In this issue:

6  On the Use of Single Wall Carbon Nanotubes and Other Graphitic Solids as Lubricating Grease Thickeners

28  The Preparation of an Aluminum Complex Grease Formulated with PAO 6 AND mPAO 65

36  NLGI Interviews Ms. Cecilia M. Mancero
    Vice President, International Sales, STRATCO, Inc.
On the Use of Single Wall Carbon Nanotubes and Other Graphitic Solids as Lubricating Grease Thickeners

J. Andrew Waynick and Dr. Haiping Hong

The Preparation of an Aluminum Complex Grease Formulated with PAO 6 AND mPAO 65

Paul A. Bessette* and Ken Hope**
*Triboscience & Engineering, Inc., Fall River, MA 02720
**Chevron Phillips Chemical Co., LP, The Woodlands, TX 77380

NLGI Interviews Ms. Cecilia M. Mancero
Vice President, International Sales, STRATCO, Inc.
Scottsdale, Arizona
Mary Moon and Raj Shah

Published bi-monthly by NLGI. (ISSN 0027-6782)
CRYS TAL O’HALLORAN, Editor
NLGI International Headquarters
118 N Conistor Street, Suite B-281, Liberty, MO 64068
Phone (816) 524-2500, FAX: (816) 524-2504
Web site: http://www.nlgi.org - E-mail: nlgi@nlgi.org
The NLGI Spokesman is a complimentary publication.
The current issue can be found on the NLGI website.
The NLGI Spokesman is indexed by INIST for the PASCAL database, plus by Engineering Index and Chemical Abstracts Service.
Microfilm copies are available through University Microfilms, Ann Arbor, MI. The NLGI assumes no responsibility for the statements and opinions advanced by contributors to its publications. Views expressed in the editorials are those of the editors and do not necessarily represent the official position of NLGI. Copyright 2018, NLGI. Send e-mail corrections to nlgi@nlgi.org.

Serving the Grease Industry Since 1933 - VOL. 83, NO. 4, SEPT./OCT. 2019

ON THE COVER
Happy Fall!
The Institute has had some exciting developments over the past couple of months. First, thank you to all of those who attended NLGI’s inaugural Hands-On Training Course September 17-19, 2019 in Holtsville, NY. This three-day training offered a mixture of classroom lecture and hands-on lab training including:

**Classroom Lecture Modules**
- Introduction to Greases
- Applications: Problem Solving
- Grease Manufacturing Overview
- Grease Testing
- Automotive Applications
- Industrial Applications
- Grease Selection and Recommendations
- Special Tests
- Applications: Grease Tribology
- Grease Composition
  - Base Oil Basics
  - Thickener Basics
  - Additives

**Lab Tests**
- D217 Penetration
- D1743 Rust Prevention
- D1831 Roll Stability
- D2265 High Temperature Dropping Point
- D2266 Four Ball Wear
- D2596 Four Ball Extreme Pressure
- D5706 EP Properties Using SRV
- D5707 Friction and Wear Properties Using SRV
- DIN 51805-2 Low Temperature Flow-Kesternick
- Tackiness Tester
- D6138 Emcor

Due to the success of the Hands-On Training Course, we plan to offer again in Fall 2020. Please stay tuned to NLGI e-mails and website for more details.

Additionally, the Board of Directors met in Toronto at the end of September. Many fruitful discussions took place regarding NLGI’s strategic priorities including membership engagement, global outreach and board governance. The board, committees and HQ work daily to execute our strategic priorities. If you’re interested in learning more or would like to participate on a committee, please contact Crystal O’Halloran, Executive Director at crystal@nlgi.org.

**UPCOMING DEADLINES**

**November 1, 2019** – Launch 2020 Call for Papers. Stay tuned for more information on proposal, paper & presentation deadlines.

**December 1, 2019** – Launch 2020 Research Grant Applications. Applications will be accepted through March 15, 2020.

**January 6, 2020** – Launch 2020 Award Nominations. Nominations will be accepted through March 1, 2020.

As a reminder, you can access technical, education and general information through the Members’ Only area of the www.nlgi.org website using your company’s member login. Please contact NLGI HQ if you do not remember your login information.

Happy Fall,
Joe Kaperick Afton Chemical
NLGI President 2018-2020
Soltex is now the named distributor for Imerys natural and primary synthetic graphite in lubricant applications throughout the Americas!

Improve your lubricants and your supply chain with TIMREX® graphite powders plus best-in-class service and support.

- High quality & purity
- Stable source of supply
- The only primary synthetic graphite
- Technical support
- Logistics solutions

Locations

USA | CANADA | ARGENTINA

orderentry@soltexinc.com | soltexinc.com | +1 281 587 0900 | +1 800 275 8580

Warm Welcome to our New NLGI Member
new member as of August 1, 2019

Candan Industries Pty Ltd
Marketing
Australia

Lubricantes Argentinos
De Alta Performance S.A. LAAPSA
Manufacturer
Argentina

Working Together to Bring You Graphite for BETTER LUBRICANTS

Advertiser’s Index

All-Weld Patterson, page 42
Chemicolloid Laboratories 43
Lubes’n’, page 44
Moly Metals, page 46
Petro-Lubricant Testing Laboratories Inc., page 38
ProSys Servo Filling Systems, page 41
Soltex, Inc, page 4
Vanderbilt Chemicals, LLC, page 39
Zschimmer & Schwarz, page 37

Industry Calendar of Events

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.)

April 25 - 28, 2020
32nd Annual General Meeting
Grand Elysee Hotel
Hamburg, Germany

February 1-3, 2020
NLGI India Chapter Annual Meeting
Indore, India
Day 1

Tribology Fundamentals
• Fundamentals on EHL Film Formation
  Amir Kadiric (Imperial College)
• The Physics of Friction
  Ian Taylor (Shell)
• Fundamentals of Bearing Tribology
  Guillermo Morales (SKF)

Mechanical Engineering
• Rotary Lip Seals: a Misaligned Approach
  F. Xavier Borras (University of Twente)
• Bearing Design for Dynamic Operating Conditions
  Hannes Grillenberger (Schaeffler)
• Grease Life in Rolling Bearings
  Piet Lugt (SKF)

Material Science
• Material Science Aspects of the Wear of Metallic Materials
  Alfons Fischer (MPI Eisenforschung)
• Cage Dynamics in Rolling Bearings by Test and Simulation
  Sebastian Schwarz (Uni Erlangen)
• Surface Texturing
  Vasilios Bakolas (Schaeffler)

Round Table Discussion

Day 2

Tribology Testing
• Roller-on-Disk Geometry for Extreme Pressure Gear Oils
  Mathias Woydt (Matrilub)
• Food Tribology: Concepts and Experimental Approaches
  Florian Rummel (Anton Paar)
• How to Approach a Real World Tribology Problem on Lab Scale
  Dirk Drees (Falex Tribology)

Lubricant Chemistry
• Chemical Approach to Energy Savings in Hydraulic Applications
  Dmitry Shakhvorostov (Evonik)
• Silicone Fluids with Optimised Tribological Behaviour through Molecule Structure Enhancement - a Solution for EV Drivetrains
  Steffen Botts (Lubevisio)
• Fretting Wear Tests – Basics, Industrial Relevance and Test Realisation
  Henrik Buse (Hochschule Mannheim)

Application
• Blink of an Eye - a Biotribology Quest Towards Patient Comfort
  Christian Mathis Ulrich (SuSoS AG)
• Grease Applications
  Aleksandra Nevskaya (DDP Specialty Products Germany)
• Lubricant Challenges in Wind Turbine Applications
  Olav Hoeger (Shell)

Round Table Discussion

If you would like to share your experience or have any questions on the above mentioned topics please submit your enquiry to europe@stle.org

For organisational questions:
Carol Koopman, ELGI, Hemonylaan 26, 1074 BJ Amsterdam, Netherlands
Telephone: +31 20 67 16 162
Email: carol@elgi.demon.nl
www.elgi.org

For technical questions Workshop Chair:
Dr. Manfred Jungk, STLE Europe Representative
Greater Frankfurt Suburb Office, Germany
Phone: +49 6722 500816  Email: europe@stle.org  www.stle.org

Dr. Hannes Grillenberger, Schaeffler Technologies AG & Co.KG
Email: grillhnn@schaeffler.com

Dr. Markus Matzke, Robert Bosch GmbH
Email: Markus.Matzke@de.bosch.com
Abstract
Carbon nanotubes have been shown previously to act as lubricating grease thickeners, with single wall carbon nanotubes (SWCNT) being much more efficient than their multi-wall counterparts. In this study, three different SWCNT’s were evaluated as grease thickeners in a polyalphaolefin (PAO) base oil blend. Several graphites of varying types and reported surface areas were tested as well. Combinations of SWCNT’s and graphites were also included in this study.

Results showed that there was a wide range of thickening ability that depended on which SWCNT (and which lot of SWNCT) was used. In this study, all graphites were significantly less effective thickeners than SWCNT’s, but some graphites were superior to other graphites. Reported surface area did not appear to correlate well with graphite thickening efficiency. Other factors, such as the inclusion of near-graphene structures, may be at least as important as surface area. One class of graphite showed evidence of a significant morphology change during the typical heating process whereby it was incorporated into the PAO base oil blend.

All greases had very high dropping points > 343 C, but only greases thickened with SWCNT’s showed excellent overall structural storage stability. Greases thickened with both an SWCNT and a graphite (or a blend of two SWNCT’s) showed significant adverse interactions where thickener efficiency was less than what would have been expected based on the performance of the individual thickeners. These thickener interactions have interesting implications for future greases where extremely high electrical and thermal conductivity are required.

Controlled shear rate rheometry of SWCNT-thickened greases as a function of temperature showed significantly different behavior for each thickener. When a combination of two SWCNT’s was used, the rheometric behavior at 1 rpm shear rate was different from what was expected on the basis of data for greases thickened by each SWCNT alone. This difference in behavior was not observed at 100 rpm.

All SWCNT’s provided a significant increase in thermal conductivity in the PAO blend compared to just the PAO blend or to more traditional lubricating greases. However, graphite-thickened greases showed an even higher thermal conductivity than SWCNT-thickened greases. This was shown to be due to the much higher concentration of graphite compared to SWCNT’s in the greases.

Introduction
Carbon nanotubes (CNT) have been the focus of much research during the last two decades [1]. There are two types of carbon nanotubes: single-wall (SWCNT) and multi-wall (MWCNT). Single wall carbon nanotubes may be considered to have a structure equivalent to a single graphene sheet rolled into a seamless cylinder with ends that are either open or capped by half fullerene groups or by other more complex structures [2][3]. They are known to exist in braided or intertwined ropes where individual
SWCNT’s have a radial diameter of 1.4 nm. These SWCNT ropes are typically about 0.5 to 40 μm (microns) in length. Thus, the aspect ratio of an SWCNT can be as large as 28,000. Multi-wall carbon nanotubes are comprised of two or more single wall carbon nanotubes that are nested within the outermost carbon nanotube.

Twelve years ago, carbon nanotubes were first shown to behave as a lubricating grease thickener \[4\]. That initial work demonstrated that SWCNT’s were about twice as efficient as MWCNT’s. Base oils that were effectively thickened included polyalphaolefins (PAO) and blends of PAO with more polar synthetic base oils such as polyol esters and alkylated naphthenes. When a 60/40 (wt/wt) blend of 40 cSt PAO and 6 cSt PAO was used, an NLGI No. 2 grade base grease was achieved with 10.5% (wt) of a specific SWCNT. All such SWCNT-thickened greases were shown to have excellent shear stability, low oil bleed, and dropping points of 343 C or higher.

Additional work was also done to show how CNT’s can act as a co-thickener when used with several other more conventional thickener systems \[5\]. However, that work did not determine how different sources of SWCNT’s might affect thickener performance. Neither did that study investigate the use of other graphitic solids as grease thickeners, either alone or in combination with SWCNT’s. The work documented in this paper addresses both of these questions.

Experimental

General Approach

Three SWCNT’s and five graphites were used alone and in various combinations as grease thickeners. The base oil for all thickened formulations was the same 60/40 (wt/wt) ratio blend of 40 cSt PAO and 6 cSt PAO that was used in the aforementioned earlier work \[3\] \[4\]. For the remainder of this paper, the term “PAO blend” will be used to describe this base oil blend. Properties measured were as follows:

1. Thickener efficiency and dropping point
2. Structural storage stability
3. Controlled shear rate rheometry as a function of temperature
4. Thermal conductivity

In this investigation, the terms “thickened blends” and “greases” are used interchangeably. Each thickened blend was prepared by weighing the required amounts of PAO and graphitic solids into an appropriately sized steel can. A small steel spatula was used to hand mix each blend until all solid material was thoroughly wetted by the PAO. Then, the mixture was heated on a hot plate with intermittent stirring until its temperature reached 150 C. For a few blends, the heating process was intentionally not done. Whether heated or not, once thoroughly mixed, all blends were promptly given multiple passes through a three-roll mill with both gaps set at 0.0025 cm (0.001 in). Roll milling was continued until no further thickening was visible. This was usually accomplished in three to four passes. One exception to this is explained below in the Results and Discussion section.

Test Methods

All weights were determined using a top loading balance capable of measuring mass to the nearest 0.01 g. All penetrations were determined in accordance to the half-scale procedure defined in ASTM D1403. Full-scale penetrations as defined in ASTM D217 were not measured due to limited amounts of SWCNT’s available to make grease.
Dropping point was determined by a modified ASTM D2265 procedure where the block temperature was set at 343 C for all measurements. This allowed each grease to experience the same thermal stress during the test. It should also be noted that ASTM D2265 defines dropping points up to 316 C, and the correlation between ASTM D2265 results and real world grease performance is not defined at any temperature. However, since the modified dropping point method employed herein is used as a tool for detecting changes in grease structural stability, these concerns did not apply because the dropping point method was used consistently for all greases in this study, and results were interpreted within the intended limitations of the investigation.

Structural stability was determined by storing samples of the thickened blends in the dark at ambient laboratory temperature (about 25 C). Maximum storage times varied, depending on when the samples were made, but ranged from four to eight months. Further details of the structural stability evaluation procedure are provided in the Results and Discussion section.

Four SWCNT-thickened greases were evaluated by constant shear rate rheometry at two shear rates (1 and 100 rpm) using a Brookfield uni-directional R/S Rheometer. The rheometry test procedure involved using a temperature ramp that started at 22 C and cooled to about -30 C in 40 min.

Thermal conductivity in units of W/mK was measured for selected thickened blends. These tests were performed with a Hot DiskTM Thermal Constants Analyzer using the following parameters:

1. 6 mm measurement depth
2. 16 s measurement time
3. 2.001 mm sensor radius
4. Ambient temperature 25 C
5. 0.025 W power setting
6. Kapton disk

All thermal conductivity measurements were precise to plus or minus 3%. Further details of the thermal stability evaluation procedure are provided in the Results and Discussion section.

**Raw Materials**

Table 1 provides a summary of the compositional properties of the three SWCNT’s used in this study as provided by their respective suppliers.

| TABLE 1: GENERAL INFORMATION ON SINGLE-WALL CARBON NANOTUBES |
|---------------|-----------|-----------|-----------|
| DESIGNATION   | SWCNT-1   | SWCNT-2   | SWCNT-3   |
| Carbon nanotubes, % (wt) | >85       | >90       | >98       |
| SWCNTs, % (wt)       | >70       | >80       | >95       |
| Amorphous carbon, % (wt) | <5        | <5        | <3        |
| Ash, % (wt)           | <2        | <2        | <1        |
| Appearance            | black powder | black powder | small black flakes |

In terms of purity (% CNT’s), the ranking of the three SWCNT’s was as follows:

SWCNT-3 > SWCNT-2 > SWCNT-1

It should be noted that SWCNT-1 was the same as SWCNT that was used in the previously cited work [3][4] where 10.5% (wt) was required to thicken the PAO blend to an NLGI No. 2 consistency.
As can be seen in Table 1, SWCNT-3 had a distinctly different physical appearance compared to SWCNT-1 and SWCNT-2. Additionally, the supply of SWCNT-3 was extremely restricted, which limited the evaluation of SWCNT-3 compared to SWCNT-1 and SWCNT-2.

Table 2 provides properties of the five graphites used in this study.

<table>
<thead>
<tr>
<th>TABLE 2: GENERAL INFORMATION ON GRAPHITES</th>
</tr>
</thead>
<tbody>
<tr>
<td>DESIGNATION</td>
</tr>
<tr>
<td>-------------</td>
</tr>
<tr>
<td>Synthetic or Natural</td>
</tr>
<tr>
<td>General Description</td>
</tr>
<tr>
<td>Surface area, m²/g</td>
</tr>
</tbody>
</table>

As can be seen in Table 2, Graphites A and D were surface enhanced natural flake graphites that differed from each other primarily in the reported surface area. A more precise explanation as to what “surface enhanced” means was not provided by the supplier. Both of these graphites were reported to contain a greater amount of very thin nano-platelet structures compared to more traditional natural graphites. Graphites B and E were double milled synthetic graphites with high surface areas that reportedly resisted re-agglomeration. Graphite C was a more traditional natural graphite with a low reported surface area.

The 6 cSt PAO and 40 cSt PAO were based on 1-decene. The properties of such PAO’s are well documented and are not further discussed here.

**Safety Considerations**

Carbon nanotubes have been a source of concern regarding their potentially serious effects on human health via inhalation and penetration through skin pores \(^6\). Accordingly, during the preparation, handling, and testing of all thickened blends, disposable personal protective equipment (PPE) was worn at all times. That disposable PPE consisted of a Tyvek \(^\circledR\) zip-up jump suits cinched at the ankles and wrists, disposable shoe covers, non-latex gloves, non-permeable hair nets, and near-HEPA air filter face masks. Additionally, clear plastic goggles were worn. At the end of each day, all the PPE except for the goggles was carefully removed and placed into a dedicated disposal container. The sealed container was then removed by a contract hazardous waste disposal company. The goggles were carefully cleaned after each use and then re-used.

**RESULTS AND DISCUSSION**

**Thickening Efficiency and Dropping Points of Carbon Nanotubes**

The ability of SWCNT-1, SWCNT-2, and SWCNT-3 to thicken the PAO blend was evaluated by preparing a series of ten thickened blends. Additionally, the effect of heating the blends before milling was evaluated for SWCNT-1 and SWCNT-2 by making replicate batches without heating. The results are provided in Tables 3 – 5.
NOTE 1: Preparation of this grease blend began with 7.5% (wt) of SWCNT-3, and additional PAO blend was added with mixing and milling until the final grease was obtained.

NOTE 2: Preparation of this grease blend began with 1.9% (wt) of SWCNT-3, and repeated mixing and milling were continued with no further addition of PAO blend until the final grease was obtained.

As can be seen in Tables 3 – 5, the dropping points of all greases were very high with the lowest value being 322 °C. This was consistent with the earlier reported work and may have been due to a combination of the dispersed intrinsic fiber-like structure and very high melting point of CNT’s.

<table>
<thead>
<tr>
<th>Blend Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 cSt PAO, % (wt)</td>
<td>35.80</td>
<td>36.40</td>
<td>37.00</td>
<td>37.00</td>
</tr>
<tr>
<td>40 cSt PAO, % (wt)</td>
<td>53.70</td>
<td>54.60</td>
<td>55.50</td>
<td>55.50</td>
</tr>
<tr>
<td>SWCNT-1, % (wt)</td>
<td>10.50</td>
<td>9.00</td>
<td>7.50</td>
<td>7.50</td>
</tr>
<tr>
<td>Heated before milling?</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Unworked penetration, 0.1 mm</td>
<td>236</td>
<td>257</td>
<td>285</td>
<td>289</td>
</tr>
<tr>
<td>Worked penetration, 0.1 mm</td>
<td>237</td>
<td>257</td>
<td>283</td>
<td>287</td>
</tr>
<tr>
<td>Dropping point, C</td>
<td>&gt;343</td>
<td>341</td>
<td>322</td>
<td>&gt;343</td>
</tr>
<tr>
<td>Dropping point, F</td>
<td>&gt;650</td>
<td>645</td>
<td>612</td>
<td>&gt;650</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Blend Number</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 cSt PAO, % (wt)</td>
<td>35.80</td>
<td>35.80</td>
<td>35.20</td>
<td>35.50</td>
</tr>
<tr>
<td>40 cSt PAO, % (wt)</td>
<td>53.70</td>
<td>53.70</td>
<td>52.80</td>
<td>53.25</td>
</tr>
<tr>
<td>SWCNT-2, % (wt)</td>
<td>10.50</td>
<td>10.50</td>
<td>12.00</td>
<td>11.25</td>
</tr>
<tr>
<td>Heated before milling?</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Unworked penetration, 0.1 mm</td>
<td>317</td>
<td>286</td>
<td>249</td>
<td>265</td>
</tr>
<tr>
<td>Worked penetration, 0.1 mm</td>
<td>317</td>
<td>286</td>
<td>263</td>
<td>265</td>
</tr>
<tr>
<td>Dropping point, C</td>
<td>324</td>
<td>&gt;343</td>
<td>&gt;343</td>
<td>&gt;343</td>
</tr>
<tr>
<td>Dropping point, F</td>
<td>615</td>
<td>&gt;650</td>
<td>&gt;650</td>
<td>&gt;650</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Blend Number</th>
<th>9(1)</th>
<th>10(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 cSt PAO, % (wt)</td>
<td>39.24</td>
<td>39.24</td>
</tr>
<tr>
<td>40 cSt PAO, % (wt)</td>
<td>58.86</td>
<td>58.86</td>
</tr>
<tr>
<td>SWCNT-3, % (wt)</td>
<td>1.90</td>
<td>1.90</td>
</tr>
<tr>
<td>Heated before milling?</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Unworked penetration, 0.1 mm</td>
<td>288</td>
<td>279</td>
</tr>
<tr>
<td>Worked penetration, 0.1 mm</td>
<td>274</td>
<td>269</td>
</tr>
<tr>
<td>Dropping point, C</td>
<td>&gt;343</td>
<td>&gt;343</td>
</tr>
<tr>
<td>Dropping point, F</td>
<td>&gt;650</td>
<td>&gt;650</td>
</tr>
</tbody>
</table>
The worked penetration data for all greases from Tables 3 – 5 are graphically presented in Figure 1.

As can be seen, 7.5% (wt) of SWCNT-1 was required to thicken the PAO blend to an NLGI No. 2 consistency. This is noteworthy since 10.5% (wt) of a different lot of this same SWCNT was required to achieve the same thickening in the same PAO blend in earlier cited work \[3\][4]. Obviously, there was a very significant difference in the manufactured lots of SWCNT-1 used in the present and previous studies.

The three SWCNT’s had significantly different thickening efficiencies in the PAO blend. SWCNT-1 was a more efficient thickener than SWCNT-2. This was the opposite of what would be expected based on the reported purity of these two SWCNT’s as provided in Table 1.

When using SWCNT-1, heating to 150 C before milling did not have a significant effect on thickener efficiency compared to not heating (Blend 3 vs. Blend 4). However, when using SWCNT-2, heating to 150 C before milling resulted in a significantly softer grease compared to the same composition without the heating (Blend 5 vs. Blend 6). This was another indication of a difference between these two SWCNT’s.

The greatest difference between the three SWCNT’s was observed for SWCNT-3. As shown in Figure 1, the thickening efficiency of SWCNT-3 was far superior to either of the other two SWCNT’s. Additionally, the behavior during the preparation of the blends with SWCNT-3 (Blends 9 and 10) was much different than the previous blends. In Blend 9, the initial amount of SWCNT-3 added to the PAO blend was 7.5% (wt). This was done based on the thickening efficiency already observed with the previous two SWCNT’s. However, the 7.5% (wt) SWCNT-3 grease became extremely hard when milled. Additional PAO blend was added in several portions with re-milling after ambient temperature mixing. Eventually, the final milled blend with 1.9% (wt) SWCNT-3 was obtained.
Blend 10 was made where 1.9% (wt) of SWCNT-3 was initially added to the PAO blend. After heating to 150 C, the blend was repeatedly roll milled. The blend slowly began to thicken, but it took more than 30 passes before further thickening apparently ceased. As can be seen, there was no significant difference between the thickening efficiency of Blends 9 and 10. Both blends had very high dropping points (> 343 C) as shown in Table 5.

Unlike the greases thickened with SWCNT-1 and SWCNT-2, Blends 9 and 10 slightly hardened upon working 60 strokes. Blend 9 hardened by 14 points; Blend 10 hardened by 10 points. This minor rheopectic tendency may indicate that the thickening efficiency of SWCNT-3 was not fully achieved in these two blends prior to working. Additional data supporting this possibility are discussed in the section on Constant Shear Rate Rheometry.

The much greater thickening efficiency of SWCNT-3 compared to the other two SWCNT’s possibly was due, at least in part, to the higher purity of SWCNT-3 (Table 1). However, since the reported purities of SWCNT-1 and SWCNT-2 did not trend with their comparative thickening efficiencies as expected, other factors may have contributed to the extremely high thickening efficiency of SWCNT-3.

The one obvious physical difference between SWCNT-3 and the other two SWCNT’s was the flaked appearance of SWCNT-3. The unique flaked appearance of SWCNT-3 suggested a possible explanation for its extremely high thickening efficiency and unique behavior during milling. Perhaps, carbon nanotubes slowly exfoliated from the flaked structure of SWCNT-3 with prolonged shearing. This gradual exfoliation could have resulted in a more effective dispersion of the carbon nanotubes throughout the PAO blend.

If a very high concentration of SWCNT-3 is initially present, the internal shearing forces experienced during mixing and heating could assist in this exfoliation process, thereby requiring less milling to achieve optimum thickening. When a much lower initial concentration is used, nearly all the exfoliation would be due to the milling, thereby requiring many more passes through the mill. While this is an interesting theory, much more work would be required to verify it.

**Thickening Efficiency and Dropping Points of Graphites**
The ability of the two surface enhanced natural graphites (Graphites A and D) to thicken the PAO blend is provided in Table 6 and graphically displayed in Figure 2. The ability of the two double-milled high surface area synthetic graphites (Graphites B and E) to thicken the PAO blend is provided in Table 7 and graphically displayed in Figure 3. The ability of the traditional low surface area natural Graphite C to thicken the PAO blend is provided in Table 8.

<table>
<thead>
<tr>
<th>Blend Number</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 cSt PAO, % (wt)</td>
<td>32.00</td>
<td>30.00</td>
<td>32.00</td>
<td>34.00</td>
</tr>
<tr>
<td>40 cSt PAO, % (wt)</td>
<td>48.00</td>
<td>45.00</td>
<td>48.00</td>
<td>51.00</td>
</tr>
<tr>
<td>Graphite A, % (wt)</td>
<td>20.00</td>
<td>25.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite D, % (wt)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unworked penetration, 0.1 mm</td>
<td>350</td>
<td>279</td>
<td>340</td>
<td>483</td>
</tr>
<tr>
<td>Worked penetration, 0.1 mm</td>
<td>361</td>
<td>267</td>
<td>355</td>
<td>ND</td>
</tr>
<tr>
<td>Dropping point, C</td>
<td>326</td>
<td>&gt;343</td>
<td>334</td>
<td>298</td>
</tr>
<tr>
<td>Dropping point, F</td>
<td>619</td>
<td>&gt;660</td>
<td>633</td>
<td>569</td>
</tr>
</tbody>
</table>

NOTE: Graphite D blends were extremely gritty. After several weeks of ambient temperature storage, significant oil separation occurred.
Figure 2
Thickener Efficiency of Surface Enhanced Natural Graphites in PAO Blend

These values are for unworked penetrations since the softest of these two blends was too fluid to measure a worked penetration. Both Graphite D blends were extremely gritty and produced significant oil separation after several weeks.

<table>
<thead>
<tr>
<th>Blend Number</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 cSt PAO, % (wt)</td>
<td>34.00</td>
<td>32.00</td>
<td>30.00</td>
<td>28.00</td>
<td>30.00</td>
<td>28.00</td>
</tr>
<tr>
<td>40 cSt PAO, % (wt)</td>
<td>51.00</td>
<td>48.00</td>
<td>45.00</td>
<td>42.00</td>
<td>45.00</td>
<td>42.00</td>
</tr>
<tr>
<td>Graphite B, % (wt)</td>
<td>15.00</td>
<td>20.00</td>
<td>25.00</td>
<td>30.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite E, % (wt)</td>
<td>25.00</td>
<td>30.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unworked penetration, 0.1 mm no grease</td>
<td>422</td>
<td>358</td>
<td>287</td>
<td>338</td>
<td>254</td>
<td></td>
</tr>
<tr>
<td>Worked penetration, 0.1 mm no grease</td>
<td>424</td>
<td>358</td>
<td>295</td>
<td>340</td>
<td>257</td>
<td></td>
</tr>
<tr>
<td>Dropping point, C no grease</td>
<td>&gt;343</td>
<td>&gt;343</td>
<td>&gt;343</td>
<td>&gt;343</td>
<td>&gt;343</td>
<td></td>
</tr>
<tr>
<td>Dropping point, F no grease</td>
<td>&gt;650</td>
<td>&gt;650</td>
<td>&gt;650</td>
<td>&gt;650</td>
<td>&gt;650</td>
<td></td>
</tr>
</tbody>
</table>
As expected, Graphite C was a very inefficient thickener, requiring 40% (wt) in the PAO blend to impart an unworked penetration of 239 and a worked penetration of 357. The extreme softening that occurred with 60 strokes of working indicated that the thickened blend had poor structural stability. Additionally, this thickened blend (Blend 24) had a paste-like consistency. It did, however, have a very high dropping point (> 343). No further blends were made using this graphite.

The data for the two surface enhanced natural graphites (Table 6 and Figure 2) showed that Graphite A was a better thickener than Graphite D. Although the worked penetration for both graphites was about the same at 20% (wt) in the PAO blend (Blend 11 vs. Blend 13), the blends made with Graphite D were very gritty. Also, they exhibited significant oil separation after only a few weeks of ambient storage. The lower surface area of Graphite D compared to Graphite A may have been a factor in this behavior.
The data for the two double-milled high surface area synthetic graphites (Table 7 and Figure 3) showed that Graphite E was a better thickener than Graphite B in the PAO blend. This was the opposite of what would be expected from the information provided on these two graphites. Graphites B and E were produced from very pure petroleum coke. They were similar except for surface area, with Graphite B having the higher surface area. Also, of the five graphites evaluated in this study, the supplier claimed that only Graphite B contained structures that approximated a true graphene. Nonetheless, Graphite E provided a higher thickening efficiency compared to Graphite B. This implied that some other factor was involved in determining the relative thickening efficiency of these two graphites in the PAO blend.

Another interesting observation was an apparent morphology change when blends containing Graphites B and E were heated to 150°C prior to milling. During the heating process, a very noticeable crackling occurred. This was accompanied by a change in physical appearance of the greases from flat (dull) black to glossy black. The texture before milling also changed from grainy to very smooth. In fact, although the 10.5% Graphite B blend (Blend 15) did not form a grease, it nonetheless remained a smooth fluid without any visible settling after one day. The two surface area enhanced natural graphites (Graphites A and D) did not exhibit any of these properties. This information continued to show that there were significant chemical and rheological differences between these two families of graphites. Additional information on the physical appearance of all thickened blends is provided below in the section on Structural Storage Stability.

The penetration data for Graphites A, B, D, and E from Tables 6 and 7 are graphically presented in Figure 4. The one significant observation provided by this comparison was that natural Graphite A (27.0 m²/g surface area) imparted a higher thickening efficiency in the PAO blend than either of the much higher surface area synthetic Graphites B and E (340 and 250 m²/g, respectively). Once again, this indicated that certain as yet undefined structural and compositional properties influenced thickening efficiency more than reported surface area.
By comparing Figures 1 and 4, it is immediately seen that all three SWCNT’s were much more efficient thickeners in the PAO blend compared to any of the graphites. This may be due to the intrinsic “fiber-like” structure provided by CNT’s, but absent in the other graphitic solids. The ranking of all carbon-based solids as thickeners in the PAO blend is summarized as follows:

SWCNT-3 > SWCNT-1 > SWCNT-2 >> Graphite A > Graphite E > Graphite B > Graphite D > Graphite C

**Thickening Efficiency and Dropping Points of Combinations of SWCNT’s**

An experiment was performed to investigate whether there might be an interaction between SWCNT-1 and SWCNT-2 to increase (or decrease) their thickening efficiency when used as co-thickeners in the PAO blend. Two greases (Blends 25 and 26) were made using both SWCNT-1 and SWCNT-2 as co-thickeners.

Greases 25 and 26 were made as follows. Figure 1 shows the linear regression relationship between carbon thickener content and grease worked penetration for each SWCNT. Using Figure 1, the amounts of each of these SWCNT’s (each as an individual thickener) needed to make hypothetical greases with target worked penetrations of 280 and 310 were determined. Using those predicted values, two grease compositions were prepared that were compositionally equivalent to 50/50 (wt/wt) blends of greases made from only SWCNT-1 and from only SWCNT-2. Greases 25 and 26 would have worked penetration values of 280 and 310 if there were no interactions between the two SWCNT’s. The compositions and test results for Greases 25 and 26 are provided in Table 9. Comparison of actual worked penetrations and theoretical values are given in Figure 5.

**TABLE 9: COMBINATION OF TWO SWCNT’S AS GREASE THICKENER IN PAO BLEND**

<table>
<thead>
<tr>
<th>Blend Number</th>
<th>25</th>
<th>26</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 cSt PAO, % (wt)</td>
<td>36.21</td>
<td>36.77</td>
</tr>
<tr>
<td>40 cSt PAO, % (wt)</td>
<td>54.72</td>
<td>55.16</td>
</tr>
<tr>
<td>SWCNT-1, % (wt)</td>
<td>3.82</td>
<td>2.84</td>
</tr>
<tr>
<td>SWCNT-2, % (wt)</td>
<td>5.05</td>
<td>5.23</td>
</tr>
<tr>
<td>Total Carbon, % (wt)</td>
<td>9.47</td>
<td>8.07</td>
</tr>
<tr>
<td>Heated before milling?</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Unworked penetration, 0.1 mm</td>
<td>295</td>
<td>342</td>
</tr>
<tr>
<td>Worked penetration, 0.1 mm</td>
<td>288</td>
<td>337</td>
</tr>
<tr>
<td>Theoretical worked penetration, 0.1 mm</td>
<td>280</td>
<td>310</td>
</tr>
<tr>
<td>Dropping point, C</td>
<td>317</td>
<td>312</td>
</tr>
<tr>
<td>Dropping point, F</td>
<td>603</td>
<td>594</td>
</tr>
</tbody>
</table>

**Figure 5**

Effect of Using Two SWCNT’s as Co-Thickeners in PAO Blend
The worked penetrations of both Greases 25 and 26 were softer than the predicted theoretical values. However, Grease 25, which was targeted at a worked penetration of 280, was only slightly softer than the theoretical prediction. The significance of these data may be somewhat obscured by the scatter in the linear relationship of the greases thickened only by SWCNT-2, as shown in Figure 1. However, it can be reliably stated that the combined use of both SWCNT’s did not result in any significant thickener yield improvement relative to what was indicated by the thickening efficiency of the two individual SWCNT’s. Dropping points for both greases were above 300 C.

If the difference between the actual and theoretical penetration values at the soft end is real, this may indicate a disrupting interaction between the two SWCNT’s at lower dispersion concentrations. If this is so, it may point to a possible increased connectivity between the two SWCNT structures throughout the grease matrix with possible increases in thermal and electrical conductivity.

**Thickening Efficiency and Dropping Points of Combinations of SWCNT and Graphite**

A series of three greases (Blends 27 – 29) were prepared using both SWCNT-1 and Graphite B as co-thickeners. SWCNT-1 was chosen since it was more efficient than SWCNT-2, and the limited supply of SWCNT-3 was used up. Graphite B was chosen since it was reputed by the supplier to be the best source of near graphene structures of any of the graphites used in this study. Also, the supply of the other synthetic graphite, Graphite E, was limited.

Using the previously determined linear regression relationship between graphitic thickener content and worked penetration for SWCNT-1 (indicated in Figure 1) and Graphite B (indicated in Figure 3), the amounts of each of these materials separately needed to achieve target worked penetrations of 280, 310, and 350 were determined. Using those predicted values, three grease compositions were prepared that were compositionally equivalent to a 50/50 (wt/wt) blend of greases made from just SWCNT-1 and from just Graphite B. These three greases should have worked penetration values of 280, 310, and 350 if there were no interactions between the SWCNT and the graphite. The compositions and test results for these three greases are provided in Table 10. Comparison of actual worked penetrations and theoretical values are given in Figure 6.
All three Greases 27, 28, and 29 made with both SWCNT-1 and Graphite B gave an almost perfect linear relationship between total carbon content and worked penetration, as was the case with Greases 25 and 26 made with SWCNT-1 and SWCNT-2 (see Figures 1 and 3). However, the worked penetrations of these three Greases 27 - 29 were significantly softer than the predicted theoretical values.

This result was very interesting, since it implied that there was some interaction taking place between the dispersed structures of the SWCNT and graphite. If this interaction was caused by or resulted in significant connectivity between the SWCNT structure and the graphite or near-graphene planes, the resulting Greases 27 - 29 could have greatly enhanced thermal and electrical conductivity compared to similar greases thickened by just the SWCNT or graphite.

This adverse interaction between SWCNT-1 and Graphite B possibly provided another explanation for why SWCNT-3 had a much higher thickener efficiency compared to the other two SWCNT’s (Figure 1). SWCNT-3 had a much higher purity of CNT’s than SWCNT-1 and SWCNT-2. The impurities in SWCNT-1 and SWCNT-2 were mostly non-CNT graphitic carbon (Table 1). Given the observed adverse effect on thickening efficiency demonstrated in Figure 6, the much higher thickening efficiency of SWCNT-3 possibly was due, at least in part, to its much lower level of non-CNT graphitic impurities. However, as already discussed, the purity of a specific SWCNT material was not the sole factor in determining its thickening efficiency compared to other SWCNT’s. The thickening efficiencies of SWCNT-1 and SWCNT-2 (Figure 1) compared to their purities (Table 1) proved this.

Dropping points of the three mixed graphitic Greases 27 - 29 ranged from 314 to 339 C. It should also be noted that by using both SWCNT-1 and Graphite B, greatly reduced levels of SWCNT-1 were required compared to using only SWCNT-1. This can be seen by comparing the % (wt) SWCNT-1 values for the three blends in Figure 6 with the corresponding values in Figure 1. This represents a potential method to further reduce the cost of SWCNT-thickened greases as the cost of these materials continues to decrease.
Structural Storage Stability of All Thickened Blends

The previously made blends, for which grease structures were obtained, were stored in their sealed steel cans at ambient laboratory conditions. Except for the three blends that were thickened by a combination of SWCNT-1 and Graphite B (Blends 27 – 29), each sample was evaluated after about four and eight months of storage for general appearance and oil separation. Blends 27 – 29 were only evaluated after 4 months due to time limitations. All blends were visually evaluated on a subjective basis with a 0 rating indicating no oil separation and a 5 rating indicating extreme oil separation. General appearance (glossy, flat, gritty) was also noted, both initially and after storage. Test results are provided for SWCNT-thickened blends (Table 11), graphite-thickened blends (Table 12), and blends thickened by a combination of SWCNT and graphite (Table 13). Compositions for all these blends, as given in previous tables, are included again for ease of reference. Also note that in Tables 11 and 12, the blends containing the three different SWCNT’s or graphites are grouped together and color coded.

### TABLE 11: STRUCTURAL STABILITY OF SWCNT-THICKENED BLENDS

<table>
<thead>
<tr>
<th>Blend Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 cSt PAO, %wt</td>
<td>35.80</td>
<td>36.40</td>
<td>37.00</td>
<td>37.00</td>
<td>35.80</td>
<td>35.80</td>
<td>35.20</td>
<td>35.50</td>
<td>39.24</td>
<td>39.24</td>
</tr>
<tr>
<td>40 cSt PAO, %wt</td>
<td>53.70</td>
<td>54.60</td>
<td>55.50</td>
<td>55.50</td>
<td>53.70</td>
<td>53.70</td>
<td>52.80</td>
<td>53.25</td>
<td>58.36</td>
<td>58.66</td>
</tr>
<tr>
<td>SWCNT-1, %wt</td>
<td>10.50</td>
<td>9.00</td>
<td>7.50</td>
<td>7.50</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>SWCNT-2, %wt</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>10.50</td>
<td>10.50</td>
<td>12.00</td>
<td>11.25</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>SWCNT-3, %wt</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>1.50</td>
<td>1.90</td>
</tr>
<tr>
<td>Heated before milling?</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Unworked penetration, 0.1 mm</td>
<td>236</td>
<td>257</td>
<td>285</td>
<td>299</td>
<td>317</td>
<td>286</td>
<td>249</td>
<td>265</td>
<td>288</td>
<td>279</td>
</tr>
<tr>
<td>Worked penetration, 0.1 mm</td>
<td>237</td>
<td>257</td>
<td>263</td>
<td>297</td>
<td>317</td>
<td>286</td>
<td>263</td>
<td>265</td>
<td>274</td>
<td>269</td>
</tr>
<tr>
<td>Dropping point, C</td>
<td>&gt;343</td>
<td>341</td>
<td>322</td>
<td>&gt;343</td>
<td>324</td>
<td>&gt;343</td>
<td>&gt;343</td>
<td>&gt;343</td>
<td>&gt;343</td>
<td>&gt;343</td>
</tr>
<tr>
<td>Dropping point, F</td>
<td>&gt;650</td>
<td>645</td>
<td>612</td>
<td>&gt;650</td>
<td>615</td>
<td>&gt;650</td>
<td>&gt;650</td>
<td>&gt;650</td>
<td>&gt;650</td>
<td>&gt;650</td>
</tr>
<tr>
<td>Initial Appearance</td>
<td>glossy</td>
<td>glossy</td>
<td>glossy</td>
<td>glossy</td>
<td>semi-flat</td>
<td>semi-flat</td>
<td>semi-flat</td>
<td>semi-flat</td>
<td>glossy</td>
<td>glossy</td>
</tr>
<tr>
<td>Appearance after 4 months</td>
<td>glossy</td>
<td>glossy</td>
<td>glossy</td>
<td>glossy</td>
<td>semi-flat</td>
<td>semi-flat</td>
<td>semi-flat</td>
<td>semi-flat</td>
<td>glossy</td>
<td>glossy</td>
</tr>
<tr>
<td>Oil Separation (rating 0 to 5) after 4 months</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Appearance after 8 months</td>
<td>glossy</td>
<td>glossy</td>
<td>glossy</td>
<td>glossy</td>
<td>semi-flat</td>
<td>semi-flat</td>
<td>semi-flat</td>
<td>semi-flat</td>
<td>glossy</td>
<td>glossy</td>
</tr>
<tr>
<td>Oil Separation (rating 0 to 5) after 9 months</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

### TABLE 12: STRUCTURAL STABILITY OF GRAPHITE-THICKENED BLENDS

<table>
<thead>
<tr>
<th>Type of graphite used</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
<th>20</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 cSt PAO, %wt</td>
<td>32.00</td>
<td>36.00</td>
<td>32.00</td>
<td>34.00</td>
<td>32.00</td>
<td>30.00</td>
<td>28.00</td>
<td>30.00</td>
<td>28.00</td>
<td>24.00</td>
</tr>
<tr>
<td>40 cSt PAO, %wt</td>
<td>48.00</td>
<td>45.00</td>
<td>48.00</td>
<td>51.00</td>
<td>48.00</td>
<td>45.00</td>
<td>42.00</td>
<td>45.00</td>
<td>42.00</td>
<td>36.00</td>
</tr>
<tr>
<td>Graphite A, %wt</td>
<td>20.00</td>
<td>25.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Graphite B, %wt</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>20.00</td>
<td>25.00</td>
<td>30.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Graphite C, %wt</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>40.00</td>
</tr>
<tr>
<td>Graphite D, %wt</td>
<td>0.00</td>
<td>0.00</td>
<td>20.00</td>
<td>15.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Graphite E, %wt</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>25.00</td>
<td>30.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Heated before milling?</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Unworked penetration, 0.1 mm</td>
<td>350</td>
<td>279</td>
<td>340</td>
<td>483</td>
<td>422</td>
<td>358</td>
<td>287</td>
<td>338</td>
<td>254</td>
<td>239</td>
</tr>
<tr>
<td>Worked penetration, 0.1 mm</td>
<td>381</td>
<td>287</td>
<td>355</td>
<td>ND</td>
<td>424</td>
<td>358</td>
<td>295</td>
<td>340</td>
<td>257</td>
<td>357</td>
</tr>
<tr>
<td>Dropping point, C</td>
<td>&gt;343</td>
<td>334</td>
<td>398</td>
<td>&gt;343</td>
<td>&gt;343</td>
<td>&gt;343</td>
<td>&gt;343</td>
<td>&gt;343</td>
<td>&gt;343</td>
<td>&gt;343</td>
</tr>
<tr>
<td>Dropping point, F</td>
<td>&gt;650</td>
<td>635</td>
<td>566</td>
<td>&gt;650</td>
<td>&gt;650</td>
<td>&gt;650</td>
<td>&gt;650</td>
<td>&gt;650</td>
<td>&gt;650</td>
<td>&gt;650</td>
</tr>
<tr>
<td>Initial Appearance</td>
<td>flat</td>
<td>flat</td>
<td>flat</td>
<td>gritty</td>
<td>flat</td>
<td>gritty</td>
<td>flat</td>
<td>gritty</td>
<td>glossy</td>
<td>glossy</td>
</tr>
<tr>
<td>Appearance after 4 months</td>
<td>flat</td>
<td>flat</td>
<td>flat</td>
<td>gritty</td>
<td>flat</td>
<td>gritty</td>
<td>flat</td>
<td>gritty</td>
<td>glossy</td>
<td>glossy</td>
</tr>
<tr>
<td>Oil Separation (rating 0 to 5) after 4 months</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>Appearance after 8 months</td>
<td>flat</td>
<td>flat</td>
<td>flat</td>
<td>gritty</td>
<td>flat</td>
<td>gritty</td>
<td>flat</td>
<td>gritty</td>
<td>glossy</td>
<td>glossy</td>
</tr>
<tr>
<td>Oil Separation (rating 0 to 5) after 8 months</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3</td>
</tr>
</tbody>
</table>
Table 13: Structural Stability of Blends Thickened by Combination of SWCNT and Graphite

<table>
<thead>
<tr>
<th>Blend Number</th>
<th>27</th>
<th>28</th>
<th>29</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 cSt PAO, % (wt)</td>
<td>34.24</td>
<td>33.04</td>
<td>32.25</td>
</tr>
<tr>
<td>40 cSt PAO, % (wt)</td>
<td>51.37</td>
<td>49.55</td>
<td>48.37</td>
</tr>
<tr>
<td>SWCNT-1, % (wt)</td>
<td>1.54</td>
<td>2.84</td>
<td>3.82</td>
</tr>
<tr>
<td>Graphite B, % (wt)</td>
<td>12.85</td>
<td>14.56</td>
<td>15.56</td>
</tr>
<tr>
<td>Total carbon, % (wt)</td>
<td>14.39</td>
<td>17.40</td>
<td>19.38</td>
</tr>
<tr>
<td>Heated before milling?</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Unworked penetration, 0.1 mm</td>
<td>364</td>
<td>331</td>
<td>287</td>
</tr>
<tr>
<td>Worked penetration, 0.1 mm</td>
<td>381</td>
<td>336</td>
<td>299</td>
</tr>
<tr>
<td>Dropping point, C</td>
<td>339</td>
<td>314</td>
<td>317</td>
</tr>
<tr>
<td>Dropping point, F</td>
<td>643</td>
<td>598</td>
<td>602</td>
</tr>
<tr>
<td>Initial Appearance</td>
<td>glossy</td>
<td>glossy</td>
<td>glossy</td>
</tr>
<tr>
<td>Appearance after 4 months</td>
<td>glossy</td>
<td>glossy</td>
<td>glossy</td>
</tr>
<tr>
<td>Oil Separation (rating 0 to 5) after 4 months</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Appearance after 8 months</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Oil Separation (rating 0 to 5) after 8 months</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

As can be seen from Table 11, blends thickened by any of the three SWCNT’s gave no significant storage oil separation as long as the worked penetrations were within the NLGI No. 2 range or harder. The one grease with an NLGI No. 1 worked penetration (Blend 5 containing 10.5% of SWCNT-2) gave significant oil separation after about four months of storage. Interestingly, Blend 6 (with the same composition but without heating to 150°C) had a much firmer structure than Blend 5 and did not exhibit any noticeable oil separation. As previously discussed, SWCNT-2 gave better thickening in the PAO blend when it was not heated before milling. SWCNT-1 did not show this property. Also, SWCNT-1 blends were always very glossy in appearance, whereas SWCNT-2 blends had a semi-flat appearance. However, they were not obviously flat or gritty as were the low surface area graphite-thickened blends (see Table 12).

As can be seen from Table 12, only blends thickened by the two higher surface area synthetic graphites, Graphites B or E, had excellent stability. Even when using those two graphites, only blends with worked penetrations of 340 or harder showed no measurable oil separation after about four or eight months of storage. Given the penetration range of the greases made using these two synthetic graphites, it appeared that NLGI No. 2 grade greases (worked penetrations between 265 and 295) would be stable with respect to oil separation. NLGI No. 1 grade greases (worked penetration between 310 and 340) may also be acceptable, although more testing would be required to be sure.

On the other hand, greases that used the lower surface area natural graphites, Graphites A and D, all had inferior stability when compared to the higher surface area synthetic graphites. They also had a dull and gritty appearance, even when freshly made, in contrast to the shiny and smooth appearance typical of the greases thickened by the higher surface area synthetic Graphites B and E. As already mentioned, Graphites B and E exhibited an apparent physical or chemical change during heating in the PAO. This change resulted in the smooth and glossy appearance of the resulting greases. It was unclear what role, if any, was played by this characteristic behavior as it related to the resulting superior grease structures.

As expected, the traditional graphite-thickened Blend 24 exhibited significant oil separation upon storage.
As can be seen in Table 13, the three greases that used a combination of SWCNT-1 and Graphite B had structural stability that varied directly with the worked penetration. The blend with a worked penetration just softer than an NLGI No. 2 range (Blend 29) had excellent stability. Blend 28 with an NLGI No. 1 consistency gave slight oil separation after four months. The grease that was at the soft end of an NLGI No. 0 grade (Blend 27) gave somewhat more oil separation. However, it was apparent that if the grease remained within an NLGI No. 2 grade, blends of both SWCNT-1 and Graphite B provided good structural stability even when the SWCNT concentration was reduced by about 50% compared to what was required for a No. 2 grease using just SWCNT-1. The implications for potential cost reduction are obvious.

The storage stability of all the thickened blends after about eight months was about the same as after about four months. This indicates that all future ambient temperature storage stability testing can likely be limited to no more than four months. Additionally, the general physical appearance of all thickened blends (glossy, flat, gritty) did not change over time.

**Controlled Shear Rate Rheometry of SWCNT-Thickened Blends**

Three previously prepared greases were selected for rheometry evaluation as a function of temperature. They were Blend 3 (thickened by SWCNT-1) and Blends 9 and 10 (thickened by SWCNT-3). Additionally a fourth blend (Blend 30) was made using a combination of SWCNT-1 and SWCNT-3. This blend was prepared in the same way as Blend 9, and it was specifically made for the rheometry evaluation in this study. A summary of the compositions of all four blends is provided below in Table 14 for ease of reference.

<table>
<thead>
<tr>
<th>Blend Number</th>
<th>3</th>
<th>9(1)</th>
<th>10(2)</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 cSt PAO, % (wt)</td>
<td>37.00</td>
<td>39.24</td>
<td>39.24</td>
<td>37.45</td>
</tr>
<tr>
<td>40 cSt PAO, % (wt)</td>
<td>55.50</td>
<td>58.86</td>
<td>58.86</td>
<td>56.17</td>
</tr>
<tr>
<td>SWCNT-1, % (wt)</td>
<td>7.50</td>
<td></td>
<td></td>
<td>6.00</td>
</tr>
<tr>
<td>SWCNT-3, % (wt)</td>
<td></td>
<td>1.90</td>
<td>1.90</td>
<td>0.38</td>
</tr>
<tr>
<td>Total carbon, % (wt)</td>
<td>7.50</td>
<td>1.90</td>
<td>1.90</td>
<td>6.38</td>
</tr>
<tr>
<td>Heated before milling?</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Unworked penetration, 0.1 mm</td>
<td>285</td>
<td>288</td>
<td>279</td>
<td>305</td>
</tr>
<tr>
<td>Worked penetration, 0.1 mm</td>
<td>283</td>
<td>274</td>
<td>269</td>
<td>288</td>
</tr>
<tr>
<td>Dropping point, C</td>
<td>322</td>
<td>&gt;343</td>
<td>&gt;343</td>
<td>342</td>
</tr>
<tr>
<td>Dropping point, F</td>
<td>612</td>
<td>&gt;650</td>
<td>&gt;650</td>
<td>647</td>
</tr>
</tbody>
</table>

**NOTE 1:** Preparation of this grease blend began with 7.5% (wt) of SWCNT-3, and additional PAO blend was added with mixing and milling until the final grease was obtained.

**NOTE 2:** Preparation of this grease blend began with 1.9% (wt) of SWCNT-3, and repeated mixing and milling were continued with no further addition of PAO blend until the final grease was obtained.

As can be seen, the Blend 30 grease exhibited the same hardening effect during the 60 stroke shearing that was observed with the Blend 9 and 10 greases. This was true even though Blend 30 contained mostly SWCNT-1 with only a minor amount of SWCNT-3. Apparently, any significant presence of SWCNT-3 imparted a mild rheopectic effect on the resulting grease during the 60 stroke shearing.
Each of the four greases was tested using a Brookfield R/S Rheometer by scanning the apparent viscosity at constant shear rate from 22 to about -30 °C. Each scan took 40 min. This test procedure was done at two shear rates, 1 and 100 rpm. Results for the 1 rpm test scans are provided in Figure 7; results at 100 rpm are provided in Figure 8. Note that since all the thickened blends of this study were made in the same PAO blend, direct comparison of the apparent viscosity curves of the resulting greases was valid.
The first obvious result of these rheometry tests was that the apparent viscosity of each grease was very strongly dependent on the shear rate. At the higher shear rate, each grease’s viscosity decreased drastically compared to the lower shear rate. This non-Newtonian behavior is usually observed in lubricating greases.

Test results at both rpm’s showed that the compositionally equivalent Greases 9 and 10 had comparable apparent viscosity scans. This indicated that the viscosity properties of the greases thickened by SWCNT-3 in the PAO blend did not depend on how the SWCNT was dispersed but only on the final composition.

At 1 rpm, Blend 3 grease with SWCNT-1 and the higher carbon content of 7.5% (wt) had higher viscosity over most of the scanned temperature range compared to Blends 9 and 10 with SWCNT-3 and much lower carbon content. However, at 100 rpm, the opposite was true. Apparently, at low shear rates, the higher thickener level in the SWCNT-1 grease (Blend 3) gave higher apparent viscosity, as expected. At much higher shear rates, the apparent viscosity of all four greases decreased drastically.

However, the apparent viscosity of the two SWCNT-3 greases (Blends 9 and 10) decreased significantly less than the SWCNT-1 grease (Blend 3). This resulted in the two SWCNT-3 greases having viscosities higher than that of the SWCNT-1 grease at the higher shear rate. This possibly was due to a further thickening effect of the SWCNT-3 during the higher shear rate measurement that partially offset the expected viscosity reduction.

This might have been another manifestation of the unique property of SWCNT-3 that resulted in a much greater amount of thickening during prolonged milling compared to what was observed with SWCNT-1. Likewise, the previously discussed hardening of SWCNT-3 greases during 60 stroke shearing may have been an indication of this property. Unfortunately, the cause of this interesting property could not be determined without more detailed compositional information for the two SWCNT’s.

At both 1 and 100 rpm, the grease thickened with both SWCNT-1 and SWCNT-3 (Blend 30) had apparent viscosity that was between viscosities for the greases separately thickened by either one of the two SWCNT’s for much of or nearly all of the temperature range. However, for the 1 rpm scan, the grease with both SWCNT’s (Blend 30) was lower in apparent viscosity at temperatures lower than about -10 C.

Except for the Blend 30 grease at 1 rpm, all greases at both rpm’s seemed to converge towards a common apparent viscosity as the temperature approached -30 C. This indicated that the viscosity properties of the PAO base oil blend exerted a leveling effect on apparent grease viscosity at very low temperatures. The departure of this behavior by Blend 30 at 1 rpm possibly indicated an advantageous property of such mixed SWCNT-thickened greases.

**Thermal Conductivity**

Selected previously described thickened blends were evaluated for thermal conductivity, Table 15. For comparison, the thermal conductivity of six commercial or experimental greases is provided in Table 16.
The thermal conductivity data from Tables 15 and 16 can be summarized as follows:

1. For greases thickened by SWCNT’s, values were from 0.230 to 0.280 W/mK
2. For greases thickened by graphites, values were from 0.300 to 0.390 W/mK
3. For conventional greases, values were from 0.164 to 0.223 W/mK

The PAO blend was also evaluated and had a thermal conductivity of 0.188 W/mK. Given the 3% precision of the equipment, the thermal conductivity of the PAO blend was considered to be within the range between 0.182 and 0.194 W/mK. Using this range as the baseline thermal conductivity for all evaluated greases, several observations could be made.

First, it was apparent that all evaluated greases thickened by SWCNT or graphite had thermal conductivities significantly greater than the PAO blend in which they were made. The graphitic thickeners were clearly responsible for this effect.

Second, the thermal conductivities of most of the evaluated SWCNT- and graphite-thickened greases were also higher than the six conventional greases. One conventional grease, Grease C, had a thermal conductivity that was significantly higher than the other conventional greases. Grease C was thickened by the same calcium sulfonate complex thickener chemistry as Greases A and B. The only compositional difference between these three calcium sulfonate complex greases was the use of a significant amount of bright stock base oil in Grease C. As can be seen from Table 16, Grease C was the only grease of the six that contained bright stock base oil. Therefore, the most likely reason for the higher thermal conductivity of Grease C was the bright stock used only in that grease.
Third, all three calcium sulfonate complex greases had thermal conductivities that were higher than the two lithium complex greases and the one aluminum complex grease. This may indicate that the much higher concentrations of lower and higher molecular weight ionic species present in these three calcium sulfonate complex greases possibly influenced thermal conductivity.

Finally, of all the graphitic material-thickened greases evaluated, graphite-thickened greases gave consistently higher thermal conductivities than the SWCNT-thickened greases. The highest thermal conductivity was observed for Blend 24 where 40% of a low surface area natural graphite was used. This was noteworthy since it has been well documented that pure SWCNT’s have possibly the highest measured thermal conductivity of any known material, with values as high as 6,000 W/mK [7].

The most likely reason for the higher thermal conductivities of graphite-thickened greases compared to SWCNT-thickened greases can be seen by examining the data as presented in Figure 9.

These data show the thermal conductivity of greases thickened by three different groupings of graphitic solids: SWCNT-1 and SWCNT-2; Graphites A and B; and Graphite C. These data as a whole clearly showed that the thermal conductivity of the greases strongly depended on the total carbon (thickener) concentration.

Figure 9 also shows that for SWCNT-1 and SWCNT-2, and for Graphites A and B, there was an almost perfect linear relationship between thickener concentration and thermal conductivity. However, the slopes of the two lines differed. The slope of the SWCNT line was significantly steeper than the slope of the graphite line. This showed that the intrinsic ability of SWCNT’s to increase thermal conductivity of greases was actually higher than that of graphites. The much lower concentration of the SWCNT’s in these greases was the reason for their lower thermal conductivities. The single Graphite C grease was plotted separately because Graphite C behaved very differently than the other graphites. The fact that the single Graphite C point did not fall on the line of the other two graphites was a further indication of this behavior.
As mentioned in the beginning of this paper, MWCNT’s required about twice the concentration as SWCNT’s to provide the same level of thickening in PAO’s. Given the relationship indicated in Figure 9, it may be expected that greases thickened with MWCNT’s might provide much higher thermal conductivities than SWCNT-thickened greases of similar worked penetration. Additionally, the current costs of MWCNT’s are significantly less than SWCNT’s, although the costs of both are still far higher than the costs of other grease thickeners, base oils, or additives. Combinations of MWCNT’s and graphites may provide even further cost reductions with the same potential for beneficial improvements in thermal conductivity. However, additional work with MWCNT’s similar to what has been herein reported for SWCNT’s must be done to verify this.

For now, given the extremely high current cost of all CNT’s, it is much more cost effective to use graphites rather than SWCNT’s to formulate greases with high thermal conductivities. It remains to be seen whether there may be other unique properties of CNT-thickened greases that could eventually justify their use, as the cost of these unique graphitic materials continues to decrease.

CONCLUSIONS
The results discussed above support the following conclusions:

1. In this study, SWCNT’s were much more efficient lubricating grease thickeners than graphites when a PAO base oil was used. SWCNT’s also generally imparted a more storage-stable grease structure than graphites.

2. As grease thickeners, all SWCNT’s were not all the same. Significant differences in thickening efficiency existed between different sources and manufacturing lots of SWCNT’s. These differences in thickening efficiency could not be entirely attributed to the purity of the SWCNT materials. More detailed information on the chemical composition of these SWCNT’s would be required to determine the source of observed differences in thickening efficiency.

3. As grease thickeners, graphites were not all the same. Different thickening efficiencies existed between different types of graphites, and reported surface area was not always a good indicator of relative thickening ability. Other compositional and structural properties of a given graphite might be more important than reported surface area when determining the thickener efficiency and final grease storage stability. The compositional information provided for graphites used in this study was not adequate to predict their relative effectiveness as grease thickeners.

4. When an SWCNT and a graphite, or two different SWCNT’s, were used together to co-thicken a grease, the two materials interacted so as to provide a co-thickening efficiency that was different than what was predicted from their individual thickening efficiencies. These differences possibly indicated a connection of the two dispersed graphitic structures that favorably impacted certain properties such as thermal and electrical conductivity.

5. The rheological properties of SWCNT-thickened PAO greases appeared to be a function of the composition and the degree of dispersion of the thickener in the base oil, but not a function of the process path by which that degree of dispersion was achieved.
6. The rheological properties of SWCNT-thickened PAO greases were not the same for all SWCNT sources. If an SWCNT has a very high thickener efficiency, it possibly could cause significant differences in some rheological properties of grease. Much more work is needed to understand this potential behavior.

7. SWCNT's and graphites imparted thermal conductivity values to the greases they thickened that were higher than what was observed for more conventional greases. However, graphite-thickened greases provided higher thermal conductivities than SWCNT-thickened greases in this study. The most likely reason for this effect was the much higher amount of graphites required for thickening compared to SWCNT's.

8. Given the current extremely high cost of SWCNT’s, their commercial usefulness as a grease thickener appears to be extremely low, if not vanishingly small. However, as more efficient (and lower cost) manufacturing methods are developed for these materials, they may find utility. One such opportunity could be applications that require extremely stable thermally conductive greases.

REFERENCES

Abstract
This paper provides a simple example of the use of mPAO 65 (metallocene polyalphaolefin oil, kinematic viscosity = 65 cSt at 100°C), PAO 6 (1-decene based, kinematic viscosity = 6 cSt at 100°C) and an aluminum-based thickener to produce an aluminum complex grease. The grease was formulated using an aluminum source that did not liberate isopropyl alcohol. Excellent properties are highlighted, although the grease was not formulated for a particular purpose but rather as an example of using PAO and mPAO in an aluminum complex grease.

Introduction
In the two previous papers in this series, the focus has been on the use of mPAO in lithium soap [1] and polyurea greases [2]. In this paper, the focus is on the usage of mPAO 65 (65 cSt at 100°C) and PAO 6 (1-decene-based, kinematic viscosity = 6 cSt at 100°C) in an aluminum complex grease. Aluminum complex greases were first invented by Bruce Hotten of the California Research Corporation in 1952 [3]. That patent described the improved melting point and water emulsification resistance of a so-called ‘di-soap’ grease. Di-soap greases are now termed complex greases since they contain more than one organic or oleophilic anions, which are typically benzoic and stearic acids. Aluminum complex greases began to appear in a commercial sense in the mid-1960s [4,5] and have found use in (and are considered as) multi-functional and multi-purpose greases. Their relatively low soap and high oil content allow for good low temperature pumpability and good stability toward mechanical shear. In addition, these greases typically have excellent heat reversion characteristics so that the consistency of the grease is regained after heating under static or low shear conditions.

Purpose
The purpose of this work was to demonstrate the viability of using mPAO 65 as a high viscosity blending component to formulate aluminum complex grease. The grease was formulated to contain 7.5% (by weight) aluminum-based thickener produced using an aluminum source that does not liberate isopropyl alcohol. The finished grease contained HX-1 additives to provide both antwear and corrosion protection. (HX-1 additives are chemical products that are listed and registered by NSF International for use in H1 lubricants. NSF-registered H1 lubricants are acceptable as lubricants with incidental contact for use in and around food processing areas according to the US Food and Drug Administration.) The stoichiometry of the grease chemistry is discussed below along with chemical and physical properties of the finished grease. The formulation was not optimized for any particular application. The mPAO 65 was blended with PAO 6 to a viscosity of 162 cSt at 40°C.

The grease composition is shown in Table 1.
Table 1: Grease composition

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickener</td>
<td>7.5</td>
</tr>
<tr>
<td>PAO-6</td>
<td>39.6</td>
</tr>
<tr>
<td>mPAO-65</td>
<td>48.4</td>
</tr>
<tr>
<td>Rust Inhibitor</td>
<td>0.5</td>
</tr>
<tr>
<td>Antiwear Agent</td>
<td>0.5</td>
</tr>
<tr>
<td>Multifunction Additive</td>
<td>0.5</td>
</tr>
<tr>
<td>PTFE</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Raw Materials

Although high viscosity PAOs have been commercially available since the 1980s [6] mPAOs are relatively newer [7] 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, a paper was presented at the NLGI annual meeting in 2016 showing the usefulness of mPAO 65 in a lithium grease [1]. 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. In 2017, another paper was presented at the NLGI annual meeting that highlighted the benefits of using a preformed diurea thickener with mPAO 65 as a base grease [2].

Table 2: Properties of mPAO base oil

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>KV at 40°C, cSt</td>
<td>ASTM D445</td>
<td>605</td>
</tr>
<tr>
<td>KV at 100°C, cSt</td>
<td>ASTM D445</td>
<td>65</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>ASTM D2270</td>
<td>181</td>
</tr>
<tr>
<td>Pour Point, °C</td>
<td>ASTM D92</td>
<td>-42</td>
</tr>
</tbody>
</table>

Grease Preparation

The thickener was prepared in all of the base oil with the exception of a small amount set aside to accommodate the additives. The particular source of the aluminum chosen does not liberate isopropyl alcohol. However, the stoichiometry of the thickener must be adjusted to account for acids present on the aluminum source.

Since PAOs have a high aniline point, the mole ratio of aluminum to acid was chosen to be 1:1.9. Table 3 provides the information pertaining to the molecular weight of the ingredients, mole ratios and unit weights.
Table 3: Stoichiometry of the grease thickener (top) and proportions, quantities used to make thickener (7.5% by weight) of 45.36 kg (100.0 lbs.) of grease, unadjusted percentages, and adjustments (see note below).

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Atomic/Molecular Weight (g/mol)</th>
<th>Mole Ratio</th>
<th>Unit Weight (g)</th>
<th>Percentages in Thickener</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum (elemental)</td>
<td>27</td>
<td>1</td>
<td>27</td>
<td>5.75</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>284</td>
<td>1.3</td>
<td>369.2</td>
<td>78.65</td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td>122</td>
<td>0.6</td>
<td>73.2</td>
<td>15.6</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>469.4</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Note: Since the aluminum source contains 2.93% stearic acid and 0.65% benzoic acid, these percentages must be subtracted from the calculated amounts to maintain proper stoichiometry.

The assay of the aluminum source is 5.3% elemental aluminum. The amount of the aluminum source required to yield 45.36 kg (100.0 lb.) grease is:

\[
\frac{0.196 \text{ kg}}{0.053} = 3.70 \text{ kg (8.16 lb.)}
\]

The approximate formula for the aluminum benzoyl stearoyl hydroxide thickener is as follows:

\[
\text{Al} (\text{C02R'}) (\text{C02R''}) (\text{OH})
\]

In the above formula, R’ refers to the stearic group, and R” refers to the benzoic group.

Experimental

All of the base oil was added to the laboratory grease vessel with the exception of a small amount necessary to dissolve the additives.

The vessel contents were then heated to 90°C and the temperature was monitored with a thermocouple.

The stearic and benzoic acids were added with constant agitation.

When both acids were completely melted, the aluminum source was added. The temperature was gradually raised to 180°C and maintained at that temperature for approximately 10 minutes.

When the batch reached 100°C, the additives were added to the vessel.

The grease was then homogenized at 6000 psi in a Gaulin homogenizer.
The aluminum source was kept at room temperature prior to use.

The vessel temperature was controlled carefully prior to adding the aluminum source and during the thickener formation reaction to prevent the sublimation of the benzoic acid.

The tests that were conducted on the finished grease are reported in Table 4.

### Table 4: Physical properties of the formulated aluminum complex grease

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Visual</td>
<td>White</td>
</tr>
<tr>
<td>Appearance</td>
<td>Visual</td>
<td>Smooth</td>
</tr>
<tr>
<td>Po</td>
<td>ASTM D217</td>
<td>285</td>
</tr>
<tr>
<td>P60</td>
<td>ASTM D217</td>
<td>322</td>
</tr>
<tr>
<td>NLGI Grade</td>
<td>ASTM D217</td>
<td>1</td>
</tr>
<tr>
<td>Oil Separation, 24h at 100°C, %</td>
<td>ASTM D6184</td>
<td>3.56</td>
</tr>
<tr>
<td>Dropping Point, °C</td>
<td>ASTM D2265</td>
<td>&gt; 260</td>
</tr>
<tr>
<td>Copper Corrosion, 24h at 100°C</td>
<td>ASTM D4048</td>
<td>1A</td>
</tr>
<tr>
<td>Four Ball Wear, mm</td>
<td>ASTM D2266</td>
<td>0.50</td>
</tr>
<tr>
<td>Apparent Viscosity, 25°C 1.94 s⁻¹ mPa.s</td>
<td>TA Rheometer</td>
<td>264,300</td>
</tr>
<tr>
<td>Apparent Viscosity, 25°C 24.98 s⁻¹ mPa.s</td>
<td>TA Rheometer</td>
<td>13,120</td>
</tr>
<tr>
<td>Chemistry</td>
<td>FT-IR</td>
<td>Figure 1</td>
</tr>
<tr>
<td>Apparent Viscosity, -40°C TC Spindle, 1 RPM, mPa.s</td>
<td>CTM Brookfield Viscometer</td>
<td>6.5 x 10⁵</td>
</tr>
<tr>
<td>Oxidation Induction Time, 150°C</td>
<td>ASTM D5483 Modified</td>
<td>&gt;120 minutes</td>
</tr>
<tr>
<td>Fineness of Grind</td>
<td>TBD</td>
<td>0</td>
</tr>
<tr>
<td>Volatility, 5% Weight Loss, °C</td>
<td>Thermogravimetric Analysis</td>
<td>261</td>
</tr>
<tr>
<td>Density at 25°C, g/cc</td>
<td>Pycnometer Method</td>
<td>0.853</td>
</tr>
<tr>
<td>Water Washout, 40°C</td>
<td>ASTM D1264</td>
<td>None</td>
</tr>
</tbody>
</table>

The apparent viscosity of the grease was determined using a TA controlled stress rheometer, Model AR 1000N. Less than a gram of grease is sandwiched between a rotating spindle and a stationary base plate. Temperature is controlled using a Peltier plate to 0.1°C. The spindle is 40 mm in diameter and has a two degree angle providing constant shear. This instrument is an ideal analytical tool to study the shear thinning behavior of viscoelastic materials.

Volatility of the grease was determined using a TA Instruments Model Q50 TGA. The instrument requires milligrams of sample and measures weight loss to 0.1 mg as a function of increasing temperature. The key components of the TGA are a microbalance and a furnace. Air or nitrogen may be selected as the purge gas.

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. The grease shown in Figure 1 has an ideal appearance for incidental food contact applications.
Figure 1: Photograph of the mPAO-based aluminum complex grease in a six-ounce (170 g) cartridge

Results

Figure 2: FTIR spectra of mPAO (top) and aluminum complex grease (bottom)
Figure 2: The expansion of the region of the FTIR spectrum where the presence of the thickener is indicated by
the triplet peaks at 1605, 1586 and 1568 cm\(^{-1}\)

Figure 3 shows the rheological profile of the grease at shear rates from 1.9 to 25 (1/sec).
The red plot shows shear stress while the blue plot is apparent viscosity, both as functions of shear rate.

Figure 3: Rheological behavior of the grease as a function of shear rate

The smooth appearance of each curve in Figure 3 is noteworthy. This behavior is usually encountered when the thickener is in a well-dispersed state.

Figure 4 is a plot of the apparent viscosity of the grease as a function of decreasing temperature. The data were generated using a Brookfield Viscometer attached to a Tenney environmental chamber. The data were generated using a T-C spindle operated at 1 RPM. Apparent viscosity data were recorded at 5-min intervals using a computer program that monitored both temperature and apparent viscosity. The recorded apparent viscosity at -40°C was 6.5 million mPa.s.
Conclusions

- A successful aluminum complex grease was prepared using mPAO 65 as the high viscosity oil blending component.
- The aluminum source released no IPA in the grease preparation. This was accomplished by carefully adjusting the thickener stoichiometry.
- Using 7.5% thickener resulted in an NLGI Grade 1 grease.
- The grease exhibited good antiwear performance in a four-ball wear test, a dropping point above \(260^\circ\text{C}\) and excellent thermal oxidative stability at \(150^\circ\text{C}\).
- After 24 hours at \(100^\circ\text{C}\), copper coupon corrosion testing resulted in a freshly polished appearance.
- This grease was not optimized for any one particular application. However, all the ingredients used were HX-1 approved for use in food grade greases.
- mPAO 65 continues to demonstrate its usefulness as viable base oil component to make greases prepared with lithium complex, polyurea, and aluminum complex thickeners.

References


Acknowledgements

- Chevron Phillips Chemical Company LP for sponsoring this work.
- Mr. Chris Horvath, Fed Chem, Inc., for graciously supplying the aluminum source to complete this project.
- Dr. Maureen Hunter, King Industries, Inc., for providing a complimentary sample of a multifunctional additive package
- The late Hank Kruschwitz, an indefatigable promoter of aluminum complex technology and wonderful personal friend.
As Vice President of International Sales, Cecilia Mancero travels all over the world promoting Engineering Services, Technology, and Equipment for STRATCO, Inc. In this interview, she shares the story of her career development, her views on opportunities and threats to the lubricating grease industry, the role of NLGI, and not one but three menus for dinners with her choice of notable guests.

Education and Career

NLGI: Please introduce yourself to NLGI members.

CM: I was born in Riobamba, Ecuador, which is a small town three hours south of the capital city of Quito. The Republic of Ecuador is located between Peru and Colombia in the northwest corner of South America. Ecuador is on the coast of the Pacific Ocean and includes the very well known Galapagos Islands. In terms of size, Ecuador is similar to the State of Nevada, and its population resembles that of New York State.

After I graduated from high school, I worked in the Banking industry in Ecuador for 4 years. In 1990, I immigrated to the USA to learn English and immerse myself in the culture and customs of this wonderful country.

I attended college at Central Missouri State University in Warrensburg, Missouri and graduated with a Bachelor Degree in Business Administration - Finance. Later on, I obtained a Master’s Degree in Social Sciences with an emphasis on Leadership at Azusa Pacific University in Los Angeles, California.

During my senior year in college, I was lucky to do my internship at STRATCO and continued to develop my career there after graduation. Now I am Vice President of International Sales. I have traveled all over the world promoting our Engineering Services, Technology, and Equipment for over 20 years.

I speak Spanish and English fluently and know ‘how to get around’ with three more languages, Italian, Portuguese, and French.

I love traveling, cooking, wine tastings, and hosting people in my home.
NLGI: What have been some ‘tipping points’ and influential decisions in your career?

CM: I had a comfortable life in Ecuador with a wonderful family, a great job, and community involvement. However, something was missing. Since an early age I had a desire to know more about the world and its cultures and customs, and I wanted to experience living in a different country. The opportunity to study in the USA came about, and I took it without hesitation.

Immigrating to the USA to go to college was a blessing to me. With courage and determination, I was able to conquer a new language, meet wonderful people, and be part of a new country that I now call my own, without forgetting my Ecuadorian background.

Another one of my personal goals was to work for a Petroleum Company. Life takes different turns, and I was able to fulfill my dream by working with STRATCO, an engineering firm that has designed equipment and provided engineering services for the Petroleum and Petrochemical industries since 1928.

The opportunity to work in International Sales for this Company has been one of the tipping points and highlights in my career. I have learned...
about the technical side of the Company and applied this knowledge in Sales to promote the business and service sides of STRATCO.

**NLGI: Do or did you have a mentor? Who or what has inspired you and your career?**

**CM:** God has been my mentor first and foremost. My parents and siblings have been strong pillars of support and mentorship in my career. Their belief in me encouraged me to pursue my dreams.

Diane Graham, Chairman/President of STRATCO since 1981, has influenced my career in the USA. I respect her desire to always help people from other cultures, whether or not they are customers, feel comfortable and appreciated for who they are. As a woman business owner in a male-dominated industry, she encouraged and challenged me to become the best professional that I could and to create long lasting relationships with Customers and Colleagues all over the world.

John Kay has been my technical mentor. He always has been patient with me as I learned about grease technology, and he explained the intricacies of the mechanical and process engineering world. Many other people have also been part of my journey and career in many other ways. I have been very blessed!
service are: Integrity, Trust, Quality, Customer Service, and Building Relationships. Great leadership, listening to our Customers’ needs, walking side by side with them on many projects, and offering the best equipment, technology, and services have led to the growth and success of STRATCO for almost a century.

Combining products and services and being responsive on a timely basis have been our mission for many years. As a Company, we want to be involved in all aspects of the production of lubricating greases. For decades, STRATCO has been the provider of state-of-the-art equipment for grease manufacturing. With our Engineers and Chemists, we have been very involved investigating the processes, chemistries, and variables that impact the production of greases.

When we start a project, we listen, brainstorm, and advise our Customers about the best way to help them achieve their goals. We perform tests in our pilot plant for Customers and for our own data base. We join forces with other Companies and suppliers in the industry to improve the quality of grease production.

We are also very concerned with the environment and the responsibility our industry has to make the world a better place.

After close to a year of research with Nynas AB (SE) and Eldon’s S.A. (GR), we co-authored a technical paper, Grease Production, CO2 emission...a New Relationship!, at the ELGI Annual General Meeting in April of 2019. One of our most important results proved that “an overall 21.5% reduction in CO2 emissions per metric ton of lithium grease made with a blend of ISO VG 220 naphthenic and Group I base oil blends in a pressurized reactor (Contactor™) versus nominally identical grease made with paraffinic oil in an open kettle”.

DAWN OF A NEW ANTIOXIDANT

VANLUBE® 407

Outstanding Performance in Both Thin-Film and Bulk Oxidation Protection.

Vanderbilt Chemicals, LLC
30 Winfield Street, P.O. Box 5150, Norwalk, CT 06856-5150
petro@vanderbilstchemicals.com
www.vanderbilstchemicals.com
(203) 853-1400
(203) 853-1452
I believe that this “green” research will also be a positive influence on the next generation of “greasers” and bring well-deserved attention to a critical industry that helps the world go ‘round!

**NLGI:** Do you have any words of wisdom for working in Sales?

**CM:** Developing relationships is very important, especially in this industry where critical or key people tend to remain in the industry. It is also very important to respond promptly to the Customers’ needs and to focus on the value of our Company’s products and services, which sets us apart from our competitors.

An important aspect of international sales is to be open-minded and accept the way that things are done in other areas of the world. My love and appreciation of other cultures has helped me listen to the needs of others to provide the best possible customer service.

During my career in international sales, I have met so many people from different backgrounds, assisted them with their particular needs, and established strong relationships that I know will last forever.

**Grease Industry**

**NLGI:** What are your thoughts about the future of the grease industry?

**CM:** It will be interesting to see how much lithium supply and demand will impact grease production. It is still very likely that lithium-based greases will continue to have a major presence in the future.
but there will certainly be an incentive for developing new products and expanding product portfolios.

The grease industry will continue to be critical in all the industries that it currently serves and will continue to grow. As competition increases, the importance of reducing manufacturing costs (material, labor, energy) will grow.

In certain areas of the world, the need for better greases, including food grade greases, is increasing. Keeping up with the types of greases produced by industrialized countries has become a major goal in developing countries.

**NLGI: What are some new or future opportunities for the grease industry?**

**CM:** It will be interesting to see how microwave heating for grease manufacturing will develop. This is one of the most recent innovations in the industry.

The increase in the use of automation and robotics in manufacturing could offer some new market opportunities.

Also, the need for grease manufacturing to become more environmentally friendly and reduce energy consumption could lead to a new NLGI/ELGI Working Group and an environmental rating system based on the grease manufacturing process.

**NLGI: What are some threats – present and future – that the grease industry faces?**

**CM:** Legislation and regulations on both regional and global levels present challenges by limiting formulations and imposing significant costs for certifications.

Second, the grease industry will always be sensitive to raw material costs, which can be impacted by competing demands from other industries, monopolies due to acquisitions

---

**FILL ACCURACY = HIGHER YIELD • FASTER PAYBACK**

**Servo Filling Systems**

**Cartridges • Squeeze Tubes • Custom Containers**

- Fill Accuracy ± 0.5% to 1% by Volume
- Recipe Saving & Recall
- Turnkey Systems & Custom Machinery
- Color Mix Options
- Accurately & Consistently Dosing High Viscosity Greases to over 3 Million Centipoise

**prosysfill.com**

- **417-673-5551**

---

- **VOLUME 83, NUMBER 4**
and consolidations, and price wars.

A third concern will be the need to replace the experts and retiring veterans in the industry with young talented engineers and chemists.

Role of NLGI

**NLGI: How do you see NLGI supporting or adding value to the grease industry?**

**CM:** Since its inception, NLGI has always added value by offering a platform for presenting new developments to the industry. NLGI Meetings continue to provide a central gathering place where all the major participants in the industry can meet one another.

NLGI provides certifications and working groups that are also important to the industry, and funding for research that offers the opportunity for new developments. It will be very important for NLGI to have more influence on regulations and standards that impact our industry.

NLGI’s efforts to expand its presence to other areas of the world are adding value to the industry. NLGI has provided global leadership for the formation of other Lubricating Grease Institutes, and there is a current focus on reviving the NLGI Latin American Chapter. NLGI continues to evolve and improve its offerings to the industry and its image and value to the market.
CM: My leadership style is that of a servant leader, someone who is always part of the group and ready to assist and roll up her sleeves if needed. Helping my team grow professionally is another aspect. Creating an environment where we are all passionate about what we do and how we serve our Customers and our own employees are priorities. One of my favorite quotes is from Richard Branson, founder of the Virgin Group, which controls 400-plus companies:

“I have always believed that the way you treat your employees is the way they will treat your customers, and that people flourish when they are praised for a job well done.”

NLGI: What are some of the most important characteristics or behaviors of good managers and leaders?

CM: A good manager is the person that focuses, goes by the rules, but does not micro-manage their employees. A good leader is the person who is always ready to assist his/her group of people, creates a critical mass to achieve the goals of the organization, and encourages people to grow and show their potential.

Experiences and Culture

NLGI: Have you worked ‘hands-on’ in a grease lab or plant? Have you made batches? Performed grease tests? Gone to field trials?

I have had the opportunity to participate in laboratory tests at our own Grease Pilot Plant with customers from all over...
Electric vehicles will change the lubricants industry. Are you ready?

Lubes’n’Greases Perspective on Electric Vehicles

is a new comprehensive annual report supported by quarterly reports so you are fully informed and kept up to date throughout the year—access to independent and trusted information is key to helping you make strategic decisions.

**Subscribe now and you will receive:**
- **A comprehensive annual report covering**
  - Mechanical aspects of EVs and hybrids
  - The pace at which vehicle populations are expected to shift
  - Implications for lubricant volume and performance demand
  - Formulation and testing
- **Quarterly reports covering fast-changing news about**
  - Impacts on lubes
  - Government policy
  - Infrastructure developments
  - OEM offerings
  - And much more …

**SUBSCRIBE TODAY for USD $2500!**
For more information visit www.LubesnGreases.com/electric-vehicles

---

Cecilia inspects the top of a STRATCO Contactor™ reactor in a grease manufacturing plant. (Photo courtesy of STRATCO)

**NLGI: Do you have any favorite stories about your experiences working in the grease industry?**

**CM:** I have many anecdotes and stories that would take me a long time to tell. My first business trip to South America as a young woman from Ecuador, working for a well-known and recognized company (but without much experience in the grease industry) was a success. At first, I was afraid to talk about grease with some of the expert greasers that I met. Then Otto Rohr, Roberto Hissa, German Ponce, and their colleagues welcomed me and helped me learn so much about this wonderful industry about which they were so passionate.

Another exciting story for me was to be able to support a Customer in Eastern Europe by contacting a Customer in Western Europe. Another Customer in Western Europe was willing to help us (STRATCO) to help his competitor in Eastern Europe. In a matter of days, with our second Customer’s help, we
were able to bring our first customer bring their plant back on-line. This again shows that relationships built over the years with our Customers are strong and allow us to be of service when the need arises. It has been a wonderful experience for me personally to be part of the Lubricating Grease Industry.

Favorites

NLGI: Where is your favorite place to travel?

CM: This is a very difficult question to answer. I consider myself a woman of the world because I have been fortunate to have traveled to almost 37 countries on six continents. Each place has its own flavor, amazing cultures, and something very unique to offer. I love so many places that I have visited, and I can’t choose just one as my favorite.

NLGI: If you could have dinner with any three people, living or deceased, who would they be and why? And what might be on the menu?

CM: Gandhi would be my first choice because he was a servant leader, in my opinion. He accomplished so much with his style of leadership while promoting partnerships through nonviolent resistance. There would be a vegetarian menu of dishes seasoned with wonderful infusions of Indian spices, and flavored tea to drink.

Margaret Thatcher is my second choice because she was a strong woman and respected by her peers. The way she handled herself in the position as Prime Minister of the UK was very impressive to me.

She actually had a Chemistry degree from the University of Oxford and worked as a research chemist at a food manufacturer. I would have loved to hear more of her experiences and how she felt about being called the “Iron Lady”.

On the menu, we might have grilled Dover Sole paired with a wonderful bottle of cold Sauvignon Blanc wine. By the way, I was fortunate to be eating lunch with two great friends at the famous Dining Room (which has a Michelin star) in The Goring, a grand hotel in London, when Margaret Thatcher strolled into the restaurant with the owner of Jet Airways Airlines to have lunch!

Warren Buffett is my third choice, as I respect him for his influence on society and the financial world. Mostly, I respect his background as someone who achieved success through hard work, and how down to earth he is despite his success. Buffett is open, shares his knowledge, and listens to ordinary people, not only his peers and influential people. I would like to have a one-on-one conversation with him, just as he talks with stockholders during Berkshire Hathaway annual meetings. His legacy will last forever!

On the menu we will have a great juicy slab of Kansas City Steak with au gratin potatoes, green beans, and a good bottle of an Insignia 2015 Cabernet Sauvignon wine.
Call For 2020 Papers
“The Music of Greases, it’s in the Composition”

Would you be interested in presenting a paper on the above mentioned theme at our forthcoming AGM 25-28 April 2020 in Hamburg, Germany?

Our 2020 theme topics of interest can include, but are not limited to:
• Performance of Greases
• Composition of Greases & Food Grade Greases
• Instruments used in the measurement & evaluation of Greases
• Conducting surveys, field tests; application ...

2020 Call for papers topic and author information
2020 Guidelines for speakers on technical presentations at the ELGI AGM

If yes, do send your paper proposal by completing the author information form by 20th October 2019 to the ELGI. Papers that tie in with the 2020 theme will be given high priority. Other topics of interest to the grease industry are welcome and will be considered too. We have space for 14 papers only, so do submit paper abstract on time.

For information, please contact our office:
Carol Koopman | T: +31 20 6716 162 | E: carol@m_gi.demon.nl | W: www.elgi.org

ADVERTISE WITH NLGI
in the NLGI Digital Spokesman

The NLGI Spokesman Magazine is published bi-monthly (6 issues per year) in digital format only.

CIRCULATION INFORMATION
The NLGI Spokesman is a trade publication sponsored by the National Lubricating Grease Institute. The circulation reaches over 45 countries worldwide.

READERSHIP
Manufacturers, suppliers, marketers, distributors, technicians, formulators, scientists, engineers and consumers of lubricating greases.

CLICK HERE
to download the current rate card.

Website advertising is also available for nlgi.org.

Inquiries and production materials should be sent to
Denise Roberts at NLGI (denise@nlgi.org)