In this issue . . .
6  2017 NLGI Awards
16 Advances in Silicone Copolymer Based Lubricants
24 Technologies to Enhance Synthetic Lubricating Greases
32 Polymers to Enhance the Performance of Inorganic Grease
38 Synthetic Grease Formulated Using PAO-6 and mPAO-65

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ON OUR COVER

The 2017-2018 NLGI Board of Directors

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We also welcome two new Board members (not pictured); Ergon, Inc. represented by Timothy Langlais and Daubert Chemical Company represented by Matthew McGinnis.

I look forward to working with you all in the coming year.

David Como
2017 NLGI AWARDS

The NLGI awards recognize those who, through their farsightedness, enterprise and innovation, pioneered significant and lasting improvements in the Institute.

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“In recognition of the three NLGI founding Companies, the Founders Award is presented to a company that has had a positive impact on the NLGI in the tradition established by these found fathers.”

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NLGI FELLOW AWARD
Sponsored by Texas Refinery Corp.
“Acknowledges valuable work within the Institute, in the technical department of greases, grease tests, or the promotion of grease usage.”

J. ANDREW WAYNICK
NCH Corporation

Waynick received a B.A., Chemistry from Central Methodist College, 1974 and an M.S., Physical Chemistry from Purdue University, 1977. He is a Research Fellow within NCH Research and Development, responsible for new product, process development and technical problem solving within fluid lubricants, greases, fuel chemistry and fuel additives. He has 30 U.S. patents, 25 research papers published and has presented at various technical meetings in the U.S., Canada & Europe. In 2016, Waynick received the NLGI Clarence E. Earle Memorial Award. He is a member of ACS, NLGI and IASH.
JOHN A. BELLANTI SR. MEMORIAL MERITIOUS SERVICE TROPHY

"Acknowledges meritorious service on the NLGI Board for three or more years, or on Technical Committee projects, or to the industry.”

RICHARD BURKHALTER
Covenant Engineering Services, LLC

Burkhalter received his bachelor’s degree in Chemical Engineering at the Missouri School of Mines and Metallurgy, Rolla, Missouri, in 1967, now known as the Missouri University of Science and Technology (MS&T). He is a registered Professional Engineer (Illinois & Missouri).

He has more than twenty years’ plant operations experience, including Plant Manager for two lubricants manufacturing plants, one of which has a grease plant that he designed and started up. He served as project manager for a leading consulting firm in the design of lubricating oil and grease manufacturing plants for twelve years. In 1995, he founded Covenant Engineering Services to serve the lubricants and chemical industries where he serves as President. His projects have ranged in value from $20,000 to $30 million, and have been located worldwide. Projects have included process studies, feasibility studies, plant modernization/upgrade, and grass roots plant design.

He is a 50-year member of the American Institute of Chemical Engineers and has been an active member of NLGI since 1986. He has served on the NLGI Board of Directors for thirteen years, authored and presented six technical papers at the annual meetings, co-chaired two panel discussions, and has been published in The Spokesman, STLE, and Machinery Lubrication. In 2015, he received the NLGI award for education excellence in recognition of his teaching in the Basic Grease Education course.

In 2009, he was inducted into the Academy of Chemical Engineers at MS&T and is the holder of one patent. In 2012, he was graduated with a Master of Arts degree in Management and Leadership from Liberty University, Lynchburg, Virginia where he was also inducted into the Sigma Beta Delta Honor Society. He also serves on the Industrial Advisory Board the Chemical Engineering Department at MS&T, and on the Engineering Advisory Board for the Engineering Department at College of the Ozarks.

Mr. Burkhalter has also retired from the US Army at the rank of Colonel with 27½ years of service, both active and reserve.
CLARENCE E. EARLE MEMORIAL AWARD
Sponsored by Rockwood Lithium
“For an outstanding contribution to the technical literature relating to lubricating greases during the year.”

CHAD CHICHESTER
Dow Corning Corporation

Chad has been with Dow Corning since 1992. He worked in operations for his first 3 years, then, moved into a reliability engineering role where he spent 11 years specializing in Condition Based Maintenance techniques including Vibration analysis, Lubrication analysis, Acoustic Emission analysis and Infrared Thermography. In 2006, Chad joined the Molykote Lubricants team as a Lubricants Application Engineer where he has provided engineering and design support to lubricant end user, focused on the industrial equipment maintenance and reliability, the oil and gas segment, and the automotive industry. Chad is a member of the Society of Automotive Engineers (SAE), has served as a chair/instructor in the Society of Tribologists and Lubrication Engineers (STLE) and the National Lubricating Grease Institute (NLGI) Educational courses, and is currently NLGI’s Technical Co-Chair.
NLGI AUTHOR AWARD – Development
Sponsored by Royal Manufacturing Co. LP
“For the best paper presented at our Annual Meeting that focuses on formulation, development, and manufacture of finished greases.”

JOHAN LECKNER
Axel Christiernsson Int’l AB
“Polypropylene – A New Thickener Technology for Energy Efficient Lubrication”

Johan has an M.S. and Ph.D. in Chemical Engineering from Chalmers University of Technology in Gothenburg, Sweden. He worked for six years as a researcher first at the Pasteur Institute in Paris and then at Chalmers University of Technology. He joined Axel Christiernsson International in 2009, as Senior Development Engineer and since 2013 he is working as R&D Manager.

NLGI AUTHOR AWARD – Development
Sponsored by Royal Manufacturing Co. LP
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RENE’ WESTBROEK
Accepting: Johanna Larsson, Axel Christiernsson Int’l AB
“Polypropylene – A New Thickener Technology for Energy Efficient Lubrication”

René has a Master’s degree in Chemical Engineering from the Delft University of Technology, The Netherlands. He worked for 8 years at PPG Industries, amongst others on product development of pigment concentrates and anti-fouling paint. In 2009, he joined Axel Christiernsson International as a Development Engineer and since 2014 he has been working as a Senior Development Engineer.
NLGI AUTHOR AWARD – Application
Sponsored by Chevron Global Lubricants
“For the best paper presented at our Annual Meeting that focuses on testing, selection, application or use of greases.”

DR. GEORGE DODOS
Eldon’s S.A.
“Study on a New Oxidation Stability Method for Lubricating Greases by Employing the Rapid Small Scale Oxidation Test”

Dr. George S. Dodos has a Diploma and a PhD degree in Chemical Engineering from the National Technical University of Athens in Greece. He is working with ELDON’S S.A., involved mainly in research and development of new innovative products and in technical services. He also holds a Research Associate position in the Laboratory of Fuel Technology and Lubricants in the National Technical University of Athens with his research activities currently being focused in the field of bio-based fuels and lubricants. He has several publications in international peer-reviewed journals and conference proceedings on topics such as oxidation stability, tribological behavior and microbial contamination of lubricants and fuels. In 2014, he received the ELGI AGM Best Paper Award. He is affiliated to a number of international organizations including ELGI, SAE and ACS. As of 2013 he chairs the ELGI Bio-based Greases Working Group.
NLGI AWARD FOR EDUCATIONAL EXCELLENCE
Sponsored by Shell Lubricants
“For outstanding instruction as exemplified by subject knowledge and presentation skills in NLGI Grease Educational courses.”

VALENTINA SERRA-HOLM
Nynas AB

Valentina Serra-Holm earned a Ph.D. in Chemical Reaction Engineering from Abo Akademi University in Finland in 2000 and a Ph.D. in Chemical Plants from Polytechnic of Turin in Italy in 1997. From 1996 to 2001, she worked as Senior Researcher at Abo Akademi University in Finland. During her academic career, she has published more than 40 scientific papers in the field of industrial catalysis and is co-assignee of a world patent for manufacturing of polyols.

In 2001, Dr. Serra-Holm joined Nynas AB, where she held several positions within the technical and marketing departments before being appointed to lead the Marketing and Technology department in 2015.

In her current position, Dr. Serra-Holm holds the global responsibility for technical development and marketing of naphthenic oils within Nynas. Her main focus areas are the application and marketing of specialty oils in finished industrial lubricants.

Valentina is President of UEIL (The Union of the European Lubricant Industry) and serves as course instructor at ELGI, NLGI and STLE.
NLGI HONORARY MEMBERSHIP
“Entitles lifetime honorary membership to those who, over a period of years, have served the Institute in some outstanding capacity and are not now with a member company”

JAIME SPAGNOLI
ExxonMobil – Retired

NLGI HONORARY MEMBERSHIP
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ROB HEVERLY
Vanderbilt Chemicals LLC – Retired
NLGI AWARD FOR ACHIEVEMENT

“The Institute’s highest award, it honors the achievement of those who have made exceptional contributions to the growth and development of the Institute.”

JOSEPH KAPERICK
Afton Chemical Corp.

Joseph Kaperick received a Master’s Degree in Analytical Chemistry from St. Louis University in 1991, as well as undergraduate degrees in Chemistry, Fine Arts and Classical Humanities. Currently, Joe is a Customer Technical Service Advisor for Grease Technology and Industrial Lubricants at Afton Chemical Corporation. Joe began working for Afton Corporation in St. Louis as an Analytical Chemist in 1991 and then moved to the Richmond, Virginia headquarters in 1994. He has been in the Industrial Technical Service area with a primary focus on grease since 1999. Joe is a Certified Lubricating Grease Specialist and has received several awards from NLGI including the NLGI Fellows Award, the John A. Bellanti Sr. Memorial Meritorious Service Award, the Clarence E. Earle Memorial Award and the NLGI Author Award. He is currently the Vice President on the NLGI Board of Directors and a member of ASTM, STLE and ACS.
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**Introduction**

One of the lubrication challenges today is the need for cost effective compromise between high temperature performance and lubricity performance like wear and friction reduction. Silicones, commonly known for their extreme temperature performance, as are other synthetic technologies like perfluoropolyether, and polyolester often trade off performance at high temperature for improved lubricity and vice versa. The following paper begins with a brief primer on siloxane based lubricants as an introduction to newly developed fluorosiloxane/phenylmethylsiloxane copolymers. Fluoro/phenyl siloxanes are built on the thermal and oxidative stability of siloxane backbone molecules, functionalized with phenyl pendant groups for great thermal stability, and fluorinated pendant groups for improved wear and friction performance. Neat fluids as well as additized fluids and formulated greases are described and performance levels will be shared in this paper. The copolymer concept brings about flexibility in high temperature, and wear and friction performance, with improved additive acceptance. Additionally, molecular structure modeling will enable design of copolymer fluids with varying degrees of polymerization, functional branch types and lengths to offer many viable lubricant application possibilities.

**Siloxane Base Fluids**

Silicon is the 14th element of the periodic table. Considered semi metallic, or metalloid silicon is widely used in the semiconductor and solar industries for its dielectric and photovoltaic properties. Silicon and oxygen bonds can be polymerized to form materials known as siloxanes. Siloxanes can be functionalized with hydrocarbon-based pendant groups, or branches to make a category of materials known as silicones. Figure 1 is a depiction of the molecular structure of one type of silicone, known as polydimethyl silicone. Different silicones with different functional groups exist for many types of applications, including silicone-based lubricants.

Siloxanes backbone molecular structures are characterized as having very strong bonds. The Silicon-Oxygen bond requires 460 kJ/mol to break as compared to Carbon-Carbon bonds, which break at 348 kJ/mol. This gives the backbone structure very high thermal stability. In addition, long bond lengths (0.164 nm) and high bond angles allow siloxanes to be extremely flexible and have low steric hindrance. Leading to low monomeric friction. Strong, flexible bonds, and low monomeric friction lead to good permanent shear stability. Siloxane backbones are already fully oxidized. This gives siloxanes great oxidative stability and low volatility. Siloxane chemistry, rooted in silicon instead of carbon, offer great chemical incompatibility, which allows utility with many plastics, elastomers, and chemicals, and generally, siloxanes are hydrophobic.

Today, many siloxane-based fluids used as lubricants fall into 3 primary categories. The molecular structure of these silicones can be seen in Figure 2. Dimethyl silicones are the most common. Made of siloxanes with methyl functional groups these silicones are typically filled with silica to be used as static lubricants on elastomers and plastics, however, dimethyl silicones are poor metal-to-metal lubricants. Phenylmethyl silicones feature phenyl functional groups and have wider temperature ranges and improved metal-to-metal...
lubricity compared to dimethyl silicones. Fluoro silicones employ fluoro functional groups for even better metal-to-metal lubricity and have excellent chemical resistance, but these features come at the expense of a slightly reduced temperature range compared to phenyl silicones.

**Phenyl-Fluoro Copolymers**

Imagine combining lubricity of fluoro silicones with thermal stability of a phenyl silicones all within the same molecular structure? This is the essence of fluoro/phenyl silicone lubricants, and is illustrated in Figure 3. These copolymers can be made having varied ratios of phenyl to fluoro content to design base fluids for either higher lubricity or higher thermal stability. Like existing siloxanes many viscosities can be produced. So far, copolymers with phenyl-fluoro ratios of; 25:75, 50:50, and 75:25 have been synthesized. Phenyl-fluoro ratios of 50:50 have been made with viscosities ranging from 400 to 5000 cSt.

**Copolymer Lubricity**

Examining lubricity aspects of silicone copolymers, Figure 4 graphically compares phenyl-fluoro silicone copolymer, fluorosilicone, perfluoropolyether, and polyalphaolefins neat and additized fluids. Silicone copolymers alone, while better than dimethyl silicones still do not perform as well in 4-ball wear testing as compared to other lubricant technologies. However, with additives silicone copolymers rival even additized PAO’s showing excellent promise for the use of additives in silicone fluids intended for lubricant materials.

Examining phenyl and fluoro silicones used as lubricants, fluids of 100% phenyl silicone show large wear scars; hence, phenyl silicones are seldom used in metal-to-metal contacts, except at low temperatures. On the other hand, fluorosilicones have better lubricity properties. When considering copolymers made of phenyl and fluoro functional groups, copolymers with higher fluoro content exhibit lower 4-ball wear scars than copolymers with lesser fluoro functional groups. One would expect wear resistance to be proportionate to the percentage of fluoro content. This is highlighted in Table 1. Interestingly, neat copolymer fluids with 25% phenyl content have lower 4-Ball wear scars than even 100% fluorosilicone fluid. This contradicts the hypothesis and is being explored; however, it will not be further discussed in this paper.

In addition, SRV testing (T = 50C, Freq = 50 Hz, Load = 300N, Stroke = 2 mm) was conducted on three ratios of phenyl/fluoro silicone copolymer as well as 100% fluorosilicone. In this case shown in Figure 5, coefficient of friction values reduce as the percentage of fluoro content increases. Supporting the idea that increased fluoro content will improve lubricity.

Broadening comparison, Table 2 shows phenyl/fluoro silicone neat fluid wear scar performance relative to other exiting base fluid technologies. The 25% phenyl/75% fluoro was nearly the best performing with a wear scar of 0.55 mm, second only to poly-glycol at 0.53mm.

Additive acceptance is another exciting property of
new phenyl/fluoro siloxane copolymers. Various wear improvement additives were added to 50:50 copolymers. Wear scars of neat fluid were compared to additized copolymers. Results are shown, graphically in Figure 6.

Wear scar reduction was observed by additizing 50:50 phenyl/fluoro silicone copolymer. At 400 N loads the highest response was obtained by using zinc diamylthiocarbamate (2.5% treat rate), resulting in a 71% reduction in wear scar. Conversely, amin alkylisooctylphosphate additive (1.0%) showed no wear scar improvement. At 400 N loads the average wear scar improvement through additization (withholding 0% response of amin alkylisooctylphosphate) was 53%. Looking at 800 N load conditions, three additives; antimony o.o-dialkylphoshorodithionate, dithiocarbamate, and zinc dialkyldithiophosphate yield a 59% reduction in wear scar. Interestingly, amin alkylisooctylphosphate, which had no impact at 400 N loads, yielded 33% reduction in wear scar. The average response of additives at 800 N was 46%. This data indicates that phenyl/fluoro silicone copolymers exhibit good wear additive response.

In summary of newly synthesized phenylmethyl/fluoro siloxane copolymer lubricity. Higher fluoro content generally offers improved wear resistance and low frictional coefficient to other silicones and other synthetics. Soluble additives in these copolymers improve wear scar values, on average 50%. This enables phenyl/fluoro copolymers to be viable lubricants.

**Copolymer Thermal Stability**

Considering high temperature aspects of phenyl/fluoro silicone copolymers. Silicones are known to have high viscosity indices (VI). Dimethyl silicones may have VI's that reach as high as 400; however they may not always be applicable as a lubricant in many applications due to poor lubricity. Phenyl silicones will have VI's around 220 and have better lubricity than dimethyl, but for metal-to-metal contacts phenyls may still be lacking. Fluoro silicones have VI's around 240, and much better lubricity than Phenyls. Phenyl/Fluoro copolymers, as expected have VI's that range between 220 and 240, depending on the ratio of phenyl to fluoro functional groups.

Higher phenyl content yields VI's closer to 220, while higher fluoro content produces VI's closer to 240.

Thermographic Analysis (TGA) was performed from 30°C to 500°C. Exposure temperature begins at 30°C and increases 10°C per minute. At 250°C approximately 99% of copolymer material remained. This is nearly the same as phenyl silicone and linear PFPE, and surpasses the performance of PAO, POE, Fluorosilicone, and branched PFPE.

Differential Scanning Calorimetry (DSC) was used to identify Onset Oxidation Temperature (OOT) of phenyl/fluoro silicone copolymers, as well as other common synthetic fluids. Phenyl silicones have the highest OOT, over 360°C, and Fluorosilicone has an OOT of about 250°C. Copolymers examined vary in OOT between 250°C and 360°C depending on the amount of phenyl content. Copolymers with higher phenyl content had higher OOT than copolymers with higher fluoro content. This consistent with what was expected given the high thermal stability of phenyl silicone.

Also observed was lower

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**Table 2: Comparison of phenyl/fluoro silicone copolymer to other synthetic base fluid technologies.**

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Viscosity -35°C</th>
<th>Viscosity 40°C</th>
<th>Viscosity 100°C</th>
<th>Viscosity Index</th>
<th>4-ball Wear Scar (DIN 51555) (400 N)</th>
<th>4-ball Wear Scar (DIN 51555) (800 N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75/25 Phenyl/Fluoro</td>
<td>304</td>
<td>408</td>
<td>63</td>
<td>229</td>
<td>1.53</td>
<td>Too high</td>
</tr>
<tr>
<td>56/50 Phenyl/Fluoro</td>
<td>Solid</td>
<td>328</td>
<td>56</td>
<td>239</td>
<td>1.62</td>
<td>3.05</td>
</tr>
<tr>
<td>25/75 Phenyl/Fluoro</td>
<td>Solid</td>
<td>314</td>
<td>55</td>
<td>242</td>
<td>0.55</td>
<td>1.81</td>
</tr>
<tr>
<td>Poly-o-olefine</td>
<td>Solid</td>
<td>345</td>
<td>37</td>
<td>155</td>
<td>0.77</td>
<td>Too high</td>
</tr>
<tr>
<td>Poly-ester</td>
<td>Solid</td>
<td>171</td>
<td>21</td>
<td>145</td>
<td>1.03</td>
<td>2.30</td>
</tr>
<tr>
<td>Poly-glycol</td>
<td>Solid</td>
<td>471</td>
<td>86</td>
<td>268</td>
<td>0.53</td>
<td>0.65</td>
</tr>
<tr>
<td>Phenyl-methyl- polyisiloxane</td>
<td>Solid</td>
<td>17,400</td>
<td>100</td>
<td>29</td>
<td>322</td>
<td>Too high</td>
</tr>
<tr>
<td>Fluoro-silicone</td>
<td>Solid</td>
<td>44,410</td>
<td>186</td>
<td>36</td>
<td>241</td>
<td>1.18</td>
</tr>
<tr>
<td>PFPE (branched)</td>
<td></td>
<td>80</td>
<td>10</td>
<td>108</td>
<td>1.01</td>
<td>1.58</td>
</tr>
<tr>
<td>PFPE (linear)</td>
<td></td>
<td>159</td>
<td>45</td>
<td>338</td>
<td>1.57</td>
<td>2.07</td>
</tr>
</tbody>
</table>
evaporation rates for all three ratios of phenyl/fluoro copolymers as compared to PAO, POE, and even pure phenyl and fluoro silicones. Phenyl/fluoro copolymer thermal performance is shown in Table 3.

Table 4 is a more complete summary of thermal and oxidative stability data generated, comparing phenyl/fluoro silicone copolymers to other common synthetic lubricants.

In addition to TGA and DSC, phenyl/fluoro copolymer thermo-viscous stability was evaluated. Samples of 25:75, 50:50, and 75:25 phenyl/fluoro ratio copolymers were exposed to 250°C environment. Samples were cooled to 40°C and viscosity measured; then, re-heated to 250°C, held for 24 hours and viscosity re-measured. This process was repeated for several consecutive days. In open cup conditions viscosity began increasing after about 21 days, 28 days, and 42 days for the 25:75, 50:50, 75:25 phenyl/fluoro ratios, respectively. The rate change of 75:25 ratio was less steep than 25:75 and 50:50 ratios. This indicates better thermo-viscous stability of copolymer containing higher phenyl content, as compared to other ratios. In closed cup conditions, viscosity decreases over time in a more linear fashion, with less change, again in the 75:25 copolymer. Both of these data illustrate better thermo-viscous stability in higher phenylated copolymer.

To summarize the thermal performance of phenyl/fluoro silicone copolymers, phenyl functional groups contribute greatly to the thermal performance of the copolymers. Copolymers with higher phenyl content have viscosity indices consistent with other silicone lubricants, and higher onset oxidation temperatures, with less evaporative weight...
loss. Phenyl/fluoro copolymers' thermal performance is very good, even among commonly used synthetics available today.

**Phenyl-Fluoro Copolymer-Based Greases**

PTFE-thickened greases were formulated using phenyl/fluoro copolymer fluids of 460 mPa-s (390 cSt) and 750 mPa-s (640 cSt) viscosities. Greases were evaluated using standard grease tests. Specifically FAG FE9 testing was selected to examine high speed, high temperature performance. FAG FE9 is a lubricant rolling element bearing test. Spindle rotates at 6,000 rpm under axial load of 1500 Newtons. The test concludes when bearing torque increases due to lubricant failure. This test was modified to run at 220°C to push the temperature limits of the phenyl/fluoro copolymer grease. Copolymer-based greases, and other types of greases often used in high temperature applications were evaluated. Results shown in Table 5. Indicate copolymer greases performed well. Logging over 60 hours until failure.

**SKF EMCOR**

Corrosion testing, shown in Table 6, was conducted on phenyl/fluoro silicone copolymer, Perfluoropolyether, pure phenyl silicone and Polyolester greases, to evaluate corrosion resistance. There was little evidence of corrosion in the EMCOR test, scoring a “0” on the EMCOR scale, indicative of little or no corrosion.

Another feature of phenyl/fluoro copolymer-based greases that may have utility is lower density compared to other high temperature greases. The density of copolymer greases is around 1.4 grams per cubic centimeter.
Shown in Table 7, this is about 30% lower in density than Perfluoropolyether-based greases.

Additional grease properties comparisons like penetration, dropping point, bleed & evaporation, etc., of phenyl/fluoro copolymer greases and other grease technologies can be seen in Table 8. It is good to point out that the copolymer greases are only base oil and PTFE thickener, with no additional additives.

Additionally, a lithium complex-thickened phenyl/fluoro copolymer grease was produced. Notable changes in performance, seen in Table 9 of the lithium complex thickened copolymer grease to the PTFE thickened copolymer grease are reduction in bleed. Previously discussed phenyl/fluoro copolymer grease, thickened with PTFE had bleed rates over 4% compared to 0.46% bleed rate for lithium-thickened copolymer.

**Future Siloxane Copolymer Development**

Recall, paper 1505 from NLGI’s 82nd Annual Meeting titled, “High Temperature Grease Utilizing New Silicone Based Fluids”, by Dr. Manfred Jungk. Summarized in Figure 8 Paper 1505 discussed techniques developed by Dow Corning Corporation in collaboration with Northwestern University, to model tribological performance of silicone based lubricating fluids through understanding rheological impacts of molecular structure.

Future work to be done includes extending molecular structure modeling techniques for silicone lubricants to include phenyl/fluoro copolymer fluids. By adding
the phenyl/fluoro copolymer branch type to the molecular modeling toolbox. One could model tribological performance of phenyl/fluoro copolymers of many different phenyl-to-fluoro ratios, at varying degrees of polymerization, which allows for many viscosity evaluations to be done at the modeling stage of product development.

Summary

In Summary, phenyl/fluoro silicone copolymers, inherently retain exceptional thermal stability, oxidative stability, and high viscosity indices, for which silicone lubricants are known. Phenyl functional groups bonded to the siloxane backbone foster excellent high temperature properties, while fluor functional groups bonded to the same backbone contribute to better lubricity through improved wear resistance and friction reduction. Varying the phenyl to fluoro ratio one can also vary the thermal and lubricity performance. More phenyl and fewer fluoro groups yield higher thermal stability, while higher fluoro content and lower phenyl content yields better lubricity. Additive acceptance of phenyl/fluoro copolymers produce on average a 50% reduction in wear scar performance as compared to neat fluids. These phenyl/fluoro copolymers can be used as lubricating fluids, or used as base fluids for grease formulations. In addition, the use of molecular modeling techniques enable tribological modeling of many siloxanes to target key molecular structure variables with tribological performance in mind. Offering a wide range of viscosities, functional groups, and branch lengths these materials can be designed with specific application performance in mind.

References

October 10 – 14, 2017
CLGI Biannual National Conference
China
Location and more information to come

October 14-17, 2017
ILMA Annual Meeting
Hyatt Regency Grand Cypress
Orlando, FL

October 31 – November 2, 2017
2017 Chem Show
The Event for Processing Technology
Javits Center
New York City, New York
www.chemshow.com

April 19-21, 2018
ILMA Management Forum
Fort Lauderdale Marriott Harbor Beach Resort & Spa
Fort Lauderdale, FL

Please contact Kim if there are meetings/conventions you’d like to add to our Industry Calendar. kim@nlgi.org
(Your company does not have to be an NLGI member to post calendar items.)
Technologies to ENHANCE

Gareth Fish, PhD CLS CLGS
and Chris Hsu, PhD
The Lubrizol Corporation

Abstract
According to the 2014 NLGI Annual Grease Production Survey, synthetic base fluid greases now account for approximately 5% of the total grease market with semisynthetics making an additional 2.5%. The majority of greases (up to 80%) made with synthetic oils use polyalphaolefins (PAO) as the main component of their base oil. In terms of oxidative and thermal stability, they have outstanding properties but they have some significant negatives being seemingly less shear stable and bleed oil more readily than the mineral oil equivalents. One further challenge for PAOs is that they respond differently to chemical additives. Packages that work well in Group I and Group II mineral oils often struggle to perform in PAO and other synthetic based greases.

Synthetic esters offer the potential to be both biodegradable and renewable, depending on what alcohols and acids are used to synthesize the esters. Synthetic diesters esters typically have low viscosities and need to be boosted with polymers and or complex esters.

Fully Synthetic calcium sulfonate and calcium sulfonate complex greases are growing, albeit at a slower rate than calcium sulfonates in general. They offer significantly improved low temperature properties and pumpability compared to mineral oil based products.

Other fluids such polyalkylene or polypropylene glycol base fluids are now more in demand as they are one of the three base oil types proposed as part of the vessel general permit (VGP) legislation.

More exotic fluids such as silicone oils, alkylated diphenyl ethers (ADE), perfluoropolyether (PFPE) and ionic fluids (IF) greases can also be used to manufacture synthetic greases, but again thickener and additive response is different. The challenge for these types of fluids that they all have negative properties which need to be counteracted with additives.

The above outlined issues will be discussed in detail and potential solutions to formulating fully synthetic greases offered.

Introduction
According to the 2014 NLGI Annual Grease Production Survey (1), synthetic base fluid greases now account for approximately 5% of the total grease market with semisynthetics making an additional 2.5%. Between 2010, when the base oil type was first recorded, the volume of fully synthetic greases has grown from 25,000 tons to a reported 40,000 tons in 2014. The volumes of many of the specialty synthetic fluids sold are very small. This paper will look at issues surrounding the formulation and development of lubricating greases in a variety of synthetic fluids.

Polyalphaolefin thickened greases
The majority of greases (up to 80%) made with synthetic oils use polyalphaolefins (PAO) as the main component of their base oil. In terms of oxidative and thermal stability they have outstanding properties but they have some significant negatives for grease. One challenge to the grease formulator as the thickener content need to make an NLGI #2 grease is typically 50% higher than for a naphthenic mineral oil of similar viscosity (2). Despite the higher soap content, PAO greases are seemingly less shear stable and bleed oil more readily than the mineral oil equivalents. If being used in sealed bearing applications, seal swell agents need to be added to the PAO grease.

A study was carried out to investigate manufacturing influences on the thickening and dropping points of PAO based synthetic lithium complex greases. Lithium complex
Greases are typically manufactured in one of two ways: two-step or one-step (2).

Traditionally a two-step process has been used. There is an initial saponification with the thickening acid, normally 12-hydroxystearic acid, followed by a second saponification or reaction with the complexing agent. If a dicarboxylic acid, such as azelaic or sebacic acid is used, the two-step process should reliably produce high dropping points in the range of 260 °C to 280 °C. A variation on this is when a boron source, such as boric acid or borate ester, is used as the complexing agent. If using boric acid mixed with water, it is reacted into the grease in a similar way to the complexing dicarboxylic acid. When using a borate ester or other oil soluble boron source, it is typically added during the cooling down phase after the batch has cooled to below 150 °C. It is however important that the boron source is added above 110 °C to enable it to be properly incorporated into the matrix of the grease. This boron-based approach to complexing will produce dropping points in the range of 260 °C to 300 °C, but this depends on how much boron is added. Comparing their thermal stability, synthetic simple lithium greases will work satisfactorily to about 130 °C. Borated complexes will work above these temperatures, but lower than the 160 °C that low acid ratio complexes will perform up to (2).

In a one-step process, the complexing and thickening acids are melted and saponified together. If lithium hydroxide in water is used as the lithium source, the complexing process is difficult to control and can result in good thickening but with scattered dropping points. A series of PAO-based greases were manufactured using either lithium hydroxide in water or an anhydrous lithium hydroxide dispersion. The fatty acid sources were either neat 12-hydroxystearic acid or its methyl ester. The complexing acid was either sebacic or azelaic acids or their dimethyl esters. Reactions were carried out in open, closed and pressurized reactors. Saponification was carried out at 90 °C for either 30, 60 or 90 minutes. FTIR Spectra were taken of the finished greases and the amount of free alkalinity determined by a modified in-house version of ASTM D128. Saponifying the lithium hydroxide in water for only 30 minutes did not run any reactions to completion. The greases were very soft. Free acid and methyl esters were detected in the greases by Fourier transform infrared (FTIR) spectroscopy. When saponifying for 60 or 90 minutes complete reaction was seen with the thickening acid or methyl ester. Neither the azelaic nor sebacic acid reacted well at 90 °C, giving greases with low dropping points. The dimethyl esters did react completely with the lithium hydroxide when saponified for 90 minutes, but the greases had scattered dropping points ranging from 200 °C to 250 °C, indicating poor complexing reactions had taken place. Similarly, when reacted under pressure with the methyl esters, the lithium hydroxide in water produced a high yield grease with a worked penetration of 200 but a dropping point of only 210 °C. The anhydrous lithium dispersion reacted satisfactorily with acids but not very well with the methyl esters, even when reacted for 90 minutes.

Many grease customers now require lithium complex greases to have dropping points >280 °C and typically in the case of fully synthetic greases >300 °C. In 2014 (3), it was reported that the only way to consistently achieve dropping points of >300 °C was to use the anhydrous lithium hydroxide dispersion. Some greases were prepared in 100% PAO using this technology. The data is included in Table 1. Similar simple lithium and lithium complexes greases were made in group I paraffinic mineral oils. The thickener content for the simple lithium was 7% for an NLGI #2 and for the azelaic lithium complex was 9%. Table 1 further illustrates the higher soap contents necessary for the 100% PAO synthetic greases.

### Table 1 – Comparison of lithium thickened PAO greases

<table>
<thead>
<tr>
<th>Grease</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
<th>P6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickener</td>
<td>Simple</td>
<td>Simple</td>
<td>Azelaic complex</td>
<td>Sebacic complex</td>
<td>Azelaic complex</td>
<td>Azelaic complex</td>
</tr>
<tr>
<td>Thickener content (%wt)</td>
<td>14.0</td>
<td>15.0</td>
<td>18.0</td>
<td>18.0</td>
<td>15.0</td>
<td>12.0</td>
</tr>
<tr>
<td>Unworked penetration</td>
<td>338</td>
<td>286</td>
<td>249</td>
<td>219</td>
<td>227</td>
<td>265</td>
</tr>
<tr>
<td>Worked penetration</td>
<td>322</td>
<td>280</td>
<td>253</td>
<td>238</td>
<td>240</td>
<td>278</td>
</tr>
<tr>
<td>Dropping point (°C)</td>
<td>&lt;200</td>
<td>&lt;200</td>
<td>311</td>
<td>No drop</td>
<td>309</td>
<td>293</td>
</tr>
</tbody>
</table>

### Table 2 – The effect of new polymer additives PAO grease bleed

As can be seen, the bleed issue can be modified by the incorporation of suitable polymers.

<table>
<thead>
<tr>
<th>Additive</th>
<th>None</th>
<th>Polymer 1</th>
<th>Polymer 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treat Rate (%wt)</td>
<td>0.2</td>
<td>0.2</td>
<td>4.4</td>
</tr>
<tr>
<td>High temperature oil bleed at 150°C (%wt)</td>
<td>13.1</td>
<td>4.4</td>
<td></td>
</tr>
</tbody>
</table>

**Bleed reducers for PAO based greases**

Two new polymers were obtained, which claimed better bleed reduction properties than the typical styrene-isoprene polymers in mineral oil based greases. They were incorporated into a fully synthetic PAO grease with a base oil viscosity of 6 mm2/s at 100 °C. The greases were tested for ASTM D6184 oil bleed at 150 °C and the results of these tests are shown in table 3.

One further challenge for PAOs is that they respond differently to chemical additives. Packages that work well in
Group I and Group II mineral oils often struggle to perform in PAO based greases. Two sebacate lithium complex greases were manufactured with lithium hydroxide monohydrate using ISO VG 150 base fluids. One utilized a mineral oil blend of Group II paraffinic oil and Group I paraffinic bright stock and the other was a blend of PAO 6 and 100. A standard zinc containing EP additive package was incorporated into the grease. Salient GC-LB grease performance tests carried out, along with some additional tests, such as pressure differential scanning calorimetry (PDSC) and these are reported in Table 3. Both greases passed the requirements of the NLGI ASTM D4950 GC-LB standard, but there were some noticeable differences in performance.

The other significant observation was the different greases failure modes seen in the wheel bearing grease life test. The mineral oil grease failed by lacquering up the bearing so that after meeting the 80 hour minimum, it would not restart after the cooling phase. The PAO based grease failed by over-torqueing during running and not at start up after the 4 hour stationary phase.

A further comparison of mineral oil and PAO base fluids was carried out looking at two different viscosity grades and thickeners. Again the wheel bearing grease life test was used to compare the behavior of greases. The results in Table 4 are not statistically significant, but again the failure modes matched what had been seen earlier with the mineral oil greases creating lacquer and the PAO based ones bleeding out.

Further work is ongoing which has shown that if the bleed and stability can be controlled by polymers then the grease will give longer life. A structurally modified version of the PAO grease in Table 4 was tested recently and gave an FE9 F50 of 150 hours at 140 °C. Post-test analysis of the used grease was carried out and showed degradation of the thickener. Increasing the level of anti-oxidants present in the grease was also seen to be beneficial, as it seemed to better protect the thickener from degradation. A further comparison of urea thickened synthetic fluid greases is now underway.

### Greases in synthetic esters

Synthetic esters are the second largest family of synthetic fluids used as the lubricating base for grease. These fluids have significantly better properties than naturally derived esters, which are typically low viscosity fluids, have poor oxidation and thermal stability (4) and need to be boosted with hydrocarbon polymers, complex and polymer esters to achieve the required viscosities of base fluids for good lubricating properties.

In 2014, Fish and Hsu (3) reported that making thickeners directly in synthetic esters was problematic. Historically, it was only possible to use inorganic thickeners such as clays or silica or pre-formed simple calcium or lithium soaps using to thicken these types of oils. Preformed calcium anhydrous (12-hydroxystearate) soaps will give grease dropping points of 140 to 160 °C and those of pre-formed lithium stearate or 12-hydroxystearate will give grease dropping points of 180 to 200 °C. To develop good grease properties, the pre-formed

<table>
<thead>
<tr>
<th>Property</th>
<th>Test method</th>
<th>Typical requirement</th>
<th>Mineral oil</th>
<th>PAO</th>
</tr>
</thead>
<tbody>
<tr>
<td>NLGI Grade</td>
<td>D217</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Dropping point (°C)</td>
<td>D2265</td>
<td>≥ 220</td>
<td>279</td>
<td>265</td>
</tr>
<tr>
<td>Bearing rust rating</td>
<td>D1743</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
</tr>
<tr>
<td>4-ball wear scar (mm)</td>
<td>D2266</td>
<td>≤ 0.60</td>
<td>0.48</td>
<td>0.52</td>
</tr>
<tr>
<td>4-ball EP</td>
<td>D2596</td>
<td>≥ 200</td>
<td>315</td>
<td>315</td>
</tr>
<tr>
<td>Weld point (kg)</td>
<td></td>
<td>≥ 30</td>
<td>47.4</td>
<td>47.4</td>
</tr>
<tr>
<td>LW1 (kg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fretting wear weight loss (mg)</td>
<td>D4170</td>
<td>≤ 10</td>
<td>8.0</td>
<td>9.6</td>
</tr>
<tr>
<td>Wheel bearing life (hours)</td>
<td>D3527</td>
<td>≥ 80</td>
<td>80</td>
<td>82</td>
</tr>
<tr>
<td>Copper corrosion rating</td>
<td>D4048</td>
<td>1B max</td>
<td>1B</td>
<td></td>
</tr>
<tr>
<td>PDSC oxidation induction time (OIT) at 180 °C (minutes)</td>
<td>D5483</td>
<td>Report</td>
<td>60.5</td>
<td>93.0</td>
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<tr>
<td>Timken OK load (pounds)</td>
<td>D2509</td>
<td>Report</td>
<td>35</td>
<td>50</td>
</tr>
<tr>
<td>F50 FE9 life at 140 °C (hours)</td>
<td>DIN 51821-2</td>
<td>&gt; 100</td>
<td>107</td>
<td>94</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Grease</th>
<th>M220 Base Oil</th>
<th>P222 Base Oil</th>
<th>P221 Base Oil</th>
<th>M150 Base Oil</th>
<th>P152 Base Oil</th>
<th>P151 Base Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>NLGI grade</td>
<td>#2 Mineral</td>
<td>#2 PAO</td>
<td>#2 PAO</td>
<td>#2 Mineral</td>
<td>#2 PAO</td>
<td>#2 PAO</td>
</tr>
<tr>
<td>ISO viscosity grade</td>
<td>220</td>
<td>220</td>
<td>220</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Wheel bearing grease life (hours)</td>
<td>120</td>
<td>80</td>
<td>80</td>
<td>100</td>
<td>80</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 3: Performance comparison of mineral oil and PAO thickened lithium complex greases

Table 4: Performance comparison of mineral oil and PAO thickened lithium complex greases
thickeners, still have to be heated to melt the soap and are not readily available as complexes. As in mineral oils, clay thickened esters do not have a dropping point and silica thickened grease have higher degradation temperatures than simple soap thickened greases. Adding a clay thickener that does not give a dropping point to an easily oxidized and thermally unstable does not make it into a higher temperature capable grease (2).

In 2015 Fish (4), reported that the manufacturing process utilizing anhydrous lithium hydroxide dispersions had been further developed. The technology was able to deliver not only simple lithium greases in synthetic and natural esters but more importantly high temperature lithium complex thickened greases with dropping points >300 °C. The small particle size (<10 µm) of the lithium hydroxide in the dispersion allows it to react very quickly with the thickener acid and the complexing acid if present. The only water present is from the saponification reaction and it is easily removed with minimal hydrolysis of the base oil. This also minimizes the foaming associated with the water removal. Further development of the anhydrous lithium hydroxide dispersion manufacturing process showed that it was the only viable option to make high quality greases in sensitive base oils was to use anhydrous lithium dispersions.

Ten different synthetic ester base fluids were procured from four different suppliers. The typical properties were determined and compared. Some of the original esters were found to have compatibility issues. Two others were identified as having supply issues and the list was reduced to the more manageable number of four. The basic properties of those four fluids are listed in table 5.

The kinematic viscosities of a series of blends of these fluids were calculated targeting at ISO VG 100, ISO VG 150 and ISO VG 220. These blends were, checked for compatibility and miscibility. Then the viscosities were determined at 40 °C and 100 °C. As reported in 2015 (4), some of the early blends produced hazy mixtures and these were discarded. In table 6, the fluid ratios of the successful blends are reported along with their determined viscosity data and calculated viscosity indices.

The process used to manufacture these greases was the revised version outlined in 2014 (5). The fluid blend is mixed and heated up to 70 °C, then the complexing acid is added. It is then heated to its melting / oil solubilization temperature. In the case of azelaic acid, the melting temperature is 101 °C and in the case of sebacic acid the temperature is 135 °C. The 12-hydroxystearic acid is added and it absorbs heat from the batch and on melting cools the mixture to the desired 85 °C to 90 °C required for the complex saponification. At a 2:1 acid ratio, the thickener delivers dropping points >300 °C, but it requires a higher thickener content. Dilithium sebacate also enhances the rust inhibition of the grease. Despite its higher melting temperature and slightly more difficult processing, sebacic acid was selected as the complexing agent at a 3:1 acid ratio.

A styrene-isoprene polymer to enhance water resistance and tackiness was also cooked into the base grease at a 2%wt treat rate. This polymer was selected because it has very good shear stability and unlike most of the typical polymers used in grease, it is readily soluble in synthetic ester base fluids. Base greases were manufactured using the base fluid blend oils listed in table 5. The greases were made slightly stiff so that they could be cut back to an NLGI grade 2 using the corresponding base fluid blend.

A standard anti-oxidant, extreme pressure (EP) / anti-wear (AW) performance package (4) that also included rust and

<table>
<thead>
<tr>
<th>Synthetic ester</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity at 40 °C (mm²/s)</td>
<td>22.3</td>
<td>87.0</td>
<td>950</td>
<td>3430</td>
</tr>
<tr>
<td>Viscosity at 100 °C (mm²/s)</td>
<td>4.85</td>
<td>12.0</td>
<td>82.6</td>
<td>236</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>148</td>
<td>150</td>
<td>168</td>
<td>198</td>
</tr>
<tr>
<td>Acid number (mg KOH / g eq.)</td>
<td>0.34</td>
<td>0.8</td>
<td>21.9</td>
<td></td>
</tr>
<tr>
<td>Copper corrosion (3 hours at 100 °C)</td>
<td>1B</td>
<td>1B</td>
<td>1B</td>
<td>1B</td>
</tr>
<tr>
<td>Pour Point (°C)</td>
<td>-40</td>
<td>-27</td>
<td>+18</td>
<td></td>
</tr>
<tr>
<td>PDSC oxidation induction time at 175 °C (minutes)</td>
<td>137</td>
<td>201</td>
<td>98.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 5 – Synthetic ester data

<table>
<thead>
<tr>
<th>ISO Viscosity Grade</th>
<th>100</th>
<th>150</th>
<th>220</th>
</tr>
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<tbody>
<tr>
<td>Blend number</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Ester A</td>
<td>60</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>Ester B</td>
<td>95</td>
<td>85</td>
<td>75</td>
</tr>
<tr>
<td>Ester C</td>
<td>40</td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td>Ester D</td>
<td>5</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>Viscosity at 40 °C (mm²/s)</td>
<td>93.8</td>
<td>95.6</td>
<td>137.8</td>
</tr>
<tr>
<td>Viscosity at 100 °C (mm²/s)</td>
<td>14.83</td>
<td>14.51</td>
<td>19.88</td>
</tr>
<tr>
<td>Viscosity index (VI)</td>
<td>167</td>
<td>157</td>
<td>166</td>
</tr>
</tbody>
</table>

Table 6 – Successful synthetic ester blend information and viscosity data
corrosion inhibitors was also incorporated into the grease. The properties of the fully formulated greases are included in table 7. As can be seen from this data, the lithium complex thickener delivered high dropping points. The styrene-isoprene polymer delivered excellent water resistance and the performance package delivered satisfactory EP and AW performance.

**Fully synthetic calcium sulfonate greases**

Fully Synthetic calcium sulfonate and calcium sulfonate complex greases are growing albeit at a slower rate than calcium sulfonates in general. They offer significantly improved low temperature properties and pumpability compared to mineral oil based products.

It is relatively easy to manufacture a fully synthetic calcium sulfonate grease. The process was described in detail (5). It starts with mixing a synthetic base fluid with a 400TBN overbased sulfonate in PAO 6 at around 50 °C, followed by the addition of a suitable organic or sulfonic acid. Acetic acid is added slowly to the mixture. The amount of acid added to destabilize the micellar structure of the sulfonate depends on the amount of free lime present in the overbased calcium sulfonate. Water and alcohol are added and the mixture is heated to the gelation temperature. It is held at that temperature until the complete conversion of the calcium carbonate from amorphous to calcite has occurred. For industrial synthetic sulfonates, there are no significant restrictions on what acids or alcohols can be used to aid gelling speed and improve the gel strength. A batch of grease was made in a laboratory kettle using a blend of PAO 6 and PAO 100 as the base oil. The blend gave a final base oil viscosity grade ISO 68. An industrial grade of alkylbenzenesulfonic acid was used along with acetic acid. A promoter and water were also added and the grease gelled in 3 hours. This was followed by stripping at 150 °C. A second grease was made in a resin flask, this time using polyisobutylene (PIB) instead of the PAO as the viscosity fortifier. By increasing the acetic acid quantity to a small excess over normal and keeping the amount of sulfonic acid and promoter constant, the gelling time was reduced from 3 hours to 45 minutes. The results of both greases are reported in the table 8 below. Both greases were made without additional additives.

Two types of synthetic calcium sulfonate complex greases have been developed. The first used a two-step process in which the sulfonate is first gelled and then 12-hydroxystearic acid, more lime and water are added. The mixture is heated and held until the saponification reaction is completed before the last of the water is stripped out and the penetration is adjusted to meet the target value. A single step process was developed in which the 12-hydroxystearic acid is added up front with the synthetic base fluid, the calcium sulfonate, and the sulfonic acid. These are mixed together and followed by the addition of water and the promoter alcohol or glycol. The mixture is heated to the gelation temperature and held until both saponification and calcium carbonate conversion reactions have run to completion, before stripping out the water and promoter. Both of these two events can be monitored by FTIR spectroscopy. It is also important that the equivalents of the acids and the bases
used are known and that the batch remains within an optimum window of basicity. If the batch has too high a level of free basicity then this will prevent or stall the calcium carbonate conversion and the batch may not process properly. If the mixture is too close to neutrality or has insufficient free basicity, there is a tendency for the conversion to become unstable and the carbonate will be converted to the undesired form of vaterite rather than calcite.

H1 incidental food contact grade fully synthetic calcium sulfonates can also be manufactured from HX-1 registered components including the 400TBN sulfonate and sulfonic acid. Some of the best acids for aiding gelation and stiffening are not approved for food grade use. The calcium salts of some acids are approved, and one of these acids needs to be chosen for use as the gelation aid. Building on what was learned about gelling with the industrial sulfonate, a process was developed to gel the sulfonate in PAO 6. A laboratory kettle batch of grease was made using an HX-1 registered 400TBN calcium sulfonate in PAO 6, food grade promoter and water, acetic and sulfonic acids, and using a blend of PAO 6 and food grade registered PIB. The data in Table 9 shows the resulting food grade grease without additional additives has good properties.

### Other Synthetic fluids

The challenge for formulators working with any of the more unusual base fluids is that there is little openly published data. It is common knowledge how much simple lithium soap thickener is needed to make an NLGI #2 in a quality naphthenic base oil with a 40 °C viscosity of 150 mm2/s. Guidelines to achieve required levels of EP or AW properties using additives are widely available. With many synthetic fluids, the only way to generate data is to manufacture base greases, incorporate additives and test the performance of the finished grease.

Other fluids such as polyethylene or polypropylene glycol base fluids are now more in demand as they are one of the three base oil types proposed as part of the vessel general permit (VGP) legislation. Formulating greases with glycols requires a different approach to that of mineral oil based greases.

More exotic fluids such as silicone oils, polyethers, perfluoropolyether (PFPE) and ionic fluids can also be used to manufacture synthetic greases, but the thickener and the additive responses are different. The challenge for these types of fluids that they all have negative properties which need to be counteracted with additives. Ionic fluids can be corrosive and it is necessary to ensure that when making grease, additional alkali is added to the saponification to neutralize the free base fluid acidity.

An alkylated diphenyl ether (ADE) fluid with a 40 °C kinematic viscosity of 100 mm2/s was obtained to do thickening and additive studies. These types of fluids are used to formulate special greases for rolling element bearings. The typical thickener used for this type of fluid is a diurea.

A sample of base grease was manufactured using this ADE base fluid with a diurea thickener based on the reaction of stearylamine (SA) with methylene bis-diphenyl diisocyanate (MDI). The grease needed to be stiffer than normal to allow for softening when the additive package was incorporated and so the thickener content was targeted at 18%. A second base grease was made using aniline, cyclohexylamine (CHA), and MDI. This second grease was too soft and so a third base grease was made with the thickener content increased to 20.2%. The data is in Table 10.

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM Test method</th>
<th>PAO FG grease</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base oil viscosity @40 °C (mm²/s)</td>
<td>D445</td>
<td>30.5</td>
</tr>
<tr>
<td>Unworked penetration</td>
<td>D217</td>
<td>285</td>
</tr>
<tr>
<td>Worked penetration</td>
<td>D217</td>
<td>281</td>
</tr>
<tr>
<td>Water washout (%)</td>
<td>D1264</td>
<td>2.0</td>
</tr>
<tr>
<td>Oil separation (%)</td>
<td>D1742</td>
<td>0.4</td>
</tr>
<tr>
<td>Water corrosion (rating)</td>
<td>D1743</td>
<td>pass</td>
</tr>
<tr>
<td>Dropping point (°C)</td>
<td>D2265</td>
<td>&gt;316</td>
</tr>
<tr>
<td>4-Ball wear scar diameter (mm)</td>
<td>D2266</td>
<td>0.42</td>
</tr>
<tr>
<td>Timken OK load (pounds)</td>
<td>D2509</td>
<td>55</td>
</tr>
<tr>
<td>4-Ball EP weld point / LWI (kg)</td>
<td>D2596</td>
<td>620 / 84.8</td>
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Table 9 – Properties of a fully synthetic calcium sulfonate grease

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>479</th>
<th>497</th>
<th>498</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di-urea thicken description</td>
<td>MDI and SA</td>
<td>MDI, aniline and CHA</td>
<td>MDI, aniline and CHA</td>
</tr>
<tr>
<td>Thickener content (%wt)</td>
<td>18.0</td>
<td>18.0</td>
<td>20.2</td>
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<tr>
<td>Unworked penetration (D1405)</td>
<td>114</td>
<td>133</td>
<td>115</td>
</tr>
<tr>
<td>Full scale equivalent (D217)</td>
<td>233</td>
<td>271</td>
<td>235</td>
</tr>
<tr>
<td>Dropping point (°C) (D2265)</td>
<td>&gt;308</td>
<td>&gt;308</td>
<td>&gt;308</td>
</tr>
</tbody>
</table>

Table 10 – properties of the diurea base greases
Two different zinc containing additive packages as previously described (6) were incorporated into the 479 and 498 base greases. The first package which treated at 4% did not show any significant softening of the 479 base grease but did in the 498 base grease. The second package with a higher treat rate, caused significant softening of both base greases. It also showed significant softening when adding gelled calcium sulfonate as a co-thickener into both bases. It was therefore decided that the MDI, aniline, and CHA thickener system need more development and so it was not investigated further at this stage.

Two finished greases based on the 479 base with the first zinc package (#23) and with one containing the gelled calcium sulfonate (#22) were finished and tested. The results of this testing are in table 11.

The presence of the gelled calcium sulfonate co-thickener boosted the EP and anti-fretting wear properties of grease #22 over #23. Overall, the wheel bearing grease life obtained at over 400 hours are outstanding results as are the very long grease lives at 177 °C in the D3336 Pope test.

**Conclusions**

It has been shown above that the formulation know-how and manufacturing technology is available to develop fully synthetic greases in a wide variety of base fluids and with different thickeners.

Formulations and packages developed for mineral oil based greases do not respond in the same way as they do in fully synthetic greases.

Fully synthetic calcium sulfonate and calcium sulfonate complexes have been manufactured and have been shown to have very good properties.

The use of an alkylated diphenyl ether as a base fluid was shown to give long life grease when thickened with an MDI-SA diurea. Adding a gelled calcium sulfonate as a co-thickener improved the final grease properties.

**Acknowledgements**

The authors wish to acknowledge many co-workers and departments within The Lubrizol Corporation for their contributions to this work.

---

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM test method</th>
<th>#22</th>
<th>#23</th>
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</thead>
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<tr>
<td>Unworked penetration</td>
<td>D1403</td>
<td>291</td>
<td>275</td>
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<tr>
<td>Dropping point (°C)</td>
<td>D2265</td>
<td>&gt;308</td>
<td>&gt;308</td>
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<tr>
<td>Water washout (%)</td>
<td>D1264</td>
<td>1.4</td>
<td>0.9</td>
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<td>4-Ball wear scar diameter (mm)</td>
<td>D2266</td>
<td>0.52</td>
<td>0.53</td>
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<td>4-Ball EP – weld point (kg) – LWT (kg)</td>
<td>D2596</td>
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<td>52</td>
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<td>Wheel bearing grease life (hours)</td>
<td>D3527</td>
<td>&gt;405*</td>
<td>&gt;460*</td>
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<td>High temperature grease life, F50 (hours)</td>
<td>D3336</td>
<td>743</td>
<td>680</td>
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<td>D4170</td>
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<td>SRV step test OK load (N)</td>
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<td>SRV – friction – wear scar (mm)</td>
<td>D5707</td>
<td>0.130</td>
<td>0.67</td>
</tr>
</tbody>
</table>

*testing was stopped without failure

**Table 11 – Tests results for ADP Greases**

**References**

(1) Grease Production Survey Report 2014, NLGI, 249 SW Noel, Suite 249, Lee’s Summit, MO 64063 (www.NLGI.org)


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(4) Fish, G., “The Development of More Environmentally Considerate Greases” presented at the NLGI 82nd Annual Meeting, Coeur d’Alene Resort, Coeur d’Alene, ID, June 2015


(6) Fish, G., Ward Jr, W.C., and Capitosti S.M. “Grease Additives for High Temperature Bearing Applications” presented at the ELGI 26th Annual General Meeting, 26th -29th April 2014, Dubrovnik, Croatia
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Polymers to Enhance the Performance of Inorganic Grease

David A. DeVore, Daniel M. Vargo, and Brian M. Lipowski
Functional Products Inc.

Abstract
A selection of polymers including PIB, OCP/EPDM, grafted OCP, and PIP was added to inorganic greases. The materials studied were mineral oil based Bentonite clay thickened and Silica thickened greases. The addition of polymers into grease changes its ability to resist water spray-off as measured by ASTM D4049. Water spray-off performance can be related to the adhesive property of the grease to the metal surface. Water washout properties were also evaluated. The effect of low temperatures on greases containing polymer additives was measured using the US Steel Grease Mobility test.

Introduction
Lubricating grease comprises two phases and three components: base fluid, thickener, and other performance additives. The liquid phase is primarily formed by the base fluid and dissolved performance additives. The solid phase is formed by a network of soap molecules or a dispersion of solid particles such as inorganic clays or other fillers such as silica. Generally, the soap thickener is a metallic salt of a long-chain fatty acid, e.g. lithium 12-hydroxystearate, which can assemble into a network structure in solution. Inorganic fillers cannot assemble into a network structure. The solid phase thickener can consist of soap molecules or inorganic fillers with or without added polymer. The base oil solubilizes polymers and performance additives and is immobilized by the soap molecule network structure, resulting in a semi-solid to solid appearance.

These properties are influenced by the selection of base oil, thickener and other additives.

Polymers incorporated into the grease can be used to enhance the properties of the grease such as consistency, shear stability, water resistance, adhesion, tackiness, and soap yield. Polymers such as polyethylene, polypropylene, polyisobutylene, halogenated polyethylene, polymethacrylate and polyurea are reported to improve the properties of greases. Olefin copolymers (OCPs), styrene-ethylene-butylene (SEBS) and OCP-anhydride (OCP-A) were studied. The type and structure of polymer selected has significant impact on grease properties including low temperature flow, thickening efficiency and shear stability.

Base greases
The selection of the base fluid used to make the grease has a large impact on the low temperature properties. At low temperatures, paraffinic oils containing significant portions of saturated hydrocarbons generally crystallize which impedes flow. Certain pour points depressants are effective at disrupting these wax crystal structures and can improve flow at low temperatures but generally require a higher treat level.

Unlike paraffinic oils, naphthenic oils generally do not contain high levels of molecules that can crystallize at low temperature. The viscosity increase at low temperature is generally due to purely thickening effects as described by the viscosity index. Naphthenic oils are generally preferred over paraffinic oils for low temperature use.

More recently, synthetics including polyalphaolefins and esters have been used as base fluids in greases for use at low temperature. Similar to paraffinic oils, polyalphaolefins may contain components that crystalize at low temperature. Esters may also exhibit poor low temperature properties if, during use, cleavage of the esters into alcohols occurs.

The selection of the thickener also has an impact on the performance of grease used at low temperature. As machine design evolves operating conditions that the grease must endure has become more severe. Also, the expectation is increased machine productivity and less downtime. This has made it difficult for lithium greases to satisfactorily fulfill these requirements. The National Lubricating Grease Institute (NLGI) GC-LB specification requires greases to surpass simple lithium 12-hydroxystearate greases.

Greases formed using inorganic fillers such as Bentonite clay or fumed silica are generally used in high temperature applications. These can include oven doors, bearings operated under low-load and low-speed conditions and chain lubricants. These types of greases are preferred in these applications because, unlike soap-based greases, they do not demonstrate a dropping point. There is no degradation of the inorganic filler at high temperature and therefore
there is essentially no change to the grease properties.

The physical form of clay and silica thickeners consists of spheres or platelets. This large surface area effectively thickens the grease to a very smooth, buttery texture which is non-melting allowing it to perform very well after careful consideration is given to its intended application.\textsuperscript{12}

Inorganic base greases are somewhat less flexible in terms of the polymer additives that will be effective. This is due to the fact that there is no soap network for the long polymer chains to entangle with or, in the case of functionalized materials, bond with. This limits the success of polymer additives to cases where a sufficiently strong polymer network can be formed in the absence of a soap network. Thus, it is more difficult to improve properties such as water resistance of base grease.

The lack of a soap network also results in grease that does not stiffen and reduce in flow at lower temperatures. This is not generally a concern for inorganic greases as they tend to be used in high temperature applications. However, pumping grease into the locations to be lubricated may occur at lower temperatures where flow is more important. The low temperature properties of inorganic greases are driven by the low temperature properties of the base oil and the components that are dissolved therein such as polymers.

**Water Resistance**

To be most effective in any application a grease must have a certain affinity for the surfaces being lubricated. This affinity or adherence can be measured by several different tests that are known in the industry. Water spray-off and water washout are two of the most commonly used tests.

The adherence of grease to the substrate is characterized by water spray-off or water washout measurements.\textsuperscript{12} In the water spray-off test, a greased metallic surface is subjected to direct water spray at elevated temperature and the adherence is determined based on the mass of grease lost over a certain time period.\textsuperscript{13, 14}

**Water spray-off test**

Water resistance of the grease samples was determined using ASTM D 4049, “Standard Test Method for Determining the Resistance of Lubricating Grease to Water Spray.” This test provides a realistic determination of how much grease will be removed when water is sprayed on it. Panel weights were determined to the nearest 0.1 g and after a 0.8 mm (1/32 in.) thick film of grease was applied to the panels they were reweighed. Any grease outside the scribe lines was removed before reweighing. The panels were inserted into the holders and then into the water spray apparatus as shown in Figure 4. The panel was centered below the spray nozzle. Water at 100 °F was sprayed at a pump pressure of 276 kPa (40 psi) onto the panel for 5 minutes. Grease outside the scribe lines was removed, and the panels were dried in an oven for 1 hour at 150 °F and reweighed. The percent grease weight loss was reported as the percent water spray-off.

**Water Washout Test**

Method ASTM D1264 tests the resistance of a grease to being washed out from a wheel bearing. The grease is packed in a ball bearing, the bearing is then inserted in a housing with specified clearances, and rotated at 6006 30 rpm. Water, at 79°C impinges on the bearing housing at a rate of about 5 mL/s. The amount of grease washed out in 1 h is a measure of the resistance of the grease to water washout.

**Grease Mobility Test**

Grease mobility at 0°F was measured by the US Steel Grease mobility method. Grease flow is a complex phenomenon determined by many factors. The most important factor is temperature. As the temperature decreases a grease will have poorer mobility. Other factors include thickener type and amount, base oil properties and other mobility improvers.

The most readily pumpable or dispensable greases are made from lithium complex or aluminum complex soaps. Less readily pumpable greases are based on calcium complex and calcium sulfonate type soaps. Calcium sulfonate greases contain a higher level of soap to attain a particular NLGI grade compared to lithium complex greases. This accounts for the decreased flow rate of calcium sulfonate greases.

The base oil accounts for 80 to 90% of a typical grease. Therefore, its properties strongly influence grease flow. High viscosity base oils result in lower mobility greases; however, in machinery operation these greases provide better lubricity through increased film thickness. Base oils with low viscosity indexes generally have poorer mobility at lower temperatures. Higher base oil pour points indicate the presence of waxy components, which restrict mobility as they crystallize at low temperature.

Mobility improvers are generally low pour point, low viscosity oils or solvents. These can include synthetic esters and polyalphaolefins.\textsuperscript{13}

---

**Figure 4. ASTM D4049 Water Spray-off Machine**
**Materials**

The base greases used were a NLGI Grade 2 clay grease containing 8.5% clay filler in ISO 460 paraffinic bright stock base oil with 0.5% antioxidant and no additional additives and a NLGI Grade 2+ fumed silica grease containing 9.2% silica. The base oil viscosity was 117 cSt at 40°C, and is a 600 Neutral Group 1 base stock.

![Chemical structures](image)

- Ethylene-propylene copolymer (OCP-L)
- Polyisobutylene (PIB)
- Polyisoprene (PIP)
- Ethylene/propylene copolymer grafted with anhydride/acid/ or amide (OCP-M)

*Figure 3: Types of polymers in solution used in this study, their abbreviations and structures.*

Polymers were incorporated into the base grease by mixing in a Hobart mixer at 80°C. The polymer additives used in this study were in solutions of mineral oil and are shown above in Figure 3. Polymers were added and mixed for 3 hours to ensure complete solubilization of the polymer.

**Experimental Methods**

**Cone Penetration**

The NLGI consistency grade of each of the unworked samples used in this study was determined using one-quarter scale cone penetration following ASTM D1403.

**Water Spray-off**

The water spray-off was determined by ASTM D4049.

**Water Washout**

The water washout was determined at 79°C (175°F) following ASTM D1264 by an outside laboratory.

**US Steel Mobility Test**

The U.S. Steel mobility test determines the resistance of lubricating grease to flow at a given temperature and pressure. Mobility is determined by the flow rate of the grease through a pressure viscometer. Typically the pressure viscometer is constructed of stainless steel and is fitted with a No. 1 (40:1 ratio) capillary. With the sample at the test temperature, the flow of grease is started under the selected pressure using a nitrogen tank and regulator. Typical test pressure is 150 psi and temperatures of ambient, 32°F, 20°F, 10°F, and 0°F. Flow rate, usually measured in grams per second, is determined by collecting the grease for a specified period.

The samples used in this testing were run at 150 psi and 32°F. Lower temperatures were not evaluated due to the pervasiveness of inorganic greases in high temperature applications.
Results and Discussion

Adding polymer additives to the silica base grease does not benefit the water spray-off performance of the grease. This is likely due to the fact that there is no soap network for the second polymer network to entangle with resulting in decreases effectiveness. Due to the ineffectiveness of the polymer additives in benefitting the water spray-off water washout testing was not performed with the silica based greases.

The polymer additives were added as solutions in light naphthenic oil. This resulted in softening of the greases containing the polymer additives. To counteract this, the grease formulator would need to decrease the amount of starting oil in the formulation resulting in a higher concentration of inorganic thickener.

Mobility

Adding polymer to the silica grease resulted in decreased flow as compared to the base grease. OCP-M had the greatest flow. Polymer molecules become more rigid as the temperature decreases. This rigidity decreases the overall flow of the grease.

Unworked penetration data

In all cases addition of liquid polymer additives to the silica base grease softened the grease. Presumably addition of the additional oil along with the polymer caused the increase in cone penetration values. As stated above the polymer becomes less effective at thickening without a soap matrix with which to entangle.

Adding solutions of polymer in oil softens the grease relative to the base grease as occurred in the cases of PIB, OCP-M, and OCP-L. The advantage is that this allows for a reduction in the base oil charge to obtain the desired consistency. The PIP stiffens the base grease because the solvent is removed from the PIP and no additional oil is added with the PIP charge unlike the other polymer components.

Water spray-off

For the clay based grease we see significant improvement in water spray-off when 1% PIP or 4% OCP-M are added. Adding OCP-L has no effect on water spray-off while adding 1% PIP is detrimental to performance. This is likely due to adding a minimal amount of very high molecular weight PIB and a proportionally larger amount of oil.

<table>
<thead>
<tr>
<th>Silica Base Grease Data</th>
<th>Cone Penetration (t/10 mm)</th>
<th>Water Spray-off (%)</th>
<th>Water Washout (%)</th>
<th>US Steel Mobility (g/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base grease</td>
<td>256</td>
<td>100</td>
<td>--</td>
<td>1.019</td>
</tr>
<tr>
<td>+1% PIP</td>
<td>309</td>
<td>100</td>
<td>--</td>
<td>0.165</td>
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<tr>
<td>+1% PIB</td>
<td>283</td>
<td>97</td>
<td>--</td>
<td>0.187</td>
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<tr>
<td>+4% OCP-M</td>
<td>310</td>
<td>100</td>
<td>--</td>
<td>0.339</td>
</tr>
<tr>
<td>+5% OCP-L</td>
<td>290</td>
<td>100</td>
<td>--</td>
<td>0.077</td>
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</table>

<table>
<thead>
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<th>Clay Base Grease Data</th>
<th>Cone Penetration (t/10 mm)</th>
<th>Water Spray-off (%)</th>
<th>Water Washout (%)</th>
<th>US Steel Mobility (g/s)</th>
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<tbody>
<tr>
<td>Base grease</td>
<td>294</td>
<td>49</td>
<td>0.007</td>
<td>0.053</td>
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<tr>
<td>+1% PIP</td>
<td>286</td>
<td>10</td>
<td>29.35</td>
<td>0.009</td>
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<tr>
<td>+1% PIB</td>
<td>339</td>
<td>57</td>
<td>-2.03</td>
<td>0.012</td>
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<tr>
<td>+4% OCP-M</td>
<td>335</td>
<td>12</td>
<td>-2.21</td>
<td>0.111</td>
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<tr>
<td>+5% OCP-L</td>
<td>350</td>
<td>48</td>
<td>1.28</td>
<td>0.034</td>
</tr>
</tbody>
</table>
Water washout

The base grease without polymer had essentially zero water washout meaning that no grease was removed from the bearing. Addition of polymer resulted in poorer performance for all of the polymer additives with the exception of OCP-L. The negative results obtained with PIB and OCP-M indicate that mass was gained during the test, presumably from entrapped water.

Mobility

Adding polymer to the clay grease resulted in decreased flow as compared to the base grease except for the OCP-M which had improved flow. Polymer molecules become more rigid as the temperature decreases. This rigidity decreases the overall flow of the grease.

Conclusion

Adding certain polymers to the clay grease effectively improves water spray-off however other properties such as grease mobility and water washout can be negatively affected. Using OCP-M results in a clay based grease with significantly improved water spray-off performance and improved flow as measured by the US Steel mobility test.

It is known that polymers generally require a soap matrix with which to interact. This interaction or interpenetration allows the polymer to effectively improve both water washout and spray-off.

In the absence of a soap matrix, judicious selection of polymer additives is required to attain an inorganic grease with the best blend of performance attributes.

Acknowledgements

Functional Products Inc. would like to thank Tony Wenzler and Rob Haak of Battenfeld Grease and Oil Corp. of NY for supplying the clay base grease and John Sander and Joanne Moore of Lubrication Engineers for supplying the silica base grease.

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**Chevron Phillips Chemical Co., LP, The Woodlands, TX 77380

Introduction:

Synthetic lubricants are superior to petroleum based products in terms of thermooxidative stability and low temperature performance. Numerous automotive requirements demand that lubricating grease function at -40°C while military specification may demand serviceability to -54°C. MIL PRF 32014 describes a lithium 12-hydroxystearate thickened blend of polyalphaolefins. The viscosity requirements of the specification can be achieved by blending PAO 6 and PAO 40. This paper describes a grease formulated with PAO 6 and mPAO 65. The high viscosity component was synthesized using a metallocene catalyst. The metallocene catalyzed PAO's differ from conventionally PAO's in that their pendent groups, the side chains, represent have a comb-like structure with a chiral center at the branch carbon. The chirality provides for a random distribution of branch stereoregularity and isomer distribution to yield excellent low temperature properties. The kinematic viscosity requirements for the base oil in the grease are quite specific. At 40°C, the maximum viscosity is 140 centistokes while at 100°C the minimum viscosity is 16 centistokes. The specified viscosity requirements have been achieved for typical greases by blending PAO 6 and PAO 40. However, the military specification requires that the low temperature torque as determined by ASTM D1478 not exceed 14,000 g/cm for the starting torque and should not exceed 2800 g/cm for the running torque. We show that decene based PAO 40 is a viable blending component to achieve the viscometrics demanded by the specification while mixed-monomer fluids can be problematical. However, our work suggests that blends using mPAO 65 can produce stellar results in terms of low temperature torque requirements at -54°C.

Figure 1. Typical traditional PAO (left) and typical mPAO structure (right)
**Grease Preparation:**

Approximately five kilograms of lithium 12-hydroxystearate grease were prepared from a blend of PAO-6 and mPAO-65 using dry thickener technology. The ratio of ingredients was chosen to produce an NLGI Grade 2 grease. All of the thickener and one half of the base oil blend were heated until the thickener was completely melted above 200ºC after which the balance of the base oil was added to rapidly quench the kettle contents. The gel and various additives were subsequently homogenized at 6000 psi. The composition of the finished grease is shown in Table 1.

Note: The formulation does not contain the necessary ingredients to meet all of the requirements of MIL PRF 32014. The main objective was to determine the viability of mPAO-65 as a blend component.

Table 2 lists the physical properties determined on the grease.

**TABLE 1**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Weight %</th>
</tr>
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<tbody>
<tr>
<td>Lithium 12-Hydroxystearate</td>
<td>9.7</td>
</tr>
<tr>
<td>mPAO-65</td>
<td>42.4</td>
</tr>
<tr>
<td>PAO-6</td>
<td>42.4</td>
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<tr>
<td>Amine Antioxidant</td>
<td>1.0</td>
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<tr>
<td>Phosphorus Antiwear Agent</td>
<td>3.0</td>
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<tr>
<td>Zinc Sulfonate Rust Inhibitor</td>
<td>1.5</td>
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</table>

**TABLE 2**

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Visual</td>
<td>Light Beige</td>
</tr>
<tr>
<td>Appearance</td>
<td>Visual</td>
<td>Smooth</td>
</tr>
<tr>
<td>KV40°C</td>
<td>ASTM D445</td>
<td>122.8 cSt</td>
</tr>
<tr>
<td>KV100°C</td>
<td>ASTM D445</td>
<td>18.06 cSt</td>
</tr>
<tr>
<td>VI</td>
<td>ASTM D2270</td>
<td>164</td>
</tr>
<tr>
<td>Po</td>
<td>ASTM D217</td>
<td>270</td>
</tr>
<tr>
<td>P60</td>
<td>ASTM D217</td>
<td>279</td>
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<tr>
<td>NLGI Grade</td>
<td>ASTM D217</td>
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</tr>
<tr>
<td>P10K</td>
<td>ASTM D217</td>
<td>321</td>
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<tr>
<td>Oil Separation, 24h at 100°C</td>
<td>ASTM D6184</td>
<td>1.7%</td>
</tr>
<tr>
<td>Dropping Point</td>
<td>ASTM D2265</td>
<td>200°C</td>
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<tr>
<td>Copper Corrosion, 24h at 100°C</td>
<td>ASTM D4048</td>
<td>1 B</td>
</tr>
<tr>
<td>Water Washout, 40°C</td>
<td>ASTM D1264</td>
<td>5.8%</td>
</tr>
<tr>
<td>Four Ball Wear</td>
<td>ASTM D2266</td>
<td>0.54 mm</td>
</tr>
<tr>
<td>Chemistry</td>
<td>FT-IR</td>
<td>Figure 1</td>
</tr>
<tr>
<td>Apparent Viscosity, -54°C</td>
<td>CTM Brookfield Viscometer</td>
<td>13.6 x 10⁶ cP</td>
</tr>
<tr>
<td>T-C Spindle, 1 RPM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidation Induction Time, 210°C</td>
<td>MIL PRF 32014</td>
<td>18.4 minutes</td>
</tr>
<tr>
<td>Volatility, 5% Weight Loss</td>
<td>Thermogravimetric Analysis</td>
<td>250°C</td>
</tr>
</tbody>
</table>
Based on the data presented in Table 2, the kinematic viscosity of the base oil meets the requirements of the specification and the desired NLGI consistency has been achieved. Moreover, the other physical and chemical properties are as expected for the grease. Figure 1 shows the infrared spectrum of the grease.

The infrared analysis clearly depicts a hydrocarbon. The asymmetric and symmetric stretching vibrations of the CH bonds occur at 2955, 2921, and 2851 cm\(^{-1}\) while low energy molecular motions occur at 1462, 1377, and 721 reciprocal centimeters. The prominent peak at 1579 cm\(^{-1}\) is the carbonyl group stretching vibration due to the thickener. The low temperature apparent viscosity of the mPAO 65 grease were compared to a similar grease that was formulated using PAO 40. The low temperature viscosity data for the two greases is shown in Figure 3.
Based on the data shown in Figure 2, mPAO 65 appears to be a suitable blending component for formulating grease to the requirements of MIL PRF 32014. However, a crucial question arose as to the low temperature performance of grease formulated from mPAO 40 versus grease prepared using mPAO 65. Usually, for a given family of oils, a higher viscosity at 40ºC implies a higher viscosity at lower temperatures. However, a blend poses unique challenges and opportunities. The viscosity conundrum is this: mPAO 40 is less viscous than mPAO 65 and requires less PAO-6 to achieve the viscosity target of MIL PRF 32014 while mPAO 65 is more viscous resulting in additional PAO 6 to attain viscosities of 140 cSt max at 40ºC and 16 cSt min at 100ºC.

Which fluid has the most influence on blend performance? The answers are provided in Table 3.

### TABLE 3

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>%</th>
<th>cSt at 100ºC</th>
<th>cSt 40ºC</th>
<th>cST -40ºC</th>
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<tr>
<td>PAO 6</td>
<td>53.0</td>
<td>16.6</td>
<td>111.0</td>
<td>42220</td>
</tr>
<tr>
<td>mPAO 65</td>
<td>47.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAO 6</td>
<td>42.6</td>
<td>16.5</td>
<td>113.2</td>
<td>55153</td>
</tr>
<tr>
<td>mPAO 40</td>
<td>57.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results shown in Table 3 clearly demonstrate the influence of PAO 6 on the low temperature viscosity of the blends. This data was further corroborated with low temperature torque data determined at -54°C shown in Table 4. The viscosity index of the PAO 6 / mPAO 65 is 163 compared to 158. The slightly higher viscosity index is also indicative of the improved viscometrics achieved with the PAO 6 / mPAO 65 blend. Furthermore, the measured -40°C viscosities shows a 12,933 cSt reduction in the viscosity representing nearly a 25% decrease.

Greases 1 and 2 meet the -54ºC torque requirements of the specification whereas the mix-monomer PAO 40 based grease does not.

### TABLE 4: Low Temperature Torque per ASTM D1474 at -54°C

<table>
<thead>
<tr>
<th>Grease</th>
<th>High Viscosity Blending Component</th>
<th>Starting Torque g/cm</th>
<th>Running Torque g/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>mPAO-40</td>
<td>5605</td>
<td>1327</td>
</tr>
<tr>
<td>2</td>
<td>mPAO-65</td>
<td>3543</td>
<td>592</td>
</tr>
<tr>
<td>3</td>
<td>mix-monomer PAO-40</td>
<td>37760</td>
<td>13570</td>
</tr>
</tbody>
</table>

Figure 4 shows the oxidative stability of the mPAO 65 grease fortified with a sulfur based EP agent with AO activity. The test was run at 210ºC according to the method in MIL PRF 32014. The extension of the oxidative induction time to nearly 60 minutes is a significant improvement over 48.7 minutes in comparison. In general, this increase is attributable to the improved oxidative stability of the mPAO component. In general, the oxidative stability tends to be governed by the weakest component when all things are equal, that is, when the additives are identical and at the same treat rates. In this case, the differences are in the amount of PAO 6 present as well as the high viscosity component. The extension of the oxidation induction time should translate to a more oxidatively stable or longer lasting material.
Summary & Conclusion

This paper has sought to examine a comparison of mPAO 65 to PAO 40 for use in grease. A simple lithium grease is used as an example although we would expect similar results for other thickener types. The results indicate that superior low temperature properties are achieved due to both a decrease in the amount of the high viscosity base oil as well as the superior low temperature properties of the mPAO. This improvement in low temperature performance is evident in the 1) -40°C kinematic viscosity and 2) viscosity index for an equiviscous base oil blend at 100°C. Furthermore, in the fully formulated grease there is also a substantial reduction in the low temperature starting and running torque for the PAO 6 / mPAO 65 based lithium grease.

Another advantage that is observed is the increase in the oxidative stability of the mPAO based grease. Although this improvement is not as great in contrast to the low temperature advantages, it nonetheless is significant.

This mPAO 65 based lithium grease is intended to serve as just an example of what can be accomplished when using this material in a grease application. The improvements in low temperature performance and high temperature oxidative stability should also be applicable to other thickener systems such as, lithium complex, calcium complex, bentonite and other thickener systems as well.
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- Low odor

<table>
<thead>
<tr>
<th>TESTS</th>
<th>Treat Level</th>
<th>Grease</th>
<th>K-CORR G-1340</th>
<th>K-CORR G-1350</th>
<th>K-CORR G-1360</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treat Level</td>
<td>-</td>
<td>1.50%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grease</td>
<td>Fully Formulated Lithium 12-Hydroxystearate without RI</td>
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<td></td>
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</tr>
<tr>
<td>EMCOR</td>
<td>4,4</td>
<td>1,1</td>
<td>0,0</td>
<td>0,0</td>
<td>1,1</td>
</tr>
<tr>
<td>ASTM D 6138 3% NaCl Solution</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Four Ball Wear</td>
<td>0.65</td>
<td>0.50</td>
<td>0.50</td>
<td>0.55</td>
<td>0.50</td>
</tr>
<tr>
<td>ASTM D 2266 (mm) 1 hour, 75°C, 40 kgf, 1200 rpm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Zinc naphthenate (10% zinc)
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