H. Norton and W. C. Pattenden, "Oxidation-Resistant Lubricating Greases Containing Inorganic Alkali Metal Compounds of High Alkalinity". US Patent 2,921,899, 19 January 1960.

[22] N. Canter, "Grease additives: Important contributors not to be overlooked," *Tribilogy & Lubrication Technology,* vol. December, pp. 24-38, December 2012.

[23] I. Couronné and P. Vergne, "Rheological Behavior of Greases: Part II—Effect of Thermal Aging, Correlation with Physico-Chemical Changes," *Tribology Transactions,* vol. 43, no. 4, pp. 788-794, 2000.

[24] S. Hurley, P. Cann and H. Spikes, "Thermal Degradation of Greases and the Effect on Lubrication Performance," *Tribology Series,* vol. 34, pp. 75-83, 1998.

[25] H. Spikes, "Friction modifier additives," *Tribology Letters,* vol. 60, no. 1, pp. 1-26, 2015.

[26] J. Lorimor, "An evaluation of the use of anhydrous lithium hydroxide dispersions in full-scale production equipment," in *NLGI Annual Meeting,* Palm Desert, 2011.

[27] J. Shu, K. Harris, B. Munavirov, R. Westbroek, J. Leckner and S. Glavatskih, "Tribology of polymer and Li-complex greases with ZDDP and MoDTC additives," *to be submitted to Tribology International,* 2017.

[28] P. M. Cann, "Starved Grease Lubrication of Rolling Contacts," *Tribology Transactions,* vol. 42, no. 4, pp. 867-873, 1999.

[29] P. M. Cann, "Grease lubrication of rolling element bearings — role of the grease thickener," *Lubrication Science,* vol. 19, no. 3, pp. 183-196, 2007.

[30] J.-S. Mérieux, S. Hurley, A. A. Lubrecht and P. M. Cann, "Shear-degradation of grease and base oil avalability in starved EHL lubrication," in *Thinning films and tribological interfaces, Tribology Series 38,* Amsterdam, Elsevir Science, 2000, pp. 581-588.

[31] P. M. Cann, "Grease degradation in a bearing simulation device," *Tribology International,* vol. 39, no. 12, p. 1698–1706, 2006.

[32] T. Cousseau, Film thickness and friction in grease lubricated contacts. Application to rolling bearing torque loss, Porto: Thesis: Faculty of Mechanical Engineering of Porto University, 2013.

[33] P. M. Cann, J. P. Doner, M. N. Webster and V. Wikstrom, "Grease Degradation in Rolling Element Bearings," *Tribology Transactions,* vol. 44, no. 3, pp. 399-404, 2001.

[34] I. Couronné, P. Vergne, D. Mazuyer, N. Truong-Dinh and D. Girodin, "Nature and Properties of the Lubricating Phase in Grease Lubricated Contact," *Tribology Transactions,* vol. 46, no. 1, pp. 37-43, 2003.

[35] S. Komatsuzaki and T. Uematsu, "Change of grease characteristics to the end of lubricating life," *NLGI Spokesman,* vol. 63, no. 12, pp. 22-29, 2000.

[36] P. Lugt, S. Velickov and J. Tripp, "On the chaotic behavior of grease lubrication in rolling bearings," *Tribology Transactions,* vol. 52, no. 5, pp. 581-590, 2009.

[37] L. Kompaniets, I. Dubnikova, N. Erina, S. Kuptsov, A. Zharov and E. Prut, "Mechanodestruction of isotactic poly(propylene) subjected to plastic flow under high pressure," *Vyso Soed,* vol. 41, no. 3, pp. 511-518, 1999.

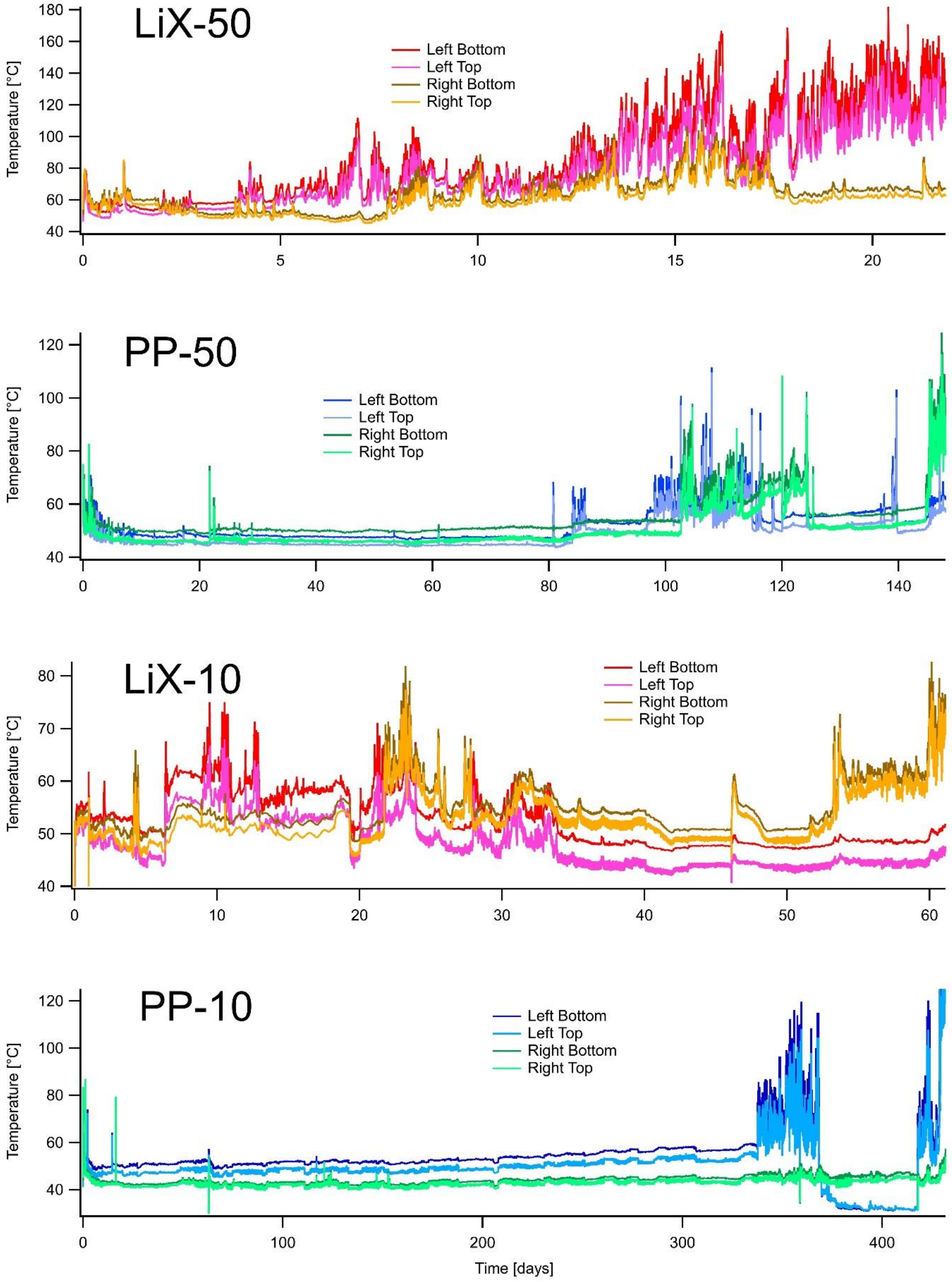
[38] L. Kompaniets, I. Dubnikova, S. Kuptsov, A. Zharov and E. Prut, "Effect of high pressure on mechanical degradation of isotactic polypropylene under plastic flow," *Polym Sci A,* vol. 43, no. 3, pp. 332-336, 2001.

[39] L. Kompaniets, S. Kuptsov, N. Erina, I. Dubnikova, A. Zharov and E. Prut, "Effect of joint action of high pressure and shear deformation on mechanical degradation of isotactic polypropylene," *Polymer degradation and stability,* vol. 84, pp. 61-68, 2004.

[40] B. Jacobson, Rheology and elastohydrodynamic lubrication, Tribology Series Volume 19, Elsevier Science, 1991.

Appendix 1:

Raw temperature data from the R2F until failure experiment for all 4 individual probes.



Appendix 2

The IR-spectra for the LiX-10 (panel A), PP-10 (panel B) and the PAO-10 oil blend (panel C) after static thermal ageing at 120°C. The detected oxidation rate as judged from the infra-red spectra is PP-10 ≈ Oil blend > LiX-10.