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New Aluminium Complex Thickener Developments

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Introduction

Aluminium complex greases

Lubricating greases can be defined as solid to semi-fluid products of the dispersion of a thickening agent in a liquid lubricant [1]. Generally the base oil content of the greases are 65-95%. Furthermore they contain additives and other materials to impart special properties, and usually the thickening agent is a metal soap (generally 5-35%) [2].

The aluminium complex grease share is ~3% of the global market (Figure 1) [4]. The production volumes were varying between 35-40 kT/year in the last couple of years, but in the recovery phase after the 2008 economic breakdown, a moderate growing trend can be seen. But as Table 1 shows, the market share of AIX greases are varying in different regions of the world.

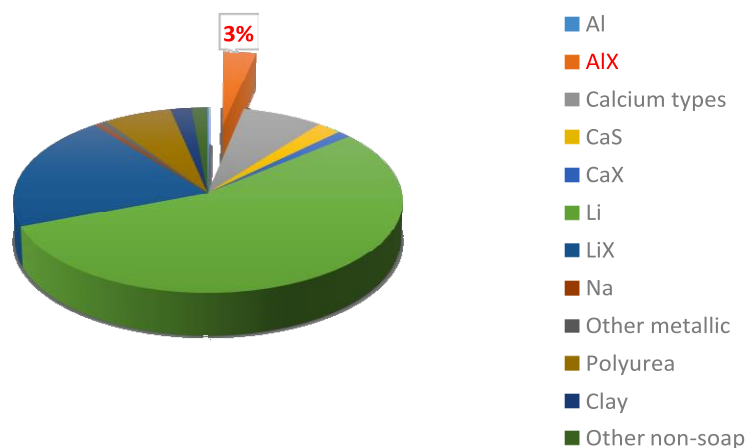


Figure 1
Global grease market share, by types

Table 1
AIX market shares in different regions

Region	AIX market share, %
North America	7,08
Europe	4,93
Pacific and Southeast Asia	5,34
India and Indian Subcontinent	0,06

Out of the aluminium complex greases one type is currently dominant in the world, which contains aluminium stearate benzoate and hydroxilate. (Figure 2).

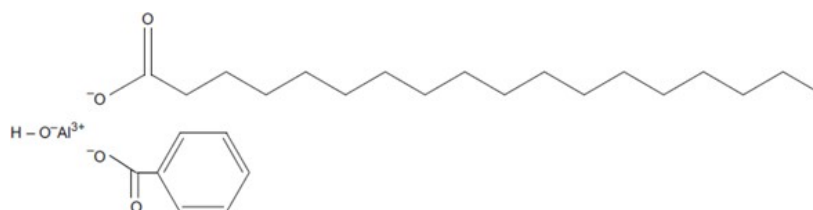


Figure 2

Aluminium stearate and –benzoate complex

Main properties of the aluminium complex greases include high dropping point and thus high maximal application temperature; excellent water resistance with a slight hardening of consistency in the presence of water; good working, mechanical and shear stability; very good oxidation stability; excellent pumpability and thus easy handling and applicability in central lubrication systems and bulk storage; wide operating temperature range; chemical resistance; good compatibility with a wide range of other greases [1].

Aluminum complex greases, in addition to having excellent heat reversion characteristics when compared to other multi-purpose greases. So they can solve intermittent heat buildup problems in its use as a wheel bearing lubricant in automotive equipment with disc brakes [5].

The aluminium complex lubricating grease have a bright future in special areas, where the mentioned properties are needed. So these greases can be applied in steel mill applications. In addition, their non-toxicity also enables their applicability in the food industry, as well as in the formulation of biodegradable lubricating greases [3]. There are other specialized areas in the field of paper- and automotive industry, construction machinery, which require the use of AlX grease lubrication. Aluminium complex greases have been used successfully to grease trailer wheel bearings and hitches [5].

Thickener development for high quality AlX grease production

In order to formulate properly the previously mentioned modern and high quality AlX greases, the continuous development of the thickeners itself are needed. Furthermore, contribution is a must from the thickener producers in the formulation experiments of the customers, which are using their current thickeners to reach the expected grease properties. Currently there are a few competitors on the market, and the thickener production volumes are expected to moderately grow parallel to the increasing AlX grease production trends.

In the paper new results are shown with our general AlX thickener which led to the introduction of our brand new grease for steel industry. Furthermore the results of our newly developed, naphthenic based thickener are presented.

Experimental

Objectives

In the frame of the development, two main goals were determined by us regarding our thickeners:

- to formulate a new, high quality AlX grease for the steel industry using our well-known general AlX thickener
- to formulate a new AlX thickener with better cold flow properties in order to achieve more comfortable handling and application of the thickener product

Feedstocks

During the experiments, different types of base oils were used: mineral Group I base oil, naphthenic base oil and white oil.

As thickener component for laboratory grease production, our general and food grade thickener product and the new experimental thickener were used. To make the aluminium complex structure, technical grade benzoic acid was used. During the formulations, polymer additives, structure modifier additives were used.

Sample production

The samples were produced in a laboratory scale open grease kettle. The whole quantity of base oil mixture was poured into the kettle. After that stirring and heating has been started. At about 60°C, powdered benzoic acid was added. After the acid was dissolved, pre warmed thickener component had been added at 70–80°C. After this the mixture has been heated to 150°C at first, for saponification. Then the temperature has been increased to the maximum of about 200–220°C, mainly depending on the type of base oil used. After reaching the maximum temperature, the grease has been cooled immediately. After cooling, finishing operations, such as milling and deaeration had been done.

Analytical methods

The analytic methods used for determining the properties of the grease samples were standardized (ISO, DIN, ASTM) methods commonly used in the grease industry.

Results and discussion

Formulation of high quality steel industry grease with general thickener

The main motivation behind this development was that softening problem was observed with one of our AlX steel mill grease under the conditions of the process and despite the continuous after-lubrication, the dismantled bearings are contained grease levels which were far from the appropriate. So developing a replacement product (with better general properties and heat stability) was needed, but using our general thickener because of economic reasons.

Before the experiments the key parameters of the new grease were set:

- Flow pressure 0°C ~ 300-400 mbar
- Penetration - NLGI grade 1-2
- Water wash out < 3 %
- Water spray off < 50 %
- Penetration change after 10000 strokes < 30 0,1mm
- Great heat stability (heat stress tests at 150°C)

In the first stage of the experiments there were proven that although the currently used product is very resistant to acidic environments, it has had some problems with tolerating the heat stress. According to the review of the additive structure of the present product, it became clear that in the next step the focus have to be on determining the right amount of polymer additive and on the careful selection of the structure modifying additive.

In the second stage four AIX base grease samples were made with different polymer and 2% structure modifier additive (SMA) contents (Table 2). As it can be seen from the results, the mechanical stability targets were fulfilled using the SMA1 structure modifier additive, except the NLGI grade and the flow pressure. To solve this issue, the thickener content was decreased significantly in the fifth formula using 2% polymer and 2% SMA1 additives (Table 3), which reduced the cost of the formula and the properties fulfilled the target values.

Table 2
Base greases with different SMAs and polymer content

	Base grease + SMA1	Base grease + SMA1	Base grease + SMA2	Base grease + SMA2
Polymer, %	1	2	1	2
Visual	homogeneous	homogeneous	homogeneous	homogeneous
Penetration change, after 10 000 strokes, 0,1 mm	7	13	10	7
Penetration change, after 100 000 strokes, 0,1 mm	26	30	50	56
Water wash out @ 79°C, %	0,4	1,4	1,1	0,2
Water spray off, %	6,49	4,9	14,7	10,5
Penetration after 60 strokes, 0,1 mm	231	225	250	249
Flow pressure 0°C, mbar	407	561	378	508

Table 3**Lab results with decreased thickener content (2% polymer, 2% SMA1)**

Visual	homogeneous
Penetration change, after 10 000 strokes, 0,1 mm	-5
Penetration change, after 100 000 strokes, 0,1 mm	13
Water wash out @ 79°C, %	4,5
Water spray off, %	31,4
Penetration after 60 strokes, 0,1 mm	269
Flow pressure 0°C, mbar	463

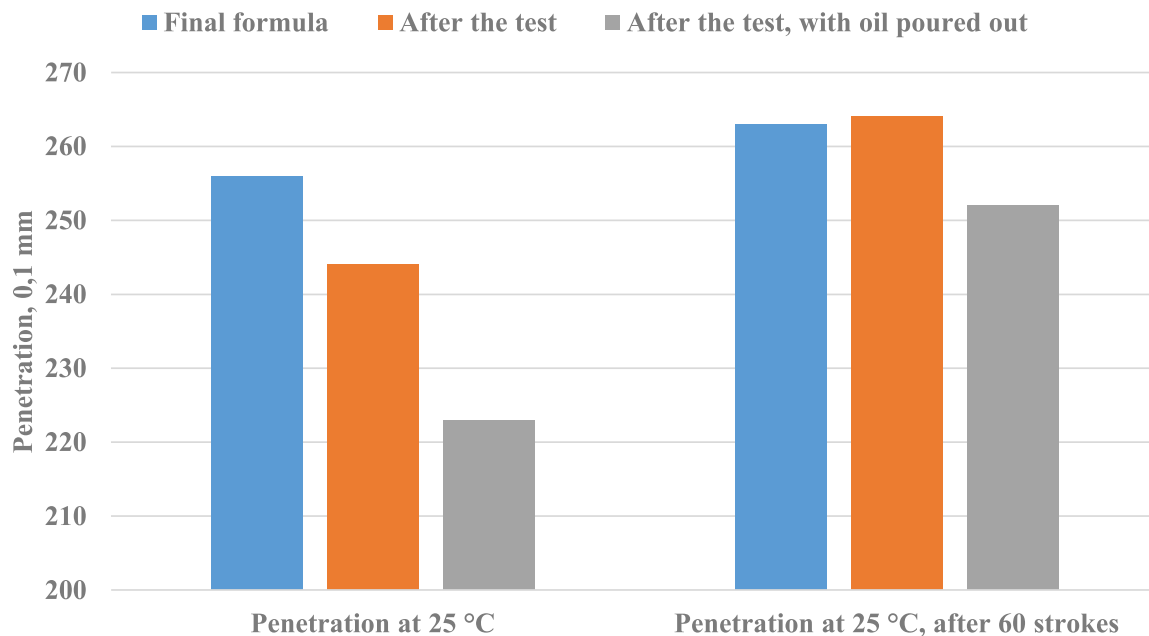
Based on the results of the second stage, in the third experimental stage the final formula was simulated in the lab: it contained not only the polymer and the SMA1 additives, but also the other needed performance additives. The results can be seen in Table 4. It can be concluded that at the end of the lab experiments, all of the target grease property values were reached.

Table 4**Lab results with fully additivated formula**

Visual	homogeneous
Dropping pont, °C	269
Penetration change, after 10 000 strokes, 0,1 mm	3
Penetration change, after 100 000 strokes, 0,1 mm	-17
4-ball method, weld load, N	2200
4-ball method, 60 min/400 N, mm	0,62
Oxidation stability (100 h, 100°C, pressure drop), kPa	20
Copper corrosion (100°C, 24 h)	1
Water wash out @ 79°C, %	2,6
Static water resistance @ 90°C	1-90
Leakage tendency, %	3,2
Flow pressure 0°C, mbar	370
Water spray off, %	41,7
Penetration after 60 strokes, 0,1 mm	285

The last task of the laboratory work was to prove that the final formula can cope with the heatstress. Two samples were heated to 150 °C temperature for 72 hours, and from one of the samples the separated oil was poured out in every 24h. The results can be seen in Figure 3. It can be concluded that the new formula stayed greasy, the hardening was not significant, although some darkening was noticed at the surface of the sample.

Figure3
Heat stress results



To summarize the results of this development: it was successfully proven, that high quality AIX grease formula can be developed using our general thickener. With the lab formula successful experimental productions in our plant was made. After the positive field test results the product was introduced into our portfolio.

The benefit of the new formula for the customer is the higher heat- and water resistance compared to the previous product, for nearly the same price.

Formulation of new AIX thickener product

The main motivation behind this development was to create a thickener, which can be used easily where the climate is cold and/or there is no possibility of using warming chamber before applying the product. So in our experiments first a modified thickener formula was formulated in the lab, and after that an experimental production was made to ensure that the quality is reproducible in the plant, too. The main properties of these products are shown in Table 5. The new thickener was different than our general thickener, it had good pour point and visually seemed more flowable, too.

Table 5
Main properties of the new thickener

Properties	Laboratory sample	Experimental production sample
Visual	clear, viscous liquid	clear, viscous liquid
Pour point, °C	-12	-18
Flash point (Cleveland), °C	215	220
Aluminium content, %	4,2	4
Stearic acid content, %	41,3	42,7

In the next experimental step the thickening effect of the new formula had to be proven. Laboratory greases were made using the experimental production sample in different amount. The new thickener was applied in Group I base oil, naphtenic base oil and synthetic base oil. The results are shown in Tables 6-8 and Figures 4-6. Based on the results it can be concluded that the new thickener behaved similarly in case of Group I and naphtenics oil based greases. The NLGI 2 grade could be reached by < 10% thickener content. The mechanical stability of these greases were normal in case of aluminium complex greases. In case of synthetic oil based greases, significantly higher thickener content have to be applied to reach NLGI 2 grade.

Table 6
Main properties of laboratory greases (Group I base oil)

Group I base oil content, %	90,59	89,41	88,54	88,24	87,07
Experimental production sample content, %	8	9	9,75	10	11
Penetration after 60 strokes, 0,1 mm	301	297	278	256	249
Penetration change after 10000 strokes, 0,1 mm	20	33	21	35	52
Penetration change after 100000 strokes, 0,1 mm	53	62	47	87	99
Oil separation 100 °C, 24h, %	10,5	8	5,1	5,1	2,5
Visual	homogeneous	homogeneous	homogeneous	homogeneous	homogeneous

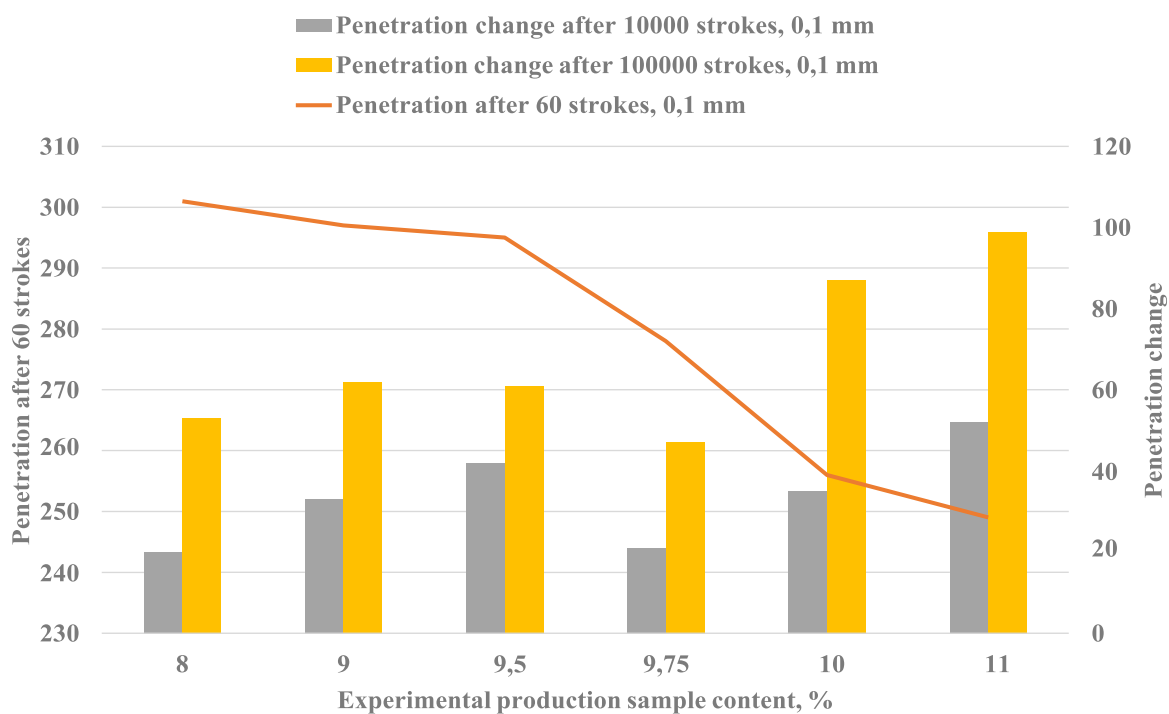


Figure 4

Consistency and stability of laboratory grease (Group I base oil)

Table 7

Main properties of laboratory greases (naphtenic base oil)

Naphtenic base oil content, %	90,59	89,41	88,24
Experimental production sample content, %	8	9	10
Penetration after 60 strokes, 0,1 mm	304	293	257
Penetration change after 10000 strokes, 0,1 mm	34	32	36
Penetration change after 100000 strokes, 0,1 mm	37	48	67
Oil separation 100 °C, 24h, %	9,1	6,7	4,5
Visual	homogeneous	homogeneous	homogeneous

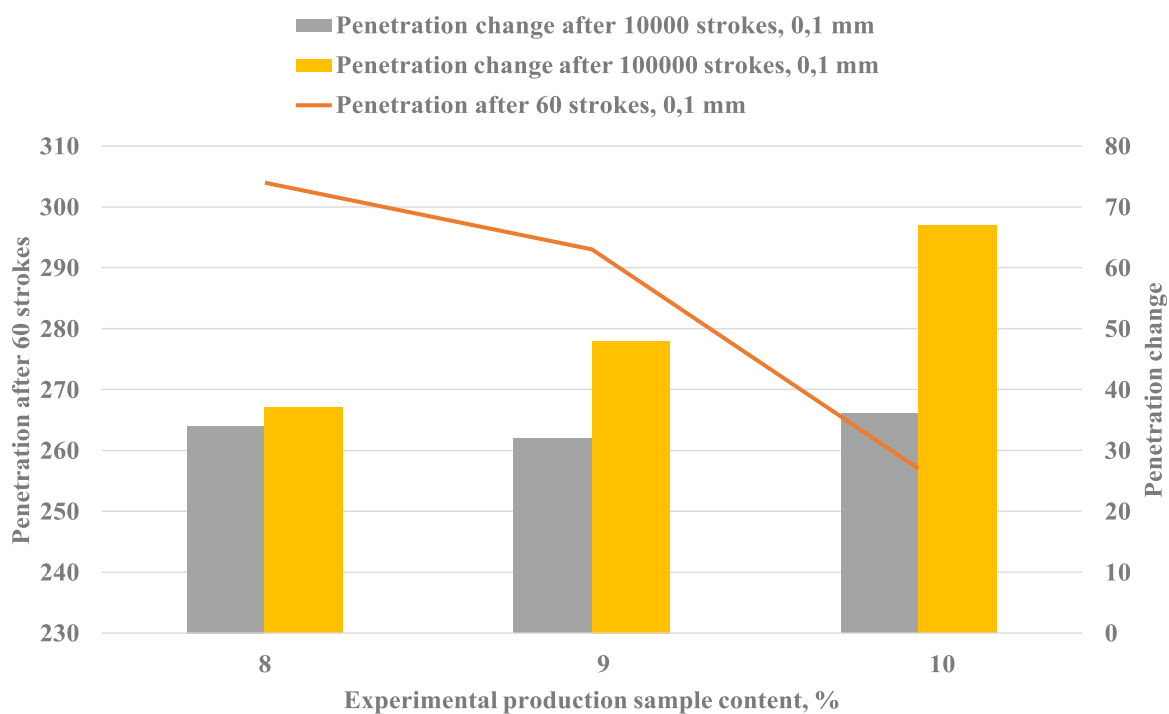


Figure 5

Consistency and stability of laboratory grease (naphtenic base oil)

Table 8

Main properties of laboratory greases (synthetic base oil)

Synthetic oil content, %	89,41	87,07	84,73	82,39
Experimental production sample content, %	9	11	13	15
Penetration after 60 strokes, 0,1 mm	405	363	323	279
Penetration change after 10000 strokes, 0,1 mm	17	27	35	46
Penetration change after 100000 strokes, 0,1 mm	27	64	19	39
Oil separation 100 °C, 24h, %	25,3	15,5	9	4,6
Visual	homogeneous	homogeneous	homogeneous	homogeneous

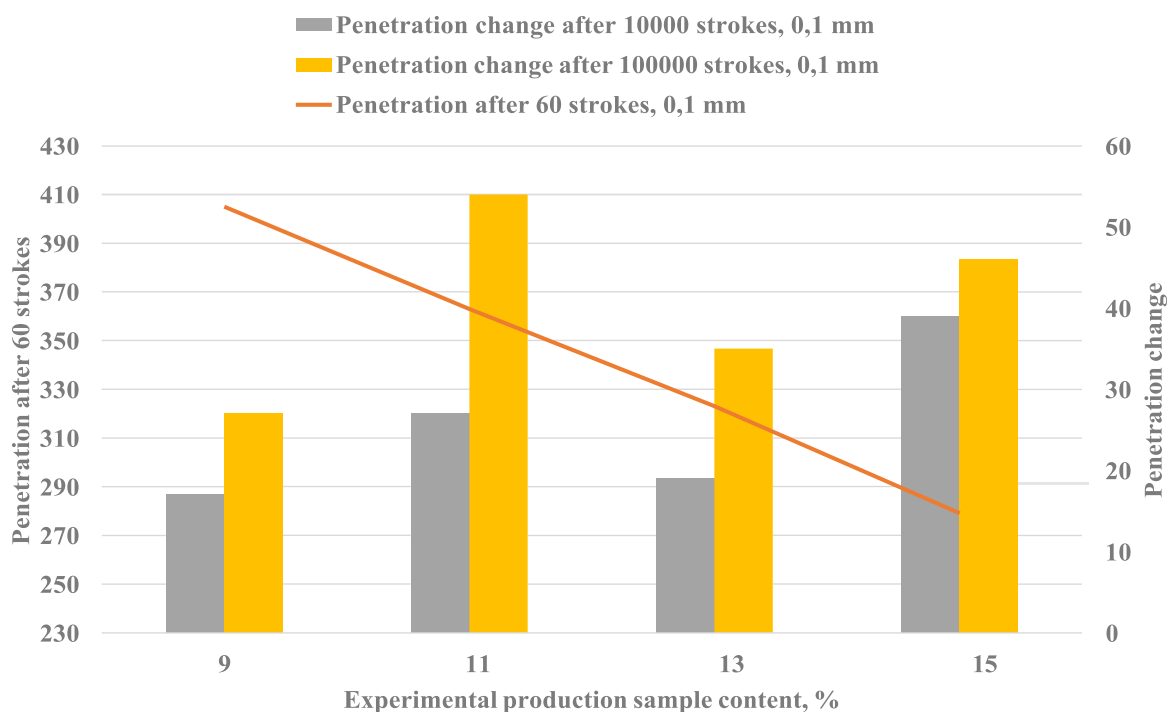


Figure 6
Consistency and stability of laboratory grease (synthetic base oil)

In the last step structural stability improvement experiments were made. It can be concluded, that with adding 1% structure modifier additive (SMA1 from the previous topic) during the laboratory grease cooking, significant improvement was experienced, as it can be seen in Figure 7.

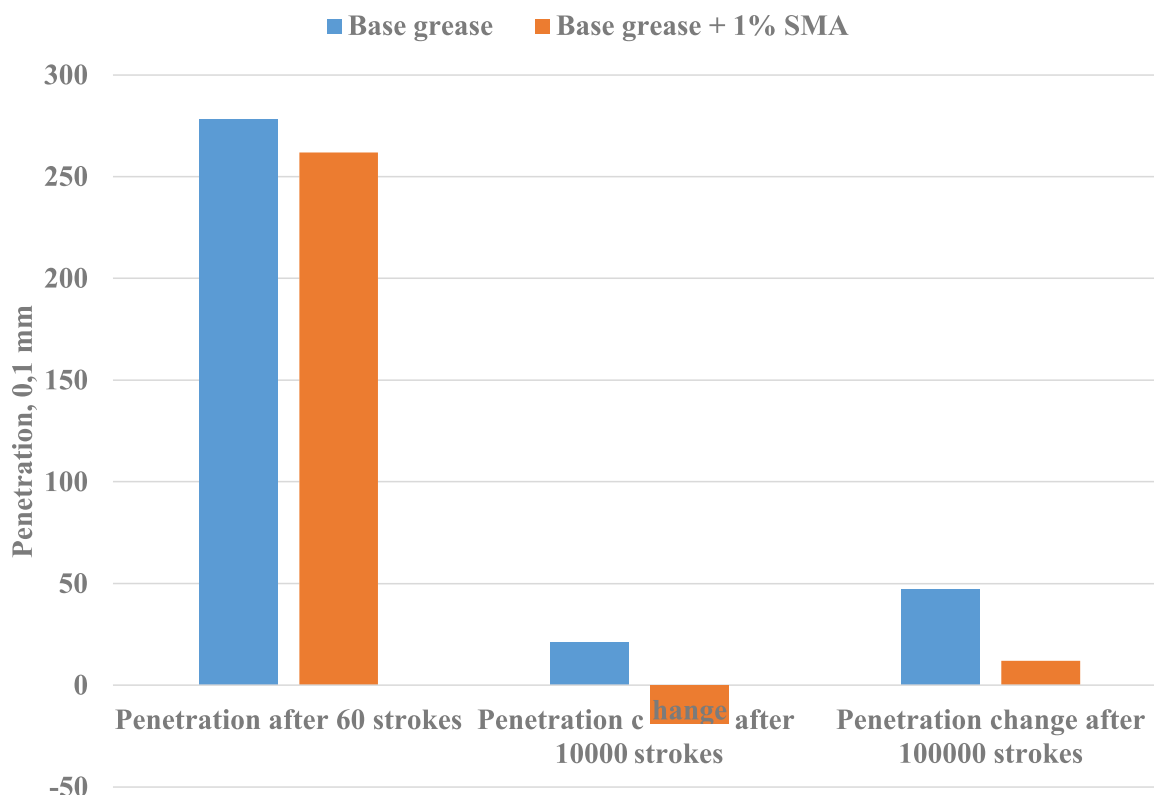


Figure 7
Structure stability improvement results

To summarize the results of this development: a new thickener was successfully developed, which can be handled more easily and its thickening effect is similar or slightly better than our general thickener. According to the first production plant experiments it can be used in grease production without any problem.

Conclusions

High quality aluminium complex greases have bright future ahead, especially in steel industry and food grade applications. For this applications constant development is needed in the field of thickener production.

In this paper the formulation process of a new high quality steel grease is presented. It was proven that by careful selection of additive structure, the development targets can be reached using our well-known general thickener.

Furthermore the development of a new thickener is presented. This product can be handled more easily during production and its thickening effect is similar or slightly better than our general thickener.

References

- [1] Mang, T., Dresel, W.: “Lubricants and lubrication”, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2007, 894 p.
- [2] Pirro, D.M., Wessol, A.A.: “Lubrication Fundamentals”, ISBN: 0-8247-0574-2, 2001, 516 p.
- [3] komadadditive.com
- [4] NLGI Grease Production Survey Report, 2016
- [5] <http://www.le-international.com>

“The Evolutions in Overbased Calcium Sulfonate Grease Technology and its Impact on its Field Performance”

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Abstract:

Calcium sulfonate greases were first reported in 1940's and several technological evolutions have taken place since then, however, their worldwide volumes have merely reached to about 2.2 %. The lithium / lithium complex greases, on the other hand, still remain the most popular greases and enjoys the whopping over 75 % of total worldwide lubricating grease market. Lithium greases, in recent past, have really been the area of some serious concern due to availability and price escalation of lithium hydroxide. The growing use of lithium in lithium ion batteries appears to drive the availability and price of lithium in future and therefore, there has been increasing efforts world over to look for alternatives. In the quest to find alternate multi-purpose and high-performance greases, overbased calcium sulfonate greases have emerged front runner, compared to other high-performance aluminum complex, polyurea, clay base greases. One of the reason of their lead is comparatively better compatibility with most widely used lithium and lithium complex greases. Calcium sulfonate greases are known to possess inherent rust preventive, excellent high temperature, extreme pressure and water resistance characteristics. However, this class of greases have inherently been associated with inferior pumpability specially at low temperatures and higher cost compared to lithium greases though , this price parity between lithium and sulfonate greases have recently been narrowed considerably due to unprecedented steep hike in lithium hydroxide prices .

Although Calcium sulfonate greases and lithium greases emerged almost during the same period, their market share have not grown up as compared to lithium greases. Besides, the comparatively higher cost of calcium sulfonate, the other impediment factor in the growth of this class of greases is lack of easily available technology to manufacture right quality greases and so far have largely been governed by patented composition and processes. While the lithium grease manufacturing technologies matured over time and almost in every continent of the world, these greases can easily be made, however, the same is not the case with calcium sulfonate greases..

On the other hand, calcium sulfonate greases are highly sensitive to composition and processing parameters. In general, originally developed calcium sulfonate lacked the stability and high temperature capabilities, though excellent rust protection, and therefore calcium sulfonate complex greases emerged in market in 1980's. These calcium sulfonate complex greases possessed excellent performance characteristics except inferior pumpability due to higher thickener content. The majority of the calcium sulfonate complex greases known in the industry are based on same or similar technology. The most significant step in manufacture of these greases is conversion of calcium carbonate to wafer like calcite form that contribute significantly

towards thickening and governing the overall thickener content. The partial / inadequate conversion and improper complexing process may lead to instability / hardening over time, high thickening content, poor lubricity at accelerated conditions like high temperature and high speeds and may even lead bearing / equipment failure.

We have been manufacturing this class greases over decades, passed through many of such technological transformations and perfected our technology over period of time where the pumpability of these greases has significantly been improved by virtue of adjusting overall overbased calcium sulfonate content suitably and improving lubricity over extended period of time under hostile environmental conditions, without compromising its other inherent performance characteristics. These greases both with and without molybdenum di-sulfide are performing excellently well in major USA steel plants and in mining application world over. Some of these interesting data will be presented in this paper.

The Tribological Performances of Molybdenum Dialkyldithiocarbamate with Highly Branched Alkyl Groups and Highly Sulfurized Core in Lubricants

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ABSTRACT: Friction-reducing (FR), antiwear (AW) and extreme-pressure (EP) performances of molybdenum dialkyldithiocarbamate with highly branched alkyl groups and highly sulfurized core (HBS-MoDTC) are reported. Four-ball tests indicate that HBS-MoDTC exhibits excellent FR and AW performances in both lubricating base oil and fully formulated engine oil. The tests also show that HBS-MoDTC possesses excellent FR and good AW, but no obvious EP capacities in lithium complex, polyurea or calcium sulfonate complex greases. MTM Stribeck curve tests in oil and MTM one-hour timed step tests in grease also prove that the HBS-MoDTC additive can effectively improve the friction performance in mixed and/or boundary lubrications. To obtain a balanced and comprehensive FR, AW and EP performance in grease, the combination of HBS-MoDTC with antimony/zinc mixed metal dialkyldithiocarbamate (Sb/ZnDTC) as EP additive was also evaluated. The copper corrosion test proves that HBS-MoDTC does not result in obvious copper corrosion in grease.

KEYWORDS: MoDTC, Highly Branched Alkyl Groups, Highly Sulfurized Core, Grease, Friction-reduction, Antiwear, Extreme-pressure

1 INTRODUCTION

Environmental protection, energy-saving and high efficiency are the key drivers for lubricant upgradation. Molybdenum dithiocarbamate (MoDTC) is a well-established phosphorus-free additive technology known to reduce friction, improve energy efficiency and prevent wear for lubricating oil and grease. In the mixed to boundary lubrication regime, use of the MoDTC additive results in a very low friction coefficient of around 0.05 making it a very effective friction modifier and an essential component of current lubricants, such as in engine oil and CVJ grease^[1-7]. Its effectiveness in friction reduction comes primarily from forming a MoS₂-containing tribofilm on the rubbing surfaces. The layer-lattice structure of the MoS₂ contributes to low friction. In MoS₂, there is powerful covalent bonding between atomic species, but between lattice layers there is only very weak Van der Waals attraction. The weak Van der Waals forces between MoS₂ layers maintain easy shear within the molecule and are responsible for the low-friction properties^[8].

MoDTC compounds can vary chemically due to differences in degree of sulfurization and types of amines used in preparation. These subtle chemical differences of different MoDTC types have a significant influence on its tribological performance and its compatibility with base oils. Recent research shows that^[9], as lubricant additive, the MoDTC with highly branched alkyl groups and highly sulfurized core (HBS-MoDTC), exhibits the extra performances as follows:

- (1) Improved low-temperature solubility in highly hydro-treated mineral oil and poly-alpha-olefin (PAO);
- (2) Better friction-reducing (FR) performance at low treat level, and lower activation temperature; and
- (3) Better FR retention capability and the formation of stronger tribochemical film.

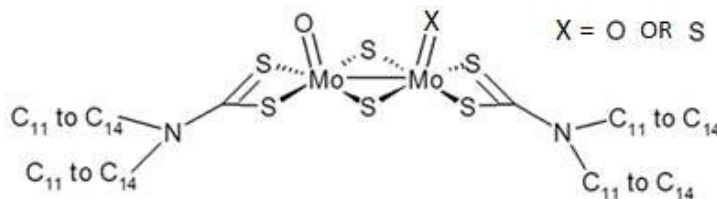
In this paper, the tribological performances of HBS-MoDTC in lubricating oils and greases are investigated.

2 EXPERIMENTAL / MATERIALS AND METHODS

2.1 Base Oil, Greases and Additives

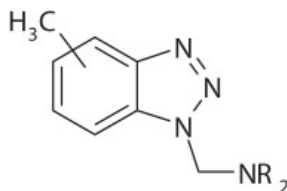
The lubricating oils used in this study are 150N Group II base oil and a fully-formulated CH-4 20W/50 engine oil. The lubricating base greases used include a lithium complex grease, a polyurea grease and a complex calcium sulfonate grease. All three base greases were obtained from real production batches by courtesy of two grease manufacturers.

The MoDTC with **H**ighly **B**ranch and Symmetrical amine and **H**ighly **S**ulfurized core is designated as HBS-MoDTC. This liquid HBS-MoDTC additive contains 10.17% of Molybdenum and 11.4% of Sulfur with the atomic ratio of S/M 3.35 (compared to S/M 3.0 in traditional MoDTC). The chemical structure of HBS-MoDTC can be described as follows:



The combination of HBS-MoDTC with Extreme-Pressure (EP) additive is also investigated. The EP additive is a di-metal salt of dithiocarbamate (Sb/ZnDTC) by *in situ* (in one kettle) synthesis^[10-11]. The Sb/ZnDTC additive has antimony, zinc and sulfur content of 5.8%, 4.5%, and 18.5% respectively.

The copper corrosion performance is also considered with HBS-MoDTC, and the metal deactivator used is a tolutrizole derivative with the following structure (R = iso-octyl):



2.2 Four-Ball Friction and Wear Test

The four-ball friction and wear test method of standard ASTM D2266 for grease and D4172 for oil were used to evaluate additive performances in lubricating oil and greases. Experimental conditions were: 20kgf, 30kgf, 40kgf and 60kgf of loads, 1200 rpm speed, 60 minutes, and 75°C. Real-time recording of coefficient of friction during the test is also available with the specific four-ball test machine used, in addition to measurement of wear scar diameters.

2.3 Four-Ball EP test

Standard ASTM D2596 four-ball EP test method was used to evaluate additive's EP performance in greases. Experimental conditions were: 1770 rpm speed, time duration 10 seconds. Both last non-seizure load (LNSL) and weld point were measured. Standard ASTM D2783 EP test method with the same test conditions was used to measure the last non-seizure load (LNSL) of the oil without and with additives.

2.4 MTM Stribeck Curve Test and Timed Step Test

Mini Traction Machine (MTM) was used to evaluate frictional characteristics in boundary and mixed lubrication regime with "Ball on Disc" configuration. MTM consists of a rotating 52100 steel ball pressed against an independently rotating 52100 steel disc immersed in oil or grease. The operating conditions are set by independently controlling the rotational velocities of the shafts that drives the ball and the disc, in order to obtain a particular combination of rolling speed and slide to roll ratio, as well as by controlling the contact force and the oil bath temperature. The operation scheme of MTM is illustrated as in Figure 1.

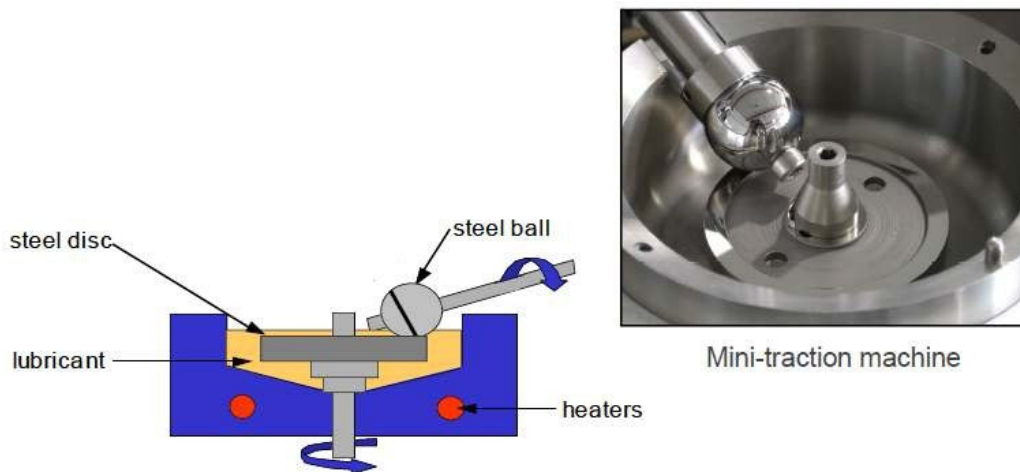


Figure 1. MTM work scheme

The Stribeck Curve test conditions for oil: 35N load (Equivalent to 1GPa Hertzian point contact load), 50% Slide to Roll Ratio (SRR), each Stribeck curves at 40°C, 60°C, 80°C, 100°C, 120°C and 140°C, Mean speed were started at 3000mm/sec and decreasing in steps of 200 mm/sec to 1000 mm/sec, and decreasing from 1000 mm/s in steps of 100 mm/s to 100 mm/s and finally decreased from 100 mm/s in steps of 10 mm/s to 10 mm/s.

Grease is not a real liquid and has trouble quickly penetrating the metal of the ball and disc making it a challenge to measure the Stribeck Curve. We choose the timed step profile to give us the most consistent measurements. The test conditions: 35N load, 200%SRR, speed 500rpm, at 60°C and 120°C. These conditions represent a sliding dominated mixed

lubrication at low and high temperatures.

2.5 Copper Corrosion Test

The copper corrosion test was run according to ASTM D4048 method. The conditions: 100°C and 24 hours.

3 RESULTS AND DISCUSSION

3.1 Tribological performances in base oil by four-ball test

HBS-MoDTC was added into the 150N Group II base oil, and the tribological performances were evaluated under different loads by four-ball friction and wear tests. The experimental results are given in Table 1.

Table 1. The EP, AW and FR Performances of HBS-MoDTC in Group II Base Oil							
	Wear scar diameter, mm			Friction coefficient			Last non-seizure load, kgf
	20 kgf	30 kgf	40 kgf	20 kgf	30 kgf	40 kgf	
150N Group II base oil	0.599	0.666	fail	0.117	0.081	fail	34
+ 0.8% HBS-MoDTC	0.469	0.504	0.514	0.074	0.079	0.073	80

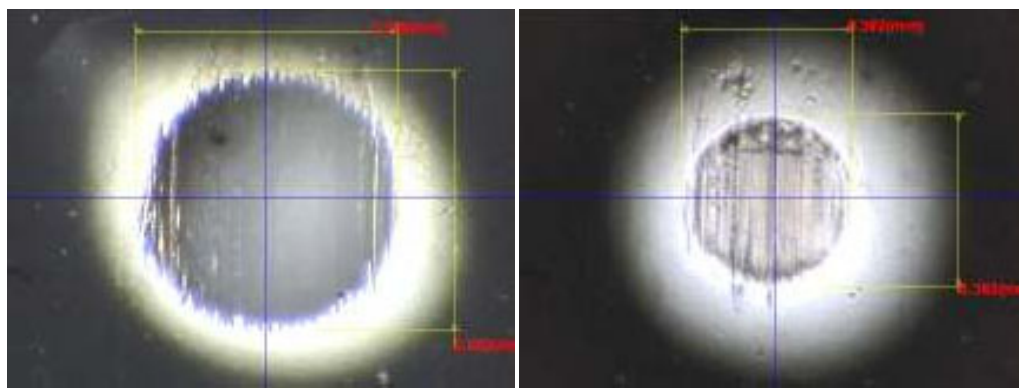
It can be seen from Table 1 that, HBS-MoDTC possesses excellent friction-reducing (FR), good antiwear (AW) performances in the base oil, and also increases the last non-seizure load of the oil, which means the strength of the tribochemical film produced in the rubbing surfaces.

3.2 Tribological performances in engine oil by four-ball test

Engine oil is a complicated system, which contains a plenty of different types of additives. To understand HBS-MoDTC's compatibility with other additives, HBS-MoDTC was added into a CH-4 20W/50 engine oil, and the tribological performances were evaluated under the load of 60kgf by four-ball friction and wear tests. This load condition is relatively very high, so we can also see HBS-MoDTC's performance under severe boundary lubrication. The test data is shown in Table 2.

Table 2. HBS-MoDTC's FR and AW performances in engine oil(Four-ball test: 60kgf, 1200rpm, 75°C, 60min.)		
	Wear scar diameter, mm	Average friction coefficient
CH-4 20W/50 engine oil	0.564	0.108
+ 1.0% HBS-MoDTC	0.380	0.063

It can be seen from Table 2 that, HBS-MoDTC possesses excellent friction-reducing (FR) and antiwear (AW) performances in the fully formulated engine oil. The wear scar and the friction curve are illustrated in Figure 2 and 3.



Wear scar by CH-4 engine oil Wear scar by CH-4 engine oil with HBS-MoDTC
Figure 2. Four-ball wear scars by CH-4 engine oil

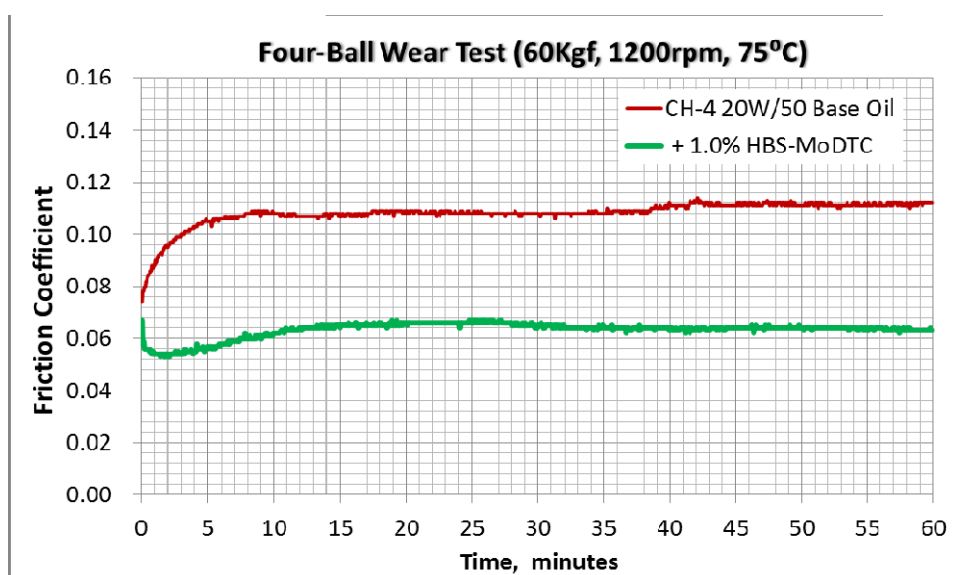


Figure 3. The FR performances of the engine oil without and with HBS-MoDTC by Four-Ball test

The outstanding AW and FR performances of HBS-MoDTC can be proved well by the Figure 2 and 3 with significant reduction in both wear scar and friction coefficient.

3.3 Tribological performances in base oil by MTM

0.8% HBS-MoDTC was added into the 150N group II base oil and the frictional properties under slide/roll conditions were evaluated using Mini Traction Machine (MTM) at 40°C, 60°C, 80°C, 100°C, 120°C and 140°C. The Stribeck curves at 60°C and 120°C are given in Figure 4 and 5. as the representatives at low and high temperatures.

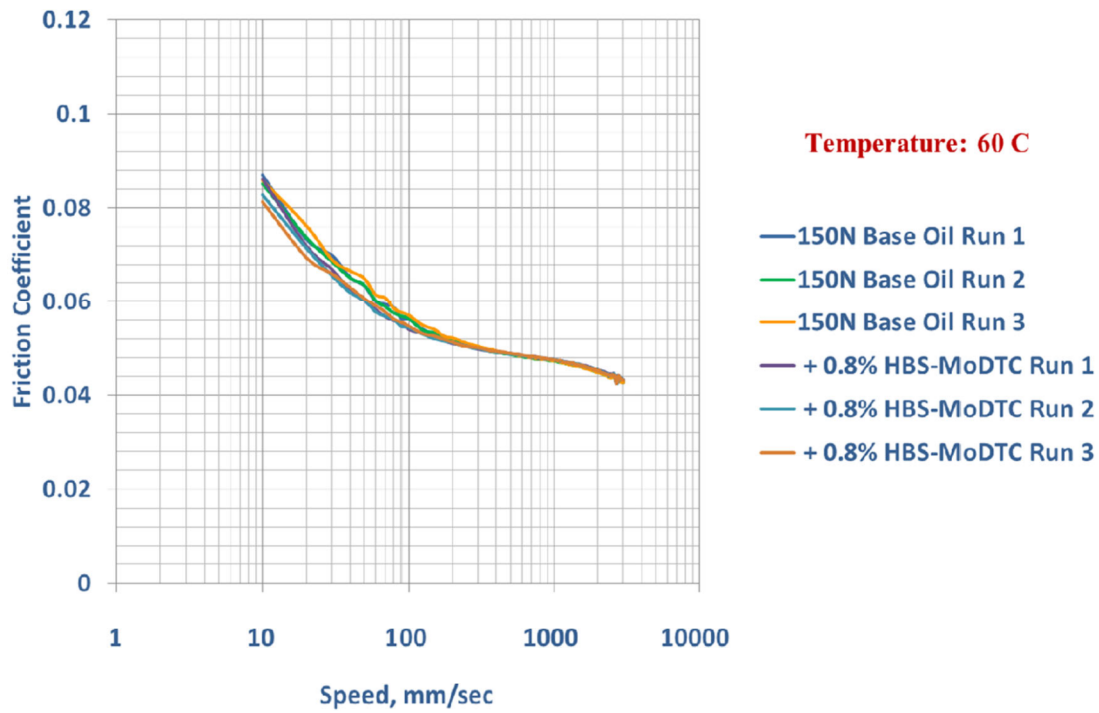


Figure 4. MTM Stribeck curve of the base oil with and without HBS-MoDTC at 60°C

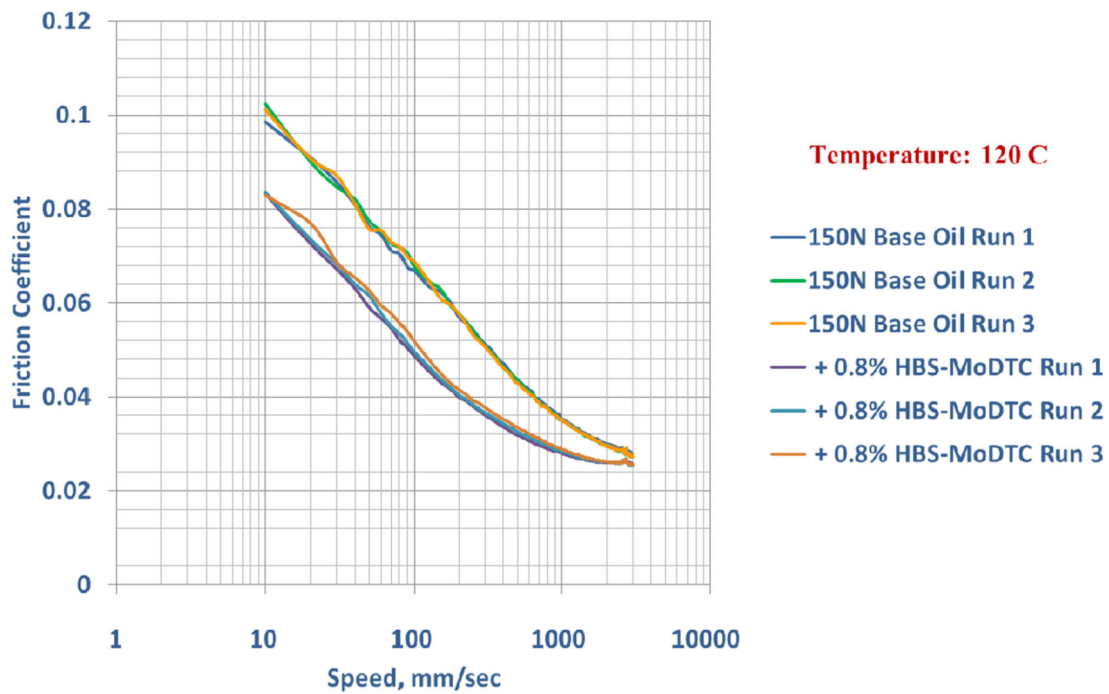


Figure 5. MTM Stribeck curve of the base oil with and without HBS-MoDTC at 120°C

From Figures 4 and 5, it can be found that the temperature is a key factor for HBS-MoDTC to develop its FR performance in the oil. At low temperature (60°C in Figure 4), we cannot identify an obvious FR characteristics by HBS-MoDTC, but at high temperature (120°C in Figure 5), HBS exhibits excellent FR properties under both mixed lubrication (1000-100 mm/s) and boundary lubrication (100-10 mm/s).

3.4 Tribological performances in greases by Four-Ball test

HBS-MoDTC was added into lithium complex, polyurea and calcium sulfonate complex base greases, and the tribological performances were evaluated by four-ball friction and wear tests. The experimental results are given in Table 3.

Table 3. The EP, AW and FR Performances of HBS-MoDTC in Greases				
	Friction and Wear Test (40Kgf, 1200rpm, 75°C, 60min.)		EP Test	
	Wear Scar, mm	Average Friction Coefficient	LNSL, Kgf	Weld load, Kgf
Lithium Complex Base Grease	0.588	0.099	82	250
+ 1.0% HBS-MoDTC	0.469	0.081	109	250
+ 2.0% HBS-MoDTC	0.445	0.074	114	250
Polyurea Base Grease	0.423	0.089	107	250
+ 1.0% HBS-MoDTC	0.464	0.090	80	250
+ 2.0% HBS-MoDTC	0.446	0.067	95	250
Calcium Sulfonate Complex Base Grease	0.375	0.098	100	315
+ 1.0% HBS-MoDTC	0.348	0.076	109	400
+ 2.0% HBS-MoDTC	0.367	0.082	126	400

It shows in Table 3 that, HBS-MoDTC exhibits excellent FR performance in all the three greases with at least 20% friction reduction, and good AW performance in the complex lithium grease. HBS-MoDTC does not improve the EP performance of the three greases. The wear scar and the friction curve by the complex Li grease with and without HBS-MoDTC are illustrated in Figure 5 and 6.

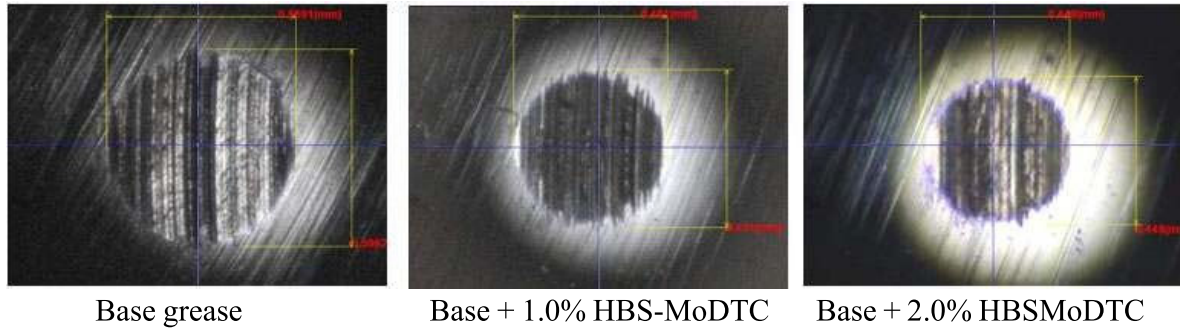


Figure 5. Four-ball wear scars by complex lithium grease

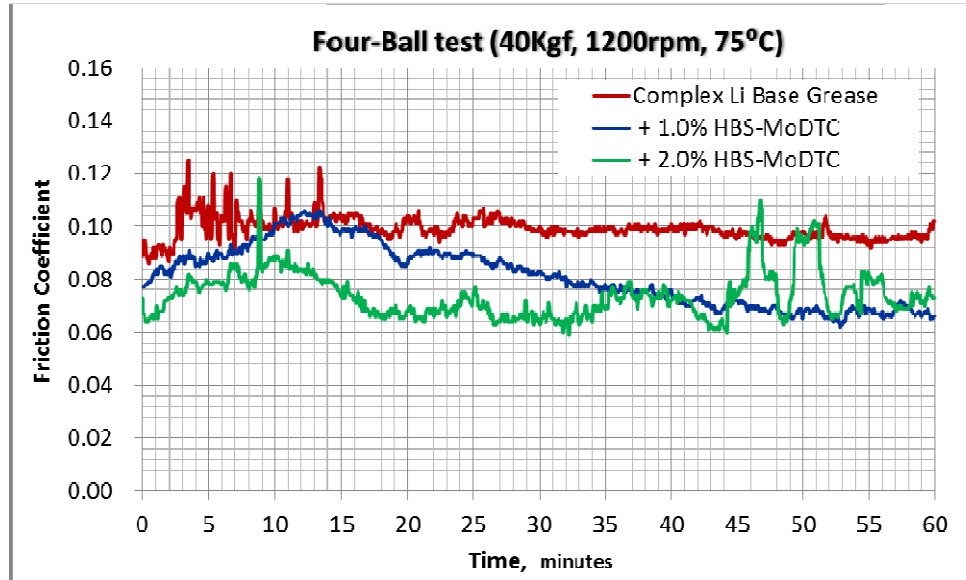


Figure 6. The FR performances of the complex Li grease with and without HBS-MoDTC by Four-Ball test

3.5 Tribological performances in greases by MTM test

Due to the difficulty running MTM grease Stribeck curve, we choose the timed step test under 35N load, 200%SRR, speed 500rpm, at 60°C and 120°C. These conditions represent a sliding dominated mixed lubrication at low and high temperatures. The friction data is showed in Figure 7 and 8.

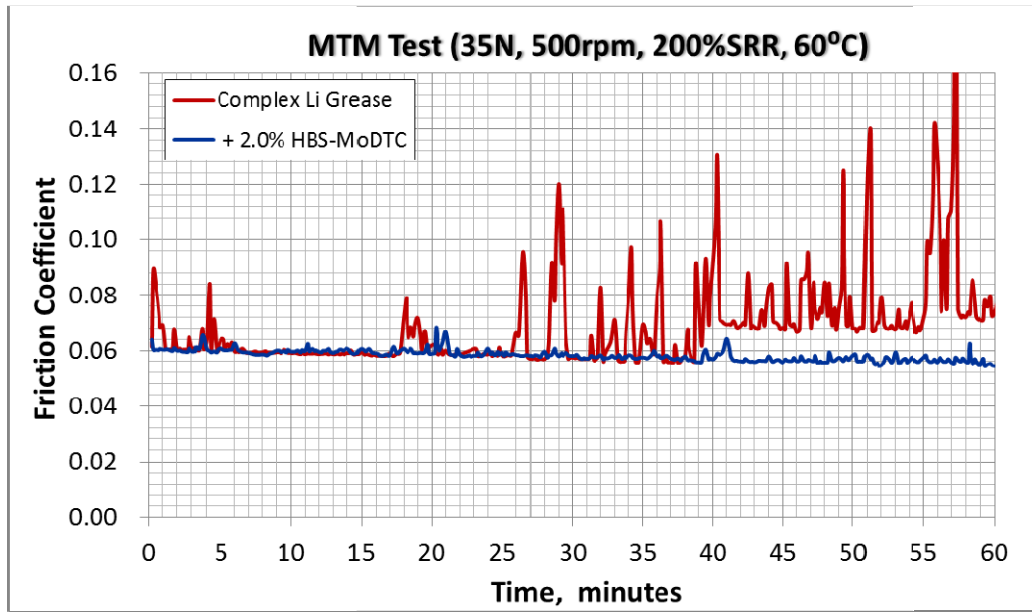


Figure 7. The FR performances of the complex Li grease with and without HBS-MoDTC by MTM timed step test at 60°C

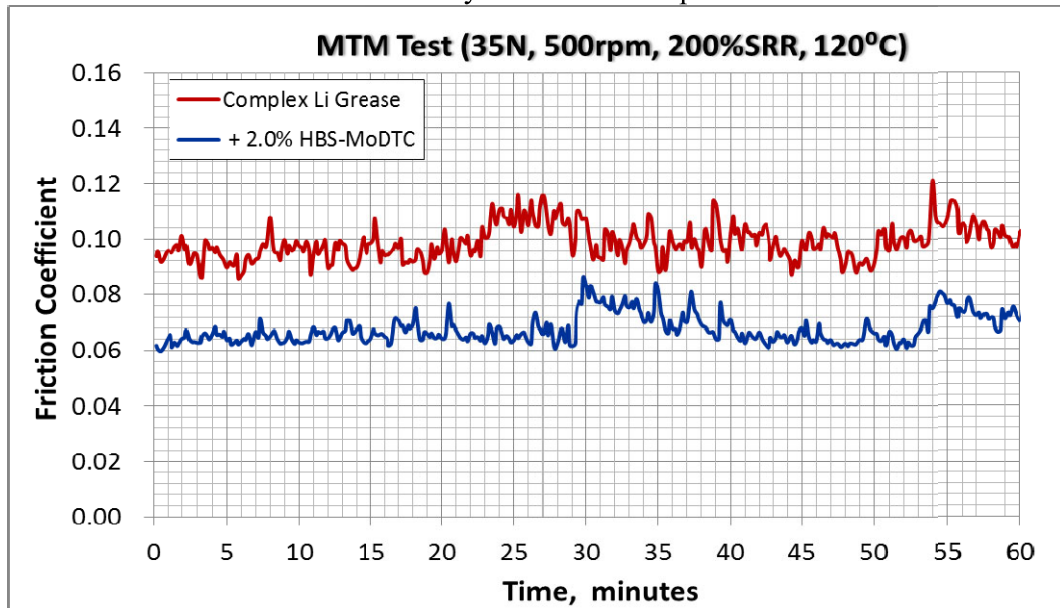


Figure 8. The FR performances of the complex Li grease with and without HBS-MoDTC by MTM timed step test at 120°C

From Figures 7 and 8, it can be found that, HBS-MoDTC does not reduce the friction significantly, but it indeed smooths the friction at low temperature (60°C, Figure 7), but at high temperature (120°C, Figure 8), HBS-MoDTC reduce the friction significantly, which ds well with the correspo

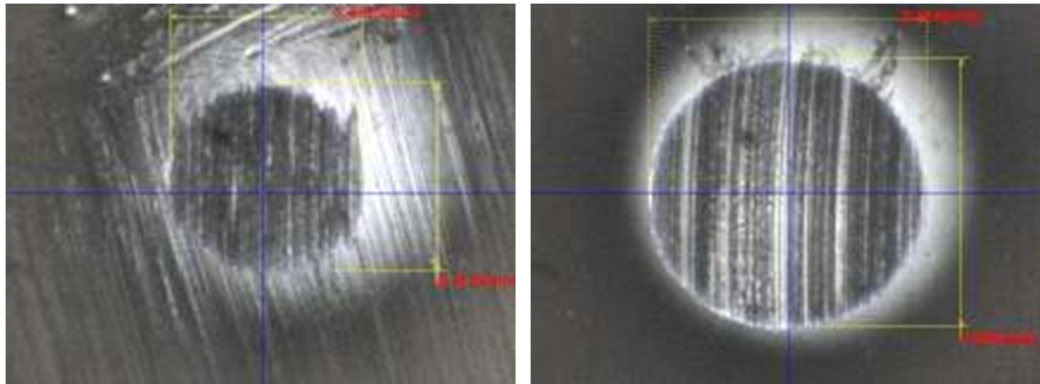
four ball friction data in Figure 6. Also again, same as in Figures 4 and 5 (MTM Stribeck curve at low and high temperature), the temperature plays a crucial role for HBS-MoDTC to develop its FR performance in lubricants.

3.6 Tribological performances with EP additive in greases

As showed in Table 3, HBS-MoDTC is an excellent FR and good AW additive for greases, but it does not exhibit EP performance, and just maintains the same weld load as the base greases. To obtain a balanced overall EP, AW and FR performance, it is necessary to consider the combination of HBS-MoDTC with EP additives. Sb/ZnDTC is an excellent EP additive in increasing four-ball weld load and Timken OK load ^[10-11]. In this paper, the combination of HBS-MoDTC and Sb/ZnDTC is investigated. Sb/ZnDTC and MoDTC were added into the polyurea base grease, and the tribological performances were evaluated by four-ball friction and wear tests. The experimental results are given in Table 4.

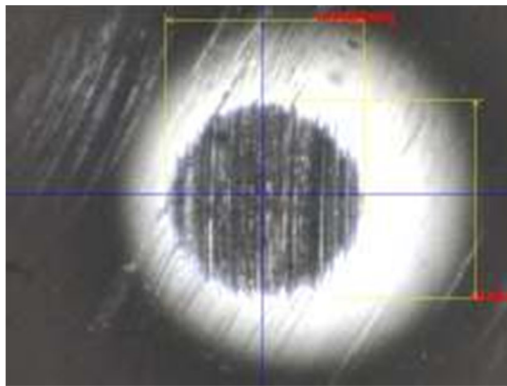
Table 4. The EP, AW and FR Performances of Sb/ZnDTC with MoDTC in Calcium Sulfonate Complex Grease				
	Friction and Wear Test (40Kgf, 1200rpm, 75°C, 60min.)		EP Test	
	Wear Scar,, mm	Average Friction Coefficient	LNSL, Kgf	Weld load, Kgf
Polyurea base grease	0.423	0.089	107	250
+ 2.0% HBS- MoDTC	0.446	0.067	95	250
+ 3.0% Sb/ZnDTC	0.614	0.106	95	400
+ 2.0% HBS- MoDTC +3.0% Sb/ZnDTC	0.410	0.066	95	400

From Table 4, it can be found that, the EP additive, Sb/ZnMoDTC carries a good EP performance with significant increase in the weld load, but its AW performance is bad with a significant size increase in the wear scar, but the combination of HBS and Sb/ZnDTC gives excellent EP, AW and FR performances simultaneously. The wear scars and the friction coefficients of the polyurea grease with MoDTC and/or Sb/ZnDTC are shown in Figures 9 and 10.

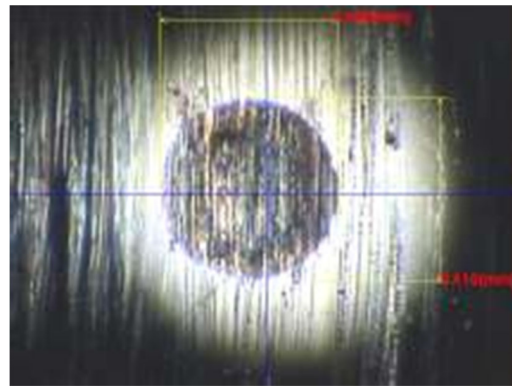


Polyurea base grease

Base +3.0% Sb/ZnDTC



Base +2.0% HBS-MoDTC



Base +3.0% Sb/ZnDTC + 2.0% HBS-MoDTC

Figure 9. Four-ball wear scars by polyurea grease

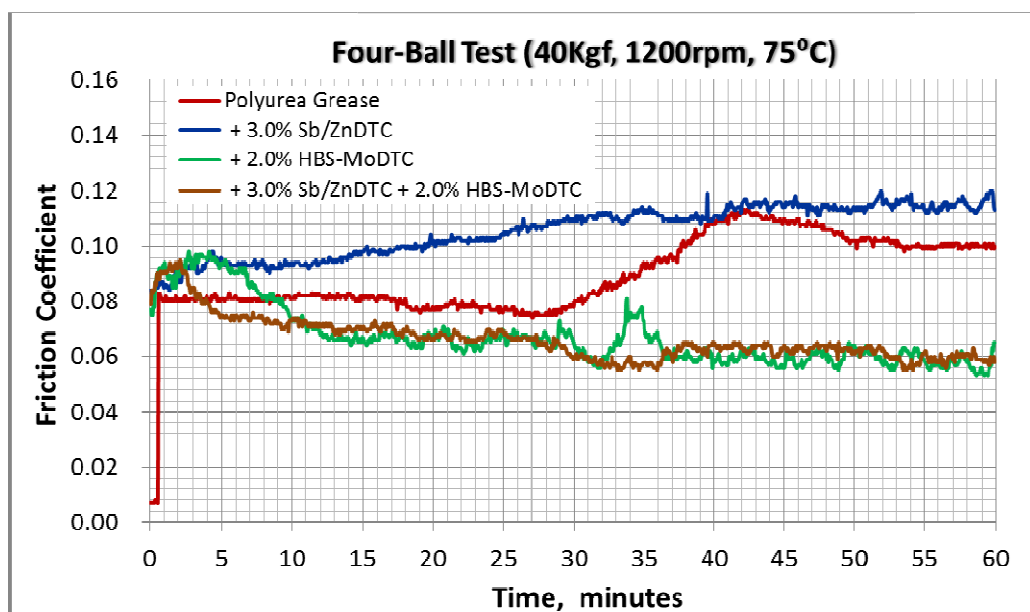


Figure 10. The FR performances of the polyurea grease with HBS-MoDTC and/or Sb/ZnDTC by Four-Ball test

It can be seen from Figures 9 and 10 that, in the polyurea grease, the combination of HBS-MoDTC and Sb/ZnDTC (as EP additive) could achieve excellent FR and AW performances, while keeping the high EP properties (weld load, from 250Kgf to 400Kgf).

3.7 Copper corrosion test

2.0% HBS-MoDTC and 0.2% tolutriazole derivative (as metal deactivator) were added into the complex Li grease, and the copper corrosion tests of the resultant greases were done at 100°C for 24 hours. The copper strips are classified as 1b and 1a for the grease containing HBS-MoDTC without and with the tolutriazole derivate respectively. Thus, HBS-MoDTC does not result in obvious copper corrosion in the grease.

4 CONCLUSIONS

- (1) Four-Ball test shows, Liquid MoDTC with Highly Branched Alkyl Groups and Highly Sulfurized Core (HBS-MoDTC), exhibits excellent Antiwear (AW) and Friction-Reducing (FR) performances in lubricating oil. MTM Stribeck curve test indicates, HBS-MoDTC can reduce the oil's friction under boundary and mixed lubrications at high temperature.
- (2) Four-ball test indicates, HBS-MoDTC possesses excellent friction-reducing performances in complex Li grease, polyurea grease and complex Ca sulfonate grease, and good antiwear performance in complex Li grease. MTM timed step test shows, under sliding dominated mixed lubrication, HBS-MoDTC can smooth the grease's friction at low temperature, and reduce the friction significantly at high temperature.
- (3) The combination of HBS-MoDTC with EP additive, Sb/ZnDTC, achieves a balanced comprehensive EP, AW and FR performances in greases.
- (4) HBS-MoDTC does not result in obvious copper corrosion in grease.

Reference

- [1] Mitchell PCH, "Oil-Soluble Mo-S Compounds as Lubricant Additives". *Wear*, 100:281-300(1984).
- [2] Gondo S, Yamamoto Y., "Mechanism of the Surface Film Formation of Molybdenum Dithiocarbamate (MoDTC) and Effect of Rubbing Materials". *Japan J Tribol*, 36(3):323-333(1991).
- [3] Graham J, Spikes H, Korcek S., "The Friction Reducing Properties Of Molybdenum Dialkyl dithiocarbamate Additives: Part I - Factors Influencing Friction Reduction". *TribolTrans*, 44(4):626-636 (2001).
- [4] Johnson M, Jensen R, Korcek S., "Additive Interactions and Depletion Processes in Fuel Efficient Engine Oils". SAE Technical Paper 971914, 1997.
- [5] Yamamoto Y, Gondo S., "On Properties of Surface Films Formed with Molybdenum Dithiocarbamate (MoDTC) Under Different Conditions". *Japan J Tribol*, 36(3):309-321 (1991).

- [6] A. Morina et al., “ZDDP and MoDTC interactions in boundary lubrication—the effect of temperature and ZDDP/MoDTC ratio”, *Tribology International* / 2006, 39(12):1545-1557.
- [7] Yasushi Kawamura et al... “Grease composition for constant velocity joints”. US patent 6,894,009 (2005).
- [8] Lansdown A R. Molybdenum Disulphide Lubrication. New York, Elsevier, 1999.
- [9] Patel Mihir, Gatto Vincent, Tynik Robert, Wallack William., “Influence of Sulfurization Level and Amine Branching on the Stability, Solubility and Tribological Performance of MoDTC”. STLE 70th Annual Meeting, Dallas, TX, May 2015.
- [10] Kevin Chase, Gaston Aguilar., “Metal Dithiocarbamates: A ‘New’ Approach to ‘Old’ Technology”. NLGI 73rd Annual Meeting, Lake Buena, 2006.
- [11] Aili Ma, Minli Gu, Junbing Yao and Patel Mihir, “The Performances of Antimony/Zinc DiamylDithiocarbamate as Grease Additive”, NLGI 83rd Annual Meeting, Virginia, 2016.

A comprehensive approach to replace Group I over a wide range of viscosities

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Abstract

The total production of paraffinic Group I is estimated to fall to about 40% of the total base oil production by the year 2020 and some estimate it down to less than 30%. Regardless the degree of the fall, a serious consequence of these changes is that the offering of the base oil industry is no longer optimized for the industrial lubricant and grease industry requirements. The deficits in solvency and viscosity might not be readily substituted by the highly refined paraffinic Group II and Group III base oils.

Higher polarity, aromaticity and sufficient solvency power constitute, beside the viscosities, the most essential parameters for process oils, metal working fluids, hydraulic oils and greases.

Within the frame of this work, a new range (NR) of base stocks, very similar to paraffinic Group I, have been developed by carefully blending naphthenic and paraffinic base oils. This new range of base oil is closely matching a broad selection of paraffinic Group I base oils, from Solvent Neutral 70 to Solvent Neutral 600 with retained kinematic viscosity and aniline point, and with improved pour point.

In order to verify some of the characteristics of these new base oils some comparative studies have been conducted where, in this paper, response of pour point depressant, the elastomer compatibility and formulation of a hydraulic fluid and lithium grease respectively, are going to be discussed.

The outcome emphasizes that this new range of base oils may replace conventional paraffinic Group I in various industrial application, in many cases without needing any significant reformulation efforts. Furthermore, the rheological characterization and measurements of the flow pressure of the greases at low temperature emphasis the improved mobility of the grease. Last but not least, the model hydraulic fluid based on NR grades demonstrates that the usefulness of the new base oil range within industrial lubes.

1. Introduction

The global ongoing rationalization of paraffinic Group I production and its potential impact on the future availability of paraffinic Group I has led several lubricant formulators to start evaluating alternative products. Almost 2 million metric tons of paraffinic Group I capacity disappeared during the last year.

Company	Refinery	Capacity (k ton)	Closure year
Colas Group	Dunkerque (France)	260	2015
Total	Gonfreville (France)	240	2015
Kuwait Petroleum	Rotterdam (Netherlands)	232	2016*
Shell	Pernis (Netherlands)	355	2015
Nynas	Harburg (Germany)	165	2015
Lukoil	Nizhni Novgorod (Russia)	220	2015
CPC-Shell	Kaohsiung (Taiwan)	270	2015
Safor	Durban (South Africa)	150	2015
ExxonMobil	Beaumont (Texas)	500	2016*
Total		2392	

Table 1. shows the closed and announced* closure of paraffinic Group I refineries

The rapid changes in the base oil market, driven mainly by the technical demand from high

performance automotive engine oil applications, are impacting all lubricant applications.

The viscosity range covered in paraffinic Group I is wider, providing much needed high viscosity to industrial gear oils, greases and engine oils. The solvency offered by paraffinic Group II and Group III, with rapidly increasing aniline points, and lower aromatic carbon type content, is far lower than that of Group I base oils. Thus, some negative effect on the blending of industrial lubricants based on Group II or Group III base oils with existing Group I based industrial product can be foreseen, and have indeed been reported from the field.

The worst case scenario could be a massive reformulation process based on trial errors which of course will be a costly and time consuming process. Hence, the questions are: Can we escape this reformulation process in the future? Can we hope that we are going to see a new shift back to a rebuilding of paraffinic Group I refineries? The most probable answer to both questions, is NO! Hence, what to do? What is the most cost efficient way out of this dilemma?

We at Nynas believe that due to the long term availability of paraffinic Group II, Group III and naphthenic oils, it is most probably that a mixtures of naphthenic oil with paraffinic Group II and Group III is a realistic, cost effective and fast solution for substitution of paraffinic Group I in various industrial applications.

This paper suggests alternatives, here called **NR**, that could be used as “drop in” or with minor adjustment as a replacement to paraffinic Group I in industrial lubricants and grease lubricated applications.

Experimental work

Nynas has created a new range of products with Kinematic Viscosity (KV), Viscosity Index (VI) and Aniline Point (AP) closely matching those of existing Solvent Neutral Group I base oils. This paper will cover some results related to the following areas:

- Response of Pour Point Depressant (PPD)
- Elastomer compatibility with respect to Nitrile Butadiene Rubber (NBR).
- Formulation and characterization of a model hydraulic fluid (HM 46)
- The behavior of two NR grades (500 & 600) in the conventional lithium grease compared to a paraffinic oil Group I (SN 500)

Response of Pour Point Depressant (PPD)

The treat rate response of a Pour Point Depressant (PPD) additive was investigated in order to better understand the properties of the NR oils. Specifically, a treat rate comparison study was made in order to elucidate the interplay between the naphthenic base oil components, and the added PPD additive.

We prepared samples, containing the six NR oils (70 to 600) and 0.25 % of PPD additive of a widely available global brand and for the reference Solvent Neutral 150 (SN 150) has been used. We found that the already good pour point of NR oils (compared with paraffinic Gr I) improves significantly, see Figure 1.

This indicates an improved low temperature performance, and a possible cost-out in formulations were PPD are going to be used.

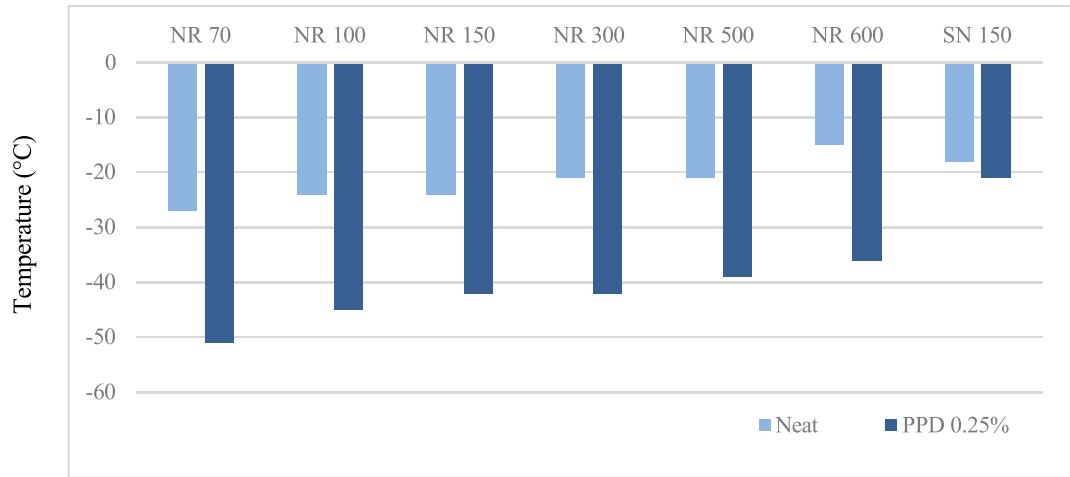


Figure 1. PPD response in the New Range base oils (NR 70 to 600) in comparison to SN 150.

Hence, an improved low temperature performance, and suggested a possible cost-out in e.g. formulations such as in hydraulic oils, shock absorber or other applications were PPD may be going to be used.

Elastomer compatibility of the base oils

Elastomer compatibility is a key property of base oils, and finished lubricants such as in hydraulic and lubricating greases. Four reference elastomer materials: two NBRs, one H-NBR and one CR, have been investigated with respect to mass and hardness changes upon immersion for 168 h at 100 °C in the new range base oils, and reference base oil.

The purpose of this test series was to establish that the new range base oils have similar effect on the elastomer materials as the reference base oil, a standard Group I, SN 150. As one example, the influence on hardness and mass of NBR, 28% Acetonitrile (AN) for the all the oils are shown graphically for hardness change, Figure 2, and mass change, Figure 3.

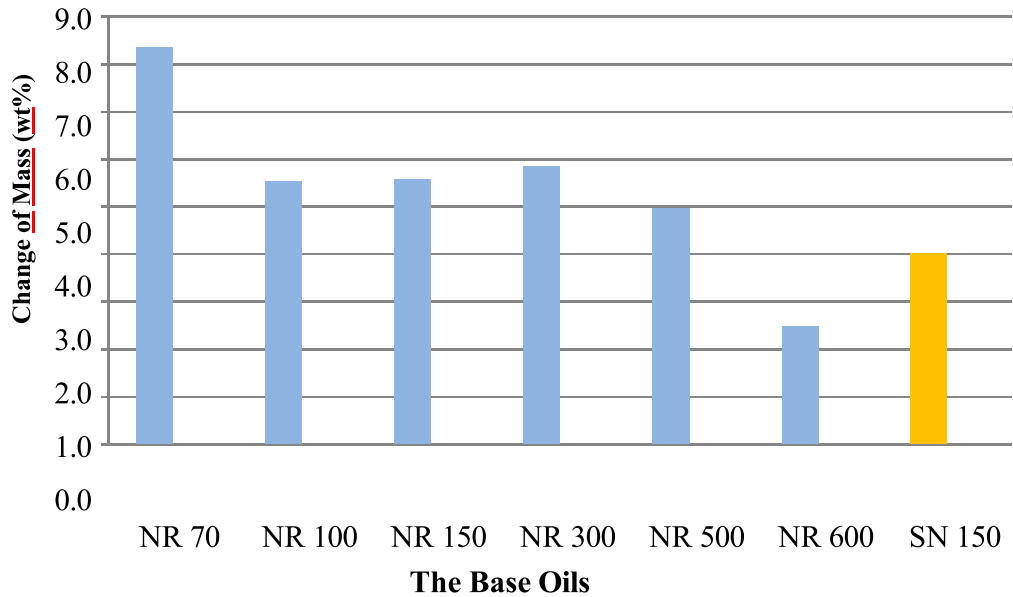
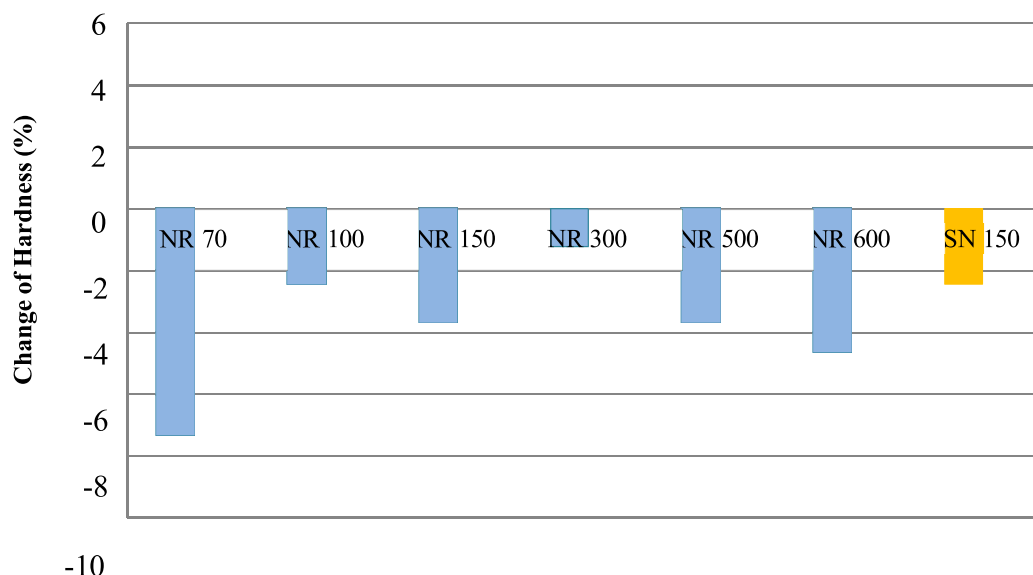


Figure 2. Hardness change of NBR 28% AN, NR 70 to 600, benchmarked against SN 150.

In Figure 2, the direction of change, moderate loss of hardness (moderate softening), is the same for all base oils, and the magnitude is small, below -5%. The commonly permissible variance of hardness is +/- 10 %, e.g. in DIN [51524].



The Base Oils

Figure 3. Mass change of NBR 28% AN, NR 70 to 600, benchmarked against SN 150.

Formulation and characterization of model hydraulic fluid (HM 46)

Hydraulic fluids are a very important lubricant segment, representing ca 10% of the global market at four million metric tonnes per year. Thus, we were keen to demonstrate the usefulness of NR base oils in this core application, and have concluded a model hydraulic fluid formulation study which shortly will be described in this paper.

A model hydraulic formulation, with a viscosity of 46 mm²/s, here after called HM 46 were prepared by using 98.9 wt.% of NR base oil and a readily available hydraulic fluid additive package (0.85 wt.%) and likewise readily available PPD (0.25 wt.%) from global commercial suppliers. The treat rate of the additive package follows the recommendation. The PPD treat rate, 50% lower than what is usually needed in Group I base oils. The new model hydraulic fluid, and one commercially available reference hydraulic fluid (M 46), were analyzed with respect to viscometric properties, pour point and flash point. Oxidation stability of our model fluids was determined by RPVOT [7]. A pass level is set to >300 minutes in the Swedish Standard [7]. In general, all properties more or less confirm to the expectations of hydraulic fluids based on our new base oils. Pour points are lower. Table 2 for the general properties of the industrial hydraulic fluids.

Characteristics	Test Method ASTM	HM 46	M 46 (ref.)
KV @ 40 °C	D 445	46,2	45,8
KV @ 100 °C	D 445	6,75	6,6
VI	D 2270	99	94
Density (g/ml @ 15 °C)	D 4052	0,873	0,879
FP COC (°C)	D 92	226	244
PP (°C)	D 97	-39	-24
RPVOT (min)	D 2270	420	nd*

*=not determined

Table 2. general Industrial hydraulic fluid properties.

To further probe the physical properties, filterability [ii], foaming tendency [iii], air release [iv], and

demulsibility [v] was investigated. These properties are influenced by the base oils, the interplay of the additives, and by the system history as the fluid ages under use, or become contaminated by dirt, dissolved substances, process fluid or other lubricants.

In Table 3, the base line properties of the hydraulic fluid, HM 46 is given. For reference, also ISO 111 58, MH [vi] limiting values are presented. The resulting data are in all aspects very promising, and well below the threshold limit values of the ISO 111 58 standard. Very fast air release, and fast and complete demulsibility stand out in this respect.

Test	Unit	HM 46	ISO ^b
Filterability I/II ^a		98/97	80/60
Foam I @24 °C	ml/ml	0/0	150/0
Foam II @93°C	ml/ml	0/0	80/0
Foam III @24°C	ml/ml	0/0	150/0
Air Release	min	3,9	10
Demulsibility	min	10	30
Oil/water/emuls.	ml	40/38/2	40/37/3

a= Dry (no added water), Applied Pressure 100 kPa, b= ISO 111 58, HM

Table 3. Physical properties of the model Industrial hydraulic fluid (HM 46).

The behavior of two NR grades (500 & 600) in lithium grease compared with a paraffinic oil Group I (SN 500) It is well known that Solvent Neutral 500 (SN 500) is traditionally used for preparation of lithium grease. Hence, this fluid is used as a reference in comparison with NR 500 and NR 600. The characteristics of these base oils can be seen in Table 4.

Characteristics	Unit	Test method	SN 500	NR 500	NR 600
Appearance			Clear & Bright	Clear & Bright	Clear & Bright
Density, 15°C	g/dm ³	D 4052	889.6	889.0	876.0
Viscosity, 40°C	mm ² /s	D 445	101	100	120
Viscosity, 100°C	mm ² /s	D 445	10.9	10.2	12.6
Viscosity Index	mm ² /s	D 2270	91	79	98
Flash Point, PM	°C		232	226	250
Refractive Index, 20 °C		D 1747	1.488	1.487	1.481
Sulphur	%	D 2622	0.944	003	0.02
Carbon-Type composition		D 2140			
CA	%		3.8	3	1
CP	%		66.7	61	69
CN	%		29.5	36	30
Viscosity-Gravity-Constant		D 2501	0.821	0.821	0.800
Pour point	°C	D 97	-12	-21	-15
Aniline Point	°C	D 611	104.3	111	123
IR, CA	%		7.8	6	2
Color	rating	D 1500	1.7	0.5	1
Copper strip, 100°C/3h	rating	D 130	1	1	1
Total Acid Number	mg KOH/g	D 974	<0.01	<0.01	<0.01

Table 4. The characteristics of the base oils used.

As it can be seen in Table 1, NR 500 and 600, in comparison to SN 500, have significantly lower Sulphur content, lower pour point and lighter in color! Thus, it is foreseen that theses improved properties will, in many cases, improve the performance and quality of the fully formulated greases.

Results ad Discussion

The grease samples have been prepared in an open kettle in which the base oils described in Table 1 were used. The target consistency for these samples was NLGI grade 2. Notable is that the greases used in this study do not contain any additives.

Characteristics	Unit	Test Method	Grease A	Grease B	Grease C
Base oil			SN 500	NR 500	NR 600
Thickener content	wt%		7.98	7.48	9.39
Penetration unworked	mm ⁻¹	ASTM D 217	285	282	278
Penetration (after 60 str)	mm ⁻¹	ASTM D 217	279	279	280
Penetration (after 10 ⁵ str)	mm ⁻¹	ASTM D 217	300	309	305
Dropping point	°C	IP 396-02	199	200	198
Cu-corrosion	rating	ASTM D 4048	1b	1a	1a

Table 5. Some properties of the grease samples

Based on the measured properties of the greases, shown in Table 5, it can be concluded that all three grease samples show good shear stability despite having different thickener content; sample C (based on NR 600) highest and sample B (based on NR 500) the lowest.

The most interesting part of this evaluation was to study the impact of significantly better pour point in NR 500 and 600 on the mobility of the greases compared with SN 500 based.

Flow pressure of the lubricating grease, measured according to DIN 51805, is widely recognized method as a relevant way to simulate pumpability of the grease in the laboratory. Hence, the flow pressure for the grease samples at various temperatures have been measured, the required pressure for each sample at six different temperatures are shown in Figure 4.

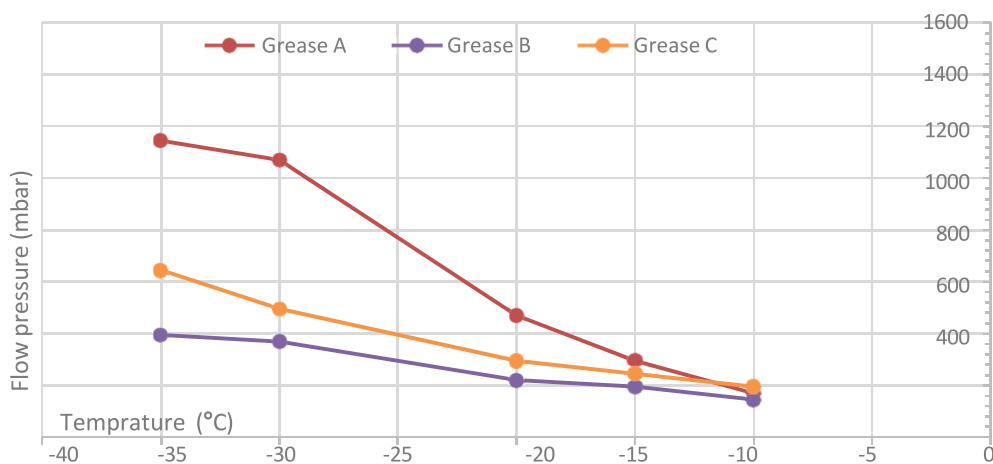


Figure 4. The required flow pressure (mbar) as a function of temperature.

The outcome emphasizes excellent performances for the two NR based greases. In fact, Solvent Neutral 500 based grease requires almost three times higher pressure than NR 500 to be mobile.

Rheological measurements

It is well known that lubricating grease is a viscoelastic material, in other words a material with a viscous part (the base oil) and an elastic part (e.g. the thickener). Parameters such as temperature and shear stress affect the oil and the thickener differently. Hence, mobility of the grease sample under controlled conditions can generate valuable information. For example, storage modulus (G') or complex modulus (G^*) of the grease can be interpreted as the real consistency of the grease, at the applied condition.

In an attempt to study the thermal behaviour of the greases the oscillatory program of a rotational rheometer has been used. The first step in the characterisation was to find out the so-called linear viscoelastic region (LVER) by applying a strain sweep program in which the frequency and the temperature were kept constant (10 Hz and 25 °C respectively), and then the strain was increased logarithmically from 0.01 to 1000%, see Figure 5.

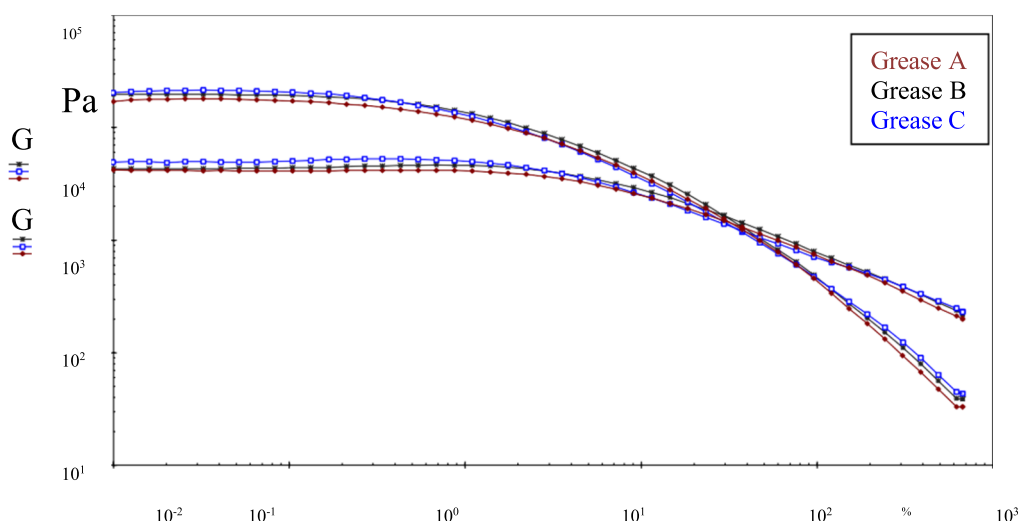


Figure 5. Storage modulus (G') and Viscosity modulus (G'') vs. Strain for the three grease samples at 25 °C

Figure 5 indicates that grease A (SN 500 based) is slightly thinner (lower G') and has shorter LVER than Grease B (NR 500 based) and C (NR 600 based) despite of the fact that all three greases have the same NLGI grade. However, the next step in this part of the study was to measure the change of the complex modulus (G^*), which is a sum of storage modulus and viscous modulus, over a wide range of temperature while the shear stress (10 Pa) and the frequency (10 Hz) have been kept constant. In order to conduct this evaluation more accurate it was decided to divide it in two steps;

Step 1) the low temperature (from +25 down to -25 °C) and Step 2) the high temperature (from +25 to +120 °C).

Step 1) The low temperature behaviour: This type of measurement reveals the degree of stiffness of a grease when the temperature is reduced. Thermal weep program was run from +25 to -25 °C.

The obtained data is shown in Figure 6.

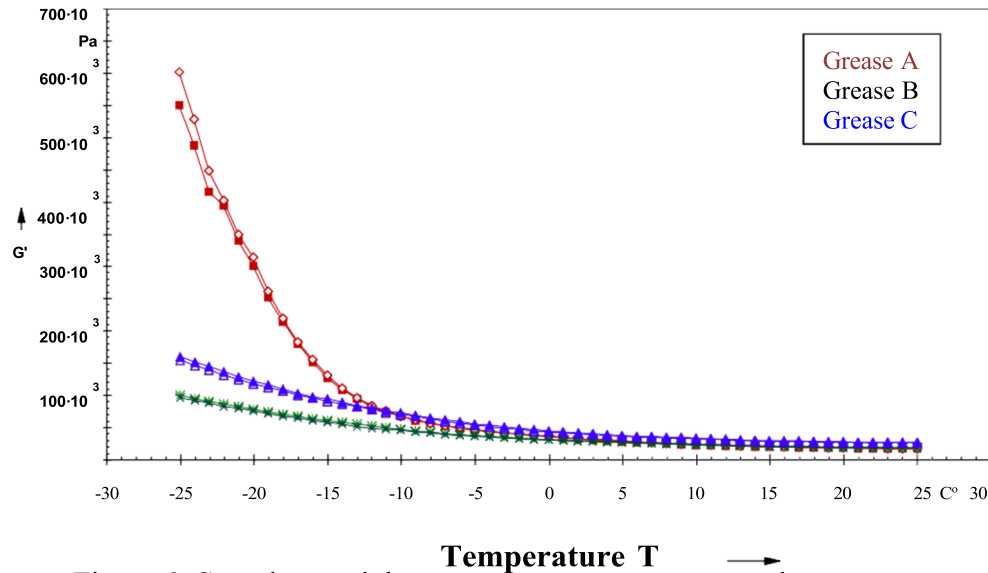


Figure 6. Complex modulus vs. temperature at constant shear stress.

Figure 6 above reveals preferably information such as:

- Grease A (SN 500 based) shows a faster degree of increased complex viscosity than the others. This increase is accelerating as applied temperature approaches the pour point of the base oil which in turn confirms the poor results from Flow pressure measurements, discussed earlier in this paper.
- Grease B and Grease C show same degree of the thickening effect within the applied temperature range and significantly better performance than Grease A.

Step 2: The high temperature behaviour: This type of measurement is targeting the degree of softening of a grease when the temperature is increased. Thermal sweep program was run from +25 to +120 $^{\circ}\text{C}$. The obtained data, shown in Figure 7, indicates that Grease C (NR 600 based) softens less than the other two greases, most probably due to the higher thickener content.

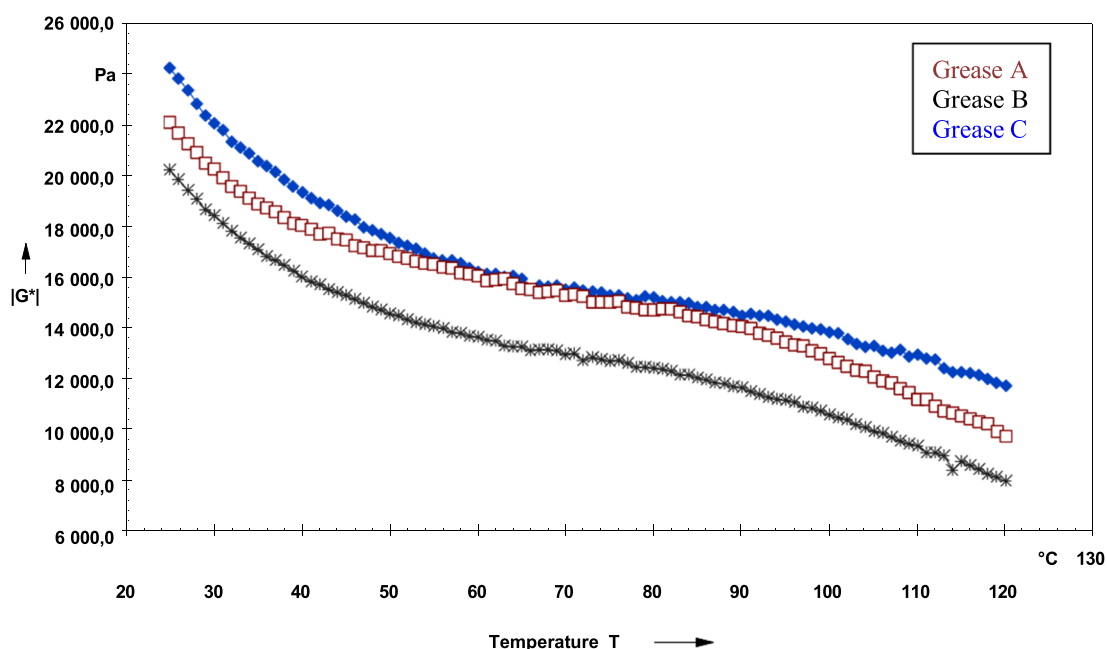


Figure 6. Complex modulus vs. temperature at constant shear stress.

Summary

The results suggest that it is indeed possible to reproduce the key features of Group I base oils, and to formulate lubricating greases and other industrial related formulations based on these.

The new range of Group I replacement fluids thus offers, besides the significant low temperature mobility, a convenient way around compatibility, solubility and extensive re-formulation issues that industrial lubricant blenders otherwise must conquer when formulating in base oils other than Group I, which will gradually be less readily available in a changing base oil market.

Reference

1. DIN 51 524 “Minimum requirement of hydraulic fluids” Part 2 and 3
 2. Phadke. M., “Synthetic Base Stocks Market –Market Trends and Outlook”, Proceedings of The 2015 European Base Oils & Lubricants Summit”, Vienna, September 2015
 3. ISO 1817:2015(E), “Rubber, vulcanized or thermoplastic- Determination of the effect of liquids”
 4. ISO 6072:2011(E), “Rubber –Compatibility between hydraulic fluids and standard elastomeric materials”
 5. www.nynas.com
- [i] ASTM D 2272-11 method A, “Standard Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel”
- [ii] ISO 13357-2:2005, “Petroleum products -- Determination of the filterability of lubricating oils -- Part 2: Procedure for dry oils”
- [iii] ASTM D 892-13, “Standard Test Method for Foaming Characteristics of Lubricating Oils”
- [iv] ASTM D 3427-12, “Standard Test Method for Air Release Properties of Hydrocarbon Based Oils”
- [v] ASTM D 1401-10, “Standard Test Method for Water Separability of Petroleum Oils and Synthetic Fluids”
- [vi] ISO 111 58:2009 ” Lubricants, industrial oils and related products (class L) -- Family H (hydraulic systems) -- Specifications for categories HH, HL, HM, HV and HG”