

NLGI THE SPOKESMAN

Serving the Grease Industry Since 1933 – VOL. 82, NO. 2, MAY/JUNE 2018

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ON THE COVER

We hope you have
an enjoyable and
relaxing summer!

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PRESIDENT'S PODIUM



Tyler F. Jark, *Chair*

NLGI GREASE PRODUCTION SURVEY

The 2017 NLGI Grease Production Survey (GPS) is almost complete and will be available after the June 9th-12th Annual Meeting in Coeur D'Alene, Idaho. As always, this year's survey results will be loaded with all of the important data upon which you've come to rely. NLGI members and survey participants will continue to receive the PDF survey results at no cost; additionally, those looking to customize the data will benefit from the time-saving Excel file format available for purchase on the NLGI website.

How much grease was manufactured in 2017? Are calcium greases increasing their market share? Are there discernable changes in lithium based greases? The NLGI GPS has the answers.

The NLGI Production Survey counts the *global* production of grease, providing a snapshot of growth (by thickener type and base oil type) and demographic (by thickener type, base oil type, and global region). Both provide an opportunity to stand up and be counted, to make a difference, to have your voice (or your production) be heard. Has grease continued to lubricate the global economy? The GPS has the answers!

The NLGI Grease Production Survey continues to be the single most comprehensive global report on grease production. The 2016 survey reflected a 1.4% global increase to 2.57 billion pounds. Did 2017 see another year of growth? Not surprisingly, mineral base oils still represent the primary fluid used globally to produce greases. This is just the tip of the information iceberg contained in the NLGI Grease Production Survey. The Grease Production Survey continues to be one of the most important member benefits provided by the NLGI to its membership. The information in the Grease Production Survey Report is a valuable source of past results and can be used as an indicator of future trends either globally or by region. This makes the Grease Production Survey Report a very useful strategic management and production tool.

The Grease Production Survey Report data for 2017 will be categorized by primary thickener types, base fluid types, and geographical region. These classifications can provide answers to many questions you may have regarding the grease industry:

- What tonnage of lithium soap grease is produced in my region of the globe?
- Are bio-based fluids increasing in percentage of grease production?
- Which region of the globe demonstrated the greatest year on year growth?

The NLGI Grease Production Survey has the answers. It is a wealth of useful information, structured and organized to assist in executing successful strategic decisions within the grease industry.

The value and accuracy of the NLGI Grease Production Survey requires your participation

and accurate reporting; we need your support. Through your active participation in next year's 2018 survey, we hope to attain a 100% participation rate, thereby reflecting the entirety of global grease production. Consequently, if you have not yet had the opportunity to participate in the NLGI Grease Production Survey, please contact Grease Technology Solutions at the address below:

Grease Technology Solutions LLC
 35386 Greyfriar Drive
 Round Hill, VA 20141-2392 USA
 Phone: 1-540-338-8040
 Fax: 1 540-338-8063
 Email: chuckcoe@grease-tech.com

Please note that the information received from individual companies is held in strict confidence by Grease Technology Solutions LLC. The NLGI Grease Production Survey Report is a valuable member benefit and your participation is integral to its continued success.

Tyler F. Jark, Chair



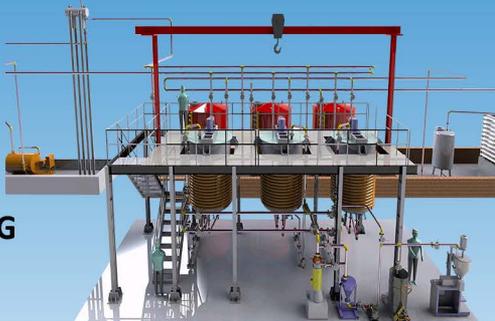
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Study of Tribological Behaviors of Polymer Greases with Fullerene-like Functionalized WS₂

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Abstract: There is a growing interest in the use of polymers as thickeners and rheology modifiers in lubricating greases. Nanoparticles of WS₂ are a well established EP and anti-wear additive for lubricants. In this work, lubricating greases were prepared from different types of polymers and a comparative tribological study was carried out with lithium grease.

These greases were formulated using fullerene-like nanoparticles of WS₂ functionalized with sodium hexametaphosphate. The tribological properties were evaluated using a four-ball tester, and coefficient of friction was determined using an Optimol SRV-III machine. The action mechanism of functionalized nanoparticles of WS₂ in polymer greases was established through analysis of the worn surface of balls with scanning electron microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDAX). The results show that the performance of WS₂ nanoparticles depends on the thickener system. The anti-wear and EP properties exhibited by WS₂ varies from polymer to polymer. Poor performance was observed with polyethylene (PE) thickener whereas performance of polypropylene (PP) and lithium greases was comparable.

1. Introduction

Polymers work as excellent thickeners and rheology modifiers for lubricating greases [1]–[6]. However, these greases have a comparatively higher wear rate than lithium and lithium complex greases, which is the biggest setback for polymer-thickened lubricating greases, especially those thickened with polypropylene (PP) and maleic anhydride grafted polypropylene (mPP) [7]. The conventional sulfur (S) and phosphorous (P) containing additives, such as zinc dialkyldithiophosphate (ZDDP), perform very well in lithium and lithium complex greases, but they are not very effective in polypropylene greases [7]. Conventional anti-wear and EP additives undergo complex physical and chemical reactions over the contact surface. During the friction process, a protective film is formed by physisorption, chemisorption and tribochemical reactions on the tribological contact surface, which is highly influenced by the interactions/synergism of the additives with the other components present in the system [8]–[10].

A plethora of published research is available on nanoparticles to investigate their effect on friction or wear properties in a variety of tribological contacts [11]–[15]. Inorganic fullerene-like metal dichalcogenides such as WS₂ show better tribological performance than carbon-based fullerenes [16], [17]. As additives, they significantly improve the tribological performance of lubricants [18]–[23]. Additionally, they are inert, nontoxic, nonmagnetic and highly resistant to oxidative and thermal degradation [24]. Unlike the S and P containing additives, these nanoparticles do not involve complex tribochemical reactions; rather, these particles are supposed to roll over the contact area, acting as a spacer to eliminate metal to metal contact between two mating metal surfaces. So, unlike ZDDP additives that are selective to thickener type, these nanoparticles are supposed to perform well in multi-component systems like greases, irrespective of the nature of the thickener.

The aim of this work is to study the tribological performance of fullerene-like nanoparticles of WS₂ functionalized with sodium hexametaphosphate [(NaPO₃)₆] under boundary lubrication as an additive in polymeric lubricating greases. In this work, the efficiency of these nanoparticle compounds in different polymer-thickened greases was tested under severe friction conditions. Coefficient of friction, four-ball weld load and wear were determined, and Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDAX) was used for analysis of worn surfaces after four-ball wear tests.

2. Experimental

2.1. Materials

Group I paraffinic mineral lubricating oil (Kinematic Viscosity 160 cSt at 40 °C) supplied by Indian Oil Corporation Ltd, India was used to prepare lubricating grease samples. PP and mPP sourced from Pluss Polymers Pvt. Ltd., Faridabad, India and linear low-density polyethylene (LLDPE), a product of Reliance Industries Ltd., India were used as thickeners. Melting temperature (T_m) and other physical properties of these polymers are given in Table 1. WS₂ functionalized with inorganic phosphates/sodium hexametaphosphate was sourced from a commercial additive supplier.

Sample	MFI (g/10 min)	Density	M_w	M_n	M_w/M_n	T_m (°C)
Polypropylene	1700	n.a.	1.20×10^5	3.8×10^4	3.2	161.5
Maleic anhydride grafted Polypropylene (mPP)	120	n.a.	1.42×10^5	5.1×10^4	2.8	160
Polyethylene (PE)	4.5	0.936	2.73×10^5	5.1×10^4	5.6	126

Table 1. Melt flow index (MFI), molecular weight (M_w , M_n), polydispersity (M_w/M_n), and melting temperature (T_m) of polymers.

2.2 Preparation of Greases

A gel-like dispersion of each polymer was prepared using a Sotalem reactor model RMP5005 through a batch process under nitrogen atmosphere. The contents were heated to between 200 and 210 °C with constant stirring at 150 rpm. After 1 h, the material was poured into a 20 litre size steel container and quenched with dry ice to between 70 and 90 °C. The material was then milled in a Frigmaires Colloid Mill to obtain grease. The processing and milling parameters for all the polymeric samples were kept identical. With the same percentage of thickener content, all the thickeners have different thickening tendencies. Hence, thickener proportion in the grease was adjusted to obtain target consistency (worked cone penetration) of 270 to 300 (1/10 mm). Four greases with different thickener proportions were prepared, and detailed compositions are given in Table 2. Lithium grease was prepared using 12-hydroxystearic acid in mineral oil in a Sotalem reactor model RMP5005 through batch process under pressure.

Grease	Thickener wt %	Unworked penetration (1/10 mm)	Worked penetration (1/10 mm)	Dropping Point (°C)
Polypropylene	18	217	270	143
Maleic anhydride grafted Polypropylene	15.5	231	287	143
Polyethylene	9	260	270	115
Li Grease	9	280	285	192

Table 2. Composition of greases, penetration values and dropping point values

2.3 DSC

Differential scanning calorimetry (DSC) was performed with a Mettler Toledo Instrument. Each test sample was weighed to about 10 ± 2 mg, sealed in standard aluminum pan and subjected to three heating cycles, first from 25 to 200 °C, then from 200 to 25 °C, and then from 25 to 200 °C at a heating rate of 20 °C/min in the first heating cycle and 10 °C/min in the second heating cycle; with nitrogen flow rate of 50 ml/min. The heat flow curve of the second heating cycle was taken for study.

2.4 Tribological Performance

The tribological behavior of all the greases was evaluated in steel/steel contacts using three types of testing methods - four-ball EP test, four-ball wear test and SRV friction test with at least two replicates for each sample.

Test method IP 239/07 was followed to study EP performance on a Stanhope-Seta four-ball EP lubricant testing machine at ambient temperature [one ball (AISI E 52100 steel balls, 12.7 mm diameter, Ra = 0.035 μm , and hardness RC 65-66) against a three-ball configuration in rotary motion; 1450 rpm].

Four-ball wear tests were carried out per ASTM D4172 test method on a Falex four-ball wear tester under similar configuration as the four-ball EP tester in rotary motion; 1200 rpm at 75 $^{\circ}\text{C}$; and a test duration of 60 min, in a sliding contact under lighter loads (392 N) than those used in the four-ball EP Test. Average wear scar diameter of the three stationary balls was calculated. A microscope with an accuracy of ± 0.01 mm was used to measure the WSDs of the balls.

Coefficient of friction was determined using an Optimol SRV-III tester [(AISI 52100 steel ball, 10 mm diameter) against a lower stationary block (AISI 52100 cylindrical steel block, 24 mm \times 7.9 mm; Ra of the block 0.08 μm)] in reciprocating sliding motion at 70 $^{\circ}\text{C}$, a frequency of 50 Hz, and a stroke length of 1 mm under step loads of 50, 100, 150, 200, 250, 300, 350 and 400 N with a test duration of 5 min under each load.

2.5 SEM and EDAX

At the end of the four-ball wear test, the lower balls were cleaned in petroleum spirit (60-80 $^{\circ}\text{C}$), and SEM and EDAX studies were performed at room temperature on the worn surface of steel balls using a Hitachi S-3400N SEM.

3. Results and Discussion

3.1 DSC

DSC measurements were carried out for all polymer samples, and the thermograms of samples corresponding to the second heating cycle are displayed in Figure 1. A single endothermic peak appears at 132 $^{\circ}\text{C}$ for LLDPE, which can be attributed to its characteristic melting temperature. The fusion endotherms of PP and mPP show the characteristic melting peaks at 161.5 and 160 $^{\circ}\text{C}$ respectively. The melting temperature and fusion enthalpy values for all the above polymers are reported in Table 1.

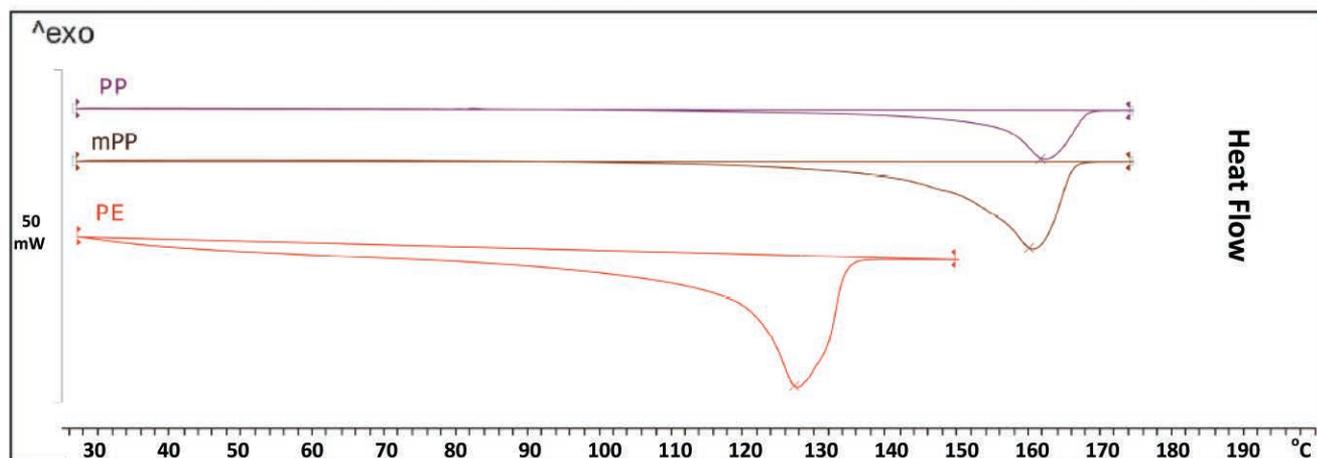


Figure 1. DSC heat flow chart of PP, mPP and PE polymers

3.2 Tribological Properties

The WSDs of additive and additive-free greases are shown in Figure 2. The results indicate that the wear performance of additive-free greases depends on the thickener type in the greases. Among all, two polymeric thickeners (PP and mPP) show higher WSDs, and WSD of PE is similar to conventional lithium lubricating grease. Moreover, the WSDs of PP and mPP greases (1.1 mm) are also higher than the WSD of base oil itself (0.9 mm), whereas the WSDs of PE

and lithium grease are the same as that of the base oil. Performance of lithium grease is consistent with earlier findings. PP and mPP in base oil behave as pro-wear components. The Authors hypothesized that under pressure, polymers flatten and oil is squeezed out of the contact zone, and then polymers retract and shrink back when pressure is released, leaving a starved surface and leading to large WSD.

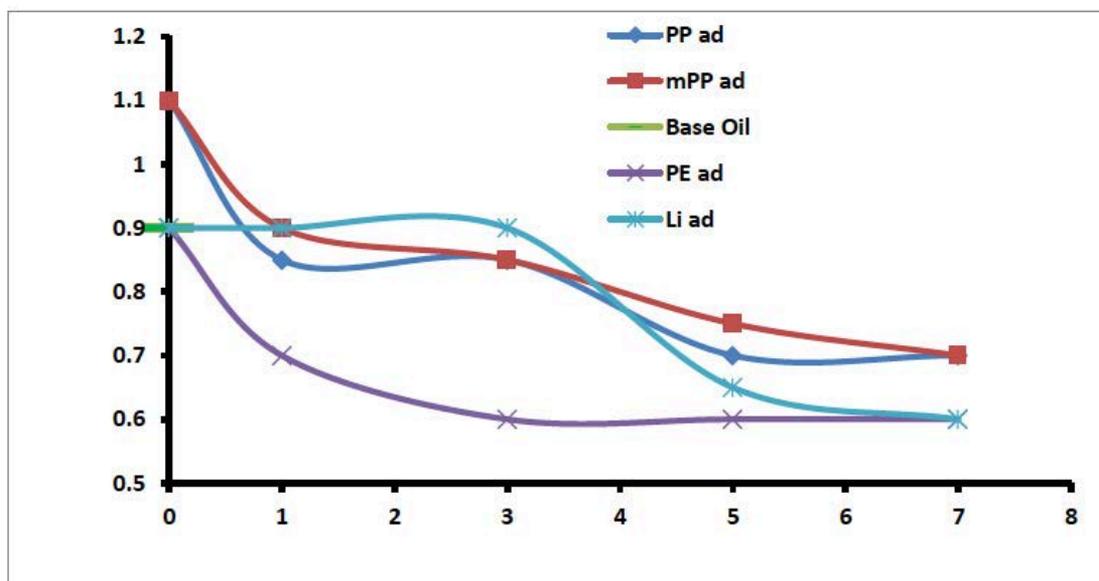


Figure 2. Wear scar diameter (Y-axis, mm) after four-ball wear tests with respect to additive concentration (X-axis, wt% WS₂)

In order to find the optimum concentration of WS₂ for obtaining the best tribological performance, several percentage compositions (1, 3, 5 and 7 wt%) of WS₂ nanoparticles were tested for four-ball wear performance. Figure 2 shows that addition of 5% or more nanoadditive was required to reduce the WSD as compared to base greases. Only PE grease showed improvement in wear at minimum additive concentration (i.e., 1%) and consistent improvement in WSD with increasing additive concentration. The best result for the nanoadditive was obtained in PE grease. PE and lithium greases have similar WSDs when the additive concentration is between 5 and 7%. PP and mPP thickened greases showed marginal improvement with low additive concentrations. Above 5% additive, PP and mPP grease showed good improvement in wear but comparatively less improvement than PE and lithium greases.

In the present study, the anti-wear performance of all the thickeners including lithium soap thickener is very good with the functionalized WS₂ nanoadditive. Performance was not similar with all the thickeners quantitatively, but was substantially good as compared to the ZDDP additive [7]. Unlike S and P type additives, which involve complex tribochemical reactions to produce tribofilms to prevent wear between the rubbing metal surfaces, nanoadditives present between the metal surfaces prevent the direct contact between them and thus prevent wear by acting as nanosized bearings [25]. The nanoadditives are more effective for the thickeners that interfere with the tribochemical reactions, thus inhibiting the anti-wear activity of the additives. On the other hand, the lubrication mechanism of this nanoadditive is based largely on physical phenomena. Thus, polymer-thickened greases like PP and mPP, which show the least anti-wear property with S and P type additives [7], showed good anti-wear response to above 5% functionalized WS₂ additive.

3.3 Coefficient of Friction and Four-Ball Weld Load

Figure 3a shows the coefficient of friction of all the base greases, and Figure 3b shows the COF of the greases additized with 5% functionalized WS₂. It is evident from the figures that the base greases show variable and very poor COFs even at a very low load of 50 N. PP thickened base grease could not sustain even a 50 N load and failed. mPP, PE and lithium greases failed at 150, 300 and 350 N, respectively.

Lithium base grease is best among all the base greases studied. Upon addition of 5% WS₂ nanoadditive, frictional performance of all the greases except PE grease improved substantially and did not fail even at a higher load of 400 N. PE thickened lubricating grease showed unexpected performance and failed at a load of 400 N. The carbon residue found on the SRV disc (Figure 4e) indicates the degradation of PE thickener component, and it is speculated that the temperature of the contacting metal surface lubricated with additized PE grease rose above >300 °C, causing thickener and additive degradation. Rapoport [26] studied fullerene-like nanoparticles of WS₂ in lubricating oil and reported that the performance of the additive diminished when the temperature of the contacting metal surfaces rose above 320 °C or above the oxidation temperature of the nanoadditive. However, more work is required to strengthen this hypothesis.

Similar performance trends were observed in anti-scuffing properties of all the greases. PP, mPP and lithium greases showed highest improvement in scuffing load, i.e., from 160/180 to 800 kg. PE grease showed slightly less improvement in scuffing load, i.e., from 180 to 700 kg (Table 3).

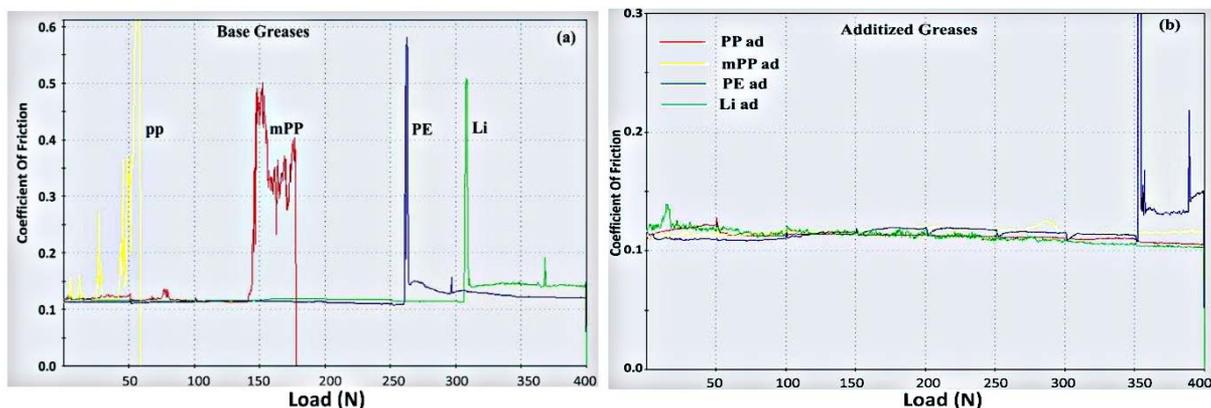


Figure 3. Coefficient of friction of base greases (a) and additized greases (b) by SRV at 50 °C

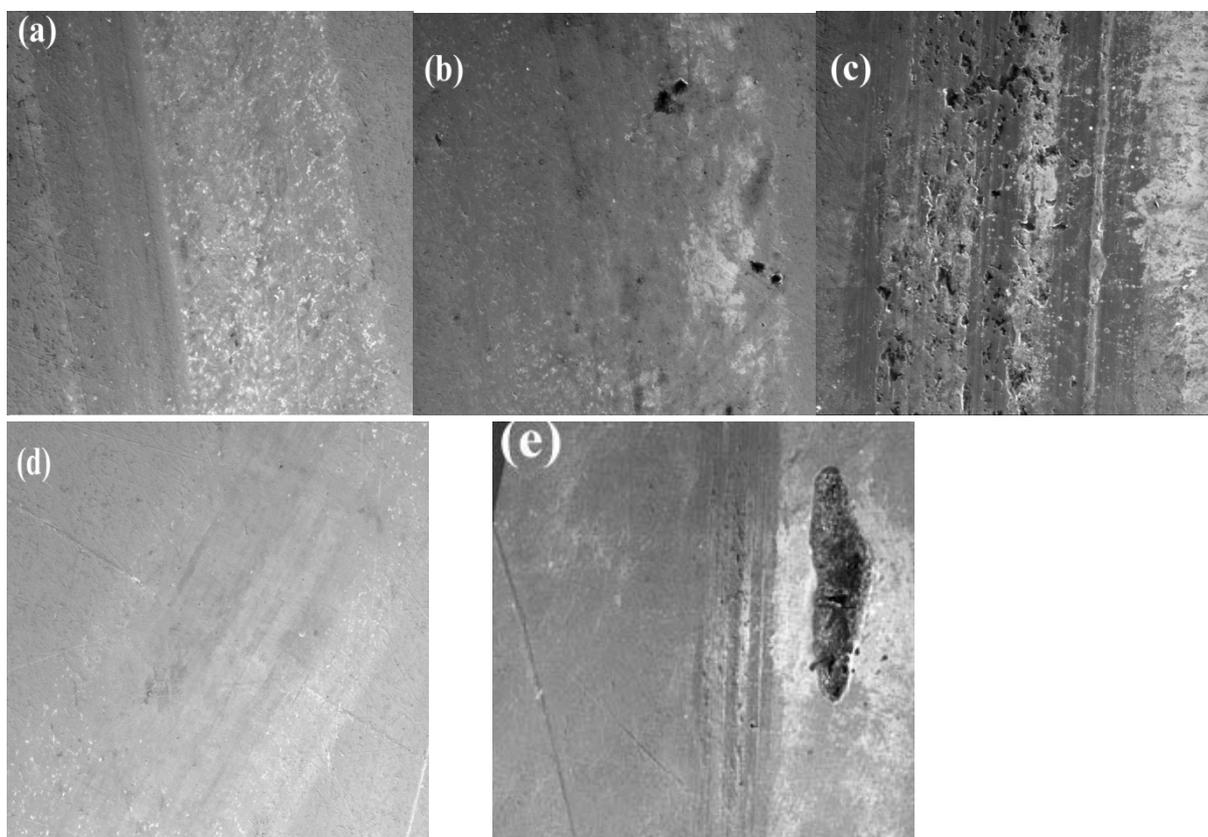


Figure 4. SEM images of worn surfaces of discs after SRV tests . Additized PP grease (a), additized mPP grease (b), additized PE grease (c), additized lithium grease (d) and low resolution image of surface (c) showing carbon deposit (e).

Grease	L_w without additive (kg)	L_w with Additive (kg)	WSD without additive (mm)
Polypropylene	160	800	1.1
Maleic anhydride grafted Polypropylene	160	800	1.1
Polyethylene	180	700	0.9
Lithium	180	800	0.9

Table 3. Load carrying capacity (L_w) of base greases (kg), L_w of greases with 7% additive and wear scar diameter of different greases without additive (mm).

3.4 SEM (EDAX)

The SEM images of worn surfaces after four-ball wear tests as well as after frictional tests are shown in Figures 4 to 6. From Figure 5, it is clearly visible that the wear profile of the balls directly corresponded to the anti-wear performance of the greases under study. The PE grease had the lowest amount of wear (Figure 2), a smooth wear track and low wear marks on the worn surfaces of steel balls after four-ball wear tests. On the other hand, lithium, PP and mPP greases had comparable wear tracks and wear marks on the worn surfaces. The smoothest wear mark was observed with the PE lubricated surface, which had the minimum WSD.

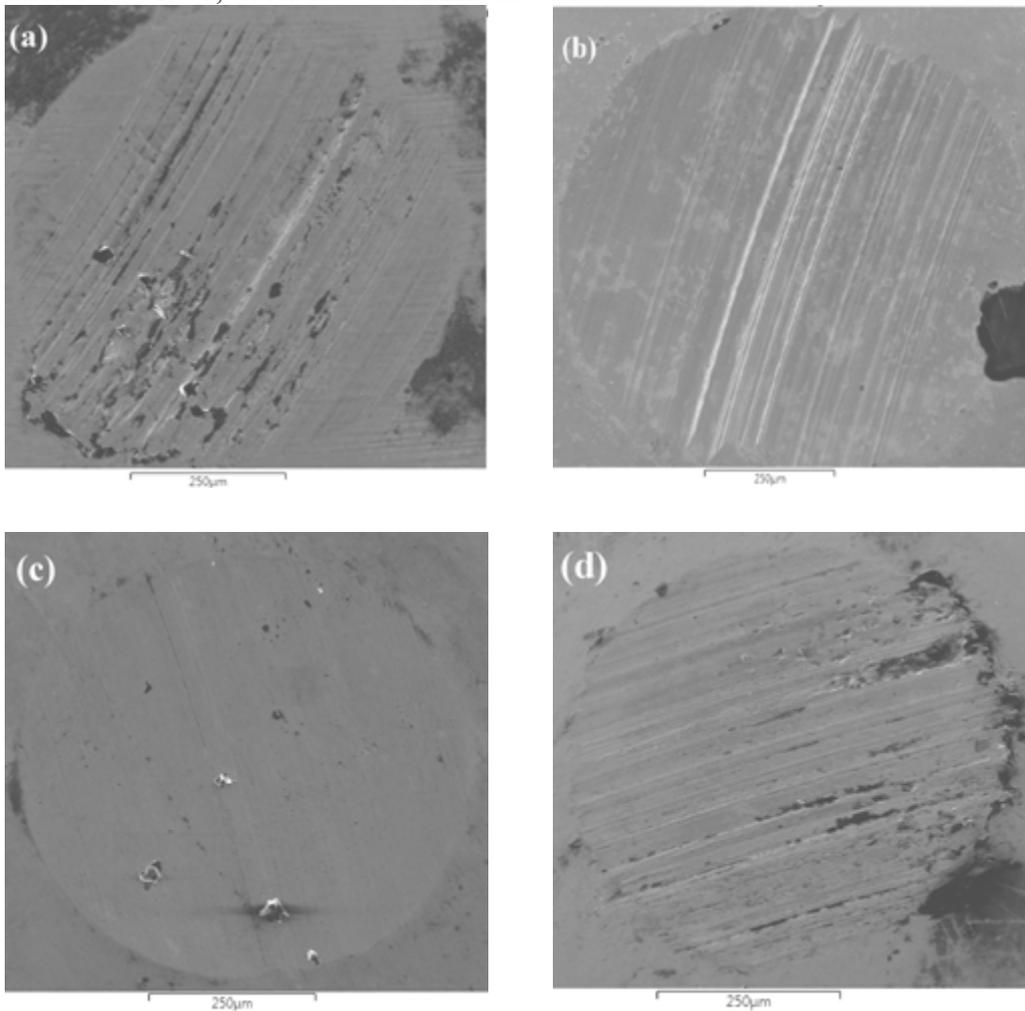


Figure 5. SEM images of worn surfaces after four-ball wear tests. Additized PP grease (a), additized mPP grease (b), additized PE grease (c) and additized lithium grease (d).

SEM images of balls and discs after frictional tests were also observed for all four samples. In Figures 4 and 6, it can be clearly seen that the samples having low COF have smooth wear marks on balls as well as discs. The discs and balls lubricated with additized PE grease, which failed in friction tests at 400 N, show patches of deep wear marks on the balls and very rough and cracked wear surfaces on the discs. All the other discs and balls have similar wear marks over the surface (including wear marks on balls lubricated with additized lithium grease, not shown here).

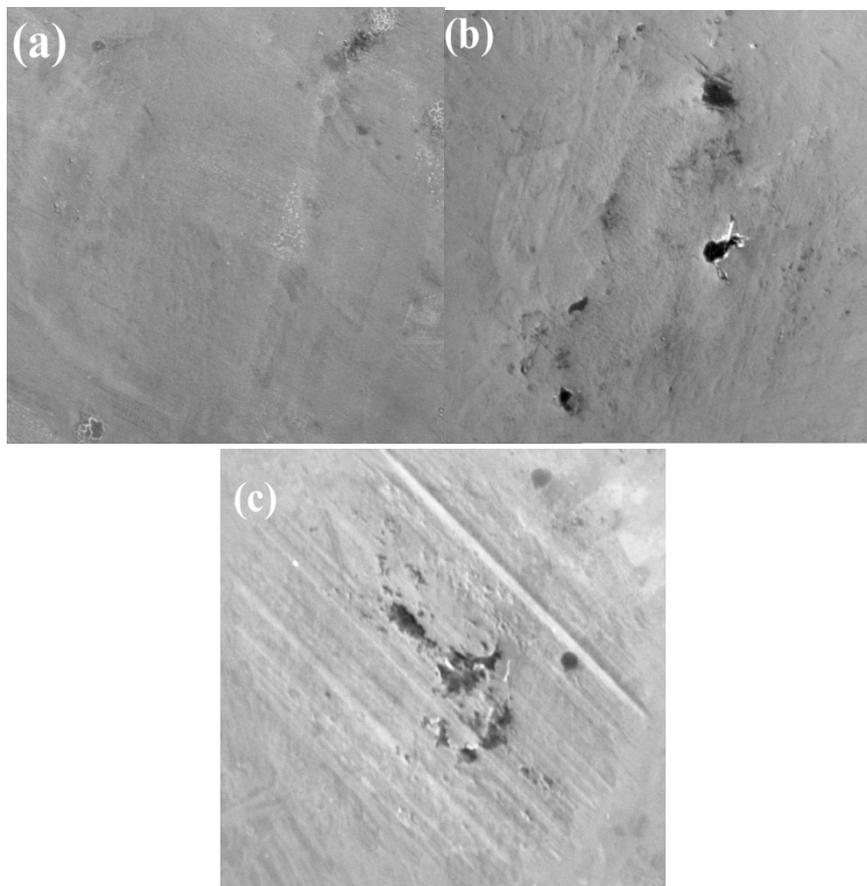


Figure 6. SEM images of worn surfaces of balls after SRV tests . Additized PP grease (a), additized mPP grease (b) and additized PE grease(c).

SEM images of all the samples after four-ball wear tests were also used to study elemental distribution on the wear surfaces. Tungsten was not found on any of the worn surfaces as expected, since WS_2 was not involved in tribochemical reactions and rather worked as a spacer between two mating metal surfaces. Only phosphorus films were observed, which could come from sodium metaphosphate functional groups on WS_2 nanoparticles.

4. Conclusions

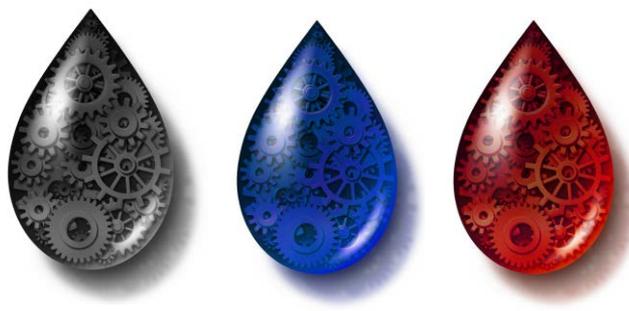
1. Tribological properties of unadditized polymer greases largely depend upon type of polymeric thickener. In the present study, anti-wear properties are in the order $PE=Li>mPP=PP$ for greases thickened with polyethylene, lithium 12-hydroxystearate, maleic anhydride grafted polypropylene and polypropylene.
2. Anti-wear and EP effects of functionalized WS_2 were similar for all the polymer thickeners except for PE thickened grease.
3. WS_2 is equally effective for improving anti-wear properties of all the greases, but PE thickener responds even at very low additive concentrations.
4. Good anti-friction and anti-scuffing properties were obtained in additized PE grease and were better than the base greases. However, the improvement was quantitatively poor compared to the other greases.

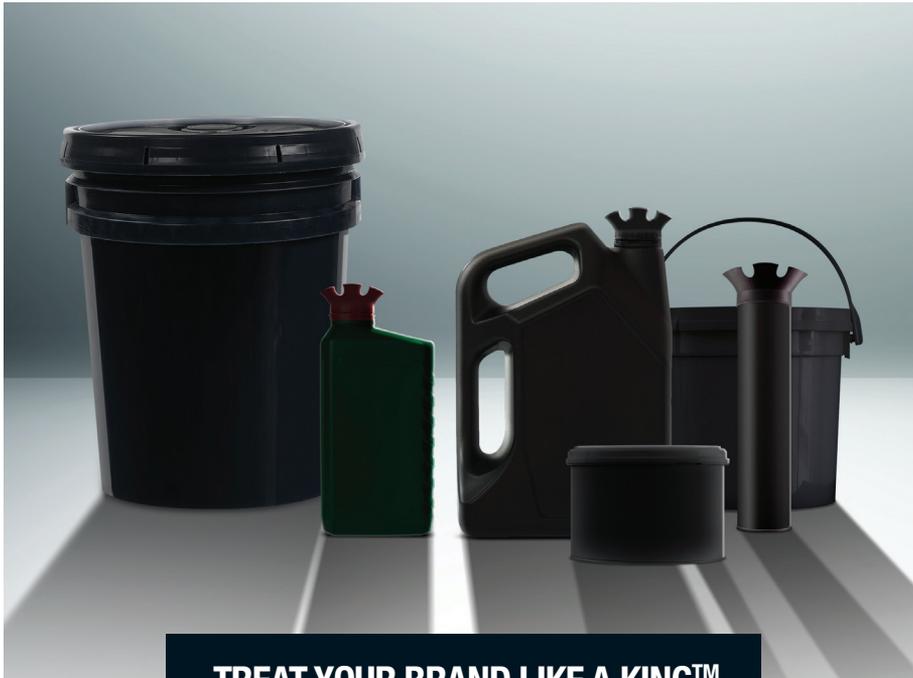
5. Functionalized nanoparticles of WS₂ were found to be a better additive for polymeric thickened lubricating greases compared to conventional S and P type additives.
6. 5 wt% is the optimum concentration of WS₂ additive for effective anti-wear and EP properties.
7. Anti-wear and EP performance of WS₂ nanoparticles is good when the temperature of the contact surface remains below a certain temperature, i.e. 300° C. Degradation of nanoparticles occurs at higher temperatures and adversely affects the tribological properties of the additive.

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CALCIUM SULFONATE POLUREA LITHIUM COMPLEX BIODEGRADABLE ALUMINUM COMPLEX SYNTHETIC CLAY BASED

“The Effect of Base Oils on Thickening and Physical Properties of Lubricating Greases”

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ABSTRACT

In general, lubricating greases are non-Newtonian fluids consisting of base oil, thickener, and additive components. The base oil is the majority component in most lubricating greases and thus significantly influences the greases' physical properties. Thickeners provide the backbone of lubricating greases, making the product semi-solid rather than liquid. Thickeners entrap base oils by various mechanisms including van der Waals interactions, hydrogen bonding, dipole-dipole interactions, and/or capillary action. The affinity of a base oil for a thickener depends greatly on the polarity of both materials. A polar thickener has greater affinity or compatibility with a more polar base oil versus a less polar base oil. In the lubricant industry, it is common practice to use the aniline point to measure the compatibility of a base stock with aniline, and to describe a base stock with relatively low aniline point (low miscibility temperature) as relatively polar or as having strong solvency. Lubricating grease manufacturers utilize a variety of base oils in their products, including aromatics, naphthenics, paraffinics, and synthetic fluids.

Historically, aromatic base oils were preferred for grease manufacturing due to their superior solvency, necessitating a smaller quantity of thickener – typically the most expensive component in a grease formulation – to reach the desired consistency. Due to advancements in refining technologies and more stringent health, safety, and environmental regulations,

naphthenic and paraffinic base oils replaced aromatics. In markets that enjoy secure access to naphthenic supply, solvency of a naphthenic base oil is preferred versus that of a paraffinic base oil due to improved grease yields; grease yield is defined as the amount of grease of a given consistency that may be made with a specific amount of thickening agent. By definition, as the yield increases, thickener content decreases. Whereas the thickener system remains the highest cost component in many grease formulations, the ability to use less equates to lower formulation costs.

This paper examines the effects of naphthenic, paraffinic, and synthetic (polyalphaolefin or PAO) base oils on the thickening capabilities of lithium 12hydroxystearate (Li 12-HSA), lithium complex (Li complex), aluminum complex (Al complex), clay base, and calcium sulfonate complex (Ca sulfonate) greases and their associated physical properties. Experimental greases were manufactured with identical proprietary processing parameters. The greases' chemical compositions were the same for each thickener type with the exception of the base oil component. Physical properties including mechanical stability, roll stability, dropping point, oil separation, and mobility are evaluated. This paper provides a detailed summary of the various base oil/thickener combinations, resulting yield levels, physical properties and the commercial implications regarding yield impacts on formulation economics.

The impact of additives, typically incorporated in low concentrations to impart certain performance characteristics to the lubricating grease, remains outside the scope of this paper.

INTRODUCTION

Lubricating greases are formulated products consisting of base oil (50-98%), thickener (2-50%), and various performance additives (0-10%) such as antioxidants, corrosion inhibitors, antiwear, and extreme pressure additives, depending on the application. Grease may be used to lubricate bearings and gears (enclosed and open), provide a protective coating, or as a parting agent and drawing compound in casting. Grease is used instead of oil in applications where retention is important, less frequent application is required, to seal out dirt and contaminants, and to protect metals from corrosion. Grease films cling to bearing surfaces better than oil and in general stay put, while oil tends to leak away. Accordingly, manufacturers and users measure several unique physical properties of grease: pumpability, dropping point, mechanical stability, and oil separation. In general, for most soap-thickened greases, base fluid viscosity and grease consistency are independent properties of a lubricating grease. The viscosity of the base fluid is determined by the base stock viscosity as well as the effect of some additives. The consistency of a grease is determined by the type and concentration of the thickener in the product.

The American Petroleum Institute (API) developed a five-part classification of base oils [1], which is used in lubrication to group oils of similar quality, from different refineries, into categories for base oil interchange purposes. The groups are defined by the level of sulfur, the percentage of saturated hydrocarbons and the viscosity index of the oil (see Table 1).

There are three basic types of hydrocarbon base oils used in grease today. These are naphthenic oils, paraffinic oils, and synthetic isoparaffinic hydrocarbons. A fourth base type, aromatic oils, has been replaced due to health and safety

concerns. The paraffinic oils can be further subdivided into Group I, Group II, and Group III. These will be discussed later. The synthetic isoparaffinic hydrocarbons are of a couple of types. Group IV polyalphaolefins (PAO) are typically oligomers of 1-decene and are the most widely used synthetic hydrocarbons for lubricant applications. Other types of synthetics include Group V polyisobutenes (PIB), which are oligomers of isobutylene, and esters, primarily dibasic esters or polyol esters. PAO remains the only synthetic base oil evaluated in this study.

Up until the '90s, essentially all paraffinic oils were API Group I type oils. In response to increasing regulation and technical demands placed on automotive engine oils (e.g., fuel economy and emissions), the refining industry transitioned from Group I base oils, typically manufactured using solvent refining technology, to Group II and III base oils, typically manufactured using severe hydroprocessing technology. In contrast to Group I, naphthenics (API Group V) can be produced via solvent extraction or hydroprocessing. Today's state-of-the-art naphthenic refineries use severe hydroprocessing to produce high-quality "clean" or low PAH naphthenic base oils that have reduced sulfur content and lower polycyclic aromatic hydrocarbon (PAH) content while preserving valuable solvency characteristics.

Advances in refining technology have greatly impacted the supply side of the market. Over the last 10 years, more than 7.5MM tonnes per year of Group I production capacity have been shuttered with most capacity additions, either expansions or new constructions, being in Group II and III products. [2]

API Group I base oils contain a considerable amount of sulfur and a saturates level less than 90%. While most commercially available Group II and Group III base oils have essentially nil aromatic content, Group I and severely hydroprocessed naphthenic base oils have been processed to remove the carcinogenic PAHs while leaving the other aromatics intact. The removal of the carcinogenic PAHs is necessary

to produce a “clean” base oil that meets the Health, Safety, and Environmental (HSE) regulations of the applications for which they are used.

Solvency is affected most by the aromatic content and then by the naphthenic (i.e., saturated ring structures) content. As the aromatic content decreases, the solvency decreases, and as the naphthenic content increases, the solvency increases. When aromatics are hydroprocessed, they are converted to naphthenes. Therefore, to maintain solvency after reducing the amount of PAHs for HSE requirements, naphthenics are an outstanding way to increase the solvency of a lubricant formulation.

Solvency is impacted by several somewhat related factors and can be assessed in terms of aniline point, viscosity index (VI), and viscosity-gravity constant (VGC). Aniline point, ASTM D611 [3], characterizes solvency via a compatibility test between the oil and aniline, which is an aromatic amine. The aniline point is defined as the minimum equilibrium solution temperature for equal volumes of aniline and the oil sample. The more soluble the oil is in the aniline, the lower the temperature required for the oil and aniline to become miscible. Less soluble oils require higher temperatures. This is an example of the industry adage, “like dissolves like”. Aniline is a polar molecule, and polar base oils are more readily miscible with aniline at a lower temperature. Less polar base oils are less miscible and require a higher temperature to ensure miscibility. The lower the aniline point, the higher the solvency of the base oil.

The viscosity index (VI), ASTM D2270 [4], which is a dimensionless number, is used to characterize the variation of the kinematic viscosity of a petroleum product with temperature. The higher the VI number, the less change in viscosity due to temperature. The VI correlates with chemical structure, with aromatics having the lowest VI, then naphthenics, and paraffins having the highest VI; therefore, a higher VI indicates a lower solvency.

Viscosity-Gravity Constant (VGC), ASTM D2501 [5], describes the general relation between specific gravity and Saybolt viscosity. The VGC is low for paraffinic (0.800) and high for aromatic (1.00) type oils. As the VGC increase, the solvency increases. VGC is often used in conjunction with aniline point since VGC is independent of molecular weight.

The thickener in a lubricating grease is the component that sets grease apart from fluid lubricants. Thickeners are molecules, polymers, or particles that are partially soluble in lubricating fluid; they arrange themselves in such a way that they impart a semi-solid consistency to the grease. Many different types of chemical compounds can be used to thicken grease.

The amount of thickener used during manufacture is linked to the desired physical properties of a finished grease. Since the soap or clay is typically more expensive than the base oil, minimizing the soap or clay content while maintaining the physical properties is paramount. The amount of thickener necessary to form the microstructure depends on the interactions between the thickener and the base oil, which depend on the solvency of the base oil. The higher the solvency, the more the interaction and the less thickener required to produce a grease with the targeted NLGI grade, which ultimately lowers the overall formulation cost.

Simple soaps are the most common grease thickeners. A simple soap is the reaction product of an organic acid (long-chain or fatty carboxylic acid) and an alkali metal to form an organic salt. Thus, simple soap is an acid-base reaction product. This reaction has a special name: saponification. Simple soaps are most commonly based on salts of lithium and calcium, and less commonly on salts of sodium, aluminum, and barium. Examples of simple soap thickeners include lithium 12-HSA and calcium stearate.

Complex soaps are also used widely as grease thickeners. The term “complex” refers to the combination of a simple soap and a complexing agent. For example, a lithium complex thickener

typically contains lithium 12-HSA (simple soap) and a salt of a shorter chain difunctional carboxylic acid, boric acid, or an aromatic acid (complexing agent). Complex thickeners are usually based on lithium, calcium, or aluminum compounds. Grease can also be thickened with non-soap materials. Common non-soap thickeners include polyurea, clay, fumed silica, fluoropolymers, and others.

Clay thickeners include the minerals bentonite and hectorite. These minerals are purified to remove any non-clay material, ground to the desired particle size distribution, and then chemically treated to make the particles organophilic (more compatible with organic chemicals). Clay particles are then dispersed in a fluid lubricant to form grease. Clay particles must be activated with a polar material to stabilize the thickener structure. No chemical reaction takes place in the production of clay thickened greases. Clay thickeners have no defined melting point, so they have been used historically in high temperature applications operating up to 200°C, such as kilns and drier ovens.

For this study, we will examine the differences between several naphthenic and paraffinic base oils, a PAO, and a bright stock as they relate to processing and properties of Li 12-HSA, Li complex, Al complex, Ca sulfonate and clay based greases. We will also illustrate simple economic benefits of lower thickener concentration.

DESIGN OF EXPERIMENT

In this study, NLGI Grade 2 greases were prepared using five different thickener systems:

- 1) lithium 12hydroxy stearate (Li 12-HSA)
- 2) lithium complex (Li complex)
- 3) aluminum complex (Al complex)
- 4) calcium sulfonate (Ca sulfonate)
- 5) clay

One exception was with the synthetic hydrocarbon clay based grease. It was not possible to produce an NLGI Grade 2 grease without drastically altering the process variables, so in this case, an NLGI Grade 00 grease was produced.

According to the 2015 NLGI Annual Production Survey [6], Li 12HSA greases account for nearly 55% of the total grease manufactured in the reporting countries. Li complex grease adds another 20%, so that lithiumbased greases account for nearly 75% of production. In North America, Li 12HSA grease is 26% while Li complex grease is 39% for total lithium based greases of 65%.

Seven base oils with different aniline points were used with each type of thickener:

- 150 N1 - Group V naphthenic base oil, ISO VG 150, 197.5 °F (91.9 °C)
- 150 N2 - Group V naphthenic base oil, ISO VG 150, 191.3 °F (88.5 °C)
- 460 N3 - Blend of 150 N1 and 1000 P3, ISO VG 460, 231.5 °F (110.8 °C),
- 1000 P3 - Group I bright stock, ISO VG 1000, 248.5 °F (120.3 °C)
- 100 P1 - Group I paraffinic base oil, ISO VG 100, 248 °F (120 °C)
- 100 P2 - Group II paraffinic base oil, ISO VG 100, 256.8 °F (124.9 °C)
- 150 S1 - Group IV PAO base oil, ISO VG 150, >300 °F (>148.9°C)

The physical properties of the base oils are given in Table 2.

The greases were all produced in the same reactor under similar conditions. Each grease was characterized by wt% thickener, unworked penetration, worked penetration (60x and 10,000x strokes), mechanical stability after 10,000 strokes, and US Steel mobility test. In addition, roll stability, oil separation, and dropping point were reported for some of the greases. In order to simplify the formulations, performance additives such as antioxidants, antiwear, and corrosion inhibitors were not included.

EQUIPMENT AND MANUFACTURING PROCEDURE

Manufacturing of greases not only depends upon the formulation technology, but is also greatly influenced by the processing parameters and scale up. All these samples were prepared in the laboratory at 1 to 5 gallon batch size. The kettles used for making these samples were Howard-type mixers, and controlled heat was provided through electric heating mantles. The greases based on Li 12-HSA, lithium complex, clay base, and aluminum complex greases were prepared with conventional processes and compositions; varying only the base oil component. All efforts were made to keep all processing parameters, composition, and operator consistent to avoid batch-to-batch variation. The Ca sulfonate grease samples in different base oils were made in counter rotating mixers using proprietary composition and process parameters. After the greases were cooked and brought to desired penetration range, all the samples were milled through the same laboratory scale homogenization mill. The finished grease samples were tested as per ASTM standard test methods, and test results are tabulated appropriately.



Figure 1. Kettle used to produce greases.

DISCUSSION

Thickener Content

The amount of grease of a given consistency that may be made with a specific amount of thickening agent, i.e., grease yield, varies by thickener type and by the solvency of the oils used to prepare the grease. As the grease yield increases, the thickener content decreases, which consequently lowers the cost of the formulation since the thickener system is generally the highest priced component.

Instead of making different types of greases using a standard amount of thickener, this study did the opposite. All the greases were prepared to an

NLGI Grade 2, and the amount of thickener was necessarily varied to obtain the same grease consistency. In this way, the properties of the greases could be compared on the same NLGI grade basis.

The data are given in Tables 3 – 7, and Charts 1 - 17. In the tables and charts, the oils are aligned in order of increasing required thickener content for the Li 12-HSA greases (see Chart 1). This alignment, with one exception, is by type (naphthenic, paraffinic, synthetic) and by decreasing solvency as defined by increasing aniline point. The one exception is with the two ISO VG 150 naphthenics from different suppliers, where the one with the slightly higher aniline point actually requires less thickener.

Thickening efficiency is the opposite of the amount of thickener used to make an NLGI grade 2 grease. It is necessary to use a larger amount of a less efficient thickener to obtain NLGI grade 2 versus a smaller amount of a more efficient thickener. In Chart 1, the thickening efficiency of L1 12-HSA was highest for 150 N1 base oil (lowest thickener content, 10.5 wt%).

In Chart 2, the oils are listed in the same order as in Chart 1 for Li 12-HSA greases. For the other thickeners in Chart 2, the amounts of thickener do not always follow the same order as for Li 12-HSA. However, the pattern of increasing thickener content does not hold, it varies with aniline indicating that the oil to thickener interaction depends on the type and chemistry of the thickener.

For all thickener types, with the exception for the calcium sulfonate grease, the use of a naphthenic ISO VG 150 base oil reduced the amount of thickener required to formulate an NLGI Grade 2 grease. For the Li 12HSA greases, the amount of thickener can be reduced by 25 to 30% when a naphthenic base oil is used instead of a paraffinic base oil, either a Group I or II. For the Li complex greases, the

decrease in the amount of thickener was 7 to 9%. For the Al complex greases, the decrease was 40 to 50%, and for the clay greases it was 20 to 30%. For the Ca sulfonate greases, the ISO VG 460 naphthenic required slightly less thickener than the ISO VG 150 naphthenic. The decrease in the amount of thickener, compared to the paraffinic base oils, was up to 20%.

Solvency

Aromatic hydrocarbons exhibit the lowest aniline points, and paraffins have the highest. The lower the aniline point, the higher or stronger the solvency of the base oil. Charts 3 – 7 plot the relationship between the aniline point of the base oil and thickener content to generate an NLGI Grade 2 grease using various thickeners. The R-squared values ranged from 0.64 to 0.97 for all thickeners except for the Ca sulfonate (R-squared = 0.09). This demonstrates the importance of the solvency of the base oil in minimizing the thickener content required to produce the target NLGI grade grease.

In general, the higher the solvency of the base oil, the lower the required thickener content. The Ca sulfonate grease behaves differently with respect to the solvency of the base oils. Of the parameters tested, none correlated to the required calcium sulfonate thickener content.

Charts 8 – 12 plot the relationship between the VI of the base oil and thickener content. Again, there are correlations (R-squared 0.57 to 0.90) between the VI of the base oil and the thickener content for all but the Ca sulfonate grease (R-squared = 0.06). The higher the VI of the base oil, the higher the required thickener content, since the VI of petroleum hydrocarbons is strongly inversely correlated with solvency.



Charts 13 – 17 plot the relationship between the VGC and thickener content. For this parameter, there were stronger correlations and the R-squared values ranged from 0.43 to 0.91 for most greases compared to Ca sulfonate (R-squared = 0.22). Li 12-HSA had the highest R-squared at 0.91. The higher the VGC, the higher the solvency and the lower the thickener content.

The authors do not have a firm understanding as to why the amount of thickener content in the Ca sulfonate greases did not correlate to differences in solvency. It is possible that other factors such as thickener structure and processing may have affected the interaction of the Ca sulfonate thickener with the base oils in this study.

Other Parameters

As noted in the experimental plan, each grease was characterized by wt% thickener, unworked penetration, worked penetration (60x and 10,000x strokes), mechanical stability after 10,000 strokes, and US Steel mobility test. In addition, roll stability, oil separation, and dropping point were measured for some of the greases. The physical property test data are given in Tables 3 – 7. All of the base oils produced greases meeting industry standards, and the data for these grease types are fairly comparable. This indicates that commercially available base oils can produce greases of comparable physical properties. The choice of the particular base oil will depend primarily on the end-use application and overall economics of the cost to produce the finished grease product.

COMMERCIAL IMPLICATIONS

These data have demonstrated that the solvency of the base oil is critical to the processing of the grease. The NLGI grade is defined by the penetration values, which are affected by the efficiency of the thickener system, the base oil and the thickener. By decreasing the amount of thickener to produce a particular grade of grease, the overall costs of the formulation can be reduced.

This is demonstrated in the following examples for the Li 12-HSA and Li complex greases as shown in Tables 8 - 9. For example, the authors estimate that using 150 N1 to make 10,000 lbs. of Li 12-HSA grease could save between \$200 and \$18,500 versus the other base oils in this study. Likewise, 150 N1 could provide similar savings for production of 10,000 lbs. of Li complex grease. Since the thickener is generally the highest priced component in a grease any decrease in the thickener concentration will have a positive impact on the overall formulation costs for a specific NLGI grade.

CONCLUSIONS

This paper examined the effects of naphthenic, paraffinic, and synthetic (PAO) base oils on the thickening capabilities of Li 12HSA, Li complex, Al complex, clay base, and Ca sulfonate complex greases and their associated physical properties. Experimental results illustrated a significant relationship between base oil solvency and thickener yield; this relationship has real economic value for grease manufacturers.



Physical properties including mechanical stability, roll stability, dropping point, oil separation, and mobility exhibited favorable results for all base oils in the study.

These observations remind us that base oil selection and preference should differ according to the requirements of the application. Paraffinic chemistries maintain a leading role in engine oil applications; however, it is evident throughout our study that a specialized application, such as grease, can benefit from high solvency and low PAH content as found in modern naphthenic base oils.

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Chart 1. Li 12-HSA Thickener Content, wt%

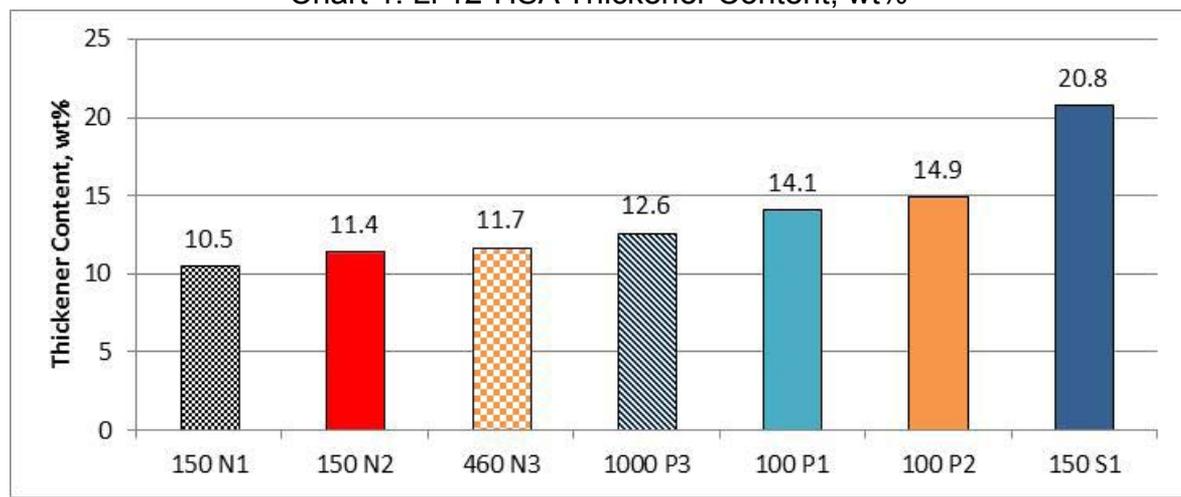


Chart 2. Thickener Content Required for Different Greases, wt%

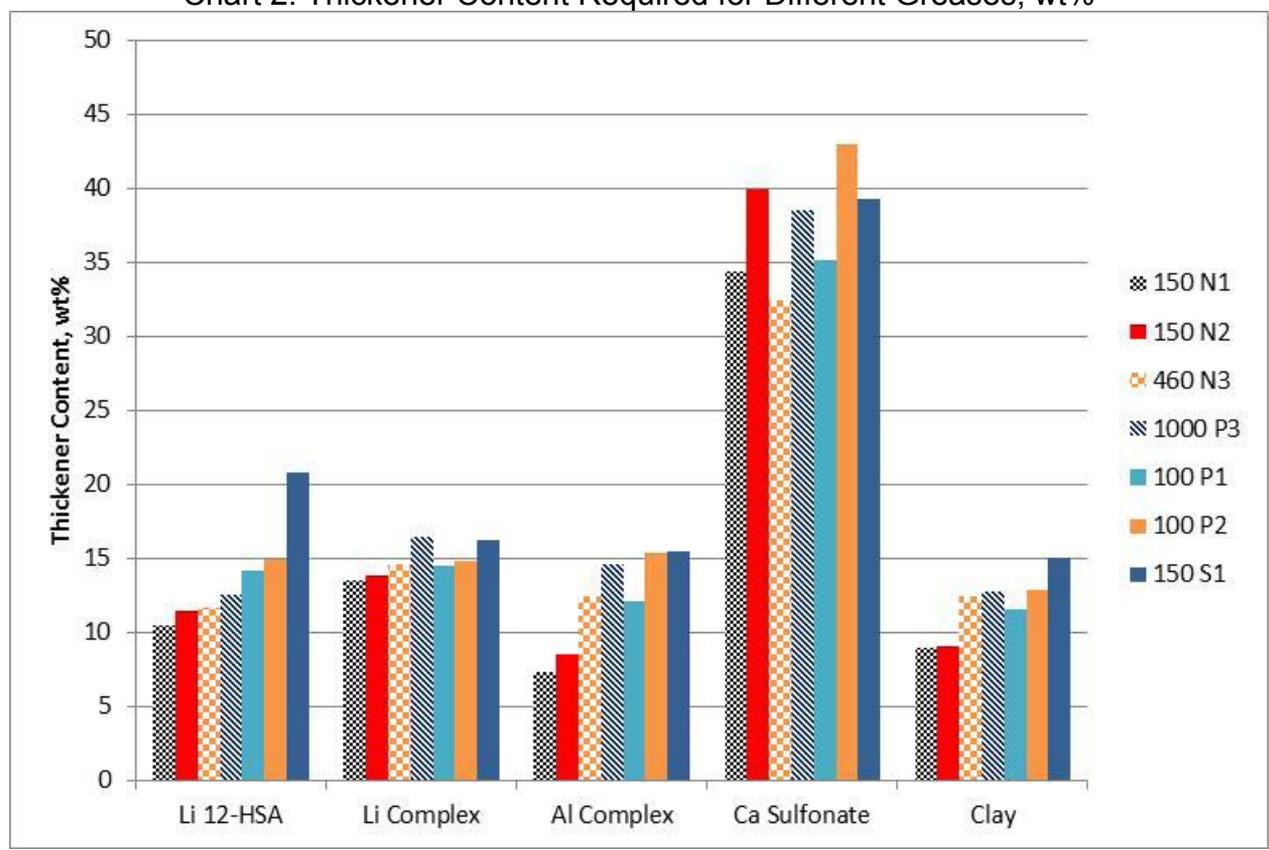


Chart 3. Aniline Point vs Li 12-HSA Thickener Content

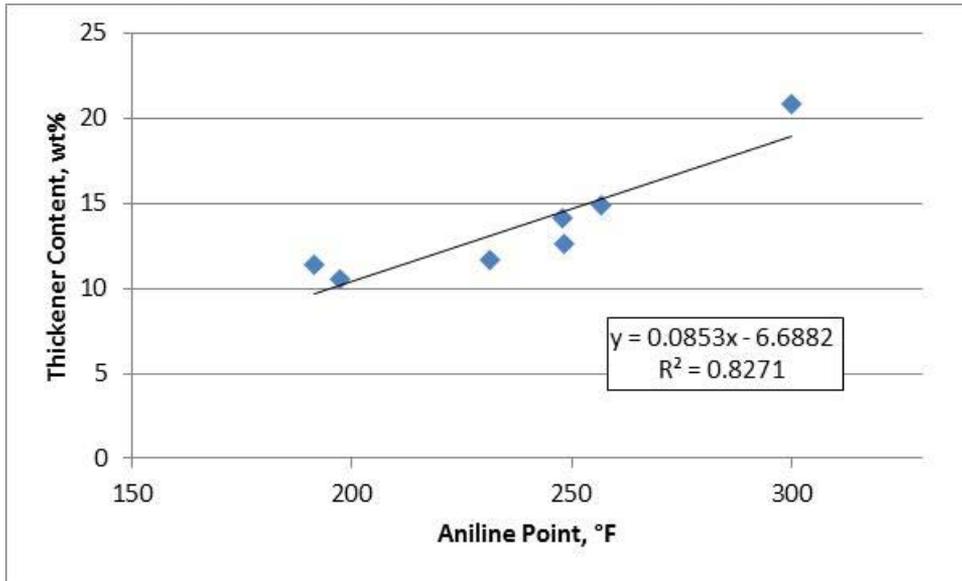


Chart 4. Aniline Point vs Li Complex Thickener Content

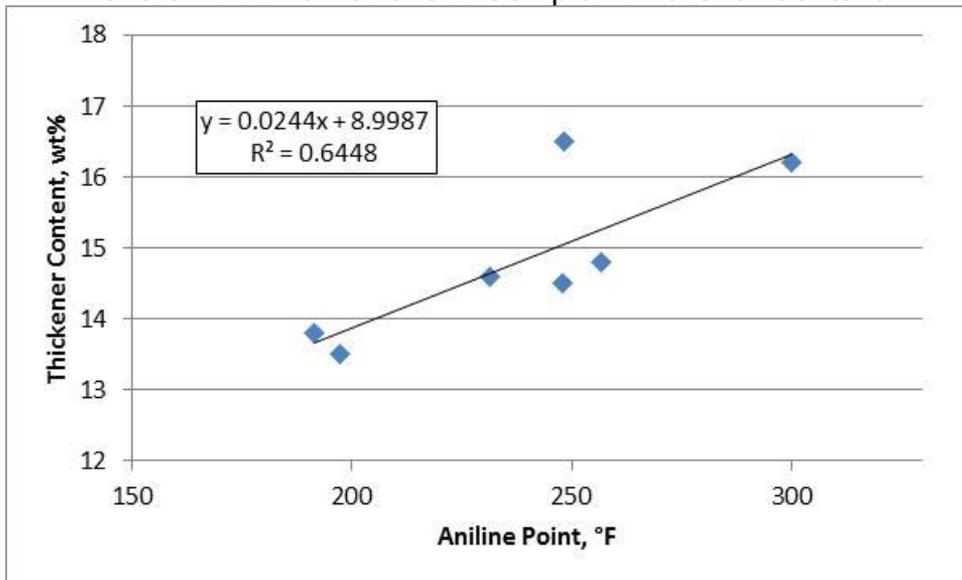




Chart 5. Aniline Point vs Al Complex Thickener Content

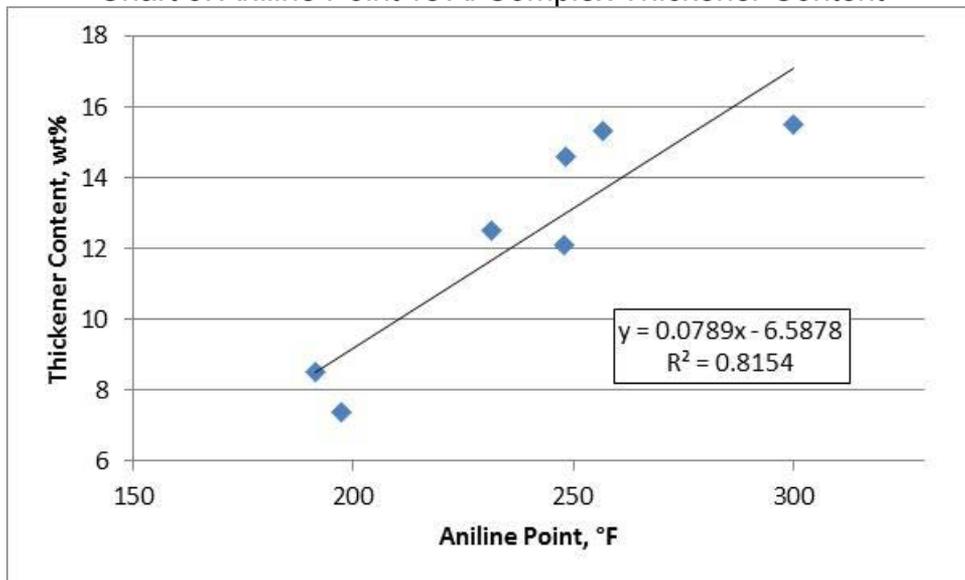


Chart 6. Aniline Point vs Ca Sulfonate Thickener Content

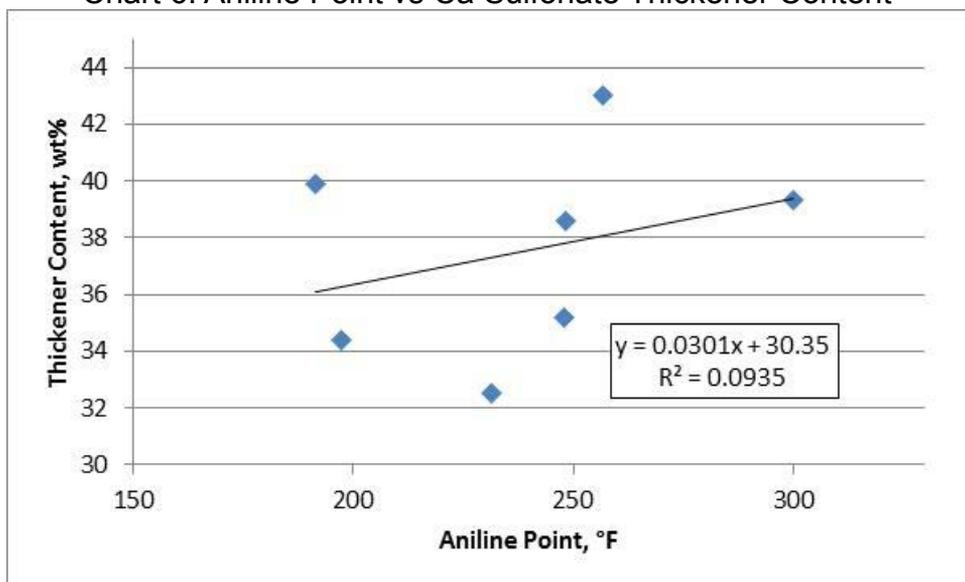


Chart 7. Aniline Point vs Clay Thickener Content

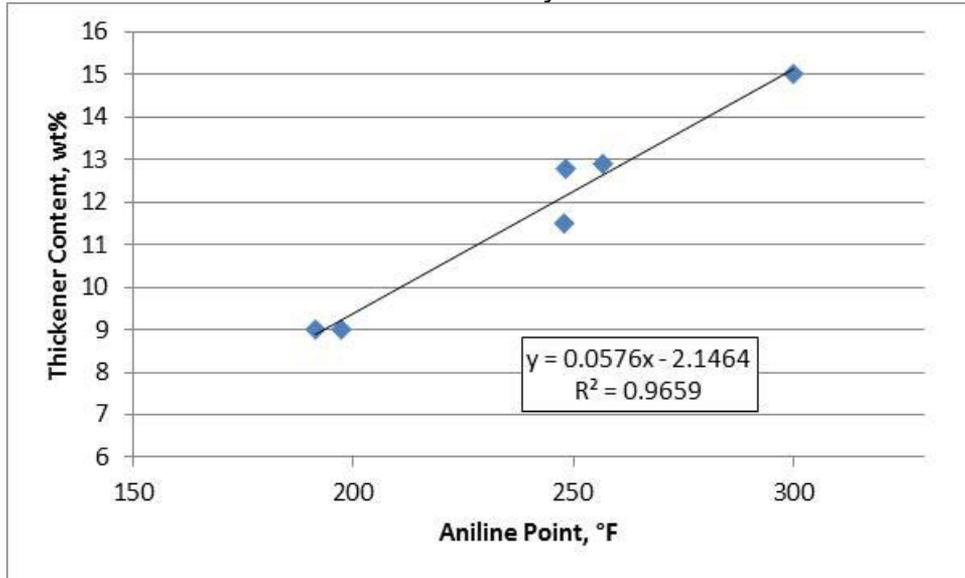


Chart 8. Viscosity Index vs Li 12-HSA Thickener Content

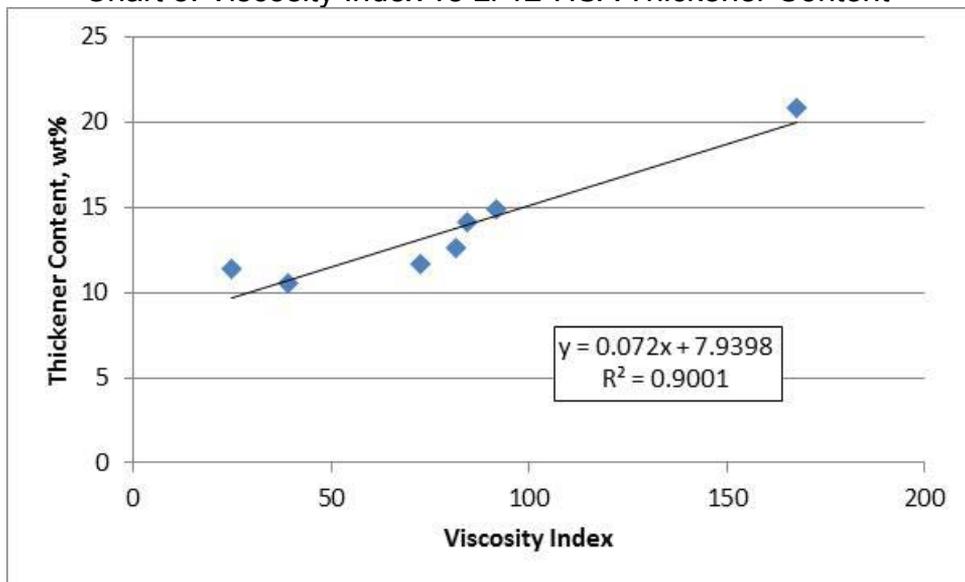




Chart 9. Viscosity Index vs Li Complex Thickener Content

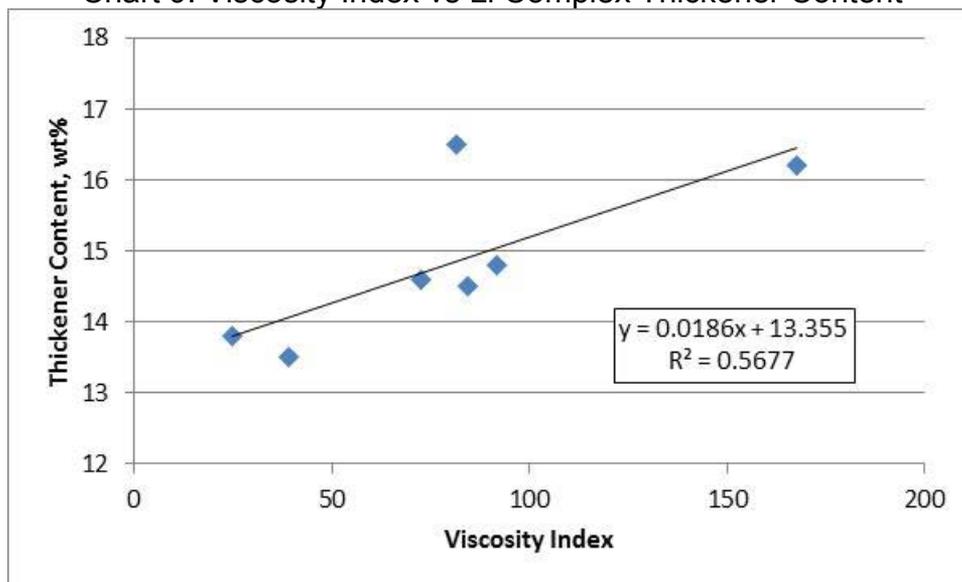


Chart 10. Viscosity Index vs Al Complex Thickener Content

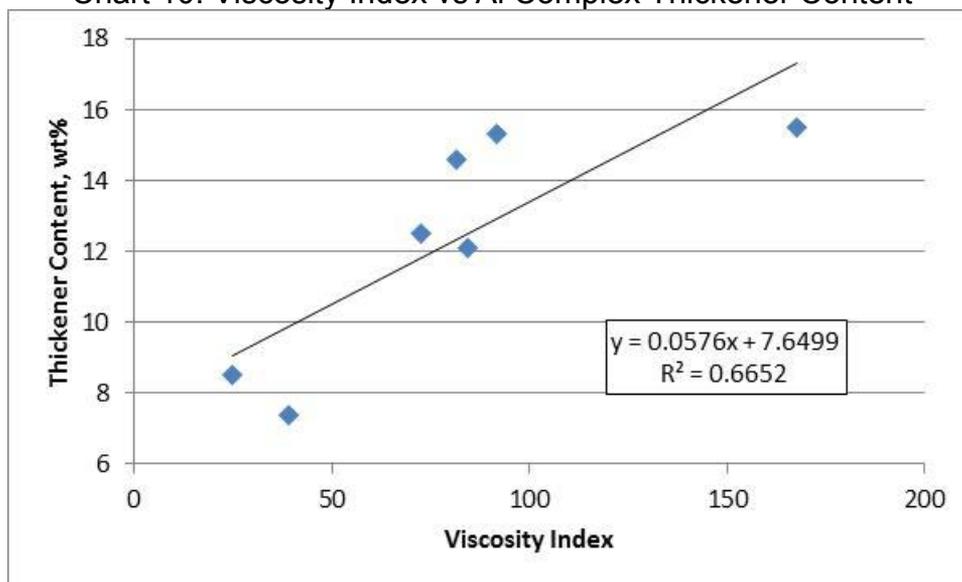


Chart 11. Viscosity Index vs Ca Sulfonate Thickener Content

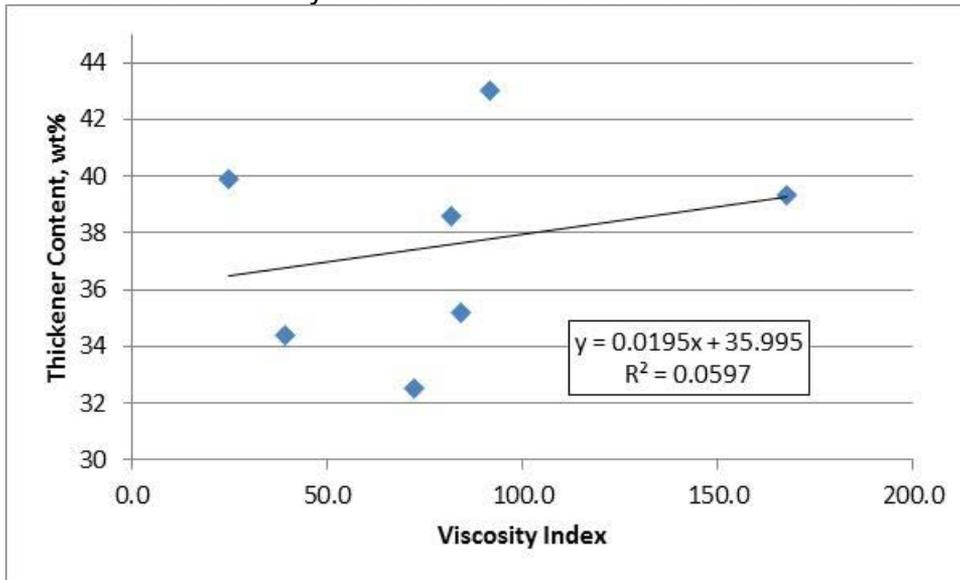


Chart 12. Viscosity Index vs Clay Thickener Content

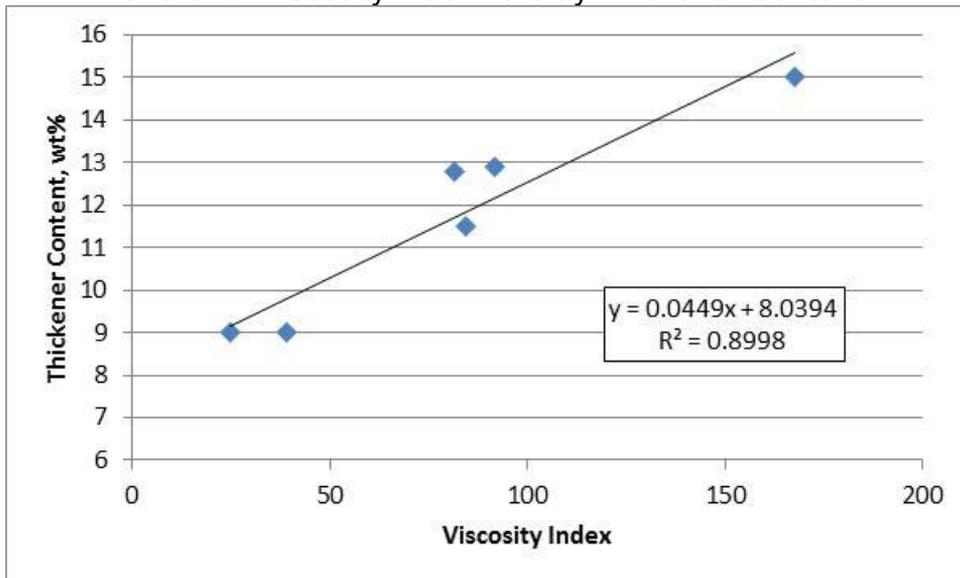


Chart 13. VGC vs Li 12-HSA Thickener Content

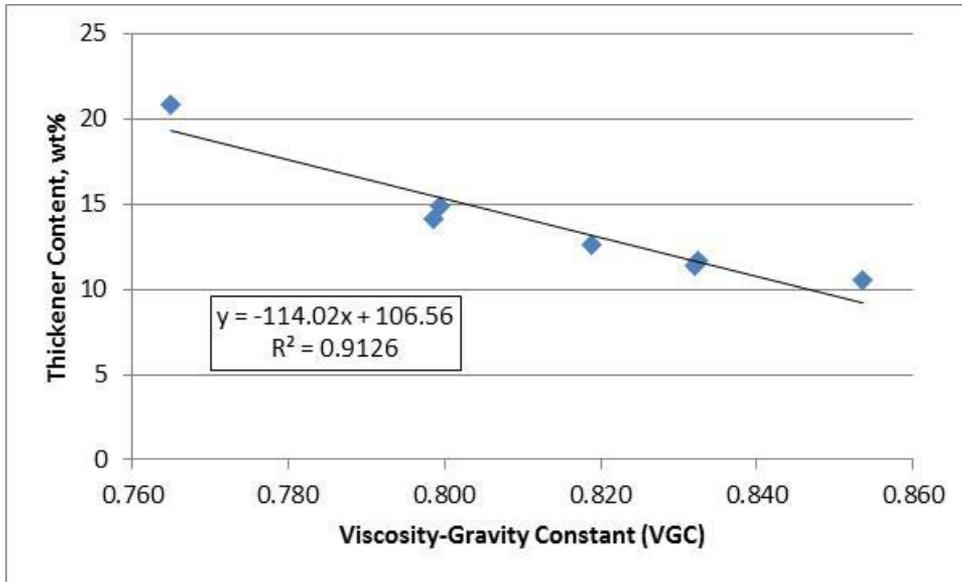


Chart 14. VGC vs Li Complex Thickener Content

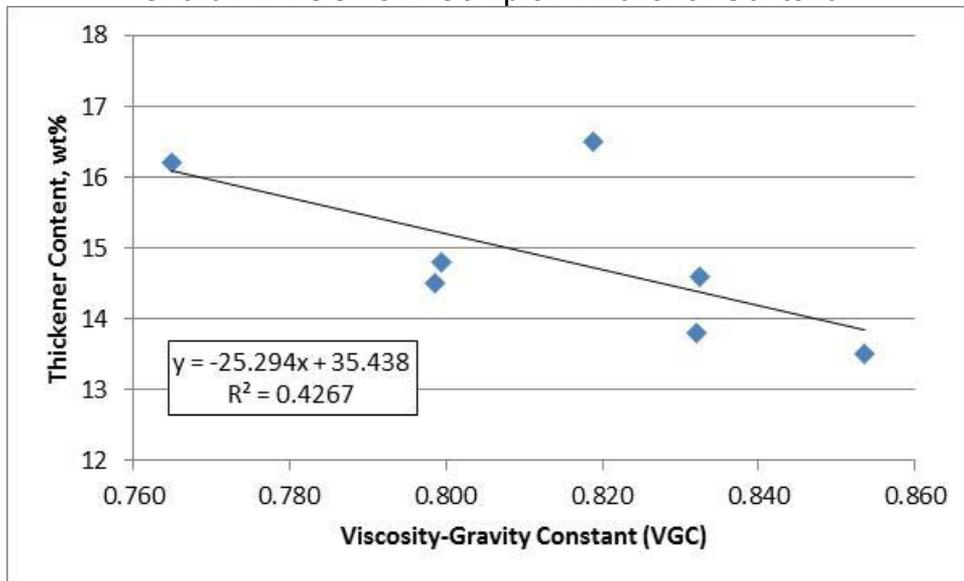


Chart 15. VGC vs Al Complex Thickener Content

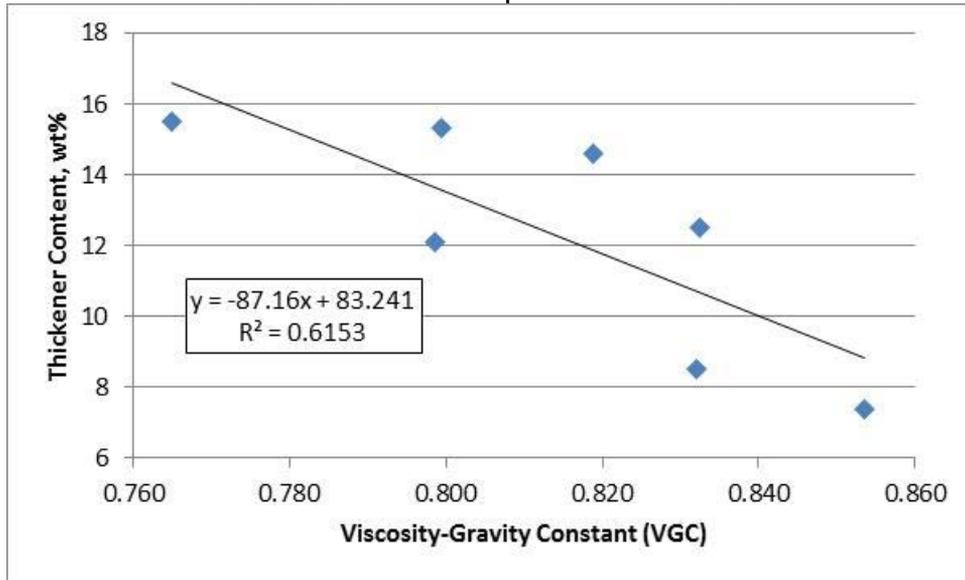


Chart 16. VGC vs Ca Sulfonate Thickener Content

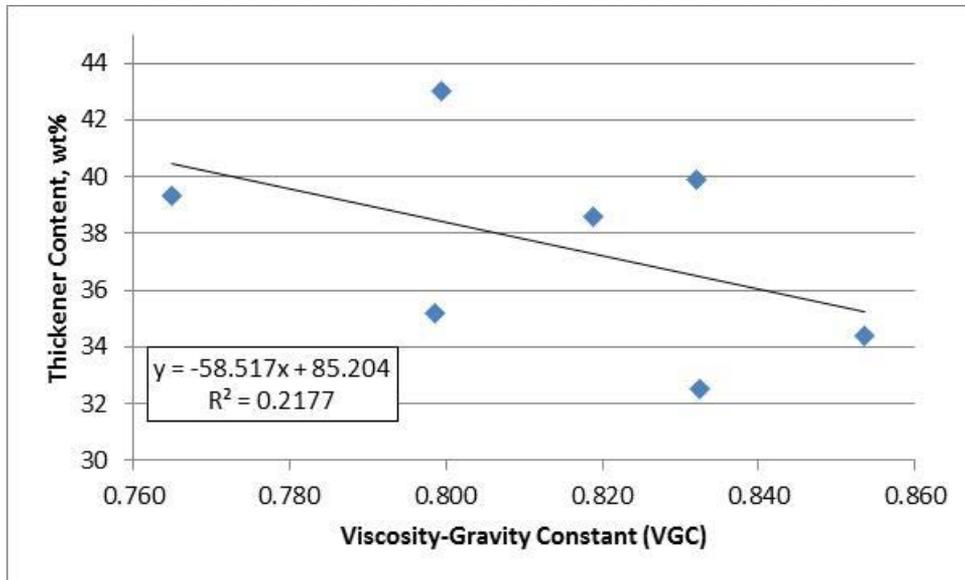


Chart 17. VGC vs Clay Thickener Content

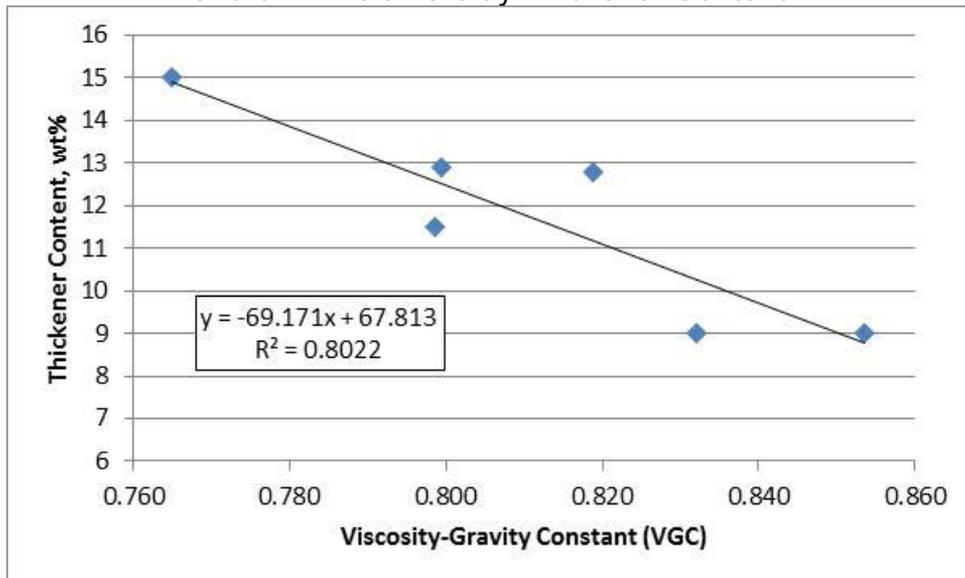


Table 1. API Base Oil Groups

Group	Sulfur, wt%		Saturates, wt%		Viscosity Index
I	> 0.03	and/or	< 90	and	≥ 80 < 120
II	≤ 0.03	and	≥ 90	and	≥ 80 < 120
III	≤ 0.03	and	≥ 90	and	≥ 120
IV	All Polyalphaolefins (PAO) C ₁₀ & C ₁₂				
V	Anything not Group I to IV; Naphthenics & non-PAO Synthetics				

Table 2. Physical Properties of Base Oils

Generic Name	150 N1	150 N2	460 N3	1000 P3	100 P1	100 P2	150 S1
Description*	Group V Nap	Group V Nap	Nap/Par Blend	Group I BS	Group I Par	Group II Par	Group IV PAO
ISO VG	150	150	460	1000	100	100	150
Vis 40°C, cSt	143.99	142.90	475.34	958.24	106.10	117.30	148.47
Vis 100°C, cSt	11.04	10.50	26.36	43.04	10.90	12.10	21.19
Viscosity Index	39	25	72	82	84	92	168
Aniline Pt, °F (°C)	197.5 (91.9)	191.3 (88.5)	231.5 (110.8)	248.5 (120.3)	248 (120)	256.8 (124.9)	>300 (>148.9)
Viscosity-Gravity Constant (VGC)	0.853	0.832	0.832	0.819	0.799	0.799	0.765
Specific Gravity, 60/60°F	0.9170	0.9017	0.9151	0.9141	0.8737	0.8756	0.8536
Carbon Type, D2140							
%C _A	11.3	19.7	9.3	7.4	0.6	0.0	0.0
%C _N	37.7	14.2	31.2	26.6	30.0	32.8	20.2
%C _P	51.0	66.1	59.5	65.9	69.4	67.2	79.8
Refractive Index	1.5028	1.5052	1.5028	1.5027	1.4798	1.4791	1.4646

* Nap = Naphthenic; Par = Paraffinic; BS = bright stock

Table 3. Properties for Li 12-HSA Greases

	Test Method	150 N1	150 N2	460 N3	1000 P3	100 P1	100 P2	150 S1
Vis, 40°C*	D445	143.99	142.90	475.34	958.24	106.10	117.30	148.47
Vis, 100°C*	D445	11.04	10.50	26.36	43.04	10.90	12.10	21.19
wt% Soap	-	10.5	11.4	11.7	12.6	14.1	14.9	20.8
wt% Base Oil	-	89.5	88.6	88.3	87.4	85.9	85.1	79.2
Penetration, 0.1 mm	D217							
Unworked		291	285	290	278	288	290	292
Worked; 60x strokes		291	289	292	284	293	295	296
10,000x strokes		300	310	307	302	306	318	315
Mechanical Stability**		9	21	15	18	13	23	19
Roll stability, % change	D1831	9.3	11.2	9	8.5	10.5	18.8	9.5
Dropping Point, °F (°C)	D2265	367	365	371	357	375	373	359
USS Mobility Test, g/min	US Steel							
@ 0°F (-17.8°C)		38.5	26.5	32.5	-	43.6	56	58
@ -20°F (-28.9°C)		15.2	10.2	12.6	-	10.7	12.9	27

* Base Oil Viscosity, cSt

** Difference in Penetration after 10,000x strokes

Table 4. Properties for Li Complex Greases

	Test Method	150 N1	150 N2	460 N3	1000 P3	100 P1	100 P2	150 S1
Vis, 40°C*	D445	143.99	142.90	475.34	958.24	106.10	117.30	148.47
Vis, 100°C*	D445	11.04	10.50	26.36	43.04	10.90	12.10	21.19
wt% Soap	-	13.5	13.8	14.6	16.5	14.5	14.8	16.2
wt% Base oil	-	86.5	86.2	85.4	83.5	85.5	85.2	83.8
Penetration, 0.1 mm	D217							
(unworked)		-	-	-	-	-	-	-
Worked; 60x strokes		278	285	295	302	278	282	296
10,000x strokes		298	310	320	330	310	305	336
Mechanical Stability**		20	25	25	28	32	23	40
Roll stability, % change	D1831	7.8	9.2	10.2	9.6	12.6	11.2	17.2
Dropping Point, °F (°C)	D2265	>550 (>288)	>550 (>288)	>550 (>288)	516 (269)	>550 (>288)	>550 (>288)	521 (272)
Oil Separation	D6184	1.91	2.32	1.56	1.12	2.8	3.2	5.2
USS Mobility Test, g/min	US Steel							
@ 0°F (-17.8°C)		13.3	11.2	4.5	1.2	9.6	8.7	25.2
@ -20°F (-28.9°C)		4.2	3.2	0.6	0	2.1	1.2	9.3

* Base Oil Viscosity, cSt

** Difference in Penetration after 10,000x strokes

Table 5. Properties for Al Complex Greases

	Test Method	150 N1	150 N2	460 N3	1000 P3	100 P1	100 P2	150 S1
Vis, 40°C*	D445	143.99	142.90	475.34	958.24	106.10	117.30	148.47
Vis, 100°C*	D445	11.04	10.50	26.36	43.04	10.90	12.10	21.19
wt% Soap	-	7.4	8.5	12.5	14.6	12.1	15.3	15.5
wt% Base oil	-	92.6	91.5	87.5	85.4	87.9	84.7	84.5
Penetration, 0.1 mm	D217							
(unworked)		-	-	-	-	-	-	-
Worked; 60x strokes		281	287	277	288	275	282	305
10,000x strokes		317	335	308	328	315	310	352
Mechanical Stability**		36	47	31	40	40	28	47
Roll stability, % change	D1831	-5.9	2.3	5.6	8.6	11.2	15.6	18.2
Dropping Point, °F (°C)	D2265	525 (274)	516 (269)	>550 (>288)	518 (270)	515 (268)	545 (285)	505 (263)
Oil Separation	D6184	3.25	2.3	1.2	0.44	2.35	3.15	0
USS Mobility Test, g/min	US Steel							
@ 0°F (-17.8°C)		9.6	7.2	6.5	0	-	5.2	20
@ -20°F (-28.9°C)		2.7	1.2	1.8	0	-	0.8	9.2

* Base Oil Viscosity, cSt

** Difference in Penetration after 10,000x strokes

Table 6. Properties for Ca Sulfonate Greases

	Test Method	150 N1	150 N2	460 N3	1000 P3	100 P1	100 P2	150 S1
Vis, 40°C*	D445	143.99	142.90	475.34	958.24	106.10	117.30	148.47
Vis, 100°C*	D445	11.04	10.50	26.36	43.04	10.90	12.10	21.19
wt% Soap	-	34.4	39.9	32.5	38.6	35.2	43	39.3
wt% Base oil	-	65.6	60.1	67.5	61.4	64.8	57	60.7
Penetration, 0.1 mm	D217							
(unworked)		-	-	-	-	-	-	-
Worked; 60x strokes		292	285	278	275	280	281	282
10,000x strokes		300	297	288	288	292	295	297
Mechanical Stability**		8	12	10	13	12	14	15
Roll stability, % change	D1831	0.0	5.1	1.2	-1.4	-	-7.4	-1.5
Dropping Point, °F (°C)	D2265	>550 (>288)						
USS Mobility Test, g/min	US Steel							
@ 0°F (-17.8°C)		23.5	18.1	12.6	2.5	18.4	45.9	171
@ -20°F (-28.9°C)		7.9	5.4	5.6	0.5	7.2	14.1	71

* Base Oil Viscosity, cSt

** Difference in Penetration after 10,000x strokes

Table 7. Properties for Clay Greases

	Test Method	150 N1	150 N2	460 N3	1000 P3	100 P1	100 P2	150 S1
Vis, 40°C*	D445	143.99	142.90	475.34	958.24	106.10	117.30	148.47
Vis, 100°C*	D445	11.04	10.50	26.36	43.04	10.90	12.10	21.19
wt% Soap	-	9	9	-	12.8	11.5	12.9	15
wt% Base oil	-	91	91	-	87.2	88.5	91.1	85
Penetration, 0.1 mm	D217							
(unworked)		287	289	-	225	285	268	400
Worked; 60x strokes		295	313	-	232	295	277	430
10,000x strokes		315	339	-	248	322	309	-
Mechanical Stability**		20	26	-	16	27	32	-
Roll stability, % change	D1831	8.5	9.9	-	7.8	9.6	12.7	-
Dropping Point, °F (°C)	D2265	0.7 (-17)	1.6 (-17)	-	0.6 (-17)	3.2 (-16)	2.7 (-16)	7.6 (-14)
USS Mobility Test, g/min	US Steel							
@ 0°F (-17.8°C)		13.3	12.8	-	0.8	10.6	14.5	36.2
@ -20°F (-28.9°C)		4	3.6	-	0	3.2	5.6	11.6

* Base Oil Viscosity, cSt

** Difference in Penetration after 10,000x strokes

Table 8. Comparative Raw Material Costs for Li 12-HSA Greases

Property	150 N1	150 N2	460 N3	1000 P3	100 P1	100 P2	150 S1
wt% Soap	10.5	11.4	11.7	12.6	14.1	14.9	20.8
wt% Base Oil	89.5	88.6	88.3	87.4	85.9	85.1	79.2
Raw Soap Price*, \$/lb	\$ 2.00	\$ 2.00	\$ 2.00	\$ 2.00	\$ 2.00	\$ 2.00	\$ 2.00
Base Oil Price**, \$/gal	\$ 2.59	\$ 2.59	\$ 3.26	\$ 3.62	\$ 2.63	\$ 2.70	\$ 17.41
Density, lb/gal	7.636	7.519	7.620	7.612	7.275	7.291	7.108
Base Oil Price, \$/lb	\$ 0.34	\$ 0.34	\$ 0.43	\$ 0.48	\$ 0.36	\$ 0.37	\$ 2.45
Formulated Soap Cost, \$/lb	\$ 0.21	\$ 0.23	\$ 0.23	\$ 0.25	\$ 0.28	\$ 0.30	\$ 0.42
Formulated Oil Cost, \$/lb	\$ 0.30	\$ 0.31	\$ 0.38	\$ 0.42	\$ 0.31	\$ 0.32	\$ 1.94
Total Formulated Cost, \$/lb	\$ 0.51	\$ 0.53	\$ 0.61	\$ 0.67	\$ 0.59	\$ 0.61	\$ 2.36
Savings \$/10,000 lbs	--	200	1,000	1,600	800	1,000	18,500

*Raw soap price estimated from market sources.

**Base oil prices as reported in ICIS Base Oils Americas - Average Market Prices on 11 Apr 2017. PAO market prices estimated from market sources.

Table 9. Comparative Raw Material Costs for Li Complex Greases

Property	150 N1	150 N2	460 N3	1000 P3	100 P1	100 P2	150 S1
% Soap	13.5	13.8	14.6	16.5	14.5	14.8	16.2
% Base Oil	86.5	86.2	85.4	83.5	85.5	85.2	83.8
Raw Soap Price*, \$/lb	\$ 2.20	\$ 2.20	\$ 2.20	\$ 2.20	\$ 2.20	\$ 2.20	\$ 2.20
Base Oil Price**, \$/gal	\$ 2.59	\$ 2.59	\$ 3.26	\$ 3.62	\$ 2.63	\$ 2.70	\$ 17.41
Density, lb/gal	7.636	7.519	7.620	7.612	7.275	7.291	7.108
Base Oil Price, \$/lb	\$ 0.34	\$ 0.34	\$ 0.43	\$ 0.48	\$ 0.36	\$ 0.37	\$ 2.45
Formulated Soap Cost, \$/lb	\$ 0.30	\$ 0.30	\$ 0.32	\$ 0.36	\$ 0.32	\$ 0.33	\$ 0.36
Formulated Oil Cost, \$/lb	\$ 0.29	\$ 0.30	\$ 0.37	\$ 0.40	\$ 0.31	\$ 0.32	\$ 2.05
Total Formulated Cost, \$/lb	\$ 0.59	\$ 0.60	\$ 0.69	\$ 0.76	\$ 0.63	\$ 0.64	\$ 2.41
Savings \$/10,000 lbs	--	100	1,000	1,700	400	500	18,200

* Raw soap price estimated from market sources.

**Base oil prices as reported in ICIS Base Oils Americas - Average Market Prices on 11 Apr 2017. PAO market prices estimated from market sources.

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The Preparation of a Polyurea Grease Using mPAO 65 and Preformed Diurea

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Abstract:

This paper provides a simple example of the use of mPAO 65 (metallocene polyalphaolefin oil, kinematic viscosity = 65 cSt at 100°C) and a preformed polyurea thickener to produce a polyurea grease. The ease of manufacturing using a preformed thickener is highlighted as well as the excellent properties that are obtained from the mPAO base oil. NLGI grade 2 grease was prepared in the absence of additives and therefore represents a base grease that provides a starting point for further formulation. The low temperature properties of this base grease are an advantage even though polyurea greases are typically known for high temperature advantages over lithium and calcium types of thickener systems. Rheological data clearly demonstrates the superior behavior of this mPAO 65 based grease. Between -30 and -40°C, viscosity was significantly lower than a polyurethane grease formulated with ISO 220 mineral oil. Dropping point (> 260°C), oxidation induction time (14.49 min at 180°C) and temperature for 5% weight loss (294°C) were impressive at high temperatures. Therefore, this grease may be suitable for formulations intended for applications over a wide temperature range. In addition, the apparent viscosity data suggest that this grease has potential to help to prevent fretting corrosion.

Introduction:

Polyurea greases are thickened with polyurea, and differ from other types of greases that are thickened with a soap or soap complex. The use of polyureas as thickeners in greases was reported initially in the 1950s [1-4]. The usefulness of these greases is due to the advantages of their high temperature performance properties, oxidative stability, water resistance, elastomer compatibility, pumpability and long bearing life [5]. Particular use has been found in rolling element bearings in electric motors, wheel bearings, spindles, constant velocity joints and even food grade applications.

A polyurea grease has a very different composition compared to other thickener types in that it is a low molecular weight polymer that is formed in the base oil. Therefore, these non-soap thickeners are more accurately considered as gel-like in nature. The gel thickener chemistry of the polyurea requires two types of chemicals: 1) isocyanates and 2) amines. The polymerization of these two components gives rise to the formation of the gel distributed in the base oil.

The chemistry of these polymers is different from other soap type thickeners since they possess a useful advantage of not being a metal salt of a fatty acid [5]. In soap thickened

greases, materials like lithium or calcium might affect the high temperature properties of a grease since they could act as catalysts for thermo-oxidative degradation of the base oil. Conversely, polyurea greases contain no metal ions from thickeners, providing a benefit for high temperature applications since there are no cations to induce catalytic degradation. Moreover, polyurea greases exhibit desirable rheological characteristics for applications susceptible to fretting wear. These greases also are noted for high dropping points and little tendency for oil separation.

These beneficial properties of polyurea grease come at the expense of the handling requirements of the components mentioned earlier, isocyanates and amines, which are considered extremely hazardous. According to Ivanhoe Industries Inc. [6], “the starting isocyanates and amines are highly toxic and require special handling equipment to handle safely.” Many grease suppliers or those that wish to produce these greases may lack the equipment and depend upon third party manufacturers to produce the polyurea grease. Safely producing the grease is all the more important as companies rightly strive toward zero safety incidents.

Given the potential consequences of working with isocyanates, it raises the question of whether there is a better way to make polyurea greases in a safer manner. This question was answered by researchers at Bayer Ag., specifically, Christian Rasp and co-workers in 1994 [7]; they described a three-step process that was employed to make a polyurea powder for the preparation of polyurea greases. Manufacturing the powder still requires the use of the hazardous chemicals, but once the powder is produced and supplied to grease manufacturers, the need to work with hazardous chemicals is minimized or eliminated altogether.

Purpose:

The primary purpose of this study was to make a polyurea grease from two relatively novel raw materials, measure its properties and assess this technology for industrial applications. Base grease was prepared from metallocene polyalphaolefin (mPAO) base stock and preformed diurea thickener. The unadditized base grease was evaluated using a set of laboratory tests commonly used for grease characterization. Potential commercial manufacturing and applications of this polyurea grease are also discussed.

The grease was made without additives to provide a baseline set of properties or starting point to show base level of performance. It is recognized that improvements can be made by the use of specific additives that are known to grease formulators.

In this paper, a polyurea grease was prepared from mPAO 65 and a preformed grade of the thickening agent. This work investigated the use of mPAO 65 as a viable ingredient for the production of urea greases. This study also tested the use of a preformed thickener to produce a polyurea grease without the need to handle difficult isocyanate raw materials. The results will help grease producers consider this simplified and relatively safe manufacturing method for polyurea grease.

Raw Materials:

Although high viscosity PAOs have been commercially available since the 1980s [8] mPAOs are relatively newer [9] with commercial grades available since 2011. The physical property advantages of the mPAO oils compared to traditional high viscosity PAOs are a higher viscosity index, lower pour point and better low temperature viscometrics. Since these mPAOs are still relatively novel for lubricant development, there are still opportunities to understand where they can or should be used to provide advantages in lubricants and greases.

Previously, we presented a paper at the NLGI annual meeting in 2016 showing the usefulness of mPAO 65 in a lithium grease [10]. In that paper, it was demonstrated that the low temperature (-54°C) torque was substantially lower than a similar grease prepared using a traditional high viscosity PAO 40 base oil. The mPAO 65 base stock was provided by Chevron Phillips Chemical Company LP, and the preformed polyurea thickener was provided by Ivanhoe Industries for this study.

TABLE 1. Properties of mPAO base oil

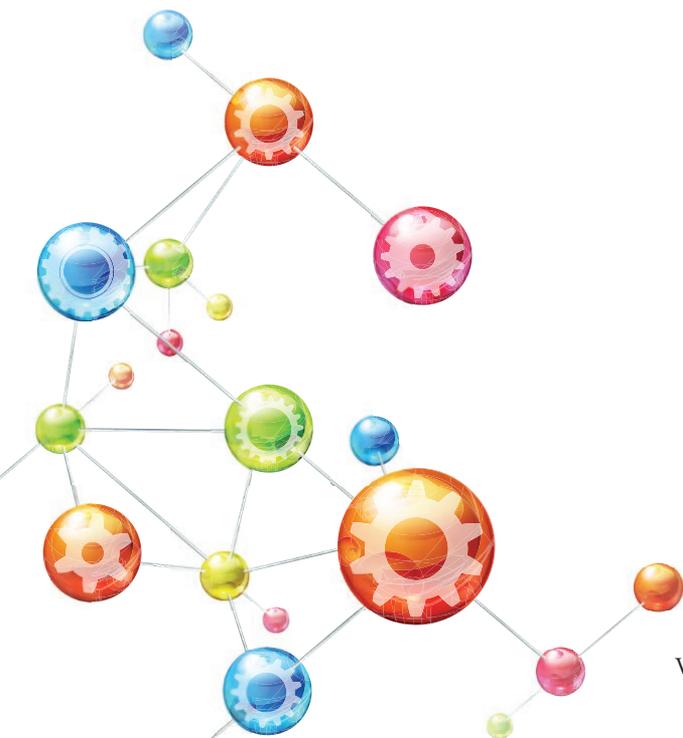
Property	Method	Result
KV at 40°C, cSt	ASTM D445	605
KV at 100°C, cSt	ASTM D445	65
Viscosity Index	ASTM D2270	181
Pour Point, °C	ASTM D92	-42

Grease Preparation:

Five kilograms of polyurea grease were prepared by mixing the diurea powder into the mPAO 65 base fluid according to the formulation in Table 2. This was accomplished by utilizing a planetary mixer and heating to approximately 180°C with constant mechanical stirring. The ratio of ingredients was chosen to produce an NLGI grade 2 grease. The gel was allowed to cool to room temperature and then homogenized at 41 mPa (6,000 psi) using a standard grease homogenizer. Only a single pass was used to homogenize the grease.

TABLE 2 PUG base grease formulation

Ingredients	Weight percent (wt%)
Diurea	20
mPAO 65	80



Experimental:

The grease evaluation was accomplished by the test methods that are listed in Table 3. ASTM methods were used unless otherwise indicated.

TABLE 3 Experimental results for polyurea base grease

Property	Method	Result
Color	Visual	Light Beige
Appearance	Visual	Smooth
Cone penetration, unworked (P0), tenths of mm	ASTM D217	285
Cone penetration (P60), worked, tenths of mm	ASTM D217	294
NLGI Grade	ASTM D217	2
Oil Separation, 24 h at 100°C, wt%	ASTM D6184	1.03
Dropping Point, °C	ASTM D2265	>260
Copper Corrosion, 24 h at 100°C	ASTM D4048	1a
Four Ball Wear, scar diameter, mm (standard deviation)	ASTM D2266	0.63 (0.044)
Apparent Viscosity, 25°C 1.94 s ⁻¹ , mPa.s	ASTM D1092	185,200
Apparent Viscosity, 25°C 24.98 s ⁻¹ , mPa.s	ASTM D1092	15,350
Apparent Viscosity, -40°C TC Spindle, 1 rpm, cP	CTM Brookfield Viscometer	6.9 x 10 ⁶
Oxidation Induction Time, 180°C, min	ASTM D5483 Modified	14.5
Temperature for 5% Weight Loss, °C	Thermogravimetric Analysis	294
Fineness of Grind, µm	ASTM D1210	65
Density, 25°C, g/cc	Pycnometer Method	0.837

Notes:

The modification to ASTM D5483 consisted of using a temperature ramp of 60°C/min.

The fineness of grind result is the gauge depth at which multiple scratches developed.

Under low magnification it was evident that the thickener and base fluid lacked the necessary affinity to produce a “microscopically smooth” structure.

A photograph of the grease is shown in Figure 1. A Nordson EFD cartridge was used to contain the grease after ultrafiltration. These cartridges allow for vacuum centrifugation of the grease to remove entrained air introduced during the filling operation. Residual air can be problematical when filling small quantities of grease into miniature bearings.



Figure 1 Photograph of the mPAO based polyurea grease

A pycnometer method was used to measure the density of the grease. The pycnometer method uses a cup or bottle that holds a known volume. The sample weight is determined by filling the cup to the appropriate volume, weighing it, and subtracting the known weight of the cup or bottle.

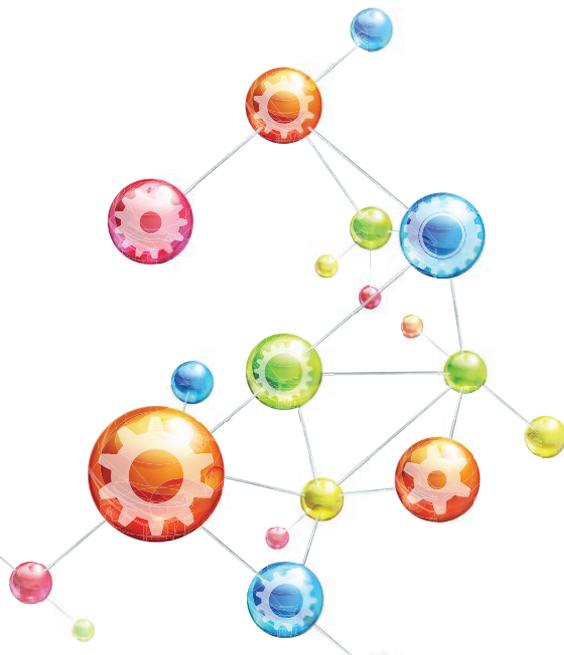
Results:

Table 3 shows some interesting results. First of all, the ratio of blended components did achieve an NLGI grade 2 grease. The cone penetration results show minor changes between worked and unworked penetration results.

The oil separation results are good as well as the copper corrosion.

Polyurea greases are known for having high dropping points, and this grease also exhibits a high dropping point in excess of 260°C, indicating suitability for applications at high temperatures. This is interesting since the grease was formulated without additives, antioxidants in particular.

The Four Ball wear scar shows reasonably good performance especially considering the absence of antiwear additives



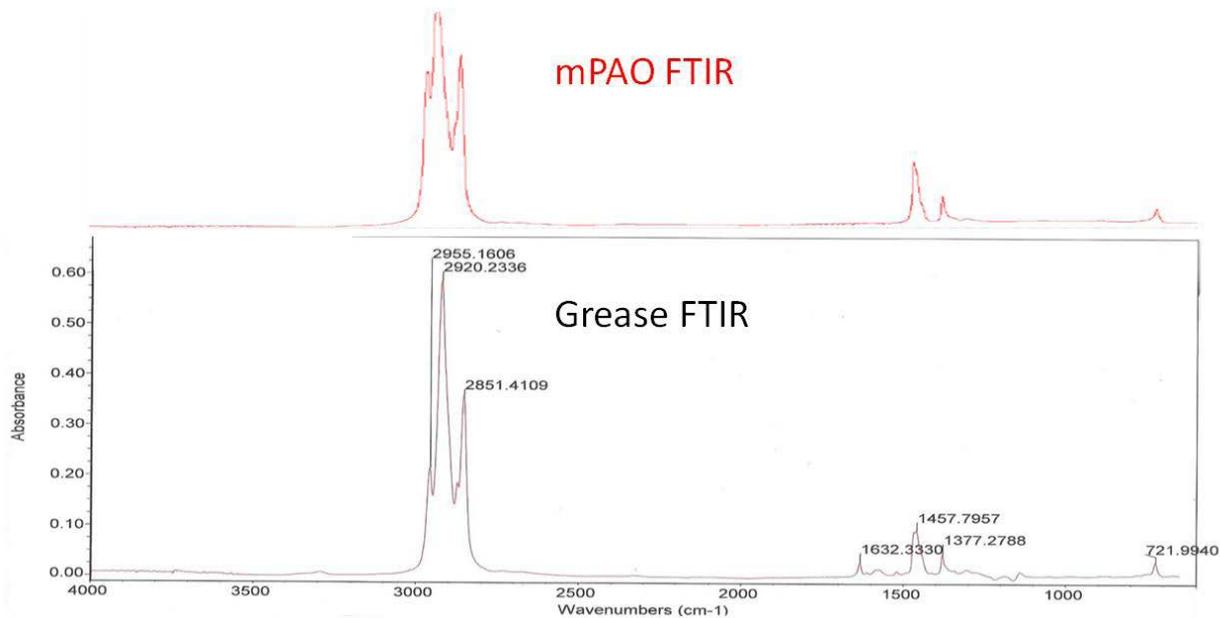
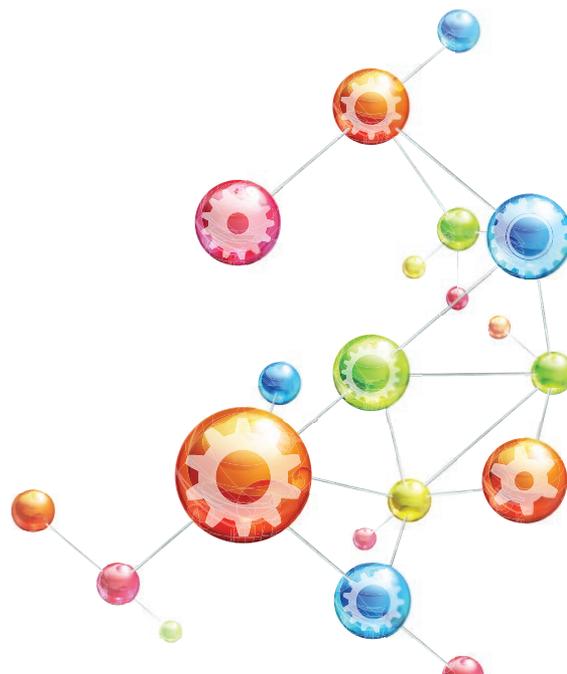


Figure 2 FTIR spectra of mPAO (top) and polyurea grease (bottom)

Figure 2 shows the FTIR spectra of the neat mPAO 65 and the polyurea base grease. Both spectra clearly depict a hydrocarbon as evidenced by the asymmetric and symmetric stretching vibrations of the C-H bonds at 2955, 2920, and 2851 cm^{-1} and lower energy transitions at 1457, 1377 and 721 cm^{-1} .

The peak at 1632 cm^{-1} is the response from the polyurea thickener and this is also noticeably absent from the neat mPAO 65 trace. The very minor baseline shift between 3000 and 3500 cm^{-1} is most likely due to the secondary amine N-H stretch from the polyurea, which is usually a broad weak peak. Nevertheless, the peak at 1632 cm^{-1} clearly indicates the presence of polyurea.



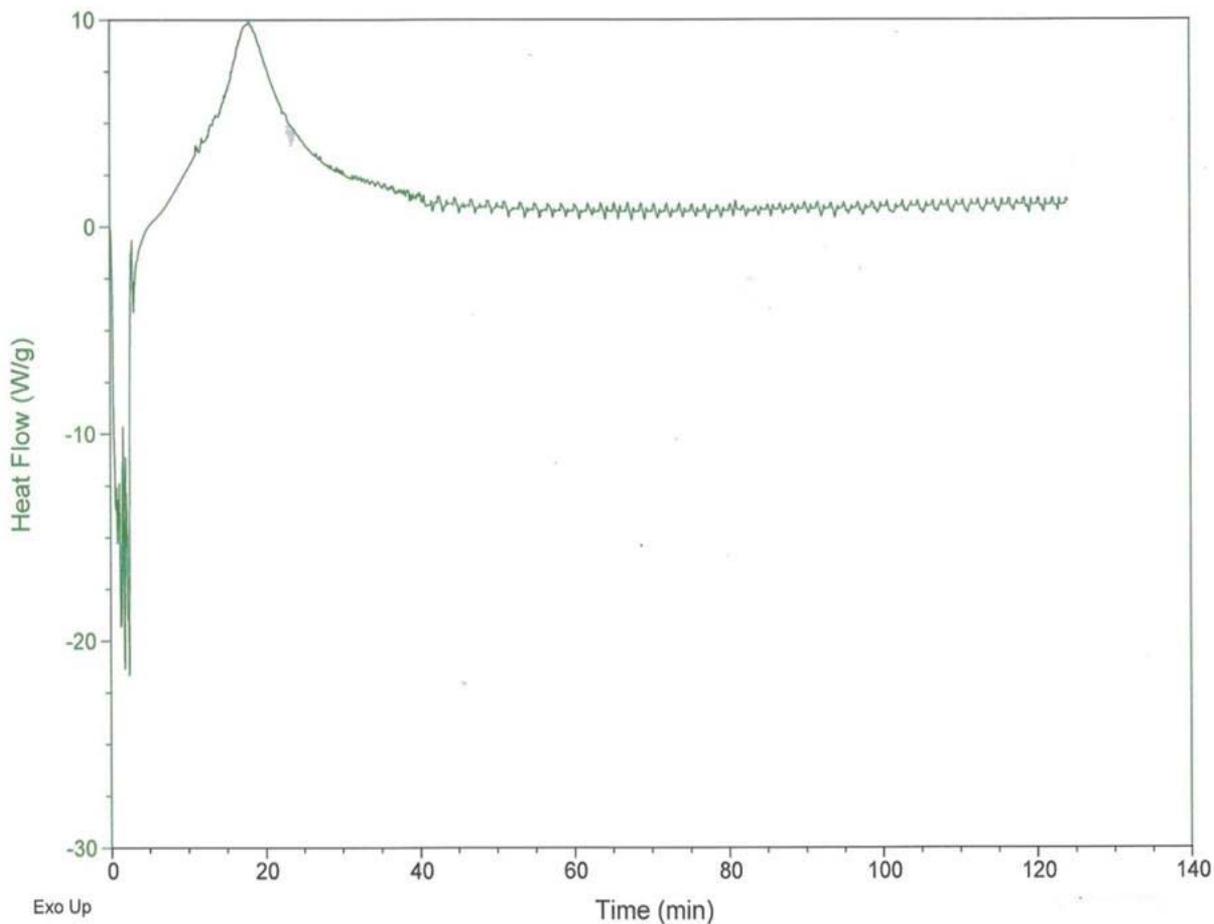
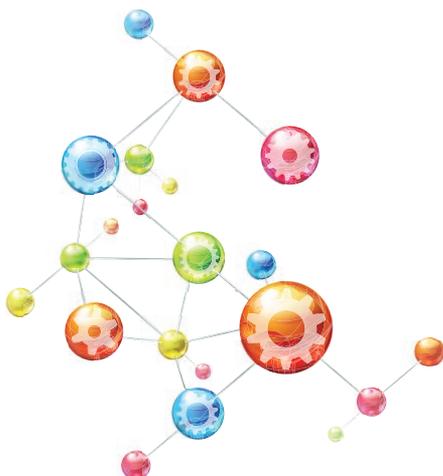


Figure 3 Pressurized Differential Scanning Calorimetry (PDSC) scan of the polyurea grease

Figure 3 shows the PDSC results of a measurement to determine the intrinsic thermo-oxidative stability of the grease. This work was conducted at 180°C in an atmosphere of pure, dry oxygen maintained at 3500 kPa. Although the exotherm occurred after 14.5 min, it is a minor peak and does not indicate significant degradation. Subsequent microscopic inspection of the grease indicated discoloration and not catastrophic degradation. When the grease was inspected under a microscope, it remained pliable when probed with a dental pick. Greases that degrade completely during PDSC testing typically liberate 400 W/g with only carbon remaining. The FTIR and high dropping point results indicate a fairly stable grease with regard to thermo-oxidative behavior.



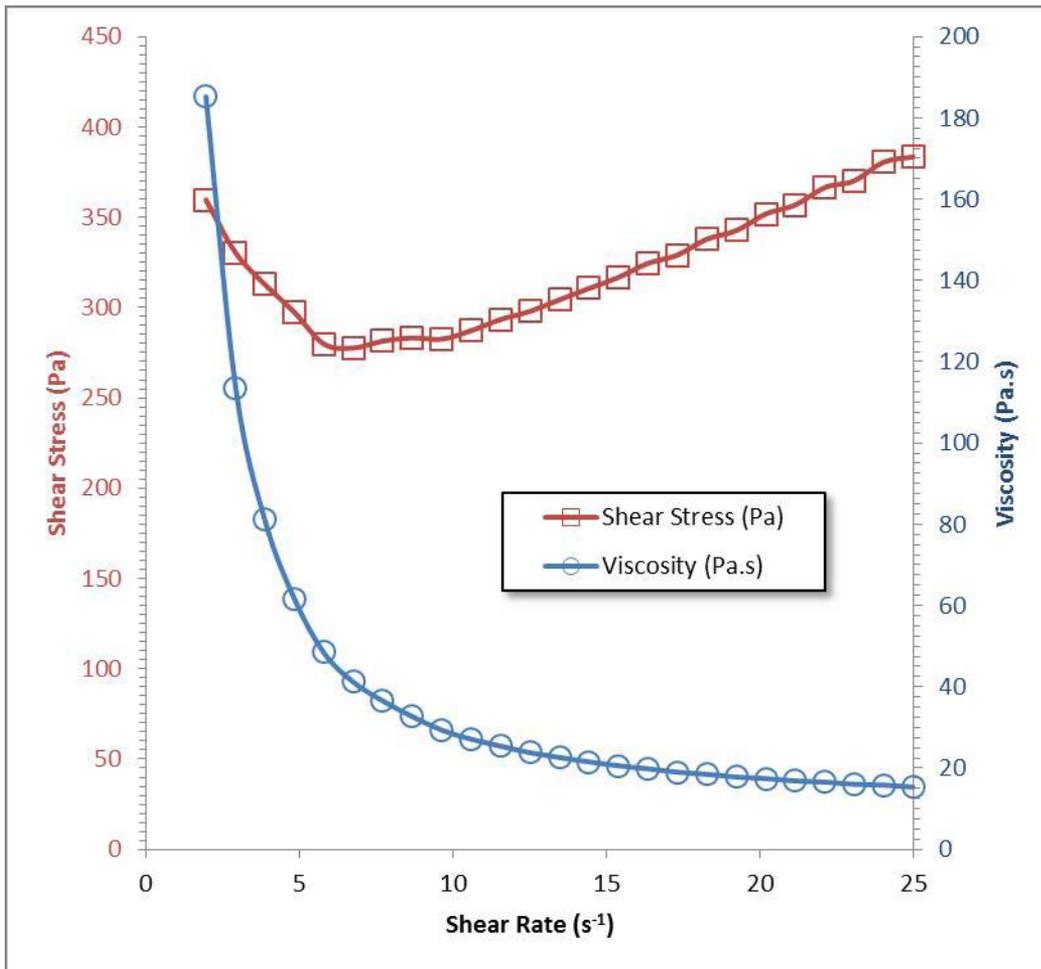


Figure 4 Apparent viscosity of polyurea grease as a function of shear rate

Figure 4 illustrates the shear thinning behavior of the polyurea base grease as a function of shear rate determined at 25°C. Over a shear rate of 23 s⁻¹ the apparent viscosity of the grease declines 169,850 mPa.s.

Since fretting wear [11] occurs due to the inability of a lubricant to gain access to the contact zone in general, greases that shear thin are more likely to be drawn into the contact and reduce the wear.

It is expected that the reduction of the viscosity due to the shear thinning behavior of the mPAO 65 grease could provide some protection against fretting wear. This is based on the assumption that lower viscosity greases would penetrate into the contact areas needing lubrication more readily than higher viscosity materials.

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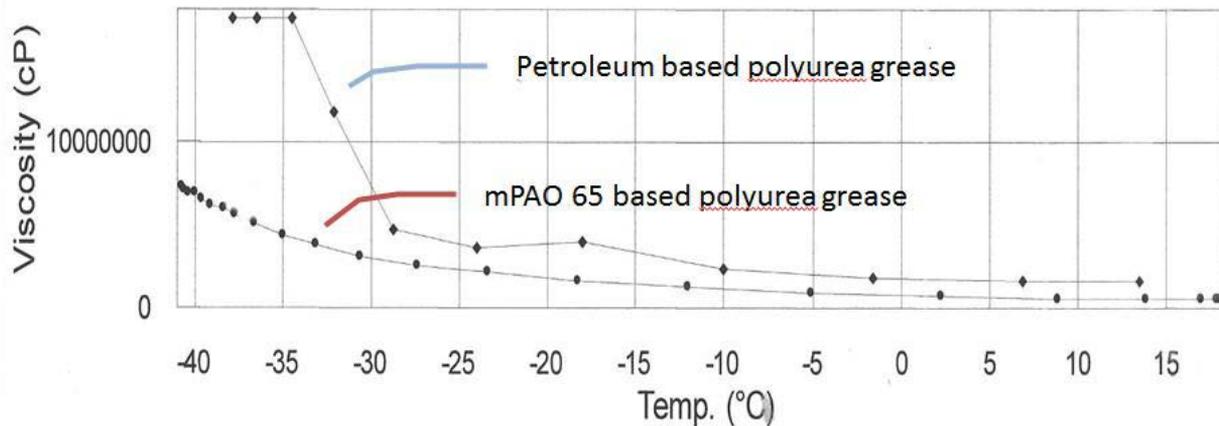


Figure 5 Apparent viscosity measurements for petroleum based polyurea grease (top) and mPAO 65 based polyurea grease (bottom)

Figure 5 compares the low temperature apparent viscosity of the mPAO 65 grease versus a petroleum based grease. These data were obtained using a Brookfield viscometer and a T-C spindle rotating at 1 rpm. Readings were automatically recorded at a fixed spindle depth. Cooling was accomplished using a Tenney Chamber programmed to -45°C . The Tenney Chamber is shown in Figure 6.



Figure 6 Tenney Chamber for temperature controlled apparent viscosity measurements

The low temperature rheological data clearly demonstrates the superior behavior of the mPAO 65 based polyurea grease below -30°C . The petroleum grease is formulated with an ISO 220 mineral base fluid and formulated to an NLGI 2 grade consistency as well. Better low temperature flow characteristics will allow the polyurea grease to function better at low temperatures. Therefore, the grease may be suitable for applications over a wide temperature range.

The thinning in the apparent viscosity upon shear stress in Figure 4 is most interesting. This is important since the thixotropic nature of the polyurea grease allows for penetrating into gaps between critical moving parts during operation and, once shear stress is reduced, then the viscosity returns to a normal grease consistency.

The viscometric properties of the mPAO 65, specifically the viscosity index of over 180, coupled with the thixotropic nature of the polyurea thickener provides an excellent combination of properties. These properties will allow facile delivery of the lubricating grease to the parts that require lubrication. One example of where this would be beneficial relates to fretting corrosion. Under fretting corrosion conditions, lubricant is usually precluded from entering the inlet and the contact starves for lubrication. Greases that are prone to soften with shear are more likely to enter the contact zone and surfaces are less likely to undergo fretting damage.

Conclusions:

A polyurea grease was formulated successfully using a preformed polyurea thickener and mPAO 65. Twenty percent thickener was required to produce an NLGI Grade 2 grease.

The dropping point of the grease exceeded 260°C

Oil separation from the grease was 1.03% after twenty-four hours at 100°C.

Although the formulation contained no yellow metal passivator, the grease demonstrated ability to prevent copper discoloration during 24 hours at 100°C.

Under microscopic inspection, inhomogeneities were observed in the grease. However, a blend of base fluids that would reduce the aniline point of the mPAO 65 would likely result in a smoother microscopic appearance.

The grease exhibits significant shear thinning which is a desirable rheological attribute for application where fretting occurs.

This paper has demonstrated that a preformed

polyurea thickener and mPAO 65 base oil can be used to produce a grease with viable properties. This formulation avoids the use of other more hazardous chemicals in the preparation of polyurea grease. This simple formulation of the thickener and base oil can naturally be improved with the use of specific additives, but this base grease provides a blank canvas for future developments with preformed polyurea thickened greases.

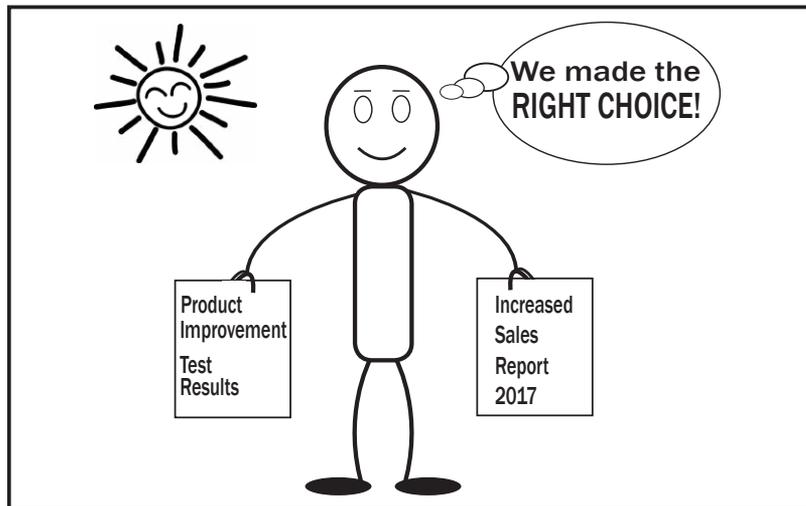
Acknowledgements:

The Authors would like to thank Chevron Phillips Chemical Company LP for supporting the work in this paper. We would also like to thank Mary Moon from NLGI for constructive conversations.

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NLGI India Presents Dr. Raj Shah with Singular Honor

Dr. Raj Shah, Director at Koehler Instrument Company, New York, was recently honored by the NLGI India chapter with its inaugural, Long Service Award, at its 20th Annual meeting held in Amritsar, India. The NLGI India chapter, which is headquartered at the Indian Oil Corporation Ltd, R & D Centre, in Faridabad, has throughout the last 20 years, grown exponentially and currently represents the best of the Indian lubricant and grease industry.

Dr. Shah was presented the award, along with the traditional shawl of honor, by Mr. Chandavarkar, CEO of Standard Greases and current president of NLGI India, due to his steadfast support and involvement in the NLGI India chapter for the last two decades. In his acceptance speech, after Dr. Shah, sincerely thanked his employer and both the board of directors of NLGI and those of the NLGI India chapter for this singular honor, he went on to say, "In NLGI India, I have witnessed unique passion, not merely shared but, perpetuated with zeal and commitment by the able group of volunteers and leaders present here, who have my unflinching admiration and gratitude, and to this commendable team that has galvanized this organization, I would like to dedicate this award."

Dr. Raj Shah, is a Fellow of NLGI, STLE and the Energy Institute and is an Eagle Award recipient from ASTM International. A previous recipient, also, of the ASTM Award of Excellence thrice in his career thus far, Dr. Shah was not long ago conferred the Distinguished Alumni Award from the Institute of Chemical Technology (ICT Mumbai), and the status of a Chartered Scientist from the Science council, UK. He recently stepped down, after serving for more than 15 years with the NLGI board of directors, but is currently still instrumental in working closely with several universities: He is on the industrial advisory board at: The Department of Chemical Engineering at the State University of New York, Stony Brook; The School of Engineering, Design, Technology and Professional programs (SEDAPP) at Pennsylvania State University, his alma mater; and the Samuel Ginn College of Engineering, Tribology and Lubrication science minor at the Auburn University. He can be reached at rshah@koehlerinstrument.com

Industry Calendar of Events 2018

*Please contact Denise if there are meetings/conventions you'd like to add to our
Industry Calendar. denise@nlgi.org
(Your company does not have to be an NLGI member to post calendar items.)*



June 9 – 12
NLGI 85th Annual Meeting
The Coeur d'Alene Resort
Coeur d'Alene, ID



October 6 – 9
ILMA Annual Meeting
JW Marriott Desert Springs Resort & Spa
Palm Desert, CA



June 19 – 20
The 5th ICIS & ELGI Industrial Lubricants Conference
Amsterdam Marriott Hotel, The Netherlands

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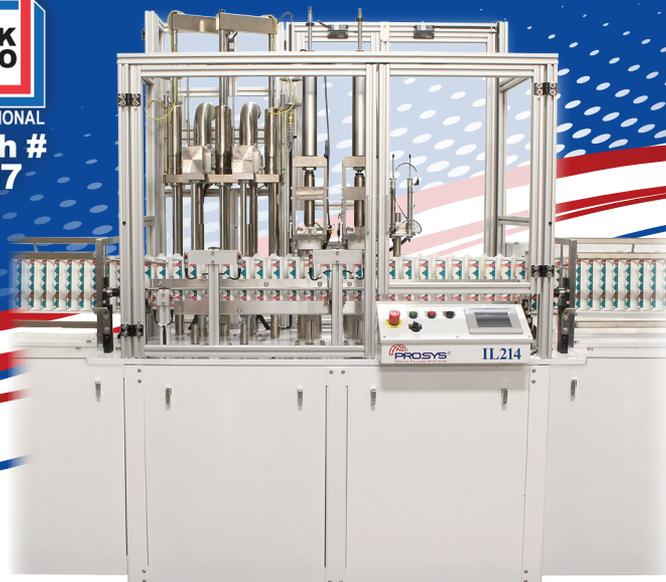
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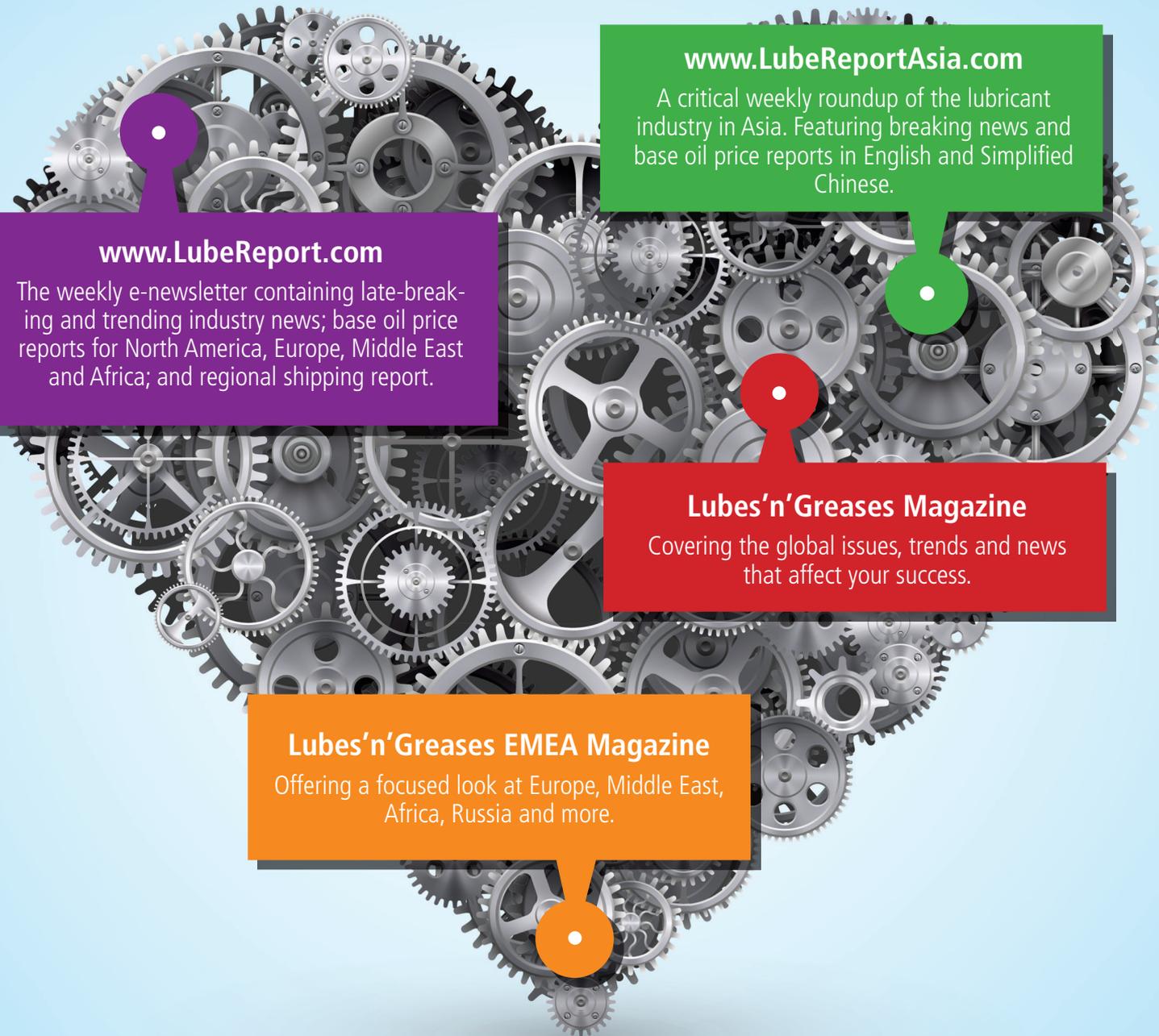
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