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The Utilization of a Commercial Vehicle Field Trial to Demonstrate the Performance of a Long-life Bearing Grease Additive Package

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Abstract

Most current commercial truck wheel bearing greases in the Indian market place are advertised as being good for up to 50,000 km between re-greasing. It was desired to generate data showing the differentiated performance of a heavy commercial vehicle wheel bearing grease utilizing a high performance long-life grease additive package and a water resisting functionalized polymer against an existing long-life grease sold in the market place. The commercial long-life grease chosen claimed that it would last for 60,000 km service intervals.

From discussions with vehicle fleet operators, it was suggested that if a grease could last 1,00,000 km or 1,20,000 km then it would help them to reduce downtime and costs. Bearing protection and seal compatibility were key requirements. It was therefore decided to run a field trial truck comparing the performance of wheel bearings lubricated with this commercial market leader and a grease which used the high performance long-life grease additive package along with the functionalized polymer.

The results of the field trial showed that grease with the high performance long-life grease additive package and functionalized polymer in a simple lithium soap thickened mineral oil grease outperformed the commercial grease in terms of surface protection and oxidation life.

The paper covers the execution of this field trial carried out in India which between 2014 and 2016 ran for approximately 1,15,000 km, the assessment of bearings used and the analysis of the used greases obtained at the end of the trial.

Introduction

For many grease applications, the technical specification is used to give the user sufficient information to say that the grease has at least the minimum basic physical and chemical properties needed for that application. However, many grease properties can only be demonstrated by running the grease in the actual equipment under actual operating conditions. Even after passing all specification tests, many grease users require demonstrable proof from field trials showing that the grease will likely work in their precise application. A vehicle fleet operator would typically run a field trial on one or two vehicles before committing to changing greases for the whole fleet. Such field trials would typically last for one to two years and would demonstrate improved performance over the existing products used.

Commercial vehicles are no exception to this approach. In North America, it is desired that fleet greases match the crankcase oil drain intervals lasting up to 30,000 miles (50,000 km) for severe duty operation but up to 60,000 miles (1,00,000 km) for mild duty intervals. In India, most currently marketed heavy-duty wheel bearing greases advertise as being good for up to 50,000 km before re-greasing. From discussions with vehicle fleet operators, it was suggested that if a grease could last 1,00,000 km or 1,20,000 km then it would help them to reduce downtime and costs. It was further indicated that bearing protection and seal compatibility were key requirements of any improved grease.

It was necessary to generate data by running a field trial to show differentiated performance between a heavy commercial vehicle wheel bearing grease (identified as Lubrizol Grease or LG) utilizing a long-life grease performance additive package with a water resisting polymer and an existing long-life grease sold in the market place. The commercial grease chosen claimed that it would last for 60,000 km service intervals and was identified as Commercial Grease or CG.

Lubricating greases for rolling element bearings

Lubricating grease represents a critical design component in the lubrication of rolling element bearings for both industrial and automotive applications. The grease functions by providing a film of lubricant to separate moving surfaces in a bearing that consists of rolling elements and a bearing raceway. The grease must also reduce the sliding friction occurring between the rolling elements, the raceways and the cage. In previous papers presented at NLGI Annual Meetings (1,2) and ELGI Annual Meetings (3,4) and the NLGI India Chapter 16^{th} Annual Meeting (5), thebasic requirements of lubricating greases for rolling element bearings were outlined. In the case of heavy loading and high temperatures necessitate other performance provided by additives in the grease including prevention of wear and scuffing through anti-wear (AW) and extreme pressure (EP) additives and reduction of oxidation with anti-oxidants (AO).

In re-greaseable applications (typically industrial, railroad, and commercial vehicles), the performance of the sealing is typically much less than that seen in sealed-for-life automotive (passenger car and light truck) bearings but is important to prevent contaminant ingress. One ofthe challenges seen with re-greaseable transportation greases is that when running, the combination of applied load, rotational speed and churning, generates heat. The sealing system typically vents when hot and then draws in air when cold. In these cases, this breathing irreversibly introduces water into the bearing. Therefore, the grease also needs to protect the mating surfaces from water induced corrosion. This can be done in one of two ways: passively by the use of polymers to make the grease water repelling or actively through surface active rust preventative additives. Railroad grease specifications typically prohibit the use of polymer additives and their formulations but this is not the case with commercial heavy-duty truck greases.

Typical passenger cars with higher speed driving use greases that have base oil kinematic viscosities in the range of 120 cSt to 170 cSt at 40 °C. The wheel on a midsized passenger car driving at 60 mph (100 kmh) will rotate at approximately 800 rpm. For heavy duty trucks at thesame speed, the rotational speed of the bearings is much lower at approximately 500 rpm. To generate similar film thicknesses, the base oil needs to be at a higher viscosity such as ISO VG220. Some of the recently reviewed North American heavy-duty truck grease datasheets for hubunits showed that they were moving away from the NLGI #2 and #3 ISO VG 220 greases to NLGI #00 grades with base oils at ISO VG 460. Historically in North America, the thickener of choice was lithium complex in a mineral oil base, but now semi-synthetic and fully synthetic base oils are widely used along with diureas and polyurea thickeners. The wheel bearings in theproposed field trial, were not installed as hub units but as serviceable bearings and so the more traditional NLGI #2 ISO VG 220 was chosen.

The greases for the field trial

The base oil viscosity was to be a blend of mineral oils at ISO VG 220. The thickener was a simple lithium soap, and the additives comprised of a long-life performance additive package and a functionalized polymer to enhance the water resisting properties of the grease. In order to ensure proper solublization of the polymer, a pre-solubilized version was used in the manufacturing which introduces some 330N paraffinic base oil into the grease mixture. This is taken into consideration when calculating the base oil ratios 500N:330N:150BS 40.0:5.6:54.4 ona weight basis. The base oil blending component identities and final blend viscometrics are listedin table 1.

In India, it is common to use hydrogenated castor oil (HCO) as a fatty acid source for soap manufacturing. Previous testing (1) had shown that free glycerin in HCO contributed to a reduction in the oxidation resistance of the grease and so it was decided to make the soap using only 12-hydroxystearic acid. Lithium hydroxide monohydrate powder was used as the alkali source. This was mixed in with 10X its weight of hot water to help facilitate the saponificationreaction. 12 kg of finished grease was made in a laboratory scale grease reactor.

Mineral oil component	Weight ratio (wt%)	Kinematic viscosity (mm^2/s)		Viscosity Index
		at 40 °C	at 100 °C	
150BS heavy paraffinic oil	54.4	485.2	31.46	95
Indian sourced 500N medium viscosityparaffinic oil	40.0	100.1	11.18	97
330N medium viscosity paraffinic oil from the polymer solution	5.6	61.1	7.98	95
Blend	100	229.8	19.26	95

Table 1 – Base oil blend selection.

The final formulation of the finished grease for the trial is listed in table 2.

Component	Weight%
Lithium 12-hydroxystearate soap	10.0
Functionalized polymer	0.23
Base oil blend	85.71
Free lithium hydroxide	0.06
Long life performance additive package	4.00

Table 2 – The formulation of the Lubrizol grease

A pail of the commercial grease was obtained for the trial. Basic chemical and physical property testing was carried out on both finished greases. Elemental analysis was carried out by microwave digestion of the grease into aqueous solution and then measuring the elemental composition by inductively coupled plasma (ICP) spectroscopy. The ICP elemental analysis is listed in table 3 below.

Elemental analysis (wt%)	Lubrizol Grease	Commercial Grease	Comments
calcium	<0.005	0.017	
iron	0.010	<0.005	
lithium	0.273	0.314	Commercial Grease has higher soap content
phosphorus	0.077	0.162	Commercial Grease has additional phosphorus additives
sodium	0.009	0.005	Insignificant traces
sulfur	1.11	0.655	Lubrizol Grease has a higher sulfur contentdue to the base oil
zinc	0.153	0.175	Commercial Grease has higher zinc dithiophosphate content

Table 3 elemental analysis of the two greases

FTIR Spectral analyses of the new greases and the samples from the bearings are shown in figures 1 and 2. In figure 3, the additive regions of the two greases are compared. The FTIR of this additive region confirmed the ICP data in that the Commercial Grease had a higher level of zinc dithiophosphate present.

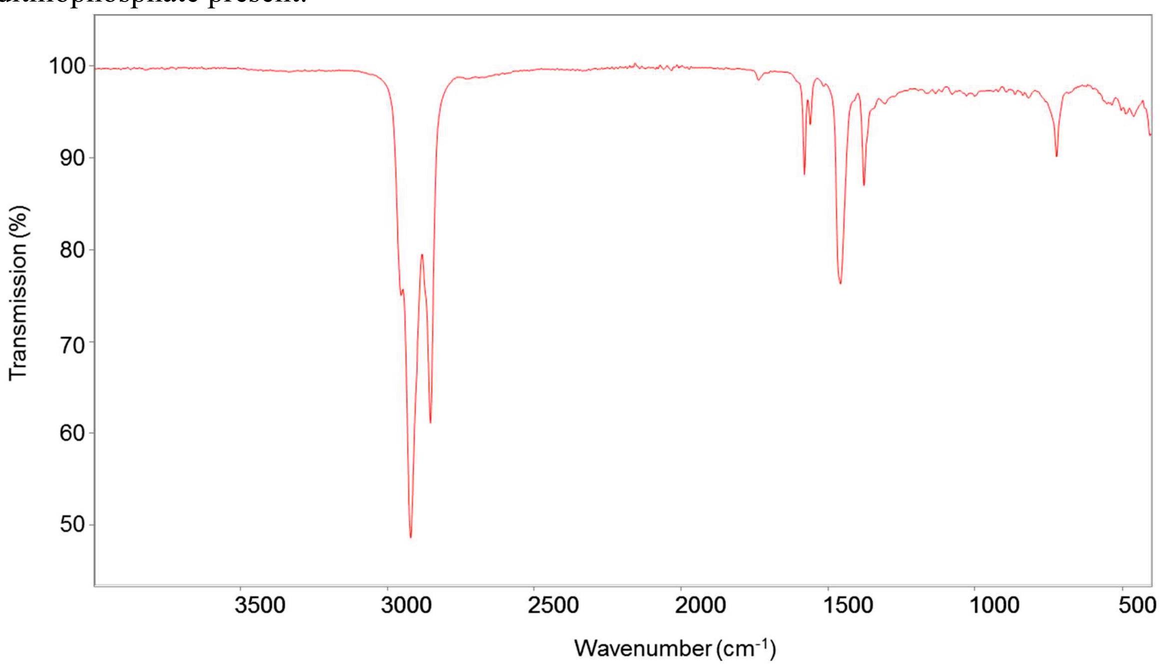


Figure 1. FTIR spectra of the Lubrizol grease as manufactured

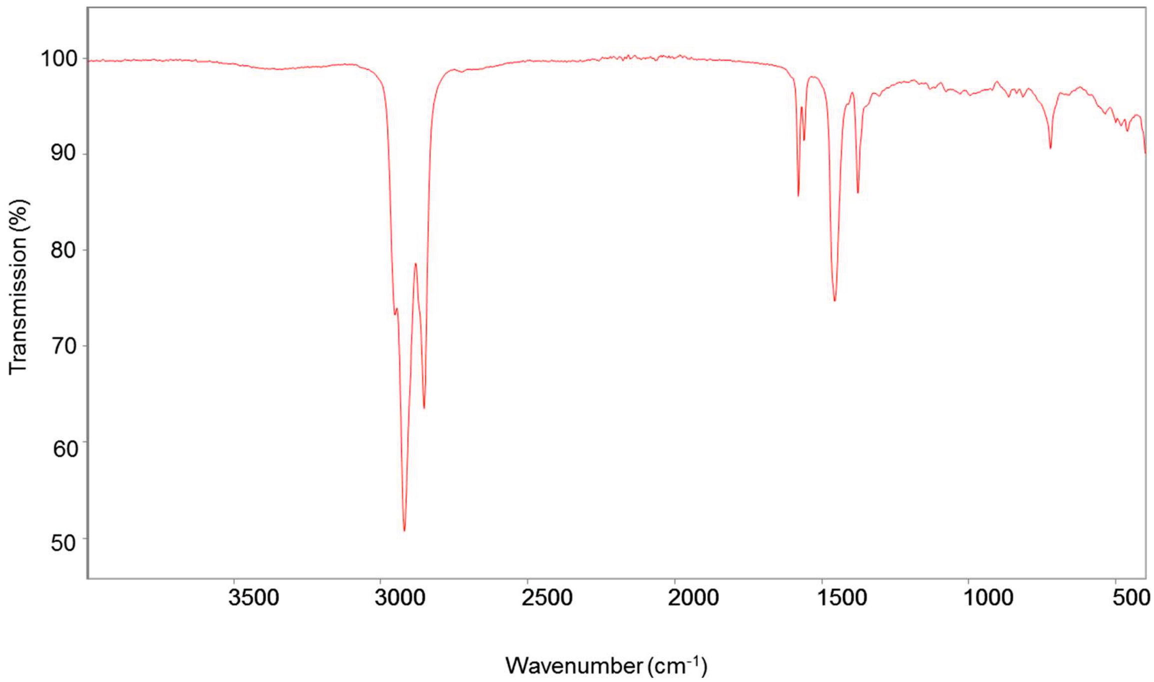


Figure 2. FTIR spectra of the Commercial long-life grease as purchased

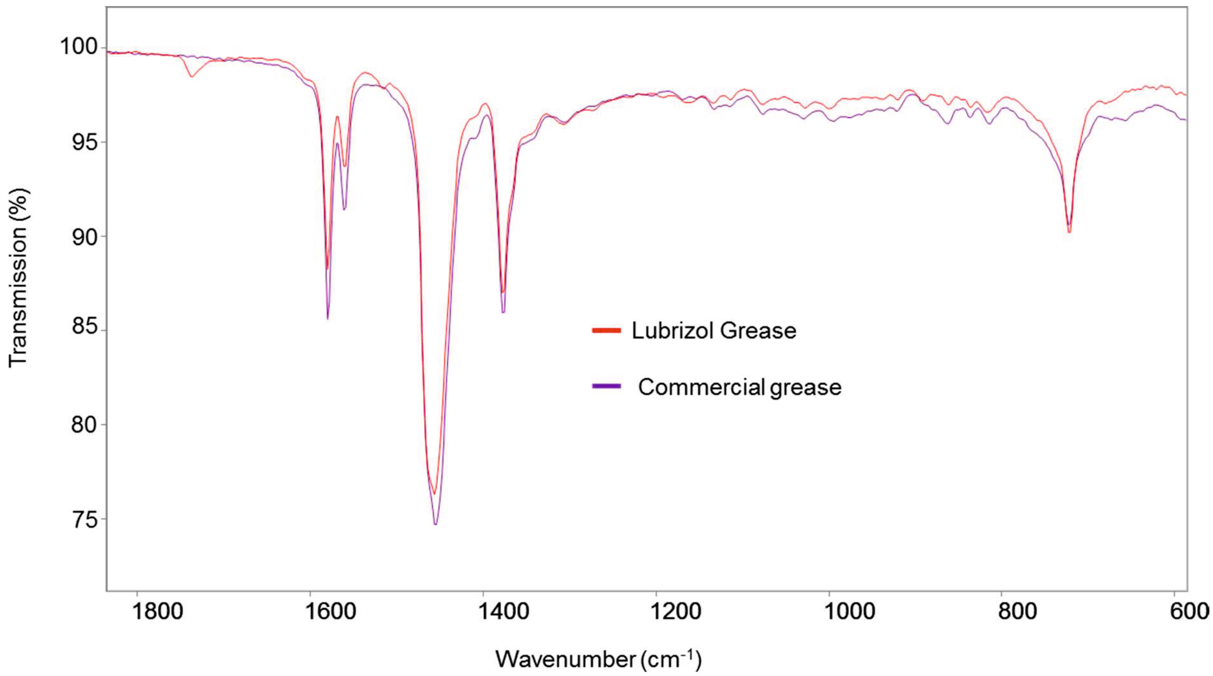


Figure 3. FTIR spectra of the comparing the additive regions of the two new greases

The Lubrizol Grease and the Commercial Grease had some basic tests carried out on them and the data is compared in Table 4 below.

Property	Test Method	Lubrizol Grease	Commercial Grease
Unworked Penetration	ASTM D217	271	235
Worked 60 Penetration		269	227
NLGI grade		#2	#3
Dropping point (°C)	ASTM D2265	201	187
4-Ball Wear Scar diameter (mm)	ASTM D2266	0.50	0.48
4-Ball EP Last non-seizure load (kg) Weld point (kg) LWI (kg)	ASTM D2596	63 315 41.3	80 250 40.1
Copper corrosion (24 hours 100 °C)	ASTM D4048	1A	1A
Pressure Differential Scanning Calorimetry(PDSC) at 180 °C Oxidation induction time (minutes)	ASTM D5483	69.4	11.7
Wheel bearing grease life (hours)	ASTM D3527	>100	60

Table 4 - Tests methods and results for the two greases

As can be seen from the data, the Lubrizol formulated grease had similar wear and EP properties compared to the commercial grease but significantly better oxidation life and thermal stability as measured by pressure differential scanning calorimetry (PDSC) at 180 °C and wheel bearing grease life at 160 °C.

Setting up of the field trial

The test vehicle was a heavy commercial diesel tractor unit fitted with a 6.7 L, 224 bhp (167 kW) turbocharged and intercooled, direct injection diesel engine. The vehicle layout is a front steering axle and a pair of driven tandem rear axles.

A complete set of new wheel bearings were fitted on the vehicle. All the bearings used for the trial were weighed before filling and after cleaning at the end of trial. Weight changes are notedin table 6 this report.

Those on the right-hand side of the vehicle (bearings #1 to #6) were filled with the Lubrizol candidate long-life grease and those on the left (bearings #7 to #12) were filled with the commercially available long-life grease.

The front axle on the vehicle has two pairs of tapered roller bearings. The inner bearings are 143mm outer diameter (SKFBT1-0500 Q) and the outer bearings are slightly smaller 114 mm outer diameter (SKF BT1-0501 Q). The inner bearings were filled with 80 grams of grease, the outer 70 grams and 300 grams were added into the hub unit after the bearings had been installed on to the vehicle, totaling 450 grams of grease per hub assembly. The middle and rear outer bearings were the same designation of tapered roller bearing, Timken 683-672 and the inner rear and middle bearings were Timken 32217. The inner bearings had 100 grams of grease in each and the outer bearings 70 grams. The hub units had 480 grams added to each one making 650 gramsper hub assembly.

Post-trial analysis

The vehicle was run across India for almost two years and completed 1,14,351 km towing a tanker trailer loaded with up to 30 tons of material.

Bearing #9 and Bearing #10 (both with the CG) suffered leakage after only 15,000 km. Thebearings were re-greased and re-sealed by the fleet operator and the trial continued.

Bearings #11 and Bearing #12 (both with the CG) were also found to be leaking at the end of trial. Brake pads were observed to be wetted with lubricant, possibly due to lubricant leak from the hub, but whether this was grease or oil could not be confirmed.

After the field trial was completed the bearings were photographed and used grease samples were taken for analysis. The greases from bearings #9 through #12 were very fluid and easily poured from the bearings when disassembled. The bearings were then cleaned and photographed, then measured for wear and weight loss. The inner and outer seals were also examined. The bearings are identified in table 5 below.

Bearing number	Grease Source	Sample Source	Grease collected from bearing (g)
1	Lubrizol	Right Hand Front Axle Inner	12.08
2	Lubrizol	Right Hand Front Axle Outer	4.72
3	Lubrizol	Right Hand Middle Axle Inner	9.51
4	Lubrizol	Right Hand Middle Axle Outer	4.99

5	Lubrizol	Right Hand Rear Axle Inner	9.13
6	Lubrizol	Right Hand Rear Axle Outer	12.65
7	Commercial Grease	Left Hand Front Axle Inner	4.17
8	Commercial Grease	Left Hand Front Axle Outer	4.02
9	Commercial Grease	Left Hand Middle Axle Inner	0.93
10	Commercial Grease	Left Hand Middle Axle Outer	0.84
11	Commercial Grease	Left Hand Rear Axle Inner	2.61
12	Commercial Grease	Left Hand Rear Axle Outer	3.30

Table 5 Grease Sample Identities and weights recovered

Bearing number	Grease	Inner ring including cage and rollers (grams)	Outer ring/bearing cup (grams)	Total Assembled bearing (grams)
1	Lubrizol	-0.71	-0.34	-1.01
2	Lubrizol	-0.40	-0.33	-0.69
3	Lubrizol	-0.71	-0.48	-1.15
4	Lubrizol	-0.21	-0.34	-0.50
5	Lubrizol	-0.60	-0.45	-1.06
6	Lubrizol	-0.45	-0.37	-0.79
7	CG	-0.76	-0.33	-1.02
8	CG	-0.26	-0.13	-0.43
9	CG	-0.54	-0.43	-0.98
10	CG	-0.38	-0.39	-0.70
11	CG	-0.51	-0.47	-0.97
12	CG	-0.29	-0.35	-0.66

Table 6 Component and Bearing assembly weight changes

It was noted that the front axle outer bearings #2 and #8 are smaller in size and have lower dynamic load capacities than the more heavily loaded inner bearings #1 and #7 and that higher wear would be expected from the front two inner bearings. The weight losses from the bearingsmatch what was expected with generally higher values for all the inner bearings.

Bearing Number	Rating	Description of distress
1 Lubrizol	1.5	Mainly discolored with trace to light rotational marking, scoring and debris denting on the roller and cup raceway surfaces.
2 Lubrizol	1.5	Mainly discolored light to medium brown banded discoloration on roller and cuprace surfaces with trace rotational marking and scoring. Trace debris denting on the roller and cup raceway surfaces.

3 Lubrizol	1.5	Mainly discolored medium to light brown banded discoloration on roller and cup race surfaces with trace to light rotational marking and scoring. Trace debris denting on the roller and cup raceway surfaces.
4 Lubrizol	1	Mainly discolored banded discoloration on roller and cup race surfaces with traceto light rotational marking and scoring.
5 Lubrizol	1	Trace to light rotational marking, scoring and debris denting on roller and cuprace surfaces. Static roller witness marking on cup race surface.
6 Lubrizol	1	Trace rotational marking with trace discoloration on roller and cup race surfaces.
7 CG	2	Trace discoloration on roller and cup race surfaces with trace to light rotational marking and scoring. Trace to medium etching and trace to light debris dentingthroughout rollers.
8 CG	2.5	Trace to light rotational marking, scoring and debris denting on roller and cup race surfaces. Trace pitting and static roller witness marking on cup race surface.
9 CG	1	Trace rotational marking and scoring with trace to light debris denting on mainlydull burnished roller and cup race surfaces.
10 CG	1	Trace rotational marking and scoring with trace to light debris denting on mainlydull burnished roller and cup race surfaces.
11 CG	1	Trace rotational marking and scoring with trace to light debris denting on mainlybright burnished roller and cup race surfaces.
12 CG	1	Trace rotational marking and scoring with trace to light debris denting on mainlybright burnished roller and cup race surfaces.
Rating Guide 1 Contact pattern noticeable, no tangible wear / pitting or micropitting 2 Loaded surface clearly marked / slight wear/ pitting or micropitting 3 Significant wear / burr formation / corrosion / wear streaks / pitting or micropitting 4 Heavy wear / pitting or micropitting 5 Very heavy wear / pitting or micropitting		

Table 7 Rating of the rolling element and outer raceway cup surfaces

In order to determine the chemical elements present, small samples of the used grease were wetash digested in a microwave oven and then analysed by aqueous ICP spectroscopy. The results are reported in table 8 for the Lubrizol Grease samples and table 9 for the Commercial Grease samples.

Lubrizol grease (wt%)	New	01	02	03	04	05	06
Aluminum	<0.005	<0.005	0.014	<0.005	<0.005	0.021	<0.005
Calcium	<0.005	<0.005	0.022	0.015	0.016	0.041	0.016
Chromium	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Iron	0.010	0.184	0.438	0.164	0.118	0.455	0.174
Lithium	0.273	0.287	0.347	0.272	0.244	0.264	0.251

Phosphorus	0.077	0.084	0.075	0.081	0.097	0.081	0.070
Silicon	0.006	0.017	0.038	0.041	0.014	0.044	0.023
Sodium	0.009	<0.005	0.010	<0.005	<0.050	0.010	<0.005
Sulfur	1.11	1.07	1.00	1.37	1.68	1.23	1.42
Zinc	0.153	0.156	0.129	0.130	0.116	0.123	0.095

Table 8 - Aqueous ICP – Lubrizol grease samples

Commercial grease (wt%)	New	07	08	09	10	11	12
Aluminum	<0.005	<0.005	0.015	<0.005	<0.005	<0.005	<0.005
Calcium	0.017	0.026	0.042	0.205	0.161	<0.005	<0.005
Chromium	<0.005	<0.005	0.011	<0.005	<0.005	<0.005	<0.005
Iron	<0.005	0.187	0.992	0.386	0.225	0.257	0.684
Lithium	0.314	0.293	0.353	0.160	0.133	0.091	0.098
Phosphorus	0.162	0.165	0.182	0.205	0.187	0.142	0.148
Silicon	<0.005	0.013	0.034	0.088	0.050	0.115	0.036
Sodium	0.005	<0.005	<0.005	<0.005	<0.050	<0.050	<0.005
Sulfur	0.655	0.686	0.713	2.45	2.50	2.43	2.06
Zinc	0.175	0.157	0.193	<0.005	<0.005	<0.005	0.058

Table 9 - Aqueous ICP – Commercial grease samples

When comparing ICP results between bearing #9, #10, #11, #12 and the new grease, the used greases show abnormally higher levels of sulfur and almost no detectable zinc, the most likely scenario is that they suffered internal seal issues between the bearing and the differential. Axle gear oil with very high levels of sulfur contaminated the bearing grease. This means that the performance of the greases from bearing #7 and #8 can be directly compared with those from bearing #1 and #2.

No clear inferences can be drawn from the oil contaminated bearings #9, #10, #11, #12 and they cannot directly be compared with bearings #3, #4, #5, and #6.

Sampling grease from used bearings can only give a rough indication of how the grease performed, especially when the majority of the grease was not collected. In the case of bearings#2 and #8, the amount of ferrous debris present was much higher than in the case of bearings #1and #7 which had higher weight loss. This is almost certainly due to the inherent variability of the grease samples collected at the end of test.

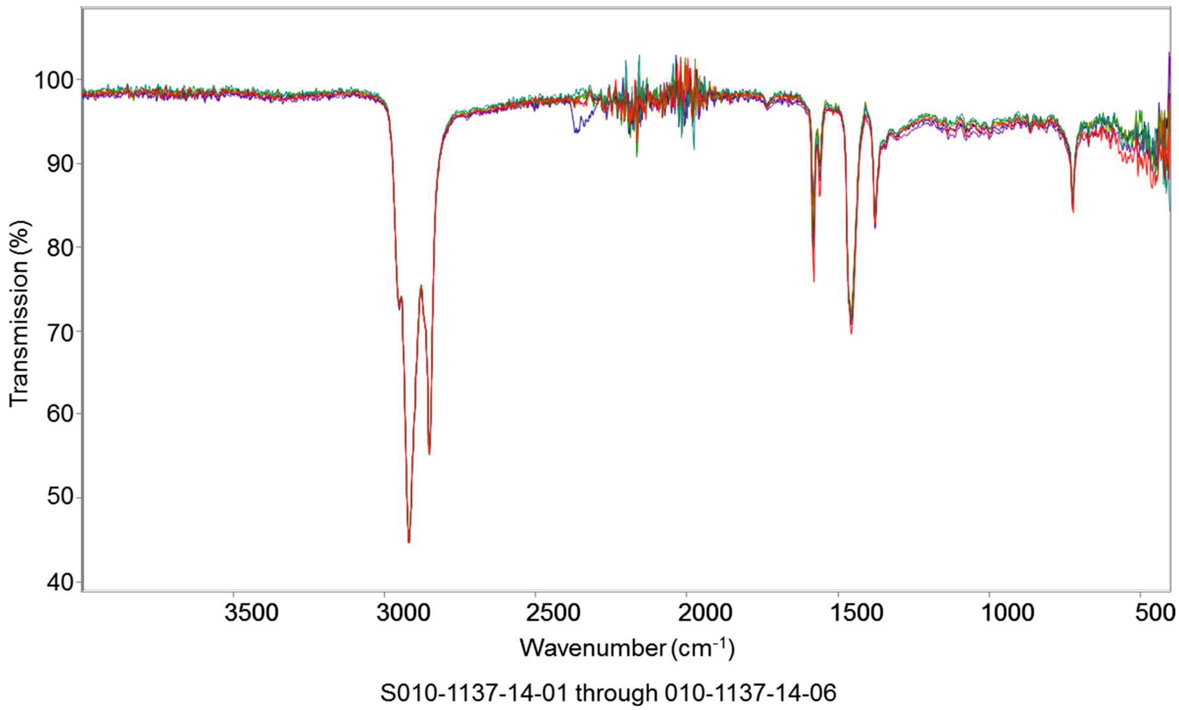


Figure 4 FTIR spectra used greases 01 through 06 (Lubrizol grease)

In Figure 4, the absence of a broad peak at 3500 cm^{-1} showed that there to be no significant water present in any of the Lubrizol used grease samples. This was similar for the greases samples from bearings #7 and #8 containing the commercial grease. Figure 5 showed that the post-trial Lubrizol Grease samples were very slightly different and the sample from bearing #2 contained a slightly higher level of soap than the sample from bearing #1. Figure 6 showed that the post-trial Commercial Grease samples were slightly different and the sample from bearing #8 contained a slightly higher level of soap than the sample from bearing #7.

Overall, the FTIR analysis of the grease samples did not show any significant differences between compared samples. The major confirmation from the Lubrizol samples and the Commercial greases from Bearings #7 and #8 showed an absence of water indicating that theouter seals were still intact.

Comparison of bearings #1 and #2 with #7 and #8 (front steering axle)

Red discoloration on the track surface of all the outer raceways from the front axle was observed after cleaning. The tracks were examined by optical microscopy which revealed that the discoloration was only in the contact areas of the tracks. It was much heavier on the Lubrizol greased bearings than on the commercial one. Sometimes red metal surface discoloration is as a result of fretting corrosion. This normally appears in patches next to contacting areas and almost never as a continuous film. In this instance, the discoloration is not fretting corrosion.

Some textbooks report that water contamination of greases can cause rusting which may appear red. However, in industry standardized rust tests such as ASTM D1743 or the Emcor test (ISO 11007), rusting appears as black discoloration on the raceways and other parts of the test bearings. No such discoloration was seen in the field-tested bearings. The FTIR spectral analysisof the used greases #1 to #6 suggested an absence of significant water contamination.

The discoloration is likely due to grease being squashed into the surface of the track whilst operating and forming the discolored red layer. This squashed down layer helps the grease to form thicker lubricating films which can add to surface protection.
No pitting was seen on the surface of either cup raceway from bearings #1 and #2. However, pitting was seen on the cup surface of both of the raceways of bearings #7 and #8 which used the commercial Grease. The absence of pitting from the Lubrizol greased bearings indicates superior surface protection and lubrication performance.

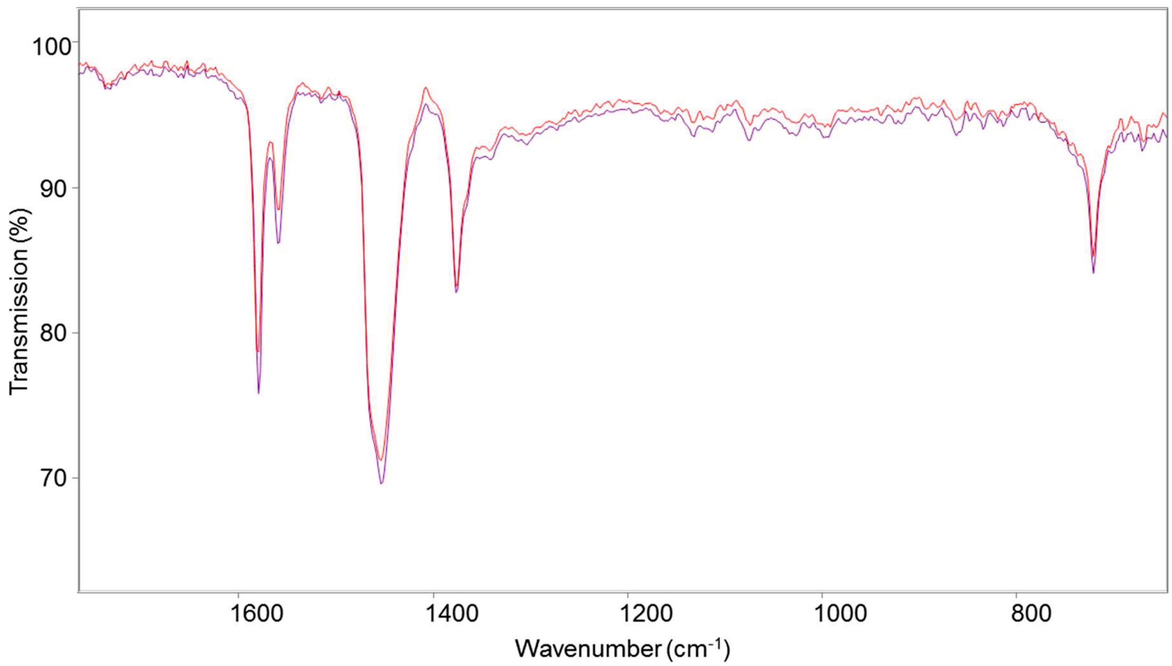


Figure 5. FTIR spectra used greases 01 and 02 (Lubrizol Grease)

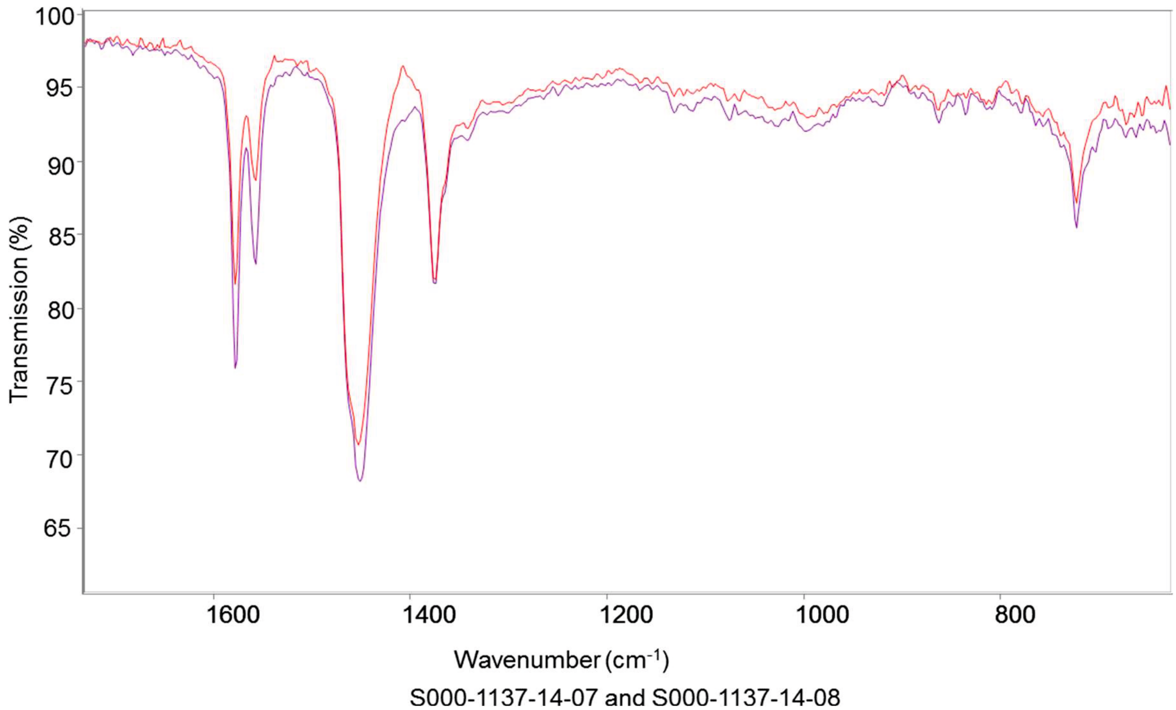


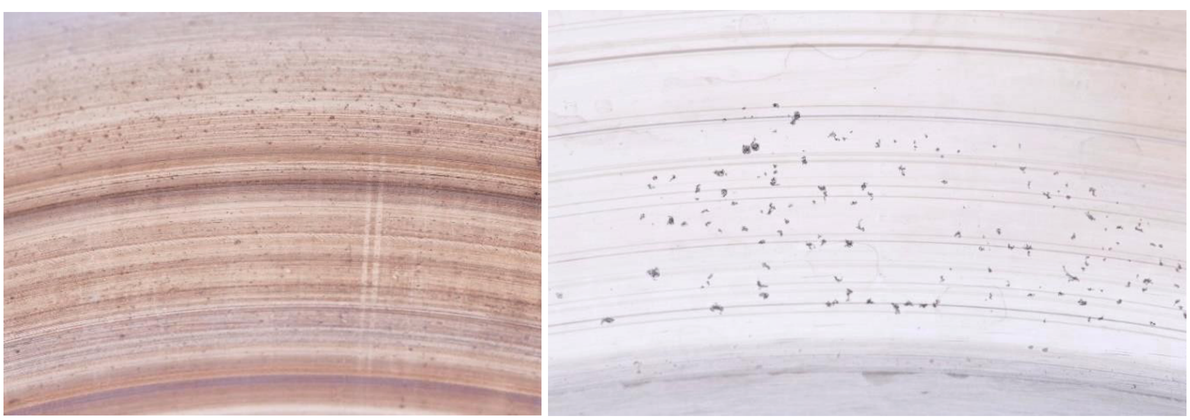
Figure 6 FTIR spectra used greases 07 and 08 (Commercial Grease)

Bearing	Cone and rolling elements	Cup surfaces	notes
#1 Lubrizol grease			Reddish discoloration in rolling area only.
#2 Lubrizol grease			Reddish discoloration in rolling area only. Two rollers have visible pitted areas

#7 Commerci algrease			Light reddish discoloration in rolling area only. Two rollers have visible pitted areas as does the cup surface
#8 Commerci algrease			Light reddish discoloration in rolling area only. Three rollers have visible pitted areas as does the Cup surface

Table 10 – Pictures of bearings #1, #2, #7 and #8 after grease removal and cleaning

To compare the raceway surface distress / discoloration better, enlarged pictures were taken of raceways #2 (Lubrizol grease) and #8 (commercial grease).



Picture 1a and 1b – Re-analysis of bearing #2 (left) and #7 (right)

Looking at picture 1a no surface pitting was found on the raceway track of bearing #2 lubricated with the Lubrizol grease but significant surface pitting was found on the surface (picture 1b) of the raceway track of bearing #7 Lubricated with the commercial grease.
In order to further verify that the Lubrizol grease had performed well, the other 4 bearingslubricated with it were further examined, photographed and rated.
As can be seen form photographs in table 11, no pitting was found on the surfaces of any of the 4 raceways examined that were lubricated with the Lubrizol grease. Because of the contamination of the Commercial greases with axle oil, no comparisons can be made between the two greases.

Bearing	Cone and rolling elements	Cup surfaces	notes
#3 Lubrizol grease			Reddish discoloration in rolling area only. No roller or cup surface pitting
#4 Lubrizol grease			Reddish discoloration in rolling area only. No roller or cup surface pitting
#5 Lubrizol grease			Reddish discoloration in rolling area only. No roller or cup surface pitting
#6 Lubrizol grease			Reddish discoloration in rolling area only. No roller or cup surface pitting

Table 11 – cleaned up pictures of bearings #3, #4, #5 and #6

Summary

The paper covers the execution and analysis of a field trial carried out in India on wheel bearings fitted to a heavy commercial truck which between 2014 and 2016 ran for approximately 1,15,000 km. The failure of the internal differential seals on the left-hand side rear axles meant that only the front wheel bearings could be properly compared.

Conclusions

The bearings from the front steer axle, the two bearings lubricated with the Lubrizol grease containing the long-life grease additive package and functionalized polymer showed much less damage and surface distress than the two bearings lubricated the commercial long-life grease. The four rear bearings on the right-hand side of the vehicle lubricated with Lubrizol grease alsoshowed no visible signs of surface distress, indicating good performance of the Lubrizol grease.

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The authors would like to acknowledge the support of the following:
Lubrizol field testing teams in both England and India, led by Kieron Donnelly Dr Chris Hsu for making the Lubrizol test grease
The chemists and technicians of Lubrizol Blend test services (BTS) for carrying out the testing on the new greases and chemical analysis of the recovered grease samples.

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Complex Issue of Dropping Point Enhancement in Grease

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Abstract

The steady increase in the percentage of complex greases in NLGI's survey of global grease production is a reflection of the demand for lubricants that will last longer in more severe, higher temperature applications. It is also a clear indicator that future research and development work will be of great value in this area of lubrication. The surge in demand for higher dropping point greases has brought additional interest in alternative methods of producing them that can reduce cycle times and, potentially, overall production costs. A study was undertaken to investigate different borate chemistries used to raise the dropping point of lithium greases to the level usually associated with complex greases. Points of focus include a design of experiment to study the impact of common factors on the effectiveness in raising dropping point, as well as a closer look at the impact of dropping point apparatus, blending temperature and correlation to effects as measured by high temperature rheology.

Introduction

According to the NLGI Annual Production Survey, lithium complex base grease production has increased by almost 50% since 2006 and has followed a steady upward trend as demands on equipment, and the greases needed to lubricate it, have grown. Last year, the share of lithium complex grease as a portion of total global production was reported at nearly 20%, or over 488 million pounds. [1]

The traditional method of making lithium complex greases typically involves the use of organic acids (such as azeleic or sebacic acid) during the soap production process which can extend the cycle time and add complexity to the production process. The more recent use of amine borates, borate esters and even boronated dispersants has offered a simplified process that has the potential to reduce cycle time and production complexity.

Background

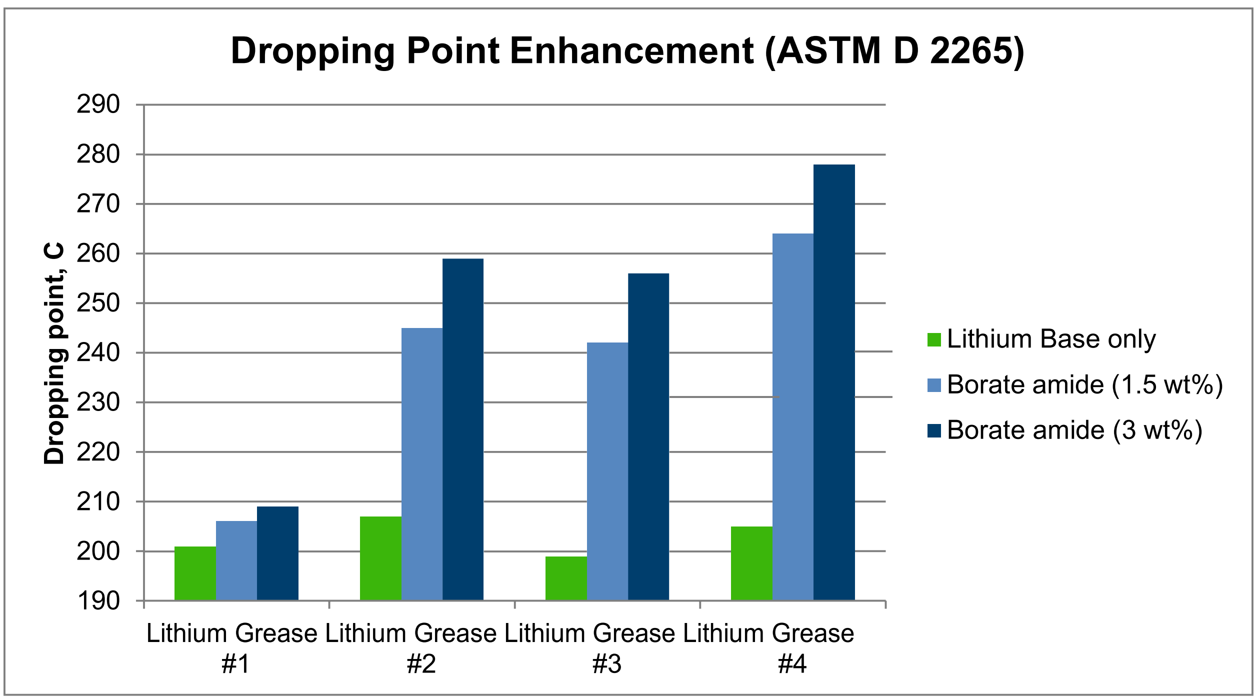
Recent work has looked at various aspects of the use of borated componentry including research by Deshmukh which focused on the use of borate esters in greases made from hydrogenated castor oil [2], and work done by Lorimor comparing the conventional complexation process using azelaic acid with a post-treatment using a boron ester. [3]

Additionally, Shiller examined the effect of some boron-containing chemistry on fretting wear using the Fafnir fretting rig (with the standard test method ASTM D 4170) and the Falex Block-on-Ring test [4], while Yao examined a synergistic interaction between borate ester and zinc dialkyl dithiocarbamate that appears to provide antiwear improvement. [5]

One of the main differentiation points between simple lithium greases and lithium complex greases is the higher dropping points measured in the complexes. Several papers have investigated the high temperature behavior of greases by a variety of methods including high temperature bearing rig tests, PDSC, high temperature rheology and dropping point. [6] [7] [8] [9] [10] [11] [12] And Coe looked at applications for grease and how the claims for high temperature performance related to dropping point, as well as to a variety of high temperature bench tests.[13]

A large variance in measured dropping points when base greases were treated with the same borate component has been observed in the authors' lab during work with a variety of customer projects. The current investigation was undertaken to further understand the interactions of different types of borate componentry with simple lithium greases made under different conditions and the reason for the large variations seen in dropping point. An example of the variation in response is seen in Table 1.

Table 1 - Variable response to borate amide in different base greases



Furthermore, some of the literature points to a synergism seen when the borate chemistry is added in the presence of zinc dialkyl dithiophosphate (ZDDP) and this interaction was included in the study.

Historically, greases made from hydrogenated castor oil (HCO) don't appear to respond well to the use of borate componentry to raise dropping point [2]. The authors hypothesized that this is due to the preferential reaction of the borate component with glycerin which is present in these greases because it is generated as a by-product of the soap process when HCO is used (see Figures 1 and 2). This means that there is very little of the boroxine componentry left to be able to crosslink (and stabilize) the lithium stearate.

A designed experiment (DOE) was used to look at the effects of three different borate components in greases along with various levels of glycerin, alkalinity, and water content. Additionally, the presence (or absence) of ZDDP was included as a variable in the study.

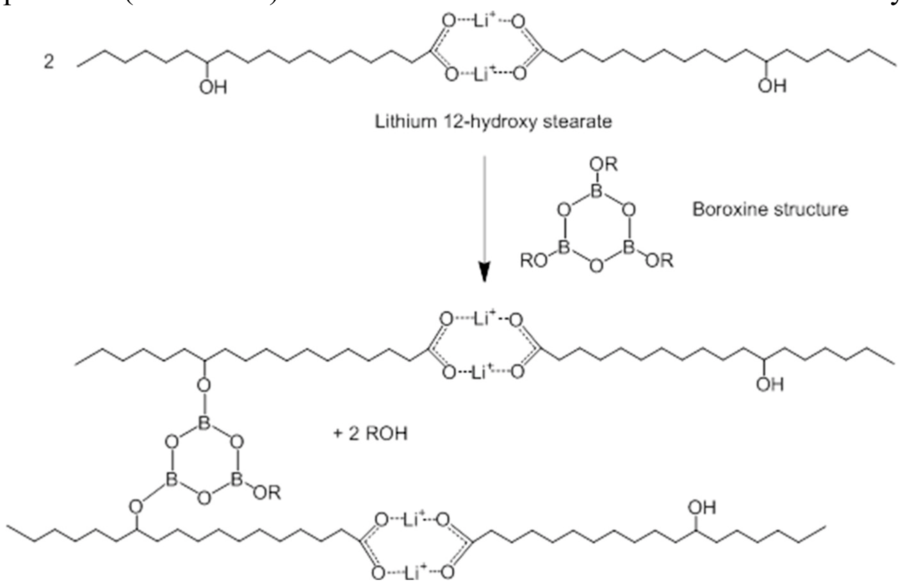


Figure 1 - Proposed mechanism for lithium stearate crosslinking through boroxine structure

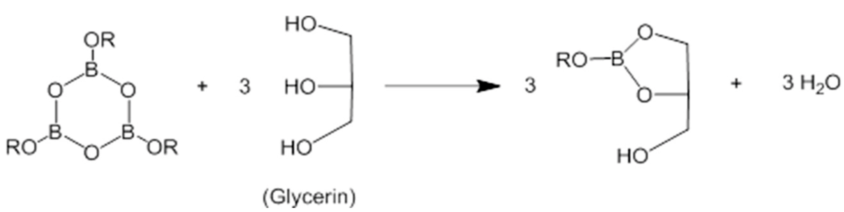


Figure 2 - Competing reaction with glycerin

Experiment

Test Methods

ASTM D2265 "Standard Test Method for Dropping Point of Lubricating Grease Over Wide Temperature Range" *[14]*

This method determines a numerical value for a grease composition representing the temperature atwhich the first drop of material falls from the test cup and reaches the bottom of the test tube. The temperature is measured using a thermometer placed near the grease sample inside a glass tube placed in an aluminum block at a preset constant temperature. A modification was used for this workin that the block temperature used for all determinations was 288 °C. This was done to ensure that the heating rate was the same for each sample. However, the dropping point was also determined using different block temperatures as described in D2265 and no statistical difference was seen between the determinations.

Base Greases

As the alkalinity of the base grease is known to affect various aspects of additive performance [15], two simple lithium base greases were made in the lab. One was targeted to be slightly basic while the other was targeted to be very basic. Both were made using 12-hydroxystearate acid (12-HSA) as the fatty acid with sufficient lithium hydroxide (LiOH) to meet the targeted alkalinity for each. Both greases were milled and diluted with base oil that had a kinematic viscosity at 40°C of 165 cSt (a mixture of AC 600N [68%] and AC bright stock [32%]) to obtain greases that were slightly harder than an NLGI #2 grade base which allowed for some softening due to addition of various componentry in the study. See Table 2 for descriptive data for these base greases.

Table 2 - Base grease measured characteristics

		Low LiOH	High LiOH
Measured free LiOH (wt%)	ASTM D128	0.014	0.093
Thickener content (wt%)	Calculated	12.04	12.01
Base Oil 40KV (cSt)	Calculated	165.8	165.5
Penetration (worked, 60x), mm-1	ASTM D1403	254	257
Dropping Point (°C)	ASTM D2266	205	211

Both greases were then dried at 80 °C in a vacuum oven for 24 hours.
Each base grease was then split into two equal parts with one part being treated with 500 ppm DI water (mixed in slowly by hand and with Hobart mixer) while the second part was kept "dry". This gave four greases (Base A through D, as shown in Table 3) to be used in the designed experiment. The dropping point of each base grease was measured as a baseline.

Grease Thickener	LiOH	Water	Dropping Point, °C
Base A	Low	Dry	201
Base B	High	Dry	194
Base C	Low	Wet	197
Base D	High	Wet	194

Table 3 - Base greases for DOE 1

<u>Additive components/levels</u>
As part of the designed experiment, a high and low level for each component was needed.
The level of glycerin added was calculated from the amount of glycerin that would have theoretically been produced as a byproduct if the laboratory-produced grease had been made with HCO instead of 12-HSA. This level was determined to be 1.2 wt%. The low level used waszero with a midpoint level of 0.6 wt%.
The specific ZDDP component used has a mixed-chain length (C4/C5/C8) and was made from a primary alcohol. The level of ZDDP used was based on that which was seen to be effective in screening work with similar greases and the borate components of interest. The high level was set at 1.13 wt%, with a low level of zero and a midpoint level of 0.56 wt%.

Table 6 - Design of Experiment 1

The level of borate used was determined empirically (see Table 4). Since the goal of the study was to be able to observe both positive and negative effects, it was decided to use a level that gave a "mid-range" result that would allow for observation of improvement or deterioration. This level (1.5 wt% of borate amide) gave a boron concentration of 300 ppm and it was decided to use this same level for each of the boronated components.

Table 4 - Borate level determination

Run	A	B	C	D
Base A (low/wet)	97.9	97.4	96.9	95.9
ZDDP	1.13	1.13	1.13	1.13
Borate Amide (BA)	**1**	**1.5**	**2**	**3**
	100	100	100	100
Dropping Point (ASTM D 2265)	**226**	**236**	**249**	**281**

The types of borates used were borate amide (BA), borated dispersant (BD) and borated/phosphorylated dispersant (BPD). The components and the treat rates used to achieve a 300 ppm boron level are shown in Table 5.

Table 5 - Boronated components

Borate type	Treat rate (wt%)	Amt in grease (ppm)
Borate amide (BA)	**1.5**	**300**
Borated dispersant (BD)	**2.3**	**300**
Borated/phosphorylated dispersant (BPD)	**3.0**	**300**

<u>Design of Experiment</u>

A statistically designed experiment was set up consisting of 24 runs and 9 midpoints (3 for each of the different borate components). See Table 6 for the entire design. It was determined that this design would allow adequate evaluation of repeatability to be able to see any significant effects due to the different variables. As described above, the dropping points were determined for the entire set using a block temperature of 288 °C (although statistical analysis of determinations run at higher and lower block temperatures showed no differences).

Table 6 - Design of Experiment 2

Run	1	2	3	4	5	6	8	7	9	10	11	12	13	14	15	16
LiOH	H	L	L	L	L	H	H	L	L	H	L	H	H	H	H	L
Glycerin	H	L	L	L	H	H	L	L	H	H	H	L	L	L	L	H
Water	L	L	L	H	H	H	L	L	L	L	L	H	L	H	H	L
ZDDP	L	H	H	L	L	L	H	L	L	H	H	H	L	L	H	L
Borates	B	A	C	C	B	A	B	B	C	C	B	C	A	B	A	A

Run	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33
LiOH	H	L	H	L	H	H	L	L	M	M	M	M	M	M	M	M	M
Glycerin	H	L	H	H	H	L	H	L	M	M	M	M	M	M	M	M	M
Water	H	H	H	H	L	L	H	H	M	M	M	M	M	M	M	M	M
ZDDP	L	H	H	H	H	L	H	L	M	M	M	M	M	M	M	M	M
Borates	C	B	B	A	A	C	C	A	A	A	A	B	B	B	C	C	C

Analysis of the data resulted in a good model ($p < 0.0001$) with the only factor of high significance(i.e. with $p<0.05$) being glycerin ($p<0.0001$). The common interpretation of this data is that the likelihood of the difference seen being due to random error is less than 0.01%. The leverage plot (see Figure 3) shows that, as hypothesized, higher levels of glycerin give lower dropping points while higher dropping points are measured in the absence of glycerin.

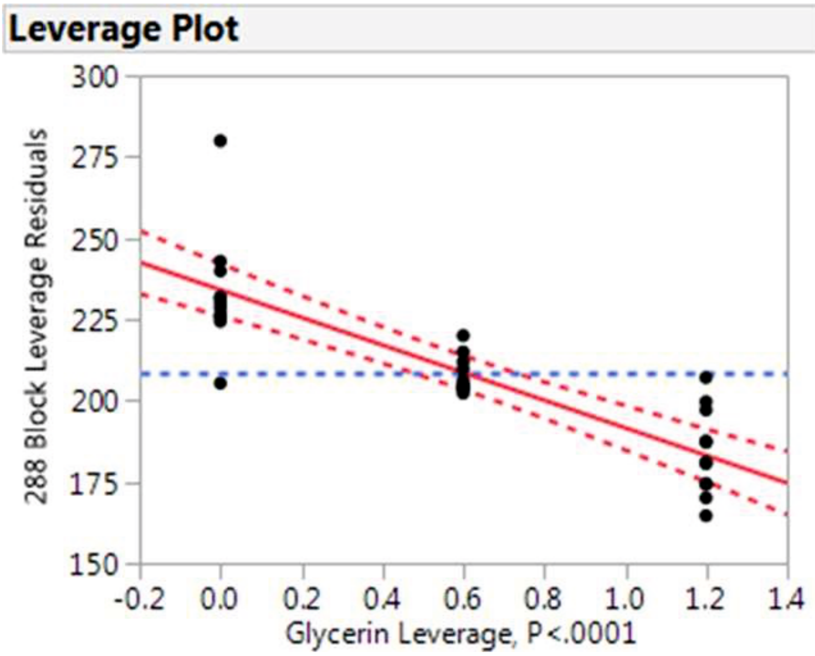


Figure 3 - Leverage plot for glycerin

There were also some indications that two of the borate species (BPD and BD) were significant although with a lower degree of probability ($0.05<p<0.10$). In both cases, it appears that higher levels of the borates can produce greases with higher dropping points.

Overall, the results of this first DOE did not appear to show the significance of the borate chemistry that was expected. It was thought that this might be due to using lower treat rates than are often used in commercial formulations. For this reason, the design was augmented with eight additional runs using twice the initial concentration of BA taking the total level of boron up to 600 ppm in each sample. The design was augmented in such a way as to keep it balanced allowing for good statistical analysis of the resulting data.

As can clearly be seen in Figure 4, when glycerin is not present the concentration of BA has an impact on dropping point whereas when glycerin is present, the level of BA present has no impact on dropping point.

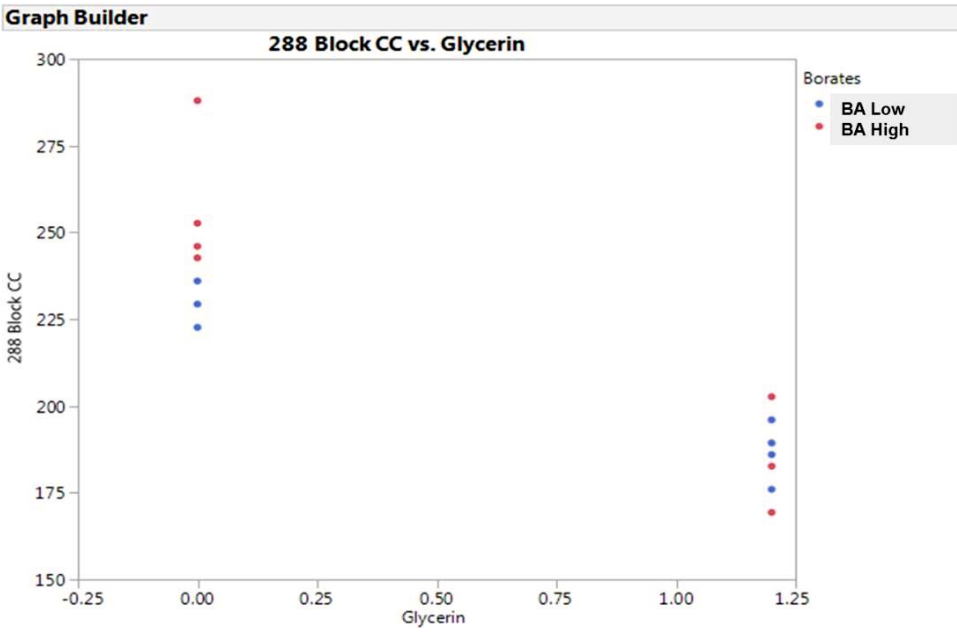


Figure 4 - Effect of glycerin in presence of borate

Due to the observed impact of the glycerin, the data without glycerin was modeled separately and while none of the individual components appeared to be significant, a three-way interaction between LiOH level, water content and ZDDP was observed. It is thought that the borate level may have been too low to show up as significant (as seen by the impact of BA at higher levels in the augmented design).

The data was then modeled including the augmented runs (in which BA was doubled for eight additional runs) and this model shows that both LiOH level (see Figure 5) and ZDDP (see Figure 6) have a positive impact on dropping point at the higher level of BA. This may confirm the original observation that the treat rates of BD and BPD were too low to be significant in the original model.

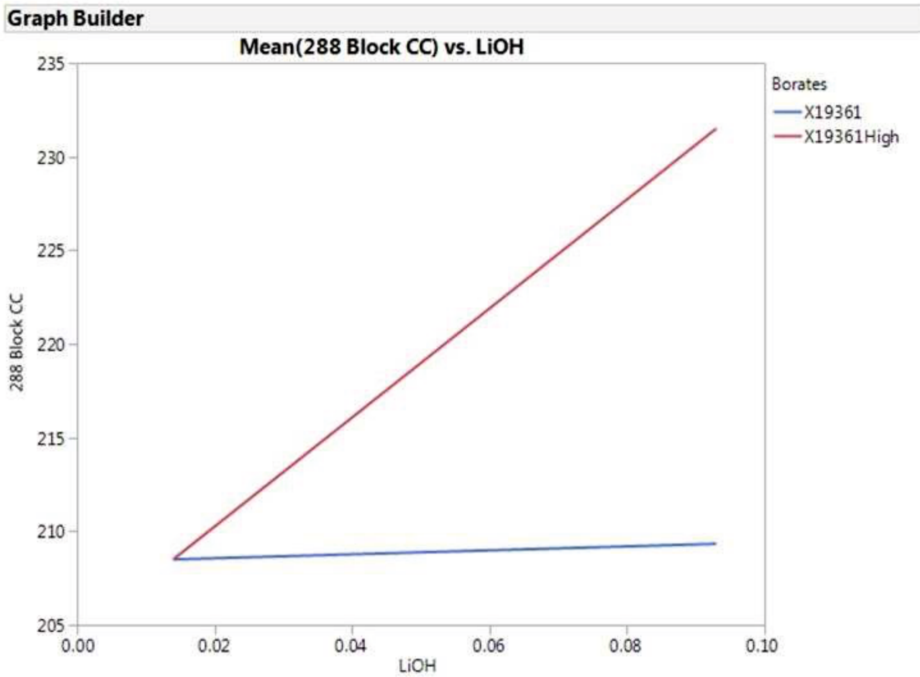


Figure 5 - Impact of LiOH at high BA level

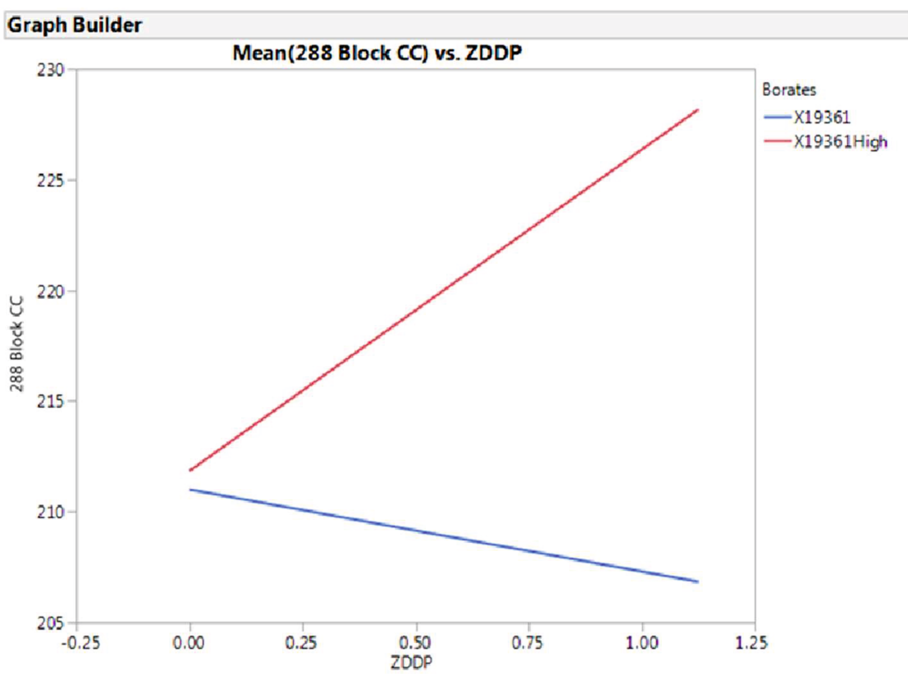


Figure 6 - Impact of ZDDP at high BA level

The overall model for the data at the high borate level (see Table 7) shows that LiOH content hasa positive impact on dropping point, while the impact of glycerin was negative. ZDDP was shownto be somewhat significant as well ($p \cong 0.1$) with a potentially positive impact on dropping point.

Analysis of Variance				
Source	DF	Sum of Squares	Mean Square	F Ratio
Model	4	12785.333	3196.33	32.7394
Error	3	292.889	97.63	Prob > F
C. Total	7	13078.222		0.0083*

Parameter Estimates				
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	231.25738	8.438145	27.41	0.0001*
LiOH	291.13924	88.44	3.29	0.0460*
Glycerin	-62.22222	5.8223	-10.69	0.0018*
Water	0.0093333	0.013974	0.67	0.5520
ZDDP	14.518519	6.210453	2.34	0.1014

Table 7 - Model for high borate level 1

Summary and Conclusions

In each of the models that were examined, glycerin was shown to be statistically significant in having a negative impact on dropping point. This would appear to support the hypotheses that glycerin is reacting with the borate species thus preventing it from helping to complex the grease and provide high temperature stability. This is further supported by the data that shows BA to have a significant impact on raising dropping point in the absence of glycerin.

The treat rate of the borates used was also shown to be important with the initial treat of 300 ppm boron content potentially being too low to show significance especially in the presence of higher levels of LiOH and ZDDP.

The three-way interaction seen between LiOH, water and ZDDP (in the absence of glycerin) was an interesting finding showing that high levels of each could have a positive impact on the ability of the borate to raise dropping point. One hypothesis to explain the observed interaction is that the excess LiOH is reacting with ZDDP to allow formation of a zinc stearate which could allow more efficient complexation by the borate chemistry. This process could be facilitated by the presence of excess water. Obviously, further study would be needed to better understand this interaction and to provide further evidence for its mechanism.

Additional Experiments

Aging of Dropping Point Cups

During the course of this work, several observations led to additional experimentation. The first observations related to the age of the brass cups used for dropping point determinations according to ASTM D2265. Though not well documented, there was some experience by laboratory personnel that pointed to different results being obtained with “new” cups as compared to “old” cups.

The ASTM method specifies:

"8.1 Thoroughly clean the cup, cup support, and test tube with mineral spirits. (Warning—Flammable. Vapor harmful.)

8.2 Use only cups that are clean and free of any residue. When the interior plating of the cup shows indications of wear, discard." [14]

A quick study was carried out doing triplicate runs of greases containing three different borates. One set of the triplicate runs was carried out with cups that had been previously used (although the age or number of runs for each cup was not known) and the second set of triplicate runs was carried out using a new cup for each determination. The results (see Table 8) show that the older cups give a higher result for seven out of the nine determinations while using the new cup resulted in a higher value only once.

Table 8 - Comparison of new and old dropping point cups

Borate	A	A	A	B	B	B	C	C	C
New	183	206	209	193	219	203	199	196	206
"Old"	203	213	209	206	206	209	206	203	209

To further study the possible effect of aging the cup on the determined dropping point, a second study was conducted in which a grease which had shown a moderately high dropping point wasrun repeatedly using the same cup which was new at the start of the study (see Figure 7).
There is an apparent increase in the obtained results that plateaus after the third run but which appears to cause an increase of about 15°C in the dropping point result. Two additional runs carried out with brand new cups appear to confirm this difference between new and used cups.

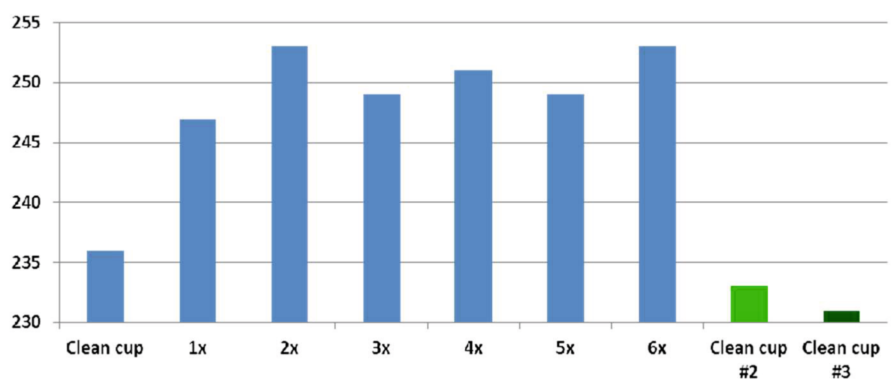


Figure 7 - Effect of aging cup on dropping point

<u>Heat/Method of Borate Incorporation</u>

A separate study was being conducted with the borate amide (BA) at 1.0 wt% and several inconsistent results were obtained ranging from 230 °C to 293 °C (see Table 9). A short experiment was undertaken to look at the effect of heating and blend order of the components used. Standard mixing had been at 60 °C in a centrifugal mixer and this was repeated at 104 °C on the original samples and a reblend. A high dropping point was obtained (No Drop) using

the original temperature of 60 °C but the higher temperature seemed to have no effect. The order of addition also seemed to show no effect. The borate was added first and homogenizedwithin the grease at 60 °C then the additional components were added at 104 °C to observe whether there was some effect of using higher heating to carry out further complexation of the grease. These components included ZDDP which can show synergistic behavior with BA as seen in the first study above.

Figure 4
Table 9 – Effect of heat and mixing on borate incorporation

Mixing	Heating	BA (1.0 wt%)	BA (1.5 wt%)
Centrifugal mixing - Original	60°C	293/243/ 231/230	311/302
Centrifugal mixing - Original	Reheated @ 60°C	225	311
Centrifugal mixing - Original	Reheated @ 104°C	242	No Drop
Centrifugal mixing - Reblend	60°C,	No Drop	312
Centrifugal mixing - Reblend	104°C	239	315
Centrifugal mixing – only Borate Amide	60°C,	229	249
Centrifugal mixing – remaining additives	104°C	232	No Drop

However, when the conditions were all repeated using a higher treat rate of the BA component (1.5 wt%), reproducibly high results were obtained under each of the conditions except for the case where the borate amide was added before ZDDP was present in the mixture (which was tobe expected given the synergistic behavior previously noted with ZDDP).

Based on these results it would appear that once there is a sufficient amount of borate in the grease to carry out the complexation completely, the heat and order of addition have little impact. When there is a lower level of borate in the grease, there is higher variability in the results obtained. This led to a closer examination of the actual determination of dropping point and observation of how the drop is formed in the apparatus.

Effect at High Temperature

It had been observed that in some determinations, a drop forms and is can be seen to continueto grow larger but before it drops (which would end the analysis according to D2265), it begins to shrink and appears to harden as the temperature in the cup continues to rise. This action is illustrated in a series of pictures (see Figure 8). This behavior would appear to indicate that some kind of physical and/or chemical change is occurring in the grease as the temperature of the cup (and grease) rises during the analysis.

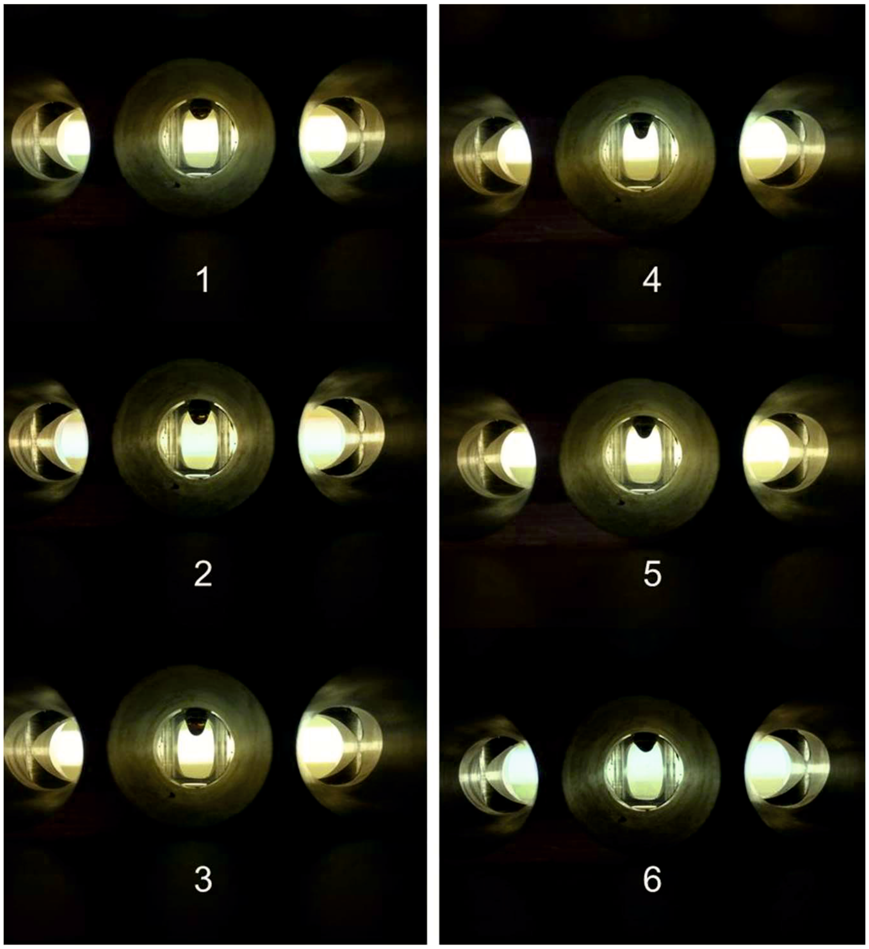


Figure 8 - Drop formation in apparatus

To further examine this aspect, a series of high temperature rheology determinations were carried out on an Anton-Paar oscillatory rheometer (MCR301). The grease samples were compressed between a temperature-controlled Peltier bottom plate and a parallel top plate. A hood which contains a temperature-controlled Peltier device was placed over the test grease and bottom plate. A temperature sweep (from 40 °C to 200 °C) was performed on the sample greases while maintaining a low strain.

The "Tan Delta" of the grease is a ratio of the loss modulus (G") and the storage modulus (G'). Higher values of this ratio indicate more liquid-like behavior in a grease and a ratio above a value of 1 (also known as the "Flow Point") indicates a change from solid to liquid behavior similar to what might be expected at the dropping point of a grease. In Figure 9, this ratio is plotted and shows the effect of raising temperature in a manner similar to that which the grease is exposed to in a dropping point cup.

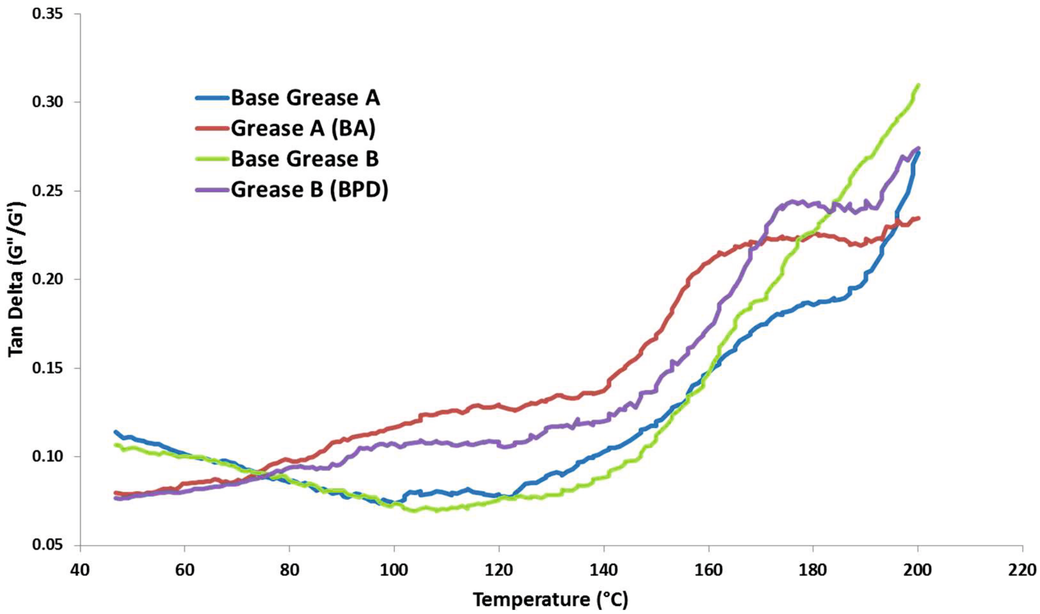


Figure 9- Rheology of grease - temperature sweeps

In this small study, Grease A is a simple lithium grease treated with the borate amide (BA) at 1.5 wt%, while Grease B is a different simple lithium grease treated with the boronated, phosphorylated dispersant (BPD) at 3.0 wt%. These plots show the behavior of the different greases in the temperature range (between 140 °C and 200 °C) at which the drop formations were observed in Figure 8 above. The plots show the relatively smooth transition from more solid to more liquid behavior of both Base Grease A and Base Grease B, whereas the additized greasesshow a clear "plateau" effect beginning at around 160 °C to 170 °C which correlates reasonably well with the apparent reversal of the drop formation and observed "solidification" of the drop in the dropping point apparatus. Both of these greases had dropping points of about 300 °C but the rheometer was not capable of going beyond 200 °C with the heating element that it was equipped with.

A rheometer with higher heating capacity was obtained and additional runs were carried out with similar high dropping point greases which were also complexed using a combination of ZDDP and borate componentry. These greases were run using the same temperature sweep programbut were able to be heated up to 300 °C by the end of the program. These plots are shown in Figure 10 along with a plot of a simple lithium base grease.

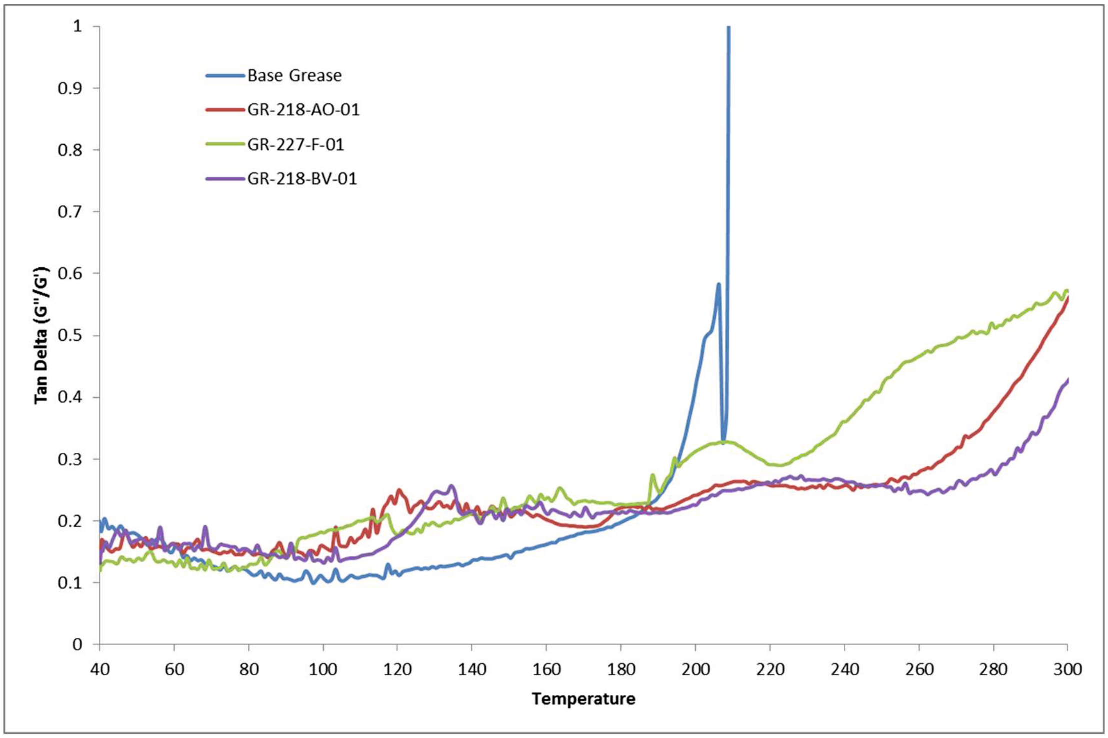


Figure 10 - Rheology of grease - high temperature sweeps

Here it can clearly be seen that the base grease reaches a Tan Delta of >1 (indicative of more liquid-like behavior) at just over 200 °C which correlates very closely with its dropping point.

The other three additized greases were all measured to have dropping points in the 300 °C range and the same "plateau" behavior is seen between 120 °C and 200 °C before the Tan Delta starts to increase again between 220 °C and 300 °C. This seems to correlate well with the plots shown in Figure 9, as well as with observations of the dropping point apparatus as illustrated in Figure 8. This also appears to provide more evidence that a physical change is occurring in these greases as they are being heated which may be affecting the ability of thesesamples to allow a drop of oil to be released during the test. It's possible that this is a chemical reaction involving the borate components. Whether or not this is reflective of what happens in high temperature applications or even in high temperature bearing rig tests is unknown and needs further study.

In summary, a designed experiment showed a large negative impact of glycerin on the ability of borates to increase the dropping point of lithium greases which provides a convincing explanation for the difficulty seen in using borates to raise dropping points in lithium greases made with hydrogenated castor oil. Additionally, the designed experiment showed the positive impact of higher levels of LiOH, ZDDP and perhaps water in raising dropping points. A possibleexplanation was proposed but would need further experimentation to provide further evidence.

Although heating to 140 °C during the mixing process didn't seem to effect results when there was an excess of borate available to react, there were inconsistent results at lower levels of borate which may be linked to the bimodal behavior seen with some greases (drop vs no drop in consecutive runs).

Additional experimentation and observations raised questions about the effect of aging on a dropping point cup with higher values being obtained with aged cups. High temperature rheometer scans showed evidence of physical changes within the grease which may correlateto observations showing drops that form but then harden rather than falling.
Additional study will focus on:

- closer investigation of the surface of aged cups and how that might be linked to the higher dropping points observed
- high temperature rheology and observation of behavior of "standard" complex greases as compared to those treated with borate chemistry
- the correlation between grease behavior observed in the dropping point apparatus compared to high temperature bearing rigs or other high temperature applications
- additional benefits of borate chemistry to other properties of a formulated grease including friction, wear and corrosion protection

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Exploratory Studies on Borate Esters as Drop Point Enhancers

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Abstract:

Borate esters are known for enhancing drop point in lubricating greases containing lithium 12-hydroxystearic acid based soap. Several vendors are supplying packages of drop point enhancers with different compositions and formulations of borate esters. Even though this technology is not very new, selecting suitable drop enhancer is not clear and no/few grease manufacturers using them in their formulations due to lack of complete study. There are only few studies showing their effectiveness as added complexing agents at the end of process, while storage stability and effect on other properties in comparison to complex greases with boric acid and other complexing acids is lacking.

The performance of these additives is thickener dependent and the borate esters liberate alcohol which either remain in grease or evaporate out. In this paper we have discussed the evaluation of different drop point enhancing borate ester packages and development of lab prepared borate ester/adduct to enhance drop point of lithium 12-hydroxysrearic acid greases with respect to process and physicochemical properties.

Key Words: Lubricating Grease, Lithium Soap, Borate Ester, Dropping Point

Introduction

Simple lithium 12-hydroxy stearate thickened greases having drop point 190-210 °C are been widely used for moderate temperatures.[1] The production and use of lithium complex steadily increasing and reported around 20% in NLGI grease production survey 2015. In high-temperature applications, complex greases to be used where, conventional complexing agent is/are usually a di-acid such as azelaic or sebacic acid with the 12-hydroxystearic acid.[2,3] But, the complexing acids are comparatively expensive and/or multi step and high temperature process to get effective drop point. These complexes generally need high thickener content and corresponding lithium monohydrate used to neutralize dibasic acids will increase the cost of the final grease. Multi fold raise in lithium price is driving grease manufactures to look for cost cutting in all the aspects in grease while maintaining the properties. Cheaper complexing agents such as acetic acid, benzoic acid does not give good high temperature greases. Boric acid is one cheaper and good complexing acid which proved to result in complex grease with high drop point in lithium 12-hydroxy stearate thickened greases.[4] The borate complexing can be done two ways; the first one is addition of boric acid or lithium borate at initial stages, which requires high temperature process of 220 °C to result in complex grease with high drop point.[5] The other way is addition of activated ester of boric acid at the end/finished grease which requires low temperature process.[6]

In recent past several reports published on lithium complex grease with borate esters including very recent Kaperick which focused on complex issues of dropping point enhancement.[7] Research articles by Deshmukh and Lorimor have shown borate complexation in lithium greases with castor oil and 12-hydroxy stearic acid respectively.[8,9]

In this paper, we compare methods of incorporating borate complexation in lithium 12-hydroxystearate grease in both ways, as boric acid, lithium borate and borate ester. The resulting greases physico-chemical characteristics such as oil bleeding, dropping points, storage stability, oxidation stability, wheel bearing leakage, water washout and rust preventive properties were evaluated. We also discuss suitability and adoptability of the methods and effect of stabilizing or activating ester by products. Several vendors are supplying packages of drop point enhancers with different compositions and formulations of borate esters. We have evaluated three drop point enhancer packages with respect to effect of alcohol used to make borate ester, their addition temperature and high temperature properties of additized grease. In order to reduce cost and make our own additive we have synthesized borate esters and evaluated against commercial borate esters.

Experimental

In the present study, first we have investigated ways of making borate complex using different form of boron source in lithium 12-hydroxy stearate grease by boric acid, lithium borate and borate ester (activated ester). The first lithium complex grease was prepared using 12-hydroxystearic acid, boric acid and stabilizing agent alcohol. The second lithium complex grease was prepared using 12-hydroxystearic acid, $Li_2B_4O_7$. The third grease was complexed with borated ester.

In second study we have investigated different commercial available borate esters along with our lab made borate esters. In this study we have studies suitability of borate ester with and without ZDDP and effect of alcohol used for making borate ester. Three greases were made with 3 different commercial drop point enhancer packages and one lab made borate ester was evaluated in comparison with other packages. The grease without borate ester is considered as base grease. The base oil used is mineral VG 150 grade blend. Other anti oxidant was added in the base grease.

Grease Manufacturing

Gr-1: Lithium complex grease made by addition of boric acid and stabilizing alcohol in initial stage of along with lithium hydroxide monohydrate and 12-HAS and used closed kettle process where final temperature of manufacturing process is 220 °C.

Gr-2: Lithium complex grease made by addition of $Li_2B_4O_7$ at initial stage along with lithium hydroxide monohydrate and 12-HAS and used closed kettle process where final temperature of manufacturing process is 220 °C.

Gr-3: Simple Lithium grease made by lithium hydroxide monohydrate and 12-HAS in closed kettle process where final temperature of manufacturing process is 200 °C. This is grease is considered as base grease used as reference and for borate ester evaluation.

Lab made Borate Ester (LBE): After screening several alcohols such as linear, branched, primary, secondary, aromatic alcohols and diols etc for synthesizing borate esters we have selected one branched alcohol is more suitable. In the present study we have used borate ester synthesized by reaction of boric acid with branched alcohol having moderately high flash point and boiling point. The borate ester is characterized by ^{1}H, ^{13}C, ^{11}B NMR, IR spectra and flame tests.

Gr-4: Base grease (Gr-3) additized with labmade borate ester at 2% by weight at 90 °C.

Gr-5 to Gr-7: Base grease (Gr-3) additized with commercial borate ester packages at 2% by weight at 90 °C.

Gr-8: Gr-3 + additized with 2% mixture having 99.4% LBE and 0.6% ZDDP

Complexation leading to high temperature initially tested by dropping point which measures the temperature at which the thickener can no longer hold the base oil, under the static conditions of the test. Other physicochemical properties also studied in detailed as shown in Table-1.

Property	Method	Gr-1	Gr-2	Gr-3	Gr-4
Appearance	Visual	Homogeneous, slight brown mass	Homogeneous, slight brown mass	Homogeneous, slight brown mass	Homogeneous, slight brown mass
Wt % of Li-12HSA	By formulation	12.0	12.0	9.5	9.5
Drop Point	D 2265	258	261	202	269
Unworked penetration	ASTM D 217	286	285	268	280
Worked penetration	ASTM D 217	291	288	270	282
Mechanical stability after 10^5 strokes	ASTM D 217	+28	+29	+18	+21
Roll Stability, 16h	ASTM D 1831	13.3%	12.0%	7.5%	8.3%
Cu-corrosion	ASTM D D 4048	Pass	Pass	Pass	Pass

Table 1. Physico-chemical evaluation of greases with boric acid and borate as complexing agents

From **Table-1** it is confirmed that all the three lithium complex greases having borate complex have shown elevation in drop point. But, making lithium complex greases with boric acid and lithium borate need higher thickener content to result in NLGI grade 2 grease and the manufacturing process is longer and need to heat at higher temperatures than simple Li-grease.

Other disadvantage is that when we use boric acid initial stage need to use corresponding neutralizing lithium hydroxide which is expensive. In the other way simple Li-12-HAS grease made by conventional method need lesser soap content and need lower manufacturing energy. Apart from that using borate ester as additive easily we can vary to get tailor made drop point based on requirement. In this regard, simple soaps additized with boron esters are faster to manufacture than conventional complex lithium soaps. Manufacturers are also able to simplify the production of lithium grease by utilizing only one cooking procedure for both simple and complex greases. The process of filling part of a batch as simple lithium grease, and then converting the remaining portion of the grease with boron ester additive to obtain complex grease allows great flexibility in manufacturing. The reduction in processing time and lower lithium requirement for the production of lithium complex grease by using boron esters creates an economic advantage to the grease manufacturer using this technology.

Gr-1 and Gr-2 shows comparatively poor mechanical stability than Gr-4. Grease additized with borate ester is found to show either similar or superior in physic-chemical properties. Since the study planned to evaluate borate complexation on high temperature properties only, extreme pressure additives/package were not added and tribological evaluation was not done.

Since making high temperature lithium complex grease is convenient and economical with borate esters we have looked into commercially available borate esters, which were found to be packages of borate ester with some % of ZDDP which also can increase drop point to some extent in lithium-12-HAS greases.[10] We have evaluated three packages from different vendors and compared with our lab made borate ester and ZDDP.

Physico-chemical properties evaluation results of greases with borate esters tabulated below (**Table-2**). All the commercial drop point enhancer packages were found to raise drop point by 30-60 units from base grease drop point at 2% treat level. While package 3 gave better result in drop point enhancement compared to other two packages. Lab-made borate ester blended with 0.6% ZDDP to equivalent to commercial packages and this additive at 2% treat rate in base grease gave desired drop point enhancement and complete evaluation results are tabulated below. Alcohol properties used to make borate ester also play important role in some aspects such as drop point, flash point and evaporation loss. If highly volatile alcohol used that can cause safety issue in process, even though the addition of borate ester done at finishing stage temperature around 90-100 °C may cause safety problems. Branched alcohols are found to be a better choice for making borate ester since they can stabilize the borate complex in grease though complex structure and have high flash point and boiling point thus making them safe to use.

Property	Method	Gr-5	Gr-6	Gr-7	Gr-8
Appearance	Visual	Homogeneous, slight brown mass	Homogeneous, slight brown mass	Homogeneous, slight brown mass	Homogeneous, slight brown mass
Drop Point	D 566	253	261	270	276
Unworked penetration	ASTM D 217	285	282	282	280
Worked penetration	ASTM D 217	290	288	282	284
Mechanical stability after 10^5 strokes	ASTM D 217	+36	+33	+23	+21
Roll Stability, 16h	ASTM D 1831	15.7%	14.2%	9.1%	8.0%
Cu-corrosion	ASTM D D 4048	Pass	Pass	Pass	Pass

Table 2. Physico chemical evaluation of greases with borate ester as complexing agent

Even though the borate ester additized grease shows better properties compared other lithium complex greases with azelaic acid, long time effect of borate complexation and the storage stability is essential to use these greases in the market application. We have studied the properties of the greases which were stored for one year and evaluated. As shown in **Table 3** the borate ester additized greases reatained the the high temperature properties as well other properties. No significant change in drop point, mechanical stability and other properties were observed.

Property	Method	Gr-5	Gr-6	Gr-7	Gr-8
Appearance	Visual	Homogeneous, slight brown mass	Homogeneous, slight brown mass	Homogeneous, slight brown mass	Homogeneous, slight brown mass
Drop Point	D 566	251	260	268	272
Unworked penetration	ASTM D 217	290	285	280	282
Worked penetration	ASTM D 217	292	288	278	286
Mechanical stability after 10^5 strokes	ASTM D 217	+40	+36	+25	+20
Roll Stability,	ASTM D	17.1%	14.5%	11.2%	9.8%

16h	1831				
Cu-corrosion	ASTM D D 4048	Pass	Pass	Pass	Pass

Table 3. Storage stability greases with borate ester as complexing agent after one year

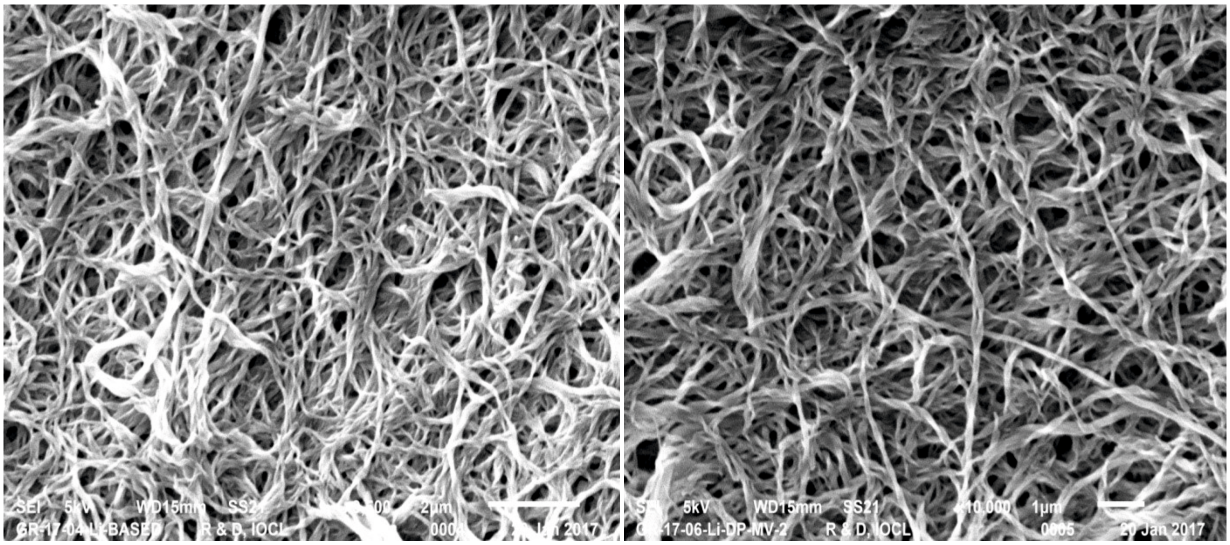

Figure1. SEM images of grease with and without borate complexation

The borate complexation in grease and mechanism involved in enhancement of dropping point is not well understood. To understand impact of complexation on structure, scanning electron microscopy (SEM) used to see any difference in the thickener fiber structure. As shown in the **Figure 1a and 1b** significant change in fiber structure does not seen. Since the fiber formed during synthesis of thickener and the borate ester was added in the finishing stage which may not alter the fiber structure but electro static attractions between boron atom and 12-hydroxy stearate. According to Siegart and Henry[11] the borate ester forms coordinated compound by electron sharing between the boron atom of the borate ester compound and the hydroxyl group of the hydroxy fatty acid soap. The coordinated interactions between soap and complexing agent holds oil intact within the thickener at high temperature which leads to result in a higher drop point in the finished grease. As per our observation borate ester being activated ester lowers activation energy to form coordinated complex with hydroxyl group of the hydroxy fatty acid soap and alcohol will be liberated out from grease if it is volatile the entire process is catalyzed by slight excess lithium hydroxide. Apart from that adding ZDDP also raises drop point to some extent. It is well known that zinc dialkyl dithio phospahate (ZDDP) also can increase drop point of lithium

12-hydroxystearate grease to some extent by forming lithium complex. The cumulative/synergic effect of borate ester and ZDDP is used in the drop point enhancement.

Conclusions

Conventional borate greases required high temperature and high cost process. Borate complexation in lithium 12-hydroxy stearate thickened grease in the finishing stage with borate ester is a simpler, faster, more economical method of producing lithium complex greases. Suitable alcohol having high flash point and boiling point in making borate ester will minimize some safety issues while using borate esters. Commercial available drop point enhancer packages evaluated to find better one. Using lab made borate ester will help in reducing cost for grease manufacturers. The storage stability of the borate additized grease is not changed significantly over one year period.

In future perspective tribological evaluation, effect of other performance improving additives and effect other thickener systems will be studied.

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