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President’s Podium

84th Annual Meeting Photos

NLGI Golf Tournament 2017

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There are many roads to Rome, but only few of them are cost efficient…A Comprehensive Approach to Replace Group I Over a Wide Range of Viscosities

Mehdi Fathi-Najafi

Days of Future Passed: A Critical Review of the Development of Highly Overbased Calcium Alkylbenzene Sulfonates

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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

Ask the Expert

Industrial Greases: Market Analysis and Opportunities

Annie Jarquin

Advertiser’s Index

Calendar of Events
I thought I would write the Podium for this issue, to sum up the past year, let you know of proposed projects for the coming year and the status of the NLGI Home Office.

Although our Annual Meeting attendance was down slightly from last year, comments from our attendees were very positive about the sessions offered and networking opportunities. I think changing the meeting format in 2015 was very successful and there are no plans to return to the “Awards Banquet”! I, along with anyone who was at that meeting in Coeur d’Alene, are very excited to be returning to Coeur d’Alene for our 2018 Annual Meeting. You may also be interested to know that NLGI has confirmed The Meritage in Napa Valley, California for its 2021 Annual Meeting. We’ve had our eye on this area for some time, so we’re very happy to have found a really amazing property there.

Our website is still a bit “under construction”. We just transferred the website to a new company and updates/corrections are being worked on. Particularly our Membership Listing and getting the technical papers back on the website.

And one of the biggest projects completed this year was the revision of the NLGI Constitution, and the creation of a Policy Manual rather than By-Laws. There were many, many conference calls and full Board discussions before this was done, almost a year and a half! The purpose of a Policy Manual is to make some decisions about the operation of the NLGI to better serve our members. This is a fluid document, and will be updated after Board of Directors meetings, if applicable. Both of these documents will be in the Members Only area on the website (eventually, see above!).

On the radar for 2018 is a project that’s been discussed for quite some time. That is to get all of the technical papers that have been presented and published in The Spokesman (back to 1935), electronically available to our Members. Currently, technical papers going back to 1999 are available electronically. Additionally, make these papers searchable. NLGI is currently talking with outside companies who can help us accomplish this goal, so stay tuned for more information. If anyone has any suggestions to assist in this effort, please let me know.

Hopefully, you all saw the announcement that NLGI has resurrected its Research Grant Program. We are very excited to have gotten this off the ground again, thanks to Lisa Tocci, Gareth Fish and a host of other volunteers. We have received a great response in our first effort, be sure to watch for the announcement of the Grant recipient and of the next Grant opportunity.
In the effort to find a new Executive Director, the Board of Directors have formed a search committee. This committee in addition to the Executive Committee, have hired an Executive Search firm and will begin conducting interviews shortly. My official last day as the NLGI Executive Director was to be October 1, 2017, however, I have agreed to remain until the new Director is on board and trained. After that, I’ll still be around but behind the scene as a contracted Meetings Manager for NLGI through October 1, 2018.

I had no idea when I walked into the NLGI Headquarters Office my first day, August 3, 2003, I would be sitting here as the Executive Director writing my farewell President’s Podium 14 years later. I would like to thank the search committee (Barbara Bellanti, Bill Kersey and Richard Howell) and the Board of Directors that gave me this opportunity in 2007. It has been such an honor and privilege to have been a part of such an outstanding group of people. I have made so many friends, worked with some great people. And will miss you. I wish you all much success in the coming years.

Warm Regards,

Kim Hartley
84th ANNUAL MEETING PHOTOS

NLGI Grease Education Course

NLGI Technical Session

NLGI/ELGI Working Groups

Keynote Speaker Frank Miles
Fascinating presentation on Birds of Prey

Always great to catch up

Featured Industry Speaker Paul Bessette

Which way again?

Yes, it snowed!
NLGI GOLF TOURNAMENT
It was a cold one!

2017 NLGI Golf Tournament Winners

1st Place
Bob Richardson
Dave Millan
Doug Church
Dave Ewanishin

2nd Place
Chip Howalt
Jim Hunt
Kevin Nolan
Gary Collette

3rd Place
Rob Zeller
Rich Niedbalski
Ken Hope
Chris Conner

Longest Drive
Alex Kocin

Closest to the Pin
Scott Dunsmoor
FMC-LITHIUM DIVISION FUN RUN
Cold and snowy!

2017 Fun Run Winners

MEN
1st Place
Jim Grabarz
2nd Place
Brian Winfield
3rd Place
Robert Zeller

WOMEN
1st Place
Christine Karako
2nd Place
Vickie Bridges
3rd Place
Johanna Larsson
TUESDAY EVENING CLOSING FESTIVITIES
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The dramatic changes in the base oil technology landscape, driven by the rapid growth in capacity for paraffinic Group II and Group III base oils, is fueled by increasing demands on automotive engine oil performance. The total production of paraffinic Group I is estimated to fall to about 40% of the total base oil production by the year 2020 and some estimate it down to less than 30%. Regardless the degree of the fall, a serious consequence of these changes is that the offering of the base oil industry is no longer optimized for the industrial lubricant and grease industry requirements. The deficits in solvency and viscosity might not be readily substituted by the highly refined paraffinic Group II and Group III base oils.

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

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

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

The outcome emphasizes that this new range of base oils may replace paraffinic Group I in various industrial application, in many cases without needing any significant reformulation efforts. Furthermore, the rheological characterization and measurements of the flow pressure of the greases at low temperature emphasis the improved flowability of the grease.

Key words: Paraffinic oil, Naphthenic oil, Pour point depressant, Elastomer compatibility, Lubricating grease

1. Introduction

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

The rapid changes in the base oil market, driven mainly by the technical demand from high performance automotive engine oil applications, are impacting all lubricant applications.

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

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

Hence, what to do? What is the most cost efficient way out of this dilemma?
We at Nynas believe that due to the long term availability of paraffinic Group II, III, and naphthenic oils, it is most probably that a mixture of naphthenic oil with paraffinic Group II and III is a realistic, cost effective and fast solution for substitution of paraffinic Group I in various industrial applications. This paper suggests alternatives, here called NR, that could be used as “drop in” or with minor adjustment as a replacement to paraffinic Group I in industrial lubricants and grease lubricated applications.

2. Experimental work

Nynas has created a new range of products with Kinematic Viscosity (KV), Viscosity Index (VI) and Aniline Point (AP) closely matching those of existing Solvent Neutral Group I base oils.

- Response of Pour Point Depressant (PPD)
- Elastomer compatibility with respect to four reference elastomer materials (two NBRs, one H-NBR and one CR)
- The behavior of two NR grades (500 & 600) in lithium grease compared to a paraffinic oil Group I (SN 500)

2.1. Response of Pour Point Depressant (PPD)

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

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

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

Hence, an improved low temperature performance, and

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

* shows the closed and announced closure of paraffinic group I refineries
suggested a possible cost-out in e.g. formulations such as in hydraulic oils or other applications were PPD are going to be used.

2.2 Elastomer compatibility of the base oils

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

The purpose of this test series was to establish that the new range base oils have similar effect on the elastomer materials as the reference base oil, a standard Group I, SN 150. As one example, the influence on hardness and mass of NBR, 28% Acetonitrile (AN), Peroxide cured (BAM E008) for the all the oils are shown graphically for hardness change, Figure 2, and mass change, Figure 3.

In Figure 2, the direction of change, moderate loss of hardness (moderate softening), is the same for all base oils, and the magnitude is small, below -5%. The commonly permissible variance of hardness is +/- 10 %, e.g. in DIN 51 524.

2.3 The behavior of two NR grades (500 & 600) in lithium grease compared with a paraffinic oil Gr. I (SN 500)

It is well known that Solvent Neutral 500 (SN 500) is traditionally used for preparation of lithium grease. Hence, this fluid is used as a reference in comparison with NR 500 and NR 600. The characteristics of these base oils can be seen in Table 2.
As it can be seen in Table 1, NR 500 and 600, in comparison to SN 500, have significantly lower Sulphur content, lower pour point and lighter in color! Thus, it is foreseen that these improved properties will, in many cases, improve the performance and quality of the fully formulated greases.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Unit</th>
<th>Test method</th>
<th>SN 500</th>
<th>NR 500</th>
<th>NR 600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td></td>
<td>Clear &amp; Bright</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density, 15°C</td>
<td>g/dm³</td>
<td>D 4052</td>
<td>889.6</td>
<td>889.0</td>
<td>876.0</td>
</tr>
<tr>
<td>Viscosity, 40°C</td>
<td>mm²/s</td>
<td>D 445</td>
<td>101</td>
<td>100</td>
<td>120</td>
</tr>
<tr>
<td>Viscosity, 100°C</td>
<td>mm²/s</td>
<td>D 445</td>
<td>10.9</td>
<td>10.2</td>
<td>12.6</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>mm²/s</td>
<td>D 2270</td>
<td>91</td>
<td>79</td>
<td>98</td>
</tr>
<tr>
<td>Flash Point, PM</td>
<td>°C</td>
<td>D 1747</td>
<td>232</td>
<td>226</td>
<td>250</td>
</tr>
<tr>
<td>Refractive Index, 20°C</td>
<td></td>
<td>D 2622</td>
<td>1.488</td>
<td>1.487</td>
<td>1.481</td>
</tr>
<tr>
<td>Sulphur</td>
<td>%</td>
<td>D 2140</td>
<td>0.944</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>Carbon-Type Composition</td>
<td></td>
<td>D 2501</td>
<td>0.821</td>
<td>0.821</td>
<td>0.800</td>
</tr>
<tr>
<td>Cₐ</td>
<td>%</td>
<td>D 97</td>
<td>3.8</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Cₚ</td>
<td>%</td>
<td>D 611</td>
<td>66.7</td>
<td>61</td>
<td>69</td>
</tr>
<tr>
<td>Cₙ</td>
<td>%</td>
<td>D 130</td>
<td>29.5</td>
<td>36</td>
<td>30</td>
</tr>
<tr>
<td>Viscosity-Gravity-Constant</td>
<td></td>
<td>D 1500</td>
<td>104</td>
<td>111</td>
<td>123</td>
</tr>
<tr>
<td>Pour Point</td>
<td>°C</td>
<td>D 130</td>
<td>7.8</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>Aniline Point</td>
<td>°C</td>
<td>D 974</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

**Table 2. The characteristics of the base oils used.**
2.3.1 Results and discussions

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

Based on the measured properties of the greases, shown in Table 3, it can be concluded that all three grease samples show good shear stability despite having different thickener content; sample C (based on NR 600) highest and sample B (based on NR 500) the lowest.

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

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

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

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Unit</th>
<th>Test Method</th>
<th>Grease A</th>
<th>Grease B</th>
<th>Grease C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Oil</td>
<td>(wt%)</td>
<td>ASTM D 217</td>
<td>SN 500</td>
<td>NR 500</td>
<td>NR 600</td>
</tr>
<tr>
<td>Thickener Content</td>
<td></td>
<td></td>
<td>7.98</td>
<td>7.48</td>
<td>9.39</td>
</tr>
<tr>
<td>Penetration Unworked</td>
<td>(mm²)</td>
<td>ASTM D 217</td>
<td>285</td>
<td>282</td>
<td>278</td>
</tr>
<tr>
<td>Penetration (after 60 str)</td>
<td>(mm²)</td>
<td>ASTM D 217</td>
<td>279</td>
<td>279</td>
<td>280</td>
</tr>
<tr>
<td>Penetration (after 10⁵ str)</td>
<td>(mm²)</td>
<td>ASTM D 217</td>
<td>300</td>
<td>309</td>
<td>305</td>
</tr>
<tr>
<td>Dropping Point</td>
<td>°C</td>
<td>IP 396-02</td>
<td>199</td>
<td>200</td>
<td>198</td>
</tr>
<tr>
<td>Cu - Corrosion</td>
<td>rating</td>
<td>ASTM D 4048</td>
<td>1b</td>
<td>1a</td>
<td>1a</td>
</tr>
</tbody>
</table>

Table 3. Some properties of the grease samples

![Figure 4. The required flow pressure (hPa) as a function of temperature.](image-url)
500 to be pushed out of the nozzle.

**Rheological measurements** of the greases have been conducted in order to create an overview over behaviour of this complex material over a wide temperature range. It is well known that lubricating grease is a material with a viscous part (the base oil) and an elastic part (e.g. the thickener). Parameters such as temperature and shear stress affect the oil and the thickener differently. Hence, flowability of the grease sample under controlled conditions can generate valuable information. For example, storage modulus ($G'$) or complex modulus ($G^*$) of the grease can be interpreted as the real consistency of the grease, at the applied condition.

In an attempt to study the thermal behaviour of the greases the oscillatory program of a rotational rheometer has been used. Notable that all the measurements were conducted by using plate on plate geometry with a gap size of 1mm. The first step in the characterisation was to find out the so-called linear viscoelastic region (LVER) by applying a strain sweep program in which the frequency and the temperature were kept constant (10 Hz and 25 °C respectively), and then the strain was increased logarithmically from 0.01 to 1000%, see Figure 5, while Figure 6 shows same measurements plotted against the shear stress.

Figure 5 indicates that grease A (SN 500 based) is slightly thinner (lower $G'$) and has shorter LVER than Grease B (NR 500 based) and C (NR 600 based) despite of the fact that all three greases have the same NLGI grade.

However, the next step in this part of the study was to measure the change of the complex modulus ($G^*$), which is a sum of storage modulus and viscous modulus, over a wide range of temperature while the shear stress (10 Pa) and the frequency (10 Hz) have been kept constant. In order to conduct this evaluation more accurate it was decided to divide it in two steps;

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

**Step 1) The low temperature behaviour:** This type of measurement reveals the degree of stiffness of a grease when the temperature is reduced. Thermal sweep program was run from +25 to -25 °C. The obtained data is shown in Figure 7.

**Figure 7 reveals lots of information such as:**

a) Grease C is thicker than other two Greases which can be supported by its higher thickener and slightly higher base oil viscosity that have been used.

b) Grease A (SN 500 based) shows a faster degree of increased complex viscosity than the others. This increase is accelerating as applied temperature approaches the pour point of the base oil which in turn confirms the poor results from Flow pressure measurements, discussed earlier in this paper.

c) Grease B and Grease C show same degree of the thickening effect within the applied temperature range and significantly better performance than Grease A.

**Step 2: The high temperature behaviour:** This type of measurement is targeting the degree of softening of a grease when the temperature is increased. Thermal sweep program was run from +25 to +120 °C. The obtained data, shown in Figure 8, indicates that Grease C (NR 600 based) softens less than the other two greases, most probably due to the higher thickener content.
3. Summary
The results suggest that it is indeed possible to reproduce the key features of Group I base oils, and to formulate lubricating greases and other industrial related formulations based on these.

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

4. Reference
1. DIN 51 524 “Minimum requirement of hydraulic fluids” Part 2 and 3
5. www.nynas.com
Join Us next year as we return to the stunning Coeur d’Alene Resort
June 9-12, 2018
ABSTRACT

Highly overbased calcium alkylbenzene sulfonates have become an important component in numerous industrial lubricants including passenger car and heavy-duty diesel engine oils, metalworking fluids, and calcium sulfonate-based lubricating greases. The latter category was, by definition, not even possible without the development of these important raw materials. The development of highly overbased calcium sulfonates began in 1942 and has continued to the present. However, as far as the author can determine, this technology development has never been reviewed in any dedicated or organized way. This paper provides such a review by concentrating on the primary source involved: the U.S. Patent literature. By systematically and critically reviewing the more than 40 U.S. Patents from 1942 to 2000 that span the development of highly overbased calcium alkylbenzene sulfonates, a picture becomes visible that provides a clearer understanding of the current calcium sulfonate-based grease technologies that use these additives. It also clearly highlights a major gap in understanding of this area of additive chemistry previously not discussed in the open literature. The recognition of this gap sets the stage for future work needed to better understand overbased alkylbenzene sulfonate chemistry and provides a new tool for the development of improved calcium sulfonate-based greases. The organization of the large amount of developmental information represented in this review paper is cast within the metaphor of a typical 24 hour day, starting just before dawn and concluding with the arrival of night – appropriate since the story of most new technology development conforms to such a picture.

THE DAY BEGINS (1942-1945)

Pinprick holes in a colorless sky,
Let insipid figures of light pass by,
The mighty light of ten thousand suns,
Challenges infinity and is soon gone…

- Graeme Edge

Today’s calcium sulfonate-based greases have as their central component highly overbased calcium alkylbenzene sulfonates. However, the impetus for the original development of those materials had nothing to do with lubricating greases, but was instead related to crankcase oils for gasoline-powered passenger cars. As the performance demands for those engine oils had increased, so had the problems of piston ring sticking and varnish buildup. In the early 1940’s, the use of performance-improving additives for motor oils
was still in its infancy. Three U.S. Patents, all filed in 1940 by Shell Development Company and issued between 1942 and 1945, addressed this problem with the development of additives based on oil-soluble metal alkylbenzene sulfonate salts. The preferred metals were those that had only one stable oxidation state; Ca, Mg, Ba, Al, and Zn were specifically mentioned. It was taught that the sulfonate salts could be either neutral or basic, with a mixture of both being preferred. However, all examples used already prepared calcium sulfonate salts with no mention as to how they were prepared or whether they were neutral, basic, or a mixture of neutral and basic. No art prior to those three patents could be found that provided any specific methods to prepare basic sulfonate salts, so there was apparently no obvious perspective that would have been easily known by those who first read those patents.

The remaining aspects of those three patents dealt with other motor oil additive components that were used to augment the metal sulfonate salts and provide additional benefits such as oxidation inhibition and further corrosion protection. This admittedly inauspicious beginning set the stage for the dawn of the development of the first documented basic metal alkylbenzene sulfonates.

**DAWN (1946-1952)**

*You look around you  
Things they astound you  
So breathe in deep  
You're not asleep  
Open your mind.*

-Mike Pinder

A series of five U.S. Patents, each assigned to a different company (except one for which the assignees were the inventors) represented the first disclosed technology for specifically forming overbased metal sulfonates. The first of these patents, assigned to Atlantic Refining, described the reaction of sulfonic acids (formed by sulfonating a hydrocarbon oil) with about twice the stoichiometric amount of hydrated lime (calcium hydroxide) by hot air agitation and direct steam heating at about 220 F to 230 F for one to two hours to produce an overbased sulfonate. No demonstration of structure was provided, and the final overbased sulfonates were considered as half-neutralized salts. Although no actual examples were provided, the chemistry described could be written as follows:

\[(1) \quad 2\text{RC}6\text{H}4\text{SO}3\text{H} + 2\text{Ca(OH)}2 \rightarrow (\text{RC}6\text{H}4\text{SO}3)2\text{Ca Ca(OH)}2 + 2\text{HOH}\]

A second patent focused primarily on reaction of metal salts of alkylbenzene sulfonic acid with either elemental sulfur or a sulfide of phosphorus. Presumably the reaction takes place across the olefinic unsaturation of the alkyl groups on the sulfonate. Although this patent did not advance the development of overbased calcium sulfonates, it did claim that the neutral metal sulfonate could be formed using bases that included not only metal oxides or hydroxides, but also metal sulfides, alkoxides, hydrides, or carbides. This concept would be used in later advances. Also, this patent introduced the concept of reacting an already formed neutral metal alkylbenzene sulfonate with inorganic metal salts including metal hydroxide. The resulting materials were claimed to be basic metal alkylbenzene sulfonates where the structure was that of a coordination complex. However, no evidence was provided to support this assertion. The examples were limited to one overbased barium alkylbenzene sulfonate and one overbased calcium tetra-isobutylphenol sulfonate. Prior to reaction with sulfur, the formation of the basic sulfonate salt in the first example would be represented by the following two reactions:

\[(2) \quad 2\text{RC}6\text{H}4\text{SO}3\text{H} + \text{Ba(OH)}2 \rightarrow (\text{RC}6\text{H}4\text{SO}3)2\text{Ba} + 2\text{HOH}\]

\[(3) \quad (\text{RC}6\text{H}4\text{SO}3)2\text{Ba} + x\text{Ba(OH)}2 \rightarrow (\text{RC}6\text{H}4\text{SO}3)2\text{Ba} \cdot x\text{Ba(OH)}2\]
The precise amount of overbasing in these two materials could not be calculated from the information provided, but it was clearly only a small amount. Therefore, $x$ in reaction (3) was likely less than or equal to 1.

A third patent dealt specifically with the preparation of basic metal alkylbenzene sulfonates using the same general approach as the above reactions (2) and (3). However, in this case, the neutral sulfonate salt was first formed using methanol/water as a solvent. Then, additional hydroxide of the same metal was added and the mixture was heated in the same solvent system. Interestingly, this patent also claimed the direct use of added metal carbonates, but nowhere provides any examples of this. Although all alkaline earth metals are taught, all three examples use only barium. The amount of overbasing in the final product was 2.5 times the amount needed for a neutral salt. Thus, the value of $x$ in the above reaction (3) would be 1.5 as it applied to this technology.

The next patent in this series of five continued the approach of the previous two in that the overbasing was accomplished by reaction of a metal-containing base with an already formed neutral metal sulfonate. No examples were provided in this patent. However, several important new concepts were introduced. First, the metal-containing base could be either hydroxide, oxide, carbonate, or bicarbonate. Second, the metal in the added base was often different from the metal in the neutral sulfonate, with sodium hydroxide often being mentioned. Most importantly, the concept of converting a final hydroxide-overbased sulfonate to the carbonate-overbased sulfonate by reaction with carbon dioxide was introduced. This was a key development that would prove vital in much of what would follow. As with earlier patents, barium appeared to be preferred in obtaining a stable product with significant overbasing. The inventors suggested that the structure of their products was a colloidal suspension. They based this on the amount of metal-containing salt present as well as the observation that their products exhibited the Tyndall Effect.

The final patent in this series taught the formation of a neutral alkaline earth metal alkylbenzene sulfonate by first forming the sodium salt and then performing a metathesis reaction with the hydroxide of the desired alkaline earth metal. All examples used either calcium or magnesium. Overbasing was accomplished by first forming the neutral metal alcoholate, then reacting it with the neutral sulfonate to form a complex. The complex was then reacted with water to convert the alcoholate to hydroxide. Thus, this patent continued the general concept introduced in the previous patent of chemically modifying the overbasing structure after the stable overbased sulfonate has been formed. The inventors posed a possible structure for these overbased materials, but presented no evidence to support it. Significantly, they made a point of not being bound to any structural theory regarding their claims. In view of what is now known about chemical bonding, their proposed structures seem unlikely.

Key advances from the patents of this section are summarized below in Table 1.

<table>
<thead>
<tr>
<th>TABLE 1: SUMMARY OF IMPORTANT ADVANCES 1946-1952</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Direct reaction of excess metal hydroxide with sulfinic acid to produce overbased sulfonate</td>
</tr>
<tr>
<td>2. Reaction of metal hydroxide with already-formed neutral sulfonate to form overbased sulfonate</td>
</tr>
<tr>
<td>3. Use of solvents to facilitate reactions</td>
</tr>
<tr>
<td>4. Barium emerging as preferred metal</td>
</tr>
<tr>
<td>5. Mixed metals possible</td>
</tr>
<tr>
<td>6. Other basic anions besides hydroxide can be used</td>
</tr>
<tr>
<td>7. Conversion of hydroxide to carbonate via CO$_2$ in overbased sulfonate possible</td>
</tr>
<tr>
<td>8. Maximum overbasing was about 1.5 times amount needed for neutral salt</td>
</tr>
<tr>
<td>9. Chemical structure of overbased sulfonates not clear</td>
</tr>
</tbody>
</table>
THE MORNING (1952-1955)

Yesterday’s dreams
Are tomorrow’s sighs

-Ray Thomas

A series of nine patents by Peter A. Asseff and co-workers, assigned to Lubrizol and issued between 1952 and 1955, represented a landmark advance in the synthesis chemistry of overbased alkaline earth metal alkylbenzene sulfonates. Most of the information found in each of these patents overlap to the others with even most of the more than 74 examples being the same. Accordingly, they will be treated as one entity instead of nine. As with all the previous patents, the driving force behind this work was the development of improved motor oil additives that could mitigate the buildup of acidic materials and varnish within critical engine areas such as piston rings, cylinder liners, and bearings.

The synthesis approach taught in all nine Lubrizol Patents was as follows:

\[
\begin{align*}
(4) & \quad 2RC_6H_4SO_3H + (x+1)M(OH)_2 \rightarrow (RC_6H_4SO_3)_2M \cdot xM(OH)_2 + 2HOH \\
& \text{or} \\
(5) & \quad (RC_6H_4SO_3)_2M + xM(OH)_2 \rightarrow (RC_6H_4SO_3)_2M \cdot xM(OH)_2
\end{align*}
\]

The key feature of this approach that distinguished it from earlier patents was that the reactions were done in the presence of water and a material called a promotor.

The term “promotor” as it applies to the synthesis of overbased metal sulfonates was used for the first time in these Lubrizol patents. Promotors were required to conform to either the formula AH or AXH, where A is an organic radical, X is either oxygen or sulfur, and H is hydrogen. Specific suggested promotors included phenolic compounds, low molecular weight sulfonic acids, alkyl nitro compounds, and thiophosphoric acids. The common structural feature of all these promotors is that they contain either acidic or tautomeric hydrogen. It should be noted that non-aromatic alcohols were not included in this initial definition of a promotor.

As indicated by both reactions (4) and (5), the Lubrizol patents taught that the starting material could be either the alkylbenzene sulfonic acid or a neutral metal salt thereof. However, starting with the sulfonic acid was taught as preferred so as to advantageously differentiate this new technology from prior patents where the already formed neutral salt was required or preferred. Even so, most of the synthesis examples in the Lubrizol patents started with an already formed neutral metal sulfonate salt.

For the first time, these patents taught that the commonly used neutralization number method (later re-defined as acid number, and later still as total acid number, TBN) was not always reliable to determine the extent of actual overbasing. The concept of metal ratio was, for the first time, introduced as a superior alternative, where the metal ratio was defined as:

\[
\text{Metal Ratio} = \frac{\text{wt} \text{ metal in overbased product}}{\text{wt} \text{ metal in neutral product}}
\]

The Lubrizol patents claimed that the highest metal ratio achieved prior to their work was 2.3, and they included two comparison examples using prior art techniques to demonstrate it. They also pointed out that none of the different chemical structures of overbased sulfonates proposed in the prior art had any real basis for proof. Instead of proposing a chemical structure themselves, Asseff and co-workers simply stated that the chemical structure was not well-understood.

The Lubrizol patents also taught the use of either CO2 or SO2 as a post-treatment to the overbased metal alkylbenzene sulfonate. This concept had been first introduced in a previous patent, but the utility of this technique was further defined by Lubrizol.

The post-treatment was done for two reasons: first, to neutralize the promotor so that it could then be stripped off by distillation; second, to convert the hydroxide to carbonate or sulfite. Examples indicated that carbonate was preferred. Several examples showed that when CO2 post-treatment was done, the metal ratio of the overbased material did not change. This observation proved that metal ratio was indeed a superior method of determining extent of overbasing compared to neutralization number, since the neutralization number of the carbonated product often was significantly reduced. It also showed that the CO2 post-treatment did not increase the amount of overbasing.

One of the nine Lubrizol patents provided a more involved reaction process that provided even higher metal ratios. This process had been discussed and used in examples in the other Lubrizol patents, but it was the specific focus of this patent. In this process, Asseff and co-workers referred to all prior art basic sulfonates as “basic salts”. They referred to their products of reactions (4) or (5) as “organic salt complexes”. In creating this name they apparently were not implying any particular chemical structure such as a true Warner complex. In the improved process described in this patent, an organic salt complex from (4) or (5) was first reacted with CO2 or SO2...
to convert hydroxide overbasing to carbonate or sulfite overbasing. Then, the resulting carbonate or sulfite-overbased organic salt complex was reacted with additional metal hydroxide to further increase the amount of overbasing. This additional reaction with metal base could be done with or without water and promoter. Finally, the product could be reacted again with CO2 or SO2 to convert the newly obtained hydroxide overbasing to carbonate or sulfite overbasing. Not including the initial water or promoter in the equations, the reaction chemistry described with conversion to carbonate could be written as follows:

\[
(6) \quad (RC_6H_4SO_3)_2M \cdot xM(OH)_2 + xCO_2 \rightarrow (RC_6H_4SO_3)_2M \cdot xMCO_3 + xHOH
\]

\[
(7) \quad (RC_6H_4SO_3)_2M \cdot xMCO_3 + yM(OH)_2 \rightarrow (RC_6H_4SO_3)_2M \cdot xMCO_3 \cdot yM(OH)_2
\]

\[
(8) \quad (RC_6H_4SO_3)_2M \cdot xMCO_3 \cdot yM(OH)_2 + yCO_2 \rightarrow (RC_6H_4SO_3)_2M \cdot (x+y)MCO_3 + yHOH
\]

Asseff and coworkers referred to the final products of this reaction process as “superbased salts”.

Collectively, the nine Lubrizol patents provided more than 74 detailed synthesis examples, with metal ratios reported for nearly all of them. Metals used were barium, calcium, and strontium. At least 62 examples used barium. The highest metal ratio achieved for an overbased barium sulfonate using the general reaction process of reactions (6) through (8) was 9.3. Most barium metal ratios were between 3.0 and 5.5 when the more simple process of reactions (4) or (5) were used. Only six examples used calcium as the metal. Metal ratios for those samples were: 1.57, 1.53, 2.36, 1.29, 3.07, and 3.94. One sample used strontium, and its metal ratio was 1.67. Empirical formulas were provided for the final products in the examples of two of the Lubrizol patents\(^\text{10,17}\). The inventors openly claimed that all overbasing techniques thus far documented, including theirs, worked best when barium was the metal. Clearly, their own data showed this to be so. However, no chemical reason for this was suggested.

Key advances from the patents of this section are summarized below in Table 2.

<table>
<thead>
<tr>
<th>TABLE 2: SUMMARY OF IMPORTANT ADVANCES 1952-1955</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Use of water and promoter to achieve highest yet levels of overbasing</td>
</tr>
<tr>
<td>2. Metal ratio defined and used to better measure level of overbasing</td>
</tr>
<tr>
<td>3. Chemical structure of overbased salts shown to be not well-understood</td>
</tr>
<tr>
<td>4. Barium clearly shown to allow the highest level of overbasing</td>
</tr>
<tr>
<td>5. Post-treatment with CO2 to allow removal of promoter</td>
</tr>
<tr>
<td>6. Post-treatment with CO2 to convert hydroxide overbasing to carbonate overbasing</td>
</tr>
<tr>
<td>7. Post-treatment with CO2 shown not to increase level of overbasing</td>
</tr>
<tr>
<td>8. Use of multiple iterations of reactions to increase level of overbasing</td>
</tr>
</tbody>
</table>

**PEAK HOUR (1958-1962)**

I see it all through my window it seems,  
Never failing, like millions of bees…  
Minds are subject to what should be done,  
Problem solved, time cannot be won…  
Peak hour…

- John Lodge
It was more than two years after the final of the nine previously discussed Lubrizol patents before the issuance of another significant patent dealing with overbased metal sulfonates. That patent, issued to Shell Development Company in 1958, provided the next important advance in this developing technology. Unlike earlier patents, this one primarily used calcium instead of barium. Promotors were not used. A neutral calcium alkylbenzene sulfonate was reacted with calcium hydroxide, water, and CO2 with heat.

Unlike all previous patents where CO2 was only used to convert hydroxide overbasing to carbonate overbasing in an already formed overbased sulfonate, this patent taught the use of CO2 as a reactant to actually increase the level of overbasing. The inventors claimed that calcium carbonate was formed in situ and then reacted with the neutral calcium sulfonate to form the unspecified overbased structure. However, they also claimed that this process would work when starting with the alkylbenzene sulfonic acid instead of the neutral sulfonate salt. They showed in two comparative examples that a stable overbased calcium sulfonate could not be formed if the sulfonic acid was reacted directly with added calcium carbonate. For the synthesis to be successful, the calcium carbonate needed to be formed (by reaction with the calcium hydroxide and CO2) as the overall reaction process occurred. This contradicted an earlier patent that claimed (without supporting data) that added metal carbonate could be used.

Most of the 20 examples started with a neutral calcium sulfonate; one started with a neutral barium sulfonate. Two started with a sodium sulfonate which was reacted with calcium chloride to form the neutral calcium sulfonate. The extent of overbasing was measured in all examples by base number. The highest base number achieved was 162 in an example that used three sequential overbasing, stripping, and filtration stages.

For the first time, this patent taught that for optimum product stability, not all the calcium hydroxide should be carbonated. The reaction chemistry, omitting the initially added water, can be described as follows:

\[
(9) \quad (RC6H4SO3)2Ca + xCa(OH)2 + (x-n)CO2 \rightarrow (RC6H4SO3)2Ca.(x-n)CaCO3. nCa(OH)2 + (x-n)HOH
\]

A second related Shell patent issued later the same year and was similar in its general approach. However, it differed from the previous Shell patent in that most of the examples used organic acids other than alkylbenzene sulfonic acids. The most common acid used was alkyl salicylic acid. Also, an alcohol, usually methanol, was added as well. The inventors claimed that the alcohol helped to provide a more stable overbased product during the process whereby the calcium carbonate was formed in situ as the acid was neutralized and overbased. The inventors did not claim the use of a promotor, and as already mentioned, the earlier Lubrizol work by Asseff and coworkers did not include non-aromatic alcohols as promotors. However, based on work that would later be published, it is likely that methanol was indeed acting as a promotor. The highest metal ratio reported was 11, and was achieved by using an alkyl naphthenic acid. As with the earlier Shell patent, the inventors claimed that it was important to not convert all the added calcium hydroxide to the carbonate.

Two patents issued to Continental Oil Company provided additional methods to prepare overbased sulfonates. The first dealt specifically with using barium, preferably as barium oxide dissolved in methanol, as a reagent. In order to overcome the poor solubility of the calcium bases in methanol, they were first converted to the more soluble calcium sulfide by reaction with H2S. The calcium sulfide was then dissolved in methanol and reacted with postdodecylbenzene sulfonic acid, water, and CO2. Highest base number achieved was 108. Electron micrographs showed that the resulting barium and calcium hydroxide in the overbased products were typically smaller than 0.03 microns. As with all patents discussed thus far in this paper, no mention was made as to whether any crystallinity was observed. As with the previously discussed Shell patents, the methanol used in these two Continental Oil Company patents may have been acting as a promotor even though the inventors made no such claim.

In a related patent that issued two years later, this technology was adapted to using calcium oxide or hydroxide instead of barium oxide. In order to overcome the poor solubility of the calcium bases in methanol, they were first converted to the more soluble calcium sulfide by reaction with H2S. The calcium sulfide was then dissolved in methanol and reacted with postdodecylbenzene sulfonic acid, water, and CO2. Highest base number achieved was 108. Electron micrographs showed that the resulting barium and calcium hydroxide in the overbased products were typically smaller than 0.03 microns. As with all patents discussed thus far in this paper, no mention was made as to whether any crystallinity was observed. As with the previously discussed Shell patents, the methanol used in these two Continental Oil Company patents may have been acting as a promotor even though the inventors made no such claim.

The next two patents both involved interesting ways to “trick” additional calcium hydroxide into an overbased structure by first forming another, less stable calcium-containing base that apparently more easily attached itself to the neutral sulfonate salt. Then the unstable base was decomposed to leave the calcium hydroxide in place as the overbasing species. The first of these two patents was issued to Texaco and described a novel method of reacting a neutral metal alkylbenzene sulfonate, water, and a metal alkoxy ethanolate to produce a hydroxide overbased sulfonate and alkoxy ethanol that was stripped off. The resulting overbased sulfonate could...
optionally be reacted with CO2 to convert the hydroxide overbasing to carbonate overbasing. Most examples used magnesium, although barium and calcium were also used. The reaction (without the carbonation step) can be described as follows:

\[
(10) \quad (RC_6H_4SO_3)_{2Mg} + xMg(OC_2H_4OR)_2 + 2xHOH \rightarrow (RC_6H_4SO_3)_{2Mg} \cdot xMg(OH)_2 + 2xHOC_2H_4OR
\]

Although the authors claimed that promotors as per the prior Lubrizol patents were not used, it is possible that the alkoxy ethanol formed during the hydrolysis reaction generated an effective promotor in situ. Metal ratios of 2-3 were obtained. So, while the chemistry is interesting, it did not seem to advance the ability to provide even higher levels of overbasing compared to previously reported work.

The second patent dealing with a novel way to introduce overbasing to alkylbenzene sulfonates and other organic dispersing agents was issued to Continental Oil Company in 1960. The unique feature of this patent was that a metal base (usually calcium hydroxide) was dispersed in an alcohol (usually methanol) and reacted with CO2 to form an alcohol-insoluble compound that was identified as a very specific methyl O-substituted calcium carbonate-methanol complex with the following structure:

\[
(11) \quad Ca(-O-CO-OCH_3)_2 \cdot nCH_3OH
\]

This complex was then added to a dispersant (such as a neutral calcium alkylbenzene sulfonate), and the mixture was heated to decompose the complex and strip off the methanol, thereby leaving the resulting calcium carbonate dispersed as part of an overbased product. Base numbers for the examples were typically between 50 and 90, although two samples had base numbers greater than 250.

Finally, in another important patent issued in 1962, Lubrizol incorporated the feature of using CO2 to actually increase the extent of overbasing into the technology that they had developed during 1952-1955. The patent was specifically for overbased calcium sulfonates. The chemistry involved reaction of a neutral calcium alkylbenzene sulfonate with calcium hydroxide, water, CO2 and an alcohol at a typical temperature of about 40°C. The term “promotor” was not used in this patent. Even so, based on later Lubrizol work discussed in the next section of this paper, it is likely that the alcohol was functioning as a promotor. The preferred alcohol was methanol, making it even more likely that some of the earlier patents that used methanol as a solvent were actually benefiting from its role as a promotor. Metal ratios of 7-8 were taught, with the highest value obtained in any example being 7.1. It should be noted that a specific step by step mechanism for the overbasing reaction that defined the exact roles of water and promotor was not proposed or even mentioned in this patent or in any previous one.

This Lubrizol patent is important for two reasons. First, it included for the first time all the compositional and process features used today for the manufacturing of 400 TBN overbased calcium sulfonates. Second, the primary inventor, Richard L. McMillen, was the person who would only four years later be the primary inventor for the first overbased calcium sulfonate-based grease patent. This fact is almost certainly not coincidental.

Key advances from the patents of this section are summarized below in Table 3.

<table>
<thead>
<tr>
<th>TABLE 3: SUMMARY OF IMPORTANT ADVANCES 1958-1962</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Use of CO2 and water to increase level of overbasing</td>
</tr>
<tr>
<td>2. Intentional incomplete carbonation of hydroxide during the overbasing reaction to improve final product stability</td>
</tr>
<tr>
<td>3. Use of methanol as solvent (promotor?) to improve reactivity of metal oxide or hydroxide with sulfonic acid or neutral sulfonate salt</td>
</tr>
<tr>
<td>4. Use of meta-stable chemically modified forms of metal bases to provide initial overbasing, followed by conversion of the overbasing to hydroxide or carbonate</td>
</tr>
<tr>
<td>5. Use of combination of calcium hydroxide, water, alcohol (promotor), and CO2 as a method to directly form carbonate overbased calcium alkylbenzene sulfonates</td>
</tr>
<tr>
<td>6. Higher levels of overbasing achieved</td>
</tr>
<tr>
<td>7. Mechanistic role of water and promotor not explained or proposed</td>
</tr>
</tbody>
</table>
THE AFTERNOON (1963-1970)

I'm just beginning to see  
Now I'm on my way  
It doesn't matter to me  
Chasing the clouds away

-Justin Hayward

The important advances mentioned in Table 3, especially items 1-5, catalyzed much new work on further methods to synthesize overbased alkaline earth metal alkylbenzene sulfonates. Unlike much of the earlier work where the more easily overbased barium was the focus, work from this point on focused primarily on calcium.

Two patents issued to Bray Oil Company described methods where calcium oxide or hydroxide was first reacted with CO2 in methanol. In the first of these two patents, the inventors claimed that calcium carbonate was formed and dispersed in the methanol, and that the dispersion could form a gel structure. After adding a light organic solvent to thin out the dispersion, it was mixed with either an alkylbenzene sulfonic acid or the neutral sulfonate salt. Heating to strip off the solvents resulted in a gel. The gel was broken by heating with added water. Base numbers as high as 350 were taught, although the highest value obtained was 306.

In a modification of this process, calcium oxide was first formed by thermal decomposition of calcium carbonate. This calcium oxide was then reacted with CO2 in methanol so that no more than 50% of it was converted to a calcium carbonate dispersion. The resulting dispersion was mixed and heated with a sulfonic acid. Additional reaction with CO2 and heat stripping of solvents resulted in a gel. The gel was broken by heating with added water. Base numbers as high as 345 were reported. It is interesting that these two patents claimed that the initial carbonated methanol dispersion contained calcium carbonate. As previously mentioned, a 1960 Continental Oil Company patent reported making very similar dispersions, and their work indicated the different structure (11) as shown above.

Several improvements to that Continental Oil Company patent were issued in 1964-1969. In the first one, issued in 1964, Mack Hunt and co-workers, also of Continental Oil Company, used a multi-step process wherein the first step was to react calcium carbide with an alcohol to produce a calcium alkoxide and acetylene.

\[(12) \text{CaC}_2 + 2\text{ROH} \rightarrow \text{Ca(OR)}_2 + \text{HCCH} \]

The calcium alkoxide was then carbonated to produce a calcium semi-alkoxide carbonate.

\[(13) \text{Ca(OR)}_2 + \text{CO}_2 \rightarrow \text{RO-Ca-O-CO-OR} \]

Note the similarity of the final product of (13) with the previous structure (11). The improvement was that when R was properly chosen, the final product of (13) was soluble in the corresponding alcohol ROH. The calcium semi-alkoxide carbonate was then reacted with either an alkylbenzene sulfonic acid or the corresponding neutral calcium sulfonate, followed by hydrolysis to decompose the carbonated alkoxide moiety. The result was a highly overbased calcium sulfonate wherein the overbasing consisted of calcium carbonate. The highest base number achieved was 364.

Two additional improvements to the 1960 Continental Oil Company patent, both issued to Mobil Oil Company, involved partial reaction of calcium carbonate overbased calcium sulfonate with formic acid or with both formic and acetic acid. The highest base number reported for each of these patents was around 290. Final products were claimed to be superior in high temperature stability for use as motor oil additives.

In 1970, a patent issued to Phillips Petroleum Company described a process where a neutral alkylbenzene calcium sulfonate was reacted with calcium hydroxide, promotor, water, and CO2. What made this process different from the previously discussed 1962 Lubrizol patent was that the promotor was an alkylated phenol sulfonic acid. When this promotor was neutralized during the reaction, it became part of the overbased sulfonate structure, and therefore its subsequent removal was unnecessary. The highest TBN value documented from the single example was 150.

Finally, several other important disclosures were made during this time period by Lubrizol. One patent was similar to Lubrizol’s 1962 patent, but eliminated the need for added water. This feature would become dominant in later work. Barium was the metal most often used in the examples, but it was an overbased calcium sulfonate that had the highest metal ratio. That value of 12.2 was achieved by forming the first overbased calcium sulfonate and then repeatedly reacting it with more CO2 and calcium hydroxide. The inventors redefined the promotor to specifically be monohydric and polyhydric non-aryl alcohols with monohydric alcohols such as methanol being preferred. They also re-iterated the two previous general theories concerning the structure of the highly overbased metal sulfonates: a formal complex where all the overbased metal cations and their anions are incorporated into a truly soluble molecular species; and, a colloidal dispersion where the overbased metal cations and their anions are dispersed by the neutral metal sulfonate. Comments on structure and mechanism will be provided in the final section of this paper.
In 1970, two of the Lubrizol patents dealing with the first overbased calcium sulfonate-based greases documented for the first time the fact that the calcium carbonate that comprised most of the overbasing was devoid of any sign of crystallinity as measured by X-ray diffraction. McMillen and co-workers referred to this as amorphous calcium carbonate. It should be noted that although the term "amorphous", from the Greek, means "no form", McMillen and co-workers did not say that the calcium carbonate had no structure whatever, simply that it did not have a measurable crystalline structure. These Lubrizol patents also refined the previous overbasing technology to provide final oil-soluble overbased calcium sulfonates with metal ratios near 20.

### TABLE 4: SUMMARY OF IMPORTANT ADVANCES 1963-1970

<table>
<thead>
<tr>
<th></th>
<th>Further methods to form meta-stable alternative bases for subsequent reaction with sulfonic acid or neutral sulfonate salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Additional methods to modify carbonate and/or hydroxide overbasing in overbased sulfonate</td>
</tr>
<tr>
<td>3</td>
<td>Expansion and further definition of what a promoter is</td>
</tr>
<tr>
<td>4</td>
<td>Establishment of non-crystalline structure of overbased calcium salts</td>
</tr>
<tr>
<td>5</td>
<td>Elimination of water as a reactant when using promoter</td>
</tr>
<tr>
<td>6</td>
<td>Attainment of higher metal ratios</td>
</tr>
<tr>
<td>7</td>
<td>Detailed structure of overbased sulfonates still not provided</td>
</tr>
</tbody>
</table>

Key advances from the patents of this section are summarized below in Table 4.


_I can see it all, from this great height,_
_I can feel the sun, slipping out of sight._
_And the world still goes on through the night._

_-Mike Pinder_

By 1970, all subsequent reported work dealt with refinements of technologies already established. Significant work was reported on whether calcium oxide or calcium hydroxide should be used in the overbasing reaction, and on how much should be left after carbonation. Final product clarity and filterability also became increasingly emphasized parameters. In a 1970 patent assigned to Texaco, it was taught that the amount of calcium carbonate formed during carbonation should consume between 50% and 83% of the stoichiometric excess calcium hydroxide used. The inventors further stated that the calcium hydroxide used in the reaction needed to have less than 1.5% calcium carbonate impurity in order to obtain a product with good filterability. Metal ratios were typically around 18 with one example having a value of 20. TBN values were as high as 375. Water was not used in the overbasing reaction, and methanol was the promoter.

In a 1973 patent assigned to Lubrizol, it was further taught that a fully ‘solubilized, homogenous” product could be obtained with as little as 75% of the stoichiometric excess calcium hydroxide converted to the carbonate. This patent also re-stated that the calcium carbonate in the overbased product showed no crystallinity by X-ray diffraction. Metal ratios reported in the examples ranged from 5.2 to about 78.

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Another patent assigned to Bray Oil Company in 1975 provided further work related to an earlier patent. A neutral calcium sulfonate was overbased by reaction of calcium oxide, methanol, and CO2. A base number of 600 was reported for an overbased calcium sulfonate made by four successive iterations of that reaction. Equipment and process flowcharts were described for using their multi-stage process.

Two patents, one issued to Witco Chemical Corporation in 1974, and one issued to Exxon Research & Engineering Company in 1983, continued to use methanol as the preferred promoter (although the Witco patent does not use the term “promotor”) and did not use water as a reactant. Both patents taught carbonation to be done in two distinct steps. In the Witco patent, preferably 90% to 95% of the total calcium oxide or calcium hydroxide was reacted. Base numbers were typically around 300. The Exxon patent differed in the way the temperature was controlled during both carbonation steps. TBN values were typically around 400. Both patents used filtration time as to measure how much of the added calcium hydroxide was utilized.

A 1978 patent assigned to Labofina S.A. taught that using a moderately reactive calcium oxide instead of calcium hydroxide in the overbasing reaction resulted in a product with superior filterability. The base number of the product from the single example was 320.

In a 1984 Texaco patent, the concept of using a very specific mixture of calcium oxide and calcium hydroxide in the overbasing reaction was first introduced. Advantages claimed included improved product clarity and less tendency to form a gelatinous rheology. The inventors also claimed that a promoter was no longer necessary, although in all examples methanol, a previously established promoter, was used. The best final products appeared to be generated when the ratio of calcium oxide to the sum of the oxide and hydroxide was between 0.2 and 0.3. Those final products also had between 5% and 10% of the stoichiometric excess calcium base remaining unreacted after carbonation. Base number values of 400 were provided.

Key advances from the patents of this section are summarized below in Table 5.


_Twilight time to dream awhile, _
_In veils of deepening blue._
_As fantasy strides, over colourful skies, _
(Of form disappearing from view.) _

_Ray Thomas_

The U.S. Patents from this period continued the focus described in the previous section, with even more detail towards the further optimization of the reaction process. A patent assigned to Phillips Petroleum Company in 1985 described a continuous reaction process to prepare carbonate overbased calcium sulfonates by reaction of a neutral calcium sulfonate with calcium hydroxide, methanol (the promoter), and CO2. The process involved using a series of reaction vessels in series, with equipment diagrams provided. A critical parameter of the process was the removal of the water formed during the overbasing/carbonation reaction so that its concentration was kept to no more than 1.5% of the reaction mixture. Methanol was also removed during each reaction stage, then re-introduced at a controlled level in the next stage. The inventors taught that this process provided a final product with a TBN of 310.

Nearly one year later, a patent assigned to the inventor, Joanne R. Whittle (previously named as inventor for a Texaco patent), taught a process of mixing a neutral calcium sulfonate, methanol, calcium oxide, and a hydrocarbon solvent. This was followed by a controlled addition of CO2 and water during a single overbasing/carbonation stage. The inventor claimed the final product had superior filterability compared to products made using a mixture of calcium oxide and calcium hydroxide such as previously taught in her earlier Texaco patent. TBN values of 300 to 416 were obtained.

Over the next five years, three patents assigned to Texaco Inc. provided what were cast as successive improvements over the previous Whittle patent. The first of these patents added the modification of adding 25% to 40% of the required water to the initial mixture of reactants. The remaining water and CO2 were gradually added at a controlled and uniform rate.

<table>
<thead>
<tr>
<th>TABLE 5: SUMMARY OF IMPORTANT ADVANCES 1970-1984</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Elimination of water as a required reactant during overbasing/carbonation further established</td>
</tr>
<tr>
<td>2. The requirement of unreacted calcium base after overbasing/carbonation further established and defined</td>
</tr>
<tr>
<td>3. Multi-step carbonation processes introduced as a method to improve final product clarity, viscosity, and filterability</td>
</tr>
<tr>
<td>4. Concept of using a controlled mixture of calcium oxide and calcium hydroxide for overbasing introduced as a method to improve final product quality</td>
</tr>
</tbody>
</table>
to complete the reaction. The inventors taught that previous processes where all the reactant water was added at once or continuously gave a product where part of the overbased calcium carbonate was crystalline and contributed to engine wear. They further taught that their process gave only amorphous calcium carbonate which did not contribute to engine wear. TBN values as high as 470 were taught.

The next Texaco patent was taught as an improvement over the previous one. In this case, a mixture of calcium oxide and calcium hydroxide was used with all the water added in the initial reaction charge. The added water was to be between 15% and 30% of the moles of calcium oxide used. The inventors claimed that previous overbased calcium sulfonates made from a mixture of calcium oxide and calcium hydroxide were hazy, had higher solids content prior to filtration, and had lower TBN values. They claimed that the products of this most recent process were clear and bright and had lower solids content prior to filtration. TBN values of 400 were reported, and IR spectra showed only amorphous calcium carbonate present.

The next Texaco patent, issued in 1991, had different inventors from the previous two, and it appeared to teach a contrary position. First, the inventors used only calcium hydroxide as the added base. Second, water was not added as a reactant. The primary feature of this patent was that before 80% of the calcium hydroxide had reacted, a zeolite adsorbent was added to remove reaction bi-product water. The carbonation step was then completed. The authors claimed that nearly all the calcium hydroxide could be converted to calcium carbonate with none of it being crystalline. TBN values up to 447 were achieved. Additionally, the inventors claimed that it was the presence of water near the end of the carbonation step that caused conversion of amorphous calcium carbonate to the crystalline form. They also taught that the previous use of calcium oxide was an attempt to remove water during the carbonation step (by reaction of calcium oxide with water to produce calcium hydroxide), but that this method was not very effective. Finally, they taught that water present near the end of the carbonation step caused an agglomeration of amorphous calcium carbonate within the core of the micelles, and that this “pre-crystallization” was what triggered the conversion to the crystalline form. They based this theory on measured values of the core sizes of amorphous and crystalline overbased calcium sulfonates, both of which were provided.

In 2000, a patent issued to Witco Corporation provided a process whereby a 400 TBN overbased calcium alkylbenzene sulfonate with 100% amorphous calcium carbonate could be converted to an overbased sulfonate with 100% crystalline (calcite) calcium carbonate. The process involved heating the initial overbased sulfonate with water, methanol, diluent hydrocarbon solvent, and either calcium acetate or acetic acid. An optional dispersant could also be included. The final product was clear and bright. TBN values were reported as high as 265, although values as high as 400 were claimed. When added to a commercially established motor oil at 5%(wt), products of this invention decreased the Four Ball Wear (ASTM D4172) scar diameter, thereby showing that their 100% crystalline calcium carbonate overbased calcium sulfonate did not increase wear, at least by the specific test used. Circumstantially, this Witco patent appeared to be something of a rebuttal to the previous Texaco patent that linked crystalline calcium carbonate in overbased calcium sulfonates with increased engine wear.

The refinement of overbased calcium sulfonate technology did not end with this Witco patent. However, this is a good point to end the review, since the successful development of both fully amorphous and fully crystalline 400 TBN overbased calcium sulfonates brings the “development day” to an appropriate nightfall.

Key advances from the patents of this section are summarized below in Table 6.

<table>
<thead>
<tr>
<th>TABLE 6: SUMMARY OF IMPORTANT ADVANCES 1985-2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Continuous process for manufacturing of overbased calcium sulfonates</td>
</tr>
<tr>
<td>2. Uncontrolled and excessive reactant water suggested as a cause of lower TBN values, hazy appearance, and poor filterability in final product</td>
</tr>
<tr>
<td>3. Water re-introduced as reactant with controlled use and removal techniques</td>
</tr>
<tr>
<td>4. Additional processes using either just calcium oxide, just calcium hydroxide, or a mixture of both</td>
</tr>
<tr>
<td>5. TBN values of 400 and higher</td>
</tr>
<tr>
<td>6. Dispersion (micelle) accepted as general structure of overbased calcium sulfonates</td>
</tr>
<tr>
<td>7. Micelle core dimensions cited for both amorphous and crystalline forms</td>
</tr>
<tr>
<td>8. Details of the exact structure of amorphous calcium carbonate within micelle still not explained</td>
</tr>
<tr>
<td>9. Mechanistic role of water and promoter still not explained or proposed</td>
</tr>
<tr>
<td>10. About 5% of stoichiometric excess calcium base required to remain for clear, bright, stable product with good initial filterability</td>
</tr>
<tr>
<td>11. One patent claims essentially 100% utilization of calcium base without product quality problems</td>
</tr>
<tr>
<td>12. Process for converting amorphous calcium carbonate overbased calcium sulfonates to corresponding crystalline (calcite) form with good product quality</td>
</tr>
</tbody>
</table>
THE NIGHT (SUMMARY AND RETROSPECTIVE)

Nights in white satin
Never reaching the end…

-Justin Hayward

The night can be a time for reflection of the day that has just ended. This section serves that purpose by summarizing and reflecting on the important topics that run through the U.S. Patents discussed in this review. Three such topics are: barium vs. calcium; evolution of techniques; and structure and mechanism. This is by no means an exhaustive list, but it is a representative one that is appropriate for the scope of this review. The discussion of these three topics will be limited to how they apply to overbased calcium sulfonates where the overbasing is in the amorphous form.

Barium vs. Calcium
The number of patent examples using barium compared to calcium as a function of issuance date is provided in Figure 1.

**FIGURE 1: OCCURRENCE OF BARIUM AND CALCIUM-BASED EXAMPLES**

![Diagram showing the occurrence of barium and calcium-based examples over time.](image)
As can be seen, the family of the nine Asseff patents as well as several others used barium as the dominant metal during the earlier years. However, calcium was also used from the beginning and eventually was exclusively used. A comparison of metal ratio values for barium and calcium-based products as a function of issuance date is provided in Figure 2. A similar plot of base number values is provided in Figure 3.
As can be seen, both metal ratio and base number were initially higher with barium. However, calcium-based values quickly dominated as overbasing technology became more effective.

As already mentioned, barium appeared to be easier to be incorporated into an overbased sulfonate structure compared to calcium. However, no stated reason for this could be found within the reviewed patent literature. However, a reasonable explanation can be found from well-known principles of inorganic physical chemistry. The aqueous solubility product constants for calcium carbonate (calcite) and barium carbonate at 25°C are $8.7 \times 10^{-9}$ and $8.1 \times 10^{-9}$, respectively. In water there does not appear to be much difference in their solubility. However, the preparation of overbased alkylbenzene sulfonates is not done primarily in an aqueous system. Both barium and calcium bear a 2+ formal charge in their compounds, but a barium cation is significantly larger (1.34 Angstroms) than a calcium cation (0.99 Angstroms). Also, the much greater number of electrons surrounding the barium cation compared to a calcium cation will provide more shielding of the positive charge borne within the nucleus. Both these factors can be expected to result in an effective charge density that is less for a barium cation than a calcium cation. Regardless of the exact structure of the micelle core where the calcium cations and carbonate anions are thought to reside, replacing the calcium with barium would be expected to decrease the affinity between the oppositely charged ions. This would explain why barium sulfonates appeared to be more responsive to most of the overbasing techniques. A brief summary of those techniques is provided next.

**Evolution of Techniques**

In 1942, the earliest overbased metal alkylbenzene sulfonates were prepared by simply heating an alkylbenzene sulfonic acid with a stoichiometric excess of the metal oxide or hydroxide. Alternatively, a neutral metal sulfonate salt was heated with additional metal oxide or hydroxide. Either way, only a very limited amount of excess metal base could be incorporated in a stable product. By 2000, the technique of getting large amounts of excess calcium to be incorporated into a clear and bright overbased alkylbenzene sulfonate had been developed. In terms of metal ratios, values went from initially being about 2.3 to eventually being 20 or more. The key aspects in this progression of overbasing technology have been captured in the previous Tables 1-6. However, it is useful to distill this technology progression into the following sequence:

1. Direct reaction of calcium oxide/hydroxide with either alkylbenzene sulfonic acid or the corresponding neutral salt
2. Use of water and promotor to increase extent of overbasing
3. Post-reaction with CO2 to convert overbasing anion to carbonate (carbonation)
4. Use of CO2 as an actual reactant to increase extent of overbasing
5. Elimination or limiting of water during the overbasing reaction
6. Fine tuning of whether to use calcium oxide or calcium hydroxide or both
7. Fine tuning of reaction conditions and separation of final product

Obviously, these seven steps did not occur independently from each other. Neither did one step become complete before another began. However, this progression does suggest certain things regarding the structure of the overbased products and the mechanism by which they were formed. This will be discussed in the final section of this review.

**Structure and Mechanism**

Given the huge difference in overbasing that exists between the earliest products and those in the final reviewed U.S. Patents, it is nearly certain that the detailed chemical structures are not the same. While the earliest products with metal ratios of about 2.3 could perhaps be something akin to a multi-centered complex, such a structure does not seem possible for products that have 20 (or more) times the amount of metal present as what is found in a neutral sulfonate salt. Likewise, the methodology used to make the overbased products with the very high metal ratios strongly suggests that something rather unusual is taking place on the atomic and molecular level.

The overall structure of today’s 400 TBN overbased calcium sulfonates is accepted to be a reverse micelle arrangement with the overbasing moieties within the core. However, the exact arrangement of the core has not been adequately described or demonstrated. Figure 4 provides a typical depiction as found in the open literature.
In some other depictions, the core is represented as having a hodgepodge of calcium cations and carbonate anions. In a few depictions, hydroxide anions are added to the hodgepodge. In all such depictions, a possible (if unintentional) implication is that the calcium cations and carbonate anions are present in some manner that is totally devoid of any structure whatsoever. While those who have used such depictions do not actually explicitly indicate this, neither do they indicate anything else concerning any specific and defined core structure. This has the potential of leaving the readers to assume that no core structure of any sort exists. As already mentioned, when the Lubrizol researchers first used the term “amorphous” to describe the calcium carbonate in the highly overbased structure, they did not claim that no structure at all existed. They simply stated that no crystalline structure as measured by X-ray diffraction could be detected.

There are several good reasons based on information discussed within this review that strongly suggest that some kind of structure does exist within the location of the overbasin calcium and carbonate ions.

1. Simple electrostatic considerations make it highly doubtful that a significant number of calcium cations and carbonate anions could exist within the measured dimensions of micelle cores without some kind of structure.

2. In nearly all overbasin techniques a relatively small amount of non-carbonated calcium base (usually the hydroxide) needs to be present so as to provide a final product that is stable. If the calcium cations and carbonate anions are randomly arranged within the core without any structure whatsoever, then why would a small amount of hydroxide anion be important to structural stability?

3. The intricate methodology involving promotor and the careful use of water during and immediately after formation of the overbased sulfonate suggests a special structural arrangement that allows such high levels of excess metal to remain within a clear and bright final product.

The last point is simply an outworking of the inevitable link between a product’s detailed chemical structure and the equally detailed chemical mechanism by which it is formed. The author could find no reference in the open literature concerning any specific and defined core structure. This has the potential of leaving the readers to assume that no core structure of any sort exists. As already mentioned, when the Lubrizol researchers first used the term “amorphous” to describe the calcium carbonate in the highly overbased structure, they did not claim that no structure at all existed. They simply stated that no crystalline structure as measured by X-ray diffraction could be detected.

There are several good reasons based on information discussed within this review that strongly suggest that some kind of structure does exist within the location of the overbasin calcium and carbonate ions.

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3. The intricate methodology involving promotor and the careful use of water during and immediately after formation of the overbased sulfonate suggests a special structural arrangement that allows such high levels of excess metal to remain within a clear and bright final product.

1. What is the exact mechanistic role of the promotor?

Specifically, does the promotor become part of the structure of the overbased sulfonate or an intermediate form, and if so, what is that structure?

2. How does the answer to question 1 depend on the chemical structure of the promotor? Why is methanol apparently one of the most effective promotors in terms of how it chemically interacts with the other reactants during the overbasin process?

3. What is the exact mechanistic role of water when used in the overbasin process? Why is too much water at the beginning or near the end of the process detrimental to the extent of overbasin, efficiency of calcium hydroxide/oxide promotion, and final product clarity/filterability? What is the mechanistic relationship between the use of various calcium bases (oxide, hydroxide, or mix of both) and initial presence of water?

4. What is the exact mechanistic role of CO2 when used to simultaneously overbase and carbonate the sulfonate? How is this mechanism different from what occurs when CO2 is used only as a post-treatment for an already formed calcium hydroxide overbased sulfonate? Are any intermediates formed that include the CO2 before the final form of the overbasin sulfonate? If so, what is the mechanistic fate of those intermediates?

5. Why is it important to product stability to have a minor amount of non-reacted calcium hydroxide in the final overbased sulfonate? Is this calcium hydroxide part of any intermediate form, and if so what is the structure? What is the role of that calcium hydroxide in the structure of the final overbased sulfonate?

6. What is the detailed structure of the overbasin moieties (calcium cations, carbonate anions, and hydroxide anions) within the region of the overbased sulfonate where they reside? What are the final mechanistic steps that place these ions within their final orientation?

7. What is the relationship between the detailed mechanism of overbased calcium sulfonate formation and the detailed mechanism of the conversion process by which they are changed into non-Newtonian greases (which also does not appear to be well-documented)?
These seven questions are not a complete list, but they are important. Complete answers to these questions would provide a good place from which significant new technology development could result. Most technology development follows the pattern intentionally used in this paper. The process begins with a dawning of understanding that accelerates, reaches a peak, and then eventually declines, i.e., the typical “S” curve profile. A radical new beginning of technology development usually feeds off of improved understanding and utilization of what has already been documented. A recent example of this was the realization that when the residual calcium hydroxide in an overbased calcium sulfonate was too low, it could affect the structural stability of the grease made from that overbased calcium sulfonate, even if additional calcium hydroxide was added before conversion. The realization of this fact was the basis for an improved understanding of the reaction mechanism of calcium sulfonate complex grease formation previously undocumented in the open literature. That in turn resulted in an advance in calcium sulfonate complex grease technology. One cannot help but wonder what advances could result from a detailed and documented understanding of the structure and formation mechanism of highly overbased calcium sulfonates.

_Cold-hearted orb that rules the night_  
_Removes the colours from our sight_  
_Red is grey and yellow white_  
_But we decide which is right._  
_And which is an illusion?_  

_-Graeme Edge_

**ACKNOWLEDGEMENT**

The organizational structure and poetic verse used in this paper are from the iconic 1967 concept album “Days of Future Passed” by The Moody Blues.

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33 Jao, Tze-Chi "Method of Preparing Overbased Calcium Sulfonates"; U.S. Patent No. 4,780,224, 1988


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43 Weynick, J. Andrew "Calcium Sulfonate Complex Greases Using Calcium Hydroxyapatite as a Hydroxide-Containing Basic Reactant"; NLGI 83rd Annual Meeting, Coeur d'Alene, ID, June, 2015
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

Abstract
It is well known that lithium grease shows good low noise property, but is poor in grease life at higher temperature than 150 degree C. 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 loss), low noise property (Anderon value, dB 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 degree C 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 degree C and above with low noise property. On the other hand, it is also well known that urea greases which have a long life at high temperature are applied for various industrial fields, such as automobile, steel making plant and household appliances.

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 at high temperature by choosing a suitable blend ratio of lithium grease and diurea grease.

This paper describes on the difference of performance (thermal stability, shear stability, low temperature property, low noise property, rust preventiveness, and grease life) among five sample greases including three blended greases.

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

2.1 Lithium Grease
2.1.1 Li Grease Sample Preparation Procedure
1. Heat lithium soap in base oil with stirring until the temperature reaches almost 215 degree C.
2. Pour the hot material into cooling pan.
3. Add an oxidation inhibitor and rust preventive agents to the resulting mixture with stirring.
4. Treat the resulting mixture by three-roll mill.

2.2 Urea Grease
2.2.1 Urea Reaction

2.2.2 Urea Grease Sample Preparation Procedure
(1) React on MDI with amines at 80~100ºC in base oil.
(2) Heat the reaction product up to150-160 ºC with stirring and maintain it at this temperature for 30 minutes.
(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 (mass %)</td>
<td>100</td>
<td>75</td>
<td>50</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>Diurea Grease (mass %)</td>
<td>0</td>
<td>25</td>
<td>50</td>
<td>75</td>
<td>100</td>
</tr>
<tr>
<td>Thickener content (mass %)</td>
<td>13 ---- 15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type of base oil</td>
<td>Ester oil</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Base oil Viscosity 40°C, mm²/s</td>
<td>30 ---- 40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Penetration 25 °C, 60W</td>
<td>NLGI 2~3</td>
<td></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 (Anderson 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 3336 modified) The test conditions are shown in Table 7.

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.
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

| Test Temperature, °C | 150, 165 |
| Test Duration, h     | 24, 50, 80, 100 |
Thin film evaporation test was done as the following photos (before and after).

The results of the evaporation loss are shown in Fig. 1 and 2.

4.2.1 Thin film evaporation loss

![Graph showing evaporation loss at 150°C](image1)

**Fig. 1 Evaporation Loss (1)**

![Graph showing evaporation loss at 165°C](image2)

**Fig. 2 Evaporation Loss (2)**
4.3 Shear stability (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>

![Graph showing shear stability](image1)

4.4 Low temperature torque (JIS K2220 18)

![Graph showing low temperature torque](image2)
4.5 Low noise property

Table 5 Low noise property (Bearing vibration tester)

<table>
<thead>
<tr>
<th></th>
<th>dB</th>
<th>Anderon (μm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparatus</td>
<td>S-0910A</td>
<td>BVT</td>
</tr>
<tr>
<td>Revolution Speed, min⁻¹</td>
<td>1500</td>
<td>1800</td>
</tr>
<tr>
<td>Test Bearing</td>
<td></td>
<td>6201</td>
</tr>
<tr>
<td>Preload</td>
<td>N</td>
<td>40</td>
</tr>
</tbody>
</table>

Fig. 5 Low Noise Property (1)

Fig. 6 Low Noise Property (2A)

Fig. 7 Low Noise Property (2B)
### 4.6 Rust preventive characteristics

<table>
<thead>
<tr>
<th>Test Method</th>
<th>ASTM D1743 Modified</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conditions</td>
<td>0.5% NaCl</td>
</tr>
</tbody>
</table>

Test results are shown in Fig.8. All the grease samples showed good results in 0.5% NaCl solution. There are no rust spots after the test.

![Fig.8 Rust Preventive Property](image)

### 4.7 Grease life test

<table>
<thead>
<tr>
<th>Method</th>
<th>ASTM D3336 Modified</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotating Speed, min⁻¹</td>
<td>10000</td>
</tr>
<tr>
<td>Test Bearing</td>
<td>6204</td>
</tr>
<tr>
<td>Test Temperature, ºC</td>
<td>150, 165</td>
</tr>
<tr>
<td>Load (Thrust/Radial), N</td>
<td>22 / 67</td>
</tr>
</tbody>
</table>

Figure 9 shows the test results of grease life at the temperature of 150 ºC and 165 ºC.

![Fig.9 Grease life test](image)

### 5 General Evaluation

![Fig. 10 General Evaluation](image)
Q: We have problems with telescopic sliders working on a tramway door. The telescope is made of C45 sliders and 100Cr6 balls. When door is opening and closing, the telescope is under rain. It seems that during intense raining (1 or 2 days), the lubricant is "washed away". The telescope makes noise and at the end, sliding friction is so high than the door stops during closing/opening.

Which criteria shall I look to, to choose a grease that will work with a high amount of water, taking into account that the doors shall be able to work at -30°C.

A: Look for data for Water Washout Test (ASTM D1264, DIN 51807-2, ISO 11009) and Water Spray-Off Resistance Test (ASTM D4049). These methods both report the amount of grease lost after exposure to water.

Q: Is there a specific place to get the latest Grease Compatibility Charts?

A: Grease compatibility charts are available online from multiple sources. Many of them do not agree with one another. A grease compatibility chart should be used as a starting point, not a definitive answer, for determining grease compatibility. It is always best to perform a laboratory compatibility test using the two products in question, or obtain information from one or both of the manufacturers of the products.

Q: I have a German made rotary hay rake that recommends a semi fluid grease in the gearbox with a NLGI 0. The closest thing I can find has a NLGI 00. In your opinion would this be acceptable? What is the correlation between a 80w90 gear oil and NLGI 0 ratings? What weight of gear oil could I use that would be close to the NLGI 0 rating?

A: NLGI 00 and 0 grade greases are both somewhat fluid products, although NLGI 00 is more fluid. NLGI 0 grade greases are fairly common, so you should be able to find a product of that consistency grade relatively easily.

There is no correlation between oil viscosity and grease consistency. Grease consistency is dependent upon the amount of thickener present in the grease. Oil viscosity is to just that, the viscosity of the oil. The oil in grease also has viscosity, and that should be taken into account when selecting the proper grease for a given application.

Q: What is NLGI-KI 2EP? Is this just a EP 2 or does the KI denote something else?

A: The designation you have quoted may be a fragment of the DIN 51825 system for classifying lubricating grease. Type K indicates the product to be grease. That system defines the types further, as follows:

Type K – Lubricating grease consisting of mineral or synthetic oil and thickener. Additives and/or solid lubricants are permitted.
Type KP – Lubricating grease with anti-wear and/or extreme pressure additives.
Type KF – Lubricating grease with solid lubricants added.
Type KPF – Lubricating grease with anti-wear and/or extreme pressure additives and solid lubricants added.

There is no KI designation. It could be K1, which would designate a NLGI 1 grade product, but then the designation you provided states 2EP, which would indicate an NLGI 2 grade consistency. In addition, DIN 51825 does not use the designation EP, since it is not universally recognized.

We suggest you contact the equipment manufacturer for clarification of what is meant by the grease designation they have provided.

Q: Is Lithium 12 H Stearate (Lithium semi complex) thickener is suitable for making transparent grease?? if yes, kindly tell me how to process it. also name some transparent additives??

The Expert
Q: Have any reports been published that actually test the performance of MIL-PRF-23827 Ty.1 and Ty.2 greases when they have been mixed together? I know of one Mobil report but was wondering if there are others. Haven’t seen anything from Aeroshell.

A: NLGI does not have any reports or papers on the compatibility of MIL-PRF 23827 Type 1 and Type 2 greases. The US FAA (Federal Aviation Administration) may have a report on that subject.

Q: Are all greases that are labeled NLGI GC-LB # 2 compatible with each other and mixable?

A: The simple answer is “no.” Greases that meet the NLGI GC and LB specifications can be made from different thickeners, some of which are not compatible with one another. When selecting a grease for automotive applications, you should look for a grease with the same thickener type as the grease that is in service. If the type of grease in service is not known, it should be displaced as thoroughly as possible when re-lubricating the equipment.
Industrial Greases: Market Analysis and Opportunities

Annie Jarquin
Kline Group

Introduction
The global industrial manufacturing sector continues to improve from the low production rates during the 2008 recession. However, the emerging scenario is vastly different from the pre-recession one. Firstly, shifting manufacturing units to low-cost offshore Asian markets is no longer attractive due to the reducing cost-competitiveness of Asian manufacturers. In fact, China is expected to achieve cost parity with the United States in the next few years due to rising wages and strengthening currency. Secondly, manufacturers in Asia are keen to improve and modernize their manufacturing process in order to better compete with their western counterparts. Thirdly, all manufacturers are increasingly focusing on improving energy efficiency, reducing emissions, and becoming more sustainable. All three factors will profoundly influence the volume and quality of industrial lubricants consumed.

Overall Grease Market
Grease consumption though small is ubiquitous, spread across all automotive and industrial end-use sectors. The focus of this paper is only the industrial segment. Estimates for the total grease market are presented here for completeness.
Globally, grease consumption is estimated to be around 1,302 KT per year, of which 48% is represented by automotive applications and the balance 52% is represented by industrial applications. The automotive segment includes initial fill and service fill of commercial vehicles, such as trucks, buses, tractors, off-highway vehicles, passenger cars, SUVs, and two- and three-wheelers. The industrial segment covers grease consumption in all industrial end-use sectors, including automotive manufacturing and off-highway transportation comprising railroad, aviation, and marine.

Figure 1: Grease Demand by End-use Sector, 2014

<table>
<thead>
<tr>
<th>End-use Sector</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Consumer</td>
<td>11%</td>
</tr>
<tr>
<td>Commercial</td>
<td>37%</td>
</tr>
<tr>
<td>Industrial</td>
<td>52%</td>
</tr>
<tr>
<td>Total</td>
<td>1,302 KT</td>
</tr>
</tbody>
</table>
**Industrial Grease Global demand**

In 2014, global consumption of grease in industrial applications is estimated at around 680.0 KT. Primary metals - steel and aluminium rolling mills and other such applications - is the largest end-use industry. The mining industry, where grease is used in applications such as open gears, chains, and conveyors, is the second-largest consumer.

The Asia-Pacific region is the largest demand center for industrial greases. A number of key end-use industries have shifted their manufacturing facilities to Asia. This has resulted in a rapid increase in demand for industrial greases in this region, with its global share growing by 7 percentage points in the last 10 years.

In 2014, global consumption of soap (conventional and complex) thickened greases accounts for about 91% of total consumption. Non-soap thickened greases, which include polyurea, clay, and other such thickeners, account for about 9% of the total consumption.

Lithium thickeners, both simple and complex, are the most commonly used in all regions and end-use industries, and account for nearly 74% of the total consumption. Lithium greases are true “multipurpose” greases, on account of their excellent properties in terms of water resistance, high temperature performance, and structural strength. Lithium complex greases
have a higher operating temperature limit, and hence they are catching up fast.

**Europe Overview**

Europe is the second largest market for grease. Primary metals industry is the largest consumer of industrial greases in Europe. The key country markets in Europe reflect the main manufacturing countries in the region: DACH (Germany, Switzerland, and Austria) and Russia are the main markets, followed by Turkey.

Primary metals covers steel and aluminum rolling and other metals. Within Europe, Russia, Germany, Italy, Spain, Benelux, France, the United Kingdom, and Poland are significant producers of steel. Russia is the largest aluminum producer, followed by Norway and Germany. Other significant producers of rolled product include the United Kingdom, Italy, Spain, France, and Hungary.

DACH is the manufacturing powerhouse of Europe, with a large share of manufacturing of automobiles, chemicals, machinery, primary metals, and other products. As a result, DACH consumes the largest amount of grease. Germany is the leading consumer of grease for automotive manufacturing, distantly followed by Spain and France.

Russia is comparatively a new and less discovered market for the major grease marketers of Europe. Due to extreme cold weather conditions, the Russian market is exhibiting a trend towards high-quality greases that can perform at low temperatures. Russia with the largest rail network in Europe is a significant grease consumer in the off-highway industry. All these trends have been drawing the interest of large grease suppliers in Europe to establish their distribution network in the country.

Turkey is the third-largest grease market in the region. The industrial sector in Turkey includes automotive production, steel, paper, and mining. In mining applications, lithium and aluminum complex greases are commonly used.

Other leading markets in Europe include Iberia (primarily Spain), Italy, Ukraine, France, Poland, and the United Kingdom. All of these markets have manufacturing activities covering automotive production, machinery production, steel and aluminum rolling, and mining which drives grease consumption. The marine industry in Europe is a significant consumer of calcium sulfonate greases, whereas the railways consume large quantities of biodegradable greases.

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**Figure 5: Industrial Grease: Demand by Thickener, 2014**

![Chart showing industrial grease demand by thickener with Sodium, Clay, Aluminum, Ployurea, Calcium, Other soap, Other non-soap, and Lithium categories. Total Demand: 680.0 KT. Source: Kline.](chart)
Figure 6: Demand in Europe by Industry, 2014

Source: Kline

Figure 7: Grease Demand in Europe by Base Oil Type, 2014

Source: Kline
Mineral oil-based greases dominate the total grease consumption in Europe with synthetic and semi-synthetic greases accounting less than 10% of the overall consumption. The European market is moving towards synthetic greases, albeit slowly. These greases are used in electrical motors, fan bearings, and other fill-for-life applications operating in extreme conditions, and also in applications where a long life is preferable, for example, wind turbines. The demand for synthetic greases is relatively higher in Northern Europe because of their superior low-temperature performance.

The demand for biodegradable greases is also on an increase in Europe. These greases currently account for less than 5% of the total consumption in the region. Biodegradable greases are primarily synthetic ester-based. Those based on vegetable oils, such as rapeseed and sunflower, are not sturdy enough for industrial applications due to poor oxidative stability. Biodegradable greases are finding use in applications such as water purification plants, water locks on rivers, agriculture, forestry, mining, and railway curve grease.

**Asia Pacific Overview**

Asia Pacific is the largest market for grease. Primary metals manufacturing industries is the largest end-user followed by mining, off-highway, and transportation equipment manufacturing. China is the leader in consumption of industrial greases in Asia Pacific by a wide margin.

The other leading markets in the region include Japan, India, South Korea, Indonesia, Thailand, and Taiwan. Together, the top five markets account for close to 90% of the total demand.

Within China, the main end-use industries include primary metals, and off-highway transportation, such as aviation, marine, and railway. In China, most of the steel production is located in the coastal areas, especially the Bohai Economic Rim. Therefore, this area is the demand center for industrial greases in China. Additionally, provinces in the East and South coast of the country, such as Shanghai and Guangdong, also have a significant demand for industrial greases, due to the presence of production plants for chemicals and related products.

In Japan, the key end-use industries consuming grease include transportation equipment manufacturing and general manufacturing, especially fabricated metal products. Japan has one of the largest automotive industries in the world and accounts for 11% of the global automotive production. The greases majorly consumed in Japan are lithium, lithium complex soap-based and polyurea-based greases. Polyurea greases are widely used in steel plants in Japan.

Within India, the key end-use industries include primary metals, transportation equipment manufacturing, off-highway transportation, cement, and general manufacturing. India is the fourth-largest producer of crude steel, second-largest producer of cement, and has the fourth-largest railway network in the world. Although conventional simple soap-based greases still account for a large share of grease consumption, there is also a trend towards using high-performance and synthetic greases in some select applications. One such application is in cement plants, where high-performance polyurea greases are sometimes used in high-temperature applications and aluminium complex greases are used in open gear girths. Polyurea greases have also made some inroads in the steel industry in India.
Mineral oil-based greases dominate grease consumption in the Asia-Pacific region. Synthetic and semi-synthetic oil-based greases account for just over 5% of the total. Synthetic greases are used primarily in severe applications like steel mills, wind turbines, and food processing. Consumption of biodegradable greases is less than 1% of total. Consumption of biodegradable greases is seen primarily in markets such as Japan and Australia.

North America is the third largest region in terms of industrial grease consumption. The mining industry, including mining of metals and non-fuel minerals is the leading end-user, followed by primary metals, and transportation equipment manufacturing industries. The United States is the largest market in North America by a wide margin, followed by Mexico and Canada.

Mining is the leading end-use for industrial grease in North America. This is followed by off-highway transportation, primary metals, and general manufacturing. The grease demand by the top three end-use segments has not shown much growth in recent years as a result of the increased consumption of high-performance and synthetic greases, and installation of grease application systems, which are designed to prevent over-greasing. Other segments that have significant demand for greases in North America include power generation, off-highway transportation, oil and gas, general manufacturing, and food and beverage processing.

The grease consumption in the three countries in the region follows the relative size of the manufacturing sector in the three economies. Within the United States, grease consumption is concentrated in the Mid-western and Eastern regions, as most of the industrial activity is concentrated in these regions. End users in the United States and Canada are increasingly moving towards high-performance synthetic greases, due to the extended effective life of synthetic greases, better performance, and low temperature characteristics. These end users are also making attempts at reducing over-greasing by installing hydraulic shut-off grease fittings in their equipment. Hydraulic shut-off grease fittings help in automatically stopping the flow of grease into the equipment once a given pressure is reached. Increasing number of end users, especially in primary steel and manufacturing, are investing in this technology. This results in reducing the consumption of grease in the equipment.

In Mexico, the leading industrial segments that consume greases include transportation equipment, fabricated metal products, primary metals, machinery, and mining. A rapid expansion of the manufacturing sector in Mexico in the recent years, especially the automotive and its ancillary industries, has contributed to a healthy growth in grease consumption in the region. However, as against the trend in the United States and Canada, end users in Mexico do not exhibit a strong trend towards high-performance and synthetic greases. End-use industries in Mexico still use conventional greases in most industrial applications.
Figure 10: Grease: Demand in North America by Industry, 2014

Source: Kline

Figure 11: Grease: Demand in North America by Base Oil Type, 2014

Source: Kline
Mineral oil is the leading basestock type used in North America, for soap as well as non-soap based greases with more than 90% of the total demand. The demand for synthetic greases, formulated using basestocks such as PAOs, phosphate esters, diesters, polyl esters, and silicone are generally limited to specialty applications, such as aerospace, where temperatures exceed 300 °C.

**Market Outlook**

Over the forecast period of 2014 to 2019, global demand for industrial grease is expected to grow at a CAGR of 0.3%, from 680.0 KT in 2014 to 691.0 KT in 2019.

- Growth in North America and Europe will remain flat as a result of slow industrial activity in these regions.
- Demand for industrial greases is forecast to decline slowly in North America, while in Europe the demand will grow slightly.
- The growth in Europe will be driven by the recovery from the current slowdown, rather than a true economic growth.
- Asia-Pacific will remain flat or even decline slightly from current levels, primarily due to a slowdown in general manufacturing and primary metals in China.
- Demand for industrial greases will grow fastest in the rest of the world, with the largest growth coming from South America.

![Figure 14: Global Grease Demand by Region, 2014 to 2019](image)

Source: Kline

![Figure 15: Global Grease Demand by Industry, 2019](image)

Source: Kline
Opportunities and Challenges

Opportunities

Product type: Mineral oil-based lithium and lithium complex soap based greases will continue to dominate the market. Lithium complex thickened greases in particular are increasingly gaining customer acceptance across a wide range of industries. These greases are cost-effective and have superior load carrying, water resistance, and temperature properties.

The thickener technology is increasingly moving towards multifunctional thickeners. A typical example is calcium sulfonate complex-based greases, where the sulfonate is not just the thickener, but it is an EP additive and corrosion inhibitor as well. These greases can resist water and prevent metal surface corrosion, along with exhibiting good load carrying properties. Due to such multifunctional characteristics, the demand for calcium sulfonate greases is increasing in heavy-duty and wet applications, such as paper machines, mining, and the steel industry.

Polyurea greases, which have good thermal resistance and provide protection against corrosion, are increasingly being used in long-life or fill-for-life electric motor bearings. These greases have also made inroads into food industry applications.

Industry:

The end-use industry is slowly but surely changing its focus from price to value. As an example, using a better and more expensive grease, the end user can improve energy efficiency and save energy costs, as well as reduce downtime and maintenance costs. End users are increasingly moving towards lithium complex greases as a replacement for multipurpose simple lithium soap greases. For more specific performance requirements, such as high-temperature performance, calcium sulfonate and polyurea greases are preferred.

In addition to this, bearing OEMs and end users are continuously looking for suppliers who can tweak their formulations to suit their specific requirements. Thus, there is always an opportunity for a customized product, but the approval process may be a barrier.

In terms of end-use industries, most growth opportunities lie in primary metals, mining, and the power generation sector. These end-use industries are rich in specialty applications in terms of high temperature, water washout, and loading, which require high-performance greases.

Grease is also becoming popular for open gears which were previously oil lubricated. Greases do not leak easily and extend the life of the gear. End users are exploring the use of soft greases with stability and stiffness for these applications.

Opportunities in food grade greases are limited. The consumption of these greases can be promoted on a platform of food safety and liability protection.

Technology: Centralized grease distribution systems are gaining popularity in industrial and heavy-duty mobile equipment, especially where repetitive lubrication is required at multiple points.

− These systems range from simple single-port lubricator to complex dual-line greasing points, operating in conjunction with timers, sensors and alarms. Centralized greases distribution helps in pumping small amounts of grease at frequent intervals to the bearings, thus keeping the bearing greased without manual intervention.

− Greases that are recommended to be used in such systems must possess excellent pumpability characteristics, particularly at a low shear rate. For example, polyurea greases, which have good pumpability characteristics and can prevent water and abrasive foreign particles from entering the bearings, are recommended for such applications. Increased interest in such centralized systems will provide grease suppliers with opportunities to push through better quality and more expensive greases in the market.

Challenges

The industrial grease market can be categorized into two broad categories: lower cost, multipurpose greases that are used in less technically challenging applications and high cost specialized greases that are used in more technically challenging applications.

The higher technology grease category is increasingly complex, with the improvements in lubrication technology, as well as with the introduction of new equipment that run at higher loads and temperatures. It has become extremely important for specialized grease suppliers to keep abreast with new technological introductions in lubrication and to tweak their products accordingly as required.

Synthetics and biodegradable greases are likely to remain niches products in most end-use industries. Although synthetic greases provide performance benefits at high temperatures, they face a strong competition from high-performance mineral oil-based greases.

This is because good quality mineral oil-based greases, such as lithium complex, are capable of withstanding peak operating temperatures of 240 °C for short periods and continuous operating temperatures of 150 °C. Synthetic basestocks are usually required when continuous operating temperatures are equal to or more than 200 °C. Biobased greases are not catching up in most regions of the world due to their inferior performance in the past. The use of these greases is limited to applications where it is mandated by law.

Approval and introduction of a new higher performance grease is usually a big challenge as end users are averse to taking risks and unwilling to take a unit offline to flush out an old grease and apply a new one.

Educating grease end users is a big issue, especially in industries where grease has a small role in overall lubrication.

− With a proliferation of grease products based on different thickeners and base oils, the end user is often at a loss in
making a choice.
− In such a situation, it is difficult to guide an end user to a higher-cost higher-performance grease when low-cost alternatives abound.

Rising raw material prices is a huge challenge especially to pure marketers. Given the low-cost image of grease, it is difficult to pass on cost increases to end users. The industry has suffered in the past from the high cost of lithium on account of its high demand from lithium batteries.
− Similarly, growth in biofuels has pushed up the prices of complexing acids.
− Group I basestock prices have also increased especially for higher viscosities

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October 31 – November 2, 2017
2017 Chem Show
The Event for Processing Technology
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www.chemshow.com

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

October 6-9, 2018
ILMA Annual Meeting
JW Marriott Desert Springs Resort & Spa
Palm Desert, CA

June 9 – 12, 2018
NLGI 85th Annual Meeting
The Coeur d'Alene Resort
Coeur d'Alene, ID

June 8 – 11, 2019
NLGI 86th Annual Meeting
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