In this issue . . .
8  Unique Spherical Nanoparticles of Tungsten Disulfide (IF-WS2) as High Performance Additives for Greases
14 Performance Evaluation of Antimony/Zinc Diamyl Dithiocarbamate as Grease Additive
22 Study on a New Oxidation Stability Method for Lubricating Greases by Employing the Rapid Small Scale Oxidation Test
36 Complex Issue of Dropping Point Enhancement in Grease
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President’s Podium

Resolve to Recognize - 2018 Award Nominations

Unique Spherical Nanoparticles of Tungsten Disulfide (IF-WS2) as High Performance Additives for Greases

Elena McDaniel, George Dilyon, PhD, Nanotech Industrial Solutions Inc.

Performance Evaluation of Antimony/Zinc Diamyl Dithiocarbamate as Grease Additive

Aili Ma, Minli Gu, and Junbing Yang, VANDERBILT (BEIJING) TRADING, LTD

Mihir K. Patel, Ruiming “Ray” Zhang, VANDERBILT CHEMICALS, LLC

Study on a New Oxidation Stability Method for Lubricating Greases by Employing the Rapid Small Scale Oxidation Test

George S. Dodos, ELDON’S S.A.

Complex Issue of Dropping Point Enhancement in Grease

Joseph P. Kaperick, Gaston Aguilar, Ken Garelick, Amanda Miller, Michael Lennon, Michael Edwards; Afton Chemical Corporation

A STUDY ON A HYBRID GREASE OF A LITHIUM GREASE AND A DIUREA GREASE Applied for Wide Temperature Range

Author: You Shu Ting,
Co-authors: Chen ShiQi, Ng Hak Hong Seiji Okamura
Hin Leong Trading (PTE) Ltd., Singapore

2018 Calendar of Events

Advertiser’s Index
President David Como Announces New Executive Director

I am pleased to announce that Crystal O’Halloran, MBA, CAE has joined the organization as NLGI’s new Executive Director. In her new role, O’Halloran will lead the institute’s global strategy and community outreach as well as manage operations and drive membership growth and engagement.

“I’m honored and pleased to join the NLGI team,” said O’Halloran. “I’m dedicated to partnering with the board of directors to make NLGI the go-to resource for grease education including information that can lead to the development of better lubricating greases for the consumer as well as provide better grease lubrication engineering service to the industry.”

O’Halloran received her undergraduate degree from Kansas State University and graduate degree from Baker University. She began her career in the hospitality industry, but quickly developed a passion for association management. O’Halloran has worked for two associations in Kansas City and has twelve years of association management experience, including seven years of trade association experience. Her skills include developing and implementing strategic plans, generating new revenue streams (including non-dues revenue), refining member engagement, recruitment and retention, launching new initiatives, providing financial oversight as well as cultivating relationships with the Board of Directors, members, staff and partnering organizations.

O’Halloran succeeds Kim Hartley, who joined NLGI in 2003, became executive director in 2007 and now moves into the newly created position of NLGI meeting planner, said Dave Como of Dow Corning, the group’s president. “The quality of NLGI’s meetings became legendary under Kim’s tenure,” he added, “and we’re delighted to see that continue for our upcoming Annual Meeting,” in Coeur d’Alene, Idaho, June 9-12, 2018.

“On behalf of the NLGI board of directors, we’re thrilled to welcome Crystal O’Halloran to our organization. Beyond her experience and successes, she is the kind of personable person you feel that you’ve known for a long time and will be an extraordinary fit for our organization,” said NLGI President, Dave Como.
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RESOLVE TO RECOGNIZE

Happy New Year! It’s that time again, time to consider resolutions for the coming 12 months. Certainly, a little introspection helps chart a path to a better, more productive, and happier self. But, one of the most rewarding feelings in life comes from recognizing the efforts and contributions of others. Here’s a great opportunity to start your year off on the right foot by recognizing the achievement or contribution of a fellow industry professional.

At the 2018 NLGI Annual Meeting, themed Grease Currents: Lubrication in an Electrified World, to be held at the fabulous Coeur D’Alene Resort in Coeur D’Alene, Idaho, June 9-12, distinguished individuals will be recognized for efforts in advancing knowledge and understanding within the lubricating grease industry. The NLGI strives to honor those who have furthered themselves, the company they represent, and the industry.

No doubt, you know of an individual deserving nomination for special recognition. It only takes a few short minutes to complete a nomination form. Make a resolution to recognize someone you know and admire.
The following prestigious awards are now open for nominations from NLGI members:

- **NLGI Award for Achievement**
  The Institute's highest award honors the achievement of those who have made exceptional contributions to the growth and development of the Institute.

- **NLGI Fellows Award**
  Acknowledges valuable work within the Institute, in the technical development of greases, grease tests, or the promotion of grease usage.

- **John A. Bellanti Sr. Memorial Award**
  Acknowledges meritorious service on the NLGI Board, or on Technical Committee projects or to the industry.

- **NLGI Honorary Membership**
  Entitles lifetime honorary membership to those who, over a period of years, have served the Institute in some outstanding capacity and are not now with a member company.

- **Award for Educational Excellence**
  For outstanding instruction as exemplified by subject knowledge and presentation skills in NLGI educational courses.

- **NLGI Author Award (Development)**
  For the best paper presented at our Annual Meeting that focuses on formulation, development, and manufacture of finished greases.

- **NLGI Author Award (Application)**
  For the best paper presented at our Annual Meeting that focuses on testing, selection, application or use of greases.

- **Clarence E. Earle Memorial Award**
  For an outstanding contribution to the technical literature relating to lubricating greases during the year.

- **NLGI Founders Award**
  In recognition of the three founding companies of the NLGI, the Founders Award is presented to a member company that has had a positive impact on the NLGI in the tradition established by these founding fathers.

[CLICK HERE to download a form](#)
Email nlgi@nlgi.org, or call 816-524-2500 to receive a Nomination Form.
Send completed forms to: nlgi@nlgi.org

Start off the year by nominating that deserving individual, then join us in Idaho for the ceremony!

**HAPPY NEW YEAR!**
*Pat Walsh*, Chair, Awards Committee
*Chuck Coe, Joe Kaperick, Anoop Kumar, David Turner*
UNIQUE SPHERICAL NANOPARTICLES of TUNGSTEN DISULFIDE (IF-WS2) as High Performance Additives for Greases

Elena McDaniel, George Diloyan, PhD
Nanotech Industrial Solutions Inc.

Abstract

Solid particles have been widely used in greases to improve EP performance in demanding applications and in various industries. The most common solid particles for the past several decades have been platelet shaped micron sized particles of 2H-MoS2 (2 dimensional hexagonal Molybdenum DiSulfide). In this paper the properties of novel spherical shaped nanoparticles of IF-WS2 (Inorganic Fullerene Tungsten disulfide) solid additives in greases will be shown as a potential replacement of micron platelet 2H-MoS2 additives.

Spherical like nanoparticles of tungsten disulfide (IF-WS2) are considered to be excellent anti-wear, antifriction and EP additives. Due to their unique spherical shape, these particles are protecting metal surfaces from load shock, micro pitting and wear from constant metal to metal contact under high temperatures and loads.

Introduction

Antifriction, anti-wear and EP (Extreme Pressure) properties in greases play a very important role in order to produce high quality products that protect equipment in industrial applications such as mining, automotive, steel production etc. There are many additives in the market that are reducing wear and friction (i.e. MoDTP, MoDTC, ZnDTP, 2H-MoS2) and increasing EP properties (i.e. heavy metals, sulfur, phosphorous).

Anti-wear characteristics of ZnDTP (Zinc dialkyl-dithiophosphate) are attributed to the formation of phosphate films that can react with abrasive iron oxides [1]. On the other hand MoDTC (molybdenum dialkyl-dithiocarbamate) has been used primarily as a friction modifier due to the formation of MoS2 at high Hertzian pressure points. MoDTP (molybdenum dialkyl-dithiophosphate) possesses combined anti-wear and friction reduction properties [2]. Both MoDTP and MoDTC require the presence of temperature and friction in order to start the generation of MoS2 layers. 2H-MoS2 particles (Figure 1a [3]) are platelet shape micron size particles that in the presence of shear stress exfoliate layers of MoS2 thus reducing friction.

IF-WS2 nanoparticles (Figure 1b) are novel spherical particles that were invented in 1992 by Professor Reshef Tenne in the Weizmann Institute of Science. These particles currently are produced on a commercial scale and are available in various forms of dispersions (water, paste, oil). In this paper the commercially available paste dispersion of IF-WS2 nanoparticles has been tested in LiX grease. Wear, friction, and EP characteristic along with other physical properties have been evaluated.

Fig. 1. SEM image of 2H-MoS2 micron size particle [3] (a) and closed-caged nanoparticle of IF-WS2 (b)
Due to their morphology and size, IF-WS2 nanoparticles provide excellent shock absorbing properties along with anti-wear, anti-spalling and pitting, friction reducing, and extreme pressure properties. Figure 2 depicts the mechanisms of IF-WS2 nanoparticles and their behavior under various conditions: static and dynamic loads, shock, shear etc. Due to the Nano range of the primary particle size (30-110nm), the treat rate of IF-WS2 in applications varies from 0.15% to 1%. In comparison 2H-MoS2 is mostly used between 3% - 10% accompanied with active sulfur to get decent EP characteristics (above 315kgf ASTM D2596).

Experimental
The grease selected for our current study was a lithium complex soap (LiX) obtained from a commercial batch of a grease manufacturer. IF-WS2 based concentrate in paste form (EMX) was used at various treat rates between 0.5% and 1.5%. 2H-MoS2 micron sized platelet shaped particles of MoS2 were used at concentration range 3-10%. EMX and 2H-MoS2 were mixed in the LiX grease followed by homogenization in the FlakTec Speed Mixer shown in the Figure 3. Wear scars were measured in optical microscope, and 3D images were obtained via RTec profilometer (Rtec Instruments).

All samples after milling were evaluated for grease consistency following ASTM D217 standard test procedures and dropping point following ASTM D2265. Table 1 shows description of each sample evaluated.

![Figure 2. Mechanism of IF-WS2 performance](image)

![Figure 3. High Speed grease mixer](image)

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>LiX base grease (soap + oil)</td>
</tr>
<tr>
<td>Sample 2</td>
<td>LiX base+0.5% IF WS2 dispersion EMX</td>
</tr>
<tr>
<td>Sample 3</td>
<td>LiX base+1% IF WS2 dispersion EMX</td>
</tr>
<tr>
<td>Sample 4</td>
<td>LiX base+1.5% IF WS2 dispersion EMX</td>
</tr>
<tr>
<td>Sample 5</td>
<td>LiX base+3% 2H-MoS2</td>
</tr>
<tr>
<td>Sample 6</td>
<td>LiX base+5% 2H MoS3</td>
</tr>
<tr>
<td>Sample 7</td>
<td>LiX base+10% 2H MoS4</td>
</tr>
</tbody>
</table>
Since IF-WS2 powder after synthesis process comes in agglomerated form, where agglomerates are several microns in size, the de-agglomeration and dispersion procedures have been conducted. Figure 4c shows IF-WS2 aggregate. Where on the edge of the aggregate can be seen spherical shape IF-WS2 primary particles. In order to make sure that all IF-WS2 particles were in primary size (30-110nm), ready to use IF-WS2 based concentrate (EMX) has been used for this study.

Table 2. List of tests conducted on samples

<table>
<thead>
<tr>
<th>#</th>
<th>Test Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ASTM D2266</td>
<td>Four Ball wear</td>
</tr>
<tr>
<td>2</td>
<td>ASTM D2266</td>
<td>Coefficient of Friction</td>
</tr>
<tr>
<td>3</td>
<td>ASTM 2596</td>
<td>Four Ball EP</td>
</tr>
<tr>
<td>4</td>
<td>ASTM D2509</td>
<td>Timken EP test</td>
</tr>
<tr>
<td>5</td>
<td>ASTM D217</td>
<td>NLGI grade</td>
</tr>
<tr>
<td>6</td>
<td>ASTM D2265</td>
<td>Dropping Point</td>
</tr>
</tbody>
</table>

Table 2 shows the list of standard tests that been conducted for each sample and parameters monitored.

Results and Discussion

The grease formulations evaluated in this study showed excellent tribological properties. Results in the table below show that the LiX grease with IF-WS2 particles even at extremely low percentages increase the performance in extreme pressure and wear. 2H-MoS2 particles showed good antifriction properties and increased EP properties, however increased wear at higher treat rates.

Low friction, wear and increased EP properties of IF WS2 based dispersion could be explained by multi-functional mechanism of IF-WS2 particles. Due to spherical morphology of IF-WS2 they behave differently under various tribological conditions. The mechanism can change from rolling, to sliding and to exfoliation under various loads, shear and shock. On the other hand 2H-MoS2 platelets reduce friction predominantly under shear/sliding motion. And due to platelet structure and big particle size (about 1.5-3 µm) could be abrasive, especially under high loadings.
Figures 5-7 show wear, friction and weld point data for all tested samples.

Figures 8 and 9 show 3D profiles of wear scars of Sample 2 and Sample 4. Figures 10 and 11 show 3D profiles of wear scars of Sample 5 and 7.

**Table 3. Summary of results**

<table>
<thead>
<tr>
<th>#</th>
<th>Test Name</th>
<th>Description</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
<th>Sample 6</th>
<th>Sample 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ASTM D217</td>
<td>Cone Penetration of Lubricating Grease</td>
<td>263</td>
<td>267</td>
<td>273</td>
<td>273</td>
<td>271</td>
<td>275</td>
<td>277</td>
</tr>
<tr>
<td>2</td>
<td>ASTM D2266</td>
<td>Four Ball wear, mm</td>
<td>0.57</td>
<td>0.515</td>
<td>0.465</td>
<td>0.425</td>
<td>0.47</td>
<td>0.54</td>
<td>0.655</td>
</tr>
<tr>
<td>3</td>
<td>ASTM D2266</td>
<td>Coefficient of Friction</td>
<td>0.0704</td>
<td>0.0648</td>
<td>0.0672</td>
<td>0.0607</td>
<td>0.0779</td>
<td>0.0745</td>
<td>0.0567</td>
</tr>
<tr>
<td>4</td>
<td>ASTM 2596</td>
<td>Four Ball EP, kg weld point</td>
<td>160</td>
<td>315</td>
<td>500</td>
<td>620</td>
<td>315</td>
<td>400</td>
<td>620</td>
</tr>
<tr>
<td>5</td>
<td>ASTM D2509</td>
<td>Timken EP test, lbs</td>
<td>N/A</td>
<td>45</td>
<td>55</td>
<td>65</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>6</td>
<td>ASTM D2265</td>
<td>Dropping Point, C</td>
<td>245</td>
<td>242</td>
<td>253</td>
<td>255</td>
<td>253</td>
<td>251</td>
<td>248</td>
</tr>
</tbody>
</table>

Figures 5 and 6 show wear and weld point data for all tested samples.

**Figure 5. Wear scar comparison of tested samples**
Figures 7, 8 and 9 show 3D profiles of wear scars of Sample 4, 5 and Sample 7 respectively.

Figure 6. EP properties comparison of tested samples

Figure 7. 3D profilometry wear scar of Sample 4
Conclusion

The work done here has compared IF-WS2 nanoparticle based concentrate and micron sized platelet form 2H-MoS2 particles in one LiX grease formulation. By using some basic tribological tests (4-ball EP (ASTM D2596), 4-Ball Wear (ASTM D2266), and Timken (ASTM D2509)), it has been shown that IF-WS2 based concentrate significantly increases the EP properties of the LiX grease used here at a much smaller treat rate (up to 1.5%) than platelet 2H-MoS2. Other physical properties of the grease such as dropping point or cone penetration were not affected. Work with additional LiX greases and other soaps have not yet been tested and documented. The work done here is representative of one type of LiX grease used, however, ongoing testing and research is still being conducted with other LiX soaps and grease types.

Reference

4. P.U.Aldana, F.Dassenoy, B.Vachera, T. Le Mognea, B. Thiebaub, A. Bouffet, Tribology Transactions, 59 (1), (2016), 178
Performance Evaluation of Antimony/Zinc Diamyl Dithiocarbamate as Grease Additive

Aili Ma, Minli Gu, and Junbing Yao
Vanderbilt (Beijing) Trading, Ltd

Mihir K. Patel, Ruiming “Ray” Zhang
Vanderbilt Chemicals, LLC

ABSTRACT

The Extreme-Pressure (EP), antiwear (AW), friction-reducing (FR) and antioxidation (AO) performances of antimony/zinc mixed metal dithiocarbamate (Sb/ZnDTC) as a grease additive are evaluated. The four-ball tests show that, the Sb/ZnDTC a mixed metal organic salt, exhibits excellent EP, good AW, but no FR performances in lubricating base oil. Whereas it exhibits good EP, but no obvious AW and FR capacities in lithium complex, polyurea and calcium sulfonate complex greases. The combination of Sb/ZnDTC and molybdenum dialkyl dithiocarbamate (MoDTC), a known AW and FR additive, could give a balanced overall performance in grease with high EP and excellent FR/AW characteristics. The MTM (Mini Traction Machine) Stribeck curves indicate, Sb/ZnDTC could effectively reduce the friction coefficients under boundary and mixed lubrication regimes in calcium sulfonate complex grease, especially at high temperature. In addition, the PDSC (Pressure Differential Scanning Calorimetry) oxidation test proves that Sb/ZnDTC is an excellent antioxidant in greases as a hydroperoxide decomposer.

KEYWORDS

Grease, Dithiocarbamate, Antimony, Zinc, Extreme-Pressure, Antioxidant

1. INTRODUCTION

Antimony, same as phosphorus, belongs to the Group VA in the periodic table of the elements, possesses some extreme-pressure (EP) and antiwear properties too. Extreme Pressure (EP) performances, especially the Timken OK loading capacity, of greases and oils have long been enhanced by the use of antimony dithiocarbamate (SbDTC)\(^1\)\(^-\)\(^4\). However, it is very important to try to limit the amount of antimony into the environment, due to the environmental and health concerns over its toxicity as a heavy metal element. It is a challenge to utilize low amount of antimony dithiocarbamate in lubricating oils and greases to achieve high EP performances. Very meaningfully, the in situ (in one kettle) preparation of zinc dialkyl dithiocarbamate (ZnDTC) in the preparation of antimony dithiocarbamate (SbDTC) has allowed for the significant reduction of the SbDTC needed while maintaining the necessary EP properties of the grease composition as determined by the Timken OK load test\(^7\)\(^-\)\(^8\). The in situ synthesis of this di-metal salt of dithiocarbamate (Sb/ZnDTC) from a secondary amine, carbon disulfide and antimony (III) oxide, Sb2O3, and zinc (II) oxide, ZnO can be describe as follows:

\[
\text{R}_2\text{NH} + \text{CS}_2 + \text{Sb}_2\text{O}_3 + \text{ZnO} \rightarrow \text{Sb}([\text{Zn}([\text{S}_2\text{CNR}_2])_2] + \text{H}_2\text{O}
\]

The EU Classification of Xn (harmful) N (dangerous for the environment) for concentration of Antimony (Sb) is: Sb ≥ 25 %, Xn, N, R20/22-51/53; 2.5 % ≤ Sb < 25 %, Xn, R20/22-52/53; and 0.25 % ≤ Sb < 2.5 %, Xn, R20/22. Therefore it is very important for the concentration level of antimony in grease to be less than 0.25%. Reduced antimony content in greases without the loss of EP capability or the need for sulfurized olefin or ester with strong odor could be achieved by this synthesis method. The Sb/ZnDTC by this in situ synthesis can guarantee an excellent EP performance, when Sb is less than 0.25% in greases. The comparison between the bi-metal salt of dithiocarbamate by in situ synthesis and its simple blending (SbDTC + ZnDTC) was given as in the Table 1\(^9\).

The Sb/ZnDTC by in situ synthesis outperforms the physical mixture of SbDTC and ZnDTC, moreover, it does not have the sulfurized olefin’s drawbacks of pungent odor and lowering dropping point of lithium complex grease.
2. EXPERIMENTAL / MATERIALS AND METHODS

2.1 Base Oil, Greases and Additives
Base oil used in this study is 650SN Group I base oil. Base greases used include a lithium complex grease, a polyurea grease and a calcium sulfonate complex grease. All three base greases were obtained from real production batches by courtesy of two grease manufacturers.

The in situ liquid Sb/ZnDTC additive has antimony, zinc and sulfur content of 5.8%, 4.5%, and 18.5% respectively, and contains 20% petroleum base oil. In this paper, the additive is designated as Sb/ZnDTC. The interaction between Sb/ZnDTC and an organo-molybdenum additive is also investigated in this paper for an overall balance EP, AW and FR performances in greases. The Molybdenum additive evaluated is a solid molybdenum dibutyl dithiocarbamate, which contains the molybdenum of 28.0% and the sulfur of 24.5%. This Mo additive is designated as MoDTC. These two additives are commercially available.

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

2.3 Four-Ball EP test
Standard ASTM D2596 four-ball EP test method was used to evaluate additive EP performance in greases. Experimental conditions were: 1770 rpm speed, time duration 10 seconds. Both last nonseizure load (LNSL) and weld point were measured.

2.4 MTM Strubeck Curve
Mini Traction Machine (MTM) was used to evaluate frictional characteristics in boundary and mixed lubrication regime (Strubeck Curve) with “Ball on Disc” configuration. MTM consists of a rotating a 52100 steel ball pressed against an independently rotating 52100 steel disc immersed in the grease. The operating conditions are set by independently controlling the rotational velocities of the shafts that drives the ball and the disc, in order to obtain a particular combination of rolling speed and slide to roll ratio, as well as by controlling the contact force and the oil bath temperature. The test conditions: 35N load (Equivalent to 1GPa hertzian point contact load), 50% Slide to Roll Ratio, each Strubeck curves at 40°C, 60°C, 80°C, 100°C, 120°C and 140°C, Mean speed were started at 1000 mm/s and decreasing in steps of 100 mm/s to 100 mm/s and finally decreased from 100 mm/s in steps of 10 mm/s to 10 mm/s. The operation scheme of MTM is illustrated as in Figure 1.
2.5 PDSC oxidation test

PDSC (Pressure Differential Scanning Calorimetry, ASTM D6186) was used to measure the oxidation in greases. A small quantity of oil is weighed into a sample pan and placed in a test cell. The cell is heated to a specified temperature and then pressurized with oxygen. The cell is held at a regulated temperature and pressure until an exothermic oxidation reaction occurs. The extrapolated onset time is measured and reported as the oxidation induction time (OIT) for the lubricating oil or grease at the specified test temperature. The test conditions: 3.5MPa pressure, 180, 200 and 210°C temperatures, 3.0 mg grease sample, and 100ml/min oxygen flow.

3. RESULTS AND DISCUSSION

3.1 Tribological performances in base oil

Sb/ZnDTC was added into Group I base oil, and the tribological performances were evaluated by four-ball friction and wear tests. The experimental results are given in Table 2.

<table>
<thead>
<tr>
<th></th>
<th>Friction and Wear Test (40Kgf, 1200rpm, 75°C, 60min.)</th>
<th>EP Test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wear Scar, mm</td>
<td>Average Friction Coefficient</td>
</tr>
<tr>
<td>650SN Base Oil</td>
<td>0.802 (30Kgf)*</td>
<td>0.100 (30Kgf)*</td>
</tr>
<tr>
<td>+ 2.0% Sb/ZnDTC</td>
<td>0.558</td>
<td>0.102</td>
</tr>
<tr>
<td>+ 3.0% Sb/ZnDTC</td>
<td>0.585</td>
<td>0.104</td>
</tr>
</tbody>
</table>

*Seizure occurred for the base oil under 40Kgf load, and the test for 60 min. failed, so just the wear scar and the friction coefficient under 30Kgf load for 60 min. was given for reference.

It can be seen from Table 2 that, Sb/ZnDTC possesses excellent EP, good AW performances, but no obvious FR capacity in the base oil.

3.2 Tribological performances in greases

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

<table>
<thead>
<tr>
<th></th>
<th>Friction and Wear Test (40Kgf, 1200rpm, 75°C, 60min.)</th>
<th>EP Test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wear Scar, mm</td>
<td>Average Friction Coefficient</td>
</tr>
<tr>
<td>Lithium Complex Base Grease</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ 3.0% Sb/ZnDTC</td>
<td>0.508</td>
<td>0.092</td>
</tr>
<tr>
<td>Polyurea Base Grease</td>
<td>0.423</td>
<td>0.089</td>
</tr>
<tr>
<td>+ 3.0% Sb/ZnDTC</td>
<td>0.614</td>
<td>0.106</td>
</tr>
<tr>
<td>Calcium Sulfonate Complex Base Grease</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ 3.0% Sb/ZnDTC</td>
<td>0.375</td>
<td>0.098</td>
</tr>
<tr>
<td>+ 3.0% Sb/ZnDTC</td>
<td>0.478</td>
<td>0.089</td>
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</tbody>
</table>
It shows in Table 3 that, Sb/ZnDTC exhibits good four-ball EP performance, but no obvious FR capacity in the greases, and the AW properties can only be found in the lithium complex base grease. Thus, Sb/ZnDTC can only be treated as an EP additive in greases, and another kind of additive is needed in combination with it to achieve an overall balanced EP, AW and FR performances.

### 3.3 Tribological performances with organo-molybdenum additive in greases

As showed in Table 3, Sb/ZnDTC is not a good AW and FR additive for greases, so AW and FR additive is needed with it for the comprehensive performances. Molybdenum dibutyl dithiocarbamate (MoDTC) is well-known for its excellent FR and AW performances in greases [9]. Actually, the successful combination of SbDTC and MoDTC in lithium, lithium aluminum mixed greases for high Timken OK load, high four-ball wear load, low wear scar and low friction has already been reported [3].

Sb/ZnDTC and MoDTC were added into the calcium sulfonate complex base grease, and the tribological performances were evaluated by four-ball friction and wear tests. The experimental results are given in Table 4.

| Table 4. The EP, AW and FR Performances of Sb/ZnDTC with MoDTC in Calcium Sulfonate Complex Grease |
|----------------------------------------------------------|----------------------------------------------------------|
| **Friction and Wear Test**                               | **EP Test**                                               |
| (40Kgf, 1200rpm, 75°C, 60min.)                           | LNSL, Kgf                                               |
| Wear Scar, mm, Average Friction Coefficient              | Weld load, Kgf                                            |
| Calcium Sulfonate Complex Base Grease                     | 0.375                                                   |
| + 3.0% Sb/ZnDTC                                          | 0.098                                                   |
| + 1.0% MoDTC                                             | 100                                                     |
| + 3.0% Sb/ZnDTC + 1.0% MoDTC                             | 315                                                     |
| + 0.0% Sb/ZnDTC                                         | 0.089                                                   |
| + 1.0% MoDTC                                             | 139                                                     |
| + 3.0% Sb/ZnDTC + 1.0% MoDTC                             | 620                                                     |

It is evident from Table 4 that, in the calcium sulfonate complex grease, the combination of Sn/ZnDTC with MoDTC can achieve excellent EP, AW and FR performances simultaneously. The wear scars and the friction coefficients of the greases with and without Sb/ZnDTC and/or MoDTC are shown in Figures 2 and 3.
It can be seen that, in the calcium sulfonate complex grease, the combination of Sb/ZnDTC and MoDTC could achieve excellent FR and AW performances, while keeping the high EP properties (weld load, from 250Kgf to 620Kgf).

### 3.4 MTM Stribeck curve
3.0% Sb/ZnDTC was added into the calcium sulfonate complex base greases, and the frictional properties under slide/roll conditions were evaluated using Mini Traction Machine (MTM). The Stribeck curves at different temperature are shown in Figure 4.

From Figure 4, it could be found that, with the increase of the temperature, the friction-reducing efficiency by Sb/ZnDTC becomes higher and higher under boundary (10-100mm/s) and mixed (100-1000mm/s) lubrication regimes.

Especially at middle and high temperatures (≥100°C), Sb/ZnDTC can reduce the grease's friction coefficient under almost whole boundary and mixed lubrication regime (10-1000mm/s).

### 3.5 Anti-oxidation performance
PDSC was employed to evaluate the antioxidation performance of Sb/ZnDTC in lithium complex, polyurea and calcium sulfonate complex base greases. The oxidation induction times at different temperature are given in Table 5.

The three base grease samples were provided by different grease maker. It seems that the simply polyurea base grease is not always better than simply lithium complex base grease under high temperature, but definitely the polyurea grease has a better response to the antioxidant.

### Table 5. The Antioxidation Performances of Sn/ZnDTC in Greases

<table>
<thead>
<tr>
<th></th>
<th>PDSC Test, Oxidation Induction Time, min.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>180°C</td>
</tr>
<tr>
<td>Lithium Complex Base Grease</td>
<td>82.7</td>
</tr>
<tr>
<td>+ 3.0% Sb/ZnDTC</td>
<td>190.2</td>
</tr>
<tr>
<td>Polyurea Base Grease</td>
<td>54.8</td>
</tr>
<tr>
<td>+ 3.0%Sb/ZnDTC</td>
<td>251.0</td>
</tr>
<tr>
<td>Calcium Sulfonate Complex Base Grease</td>
<td>9.8</td>
</tr>
<tr>
<td>+ 3.0% Sb/ZnDTC</td>
<td>86.0</td>
</tr>
</tbody>
</table>
Figure 4. MTM Stribeck curve of the calcium sulfonate complex grease with and without Sb/ZnDTC at different temperature
It is evident from Table 5 that, Sb/ZnDTC possesses excellent antioxidation performance in all these three greases, which increases the oxidation induction times significantly. Due to the chemical characteristics as dithiocarbamate derivative, Sb/ZnDTC serves as a hydroperoxide decomposer. The PDSC oxidation diagrams of the polyurea greases with and without Sb/ZnDTC are illustrated in Figure 5. It shows in Figure 5 that, Sb/ZnDTC could increase the OIT of the base polyurea grease more than 3.5 times, which demonstrates Sb/ZnDTC’s outstanding antioxidation capacity in grease.

4. CONCLUSIONS

(1) The di-metal salt of dithiocarbamate (Sb/ZnDTC) by in situ synthesis possesses excellent EP, good AW, but no FR performances in base oil;
(2) Sb/ZnDTC exhibits good EP performances in lithium complex, polyurea and calcium sulfonate complex greases.
(3) The combination of Sb/ZnDTC and molybdenum dialkyl dithiocarbamate (MoDTC) as AW and FR additive, could give a balanced overall performances in grease with high EP and excellent FR/AW characteristics.
(4) The MTM (Mini Traction Machine) Stribeck curves indicates, Sb/ZnDTC could effectively reduce the friction coefficients under boundary and mixed lubrications in calcium sulfonate complex grease, especially at high temperature.
(5) The PDSC (Pressure Differential Scanning Calorimetry) oxidation test proves that Sb/ZnDTC is an excellent antioxidant in greases as hydroperoxide decomposer.

Reference
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STUDY ON A NEW OXIDATION STABILITY METHOD for Lubricating Greases by Employing the Rapid Small Scale Oxidation Test

George S. Dodos
ELDON’S S.A.

Abstract
In recent years an accelerated oxidation test has been developed and was initially introduced as a standard ASTM method for screening the ageing reserve of fuels and biofuels. This is namely the Rapid Small Scale Oxidation Test (RSSOT) which is based on an automated and customizable oxidation tester that could be also adapted for measuring lubricating greases. Therefore, the aim of this study is to evaluate the RSSOT as a new potential method for screening the oxidation stability of lubricating greases. Different types of commercially available conventional and biobased grease samples were examined and were subjected to accelerated oxidative deterioration in the RSSOT unit under a series of testing protocols by modifying either the temperature, the oxygen pressure or the final breakpoint. By varying the test parameters, alterations in the relative oxidative characteristics of the samples were determined as well. A comparative assessment was carried out with the results obtained from the ASTM D942 method. The RSSOT can give a rapid screening of a grease’s aging resistance while the results seem to be consistent and in good agreement with the conventional test. Overall, it appears to be a promising method for the determination of the oxidation stability of lubricating greases that can be used as an alternative to conventional ones with certain advantages over the latter.

Keywords: Lubricating greases, oxidation stability, test method, Rapid Small Scale Oxidation Test (RSSOT).

Introduction
The ability of a lubricant to resist to thermal and oxidative deterioration is considered a key feature for an extended useful life and an untroubled service life. This is for certain the case for lubricating greases as well. The need to control and measure the oxidative behaviour of greases, has led to the development of several standard methods that evaluate oxidation stability either under dynamic or static conditions [1-5]. Nowadays, of the so-called static accelerated oxidation stability test methods ASTM D942 and ASTM D5483 are most commonly described in various grease specifications.

The ASTM D942 is the standard method for measuring the Oxidation Stability of Lubricating Greases by the Oxygen Pressure Vessel Method (OPVM). Widely known as the “bomb” oxidation method (Norma - Hoffman), this test was originally designed to predict shelf storage life of greases in pre-packed bearings and was introduced to the ASTM in 1938 [1,6]. It determines the resistance of lubricating greases to oxidation when stored statically in an oxygen atmosphere in a sealed system at an elevated temperature. Being the only available oxidation bench test for many years, the “bomb” became an established method for assessing storage and service oxidation stability that served the industry for a long time and is still used to meet various grease specifications. During the years several modification in the procedure have been proposed (such as temperature increase or addition of metal catalyst) however none of them was ever incorporated in the official standard [4,6]. On the other hand the “bomb” method is a time-consuming test with its own limitations. It has received criticism mainly for the very poor precision it has and for the limited validity in predicting oxidation in service life.

The advances in grease technology and manufacturing has motivated the search for an alternative to the ASTM D942. In the early 1990s the U.S. Army developed a new oxidation stability test for lubricating greases based on Pressure Differential Scanning Calorimetry (PDSC) [2], a technique widely used in polymer science. Eventually this was adopted as the ASTM D5482 standard method for measuring the Oxidation Induction Time of Lubricating Greases by PDSC. In general this is a considerably faster method with a good sensitivity and very small sample requirements. On the other hand the fixed and running cost is high, let alone the need for specialized staff. Also the current precision statements cannot fit to all existing makes of equipment and - similar to the “bomb” method - no correlation has been determined between test and service performance [1,7]. Additionally, some product
types (esp. biobased greases) have been found to give results below the marginal value of 10 minutes even at the lowest ASTM recommended temp of 1550C. These two methods, the oxygen “bomb” and the PDSC, had been shown to give good correlation, but only when the same oxidation mechanism occurred [8].

In the meantime, the increasing demand for biobased lubricating greases has also propagated the search for test methods that would be more applicable in this type of renewable products. The joint ELGI- NLGI Biobased Working Group has recently conducted an extensive round robin tests on methodologies for determining the oxidation stability of biobased lubricating greases including the OPVM, the PDSC and the new proposed method, the Rapid Small Scale Oxidation Test (RSSOT) [9].

The Rapid Small Scale Oxidation Test (RSSOT) - A new potential method for measuring oxidation stability of lubricating greases.

In recent years a new accelerated methodology was developed for measuring the oxidation stability called the Rapid Small Scale Oxidation Test (RSSOT). This test method was initially introduced as a rapid method to screen the oxidation stability of fuels and biofuels. It has been incorporated in the standard methods ASTM D7545 and ASTM D7525 for middle distillate fuels (diesel + renewable alternatives) and spark ignition fuel (gasoline + alternatives) respectively. Like the ASTM D942 method, this is a test based on determination of oxidation stability via oxygen depletion. The automated oxidation tester comprises of a heating block and pressure vessel in which a small amount of sample is placed (Figure 1).

According to the ASTM D7545 standard method, after the introduction of the sample, the pressure vessel of the apparatus is charged with oxygen to 700kPa at ambient temperature. The test is initiated by rapidly heating the pressure vessel to the selected temperature of 140oC. The pressure in the test apparatus is continuously recorded until it is 10% below the maximum observed pressure. The elapsed time between starting the heating procedure of the sample vessel and the break point is reported as Induction Period in minutes. (IP-min) [10].

Nevertheless the apparatus can be also set up to measure lubricants and greases as it was reported in a previous published work of the author [11]. in which, a preliminary study has been presented on the applicability of the RSSOT on lubricating greases. The potential of this method on lubricating greases has been shown, along with a good correlation with the conventional ASTM D942 method. In this initial study a gold-plated version of the unit has been used and the grease samples were introduced in the unit via a glass dish identical to the one used in the D942 method. The samples were tested under conditions similar to ASTM D7545.

In the present study, the previous work is extended by examining the following parameters:

- An alternative stainless steel version of the apparatus was employed.
- A PTFE dish was used instead of the glass dish.
- Oxidation stability of lubricating greases was evaluated under various testing protocols by altering the test temperature, the oxygen pressure and the actual mass of the sample.
- RSSOT results were compared with those from ASTM D942 and ASTM D5483.

Table 1. List of the lubricating grease samples utilized in this study

<table>
<thead>
<tr>
<th>Thickener Type</th>
<th>Base oil type</th>
<th>NLGI No</th>
<th>Thickener Type</th>
<th>Base oil type</th>
<th>NLGI No</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1 Ca Sulfonate complex</td>
<td>M</td>
<td>2</td>
<td>BG1 Anhydrous Ca</td>
<td>B</td>
<td>0</td>
</tr>
<tr>
<td>G2 Ca Sulfonate complex</td>
<td>M</td>
<td>2</td>
<td>BG2 Li complex</td>
<td>B</td>
<td>2</td>
</tr>
<tr>
<td>G3 Li complex</td>
<td>S</td>
<td>2</td>
<td>BG3 Anhydrous Ca</td>
<td>B</td>
<td>2</td>
</tr>
<tr>
<td>G4 Li complex</td>
<td>S</td>
<td>2</td>
<td>BG4 Li complex</td>
<td>B</td>
<td>2</td>
</tr>
<tr>
<td>G5 Lithium</td>
<td>S</td>
<td>2</td>
<td>BG5 Lithium</td>
<td>B</td>
<td>2</td>
</tr>
<tr>
<td>G6 Anhydrous Ca</td>
<td>M</td>
<td>2</td>
<td>BG6 Al complex</td>
<td>B</td>
<td>2</td>
</tr>
<tr>
<td>G7 Li complex</td>
<td>M</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G8 Inorganic (silicon)</td>
<td>S</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G9 Anhydrous Ca</td>
<td>M</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G10 Lithium/Calcium</td>
<td>M</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G11 Lithium</td>
<td>M</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G12 Inorganic (clay)</td>
<td>M</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G13 Calcium</td>
<td>M</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*B: Biobased; M: Mineral; S: Synthetic
Experimental

Grease samples

Nineteen (19) different samples of lubricating greases were employed in this study in order to assess their stability in the RSSOT accelerated oxidation method. The grease samples are listed in Table 1 that summarizes the thickener type they contain, their main base oil type and the NLGI classification. All samples were finished, commercially available lubricating grease products. Samples BG1 - BG6 are characterized as biobased lubricating greases.

Oxidation Stability in the Rapid Small Scale Oxidation Test (RSSOT)

A Rapid Small Scale Oxidation Test unit (RapidOxy-Anton Paar) was utilized in order to assess the oxidation stability of the lubricating greases (Figure 2). As reported above, this is an automated and customizable tester comprising fundamentally of a heating block and a pressure vessel (chamber) that carries the test sample. The latter is subjected to accelerated deterioration under the effect of temperature and oxygen and the oxidation stability is determined via oxygen consumption.

Each time a PTFE sample dish of 9cm³ (9ml) capacity was fully filled with the lubricating grease in a uniform layer with a smooth upper surface. A steady-volume approach was followed so approximately 9cm³ of grease was inserted in the dish. The latter was placed in the test chamber which was then charged with oxygen and heated rapidly per the selected parameters. The samples were subjected to accelerated ageing until a 10% pressure drop below Pmax was detected (breakpoint). The elapsed time between starting the heating procedure and the break point was reported as Induction Period in minutes (Figure 3). All measurements were conducted at least in duplicate.

Effect of temperature

The relative oxidative behaviour of the grease samples in the RSSOT was examined under a series of testing protocols (TP) as listed in Table 2. The main variations in the conditions relate to test temperature and the breakpoint. Temperatures of 100°C, 120°C, 140°C, 150°C and 160°C were applied, while in one case an extended break point, equal to 25% pressure drop was employed. TP1 is equivalent to ASTM D7545 standard method for middle distillate fuels and TP-7 was used in order to simulate the parameters of ASTM D942 standard method with a breakpoint set to 35kPa [12].

Figure 2. The RSSOT unit and the introduction of grease samples in the tester.

Figure 3. Determination of the Induction Period (oxidation stability) of greases in the RSSOT.
Effect of oxygen pressure
The effect of the initial oxygen pressure in the test chamber with regards to the depicted induction period was evaluated. One of the samples (BG6) was tested under increasing increments of pressure at a temperature of 100 oC and 140 oC as shown in Table 3. Testing protocols 8-10 and 11-13 were compared with results from TP-1 and TP-3 respectively.

Effect of the O-ring seal type
During the test, the pressure chamber is closed hermitically via an O-ring type seal. Since there are two types of available sealing (standard rubber type and PTFE type) that can be utilized, a comparative assessment of the results obtained by using either O-ring type was carried out. Again, one of the examined greases (BG5) was subjected to oxidative deterioration under the testing protocols in Table 1, by using each time a different type of sealing.

Steady volume vs. steady mass approach - Effect of sample mass
All the previously mentioned testing protocols were conducted on a steady volume basis i.e. by inserting each grease in the PTFE dish in such a way that the latter was completely filled (9cm3) with a sample having a smooth, even finished surface. In order to examine the effect on the reported Induction Period of the quantity of the grease that is placed in the PTFE dish, samples were tested again under TP-3 (140oC, 700kPa, 10% break point), but this time a pre-determined fixed mass of 5g was placed in the dish.

Results and Discussion
The oxidative behaviour of the examined greases under the various testing protocols (TP1 -TP7) in the RSSOT apparatus are given in Figure 4.

The analysis of the data show that the RSSOT can give a

---

**Table 2. Testing protocols in the RSSOT - variation in temperature**

<table>
<thead>
<tr>
<th>RSSOT Testing Protocol</th>
<th>Temperature (ºC)</th>
<th>Oxygen Pressure (kPa)</th>
<th>Break Point (% Pmax drop)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP -1</td>
<td>100</td>
<td>700</td>
<td>10</td>
</tr>
<tr>
<td>TP -2</td>
<td>120</td>
<td>700</td>
<td>10</td>
</tr>
<tr>
<td>TP -3 (ASTM D 7545)</td>
<td>140</td>
<td>700</td>
<td>10</td>
</tr>
<tr>
<td>TP -4</td>
<td>140</td>
<td>700</td>
<td>25</td>
</tr>
<tr>
<td>TP -5</td>
<td>150</td>
<td>700</td>
<td>10</td>
</tr>
<tr>
<td>TP -6</td>
<td>160</td>
<td>700</td>
<td>10</td>
</tr>
<tr>
<td>TP -7</td>
<td>99</td>
<td>600</td>
<td>35kPa (abs. Pres. drop)</td>
</tr>
</tbody>
</table>

---

**Table 3. Testing protocols in the RSSOT - variation in pressure**

<table>
<thead>
<tr>
<th>RSSOT Testing Protocol</th>
<th>Temperature (ºC)</th>
<th>Oxygen Pressure (kPa)</th>
<th>Break Point (% Pmax drop)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP -8</td>
<td>100</td>
<td>500</td>
<td>10</td>
</tr>
<tr>
<td>TP -9</td>
<td>100</td>
<td>300</td>
<td>10</td>
</tr>
<tr>
<td>TP -10</td>
<td>100</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td>TP -11</td>
<td>140</td>
<td>500</td>
<td>10</td>
</tr>
<tr>
<td>TP -12</td>
<td>140</td>
<td>300</td>
<td>10</td>
</tr>
<tr>
<td>TP -13</td>
<td>140</td>
<td>100</td>
<td>10</td>
</tr>
</tbody>
</table>
rapid screening of a grease's oxidation stability compared to the conventional oxygen pressure vessel test. (ASTM D 942). When tested at temperatures higher than 120°C, and with a breakpoint at 10% pressure drop, all determinations were terminated at less than 24h. The results obtained in this study appear to be consistent and reasonable and the method seems to provide good sensitivity and discrimination between the different products. Only TP-7, that was used in order to simulate conditions similar to ASTM D942, was not capable of producing reasonable oxidation stability data.

The order of increasing oxidation stability was found to be more or less similar under the various test conditions with the exception of grease sample G8. This was the only sample that showed a different behaviour when the breakpoint of the test was increased from 10% to 25% pressure drop. For some reasons in this particular sample the oxidation rate is higher in the beginning, however afterwards it appears to proceed extremely slow as depicted by the remarkably elongated induction period in TP-4. Nevertheless, regarding the conventional greases, the calcium sulphonate complex samples and the synthetic-based Li complex proved to be the most...
resistant to oxidative deterioration, whereas the hydrated calcium and inorganic clay grease were the least stable.

Concerning the biobased examined samples, it appears that this method could be applicable in this type of greases. It can give a quick estimate of their ageing reserve, it can differentiate between the different types of biobased material utilized (vegetable oils / biobased esters) and could be utilized for R&D purposes for developing more efficient and resistant renewable products. As a matter of fact it is worth noticing that by employing the RSSOT method a direct comparison of the oxidation stability of biobased greases to conventional ones can be directly done, without any discrepancies due to sensitivity limits as shown in PDSC testing.

**Effect of temperature**

The effect of temperature in the oxidation stability measurements in lubricating greases is given in Figure 5, in terms of the average percentage reduction in the Induction Period (ΔIP%). The behavior of the greases under elevated oxidizing temperature was also examined by visually observing the relative alteration in the appearance of the samples after the test. Such an example is demonstrated in Figure 6 regarding sample BG5. An increase by 10°C in the test temperature led to a 30%, in average, drop in the oxidation stability. A halving in the induction period was observed when temperature was increased by 20°C. When temperature was 30°C and 40°C higher, the decrease in the IP was in average 67% and 75%, respectively. IP was substantially suppressed by further increasing the test temperature.

![Figure 4. RSSOT oxidation stability determinations of the grease samples](image1)

![Figure 5. Effect of temperatures on the RSSOT determinations](image2)
The selected test temperature also affects the corresponding maximum oxygen pressure ($P_{\text{max}}$) in the test chamber. In Table 4 the average $P_{\text{max}}$ for each testing protocol (TP1-TP6) is reported along with the calculated standard deviation (SD). As expected, $P_{\text{max}}$ increases with the increasing test temperature, however, taking into account the SD values, in practice it appears to be unaffected by the type of the lubricating grease. This means that irrespective of the grease sample, the $P_{\text{max}}$ would be more or less the same for each given test temperature and consequently the 10% (or 25%) pressure drop would reflect a comparable difference in the absolute pressure drop. Nevertheless, when the test temperature is plotted against the average $P_{\text{max}}$ a strong linear relationship is observed, as depicted in Figure 7.

**Table 4. Effect of test temperature on the average $P_{\text{max}}$**

<table>
<thead>
<tr>
<th>Testing Protocol</th>
<th>Temperature ($^\circ$C)</th>
<th>Average $P_{\text{max}}$ ± SD (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP -1</td>
<td>100</td>
<td>900 ± 13</td>
</tr>
<tr>
<td>TP -2</td>
<td>120</td>
<td>948 ± 9</td>
</tr>
<tr>
<td>TP -3 (ASTM D 7545)</td>
<td>140</td>
<td>1001 ± 10</td>
</tr>
<tr>
<td>TP -4</td>
<td>140</td>
<td>1006 ± 13</td>
</tr>
<tr>
<td>TP -5</td>
<td>150</td>
<td>1035 ± 16</td>
</tr>
<tr>
<td>TP -6</td>
<td>160</td>
<td>1068 ± 14</td>
</tr>
</tbody>
</table>

**Figure 6. Visual observation of oxidized grease (BG-5) under increasing test temperature.**

**Figure 7. Relationship of $P_{\text{max}}$ with increasing test temperature**

(initial filling pressure: 700kPa)
Effect of oxygen pressure

The effect of the applied oxygen pressure on the induction period is given in Figure 8. BG6 grease samples were tested at a range of decreasing pressure increments at test temperatures of 100°C and 140°C. It is evident that the pressure as a test parameter may play a role in the oxidation rate of this grease depending on the test temperature in the RSSOT method. At 140°C the induction period doesn’t seem to be affected by the oxygen pressure and, thus, the variation in the results is not significant. On the contrary when the same sample was tested at a lower temperature of 100°C, the initial filling pressure considerably affected the outcome. In particular, with decreasing pressure increments, a gradual reduction in the induction period was observed, though one might expect either the opposite or at least a minimal effect. The mild test temperature along with the breakpoint approach that is determined as a percent rather than as an absolute pressure drop could explain this behavior.

Effect of sealing type

A similar observation was made when measurements were carried out by using the two different types of the O-ring sealing. As shown in Figure 9 one grease sample (BG5) was tested under various testing protocols and in all cases the IPs were found to be more or less identical, irrespective of the type of seal that was employed.

Fixed volume vs. fixed mass approach - effect on the IP

When the PTFE dish is completely filled with the examined grease, the volume of each sample is constant (9cm³) but depending on the specific gravity of the sample, a slight variation in the inserted mass can be observed. Table 5 shows the mass of each grease when the measurements of all previously reported determinations were carried out under TP 1-13 (approach A - fixed volume). In most cases a quantity of approximately 8g was needed to completely fill the PTFE, except for G1, G2 and G6 in which the volume of 9cm³ corresponds to approximately 9g of sample in the dish.

![Figure 8. Effect of oxygen pressure on the RSSOT determinations](image)

**Figure 8. Effect of oxygen pressure on the RSSOT determinations**

![Figure 9. Effect of the O-ring type on the IPs in the RSSOT](image)

**Figure 9. Effect of the O-ring type on the IPs in the RSSOT**

| Table 5. Mass of grease sample involved in the TP-3 runs under (A) and (B) approach |
|---------------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| G1 | G2 | G3 | G4 | G5 | G6 | G7 | G8 | G9 | G10 | G12 | BG1 | BG2 | BG3 | BG4 | BG5 | BG6 |
| A(g) | 8.9 | 8.7 | 7.6 | 8.0 | 7.8 | 8.0 | 8.0 | 8.8 | 8.1 | 8.0 | 8.3 | 8.0 | 8.0 | 8.1 | 8.2 |
| B(g) | ---5g in all determinations--- | | | | | | | | | | | | | | | |

**Notes:****A:** Steady volume - completely filled PTFE dish / 9cm³  
**B:** Steady mass - PTFE dish filled with 5g of grease
In order to examine how the determined induction periods in the RSSOT are affected when a steady-mass approach is followed, the grease samples were re-run under TP-3 test conditions but this time the PTFE dish was filled with 5g of each grease (approach B). Figure 10 shows the difference in the preparation of the sample to be examined under the steady volume vs. steady mass approach.

The results that were obtained from the steady-mass approach are presented in Figure 11 and compared with the corresponding measurements from the steady volume determinations. Though the 5g sample preparation results in a relatively larger outer surface of the sample that is in direct contact with the oxygen, the lower mass appears, in general, to give rise to elongated induction period. At low IPs, i.e. ≤ 100 min, the determinations were not significantly affected by the quantity of the sample employed and the results were comparable between the two approaches. On the other hand, as the relative oxidation stability increases, considerably higher induction periods are generated at the 5g sample approach. This indicates that the quantity of the sample that is inserted in the PTFE dish plays an important role in the time that is needed to achieve the pre-determined breakpoint of the test. Nevertheless, the fixed mass approach doesn’t seem to substantially alter the observed order of stability of the tested greases compared to the fixed volume approach. The corresponding IPs are plotted in Figure 10 (b) and with the

![Figure 10. Preparation of grease sample (a) fully filled dish/ steady volume of 9cm³ . (b) 5g sample/ steady mass](image)

![Figure 11. (a) Effect of grease sample mass on the RSSOT determinations, (b) steady volume vs. steady mass approach](image)

| Table 6. Precision of the RSSOT results - Repeatability (r) |
|---|---|---|---|---|---|---|---|
| Sample | T (°C) | P (kPa) | Breakpoint | 1st | 2nd | 3rd | 4th | Mean | SD |
| BG5 | 140 | 700 | 10% | 94 | 98 | 92 | 95 | 95 | 2.5 |
| G2 | 140 | 700 | 10% | 576 | 569 | 589 | 593 | 582 | 11.2 |
| G12 | 150 | 700 | 10% | 84 | 76 | 80 | 77 | 79 | 3.6 |
| G12 | 160 | 700 | 10% | 68 | 70 | 64 | 67 | 67 | 2.5 |
exception of G8 (red dot) - that has a distinct behaviour as it was previously mentioned - the scatter implies more or less an analogous trend in the oxidation stability classification.

**Repeatability of the RSSOT method**

Repeatability (r) is a standardized term and it is associated with the precision of measurements generated on the same material using the same apparatus/method by the same operator under constant operating conditions. For a method, a satisfactory test-retest reliability should be demonstrated so as to have the potential of being widely acceptable.

Since RSSOT is not a standard method for measuring the oxidation stability of lubricating greases, no pre-determined precision values are yet available. Subsequently a preliminary evaluation of the repeatability was performed. At first, it should be noted that the results shown in Figure 8 can provide an initial perspective of the very good precision of the RSSOT method. In addition to this, a series of grease samples were repeatedly subjected to accelerated oxidative deterioration in the RSSOT under identical conditions in order to further examine the repeatability of the method. The determinations are shown in Table 6 along with the calculated mean and standard deviation (SD) values. These first experimental outputs depict the very good repeatability of the measurements and could be characterized as encouraging concerning the precision of the RSSOT on grease testing.

**Reproducibility of the RSSOT method**

Similarly to repeatability, reproducibility (R) is also a standardized term relating to the precision of a method under conditions where results are obtained with the same method on identical test items in different laboratories with different operators using different equipment. The ability of a test method to be replicated with a high level of agreement is important for its credibility to provide universally acceptable results. In order to examine whether the oxidation stability measurements of lubricating greases in the RSSOT are reproducible, seven (7) lubricating grease samples were also analyzed in an independent laboratory (lab-2) by another operator under the same test conditions. The samples were subjected to oxidative deterioration in an identical RSSOT unit (RapidOxy with stainless steel chamber) under TP-3 (140°C, 700kPa, 10% break point). Oxygen of equal purity was employed while 5g of the sample was inserted each time in the PTFE dish. The results that were generated by the two independent laboratories are depicted in Figure 12. A high degree of agreement between measurements is clear in this tentative assessment which can be regarded as a good evidence of the ability of the RSSOT method/unit to provide consistent results.

**Comparison of RSSOT with conventional oxidation stability standard methods**

In the previous section the ability of the RSSOT method to provide rapid, reliable and consistent results was displayed. In order to check to what extent these data compare with results provided by the standard ASTM method for oxidation stability of lubricating greases, some of the examined samples were analyzed per ASTM D942 - OPVM methodology and ASTM D 5483 - PDSC methodology.
A. RSSOT vs. D942 (OPVM)

Fifteen (15) of the grease samples were tested per ASTM D 942 (99oC, 758kPa, 100h) and the results are presented in Table 7 in terms of the measured oxygen pressure drop after 100h. Exactly the same oxygen grade was used in these measurements as in the RSSOT determinations.

The corresponding data were analyzed using a statistic method and plotted in a graph against the IPs provided by testing protocols (TP) 1 to 6 as presented in Figure 13. Under the examined test conditions, the RSSOT induction periods are in good agreement with the results of the ASTM D942 method. A satisfactory coefficient of determination (R2) ≥0.91, was observed in all cases. The fact that in both methods the determination of the oxidation stability is based on measuring the oxygen depletion might also contribute to the strength of this relationship. The best correlation was reported for TP-3 where both approaches (steady mass and steady volume) showed a R2 value higher than 0.98. TP-3 test conditions are equivalent to D7545 protocol and this might imply that a temperature of 140oC and a 10% pressure drop breakpoint could be an applicable approach for the case of lubricating greases, as well. A good relationship was also evident in TP-2 (120oC in the RSSOT), however at a lower temperature of 100oC, the data comparison depicted less agreement although this temperature is almost identical with the ASTM D942. The weakest relationship was spotted with TP-6, probably due to the fact that at this high temperature (160oC) the dropping point of some samples is exceeded leading to results that do not actually correspond to a uniform grease formulation.

B. RSSOT vs. D5483 (PDSC)

Twelve (12) of the previously examined samples were

---

**Table 7. ASTM D942 results**

<table>
<thead>
<tr>
<th></th>
<th>G1</th>
<th>G2</th>
<th>G3</th>
<th>G5</th>
<th>G6</th>
<th>G7</th>
<th>G9</th>
<th>G10</th>
<th>BG1</th>
<th>BG2</th>
<th>BG3</th>
<th>BG4</th>
<th>BG5</th>
<th>BG6</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2 pressure drop after 100h, (kPa)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>10</td>
<td>15</td>
<td>15</td>
<td>20</td>
<td>35</td>
<td>15</td>
<td>30</td>
<td>170</td>
<td>300</td>
<td>260</td>
<td>640</td>
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</tbody>
</table>

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**Figure 13. Comparison of RSSOT with D942 results**

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**Table 8. ASTM D5483 data**

<table>
<thead>
<tr>
<th>OIT, (min)</th>
<th>G1</th>
<th>G2</th>
<th>G3</th>
<th>G4</th>
<th>G5</th>
<th>G6</th>
<th>G8</th>
<th>G10</th>
<th>G11</th>
<th>G12</th>
<th>G13</th>
<th>BG5</th>
</tr>
</thead>
<tbody>
<tr>
<td>180°C</td>
<td>93.5</td>
<td>73.8</td>
<td>10.3</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
</tr>
<tr>
<td>155°C</td>
<td>84.5</td>
<td>32.5</td>
<td>59.0</td>
<td>39.8</td>
<td>bdl</td>
<td>28.3</td>
<td>16.2</td>
<td>10.4</td>
<td>bdl</td>
<td>11.3</td>
<td>bdl</td>
<td></td>
</tr>
</tbody>
</table>

bdl: below detection limit, <10min
analyzed in a PDSC unit (TA Instruments, Model Q10/Q20) in an independent laboratory. The measurements were conducted according to ASTM D5483 standard method and the oxidation induction time (OIT) of the samples was determined by

subjecting them to oxygen of 3.5MPa and temperatures of either 155oC or 180oC. The provided data are listed in Table 8.

At first it is observed that the low oxidation stability greases (G12, G13 & BG5) are either close to the detection limit of the PDSC method, i.e. 10 min, or below this, whereas in the RSSOT even samples with very poor oxidation stability could be rapidly evaluated without such sensitivity limitations. On the other hand grease samples G1 and G2, as excepted, show by far the best oxidative resistance - compared to the rest of the samples - taking into account the considerably elevated OIT values at the higher temperature of 180oC. It is worth noticing that grease G8 failed to return a valid result even at the lower temperature of 155oC, although under all RSSOT testing conditions it was found to be more stable compared at least with G10-G13 and BG-5 samples. In order to examine the relationship between the results obtained from the PDSC unit and the various testing protocols in the RSSOT the samples -except for G8 - were classified per their decreasing order of oxidation stability as demonstrated by the corresponding measurements. The relative classification is given in Table 9. The PSCDC data were found to be more close to the classification that was shown by the TP-6 in the RSSOT. It is noteworthy that in this testing protocol the temperature was 160oC which is close to the test temperatures that were employed in the PDSC determinations.

In addition to this, an attempt to explore any tentative existing relationship between these two methods was made. For this reason only the PDSC data that were obtained at the test temperature of 155oC were utilized, since the majority of the samples were not capable of providing results above the detection limit when tested at a higher temperature. The data were analyzed and plotted against the RSSOT determinations as shown in Figure 14. A fair linear relationship could be observed particularly when compared with the TP 3-6 data in the RSSOT, however the TP-1 and TP-2 determinations were not in such a good agreement with the PDSC OIT values as it was in the case of the OPVOM measurements. Nevertheless, this preliminary evaluation indicates a potential for an acceptable correlation between these two methods under certain test conditions and probably similar degradation mechanism to compensate for the different evaluation technique. Clearly, further studies could provide a larger set of data points to show whether PDSC and RSSOT measurements are related either under the standardized test conditions in the PDSC or at a lower temperature and/or pressure.

| Table 9. Order of decreasing oxidation stability in the RSSOT and PDSC |
|---------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|               | G1 | G2 | G3 | G4 | G5 | G6 | G10 | G11 | G12 | G13 | BG5 |
| PDSC          | 1  | 2  | 3  | 6  | 4  | 5  | 7   | 8   | 9   | 11  | 10  |
| TP-1 (100oC)  | 1  | 3  | 2  | 4  | 6  | 5  | 8   | 7   | 9   | 11  | 10  |
| TP-2 (120oC)  | 1  | 2  | 3  | 4  | 5  | 6  | 8   | 7   | 9   | 11  | 10  |
| TP-3 (140oC)  | 1  | 2  | 3  | 4  | 5  | 6  | 7   | 8   | 9   | 10  | 10  |
| TP-4 (140oC)  | 1  | 3  | 2  | 5  | 4  | 6  | 8   | 7   | 9   | 10  | 10  |
| TP-5 (150oC)  | 1  | 2  | 2  | 5  | 4  | 6  | 8   | 7   | 9   | 10  | 10  |
| TP-6 (160oC)  | 1  | 2  | 3  | 6  | 4  | 5  | 7   | 8   | 8   | 10  | 10  |
| TP-3 (5g)     | 1  | 2  | 3  | 5  | 4  | 6  | 7   | n/a | 8   | 8   | 8   |

Figure 14. Comparison of RSSOT with D5483 results at 155°C
**Conclusions**

In this study the Rapid Small Scale Oxidation Test (RSSOT) was presented and thoroughly examined as a new potential method for determining the oxidation stability of lubricating greases. A series of nineteen conventional and biobased grease samples were evaluated under various testing protocols and the effect of test parameters - such as test temperature, oxygen pressure and sample mass/volume - on the induction period was assessed. The analysis of the results show that the RSSOT is a rapid method with high sensitivity and good discrimination for different kind of greases, utilizing a small sample with no special preparation techniques and providing customizing capabilities for selecting the optimum test conditions. Additionally, the preliminary examination of the precision provided encouraging data regarding the potential repeatability and reproducibility of this new oxidation methodology on greases. Under the test conditions employed, the induction periods that were obtained by the RSSOT method depicted high degree of agreement with the results of the ASTM D942 (OPVOM) method and a fair relationship with the PDSC data was reported for certain test conditions.

The RSSOT could also be more adaptive in the case of low oxidation stability lubricating greases and this might pose an advantage over both ASTM D942 and ASTM D5483 method, especially for measuring the ageing reserve of biobased greases. Moreover, it could serve as a fast method for production control, process optimization and R&D activities. The sample obtained after oxidative procedure is enough to combine this method with further analysis such as FTIR, etc. Overall the Rapid Small Scale Oxidation Test appears to be a promising method for the determination of the oxidation stability of lubricating greases that can be used as an alternative to the conventional methods with certain advantages over the latter.

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**Acknowledgments**

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**Abbreviations**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BGx</td>
<td>Biobased Grease sample</td>
</tr>
<tr>
<td>ELGI</td>
<td>European Lubricating Grease Institute</td>
</tr>
<tr>
<td>Gx</td>
<td>Grease sample (non-biobased)</td>
</tr>
<tr>
<td>IP</td>
<td>Induction Period</td>
</tr>
<tr>
<td>NLGI</td>
<td>National Lubricating Grease Institute</td>
</tr>
<tr>
<td>OIT</td>
<td>Oxidation Induction Time</td>
</tr>
<tr>
<td>OPVM</td>
<td>Oxygen Pressure Vessel Method (Norma-Hoffman)</td>
</tr>
<tr>
<td>PDSC</td>
<td>Pressure Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>PTFE</td>
<td>Poly-Tetra-Fluoro-Ethylene (Teflon)</td>
</tr>
<tr>
<td>RSSOT</td>
<td>Rapid Small Scale Oxidation Test</td>
</tr>
<tr>
<td>TPx</td>
<td>Testing Protocol</td>
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Abstract
The steady increase in the percentage of complex greases in NLGI's survey of global grease production is a reflection of the demand for lubricants that will last longer in more severe, higher temperature applications. It is also a clear indicator that future research and development work will be of great value in this area of lubrication. The surge in demand for higher dropping point greases has brought additional interest in alternative methods of producing them that can reduce cycle times and, potentially, overall production costs. A study was undertaken to investigate different borate chemistries used to raise the dropping point of lithium greases to the level usually associated with complex greases. Points of focus include a design of experiment to study the impact of common factors on the effectiveness in raising dropping point, as well as a closer look at the impact of dropping point apparatus, blending temperature and correlation to effects as measured by high temperature rheology.

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

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

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

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

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

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

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

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

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

**Experiment**

**Test Methods**


This method determines a numerical value for a grease composition representing the temperature at which the first drop of material falls from the test cup and reaches the bottom of the test tube. The temperature is measured using a thermometer placed near the grease sample inside a glass tube placed in an aluminum block at a preset constant temperature. A modification was used for this work in that the block temperature used for all determinations was 288 °C. This was done to ensure that the heating rate was the same for each sample. However, the dropping point was also determined using different block temperatures as described in D2265 and no statistical difference was seen between the determinations.
Base Greases
As the alkalinity of the base grease is known to affect various aspects of additive performance [15], two simple lithium base greases were made in the lab. One was targeted to be slightly basic while the other was targeted to be very basic. Both were made using 12-hydroxystearate acid (12-HSA) as the fatty acid with sufficient lithium hydroxide (LiOH) to meet the targeted alkalinity for each. Both greases were milled and diluted with base oil that had a kinematic viscosity at 40°C of 165 cSt (a mixture of AC 600N [68%] and AC bright stock [32%]) to obtain greases that were slightly harder than an NLGI #2 grade base which allowed for some softening due to addition of various componentry in the study. See Table 2 for descriptive data for these base greases.

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

Additive components/levels
As part of the designed experiment, a high and low level for each component was needed. The level of glycerin added was calculated from the amount of glycerin that would have theoretically been produced as a byproduct if the laboratory-produced grease had been made with HCO instead of 12-HSA. This level was determined to be 1.2 wt%. The low level used was zero with a midpoint level of 0.6 wt%.

The specific ZDDP component used has a mixed-chain length (C4/C5/C8) and was made from a primary alcohol. The level of ZDDP used was based on that which was seen to be effective in screening work with similar greases and the borate components of interest. The high level was set at 1.13 wt%, with a low level of zero and a midpoint level of 0.56 wt%.

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

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

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

![Table 6 - Design of Experiment](image)

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

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

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

As can clearly be seen in Figure 4, when glycerin is not present the concentration of BA has an impact on dropping point whereas when glycerin is present, the level of BA present has no impact on dropping point.
Due to the observed impact of the glycerin, the data without glycerin was modeled separately and while none of the individual components appeared to be significant, a three-way interaction between LiOH level, water content and ZDDP was observed. It is thought that the borate level may have been too low to show up as significant (as seen by the impact of BA at higher levels in the augmented design).

The data was then modeled including the augmented runs (in which BA was doubled for eight additional runs) and this model shows that both LiOH level (see Figure 5) and ZDDP (see Figure 6) have a positive impact on dropping point at the higher level of BA. This may confirm the original observation that the treat rates of BD and BPD were too low to be significant in the original model.
The overall model for the data at the high borate level (see Table 7) shows that LiOH content has a positive impact on dropping point, while the impact of glycerin was negative. ZDDP was shown to be somewhat significant as well (p 0.1) with a potentially positive impact on dropping point.

**Summary and Conclusions**

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

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

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

Additional Experiments

Aging of Dropping Point Cups

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

The ASTM method specifies:

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

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

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

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

Heat/Method of Borate Incorporation

A separate study was being conducted with the borate amide (BA) at 1.0 wt% and several inconsistent results were obtained ranging from 230 °C to 293 °C (see Table 9). A short experiment was undertaken to look at the effect of heating and blend order of the components used. Standard mixing had been at 60 °C in a centrifugal mixer and this was repeated at 104 °C on the original samples and a reblend. A high dropping point was obtained (No Drop) using the original temperature of 60 °C but the higher temperature seemed to have no effect. The order of addition also seemed to show no effect. The borate was added first and homogenized within the grease at 60 °C then the additional components were added at 104 °C to observe whether there was some effect of using higher heating
to carry out further complexation of the grease. These components included ZDDP which can show synergistic behavior with BA as seen in the first study above.

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

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

**Effect at High Temperature**

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

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

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

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

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

Here it can clearly be seen that the base grease reaches a Tan Delta of >1 (indicative of more liquid-like behavior) at just over 200 °C which correlates very closely with its dropping point. The other three additized greases were all measured to have dropping points in the 300 °C range and the same “plateau” behavior is seen between 120 °C and 200 °C before the Tan Delta starts to increase again between 220 °C and 300 °C. This seems to correlate well with the plots shown in Figure 9, as well as with observations of the dropping point apparatus as illustrated in Figure 8. This also appears to provide more evidence that a physical change is occurring in these greases as they are being heated which may be affecting the ability of these samples to allow a drop of oil to be released during the test. It’s possible that this is a chemical reaction involving the borate components. Whether or not this is reflective of what happens in high temperature applications or even in high temperature bearing rig tests is unknown and needs further study.

In summary, a designed experiment showed a large negative impact of glycerin on the ability of borates to increase the dropping point of lithium greases which provides a convincing explanation for the difficulty seen in using borates to raise dropping points in lithium greases made with hydrogenated castor oil. Additionally, the designed experiment showed the positive impact of higher levels of LiOH, ZDDP and perhaps water in raising dropping points. A possible explanation was proposed but would need further experimentation to provide
Although heating to 140 °C during the mixing process didn’t seem to effect results when there was an excess of borate available to react, there were inconsistent results at lower levels of borate which may be linked to the bimodal behavior seen with some greases (drop vs no drop in consecutive runs).

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

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

References

A STUDY ON A HYBRID GREASE OF A LITHIUM GREASE AND A DIUREA GREASE
Applied for Wide Temperature Range

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Co-authors: Chen ShiQi, Ng Hak Hong Seiji Okamura
Hin Leong Trading (PTE) Ltd.
Singapore

Abstract
It is well known that lithium grease shows good low noise property, but is poor in grease life at higher temperature than 150 ºC. On the contrary, urea grease shows longer grease life at high temperature. But urea grease is poor in low noise property.

As to five sample greases which consist of lithium soap(A) and ester oil, diurea(B) and ester oil and mixed thickener(A+B) and ester oil, we evaluated them on the items related to actual performance applied for shield/sealed bearings.

They are grease life, thermal stability (thin film evaporation test), low noise property (Grease particle, dB value, Anderon value), shear stability, rust preventiveness and low temperature property.

We developed the well-balanced grease (Hybrid grease) by blending lithium grease and diurea grease (blend ratio, A/B=75/25). This grease showed longer grease life by two to three times than lithium grease at 150 ºC and also showed good low noise property as the same as Lithium grease.

1. Introduction
On the one hand, it is well known that Li greases which have excellent low noise property are applied for electric motor bearing. Also, the market is demanding greases which are applied at higher temperature such as 150 ºC and above with low noise property. On the other hand, it is also well known that urea greases which have long life at high temperature are applied for various industrial fields, such as automobile, steel making plant and household appliances.

And also, as to urea greases, many test results on grease life at various high temperatures are reported[1],2),3),4).

Generally speaking, low noise property of urea greases is not so good.

We studied on the possibility of balancing low noise property and long life performance at high temperature by choosing a suitable blend ratio of lithium grease and diurea grease.

In this paper, we defined the mixture of Li grease and Urea grease as Hybrid grease. This paper describes on the difference of performance (thermal stability, shear stability, low

2. Grease Sample preparation
We prepared five grease samples which consist of lithium soap /urea compound and ester oil as base oil. The base oil viscosity is approx. 30-40 mm2/s.

2.1. Lithium Grease

2.2. Urea Grease

2.2.2 Urea Grease Sample Preparation Procedure
(1) React on MDI with amines at 80~100ºC in base oil.
(2) Cool it down to 80ºC with stirring and add an antioxidant and rust inhibitors.
(3) Cool it down to 80ºC with stirring and add an antioxidant and rust inhibitors.
(4) Treated by three roll mill after cooled down to room temperature.
(5) Grease samples are prepared after filtration and deaeration.
The composition and physical properties of sample grease are respectively given in Table 1 and 2.

### Table 1 Composition of the grease samples

<table>
<thead>
<tr>
<th></th>
<th>G1</th>
<th>G2</th>
<th>G3</th>
<th>G4</th>
<th>G5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Grease</td>
<td>mass %</td>
<td>100</td>
<td>75</td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>Diurea Grease</td>
<td>mass %</td>
<td>0</td>
<td>25</td>
<td>50</td>
<td>75</td>
</tr>
<tr>
<td>Thickener content</td>
<td>mass %</td>
<td>13-15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type of base oil</td>
<td></td>
<td>Ester oil</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Base oil Viscosity 40°C, mm²/s</td>
<td></td>
<td>30-40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Penetration 25°C, 60W</td>
<td></td>
<td>NLGI 2-3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. **Evaluation**

1. Physical properties are shown in Table 2
2. Thermal stability (Thin film evaporation test)
   - Making a thin film grease sample (Approx. 1mm thickness and 50 mm in diameter on a steel plate) and put it in the oven. Measure the evaporation loss. The test conditions are shown in Table 3
3. Shear stability (ASTM D 1831 modified) The test conditions are shown in Table 4.
4. Low temperature characteristics
   - Low temperature torque at -40°C (JIS K2220 18)
5. Low noise property
   - 5.1. Particle size
   - 5.2. Andersson value, dB value
   - The test conditions are shown in Table 5
6. Rust preventive characteristics (ASTM D 1743 modified) The test conditions are shown in Table 6.
7. Grease life test (ASTM D 1336 modified) The test conditions are shown in Table 7.
8. Bearing leakage test. The test conditions are shown in Table 8.
9. Bearing surface analysis by XPS (X-ray Photoelectron Spectroscopy) The test conditions are shown in Table 9.

4. **Results and Discussion**

4.1. Physical property

Physical property of the grease samples is shown in Table 2. Penetration of the grease samples is NLGI 2-3.

### Table 2 Physical Property

<table>
<thead>
<tr>
<th>Test item</th>
<th>Grease No.</th>
<th>G1</th>
<th>G2</th>
<th>G3</th>
<th>G4</th>
<th>G5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Yellow brown, Smooth</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Penetration 25°C, 60W</td>
<td></td>
<td>263</td>
<td>268</td>
<td>263</td>
<td>257</td>
<td>249</td>
</tr>
<tr>
<td>Dropping Point  °C</td>
<td></td>
<td>195</td>
<td>213</td>
<td>238</td>
<td>240</td>
<td>260(+)</td>
</tr>
<tr>
<td>Copper Corrosion 100 °C, 24h</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td></td>
</tr>
<tr>
<td>Oil Separation 100 °C, 24h</td>
<td>mass %</td>
<td>0.9</td>
<td>0.4</td>
<td>0.2</td>
<td>0.6</td>
<td>0.9</td>
</tr>
</tbody>
</table>
The dropping point varies with sample greases from 195 °C to 280 °C and above. As to the copper corrosion and the oil separation, there is not so much difference among samples.

4.2 Thermal Stability

Thin film evaporation test

Table 3 Thin film evaporation test

<table>
<thead>
<tr>
<th>Test Temperature, °C</th>
<th>150, 165</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test Duration, h</td>
<td>24, 50, 80, 100</td>
</tr>
</tbody>
</table>

Thin film evaporation test was done as the following photos (before and after).

In the test results at 150 °C, there is not so much difference among five grease samples G1-G5. But, in the test results at 165 °C, G1 shows the higher evaporation loss by two to three times in comparison with other four greases (G2, G3, G4, and G5) which include urea grease. Urea greases have good thermal stability.

4.3 Shear stability (Shell Roll test)

Table 4 Shell Roll test

<table>
<thead>
<tr>
<th>Test Method</th>
<th>ASTM D1831 Modified</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test Temperature, °C</td>
<td>150</td>
</tr>
<tr>
<td>Rotation Speed, min⁻¹</td>
<td>165</td>
</tr>
<tr>
<td>Test Duration, h</td>
<td>100</td>
</tr>
</tbody>
</table>
The test results of G3 and G4 showed more than 400 in penetration. G1 and G2 showed better results, respectively, 355 and 344 in penetration. G2 was best among five grease samples. Usually, urea greases are apt to harden in penetration under high temperature. But by shearing, grease becomes softer in penetration.

If hardening does not occur under high temperature, the penetration after the test becomes softer. Then test results after shell roll test are easy to fluctuate. The better grease such as G2 is well balanced in hardening and softening.

### 4.4 Low temperature torque (JIS K2220 18)

Figure 4 shows the test results of starting torque at -40 ºC. G1, G2 and G3 showed better results among five samples. The reason why G4 and G5 show higher value than G1, G2 and G3 is that the unworked penetration of G4 and G5 may be harder.

### 4.5 Low noise property

#### 4.5.1 Photos of grease particle

Micrographs of grease samples after three roll mill treatment are shown in Fig 5. In G1, we cannot find any particles, but G5 and G4 contain too many particles.

#### 4.5.2 Bearing noise testers

The test conditions on dB value and Anderon value by bearing noise testers are shown in Table 5 and the test results are shown in Fig 6 and Fig. 7-8 respectively.

#### 4.5.2.1 dB value

dB value of G1 shows the lowest value and the dB value of G2 is near to G1. It becomes higher in order of G5 > G4 ≧ G3 ≫ G2 > G1. This may be based on a number of grease particle and the initial penetration (consistency).

#### 4.5.2.2 Anderon value

G1 and G2 show almost the same value in both medium band and high band. G3, G4 and G5 show higher value than G1 and G2 and the value of G3, G4 and G5 are also fluctuating. G1 and G2 show good low noise property.

#### 4.6 Rust preventive characteristics

Test results are shown in Fig.9. All the grease samples showed good results in 5000 ppm NaCl solution. There are no rust spots after the test.

#### 4.7 Grease life test

Figure 10 shows the test results of grease life at the temperature of 150 ºC and 165 ºC. As to the test results at 150 ºC, G2 shows longest grease life among five greases and G2 showed almost two to three times longer than that of G1. In 165 ºC, G2 shows longer grease life almost three times than that of G1.

Other grease samples including urea grease (G3, G4 and G5) also show longer life by almost 3 to 4 times in comparison with G1. All the grease samples including urea grease are longer in grease life than G1.

### 5. General Evaluations

Fig.11 shows the general evaluation on three greases (G1, G2 and G5).

As to low temperature property and rust preventiveness, there is not so much difference among them. All the greases show better results.

G2 is superior to G1 in grease life, thermal stability and shear stability.

As to low noise property, G2 shows the better results almost as same as G1. It is said that G2 is well-balanced grease having many good properties.

### 6. Verification of the test results

G2 grease (hybrid grease) showed longer life by almost two to three times than that of G1 grease (Li grease). To verify the reason why G2 showed longer life, bearing leakage test and bearing surface analysis by XPS were done.

Bearing leakage test was done to look into
the leakage tendency among G1, G2, and G5. XPS analysis was done to look into whether nitrogen (N) on the bearing surface by urea compound is detected or not.

6.1 Bearing leakage test
Fig. 12 shows the test results of bearing leakage test. Leakage tendency is different among three greases (G1, G2 and G5).

In comparison of G1 and G2, G1 is on the increase in leakage with time lapse. On the contrary, G2 is remains at almost the same level after 50 hours.

As to G5, the leakage is kept at the lower level than 30% for 100 hours. Judging from the above-mentioned facts, followings can be estimated:
A: G1 reached the grease life in a short time by much leakage at high temperature.
B: G5 reached the grease life by decreasing of oil supply from the grease which is caused by hardening in penetration at high temperature.
C: G2 may show longer grease life by well-balanced intermediate behavior between G1 and G5.

6.2 Bearing surface analysis by XPS
Test results are shown in Table 10 and Fig.13. As to G2 ball, it showed 2.2 percent of Nitrogen. There seems to be significant difference among G1, G2 and G5. Detection of N element suggests that nitriding may occur on the surface of the ball and also suggests that the chemisorption film (characteristic of covalent bonding) by the reaction with urea compound may be formed on the surface of the ball, not usual physisorption film (characteristic of weak van der Waals forces).

On this interesting behavior, it is needed to be more closely examined.

7. Conclusion
7.1 G2 grease which we developed is well-balanced grease which has longer grease life at high temperature with good low noise property.

7.2 As to the optimum blend ratio of Li grease and Urea grease, around 75/25 ratio is suitable.

7.3 Verification on the reason why G2 showed longer life.
7.3.1 Leakage tendency is different among G1, G2 and G5. G2 may show longer grease life by well-balanced intermediate behavior between G1 and G5.
7.3.2 As to the surface analysis of tested bearing by XPS, N element on the G2 ball is detected much more than that of other samples. This suggests that nitriding may occur and that the chemisorption film may be formed on the ball surface.
7.3.3 It is needed to be more closely examined on this matter.

References
(1) S. Okamura et al, NLGI Spokesman, 56 (1992), 94
(2) Kenji Yuki et al, Proceedings of World Tribology Congress, Kyoto, 2009, 185
(3) Chen Shi Qi et al, EUROGREASE Magazine,1(2015),42-50
(4) You Shu Ting et al, Proceedings of CLGI, Nanning, 2015, 99-103
(5) Akimitsu Furukoshi, Monthly Tribology (Japan),12(2012), 42
Fig. 7 Low Noise Property (Anderton value)

Fig. 8 Low Noise Property (Anderton value)

<table>
<thead>
<tr>
<th>G1</th>
<th>G2</th>
<th>G3</th>
<th>G4</th>
<th>G5</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl (5000ppm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test Result</td>
<td>Pass</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 9 Rust Preventive Property

Fig. 10 Grease Life Test

Fig. 11 General Evaluation
Fig. 12 Bearing Leakage Test

Fig. 13 XPS Analysis

Table 10  XPS Test Result

<table>
<thead>
<tr>
<th></th>
<th>G1 Ball</th>
<th>G2 Ball</th>
<th>G5 Ball</th>
<th>G1 Plate</th>
<th>G2 Plate</th>
<th>G5 Plate</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>66.2</td>
<td>66</td>
<td>60.4</td>
<td>55</td>
<td>58.5</td>
<td>78.1</td>
</tr>
<tr>
<td>O</td>
<td>29</td>
<td>29.4</td>
<td>34.5</td>
<td>35.1</td>
<td>37.2</td>
<td>20.7</td>
</tr>
<tr>
<td>Fe</td>
<td>4.7</td>
<td>2</td>
<td>4.9</td>
<td>9.3</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>2.2</td>
<td>0.6</td>
<td>0.6</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Unit: %

Fig. 14 Example of Chemisorption

\[
R_1\text{-NH-CO-NH-R_2\text{-NH-CO-NH-R}_3} + H_2O \rightarrow R_1\text{-NH-CO-NH-R}_2\text{-NH-H} \text{ HO-CO-NH-R}_3 \\
O-CO-NH-R_3
\]

Urea Compound

Carbamic Acid
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NLGI India Chapter Annual Meeting
Hotel Taj Swarna
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March 6 – 9
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The Four Seasons Macao
Cotai Strip

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

April 21 – 24
ELGI Annual General Meeting
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London, United Kingdom

May 20 – 24
STLE Annual Meeting & Exhibition
Minneapolis Convention Center
Minneapolis, MN

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

October 6 – 9
ILMA Annual Meeting
JW Marriott Desert Springs Resort & Spa
Palm Desert, CA
30th ELGI AGM
Annual General Meeting

21st – 24th April 2018
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