NLGI SPOKESMAN

Serving the Grease Industry Since 1933 - VOL. 86, NO. 2, MAY/JUNE 2022

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ON THE COVER

Happy Summer!

PRESIDENT'S PODIUM

Jim Hunt
NLGI President
2020 – 2022

Dear NLGI Family,

As always, we hope that you and your families are healthy and happy. Where has the time gone? Seems like only yesterday I was handed over the virtual gavel in my incoming NLGI President speech. Never dreamed my NLGI Presidency would be shadowed by a global pandemic. Sometimes that is the unfortunate luck of the draw. The good news is that the NLGI was still very successful in achieving our key strategic priorities. The situation may have changed but the NLGI's commitment remained stronger than ever. The NLGI has revamped our key strategic priorities and we will continue to work diligently to accomplish each and every one of them to ensure we bring value to all our NLGI members.

I would like to take the opportunity to thank the NLGI BOD and members for allowing me this humble opportunity to be your " El Presidente" during these unprecedented times. I have many fond memories and some regrets during my NLGI Presidency but, mostly fond memories. My biggest regret was not having the opportunity to spend more personal time with each and every NLGI member to ensure that the NLGI is providing the level of service and value they expect. Your feedback is so welcome and insightful. I also wanted to have more discussions with our NLGI members to define how we can continue to improve the value we offer our members. Although I am no longer the NLGI Membership Chair, ensuring the overall satisfaction of our NLGI members will always be a high priority for me personally. Once again, the NLGI is truly a family and keeping the family members happy and safe will always be our ultimate goal.

Please keep in mind that the 89th NLGI Annual meeting will be at the Westin Harbour Castle in Toronto Canada on June 12-15. Please plan to join us this year for what we expect this to be one of our best annual meetings ever. There will be numerous opportunities to network with your friends and business associates. The NLGI AM will also offer exciting speakers presenting valuable industry related topics. We will continue to provide stellar educational classes instructed by some of the most knowledgeable professionals in the grease industry. If you have not signed up for the meeting, we highly recommend that you do so to ensure that your hotel room is secured. Looking forward to seeing you all there and getting the band back together.

As I ride out into the sunset as your NLGI President, please know that I will continue to work diligently behind the scenes with the rest of your NLGI BOD on your behalf. It is also important that you all know that the NLGI BOD members are honored to represent our NLGI members and our companies. Truly an amazing blessing for us all. One we do not take for granted. Truly look forward to seeing you all at the NLGI meeting. We will have the opportunity to celebrate life in style.

In closing, I thought it may be appropriate to quote a verse from a very famous song. "And now, the end is near and so I face the final curtain. My friends, I'll say it clear I state my case in which I'm certain. I've lived a life that's full. I traveled each and every highway. But more, much more than this. I did it my way. Yes, I did and I am grateful for the amazing opportunity .

 Once again, we want to wish all of you and your families the very best life has to offer.

Hope to see all of you at the NLGI AM in June.

Jim Hunt
NLGI President

Industry Calendar of Events 2022

2022 NLGI 89th Annual Meeting	**June 12 - 15, 2022**	Toronto, ON Canada	NLGI 89th Annual Meeting
Lubricant Expo	**September 6 - 8, 2022**	Messe Essen, Germany	Lubricant Expo
ILMA 2022 Annual Meeting	**October 1 - 4, 2022**	Marco Island, FL	ILMA Meetings
ELGI Autumn Events	**October 24 - 27, 2022**	Amsterdam, Netherlands	ELGI Autumn Events

Warm Welcome to our New NLGI Member

Dynamic Green Products Inc	*Marketer / Distributor*	USA
Pilot Thomas Logistics	*Marketer / Distributor*	USA
SMART PETROLEUM TECH, LLC	*Technical*	USA

Advertiser's Index

LUBRICANT EXPO

THE BEARING SHOW

6 - 8 September 2022
Messe Essen, Germany

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TWO CONNECTED INDUSTRIES:

Lubricant Expo & The Bearing Show combine together to provide attendees with the largest exhibition and conference from these industries. The free-to-attend event features the full range of lubrication and bearing solutions, spanning each value-chain, from raw chemicals and additives, instrumentation, equipment, manufacturing and testing solutions, to cutting edge finished lubricants and the latest bearings for high-performance applications.

CONFIRMED SPEAKERS:

Tanja Illic
Managing Director
Nanol Technologies

Juergen Ulmer
Country Manager
Chevron Deutschland GmbH

Annie Jarquin
Director of Global Business Development
Kline's Energy Management Consulting Business

Apu Gosalia
Sustainability Expert Adviser, Senator at **Senate of Economy** Partner at **Fokus Zukunft**

Maurizio Abbondanza
Sustainability Director
Infineum International Ltd

Prof. Thomas Norrby
Technical Manager – Lubricants
Nynas AB

Conference Themes will Include:

- Lubricants sustainability
- Meeting the Evolving Needs of Lubricant Customers
- The Lubricants Supply Chain – Challenges and Management
- Solutions for e-mobility and advanced ICE applications
- Lubricant R&D innovations
- Gaining energy efficiency in demanding environments
- Plant lubrication strategies
- Digitalisation
- Increasing performance for OEM's

Register for your free pass at www.lubricantexpo.com

#LEX22 #TBS22

NLGI 89TH ANNUAL MEETING
Finding The Green In Grease

JUNE 12-15, 2022
Westin Harbour Castle | Toronto, ON Canada

Agenda	Price List	Hotel / General Info	COVID-19 Info / FAQs
Exhibitors & Sponsors	Industry Speaker	Educational Courses	Optional Events
Register HERE	Attendee List	2022 Award Information	Technical Sessions

Cancellations received in NLGI's office through May 6, 2022, will received a 100% refund.
Beginning May 7, 2022, cancellation will only receive a 50% refund.

NLGI 89TH ANNUAL MEETING
Finding The Green In Grease

JUNE 12-15, 2022
Westin Harbour Castle
Toronto, ON Canada

SUNDAY June 12, 2022

6:30 AM - 1:30 PM	Golf Tournament	Offsite - Lionshead Golf Course
8:00 AM - 5:00 PM	Basic Education Course Day 1	Marine
8:00 AM - 5:00 PM	Advanced Education Course Day 1	Pier 2 & 3
12:00 PM - 2:00 PM	Exhibit setup	Metropolitan Ballroom
2:00 PM - 5:00 PM	Registration / Exhibits Open	Metropolitan Ballroom
2:30 PM - 4:30 PM	Board of Directors Meeting	Harbour A
4:45 PM - 5:45 PM	New Member/First Timer Reception	By Invitation Only
5:45 PM - 6:45 PM	Welcome Reception	Harbour Ballroom & Foyer

MONDAY June 13, 2022

7:00 AM - 5:00 PM	Registration Open	Metropolitan Ballroom
7:00 AM - 8:00 AM	Networking Breakfast (dedicated exhibitor time)	Metropolitan Ballroom
8:15 AM - 8:45 AM	Opening General Session	Frontenac Ballroom
8:45 AM - 9:55 AM	Industry Speaker Panel Discussion	Frontenac Ballroom
10:15AM - 5:00 PM	Basic Education Course Day 2	Marine
10:25 AM - 5:00 PM	Advanced Education Course Day 2	Pier 2 & 3
10:00 AM - 10:30 AM	Break	Frontenac Ballroom Foyer
10:30 AM - 11:55 AM	Technical Session 1	Frontenac Ballroom
11:55 AM - 12:55 PM	Networking Lunch (dedicated exhibitor time)	Metropolitan Ballroom
1:00 PM - 1:45 PM	Awards Ceremony	Frontenac Ballroom
1:45 PM - 2:00 PM	Break	Frontenac Ballroom Foyer
2:00 PM - 3:30 PM	Technical Session 2	Frontenac Ballroom
3:00 PM - 3:30 PM	Break	Frontenac Ballroom Foyer
3:30 PM - 4:45 PM	Bio-Based Working Group Meeting	Frontenac Ballroom
5:00 PM - 6:00 PM	Exhibitor Happy Hour (dedicated exhibitor time)	Metropolitan Ballroom

TUESDAY June 14, 2022

6:15 AM - 8:00 AM	Fun Run	Main Lobby
7:00 AM - 5:00 PM	Registration Open	Metropolitan Ballroom
7:00 AM - 8:30 AM	Networking Breakfast (dedicated exhibitor time)	Metropolitan Ballroom
8:15 AM - 12:10 PM	Technical Session 3	Frontenac Ballroom
10:00 AM - 12:30 PM	Spouse / Guest Activity	Off-site Above E11even
12:10 PM - 1:15 PM	Networking Lunch (dedicated exhibitor time)	Metropolitan Ballroom
1:15 PM - 2:30 PM	Grease Particle Working Group Meeting	Frontenac Ballroom
2:00 PM - 4:00 PM	CLGS Exam	Marine
2:30 PM - 2:45 PM	Break	Frontenac Ballroom Foyer
2:45 PM - 5:00 PM	Technical Session 4	Frontenac Ballroom
3:15 PM - 3:30 PM	Break	Frontenac Ballroom Foyer

WEDNESDAY June 15, 2022

7:00 AM - 1:00 PM	Registration Open	Metropolitan Ballroom
7:00 AM - 8:30 AM	Networking Breakfast (dedicated exhibitor time)	Metropolitan Ballroom
7:00 AM - 8:30 AM	Board of Directors Meeting	Marine
8:30 AM - 9:45 AM	Sustainability Town Hall	Frontenac Ballroom
9:45 AM - 10:00 AM	Break	Frontenac Ballroom Foyer
10:00 AM - 12:10 PM	Technical Session 5	Frontenac Ballroom
12:10 PM - 1:15 PM	Networking Lunch (dedicated exhibitor time)	Metropolitan Ballroom
1:30 PM - 3:00 PM	Exhibit Teardown	Metropolitan Ballroom
1:30 PM - 3:45 PM	Technical Session 6	Frontenac Ballroom
3:45 PM - 4:00 PM	Break	Frontenac Ballroom Foyer
4:00 PM - 5:15 PM	Food Grade Working Group Meeting	Frontenac Ballroom
6:00 PM - 9:00 PM	Closing Party	Off-site Hockey Hall of Fame

COVID-19 FAQs

*Information provided as of June 6, 2022

NLGI 89TH ANNUAL MEETING
Finding The Green In Grease

1. **You must use ArriveCAN to provide the mandatory travel information before and after your entry into Canada.**
   - This can be downloaded via Apple Store or Google Play. The link below gives you specific step by step instructions of what is required for you to prepare and upload to the app prior to your travel to Canada. https://www.canada.ca/en/public-health/services/diseases/coronavirus-disease-covid-19/arrivecan.html
   - Attendees should plan to bring their passport and proof of vaccination.

2. **What COVID-19 requirements are there to enter Canada?**
   As of April 2022, those entering Canada must:
   1. be fully vaccinated, meaning:
      - have received at least 2 doses of a vaccine accepted for travel, a mix of 2 accepted vaccines
      - or at least 1 dose of the Janssen/Johnson & Johnson vaccine
      - have received your second dose at least 15 calendar days before you enter Canada

   - Please click here to search requirements for entry into Canada, as each country may be different.

   - Click here for COVID-19 travel / testing requirements.

3. **Is a negative test required to enter Canada?**
   You <u>do not</u> need a negative test to enter Canada; however, you must be fully vaccinated. You are not required to have the booster.

4. **Is a negative test required to return home?**
   You will need a negative test to re-enter the United States if returning by air. If traveling home to another country, please check your local country's government website as each country's testing requirements may be different. Click HERE for additional information on returning to the United States. There are a couple of ways to obtain a negative test:

   1. Obtain a test at a local Shoppers facility. There are several located nearby the hotel, including the three listed below. The cost of the test is $40 CAD. If choosing this option, we encourage you to pre-schedule your re-entry test since there will be a large number of NLGI conference attendees testing on Wednesday, June 15. Below is a link to set up a rapid antigen test. https://shoppersdrugmart.medmeapp.com/schedule/groups/Covid-19-Rapid-Screening

   2. Another option for testing without leaving the hotel is to do a telehealth test. Pack a NAAT or antigen test in your suitcase and sign up for a telehealth appointment via https://onpoint-testing.com/product/certified-teleservice-covid-testing/?gclid=EAIaIQobChMIw-vfIu2U-AIVs-zjBx3DEwZoEAAYASAAEgIZSPD_BwE.
   An administrator will watch you take the test. When it shows negative, they e-mail you the negative document you need to fly home. The test can be done from the privacy of your hotel room, so it's a great option for attendees who don't have time to leave the hotel on Wednesday to get tested due to meetings, etc. If you cannot find an at-home NAAT or antigen test at a local store, you can order one off this website before you leave for Toronto (choose 1-2 days for expedited shipping): https://www.qured.us/shop/products

5. **Will I be subject to random testing?**

    Upon your entry to Canada by air or at a land border crossing, the border services officer may notify you that you have been randomly selected for a mandatory arrival test. Fully vaccinated travelers are not exempt from mandatory randomized arrival testing. If selected for random testing, you no longer have to quarantine as you await your results.

6. **How do I obtain a Visa to attend the meeting?**

    Please click here to search requirements for entry into Canada, as each country may be different. Please contact NLGI HQ (nlgi@nlgi.org) if a visa letter is needed.

7. **What safety protocols will NLGI have in place during the meeting?**

    NLGI will require each attendee to complete a COVID screening form (and potentially an updated waiver if regulations have changed since registration launched in February 2022). Anyone experiencing symptoms will not be allowed to attend the meeting until their symptoms subside. Additionally, NLGI will have hand sanitizing stations throughout the meeting space, provide masks for attendees, offer colored sticker options for badges to identify attendee's comfort level with contact, designate separate entrance and exit doors and provide social distancing as much as possible.

8. **What are current policies at Toronto airports?**

    For all passengers and employees, regardless of vaccination status: To help reduce the spread of COVID-19, all passengers and airport employees must wear a mask at all times. This includes the pre- and post-security screening areas of the terminals, parking facilities, inter-terminal train, sidewalks/curbs outside the terminals and other outdoor public areas. Please note when sitting at a dining establishment while not eating or drinking, you must still wear your mask at all times.

9. **What local mandates or regulations are in place for the Annual Meeting?**

    Patrons no longer have to show proof of vaccination to enter hotel / restaurants / bars. However, in Toronto, masks are required to be worn in indoor public spaces. A mask must cover the nose, mouth and chin without gapping. Face shields and neck gaiters are not alternatives to a mask.

    All annual meeting participants will be asked to complete a COVID-19 health screening waiver before picking up their badge.

    If you have recently had COVID-19, you may want to obtain a letter from your doctor stating that you have had COVID-19, but have recovered and are no longer infected/contagious, even though you continue to test positive. This letter would be needed for the re-entry test to the U.S.

    NLGI encourages you to pre-schedule your re-entry test since there will be a large number of NLGI conference attendees testing on Wednesday, June 15. Below is a link to set up a rapid antigen test. We encourage you to check your local country's government website as each country's testing requirements may be different.

    https://shoppersdrugmart.medmeapp.com/schedule/groups/Covid-19-Rapid-Screening

    In the search field, indicate which Shoppers location you'd like to have the test. Below are a few testing location nearby the hotel:
    - 0.8 mi – Shoppers Drug Mart, 390 Queens Quay W, Toronto, ON M5V 3A6
    - 1.1 mi – Shoppers Drug Mart, 279 Yonge St, Toronto, ON M5B 1N8
    - 1.2 mi – Shoppers Drug Mart, 388 King St W, Toronto, ON M5V 1K2

10. **What is the current COVID-19 situation in Toronto? (cases, hospitalization, etc.)**

    You can view the City of Toronto COVID-19 Dashboard here: https://www.toronto.ca/home/covid-19/covid-19-pandemic-data/covid-19-monitoring-dashboard-data/

TECHNICAL SESSIONS

NLGI 89TH ANNUAL MEETING
Finding The Green In Grease

Monday, June 13

10:30 AM - 11:10 AM	2214	Novel Basestock Technology for EV Bearing Grease Applications	**Sven Meinhardt** *ExxonMobil Chemical Company*
11:15 AM - 11:55 AM	2206	Low Temperature Fluidity of Polymer-Modified Greases	**Erik Willett** *Functional Products, Inc.*
11:55 AM - 12:55 PM		NETWORKING LUNCH	
2:00 PM - 2:40 PM	2208	Polyalkylene Glycols - Synthetic Base Oil Components in Modern Greases with Superior Lubrication and Heat Transfer Properties	**Cristina Schitco** *Clariant* **Stephanie Cole** *Clariant*
2:45 PM - 3:25 PM	2204	A Comprehensive Evaluation of Sustainable Raw Materials in Grease Production	**Mark Miller** *Biosynthetic Technologies* **Matt Kriech** *Biosynthetic Technologies*
3:00 PM - 3:30 PM		BREAK	

Tuesday, June 14

8:15 AM - 8:55 AM		2021 Grease Production Survey	**Chuck Coe** *Grease Technology Solutions LLC*
9:00 AM - 9:40 AM	2211	Fully Loaded: A Study of Additive Response in Meeting NLGI's New HPM + HL Grease Specification	**Shawne Edwards-Zollar** *Afton Chemical Corporation* **Joe Kaperick** *Afton Chemical Corporation* **Amanda Stone** *Afton Chemical Corporation* **Mike Lennon** *Afton Chemical Corporation*
9:45 AM - 10:25 AM	2213	Grease Component Selection Emphasizing Environmental Responsibility and Sustainability	**Cassie Fhaner** *DuPont*
10:45 AM - 11:25 AM	2215	Evaluating Polymer Structure - Property Relationship in Lubricating Greases	**Pang Lin Ong** *Infineum USA L.P.* **Thomas McEleney** *Infineum USA L.P.* **Xiaobo Shen** *Infineum USA L.P.*
11:30 AM - 12:10 PM	2216	Thixotropic Recovery of Lubricating Grease of Varied Thickener Types	**Jacob Bonta** *Valvoline, Inc.* **Johnathan Pham** *University of Kentucky*
12:10 PM - 1:15 PM		NETWORKING LUNCH	
2:45 PM - 3:25 PM	2217	The Response of Phosphonium Ionic Liquid in Lubricating Greases with Respect to Various Tribological Contacts	**Eamonn Conrad** *Solvay* **Jean-Noel Tourvielle** *Solvay* **Derek Voice** *Solvay* **Jinxia Li** *NYNAS* **Mehdi Fathi-Najafi** *NYNAS*

Time	#	Title	Authors
3:15 PM - 3:30 PM		BREAK	
3:30 PM - 4:10 PM	2218	Ball Screw Grease for Responding to Electrification of Automobiles	**Ryosuke Saito** *Kyodo Yushi Co., Ltd.* **Daisuke Tsutsui** *Kyodo Yushi Co., Ltd.*
4:15 PM - 4:55 PM	2219	Sustainable Grease Solutions for a Bevel Gear - A System Perspective	**Johan Leckner** *AXEL Christiernsson International AB*

Wednesday, June 15

Time	#	Title	Authors
10:00 AM - 10:40 AM	2221	High Performance Lubricating Grease, Sustainability and Formulation Suggestions	**George Diloyan** *Nanotech Industrial Solutions, Inc.* **Vasyl Ignatyshyn** *Nanotech Industrial Solutions, Inc.* **Mehdi Fathi-Najafi** *NYNAS AB* **Jinxia Li** *NYNAS AB*
10:45 AM - 11:25 AM	2223	Enabling Technologies for Enhanced Open Gear Greases and Fluids	**Jennifer Clark** *The Lubrizol Corporation* **Dr. Gareth Fish** *The Lubrizol Corporation* **Carlos Nazzario** *The Lubrizol Corporation* **Dr. Robert Dura** *The Lubrizol Corporation*
11:30 AM - 12:10 PM	2224	Ferrous Wear: Effects on Grease Testing & Interpretation	**David Tingey** *POLARIS Laboratories*
12:10 PM - 1:15 PM		NETWORKING LUNCH	
1:30 PM - 2:10 PM	2225	High Performance Biobased Greases for a Circular Economy	**Eric Cline** *Hydrotex* **Krista Pallay** *Hydrotex* **Asghar Shirani** *Hydrotex*
2:15 PM - 2:55 PM	2226	Grease Lubrication of Motor Operated Valves - A Sustainable Approach For the Nuclear Industry and Beyond	**Solongo Lewis** *Canoil Canada Ltd.* **Dr. Henry Sapiano** *Canoil Canada Ltd.* **Dr. Gamil Alhakimi** *Canoil Canada Ltd.*
3:00 PM - 3:40 PM	2228	The Effect of the Combination of Different Types of Extreme Pressure and Antiwear Agents	**Kenji Yamamoto** *ADEKA Corporation* **Akihiro Kotaka** *ADEKA Corporation* **Shinji Iino** *ADEKA Corporation*
3:45 PM - 4:00 PM		BREAK	

2214

Novel Basestock Technology for EV Bearing Grease Applications

The automotive industry is shifting from internal combustion engines (ICE) to alternative driveline concepts such as hybrid or full electric engines in order to reduce CO2 emissions and to improve fuel economy. As a consequence novel lubricant solutions are required that are suitable for extreme conditions such as ultra-high temperatures (>180°C), high speeds (>10.000 rpm) and an electrical environment in more compact systems with higher power densities. Furthermore lower base oil viscosities are anticipated to achieve additional energy efficiency improvements of the driveline equipment. In this context advanced base oil technologies for EV bearing greases can provide enhanced oxidation stability for longer bearing life and improved frictional properties for increased energy-efficiency.

This presentation examines the base oil impact on durability and energy efficiency in EV bearing greases based on Lithium Complex and PU thickener technology. For this study greases with GrIII, GrIV and novel GrIV basestock technology were tested in deep groove ball bearings on a high-speed bearing test rig. The high-temperature stability was determined by FAG FE9 testing.

Sven Meinhardt *is a Marketing Technical Support Engineer for ExxonMobil Chemical's Synthetics business. As a Phd Chemist, he has worked with the chemical and lubricants industry in a variety of areas for 23 years. A native of Essen, Germany, he studied Chemistry at the University of Dortmund with a focus on Organic Chemistry before joining Mobil Schmierstoff GmbH in Hamburg as Sales Representative for industrial lubricants in 1998. Following the Exxon-Mobil merger he was hired by ExxonMobil Chemical working in various commercial functions before joining the Synthetics Business Unit as a Business Development Manager in 2010. In his current assignment he builds on his extensive technical knowledge in lubricant applications and advises customers on the use of synthetic basestocks for the development of next-generation lubricants that can meet the increasing performance requirements.*

2206

Low Temperature Fluidity of Polymer-Modified Greases

Greases are often modified with an array of polymeric additives ranging from natural rubber latex to highly engineered synthetic viscosity modifiers and base stocks. These additives can provide quantitative benefits to water resistance, oil bleed reduction, improved yield, and mechanical stability when properly selected.

However, polymer additives are often scrutinized as limiting factors in achieving good low temperature fluidity for applications under cold conditions. For lubricants, it has been shown that proper selection and treat of polymers is key. We now seek to explore this relationship in grease and test anecdotal evidence about polymers and their effect on fluidity.

This work addresses the questions:
• Do high molecular weight materials (i.e. polymers) grease affect low temperature fluidity?
• If so, how does the structure and molecular weight correlate with effect on fluidity?

A variety of commercial polymer chemistries have been evaluated in #2 simple lithium greases. ISO 150 base fluids were made using PAO6 plus various viscosity modifiers and heavy base stocks. PAO6 acts

An initial screening of low temperature fluidity is made using a modification of ASTM D2983 'low temperature Brookfield viscosity' for high throughput screening of many samples. Select samples of interest were then evaluated by DIN 51805 Kesternich and ASTM D1478 low temperature torque against NLGI grease specifications.

Erik Willett *is vice president of technology and development at Functional Products Inc. He earned his doctoral degree in polymer science at the University of Akron and has received the NLGI Development Author Award and PCC Gonsalves Memorial Award. Erik leads the development of polymer-based lubricant additives and demonstrates his team's work in trade magazines like NLGI Spokesman, Lubes n' Greases, and TLT.*

2208

Polyalkylene Glycols - Synthetic Base Oil Components in Modern Greases with Superior Lubrication and Heat Transfer Properties

A grease formulator must consider many criteria when selecting proper components to manufacture a grease. The selection includes a variety of considerations, such as choosing the oil type and viscosity, thickener type, additives, the stability of the entire composition, application condition, to name a few. The base oil can make up to 90% of the grease composition and influences several grease properties, e.g., lubrication, low and high-temperature behavior, material and chemical compatibility, thermal and electrical conductivity. This presentation aims to show how a class of synthetic oils, called generically polyalkylene glycols, can bring significant value when formulating greases and meet the grease formulators' modern requirements. The structure and several relevant properties of polyalkylene glycols are discussed. A few grease formulations based on this class of synthetic oils and their properties are shown. The polyalkylene glycols class of synthetic base oils possesses especially superior lubrication properties and excellent heat transfer properties.

Cristina Schitco *is Technical Application Manager at Clariant based in Clariant Innovation Center in Frankfurt am Main, Germany. Cristina is responsible for the product management of the industrial lubricants portfolio in the EMEA region. Her work involves cross-functional work with various interfaces such as Research & Development, Marketing, Sales, Production, and Quality Assurance. Cristina's educational background includes a Ph.D. in Materials Science focusing on ceramics for energy applications awarded in 2016 from Technical University Darmstadt, Germany. Before joining Clariant, Cristina held a Research Engineer position in metal processing*

Stephanie Cole *joined Clariant Corporation in July of 2019 and is working as the Sr. Formulation Chemist for the Industrial Lubricants business unit in North America. Stephanie received her Bachelor of Science in Chemistry and a minor in marketing at the University of Houston, located in Houston, Texas. Stephanie has eight years of knowledge in the industrial lubricant field, including industrial cleaning formulation and application and metalworking fluid formulation and application. Her current position at Clariant Corporation is to translate customer needs to technical solutions by understanding the application benefits of Clariant's portfolio through formulation and data generation.*

2204

A Comprehensive Evaluation of Sustainable Raw Materials in Grease Production

The market demand for sustainable, bio-based base oil and additives is growing, but what makes these greases sustainable? The terminology in the sustainability landscape is confusing. In this session, the speaker will clarify key terms such as biobased, biodegradable, decarbonization, carbon footprint, bio-content etc. The speaker will also address the latest regulatory requirements and addresses the key issues of performance. From this session, attendees will learn about the key terms prevalent in the grease industry today, ad what key pitfalls to look out for in developing a sustainable grease offering. As many grease manufactures adopt strategies toward sustainable products and carbon negative footprint goals, the definitions become more important. In this session we will distinguish facts from fiction when it comes to sustainability and discuss the advantages and disadvantages of said strategies. In addition, we will cover the importance of a Life Cycle Assessment and
all that assessment encompasses and how to effectively dissect the important elements of a Life Cycle Assessment.

Mark Miller *is the CEO of Biosynthetic Technologies (BT), an Indianapolis-based company that provides high performance, renewable, non-toxic, biodegradable petroleum replacement. Prior to BT, he co-founded and was CEO of Terresolve Technologies, Ltd. A globally recognized environmentally safe chemical products company. He has engineered, sold and marketed environmentally acceptable lubricants and base oils for over 30 years. Mr. Miller is Vice Chair of ASTM Subcommittee D02.12 on Environmental Standards for Lubricants and the 2022 Technical Editor for STLE's TLT magazine. He has a B.S. in Chemical Engineering from Tufts University and an M.B.A. from Manhattan College and is the Entrepreneur-in-Residence and a business professor at The Ramapo College of New Jersey. Mark also sits on the Board for The National Foundation For Animal Rescue (NAFFAR) and he and his wife, Shari, have adopted more than their share of homeless critters.*

Along with being COO of Biosynthetic Technologies, **Dr. Matthew Kriech** *supports Heritage Research Group and The Heritage Group in evaluation of potential new projects and investments. Prior to his current role, he led the transition team for THG- The Center and worked for Asphalt Materials Inc. in developing predictive economic models. He has also served as General Manager of PIZO and Supply Chain Manager, Tolling Manager, and Business Excellence leader for Monument Chemical. Matt received his B.A. from Wabash College in 2000 and his Ph. D. from the University of Utah in 2005, where he studies protein-lipid interactions using non-linear optical spectroscopy. Prior to returning to Indiana, he worked for ATK as a "Rocket Scientist" in Utah, helping to test and develop state of the art rocket propellants. Matt serves on local charity boards for cancer and diabetes. In his spare time, he enjoys outdoor activities, spending time with his family, and brewing beer as owner of Wabash Brewing.*

2021 NLGI Grease Production Survey

The NLGI Grease Production Survey continues to be the single most comprehensive global report on lubricating grease production. It tabulates the global production of grease providing a snapshot of growth by thickener type and base oil type, organized by geographic region of the world. This paper will provide a summary overview of the key results and trends from the completed 2021 production survey.

Chuck Coe *holds a BS Chemical Engineering from the Pennsylvania State University, along with the NLGI CLGS professional certification. He worked for Mobil and ExxonMobil for over 32 years, including 6 years as ExxonMobil's Global Grease Technology Manager and many years as an industrial oil and grease formulator and technical advisor. He retired from ExxonMobil and launched Grease Technology Solutions LLC, a grease training and consulting business in 2009.*

He is a past president of NLGI, currently on the Board of Directors, and is the Grease Education Course Chair of STLE. He has authored a number of technical papers and articles on grease and received Best Marketing Paper and Best Paper awards from both NLGI (2008) and ELGI (2009), and both the John A. Bellanti Memorial Meritorious Service Award (2012) and the NLGI Fellows Award (2015) from NLGI, along with the NLGI Award for Educational Excellence (2019), and in 2021 he received the Award for Achievement, NLGI's highest award. He was most recently the technical lead for the development of the new NLGI High-Performance Multiuse (HPM) grease specification.

2211

Fully Loaded: A Study of Additive Response in Meeting NLGI's New HPM + HL Grease Specification

While much of the sustainability discussion with regard to lubrication is focused on the footprint of the lubricant, the reduction of wear and improved protection under extreme pressure leads to a net positive benefit on the environment by extending machine life, lowering friction and improving overall efficiency. This so-called "handprint" can be greatly influenced by additive selection and optimized grease formulations for specific applications.

NLGI's new set of industry specifications for High Performance Multiuse (HPM) greases includes a category designed for applications needing additional performance under High Load (+HL). This category targets higher performance in standard bench tests such as 4 Ball EP and Wear but also introduces two relatively new methods for grease evaluation using the Optimol SRV instrument. These new tests are both ASTM standards and evaluate greases for extreme pressure performance (ASTM D5706) and fretting wear protection (ASTM D7594). A study was carried out in lithium complex grease to understand the appetite of these two oscillating, ball-on-disc tests for additive componentry and to allow optimization of a grease formulation to meet all four of these "+HL" tests. The work was carried out using advanced statistical techniques to make the best use of time and resources. Discussion of the approach, process and conclusions will be presented.

Shawne Edwards-Zollar *is a Customer Technical Service Specialist for the North American Industrial and Grease teams at Afton Chemical Corporation. Over the last four years, she has provided support for National and ILMA accounts focusing on Grease, Hydraulics, Gears, Turbine, and Slideway technologies.*

Shawne has a plethora of experience in Environment, Health & Safety with expertise in the Globally Harmonization System for Classification and Labeling of Chemicals (GHS), Responsible Care Management System (RCMS), Global regulations and hazard communications. Additionally, she is a chapter author for NLGI Grease Guide.

Shawne is a member of the National Association of Lubricating Grease Manufacturers, Inc. (NLGI), Society of Tribologists & Lubrication Engineers (STLE), ILMA's SHEERA and MW committees, the American Chemistry Council's Regulatory Advocacy and Information Network (RAIN) team, as well as a reviewer for NLGI's Editorial Review Committee.

Joe Kaperick *is a Senior R&D Advisor for Greases at Afton Chemical Corporation. Joe began working for Afton in their St. Louis manufacturing facility as an Analytical Chemist in 1991 and moved to their Richmond, Virginia headquarters in 1994. Joe received a Master's Degree in Analytical Chemistry from St. Louis University as well as undergraduate degrees in Chemistry, Fine Arts and Classical Humanities. He has been in the Industrial R&D area with a primary focus on Grease since 1999.*

Joe has been serving on the NLGI Board of Directors since 2007 and has been recognized as a Certified Lubricating Grease Specialist by NLGI. He is a member of STLE, the chair of the joint NLGI/ELGI Working Group on Grease Particle Evaluation, the Chair of Section G.01 Chemical and Laboratory Tests for ASTM and is currently serving as Previous Past President on the NLGI Board.

Amanda Stone *is a Statistics Specialist for all R&D at Afton Chemical Corporation. Amanda began working for Afton in their Richmond, Virginia headquarters as a Statistician in 2016.*

Amanda received a Master's Degree in Statistics from Virginia Polytechnic Institute and State University, as well as undergraduate degrees in Statistics and Mathematics from James Madison University. She has been working with Industrial R&D for her entire career, since 2016.

Mike Lennon *joined Afton Chemical in 2012 and has spent the last 8 years in the Industrial R&D lab in Richmond, VA with a primary focus on grease manufacturing and testing techniques. He has actively supported many Afton publications in the grease area with his testing expertise and knowledge. He is also an active member of the Grease Particle Evaluation Working Group and was an instructor in the NLGI Hands-On Training Course in 2019.*

2213

Grease Component Selection Emphasizing Environmental Responsibility and Sustainability

As industry sustainability emphasis grows, attention must also be given to environmental and health hazards present and/or created during grease manufacturing and end-use. Achieving "clean" products is not simple and takes careful consideration of raw material sources, synthesis processes, additives, composition changes during storage, grease-substrate interactions, grease contaminants, and end-of-life grease disposal. Monitoring and analyzing complete grease lifecycles, and all subsequent low-concentration contaminants is not feasible. However, reduction of the creation of harmful substances such as aldehydes, peroxides, cyclics, PFAS, etc. can be achieved through vigilant chemical consideration of base oil, thickening system, manufacturing process, and mindful end-use selection. In this paper, some well-known and not-so-well-known raw material and grease manufacturing byproducts as well as degradation products are discussed with insights as to why they exist and how to avoid them to help our industry keep pace with environmental responsibility and sustainability.

Cassie J. Fhaner *is a Research Investigator with MOLYKOTE® Specialty Lubricants at DuPont where her responsibilities include new product development of greases and compounds in the laboratory, as scale-up and analytical support of new and current products, and technical review of new product ideas. From 2014 to 2017, she was a Senior Chemist in Analytical Sciences, focusing on small molecule structural identification (liquid chromatography-mass spectrometry) and small molecule quantification (liquid chromatography and gas chromatography) while also serving as subject matter expert in bioanalyses of bacteria and yeast. She holds an Associate in Science in Chemistry from Delta College, Bachelor of Science in Chemistry from Saginaw Valley State University and a Ph.D. in Analytical Chemistry from Michigan State University. She is also a member of the American Chemical Society (ACS) and received an ACS Salute to Excellence Award in 2016.*

2215

Evaluating Polymer Structure-Property Relationship in Lubricating Greases

Polymers are versatile additives widely used in lubricating grease formulations to boost viscosity and viscosity index, enhance water resistance and low temperature performance, control oil bleed, strengthen mechanical stability, increase yield and optimize cosmetics. Unlike other functional additives, one unique aspect of polymer additive selection important to grease manufacturers is ease of use (e.g. handling, incorporation) during the grease manufacturing process. Today, there is a wide variety of polymer chemistries and architectures for grease formulators to choose from, although knowledge and guidance specific to greases may not be readily available or up-to-date. Meanwhile, advance in polymer technological capabilities means growing possibilities for new designs. To provide insights into polymer selection and help guide further design optimization, an updated understanding of the structure – _property relationship in grease context will be desirable.

This study focuses on comparing and understanding the performance attributes and ease of use of polymers of different characteristics. A representative grease manufacturing process with an R&D kettle was used to cook primarily lithium-based greases in mineral and synthetic base oils. The two main polymer types under investigation are olefin co-polymer (OCP) of different shear stability indices and hydrogenated styrene-diene co-polymer in linear and star architectures. In addition to standardized performance tests, customized tests such as rheology are used to assist mechanistic understanding. The effect of polymer composition, molecular weight, architecture and morphologies will be discussed.

Pang Lin Ong

Thomas McEleney *is a Technologist in the Product Innovation and Engineering group at Infineum developing new polymers and functional additives for the grease industry. He has prior experience as an R&D engineer formulating and evaluating synthetic greases for automotive applications. He earned a Bachelor's degree in Chemical Engineering from Villanova University and a Master's Degree in Mechanical Engineering from University of Massachusetts Dartmouth. Tom is a member of NLGI, STLE and AIChE.*

Dr. Xiaobo Shen *is currently a Technologist in the Product Innovation and Engineering group at Infineum USA L.P. Xiaobo graduated from Zhejiang University in 2009 with a B.S. degree in Polymer Science and Engineering and subsequently received his Ph.D. degree from the Polymer Science and Engineering Department at the University of Massachusetts Amherst in 2014.*

Xiaobo joined Infineum USA L.P. in 2014 and has been leading work on developing and commercializing functional polymer additives for passenger car and heavy-duty diesel engine oils and lubricating greases. Xiaobo was awarded the Best Presentation Award at the SAE 2016 International Powertrains, Fuels & Lubricants Meeting. He is a finalist for the 2020 ICIS Rising Star Award Pan America. Xiaobo is a member of NLGI.

2216

Thixotropic Recovery of Lubricating Grease of Varied Thickener Types

In this study, the mechanical degradation and thixotropic regeneration of different lubricating greases are examined using a parallel plate rheometer. Physical degradation and subsequent regeneration are associated with the microstructure of the thickeners when exposed to cycles of shear and rest. Three greases are prepared: lithium 12-hydroxystearate, fumed silica, and polyurea. All materials are based on ISO 150 naphthenic base oil, allowing for a systematic, fundamental investigation of thickener effects on rheological response. Small amplitude oscillatory testing is first used to evaluate the storage and loss moduli of the materials in an undisturbed state. Results from the undisturbed moduli and ASTM D1403 (worked and unworked penetration) are compared. A 1-hour steady shear program is applied to each material, after which G' is tracked over time to gain insight into the microstructure regeneration kinetics. The effect of temperature on the break-down and recovery microstructure is also explored across the materials. Additionally, the impact of % strain used during the recovery phase is explored in one material. The studies carried out detail significant differences in the shear-thinning and thixotropic recovery of the different structural components. The recovery profile of each is fitted to a power law as a quantitative comparison of the time and temperature-dependent microstructural recovery in the materials. This study suggests that rheological analysis may provide significant insight into grease properties that are not observed in the grease structural analyses used in industry. Further expansion on these techniques will provide insights critical to grease design and ultimate use in applications.

Jacob Bonta has 7 years of experience in designing and testing new chemical products for various industrial sectors. He earned his B.S. in Chemistry from Eastern Kentucky University in 2015 and is expected to have his Ph.D. in Materials Science and Engineering from the University of Kentucky by 2024.

Hired by Valvoline in 2018, he leads lubricating grease research and development in North America and supports grease related operations for Valvoline globally as a Product Development Chemist. His graduate research is focused on lubricating grease fundamental material properties. He has multiple patents issued or pending for chemical products with three being specific to lubricating greases. He is a member of SAE, STLE, and NLGI and holds the NLGI CLGS certification.

Jonathan Pham is an Assistant Professor in Chemical and Materials Engineering at the University of Kentucky, leading a group focused on soft materials and interfaces. He received a BS (2010) in Materials Science and Engineering from The Ohio State University and earned a PhD (2015) in Polymer Science and Engineering from the University of Massachusetts Amherst. Prior to joining Kentucky, he was a Humboldt Postdoctoral Fellow at the Max Planck Institute for Polymer Research working on a range of topics, including cell-surface interactions, drop-surface interactions, and soft materials adhesion. Jonathan has been recognized for his efforts in soft materials, most recently through an NSF CAREER award, an ACS PRF doctoral new investigator award, and a 3M non-tenured faculty award.

2217

The Response of Phosphonium Ionic Liquids in Lubricating Greases with Respect to Various Tribological Contacts

There are many challenges facing today's electric vehicle (EV) manufacturers. When selecting EV lubricants and greases, companies often rely on iterative improvements to formulations designed for internal combustion engines. These lubrication systems present challenges and fail to substantially improve system efficiency. Engines running with conventional or modified lubricants in EV lose as much as 30% of efficiency due to losses directly related to lubrication. This presentation demonstrates the responses of phosphonium ionic liquids as metal free/ashless additives to deliver AW/EP properties and thermal/electrical conductivity improvements, beneficial to this application with specific focus on lubricating greases.

Eamonn Conrad *completed his Ph.D. in 2014 in phosphorus chemistry at Dalhousie University (Canada) and followed this with a post-doctoral fellowship at the University of British Columbia (Canada). After completing this he joined Cytec which was later acquired by Solvay. He has been with the company for 8 years first in research and is currently a Global Business Development Manager in the Phosphorus Specialties GBU. With other 15 years' experience in phosphorus chemistry. He supports topics of lubrication, catalysis, thermosets and many others.*

Jean-Noël Tourvielle *earned his PhD in 2014 in the field of process intensification and heterogeneous catalysis from Claude Bernard University (France). After a post-doctoral stay at Quebec University working on tar sands, he joined the Laboratory of Future, a Solvay-CNRS joint lab based in Pessac (France) in 2015. With an initial mission focused on the development of experimental methodologies for data acquisition based on automation & micro/millifluidics, he is currently leading projects on the characterization of physical-chemical properties of Solvay's products.*

Derek Voice *completed his undergraduate studies in Biochemistry and Mathematics at Queen's University (2009) before completing a Master's Degree in Biomedical Engineering at the University of Toronto (2012). He has been employed with Solvay for the past ten years, most recently as a Research Chemist in the Phosphorus Specialties business unit. His work is focused primarily on the development and scale-up of alkylphosphines and derivative products, including phosphonium salts.*

Jinxia Li *received her PhD in Grease Flow and Rheology at the Luleå University of Technology in Sweden. She has a MSc in Advance material Science and Engineering from Luleå University of Technology, and Institute National Polytechnique de Lorraine (INPL), France. She has also a MSc in Chemical Engineering and Technology from Zhejiang University, China. Since January 2016 she joined at Nynas, and her current position is senior engineer to be responsible for the product development of naphthenic base oil in lubrication and grease application with focus on the rheology and tribology perspective.*

Mehdi Fathi-Najafi *earned a MSc in Chemical Engineering and a Licentiate degree in Chemical Engineering Design from Chalmers University of Technology of Gothenburg in Sweden. Mehdi more than 25 years of experience from the global base oil and grease industry and the recipient of Clarence E. Earle Memorial Award. He has one patent and numerous articles published in a dozen publications covering a variety of specialist area, including Filtration, Base oils, Lubricating Greases, Applied Rheology and Tribology. Mehdi joined the Department of Technical and Market Support at Nynas in 2008. His current function is Chief Specialist with focus to support the Lube & Grease industry.*

2218

Ball Screw Grease for Responding to Electrification of Automobiles

Reduction of CO_2 emissions by the electrification and efficient operation of automobiles has proved critical in our efforts to realize the sustainable society as laid down in SDGs, that is largely relied on technological advances in CASE; Connected, Autonomous/Automated, Shared and Electric. To cope with automation and electrification as the fundamental CASE technologies, grease-lubricated automotive components such as linear motion mechanisms with ball screws for electric power steering and electric brake booster are commonly used.

This paper focuses on the development of a CASE-compatible grease, where the formulation and tribological characteristics of grease were examined to solve technical challenges including torque reduction and life extension of ball screw.

Ryosuke Saito graduated from the Faculty of Engineering, Kanagawa University and joined Kyodo Yushi Co., Ltd. in 2012 where he was assigned to the Grease Technology Dept, learning the fundamentals of grease evaluation. Engaged mainly in the development of automotive hub unit grease to promote the fuel efficiency of vehicles. Ryosuke also became involved in the development of lubricating oil and grease for industrial robot reducer and achieved the long life and improved work efficiency of industrial robots. Currently, participating in the development of greases for various electric vehicle parts including electronic power steering and electric brake booster to improve CASE (Connected, Autonomous/Automated, Shared, Electric) technology.

Daisuke Tsutsui graduated from the Graduate School of Science and Technology, Tokyo University of Science in 2005 and then joined Kyodo Yushi Co., Ltd. Was involved in the development of lubricating grease for automotive electronic power steering, achieving the long life and high output of EPS and the development of automotive hub unit grease to promote the fuel efficiency of vehicles.
Currently, Daisuke is involved with managing grease development for various electric vehicle parts including electronic power steering and electric brake booster to improve CASE (Connected, Autonomous/Automate, Shared, Electric) technology.

2219

Sustainable Grease Solutions for a Bevel Gear - A System Perspective

This paper summarizes two recent studies which together highlight both the importance and the complexity of including in-service performance when assessing the environmental footprint of a lubricant.

The first study focuses on the development of a new grease for nutrunner bevel gears. Here we show that the durability and energy efficiency of both the gear and the grease can be significantly enhanced when modern grease formulation solutions are applied. More specifically, the benefits of switching from a mineral oil-based, lithium soap thickened grease to a polypropylene thickener system with synthetic oil is presented.

The second study compares the greases using two different Life Cycle Assessment approaches that highlight the importance of a more holistic, cradle-to-grave approach, incorporating data from bench and field tests, versus a more limited cradle-to-gate approach. The outcome from this study is that including the in-service data reverses the outcome from the cradle-to-gate assessment, demonstrating that a the fully synthetic grease is a much more sustainable alternative when the usage phase is included.

In essence, the core message of this paper is that the performance of lubricated machine elements can have a very significant impact on sustainability assessments and that a grease providing better performance can, even if it requires more resources to produce, be the superior solution.

Johan Leckner *has an MS and PhD in chemical engineering from Chalmers University of Technology in Gothenburg, Sweden. He worked for six years as a researcher, first at the Pasteur Institute in Paris and then at Chalmers University of Technology. In 2009 he joined Axel Christiernsson International as Senior Development engineer and since 2016 he is working as Group Technical Manager. Since 2021, Johan is also part-time Professor in Lubricant Design at KTH Royal Institute of Technology in Stockholm.*

2221

High Performance Lubricating Grease, Sustainability and Formulation Suggestions

Proper lubrication is one of the critical tasks to maintain equipment in working condition, reduce costly downtimes and reduce energy consumption, hence lower CO_2 emission. In a recent industrial scale study [1]. In this study, it was clearly demonstrated a new and profitable relationship between the energy efficiency and reduction of CO_2 emission.

However, it is well known that in order to meet industry demands, grease manufacturers continuously improve the performance of their lubricating greases. The vital parameters such as load carrying capacity, shock absorbance, anti-wear, anti-friction, shear stability, temperature tolerance and ability to handle presence of water are critical for effective performance of the grease and subsequently the life of the tools and/or equipment. Thus, formulators of the lubricating greases have to consider all the above parameters when designing a high performance grease.

This paper presents results of a comparative study of inorganic solids such as molybdenum disulfide (MoS2) and Fullerene-like inorganic particles of tungsten disulfide (IF-WS2) in various type of greases (Li, LiX, AIX and bentonite clay) as well as the impact of the base oils on the overall performance. The results showed up to 50% reduction in wear, up to 3 load stages increase in EP for greases contained IFWS2 against same treat rate of MoS2. Furthermore, we are anticipating a field trial reports.

Dr. George Diloyan *has been spearheading scientific research, new product, and markets development at Nanotech Industrial Solutions, Inc., since 2012. Dr. Diloyan has received his Ph.D. in Mechanical Engineering from Temple University, focusing on nanotechnology, electrochemistry, and material science. Dr. Diloyan also holds two MS degrees in Computer Science and Thermodynamics.*

In his line of work, Dr. Diloyan interacted with over 300 industrial and high-tech companies from Lubrication, Energy, Automotive, Mining, Oil and Gas, and other sectors. A frequent guest at Scientific forums and Industrial conventions, Dr. Diloyan has published several editorials on the benefits and applications of high performance, antifriction, and antiwear components based on inorganic fullerene-like submicron particles of tungsten disulfide, the IF-WS2. The most recent one is about the latest development of water-based, zero-oil, eco-friendly Metalworking fluids and extreme performance super-thin coatings with IF-WS2 at the core.

Dr. Diloyan's extensive experience with applications of nanomaterials is behind his passion for solving industrial problems, but first and foremost - eliminating downtimes, reducing energy consumption, and minimizing environmental impact.

Vasyl Ignatyshyn *is an experienced Mechanical/ Chemical Engineer with a demonstrated history of working in the nanotechnology industry, building complex industrial production system and development processes from lab to commercial scale up.*

Skilled in nanoparticle-based lubricant product and technology development, Over 7 years' experience in nanoparticle dispersant development.

Mehdi Fathi-Najafi *earned a MSc in Chemical Engineering and a Licentiate degree in Chemical Engineering Design from Chalmers University of Technology of Gothenburg in Sweden.*
Mehdi more than 25 years of experience from the global base oil and grease industry and the recipient of Clarence E. Earle Memorial Award.

He has one patent and numerous articles published in a dozen publications covering a variety of specialist area, including Filtration, Base oils, Lubricating Greases, Applied Rheology and Tribology.

Mehdi joined the Department of Technical and Market Support at Nynas in 2008. His current function is Chief Specialist with focus to support the Lube & Grease industry.

Jinxia Li *received her PhD in Grease Flow and Rheology at the Luleå University of Technology in Sweden. She has a MSc in Advance material Science and Engineering from Luleå University of Technology, and Institute National Polytechnique de Lorraine (INPL), France. She has also a MSc in Chemical Engineering and Technology from Zhejiang University, China.*

Since January 2016 she joined at Nynas, and her current position is senior engineer to be responsible for the product development of naphthenic base oil in lubrication and grease application with focus on the rheology and tribology perspective.

2223

Enabling Technologies for Enhanced Open Gear Greases and Fluids

Reduced environmental impact through the choice of suitable lubricants has become an important consideration of many end users of heavy industrial equipment. Traditional base fluids used for the lubricants in these applications were asphalts, residual oils and brightstocks. The asphalts and residual oils have been phased out favor of polyisobutylene (PIB). With the migration to API Group II and higher paraffinic base fluids, there is now a shortage of affordable good quality brightstock.

Polyisobutylenes offer the advantage that they are clear and mating components can be more easily inspected than with traditional black oils that have to be removed in order to complete the inspection. When comparing the efficiency of bright stock and polyisobutylene, no significant differences between them were identified. Polyalphaolefin (PAO) based fluids, gave improved efficiency and gears ran at cooler running temperatures.

As an alternative to the PIB and PAO, a new family of liquid ethylene-propylene polymers were used to develop both grease and fluid lubricants for Open Gear applications. Lubricants utilizing these alternative fluids as base stocks provide a substantial decrease in operating temperature, an improvement in energy efficiency and reduced product consumption compared to traditional lubricants. Additive technologies to further enhance the new open gear lubricants were also explored.

This paper will discuss technologies that can enable grease producers to improve and enhance the development of greases and fluids for open gear applications. By combining these technology approaches of new base fluids and additive systems, lubricants can be developed to meet current and future requirements.

Dr. Jennifer Clark *received her Bachelor of Science at John Carroll University in 2007 and continued her education at SUNY Buffalo where she received her PhD in Organic Chemistry in 2012. In 2012 Jennifer began her career at Lubrizol as a chemist in the Industrial Metalworking group where she focused on rust preventive technologies. After 7 years in Industrial Metalworking, Jennifer became a Product Development Chemist for Grease Additives at Lubrizol. In this role Jennifer focuses on Open Gear Lubricant technologies, grease additives and the development of energy efficient greases.*

Dr. Gareth Fish *works for The Lubrizol Corporation; he started there in 2007. Now a Technical Fellow in the Industrial Additives Technology Group. He is a multiple time (10x) Grease Industry Award winner, including 2 Clarence E Earle Memorial awards and in 2020 the NLGI Award for Achievement. More than 60 papers and 70 teaching classes presented, 3 book chapters and 4 patents.*

Carlos Nazario *is the North America Product Manager of Grease Additives for Lubrizol. He has over 15 years of experience in the lubricants industry and have worked extensively in developing and applying new lubricants for heavy-duty equipment and has formulated specialized extreme pressure greases, gear oils, open-gear lubricants, energy efficient and environmentally acceptable lubricants for heavy-duty equipment and for the general industry.*

Dr. Robert Dura *earned his PhD in Organic Chemistry (2008) at The Ohio State University and a BSc in Chemistry (ACS Accredited) (2002) at Cleveland State University. His postdoctoral studies were in catalyst design at the University of Pittsburgh, from 2008 to 2010. Dr. Dura was involved in small molecule synthesis and drug design at Curragh Chemistries from 2000 to 2003 and from 2010 to 2014, he was with Ben Venue Laboratories studying Lyophilization and Manufacturing support, process intensification and new product development. Dr. Dura joined The Lubrizol Corporation in 2014 and is currently the Grease Technology Manager.*

2224

Ferrous Wear:
Effects on Grease Testing & Interpretation

Recently created ASTM standards (D7718 and D7918) have created a valuable opportunity to examine in-service grease health, asset reliability, and root cause analysis.

When screening grease for various routine properties, environmental contaminants, or root-cause analysis, metallic wear from the component operation is frequently present in the sample. Ferrous content in grease samples can provide some very valuable insight into abnormal mechanical events or possible clues as to installation or application faults. However, these very same metallic particles can also have an impact on a number of different grease testing parameters.

We will shed some light on the major impacts of ferrous wear on in-service grease testing in this informative and illuminating session. Learn more about popular testing methods, as well as their common results and interferences. Discover the how, and the when, of applying the appropriate interpretation of results utilizing the new ASTM D7718 protocols. Follow along as we unearth the importance of accurately understanding the story the results are telling about the grease and component.

Recognizing and perceiving how these interferences can influence the test results is paramount to making informed maintenance decisions that could prolong both the useful life of the grease and the integrity of the asset.

Dave Tingey *has more than 35 years of experience in power generation, industrial, mobile and lubrication engineering industries. His areas of expertise include specialty testing, grease testing, and filter debris analysis. As a Journeyman Millwright/Machinery Repairman in the U.S. Navy, his experience includes repairing and maintaining turbines, power generation, and industrial machinery equipment. Dave has been with POLARIS Laboratories for more than 16 years and is CLS and OMA certified by STLE.*

2225

High Performance Biobased Greases for a Circular Economy

Sustainability and ESG [environmental, social, and governance] are a strategic imperative for companies as consumer demand and government regulation move the world towards a circular economy. High performance biobased lubricants will play a crucial role for improved sustainability within product lifecycles - everything from production to operation to end-of-life considerations - as energy efficiency and environmental impact become a societal imperative for machines of the future. Half of all lubricants used worldwide end up in the environment (Mbohwa 2016), and, while biobased, biodegradable, non-toxic lubricants have long been available, often performance is sacrificed for environmentally friendliness. This study describes the development of biobased greases using advanced base oils and non-toxic additives for enhanced performance in a wide range of applications. The product formulations promise to improve energy efficiency, protect against wear, extend maintenance intervals, and contribute to longer machine life while minimizing harm upon environmental release.

Eric Cline, PhD serves as Chief Science Officer responsible for research and technology development, customer field trials, and scientific outreach at Hydrotex. Two decades of experience R&D includes expertise in lubricants and fuel improvers, pharmaceuticals, photocatalysis, and materials science. Prior to joining Hydrotex, Dr. Cline served as CEO of a technology startup developing antireflective coatings for solar energy and defense applications. Earned a BS in Biochemistry from Trinity University and a PhD in Physical Inorganic Chemistry from Princeton.

Krista Pallay serves as Process Engineer responsible for grease formulation development and technology transfer at Hydrotex. Ms. Pallay started her professional career in a rotational program with Air Liquide progressing to Plant Zone Engineer in Houston, TX followed by Process Safety Engineer for Dyno Nobel in Carthage, MO. Earned a BS ChE from Rensselaer Polytechnic Institute and a MS ChE from Georgia Tech.

Asghar Shirani, PhD serves as Research Scientist responsible for advanced tribology and lubricant applications at Hydrotex. Dr. Shirani earned his PhD in Materials Science from the University of North Texas and has seven years of experience in materials development, thin-film and vacuum processing, formulating bio-lubricants, depositing ultra-high temperature resistance films, and engineering self-lubricating coatings.

2226

Grease Lubrication of Motor Operated Valves – A Sustainable Approach for the Nuclear Industry and Beyond

Valves are a crucial component needed to control the flow of fluid in a process system. For valves that are motor operated, unique lubrication requirements need to be met. This paper looks at a calcium-sulfonate complex grease that continues to meet those needs in several industries, including the nuclear industry. The paper will outline how this grease eliminates the need for multiple products within the valve system and will explore how the performance of this grease contributes to overall sustainability.

Solongo Lewis *is a graduate of the University of Toronto's Chemistry Specialist program (2007) with fifteen years experience in the lubrication industry spanning areas such as used oil analysis, metalworking fluids, regulatory affairs and grease formulation. Solongo is a member of NLGI and STLE and has previously served as Chair of the STLE Toronto Section. She is currently a Senior Products Specialist at Canoil Canada Ltd and has been a Certified Lubrication Specialist (STLE) since 2013.*

Dr. Henry Sapiano *graduated from the University of Windsor with a BSc and PhD in Chemistry. He started his successful 38-year career with British Petroleum, which later became Suncor Energy where he gained experience in the petroleum refining and lubricants industry. Through the span of his career his experience grew, covering all aspects of the industry including supply, logistics, manufacturing and quality control, ultimately landing him in the role of Manager of Research and Development. In this role, he was responsible for and directed the development of Suncor's entire line of industrial products and greases. After an esteemed career with Suncor Canada, Henry's unceasing ambition led him to become one of two owners and Director of Operations, Supply and Product Development at Canoil Canada Ltd.*

Dr. Gamil Alhakimi *gained his BSc/M.Sc from Martin Luther University in Germany and his PhD in Organic Polymer Chemistry from Friedrich Shiller University in Germany. He took a position as R&D manager for a petrochemical complex in North Africa. In the year 2000 Gamil joined the University of Toronto as a research associate. After that he joined Petro-Canada Lubricant R&D in the analytical and de-formulation department. In 2008, Gamil started GL Chemtec International serving the pharmaceutical and biotechnology sector. During this time, Gamil graduated from the Wilfrid Laurier MBA program. In 2010, he bought Canoil Canada Ltd. with his current partner who is an industry veteran. Canoil is currently experiencing a steep growth under the two-partner leadership.*

2228

The Effect of the Combination of Different Types of Extreme Pressure and Antiwear Agents

Several types of antiwear (AW), extreme pressure (EP) agents are known for a grease application, such as ZnDTP, MoDTC, Phosphates, sulfurized olefin and adsorbing type polymers. The effect of each components and combinations are evaluated under the friction and corrosion tests which are listed for NLGI HPM HL specification, such as 4-ball, SRV and CCT. Although the effect of each single components are limited or harmful in some case, combination of those can provide beneficial performance balance. ZnDTP, a traditional EP agent for lubricants, shows positive impact for AW/EP performance especially under 4-ball test but has no or negative impact under SRV. The combination of MoDTC and sulfurized olefin can show synergistic effect, and addition of adsorbing type polymers further enhances the balance of EP and AW performance level. Phosphate reduced fretting wear but sacrifices EP capability. Corrosion inhibitors which are supplementary added to grease formulation to mitigate the corrosion impact of EP agents, occasionally negates the effect of AW/EP performance because of its strong adsorbing property on the metal surface. The choice of base oil can help to maintain the surface phenomena and improve the balance of performance between friction and corrosion. The results indicate careful selection of surface active components is essential for achieving required balance for NLGI HPM HL specification.

Kenji Yamamoto *earned a BA in Functional Polymer Science in 2002 and a Master of Engineering in 2005 from Shinshu University. He joined ADEKA in April 2005 and is a lubricant research engineer in R&D division of ADEKA Corporation. In April 2016, Kenji received the Technology Award from the Japanese Society of Tribologists. Kenji is working for developing friction modifiers, anti-wear agents and EP agents which are consisting of ashless type, phosphate type and organic metal compounds. Mr. Yamamoto has over 50 publications including patents, peer reviewed journal articles, and conference presentations. He is now focusing on energy saving technology for contributing a carbon neutral technology such as friction modifiers, antiwear agents and extreme pressure agents.*

Akihiro Kotaka *graduated in Automobile Maintenance Department from the Hama College of Technology, and joined ADEKA Corporation in 2006. He is the leader of the testing and analytical evaluation team of lubricant department. He is working for Research and Development of lubricating additives including friction modifiers, antioxidants and anti-wear agents, with his specialties in friction tests, engine tests and chemical analyses of lubricants and materials. He is now focusing on energy saving technology for further contribution towards carbon neutrality.*

Shinji Iino *earned a BA in Analytical Chemistry from Keio University in 2002, a Master of Integrated Design Engineering from Keio University in 2004 and in April 2004 he joined ADEKA. Shinji is a lubricant research engineer in R&D division of ADEKA Corporation. He is working for developing friction modifiers, anti-wear agents and EP agents, antioxidants and synthetic base oil for grease applications. Mr. Iino has over 15 patents and international conference presentations. He is interested in product development that contributes to energy conservation and carbon neutral.*

elgi

Save the dates

24th – 27th October 2022

Events Planned

- **ELGI Bi-Annual Working Group Meetings**
  Monday 24th October 2022
- **ELGI Advanced Grease Training Course**
  Tuesday 25th October 2022
- **ELGI-STLE Tribology Exchange Workshop**
  Wednesday 26th & Thursday 27th October 2022

The ELGI Autumn Events will be held in Amsterdam at the Marriott Courtyard in the beautiful surroundings of the Haarlemmer Woods and Lake. Conveniently located 12 minutes from Amsterdam Schiphol Airport with shuttle service for ELGI guests.

A Comparative Study of Greases Manufactured Using Microwaves with Greases Manufactured using Conventional Heating

Lou Honary, Environmental Lubricants Manufacturing, Inc.

Background

Papers about the use of microwaves as a heating source for processing grease have been presented at previous NLGI annual meetings and published in earlier issues of the Spokesman. The invention of microwave grease processing came about after a devastating fire at a biobased grease manufacturing plant (Figure 1) that completely destroyed the plant.

Figure 1 In 2007, a heat transfer fluid leak started a chain of events that led to a fire at a biobased grease plants

Instead of using heat transfer oil or steam in jacketed vessels to heat products for reaction; the energy from magnetic fields of radio waves applied at 915 Megahertz (industrial microwaves) or 2450 Megahertz (household microwaves) interact with the molecules of products resulting in frictional heat. The process which was patented in 2012 at the University of Northern Iowa has been in use in a grease manufacturing plant since 2010. The original design of the microwave-based grease processing was based on manufacturing biobased greases. While this has offered an effective economical solution for manufacturing biobased products, questions remained about the viability of the process for mineral oil-based grease processing. However, after over a decade of improvements and two additional patents the technology was improved to the point of making the process universal to all products including mineral oils.

Simplified, microwaves are most effective when applied to substances with dipolar molecules. They have two waveforms representing their electrical field and magnetic field. It is the magnetic fields of the waves that interacts with the north - south poles of the dipolar molecule to create movement, excitation, and frictional heat. Figure 2 shows a representation of the interaction of the magnetic field of microwaves with a dipolar molecule.
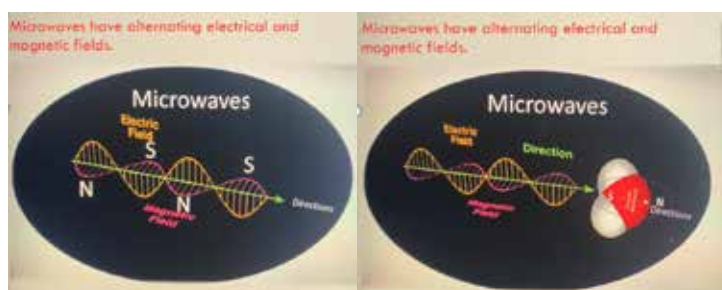

Figure 2 A representation of the interaction of the magnetic field of microwaves with a dipolar molecule.

The polarity of the molecules in mineral oils is different in that more than two dipoles are present thus weakening the overall magnetic energy of each dipole. This in turn results in less excitation and lesser amount of frictional heat in mineral oils when exposed to microwaves than it would with polar materials. To solve this shortcoming, a special coating was incorporated into the vessel that converts the microwave energy to heat and infrared energy. This way, if the polarity of product molecules is such that microwaves pass through it with little loss of magnetic energy, then the wave would excite the coating to result in heat and infrared energy to in turn heat the product. This coating is already used in the food industry for such items as sandwich wraps to allow toasting of bread in microwaves or more prevalently microwave popcorn having a special coating in one side of the bag (the side of the bag with special coating is placed down).

In the original technology for manufacturing biobased grease, microwaves were applied from the top of the vessel which presented a headspace above the product likely filled with evaporative materials some of which could be volatile. Since biobased oils in general have about 200°F higher flash point than mineral oils of the same viscosity, the possibility of flash fire due to surface overheating and arcing is minimal. However, to increase the safety of microwave processing for mineral oils, a patented barrier was designed to allow microwaves entering the vessel from the bottom. This approach eliminated any exposure of microwaves to potentially flammable vapors within the headspace above the products in the vessel.

The technology for universally heating all products regardless of their polarity has been commercialized with commercial vessels in beta testing. Figure 3 shows a picture and an illustration of a commercial vessel with a dual motion system with waves entering near the bottom of the vessel that has a special coating.
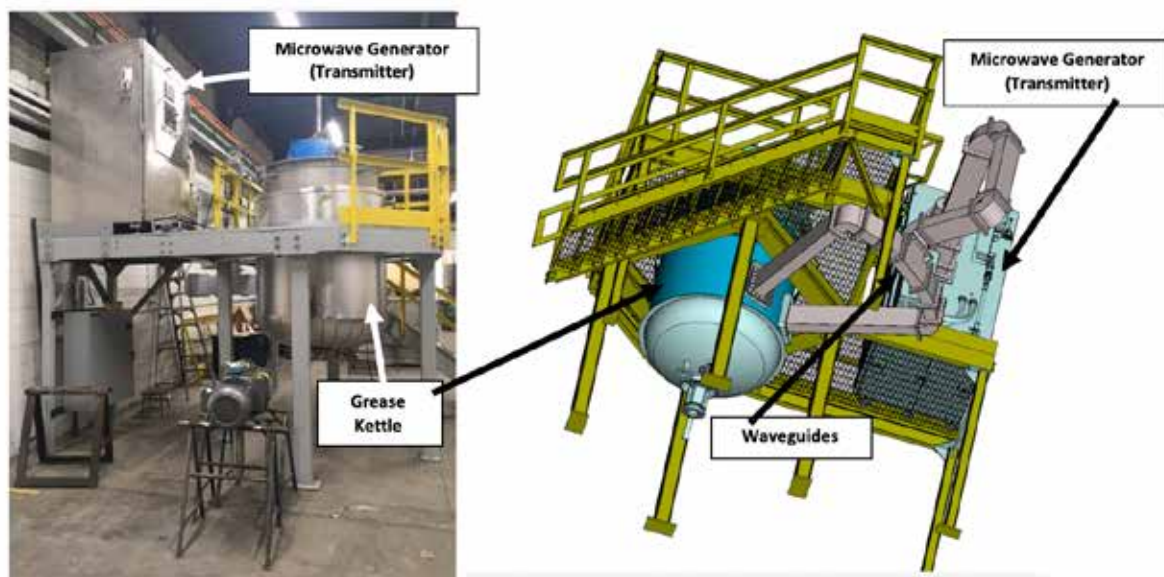
Figure 3 (Left) A picture of a commercial dual motion vessel with waves entering from below the product and has a special coating and (right) an illustration of the same vessel: Courtesy of Patterson Industries

Research Method
At the time of this report the actual microwave kettle capable of heating mineral oils for production quantity was not ready for testing as planned. Instead, the testing was performed in a laboratory setting using a conventional household microwave oven. Since the goal of this project was to test

mineral Oil based greases made in microwaves and by conventional heating, products with two mineral base oils were prepared as follows:

1. Aluminum Complex Grease made with a mixture of Polyalphaolefins (PAO)-100 and Polybutene (PB) as base oil using a mantle for heating -- (two batches made)
2. Aluminum Complex Grease made with PAO-100 and PB as base oil made in a laboratory microwave (2450MHZ) -- (three batches made)
3. Aluminum Complex Grease made with naphthenic base oil (600 cSt at 40°C) on a mantle for heating -- (two batches made)
4. Aluminum Complex Grease made with the same naphthenic base oil in a laboratory microwave (2450MHZ) -- (two batches made)

Grease Process
Despite common misconceptions that microwaves cannot be applied to metallic vessels, microwaves can be applied to many metals and metallic vessels provided the metal is not ferromagnetic. Additionally, the reason for arcing when some metals are placed in a microwave could vary from overly high amount of energy being applied to metallic gaps that facilitate arcing. So, microwaves can be applied to a stainless steel (non-ferromagnetic) bowl the same way it can be applied to a glass beaker. For this experiment, a microwave oven rated at 1.3 KW was used with a stainless-steel bowl. For each experiment 500 grams of base oil was used. Because the base oil was mineral oil, the bowl was coated with a layer of susceptor materials as described earlier. The processes for microwave and conventional heating are described below.

For Microwave Heating:
1. Base oil in a COATED stainless-steel bowl was heated to 75°C in a microwave oven at 1-minute intervals interspersed by 30 seconds of stirring
2. Fatty Acid 1 and Fatty Acid 2 were added to the base oil at 75°C
3. Product was then heated to 95°C
4. Aluminum complex thickener was added at 95°C
5. Mixture was heated to 200ºC while mixing for 30 seconds between one-minute heating intervals
6. From 140°C to 200°C samples were taken every 10 degrees
7. Cooling oil added to the mixture and grease was allowed to cool
8. Grease was milled in a three-roll laboratory mill
9. Penetrometer and dropping point tests were performed and reported
10. Samples taken at 140 to 200°C were tested using an FTIR.

For Conventional Heating:
1. Base oil in a stainless-steel bowl was heated to 75°C on a mantle while mixing continuously
2. Fatty Acid 1 and Fatty Acid 2 added to the base oil at 75°C
3. Product was then heated to 95°C
4. Aluminum complex thickener was added at 95°C
5. Mixture was heated to 200°C while stirring continuously
6. From 140°C to 200°C samples were taken every 10 degrees
7. Cooling oil added to the mixture and grease was allowed to cool
8. Grease was milled in a three-roll mill
9. Penetrometer and dropping point tests were performed and reported
10. Samples at 140°C through 200°C were tested using an FTIR
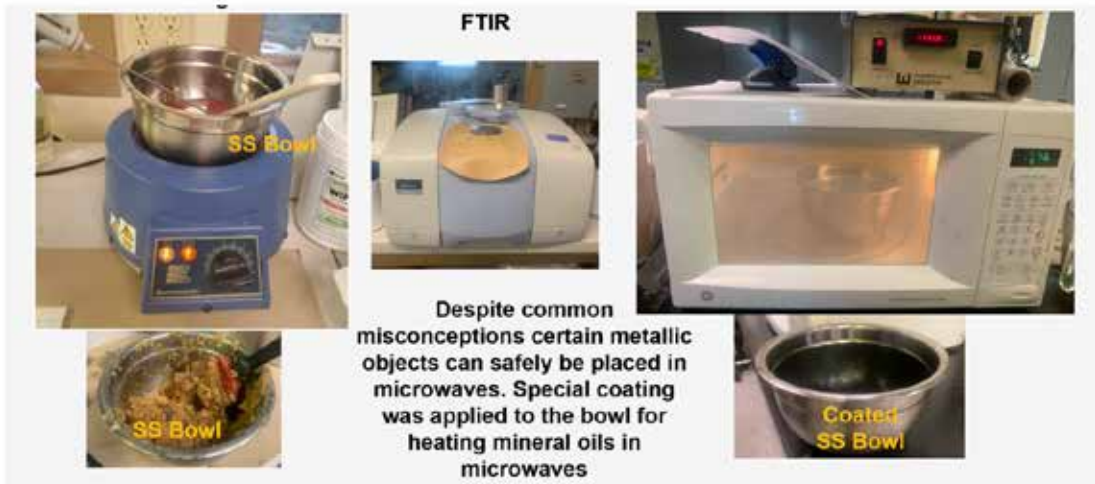
Figure 4 Equipment used for the experimental work in a laboratory setting including a 1.3kW microwave oven, a 2000-Watt heating mantle, one uncoated and one coated stainless-steel bowl, and an FTIR

To confirm that mineral oils do not respond to microwaves, first an attempt was made to make a batch of grease in an uncoated stainless-steel bowl in the microwave oven. Figure 5 shows the Time-Temperature report. While there was some temperature increase, the process was abandoned when no grease was formed after 120 minutes of heating. It should be noted that the reflected microwaves that are not absorbed by the mineral base oil would cause the air in the oven chamber to heat up causing some increase in the oil temperature. Also, once the fatty acids are introduced into the mineral oil , the microwave absorption is increased causing faster heating. But achieving the upper reaction temperatures become slow and impractical. As shown later, with a properly treated bowl, the process is rapid and can be completed in under 20 minutes.
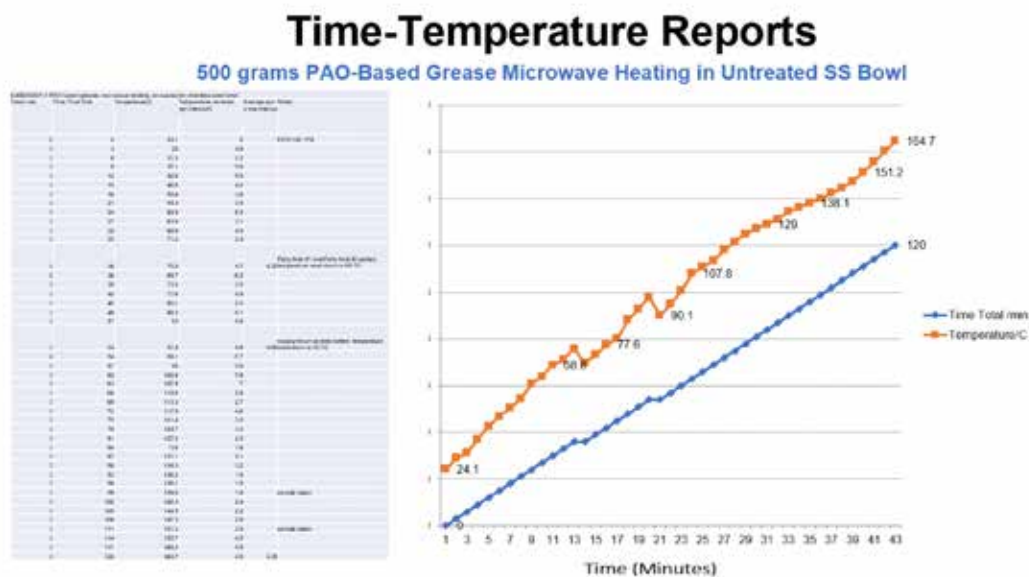
Figure 5 Time-Temperature report for the failed attempt to process mineral oil grease in an untreated stainless-steel bowl

Grease produced using mantle heating. The PAO-Based grease was made on a mantle and followed the process as explained in the conventional grease process above. The Time-Temperature report is shown in Figure 6. The product in the bowl was exposed to ambient temperature while being hand stirred. So, some heat loss from the surface of the product was expected which may not be the same in a microwave oven chamber. Nevertheless, the time required to reach 200°C was **50.2 minutes**. A duplicate batch was made to confirm the data. The second batch required less time of 42 minutes as shown in Figure 7. The average temperature for the two batches was 46.1 minutes.
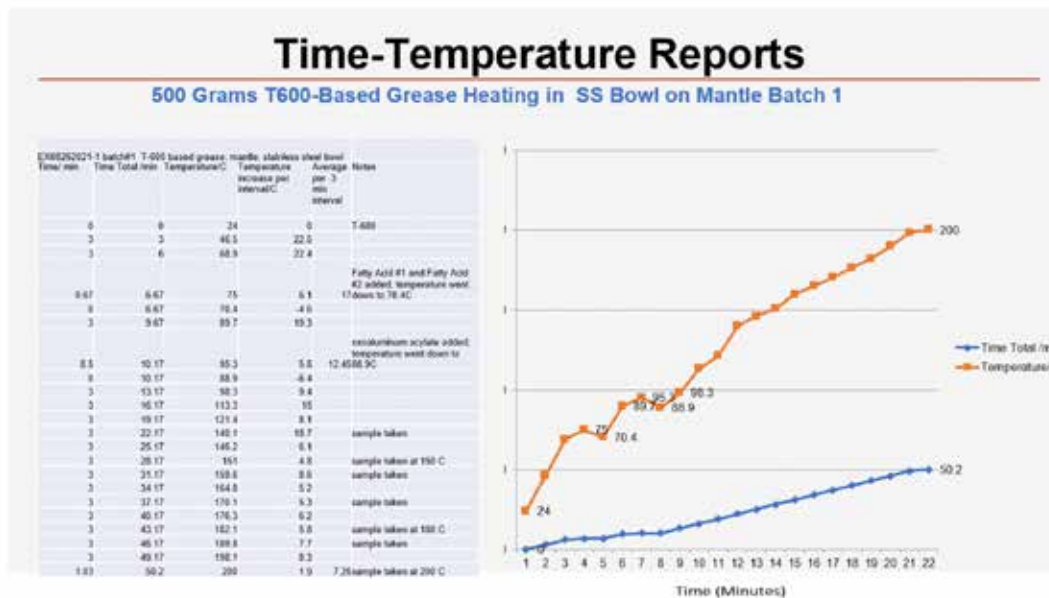
Figure 6 Time-Temperature report for grease made on mantle as in conventional process Batch 1
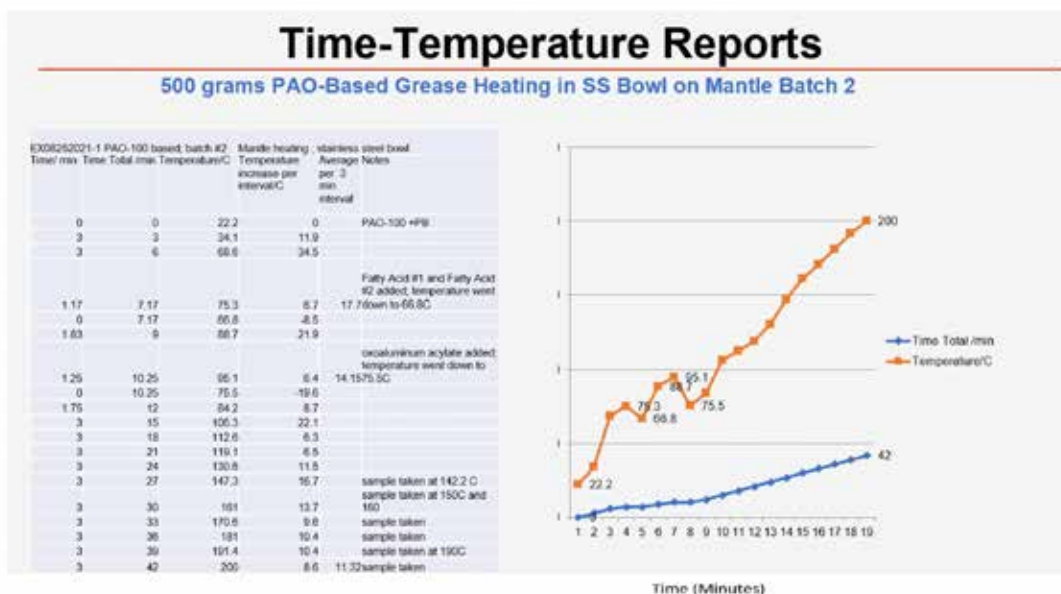
Figure 7 Time-Temperature report for grease made on mantle Batch 2

Grease produced using microwave heating. The PAO-Based grease was made in a special susceptor coated stainless-steel bowl. The process was performed as explained above. Since continuous stirring was not possible, the product was heated in one-minute intervals interrupted by 30 seconds of stirring. Figure 7 shows the Time-Temperature report indicating a total time of 17 minutes to complete the process and achieve a 200°C temperature. The average temperatures for the two batches made in the microwave was 17.5 minutes.
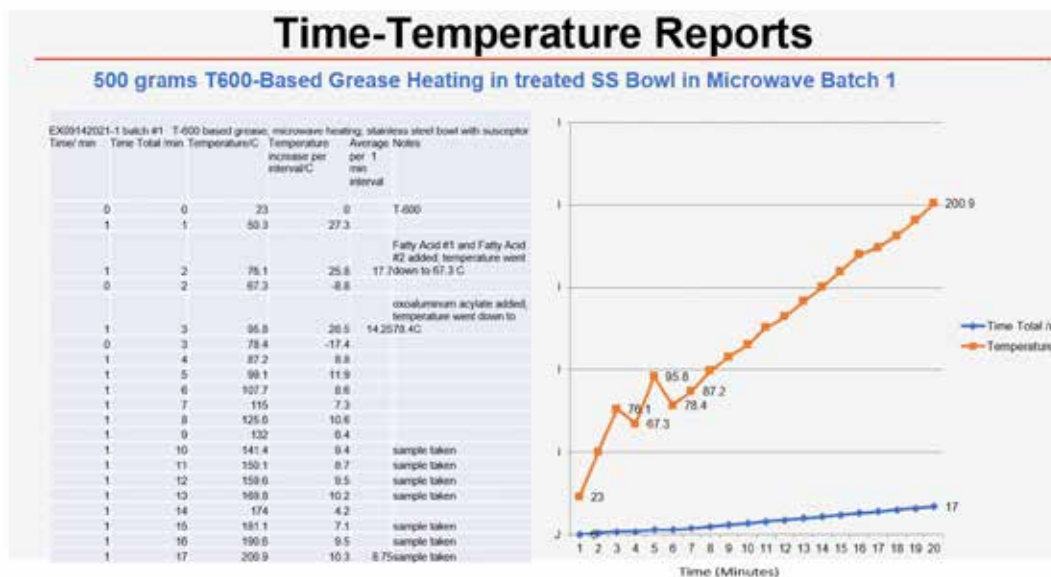
Figure 8 Time-Temperature report for microwave processing of mineral oil-based grease
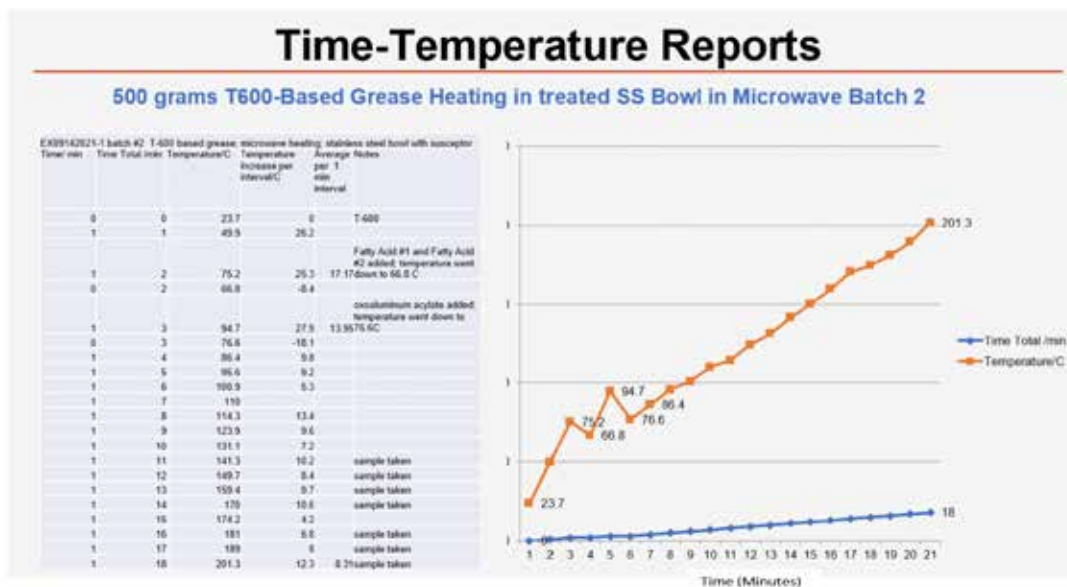
Figure 9 Time-Temperature report for microwave processing of mineral oil-based grease Batch 2

To confirm the data, a second batch of the same grease was made in the microwave using the coated stainless-steel bowl. Figure 8 shows the Time-Temperature report with near identical performance. In terms of time-temperature evaluation, the average time for making two identical batches of a mineral oil-based grease on a heating mantle was 46.1 minutes. In comparison, the average temperature for making two identical batches of a mineral oil-based grease in a microwave oven was 17.5 minutes. This represented a 2.61X faster process time when using microwaves for heating the mineral oil-based grease. An earlier presentation by this author has shown that the same amount of time difference is observed when manufacturing biobased grease using microwaves compared with conventional jacketed grease kettles and heat transfer oils. [1]

The grease made with mantle heating ended up having a darker color since the walls of the bowl being exposed to the heating elements would superheat the layers of oil that are in touch with the bowl. Continuous stirring was necessary to prevent product coking on the bowl surface. FTIR tests of the grease made in each process confirmed that both greases were fully reacted and did not show any differences. Figure 9 shows the FTIR reports on both processed greases indicating the two heating methods resulted in identical final product.
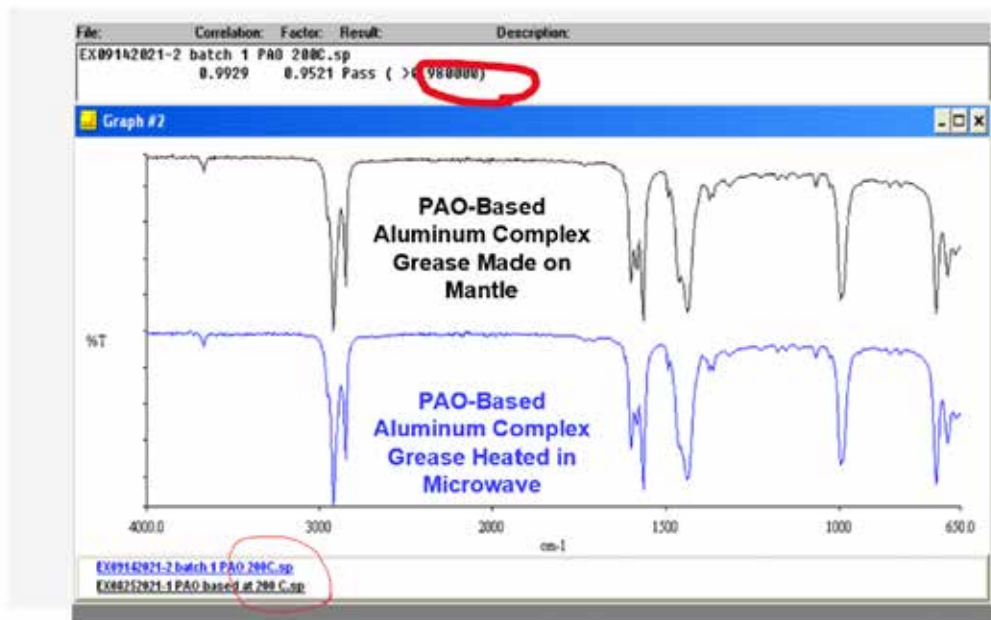
Figure 10 FTIR reports on both processed greases showing near identical results

In addition to the FTIR analysis of the products, the worked and unworked penetrometer as well as the average dropping points of the final batches of each grease process were tabulated. Table 2 shows the results. Greases made using PAO+PB as base oil showed an average dropping point of 278°C and greases made with the naphthenic oil had a slightly higher dropping point of 284°C which is in line with the dropping points expected of complex greases. But greases made with PAO and PB as base oil showed a much softer penetration reading of 402 for unworked penetrometer compared with the average unworked penetrometer reading for the mineral oil-based product of 147.25. But the results were the same regardless of using microwave or mantle heating. The data also include the degrees of Centigrade per minute in temperature rise.

Grease		Heating Time	Average temperature increase	Worked	Unworked		
Base Oil Type	Heating Method	in minutes	C per minute	Penetrometer	Penetrometer	Dropping Point	Notes
PAO+PB Batch 1	Mantle	38.01	4.81	495	405		Stainless Steel Bowl
PAO+PB Batch 2	Mantle	42	4.8	495	404		Stainless Steel Bowl
						278°C	
PAO+PB Batch 1	Microwave	120	1.38	Failed	Failed		Stainless Steel Bowl
PAO+PB Batch 1	Microwave	19	12.96	495	401		Treated Stainless Steel Bowl
PAO+PB Batch 2	Microwave	20	12.23	490	400		Treated Stainless Steel Bowl
T-600 Naphtenic Oil	Mantle	50.2	4.08	148	147		Stainless Steel Bowl
T-600 Naphtenic Oil	Mantle	52.92	4.42	144	146		Stainless Steel Bowl
						284°C	
T-600 Naphtenic Oil	Microwave	17	13.57	142	148		Treated Stainless Steel Bowl
T-600 Naphtenic Oil	Microwave	18	12.3	143	148		Treated Stainless Steel Bowl

Table 2 A summary of the data on temperature rise, penetrometer readings and dropping points of the samples

Summary and Conclusions

Since the actual modified grease kettle with the proper coating for processing mineral oil base greases was not ready for use, laboratory batches of PAO+PB based and 600 cSt naphthenic oil based greases were prepared on a mantle and in a microwave oven. **These tests would lead to the following conclusions:**

1. A specially coated metal bowl performed better when heating mineral-based oils in a lab microwave (2450 MHZ vs. industrial microwaves that are 915MHZ).
2. Greases made with the naphthenic base oil showed same properties when prepared using a heating mantle and in microwave.
3. Greases made with PAO and PB presented the same properties when prepared using a heating mantle and in a microwave but with higher penetrometer readings (much thinner). This is not entirely surprising, since it is well known that greases made with PAOs are less efficient than mineral oils (more thickener required for PAO grease to make equivalent consistency).
4. The time requirement for heating with microwaves was consistently about 50% less when compared with heating using the mantle – the microwave oven had a closed chamber which partially contributed to the shorter process time.
5. While the efficacy of using microwaves for producing biobased greases had been shown in previous papers, this presentation concludes that a specially designed microwave vessel can be used to manufacture mineral oil-based greases using this processing method.

The process of making *biobased* greases using microwaves is over a decade old and has been in use for commercial quantity grease. But new advances have made it possible to use microwaves for processing *mineral oil-based* greases. This report, although limited to laboratory experiments, confirmed that with a special coating of a stainless-steel vessel, microwaves can be used to process mineral oil-based greases.

References
1. Honary, L. (2019) Transforming Technologies in Grease Industry – Biobased Content - Microwave Based Reactors - Alternative Cooling. Presentation at the Annual Meeting of NLGI

NLGI Interviews Ms. Sandy Cowan
Grease Technology Manager,
CITGO Petroleum, Oklahoma City, OK

By Mary Moon and Raj Shah

Ms. Sandy Cowan

Sandy Cowan's interest in chemistry was the root of her career in quality control, R&D, management, and technical service in the petroleum refining and grease industries. She served on the NLGI Board of Directors for a decade, including two years as President, chaired the Editorial Review Committee and the Certification Mark Committee, and helped found the CLGS Committee and develop the first exam for this certification. At present, Sandy holds CLGS, OMA, and CLS certifications and is a member of the Test Method, Food Machinery, and Grease Cleanliness working groups. In this interview, Sandy shares her views on the grease industry, NLGI meetings, and her favorite grease. To learn more plus tips for passing the certification exams, read on!

Education

NLGI: Please tell us a little bit about where you grew up.

SC: I was raised on a farm in central Oklahoma. My hometown had a population of around 700, and there were only 23 people in my graduating class. It was great to grow up on a farm and in a place where everyone knew each other. I spent much of my childhood hiking in the canyons and riding my horse.

NLGI: Did you develop your interest in engineering and science as a student or later, during your career?

SC: I have always been interested in science. It was my favorite subject. I took every science class offered in my high school and received the outstanding science student award in my graduating class.

NLGI: Where did you go to college, and what did you study?

SC: I went to Southwestern Oklahoma State University in Weatherford, OK. I started out as a Medical Technology major. At that time, there was a high demand for Med Techs. I soon learned that I was much more interested in my chemistry classes than the biology courses. I think I made the decision to change my major while dissecting a cat in one of the biology courses. I graduated with a major in chemistry and a double minor in math and biology.

NLGI: What was your favorite course or professor?

SC: I enjoyed all the chemistry courses and labs. SWOSU was a small campus where all courses were taught by the professors instead of graduate assistants. Students got to know all the chemistry professors well by the time we graduated.

NLGI: Did you go straight from college to graduate school?

SC: No. After I received my bachelor's degree I worked as a statistical control technician at 3M for a couple of years. I didn't realize it at the time, but 3M's quality system was amazing. It was a great place to learn how quality control should be handled.

NLGI: What inspired you to continue your education? Where did you earn your master's degree, and what was your field of study?

SC: I moved to a small town that had very few opportunities for a chemist, so I went back to college to obtain a master's degree in education with natural science specialization. My experience in the field of education has been useful throughout my career. I taught for a few years before accepting a job as the chief chemist at a new refinery that supplied jet fuel to the U.S. military.

Career

NLGI: What was it like to work at a newly constructed refinery?

SC: It was great! The employees were new to their jobs, the refinery was new, and the lab equipment was new. I had a few weeks to train my chemists and set up the new lab instruments before the refinery started production. We would fill a storage tank with jet fuel and seal the tank, and then a government inspector would pull samples from the tank and observe while we ran all the QC tests. We had a perfect record and never had a batch fail any of the tests.

My job at Oklahoma Refining Company led to an opportunity to work as the Chief Chemist for Kerr McGee's QC lab. We had a miniature refinery set up in our lab. Our job was to fractionate samples of crude and determine the quality and quantity of the products that could be produced at the company's full-scale refinery.

NLGI: How did you become involved in the grease industry?

SC: Kerr McGee decided to close the QC lab where I worked, but Cato Oil and Grease (also owned by Kerr McGee at the time) had an opening for a Quality Control Administrator. My experience in QC at 3M helped me to obtain the QC position at Cato. The nice thing about that job was that I got to see how all parts of the plant operated, and I got to know the employees in all the areas of the plant.

When there was an opening for a grease chemist, I jumped at the opportunity. It was great to get back into chemistry. From there, I was promoted first to Chief Chemist and then to the Grease Technology Manager. I spend most of my time developing new grease products, but am also involved with providing training, tech support, and assisting with investigations.

NLGI: Please tell us a little bit about Cato.

SC: Cato Oil and Grease was founded in 1922 by Harris Cato, Claude Huffman, and James Corbett. They started out with no customers, one metal building, three storage tanks, and three vehicles. Their initial product line only consisted of 5 or 6 products in very plain packaging. Mr. Corbett made the products, Mr. Cato sold the products, and Mr. Huffman handled the accounting. Mr. Huffman still attended some of our company luncheons when I first started working at Cato over 30 years ago. Early products include Merit, Penntroleum, and Wanda. The Mystik® brand was first used in 1954. The company was founded on the principal of providing quality products and good service. The company continued to grow and is now one of the largest grease manufacturers in the United States.

Sandy with the members of the Grease Group at CITGO

The original founders sold Cato to Kerr McGee in 1957, and Kerr McGee sold Cato to CITGO Petroleum Corp. in 1995. We have lubricant manufacturing plants in Oklahoma City, Atlanta, and Cicero (Chicago area). The Oklahoma City lubricant plant, where Cato originated, is celebrating its 100-year anniversary this year.

CITGO Petroleum Corporation traces its roots to the Cities Service Company, which was founded in 1910 by Henry Doherty to supply energy to small utilities. The name CITGO first debuted in 1965. Today, the company takes pride in sponsoring organizations such as the Muscular Dystrophy Association and other charitable causes. CITGO is the fifth-largest independent refiner in the U.S. with headquarters in Houston, Texas.

NLGI: Do you have any words of wisdom for readers who might be thinking about going into the grease industry?

SC: This is a great industry to work in. It is never boring because there are always new things to learn. It is interesting to work with our customers to select the right product or to develop optimized greases for their specific applications. It is rewarding to help solve lubrication problems and improve the performance and extend the life of equipment.

Unlike many industries, people who work for competitors are also good friends.

NLGI: Do you have a philosophy for managing people, or working with customers, or responding to pressure from senior management?

SC: My philosophy is to be considerate, treat others fairly, and do what I can to help others achieve their goals. More can be accomplished when working together as a team, and there is much to be gained from sharing ideas with others. It is important to enjoy one's job and to work with people who inspire you. I am very fortunate to work with a great team.

> *My philosophy is to be considerate, treat others fairly, and do what I can to help others achieve their goals.*

Grease Industry

NLGI: What are your thoughts about the lubricating grease industry? What do you think about its future?

SC: There will always be a need for quality lubricants. I think there will be more fill-for-life applications and a trend to extend re-lubrication intervals. I also think there will continue to be a market for multi-purpose greases with good performance at a cost competitive price.

NLGI: Are there new or future applications of greases?

SC: I expect there will be more automation in the future. There will be a trend for equipment to run faster and more efficiently. If energy costs continue to escalate, we could see an increased need for greases that help conserve energy.

NLGI: Are there new chemistries for greases?

SC: Definitely. There will continue to be new technologies and improvements for grease formulations.

NLGI: Are there new tests and specifications for greases?

SC: As technology advances and new applications are developed, tests will be developed to quantify the traits needed for future lubricants.

> *Lithium complex grease is my favorite - it works well in so many applications, is compatible with other thickeners, and is cost effective.*

NLGI: Do you have a favorite grease chemistry?

SC: Lithium complex grease is my favourite because it works well in so many applications, has great compatibility with most thickener types, and is cost effective. I am also a big fan of polymers because they can impart traits such as

keeping the grease in place in applications, increasing the viscosity index to make the grease perform more consistently over a wide operating temperature range, and improving the water resistance.

NLGI

NLGI: How did you become involved in NLGI?

SC: Cato has a long history with NLGI and was one of the founding members of the organization. When I

started working for Cato, I started attending NLGI annual meetings, which is a great way to learn more about all aspects relating to grease.

NLGI: Can you tell us about some of your NLGI activities?

SC: I served on the NLGI Board of Directors for around 10 years, as Treasurer for 2 years, and as President of NLGI for 2 years. I am a former Chair of the Editorial Review Committee and the Certification Mark Committee, and I was the founding Chair of the CLGS Committee. I helped develop the first exam for this certification. I have been an instructor in the NLGI Advanced Grease Course, and I am a member of the Test Method, Food Machinery, and Grease Cleanliness working groups.

The best way to prepare for the CLGS and CLS exams? Get experience, attend meetings and education courses, and read the trade journals and reference materials.

NLGI: You are certified as OMA, CLS, and CLGS. What do these certifications cover? How do they differ? Were the certification exams difficult? How did you prepare to take these exams (and pass)?

SC: The first certification I obtained was the STLE

CLS (Certified Lubrication Specialist) certification. This certification requires knowledge in a wide variety of tribology related areas including all types of lubricants, applications, test methods, fundamentals, manufacturing, etc.

The NLGI CLGS (Certified Lubricating Grease Specialist) certification requires detailed knowledge of grease related topics.

The STLE OMA 1 (Oil Monitoring Analyst) certification requires knowledge related to oil monitoring programs and testing.

The best way to prepare for these exams is to obtain work experience in the lubricant industry, attend industry meetings and relevant training courses, and read the trade journals and the reference material recommended on the NLGI and STLE websites.

NLGI: Do you have any suggestions or advice to encourage someone who hasn't attended an NLGI Meeting in the past to decide to attend the 2022 Meeting?

SC: People interested in grease or grease-related applications should definitely attend. The NLGI Annual Meeting is a great place to meet others in the industry and to learn more about grease. The technical

presentations and grease courses are outstanding. There are many networking opportunities. It is a great opportunity to learn how to make better products and to meet with customers and suppliers.

The NLGI Annual Meeting is a great place to meet others in the industry and learn more about grease.

Perspectives

NLGI: Please tell us a little about your home, family, and hobbies.

SC: I live in central Oklahoma and am very fortunate to live close to my family. My daughter is a nurse manager at Mercy Hospital. My grandson will be 6 years old this summer. I am blessed to be able to spend much time with them. My sister and her family also live within a 1-hour drive from my home. I spend many weekends at the lake and enjoy kayaking and paddle boarding. I also enjoy reading, painting, crafts, hiking, going to museums, trying new restaurants, and playing golf.

NLGI: Please tell us about your favorite places to travel.

SC: I enjoyed visiting the sites in France, Greece, Cyprus, Croatia, Spain, the Czech Republic, Sweden, Scotland, and Germany. I also enjoy most places that are near an ocean.

The Smithsonian and Louvre are amazing museums. Hawaii, Maine, and Florida are also great places to visit.

NLGI: If NLGI members travel to Oklahoma City, please recommend special things for them to do, the best things to eat, or interesting sites to visit.

SC: We have some great places to eat in OKC. The steaks and barbecue are excellent. The Cowboy Hall of Fame, Omniplex, and Museum of Art are interesting and unique. We have many state parks and lakes in Oklahoma. These are great places to go to relax and enjoy the outdoors.

NLGI: Please recommend some of your favorite grease related books or technical journals to NLGI members.

SC: *The NLGI Spokesman* and *Eurogrease* contain great information for people who want to learn more about grease. Information in the early journals is still relevant today. I also enjoyed the books by C. J. Boner and Arthur Polishuk.

This interview series, started in 2019 by Dr. Moon and Dr. Shah, gives NLGI members a bit of insight into the professional and personal lives of their colleagues, developments in the grease industry, and the role of NLGI worldwide. If you would like to suggest the name

> ### *Sandy's Bookshelf*
>
> ***Modern Lubricating Greases and Manufacture and Application of***
>
> ***Lubricating Greases by C. J. Boner***
>
> ***A Brief History of Lubricating Greases by Arthur Polishuk***
>
> ***Eurogrease***
>
> ***The NLGI Spokesman***

of a colleague for an interview (or volunteer to be considered as a candidate), please kindly email Mary at mmmoon@ix.netcom.com *or Raj at* rshah@koehlerinstrument.com.

Dr. Mary Moon is Technical Editor of The NLGI Spokesman. She writes scientific and marketing features published in Lubes'n'Greases and Tribology & Lubrication Technology magazines, book chapters, specifications, and other literature. Her experience in the lubricant and specialty chemicals industries includes R&D, project management, and applications of tribology and electrochemistry. She served as Section Chair of the Philadelphia Section of STLE. She consults, works in the publishing industry, and is a member of the National Association of Science Writers.

Dr. Raj Shah is currently a Director at Koehler Instrument Company, Long Island, NY where he has lived for the last 25 years. An active NLGI member and he served on the NLGI board of directors from 2000 to 2017. A Ph.D in Chemical Engineering from Penn State University and a Fellow from the Chartered Management Institute, London, Dr. Shah is a recipient of the Bellanti Sr. memorial award from NLGI. He is an elected fellow by his peers at NLGI, IChemE, STLE, INSTMC, AIC, MKI, Energy Institute and the Royal Society of Chemistry. He has over 300 publications and is currently an Adjunct Professor at the Dept. of Material Science and Chemical engineering, State University of New York, Stony Brook. Currently active on the board of directors of STLE he volunteers on the advisory boards of several universities. More information on Raj can be found at https://www.nlgi.org/nlgi-veteran-member-raj-shah-presented-with-numerous-honors-in-2020/

NLGI COMMITTEE UPDATE

Membership

Membership Committee Chair: Tom Schroeder

The Membership Committee focuses on membership growth by recruiting new member companies including international expansion. Additional focuses of the Membership Committee include member benefits, membership value and retaining current members.

The Membership Committee achieved 94% retention for 2022!

Welcomes our 4 new members so far for 2022
- Barentz North America   *Supplier*
- Dynamic Green Products Inc.   *Marketer / Distributor*
- Pilot Thomas Logistics   Marketer / Distributor
- SMART PETROLEUM TECH, LLC   Technical

Over the last year, the Membership Committee completed:
- a full audit of current membership categories
- revised categories and descriptions
- added a new Associate category

*If interested in serving on a committee/sub-group, complete the volunteer form on the NLGI website. Please don't hesitate to contact NLGI HQ with any questions: 816.524.2500 or nlgi@nlgi.org.

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RETROSPECTIVE

Infrared Spectroscopy in the Development and Manufacture of Lubricating Greases

The use of infrared spectroscopy as a tool in the analysis of grease thickener systems is well-known and used today in development, production and identification of greases. While the techniques have advanced becoming easier and providing more information with the introduction of Fourier Transform techniques (FTIR), Attenuated Total Reflectance (ATR) and tools like infrared microscopes, the basic tenets remain the same and many researchers still refer back to some of the early papers published on the subject for guidance and reference in their work today. With this in mind, NLGI is pleased to present this retrospective look at work first published in the NLGI Spokesman in 1983, "Infrared Spectroscopy in the Development and Manufacture of Lubricating Greases" by A. Izcue G.

Infrared Spectroscopy in the Development and Manufacture of Lubricating Greases

By A. Izcue G., Krafft, S.A.

Summary

Infrared spectroscopy (IR) has become a valuable tool for the specialist in the development and production of lubricating greases. Although this fact has been acknowledged previously, few authors have devoted more than brief reference to the use of this technique during the early stages of the grease production process. Various spectra related to this subject are presented and discussed in this work to demonstrate the potential of IR in this field.

Introduction

As infrared spectroscopy (IR) left the isolation of research centers and reached the domain of industrial laboratories, its use and scope of application experienced spectacular growth. Unlike other instrumental techniques, IR represents a simple procedure which can be easily applied empirically and therefore has been readily accepted by the industrial chemist as a useful tool.

In the field of lubricants, the application of IR to the analysis of greases attracted special attention. In addition to its applications to base oils and additives, IR provides an invaluable method for the identification and classification of greases, as it can yield much information with economy of time and product.

IR has given industrial chemists better insight into the development and manufacture of greases and into the possible product changes that may occur during storage and use. This research has brought about a wealth of information on IR related to lubricating greases.

During the production process, the correct formation of the thickening agent is fundamental for achieving the desired quality in the finished product. Nevertheless, modern design and operating conditions of kettles and reactors ensure success in these early stages, provided the raw materials, their proportions, and the dispersing agent have been correctly selected. Classical laboratory analysis have been used for quality control, and the use of IR as an additional monitoring technique during the formation stage of the thickening agent had appeared superfluous, hence the scant bibliography on the subject, which only includes short or occassional comments.[1,2,3]

Through the presentation and discussion of several spectra examples, this study attempts to demonstrate the usefulness of IR in following the formation of various types of thickening agents during the production process of lubricating greases. The spectra provide a sufficiently accurate picture of each stage of process. When related to other data, such as temperature and appearance of the system, they permit the establishment of more favorable working conditions and a monitoring procedure on subsequent routine operations. In many cases, the use of this technique for product development brings about better insight and conclusions instrumental for achieving an optimum product.

Equipment and Procedure

The spectra in this work were recorded in the frequency range from 4000 cm^{-1} to 600 cm^{-1} with a double beam Perkin-Elmer 397 spectrophotometer. Cooled samples were placed between sodium chloride crystals of a cell assembly, sample thickness varied from thin film to about 0.1mm, as required to obtain suitable spectra.

It is important to note that most of the spectra in this paper were obtained at the laboratory development stage or production level for the sole purpose of monitoring the development of a process. Therefore, they consist of routine monitoring spectra in which scanning speed was more important than the determination of exact frequencies. Bands slightly displaced from their theoretical position may therefore be found in some cases due to minor deviations because of the instrument operating parameters selected. This fact does not alter their interest within the objectives of this report.

The primary purpose of these spectra was to monitor the relative concentrations of the reacting components and their resulting products and/or to monitor the evolution of their bands to obtain data on the kinetics of the reaction and its termination. The evolution in intensity and possible alterations of the bands of the thickening agent provide data on the process and represent valuable parameters for control and interpretation.

As a rule, this technique does not attempt to define the actual concentration of any of the components in the samples examined. Different aspects described in the literature[4-11] have a real influence on the shape of the recorded spectra. Therefore, any quantitative determination would complicate the process enormously, and yield data mostly irrelevant to the objectives of the method.

Occasionally at various stages in the process, mainly during the development of new or alternative products, two phases resulting from incompatibility or relative insolubility are found. It may then be of interest to record separately the spectrum of each phase. Conclusions may thus be obtained concerning component distribution which are not obtainable from a single spectrum of the homogeneous compound.

General Reactions: Neutralization and Raw Materials

The majority of the thickening agents used in lubricating greases are soaps prepared *in situ*. The following reactions summarize the chemical aspect of the early stages of compounding of most of these soaps:

-Neutralization reaction: $R\text{-}COOH + MEOH \quad R\text{-}COOME + H_2O$
-Saponification reaction: $R\text{-}COOR' + MEOH \quad R\text{-}COOME + HOR'$
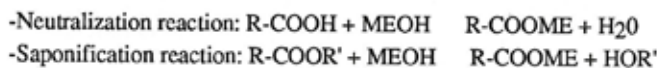
Generally, the above reactions specify the nature of the molecules participating in the process, and therefore implicitly define the most characteristic absorption bands found in the IR spectra of the greases during their preparation.

It is easily noted that most of the information is supplied by bands corresponding to the vibrations of the hydroxyl group (OH) and most particularly by those of carbonyl (C=0), for esters, acids and soaps. These important bands with corresponding intensities and wavelengths were already identified in the earliest development of the IR technique [12,13].

It is well known that the presence of soap in lubricating greases is detected by the appearance in the spectra of one or more bands in the range of 1610 to 1500 cm^{-1}, which are due to asymmetrical stretching vibration of the C00$^-$ group of the thickening agent.

These bands have a tendency to appear at lower frequencies as the atomic weight of the metal contained in the soap is increased [1,3,14]. The case of aluminum is an exception due to bonding of the non-neutralized OH groups in the soap molecule.

These asymmetrical-stretching bands represent a fundamental basis for monitoring the reaction progression and shall be developed in detail with the discussion of each case.

In many cases a weaker and much less significant symmetrical stretching vibration of the same C00$^-$ group, is found between 1450-1400 cm^{-1}. This overlaps the deformation band of the CH (asymmetrical deformation of CH_3 + deformation of CH_2) at 1460 cm^{-1}. Several other, generally weak, bands also exist which, with the exceptions to be mentioned subsequently are not of significant interest in our work. However, in the analytical field these bands are of complementary interest for the identification of different greases[15].

Neutralization in Lubricating Greases: Titrimetry and IR

The monitoring of neutralization in a grease is usually carried out by titration with an indicator in an organic or mixed medium. Data may be found in literature (16) which point out the lack of uniformity among results obtained with different methods with the same grease. Results obtained with greases of different soap bases using the same indicator are also dissimilar. From a manufacturing standpoint, it is usually possible to select an indicator which will be adequate for the reaction contemplated. In other cases, the nature of the reacting agents makes the task difficult or even impossible.

Under the conditions prevailing in a direct titration test, the esters cannot be evaluated. Thus, a grease compounded with glycerides may yield a neutral reaction if the alkali content is lower than that calculated. When the alkali is consumed, the excess ester will not be detected. If for any reason the saponification reaction is not complete with respect to the alkali present, a basic reaction will be obtained with titration in spite of the alkali being stoichiometrically deficient. Neutralization by the addition of fatty acid, would imply an even higher imbalance in the original formulation. In all the cases described the spectra contain the ester band at 1720 cm^{-1}.

In the case of excess acid, the acid will be detected easily during titration. IR will likewise enable us to identify this by the existence of a band near 1700 cm^{-1}. However, cases may arise in which the reaction between the alkali and the acid has not been completed. In these cases, it is very likely that an this reaction will be completed in the course of dissolution of the sample of titration in a much less viscous, more polar medium. The result of the evaluation will reflect this new situation which obviously does not correspond to the original, whereas a spectrum will point out more reliably the presence and approximate proportion of each component and its condition.

Determining excess hydroxide in the case of alkaline soaps lies within the realm of titrimetry almost exclusively because the OH band of the hydroxide is not often detectable. However, in the specific case of certain complex lithium greases, titrimetric analysis does not yield satisfactory results since some of these greases can present very strong alkaline reaction after they have correctly neutralized. Sometimes IR may detect the presence of free hydroxide in some precise stages of the manufacturing of these greases, but its use is very limited.

With aluminum-based greases, the possibilities for titration are nil or exceedingly limited due to the low basicity of the alumina, to the strong tendency of its soaps to hydrolyze and to its insolubility and ill-defined polymer structure in which non-reacted acid may be found[18]. The use of preformed soap solves these problems.

However, with the development of complex aluminum greases, the *in situ* compounding of soaps from aluminum isopropoxide and its derivatives raises a peculiar problem in the monitoring of a neutralization reaction in which titration methods are not applicable. Since organoaluminum derivatives are particularly moisture sensitive and loss by sublimation of certain components at some stages of the production process, may occur, initial proportions of the starting material may have to be adjusted accordingly.

IR does not provide an ideal solution, either. It does not adequately reflect the disappearance or decrease of alcoholate bands due to interaction with other components. If hydrolyzed

alumina is present, a sharp drop in IR transmission is likely to occur near 1200cm $^{-1}$. Furthermore, multistage reactions may complicate the spectrum. Despite these difficulties, IR can provide useful information which is rendered even more valuable by lack of other suitable control methods.

Acid Grease Components From an IR Viewpoint

Two major groups of products exist which can react with alkalis to form soaps: 1) vegetable or animal fats consisting of glyceryl esters which can be modified or used directly after refining, and 2) free acids obtained from these fats. Both types are often used together, and while the ester has the advantage of a lower price, the acid features better reactivity and does not introduce by-products, such as glycerine, which can modify the structure of the finished grease. Alternatively, other esters such as methyl esters can be used, which react easily and do not produce the by-products.

These raw materials are fluids or have relatively low melting points. It is therefore easy to obtain an infrared spectrum in liquid phase. Under these conditions, the spectrum is simple due to the superposition of all the possible vibrations in the free molecule, in which ester or acid bands are easily identified. Other types of information can also be obtained, such as the presence of unsaturation and water.

Solid-state spectra as a result of the orientation of the molecules, are at once both more clearly defined and complex. Thus, more information can be obtained on the nature and properties of the products from the bands in "the fingerprint region" [19]. At any rate, such information, while useful, is not necessary for the purpose of this discussion.

Figure 1 shows various spectra of solid and liquid acids and esters as follows:
a) melted tallow fatty acids
b) melted tallow
c) a solid stearic-polmitic acid (7:3) in 20 percent Nujol.
d) solid 12-hydroxystearate acide in 20 percent Nujol
e) methyl 12-hydroxystearate in 20 percent Nujol
f) triglyceryl 12-hydroxystearate (hydrogenated castor oil) in 20 percent Nujol.

The presence of a strong stretching carbonyl (C=0) band near 1700 cm $^{-1}$ is unmistakable in all cases. This is a fundamental band which, due to its intensity, isolated position, and absence of interference, represents the ideal band for the monitoring of the neutralization and saponification reactions. In the case of the esters (Figures 1b, 1e, 1f) it appears at a frequency approximately 20 cm $^{-1}$ higher than in the case of the acids.

Between 3600 and 3000 cm $^{-1}$ the broad OH stretching band can be seen in the acids. In the case of the hydroxystearic acid esters, OH band in the 3500-3100 cm $^{-1}$ range is due to the presence of the alcohol group.

On the other hand the acids have a band (out-of-plane deformation of the OH) at approximately 920 cm $^{-1}$ although its intensity differs from one case to the others.

In addition, in the esters the asymmetrical stretching band of the C-0 link becomes detached at approximately 1180 cm-1, and in the case of the liquid ester (Figure 1b), the symmetrical stretching band is observed at approximately 1100 cm-1.

Alkaline Grease Components From an IR Viewpoint

Figures 2a through 2d are spectra of Nujol-dispersed lithium hydroxide showing the influence of particle size, crystallization water, and polar compounds on the intensity and disposition of the OH stretching frequency. These together with its high water solubility, with resulting solvation and complete disappearance of the bands, disqualifies IR as a reliable tool to monitor the presence of lithium hydroxide in the grease production process.

The occasional appearance of the weak and fleeting LiOH bands can be related to specific occurrences, such as water-poor media, a dehydration due to heat or an incomplete saponification reaction with glycerides. Their detection is unimportant, for, although the presence of a highly alkaline medium is revealed, the existing imbalance is much more clearly indicated by the corresponding stronger, clear-cut ester band.

In contrast, calcium hydroxide with much lower water solubility and affinity, in very fine powder form, shows a single, permanent band at approximately 3615 cm $^{-1}$ (Figure 2e). This band is located between the two bands of anhydrous lithium hydroxide. This band, which overlaps to a lesser degree the wider water bands, (Figure 2f), is worthy of interest as a complement in the monitoring of grease neutralization. In this case, a moderately strong ester or acid band, together with the absence of the corresponding lime band, points unmistakably to an imbalance in the formulation.

It is not easy to assign a value to the lowest concentration of free lime in a grease which can be determined by IR, as monitoring of low concentrations is also affected by the overlapping of the water bands, the content of which can differ from case to case. Lime content of 0.2 percent can be determined from an ordinary spectrum. With practice and the use of adequate thicknesses, attenuation and low-scanning speeds, the limits of detection can be expanded. By heating a small amount of sample, most of the interfering water can be removed and the soap-oil equilibrium stabilized by the wetting effect of the water is simultaneously broken. Both components are effectively separated; the water is driven off and the lime is integrated in the soap phase. The spectrum produced by this phase can detect contents even lower than the above-mentioned 0.2 percent of the total grease. If the monitoring has been conducted as described, the free-lime content in the finished product can be detected in the one-hundredth percent bracket. This is more than acceptable, considering the relatively wide tolerance of these greases to neutralization deviations.

The sodium hydroxide spectrum coincides with that of Li OH.H$_2$0 sodium hydroxide (Figure 2a) has an even greater affinity for water than does lithium hydroxide. At any rate, because of its reactivity, it is not often that we encounter NaOH in a free state in the course of an advanced production process. If the relative content in the formulation is excessive, this can be easily evaluated by titrimetry and neutralized thereafter.

Calcium Greases

Thus in the following discussions, special attention is paid to

the calcium greases.

Lime Greases

Variability is a frequent characteristic in calcium-grease production. From a scientific point of view, they are the least defined products among the lubricating greases. The large number of possible raw materials which may be used in conventional lime greases, and the requirement for water as stabilizer in indefinite and variable proportions, makes the process a purely practical skill.

Figure 3 shows several typical spectra recorded during the formation of a classical lime grease. Figure 3a is a spectrum of a blend of acids and glycerides dissolved in oil prior to the incorporation of the lime. The acidic proportion is slightly in excess of that of the alkali which is to be neutralized. In the OH stretching frequency range, 3500-2500 cm^{-1}, a very wide band of the associated OH acid group is observed. The C=0 stretching frequency of the ester group appears near 1735 cm^{-1} and that of the acid at 1700 cm^{-1}, overlapping the former. The C-O-C stretching band of the ester is found at 1160 cm^{-1}. The weak triplet at 1560-1520 cm^{-1}, adjoining a weak band of the aromatic portion of mineral oil is due to hydrated calcium soap, probably residual contamination from a previous test.

Figure 3b shows the spectrum obtained after incorporation of the lime. The lime reacts with the acid to form a soap, but under these moderate conditions the glyceride does not react. In the 3700-3000 cm^{-1} range, the sharp OH band of the portion of lime which has not reacted with the ester may be seen. This is followed by a wider band due to the associated OH of the water molecules produced during neutralization. The wide band of the acid group has disappeared. In the 1800-1400 cm^{-1} carbonyl stretching region, the unaltered ester band may be observed at 1720 cm^{-1} but the acid band at 1700 has totally disappeared.

Two very intense peaks of hydrated lime soap appear between 1600 and 1500 cm^{-1}. This band, which is common to all hydrated calcium soap greases, has a much more complex structure than that of a mere doublet, as each peak bends slightly before its end. This is not visible in all the spectra, the ends being slightly rounded rather than sharp. In the overlapping point of both peaks, the same tendency is seen. As shall be seen later, this feature is important for a better understanding of the relationship among the different types of calcium greases.

In Figure 3c, the effect of dehydration on the product can be seen. The soap band is resolved into a single band at approximately 1540 cm^{-1}, the lower end of which is not clearly defined. The OH band of the lime is intensified, indicating an accumulation of this ingredient in the segregated soap phase. On the other hand, a diminished ester band can be seen, this having been partially dissolved in the oil phase (this distribution can vary substantially from one case to another depending on the nature and proportion of the other ingredients). Dehydration is reflected by the significant decrease of the wide band of the water at 3500-3200 cm^{-1}.

Figure 3d shows the grease spectrum obtained after completion of the saponification reaction following dilution and rehydration of the soap. Again, the characteristic soap doublet can

be seen just as it appears in finished greases. A small ester band confirms the excess introduced at the start of the process.

For comparative purposes, Figures 4a-4e shows a similar situation with fatty acids only, i.e., without the glycerides. In addition, spectra (in the 4000-1200 cm^{-1} range) for a product containing excess lime and a neutral grease are shown.

With calcium hydroxystearate greases it is possible to closely follow the dehydration and rehydration of calcium greases as shall be explained later. However, this does not occur with classical lime greases where the first trace of dehydration is brought about by the change of appearance of the mass. It is not easy to determine by examination of a spectrum whether non-hydrated soap portions exist in a lime grease. However, remnants of these anhydrous soaps in the oil phase can occasionally be detected while analyzing a grease. With some types of hydrated soaps produced from certain animal fats, these remnants are not easily separated from the oil which hinders its correct determination and alters its viscosity and other properties.

Complex Calcium Greases

The development of calcium complex greases from an IR standpoint parallels that of lime greases. To avoid duplication, only some specific aspects are outlined to complement the points already discussed. The principal difference consists of the presence of other compounds, such as short chain acids, which introduce spectral variations requiring interpretation.

Figures 5a-5c show full similarity as to the location of their bands and differ only in their relative intensity. Figure 5a corresponds to a dispersion of calcium acetate in an oil containing the Ca $(OH)_2$ (sharp band at 3630 cm^{-1}) required to neutralize the fatty acid. Figure 5c corresponds to finished grease which still contains a slight excess of lime. The intensity of the band at 1610 cm^{-1} compared to the 1580-1540 cm^{-1} range has decreased considerably due to the presence of the dehydrated calcium soap formed after the addition of the acid the band of which is added to that of the acetate at 1540 cm^{-1}. The only IR evidence of the presence of soap in the finished grease is the difference in intensity; this can be useful in estimating the soap-acetate relationship.

During the soap formation phase the situation is the opposite, regardless of the time and sequence of incorporation of the ingredients. In Figure 5b in which a portion of the fatty acid is incorporated, the band of hydrated soap fully dominates the 1600-1500 cm^{-1} range. Despite the band at 1610 cm^{-1}, the fact that an identical band may appear and even eventually persist to the end in certain ordinary lime greases shows that the only sure way of detecting the complex nature of the grease at this phase is by means of the bands in the ranges between 1100-1000 cm^{-1} and, above all, those between 700-600 cm^{-1}.

The dehydration process develops in much the same manner as with ordinary greases, except that the presence of the acetate or an equivalent product stabilizes the anhydrous soap thereby preventing separation. This applies also to cases in which hydroxystearic acid and moderate quantities of di-acids are used.

Calcium Hydroxystearate Greases

The so-called anhydrous greases, which do not require water for stabilization, have a clearly defined composition produced by reacting hydroxystearic acid with lime. From a kinetic point of view, the reaction may be highly erratic, sometimes with absolute refusal of the components to react, or to react in a sudden, violent way, either completing the reaction or interrupting it before completion.

The various stages of thickener build-up in an anhydrous calcium hydroxystearate grease are shown in Figures 6a-6e.

With such greases, the initial reaction occurs when the acid reacts with the lime in an oil vehicle under adequate conditions. In the 3700-3000 cm^{-1} OH stretching-frequency range, the sharp band of the non-reacted lime at 3620 cm^{-1} is followed by the wide band of the associated OH of the hydroxystearic acid and alcohol groups. In the 1800-1400 cm^{-1} range corresponding to the C=0 vibration, a sharp band from non-reacted dimerized acid occurs near 1700 cm^{-1} Between 1600 and 1500 cm^{-1}, the asymmetrical stretching vibration of the low proportion COO$^-$ soap group is found. This band appears in the typical doublet form peculiar to hydrated calcium soaps and is accompanied by the weak symmetrical stretching vibration band at approximately 1410 cm^{-1}.

Figure 6b is a spectrum from the highly advanced neutralization reaction. There is a strongly attenuated free lime band overlapping the OH band of the reaction-generated water. Also, there is a sharply diminished acid band at 1700 cm$^-$ ^{1}preceded by a previously unnoticeable weak band in the ester range at 1730 cm^{-1} and a very strong hydrated soap band. At this stage, the product thickens greatly.

Figure 6c was obtained in the beginning of the dehydration stage. Water evaporation weakens the OH band. The hydrated soap band starts evolving into the anhydrous form, and the acid band almost totally disappears.

Dehydration continues and when well advanced, the spectrum in Figure 6d is obtained. The intermediate shoulder visible in the hydrated soap band evolves into an inflection, but the very weak bands at 1730 and 1700 cm^{-1} persist.

Upon total dehydration, the spectrum in Figure 6e is obtained. There is a sharp soap band peculiar to anhydrous calcium greases. There are two slight inflections which might be related to non-dehydrated soap remnants. However, views questioning this interpretation will be presented later.

Above all, it should be noted that calcium hydroxystearate, at the time of its formation, displays a double band at 1600-1500 cm^{-1}, similar to the soaps of ordinary lime greases; only from this point can the single band peculiar to anhydrous calcium be obtained through gradual evolution. With hydroxystearic acid, this evolution is easily reversible depending on water content and temperature. During the incorporation or removal of water, the grease does not noticeably change in appearance, and the dropping point is remarkably identical in both variants.

Additional Observations With Calcium Greases

It would appear that, after service in a water environment at moderate temperatures, a calcium hydroxystearate grease would transform into the hydrated form, with resulting significant change in its spectrum. One such grease of this base (conforming to MIL-G-10924 C) did not show hydration after the ASTM D-1743 corrosion-protection test or after being worked 100,000 strokes with 10 percent water, but as soon as that same product was stored at 90°C, hydration invariably occurred (Figures 7a, 7b, and 7c.) Such a temperature and possible presence of moisture is unquestionably within the scope of the service applications of this grease. For this reason, IR analysis of such a grease subjected to these conditions could confuse the identification of the product; in addition, the presence of water alters the shape of OH band and causes an inflection at 1600 cm^{-1}, thereby increasing the similarity of this product with lime greases.

Another interesting aspect is contributed by the weak absorption bands, overlapping and corresponding to independent vibrations near 1730 and 1700 cm^{-1}. These bands are visible in the spectra when the strong acid band starts to disappear by neutralization, as shown in Figure 6b, 6c and 6d. In spite of its frequencies being near (in one case) or coincident (another case) with the acid stretching bands, experience has shown that it is impossible to eliminate them by neutralization. Both bands accompany the hydroxystearic acid and may vary in intensity, independently of each other, according to the origin of the acid.

For comparative analysis, the spectra resulting from complete neutralization, under mild conditions, of the hydroxystearic acid dissolved in mineral oil with a large excess of lime was recorded. The higher frequency band appears to be related to the presence of estolides that is polymeric esters and lactones esters which are only slightly reactive and do not completely split with the lime under the conditions existing in the production of calcium greases. Their formation and location are shown in Figure 8: A sample of hydroxystearic acid diluted in oil was divided in two parts one of which was stored at 90°C for 12 hours. Following neutralization of both parts: the sample kept at room temperature (Figure 8a) gave both bands with similar intensity whereas the heated sample (Figure 8b) gave an increase in the higher frequency band due to the formation of a new quantity of the above-mentioned estolides. The lower frequency band has a different origin and will be discussed more fully in the section devoted to lithium greases, but it is apparent that the presence of these two bands conceals the last remnants of free hydroxystearic acid.

Calcium Greases in Anhydrous Medium

The fact that the calcium greases referred to as being anhydrous actually show a hydrated soap band during the initial stage of their formation poses the question of how the build-up of soap will develop, and what would be the properties of a product obtained in a totally water-free medium, water generated by neutralization itself notwithstanding.

In order to examine this question more fully, we selected hydroxystearic acid. Once the grease has been obtained, it was tested without further water addition to stabilize the product.

Calcium methoxide, used as a base, was obtained by reflux

boiling the necessary amount of calcium hydride with excess sodium-dehydrated, distilled, absolute methanol, while protecting the system against moisture absorption.

The product, a dispersed solution of the methoxide in the excess methanol, was directly taken to a reactor where the required amount of oil had already been placed. The whole was then heated and stirred. Upon evaporation of the methanol, a dispersion of methoxide in oil remained. The strong band near 1050 cm^{-1} and its likely overtone at 2075 cm^{-1} (Figure 9) are attributed to the alcoholate.

The development of the reaction can be followed in Figure 10. The soap is formed without difficulty in its anhydrous form. In Figure 10a, the immediate, total disappearance of the methoxide bands was observed after the addition of what is deemed a stoichiometric quantity of acid, while a strong band of non-reacted acid was observed near the weaker soap band. In subsequent spectra, it appears that the soap content increases, whereas the acid content decreases. This seems to indicate that the excess acid, according to the spectrum, is only apparent. As the reaction progresses, (Figures 10b and 10c) a weak, but well-defined band near 3625 cm^{-1} becomes evident and is attributed to calcium hydroxide. It may be due to hydrolysis of the methoxide by ambient moisture, or to reaction with the alcohol group of the 12-hydroxystearic acid. At termination of the process (Figure 10d) this band disappears probably due to reaction with the last residue of acid. Once more the estolides and their neighboring bands are apparent in this Figure.

An interesting detail is the presence of very weak inflections in the soap band between 1575 and 1530 cm^{-1}, in spite of there not having been a hydrated form. This fact is consequential in that it coincides with characteristic frequencies appearing in the hydrated soap band precisely where dehydration usually starts. The dehydrated band usually maintains the same inflections in position and intensity as those of an anhydrous soap.

The grease thus obtained had the following composition:

- Calcium methoxide   2.32%
- Hydroxystearic acid   12.75%
- Mineral oil   84.93%

Its characteristics were as follows:

NLGI grade: 2-3
P= 253 mm/10
P (60) = 255 mm/10
P (10^5) = 272 mm/10
Dropping point: 145°C
Acidity Index: Alkaline reactions equivalent to 0.23 mg KOH/g according to the method of Dagaeva et al. [17]. The result excludes any mistake in the proportions of acid and methoxide used.

The spectra in Figure 11 show conversely the gradual decrease of the alcoholate band when the above formulation is reproduced by incorporating the acid step by step. In this case, no free acid band appears at any time. The acid was incorporated from a 25 percent solution in mineral oil at 90°C. The product thus

obtained yields the following values:
NLGI grade 2.:
P=270 mm/10;
P(60) = 267 mm/10
P (10^5) - 267 mm/10
Dropping Point: 146°C

In view of these results, the behavior of a stearic-palmitic acid (7:3) such as those used in hydrated lime greases was investigated. The evolution of the process is shown in Figure 12.

Figure 12a: The addition of a portion of acid diluted in oil to the methoxide dispersion caused a quick formation of soap which produced a band practically identical to that of the anhydrous soap of the hydroxystearic acid. The existence of the same, equally weak inflections is significant.

Figure 12b: The addition of 50 percent acid induced a strong imbalance in the relative intensities of the soap band although their frequencies remain substantially constant. The methoxide band is weakened. The acid band does not appear.

Figure 12c: The addition of the remaining acid caused a situation of transitory non-neutralization. However, unlike the hydroxystearic acid, all the components are visible in the spectrum although it is not known whether the intensities of the bands reflect the actual concentrations or indicate some type of interference. The incorporation of all of the acid causes normalization of the soap band. The grease appears as an unctuous, medium-viscosity oil throughout.

Figure 12d: Neutralization has been completed. When cooled to approximately 70°C, the mass formed a gel which is easily destroyed by working between the fingers, but shows no tendency toward phase separation as when dehydrating an ordinary lime grease. The dropping point of this mass was 103°C. It is remarkable that, despite its definitely unstable structure from a mechanical viewpoint, this grease yields a dropping point similar to that of an ordinary hydrated grease. Incorporation of water at 0.4 percent with stirring and heating at 70°C brings about the hydrated form.

In conclusion, we have not found the reason for the disappearance of the methoxide bands by addition of all the hydroxystearic acid at one time during the first of the three tests (Figure 10a). The fact that the same effect has not been observed with stearic acid under similar, although not identical, conditions points to a reaction in stages with possibly a rapid first stage including the alcoholic OH of the hydroxystearic acid, which would cause the disappearance of the band, followed by neutralization by the acid.

Characteristics of Calcium Soap Bands

Besides demonstrating the possibility of avoiding the hydrated form in the compounding of calcium greases, these procedures permit comparative observations which would not be possible under normal conditions.

The obvious similarity between the IR bands of hydrated calcium hydroxystearate grease bands and those of ordinary lime greases, and the similarity between those of anhydrous hydroxystearate with those of stearate-palmitate compounded in a water-free medium, points to common origin in all cases.

This possibility has led to a careful determination of the position of certain bands with respect to polystyrene reference frequencies at 1583.1 and 1601.4 cm^{-1} (Figure 13). We may note the coincidence among the different anhydrous bands and among the hydrated bands whatever their origin. In view of these results, it seems reasonable to ascribe a common original band to calcium soaps which is shown in the expanded abscissa in Figure 14.

Maximum absorption (Figures 14a and 14b) of this band occurs at approximately 1585 cm^{-1}, and there are sharp inflections at 1561 and 1541 cm^{-1}. The band also shows less defined inflections at other wave numbers. The inflection at 1541 cm^{-1} evolves with hydration (Figure 14c), creating a new band with a resulting doublet with two maximum absorption peaks. Each of the peaks in turn is slightly split in pairs at 1583-1579 cm^{-1} and 1543-1538 cm^{-1} (Figures 14d and 14e).

In both cases, shoulder between both pairs is observed; both branches of each band converge, coinciding with the anhydrous band inflection at 1561 cm^{-1}. The three most important frequencies are clearly shown in the anhydrous band, but upon a careful examination, one finds very weak inflections associated with frequencies related to the remaining hydrated band frequencies.

Other complexities in the calcium soap bands were noted. When complete dehydration of an ordinary lime grease was attempted, the distortions appearing in the soap band were found. These are possibly associated with stubborn water residues, and most certainly with glycerine when it is present. It is noteworthy that hydrated hydroxystearate grease, with a stationary, stale OH, dehydrates easily without change in its appearance, modifying its band very gradually and regularly. However in the presence of highly excessive, highly polar, soluble compounds, such as hydroxystearic acid, this hydrated band may remain unchanged at temperatures as high as 170°C. The behavior of the calcium ricinoleate is also remarkable; the variations in soap band at several temperatures, especially in the presence of glycerine, are fairly erratic. The anhydrous band is not clearly defined, and its behavior more closely resembles that of other acids rather than that of the hydrostearic. Generally the influence of other components on the stability of the calcium hydrated soap band seems to be related to the stability provided to the soap-water-oil system by certain components , as some authors have shown [20].

However, there is another influence on the indefinite band which results from the attempt to dehydrate a lime grease. If the dehydrated product is milled and the infrared spectrum freshly recorded, one can note the tendency of the hydrated band to regenerate. The more thorough the refining, the more remarkable this phenomenon, and its persists even in greases exposed to more than 200°C, as can be seen in Figure 15. In view of these results, it is apparent that a decisive influence over the form of these bands can be attributed to the state of aggregation. An already formed hydroxystearate grease, with its sharp dehydrated band, will develop into a wider band with indefinite outline upon disintegrations"" of the grease. A similar effect is also achieved by addition of a large excess of a fatty acid, although in this case the effect is accompanied by a drastic decrease of the intensity of the band. Logically, in this case refining the dehydrated sample does not present the slightest tendency to regenerate any doublets, the characteristic single band of the anhydrous soap remains.

Finally, there are some calcium soaps which do not show the characteristic doublet in the presence of water. This occurs in some products with high resinic acid content, such as those used in old axle greases. These can yield a single band insensitive to the presence of water, even in large quantities, from room temperatures to more than 100°C. Although several soaps of these characteristics exist, universally they have little or no thickening power.

Lithium Greases

Today, lithium greases are probably the most important of all lubricating greases available on the market. The process of lithium soap formation in greases parallels that of calcium greases. To avoid unnecessary repetition, only isolated spectra will be presented for cases of specific interest or complementary to the general subject.

In Figure 16a the lithium hydroxide band at 3650 cm^{-1} is perceptible. However, this hydroxyl band is extremely weak compared with that of the calcium hydroxide band under similar circumstances. A hydrogenated castor oil can be deduced from the strong ester band at 1730 cm^{-1}, and the weak soap band at 1575 cm^{-1} shows the reaction is just starting.

Figures 16b and 16c are from greases having the soap practically formed, as shown by the absence of strong bands in the range from 1800-1700 cm^{-1} which excludes the presence of esters and acids in substantial quantities. In both cases, the characteristic double band of lithium soap is observed at 1575 and 1555 cm^{-1} .

The grease of Figure 16b was produced by saponifying a mixture of a hydrogenated castor oil blend and free 12-hydroxystearic acid, whereas Figure 16c came from the neutralization under moderate conditions of 12-hydroxyoleic acid (ricinoleic acid). In both cases, excess water produced an intense, associated OH band in the 3700 to 3100 cm^{-1}. The high water content is confirmed by the wide, weak bands at 2400 - 2000 cm^{-1} and 1640 cm^{-1}. Two major differences between Figure 16b and 16c are noted: one corresponds to the presence in the ricinoleate of a weak shoulder at 3010 cm^{-1} due to the double bond c=c; the other is related to the symmetrical band at the 1400 cm^{-1} of the C00 group, which is normally present in all lithium soaps with the exception of the hydroxystearate, which shows a barely visibvle, slight band, and even this slight band could be attributed to the minozitary components in the commercial acid, rather than to the acid itself.

Figures 16d and 16e show a more advanced phase of process of these greases. In both spectra, the strong water band between 3700 and 3100 cm^{-1} has been replaced by the weaker alcohol group of the hydroxylated soaps. The disappearance of the band at 1640 cm^{-1} permits observation of details in the area of 1700 cm^{-1}. In both spectra there is a weak band at this frequency, and in the case of the ricinoleate, there is another band near 1730 cm^{-1}

[1]. Considering that free ricinoleic acid yields estolides more easily than hydrostearic acid, and that neutralization reaction conditions have been moderate, the presence of an estolides band near 1730 cm^{-1} is justified. However, Figure 16e corresponds to a product made under more severe reaction conditions. It does not show the ester band, indicating a complete splitting of the glyceride and estolides. Generally, lithium hydroxystearate greases produced with acid or with its blends with glyceride, do not usually have ester bands, provided the quantity of lithium and reactions are sufficient. Nevertheless, the effects of the presence of estolides on the greases is controversial. Their usefulness has been claimed in patents [21], whereas in some opinions their presence is considered undesirable.

In spite of its position in the spectrum, it is difficult to relate the band at 1700 cm^{-1} to free acid, especially considering its persistence through a process in which enough strong alkali was used to completely split the very stable glycerides and estolides. This anomalous band also appears in the spectrum of greases with an alkaline excess yielding a strong alkaline reaction. This band is limited to greases containing hydroxystearates, and castor oil soaps, but is not found in greases based on animal or vegetable fat except those listed. Its presence seems to originate from small quantities of 12-ketostearic (perhaps 12-ketooleic) acid, existing in castor oil. The following spectra tend to reinforce this supposition.

Figure 17a shows a nujol mull of 12-ketostearic acid obtained from the oxidation of 12-hydroxystearic acid in acetone with chromium trioxide. The weak doublet at the end of the band at 1700 cm^{-1} suggests the existence of two very close overlapping bands, one ascribable to the acid carbonyl group and the other to ketonic carbonyl. This latter group is clearly evident in the spectra of the 12-ketostearic derivatives, in which the acid group has been replaced by a soap or an ester, as can be seen in the following spectra.

With Lithium 12-ketostearate (Figure 17b) the band at 1700 cm^{-1} no longer presents a tendency to splitting and the stretching band at 3500-3000 cm-1 has disappeared. The alcohol band does not appear as it did in the case of the hydroxystearates and ricinoleates, but only as a weak absorption at 3370 cm^{-1} as which may be a possible harmonic of the carbonyl band at 1700 cm^{-1} is also visible in the spectrum of the acid. The clearly outlined asymmetrical stretching bands at 1575 and 1555 cm^{-1} and a symmetrical band at 1400 cm^{-1} are characteristic of lithium soaps.

Figures 17c and 17d show the anhydrous and hydrated forms of calcium 12-ketostearate grease. The behavior of these products correspond to that of the conventional lime grease; all of the bands, except that belonging to the ketone group, correspond with those of any other grease of its kind.

Figure 17e was obtained from melted methyl 12-ketostearate produced by esterification of the acid with methanolic boron trifluoride. In this case, separation of the carbonyl bands of the ester (near 1735 cm^{-1}) and the ketone (1700 cm^{-1}) is much more distinct than in the case of acid. The presence of the ketone band may raise serious doubts as to the complete transformation of the acid into an ester. It is similar to that of acids (such as naphthenic acids) which, under moderate conditions such as those used here, do not achieve full esterification and yield similar spectra due to the simultaneous presence of ester and unreacted acid.

Figure 17f corresponds to a lithium stearate grease (9 percent soap in Nujol as an oil) with a slight excess of unreacted glyceride. The same product after the incorporation of 3 percent equivalent grease formulated with 9 percent lithium ketostearate soap is shown in Figure 17g. In this spectrum, the 0.27 percent ketostearate is clearly visible in spite of the presence of the ester band, and the similarity with the hydroxystearate and ricinoleate spectra (already discussed Figure 10d and 16e) is noteworthy. The proportion of 3 percent ketostearate with respect to the soap corresponds roughly to the percentage of 12-ketostearic acid usually found in gas chromatographic analysis of a commercial 12-hydroxystearic acid.

Figure 18a is a spectrum of 15 percent naphthenic acid solution in mineral oil, and Figure 18b of 10 percent lithium naphthenate obtained by neutralizing the former acid solution. The latter product is useless as a direct thickening agent, albeit under certain conditions it adds interesting features to the systems formed by other soaps; its spectrum differs from that of the normal greases. The COO asymmetrical stretching band is single, wider, and appears at a slightly higher frequency than that of classical lithium soaps. The symmetrical band at 1400 cm^{-1} is also found in this case. In the initial stages, this product does not thicken, but as the temperature is increased, there is a tendency to form a light gel reminiscent of soft aluminum greases. Above 160°C the product changes to one that can be firmed by refining at these temperatures. This behavior is similar to that of classical greases, but they are not resistant to further working. It is very difficult to achieve complete dispersion or dissolution of preformed lithium naphthenate in oil, even at 200°C. The product thus obtained has a gel appearance and is strongly thixotropic. Its spectrum is similar to that the product formed *in situ* (Figure 18b) except it shows a clearly defined band at 1540 cm^{-1}, remembering that of the ordinary lithium soaps. It is interesting to note that many other metallic soapd (lithium included) with poor or null thickener properties shows a soap band highly similar to that of the Figure 18b.

Sodium Greases

From the viewpoint of this paper, sodium greases do not present any special aspects other than those already outlined. Infrared monitoring of sodium soap processing is of less interest due to the smaller number of chemical problems associated with high reactivity of the alkali. The chemical problems are of less concern than the physico-chemical and mechanical aspects, such as dehydration, foam formation, difficulty in rehydration, agitation of fibrous mass, and oil blending. For these reasons and taking into account that excess ester is still difficult to determine by titration, Figure 19 shows the spectra of a sodium grease formulation starting with a blend of acid and glyceride.

In Figure 19a the fats and fatty acids are dissolved in oil prior

to reaction with the alkali. Acid bands are seen at 3600-3000 cm^{-1} and ester bands at 1730 and 1150 cm^{-1}. In Figure 19b the grease has been formed and its characteristic soap bands near 1555 and 1420 cm^{-1} are prominent. The wide band at 3300 cm^{-1} is due to water and glycerine; a weak residue of ester is seen at 1730 cm^{-1}.

Figure 19c shows an intermediate phase with the acid fully neutralized and the ester only partially neutralized; a large amount of soap has already been formed. The strong band at 3350 cm^{-1} and the weaker band at 1640 cm^{-1} are due mainly to water.

The grease depicted in Figure 20 was selected because NaOH was used as a neutralizing agent. The product itself is not characteristic of other sodium greases, and the possibility of using alternative bases has been described previously [22]. In the case of greases prepared from saponification of the methyl ester of the N-octadecylterephthalamic acid with caustic soda, the formation process of the thickening agent is similar to that of other greases, and the reaction monitoring is the same as that described previously. However, there are some unusual aspects due to the peculiar structure of the primary component which contains an aromatic ring and a secondary amide group:

$$-C_6H_4 \left\langle \begin{array}{l} CONH-C_{18}H_{37} \\ COOCH_3 \end{array} \right. + NaOH \rightarrow -C_6H_4 \left\langle \begin{array}{l} CONH-C_{18}H_{37} \\ COO \quad Na \end{array} \right. + CH_3OH \uparrow$$
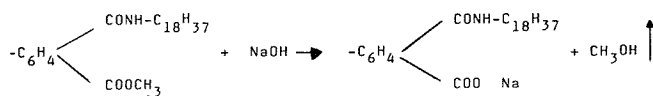
The amide group produces bands of greater intensity than those of the ester and of the resulting soap. For this reason and although clearly visible in the IR, they are not easily distinguishable from each other. Small differences in spectra of different batches can be attributed to the tendency of amides associate through hydrogen bonding, yielding cis-trans rotational isomerism.
combined with strong interaction with the strong polar ester and soda groups.

Figure 20 shows the development of this grease. Figures 20a and 20b show the spectra of two different batches of methyl-octadecyl-terephthalamate in a ten percent solution-dispersion in mineral oil. There are differences worth noting. The NH stretching vibration can be seen at approximately 3330 cm^{-1}. The stretching frequency band of the ester carbonyl is near 1720 cm^{-1}; this band is unusually weak and appears split in Figure 20a. A second stretching carbonyl band, belonging to the amide carbonyl (Amide I band), is at 1640-1620 cm^{-1}, with splitting in this case (Figure 20b). At approximately 1530 cm^{-1} Amide II band is noted, apparently arising from N-H and C-N motions. Following the methylene and methyl bending bands at 1460 and 1380 cm^{-1} respectively, a band is noted near 1280 cm^{-1}; this can be attributed to the Amide III band (C-N and N-H motions) and to the asymmetrical stretching motion of the C-0 link in the ester group. The intensity of this band leads us to assume that it belongs to the ester which is confirmed as the saponification process progresses by the gradual disappearance of this band along with that at 1720 cm^{-1}. The major band at 1110 cm^{-1} probably corresponds to the C-0 symmetrical stretching motion of the ester. Its decline, along with those at 1720 and 1280 cm^{-1}, plus the appearance and growth of the soap band constitute the criteria for monitoring the reaction. Finally, the strong band between 780 and 700 cm^{-1} could be the result of several overlapping vibrations, such as the Amide V band (NH out-of-plane bending) and the rocking skeletal-motion band of the long-chain methylene groups of the octadecyl group and the hydrocarbons of the mineral oil.

In the progression from Figure 20a to 20c, the decrease in the bands of the reacting ester have not yet become visible. After the addition of the alkali, the beginning of a small soap band at approximately 1580 cm^{-1} is already visible. At 1635 cm^{-1} the Amide I band flexes slightly as a precursor to the forthcoming doublet.

In Figure 20d, there is a marked increase of the soap band at 1580 cm^{-1} with simultaneous disappearance of the ester bands at 1720, 1280 and 1110 cm^{-1} and a change in the shape of NH band at 3300 cm^{-1}. The Amide I band at 1630 cm^{-1} has split and decreased. All of this seems to reflect the changes in the polarity of the molecules in the system due to presence of sodium hydroxide and the formation of soap.

Figure 20e was obtained as saponification progressed; there was a very light change in the N-H band at 3300 cm^{-1}.

Finally, in Figure 20f, the spectrum of the finished product shows a configuration of the N-H bands with disappearance of the wide part and slight modification of the doublet. The ester band has disappeared. As stated at the beginning, the comparatively low intensity of the soap band is significant, as well as the scarce indications of the presence of the aromatic ring.

Aluminum Complex Greases

Discussion is limited to the field of complex aluminum greases. Conventional aluminum greases are not discussed because they are made predominately with premanufactured stearates and there are no chemical reactions amenable to IR monitoring. It must be noted however that aluminum soaps and their structure have been studied in depth and that IR has played a major role in this task [23, 24, 25, 26, 27].

Soaps generally used in the production of greases correspond to the $(R-COO)_2$ AlOH type. Aluminum-grease IR bands have been clearly defined and accurately ascribed to specific molecular groups through comparison with equivalent spectra of deuteroxy soaps and those of gallium and indium [26]. Also, attention has been given to the sensitivity of the major aluminum soap bands to the presence of specific products, particularly those liable to form hydrogen bonds with a simultaneous break of the polymeric, octahedric structure of the aluminum soap and the consequential decrease in intensity of the three most characteristic bands of the $(R-COO)_2$ AlOH molecule: the OH stretching at 3650 cm^{-1}, the asymmetrical stretching of the COO at 1588 cm^{-1}, and the AlOH band at approximately 990 cm^{-1} [26,27].

Complex aluminum soaps are obtained through reaction of a short chain acid (e.g. benzoic) and a long chain one (e.g. stearic) with aluminum alcoholates. Taking into account that as with ordinary soaps, complex soaps are monobasic with free OH, we can establish the following two stage reaction when aluminum

isopropoxide is used:

a) $R-COO\ H + R'-COOH + (C_3H_7O)_3Al \longrightarrow$ $\begin{array}{c} R-COO \\ \diagdown \\ R'-COO \end{array} AlOC_3H_7 + 2C_3H_7OH$ (Isoprop. olc.)

b) $\begin{array}{c} R-COO \\ R'-COO \end{array} \diagup Al\ OC_3H_7 + H_2O \longrightarrow \begin{array}{c} R-COO \\ R'-COO \end{array} \diagup AlOH + C_3H_7OH$
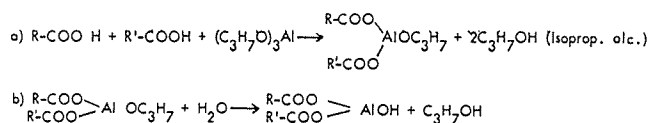
A cyclic trimer alcoholate, derived from the former isopropoxide, can also be used, from which the following reactions would originate [28].
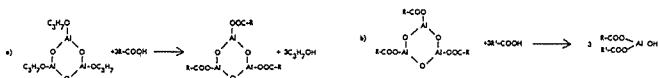
Obviously, the use of a single ordinary fatty acid will result in a classic aluminum grease without special characteristics.

Spectra of aluminum isopropoxide (Figure 21a) and of the trimer (Figure 21b) both in mineral oil, of isopropyl alcohol (Figure 21c) are shown for comparison. Apart from the weak band at 2620 cm^{-1}, the only difference that distinguishes the alcoholates from free alcohol is the band at 1030 cm^{-1}. Its position is similar to that of other alcoholates such as calcium and lithium methoxides. In practice, this band easily disappears, and for this reason its usefulness is limited.

For a better understanding of the reactions and in order to precisely monitor the phases previously described in the formation of a complex soap starting from acid mixtures, the reaction between the trimer alcoholate with the pure benzoic acid and of the trimeralcoholate with a fatty acid are shown in Figures 22 and 23 respectively.

The spectrum of benzoic acid in mineral oil (Figure 22a), shows the wide stretching bands of the OH of the acid groups overlapping the band at 3050 cm^{-1} of the aromatic C-H as well as the hydrocarbon bands at 3000-2800 cm^{-1}. The stretching band of the C=O of the acid is seen at 1680 cm^{-1} along with the skeletal-in-plane bands of the aromatic ring near 1600 cm^{-1}. The wide deformation band of the acid at 930 cm^{-1} and the aromatic monosubstitution at 710 cm^{-1} stand out among the remaining bands.

The acid and trimer were each diluted in oil and mixed at room temperature at a mole ratio of 3 acid: 1 trimer. In Figure 22b, recorded after settling, the acid bands have disappeared with the exception of small remnants at 1690 and 940 cm^{-1}; an OH band is visible at 3350 cm^{-1} and is probably due to the isopropyl alcohol formed by the reaction. The bands at 1580 and 1600 cm^{-1} are caused by the COO of the benzoate-aluminum link.

When the product was heated to 225°C the acid and alcohol residues disappeared (Figure 22c). It is interesting to note the absence of the characteristic aluminum grease bands at 3650 cm^{-1} and 990 cm^{-1}. This confirms the absence of OH and permanence of the trimer ring which remains stable in spite of the high temperature. The product does not thicken and appears to be a dispersion.

The addition of a new portion of benzoic acid at room temperature shows no further reactions (Figure 22d) up to at least 80°C. At 110°C, the acid band at 1680 cm^{-1} starts to decrease (Figure 22e) and the bands at 3650 and 980 cm^{-1} indicate the beginning of ring fracturing. The reaction is complete at 200°C. As seen in Figure 22f, the acid has disappeared and the aluminum dibenzoate formed presents the characteristic OH band at approximately 3650 cm^{-1}. The Al-OH link near 1000 cm^{-1} is slightly split and the two bands near 1600 and 1580 cm^{-1} correspond to the boundary peaks of the triplet usually found in complex aluminum soaps as should be expected the mass has not thickened.

In Figure 23 the previous process has been repeated using C_{16}-C_{18} fatty acids instead of benzoic acid. The addition of fatty acid in oil to the trimer, also in oil, at a mole ratio of 3:1 yields a spectrum (Figure 23a) of similar structure to that of the benzoate at the same stage, except for the absence of the aromatic ring. Absence of bands at 3650 and at 990 cm^{-1} shows that the trimer ring has not yet split. The single wide band at about 1585 cm^{-1} appears instead of the two benzoate bands at 1600 and 1580 cm^{-1}. When the product was heated to 225°C, the only significant change was the development of a band near 1720 cm^{-1} (Figure 23b). This development began at 130°C and increased gradually. It could be related to the formation of isopropyl ester of the fatty acid.

The addition of the second half of the fatty acid at room temperature showed the same behavior as with benzoic acid. Figure 23c shows essentially the previous spectrum with the addition of the acid bands at approximately 3500-3000 cm^{-1} and 1700 cm^{-1}. The product itself changed to a semisolid translucent mass. When it was heated to 90°C, a drastic change occurred and the mass developed all the characteristics of a conventional aluminum grease. This was reflected in the spectrum (Figure 23d), with bands appearing at 3650 and 980 cm^{-1} the soap band increased as the acid vanished almost totally. Simultaneously, the band at 1720 cm^{-1}, previously obscured by the acid band, has reappeared. Heating the grease to 140°C gave a typical spectrum of a neutralized aluminum grease with the exception of the band near 1720 cm^{-1} regenerated in the previous phase (Figure 23e).

From a comparison of Figures 22f and 23e, and particularly of the respective soap bands, it can be inferred that the soap triplet of complex aluminum greases is derived from the superposition of the bands of ordinary soap and the short chain acid salt, in this case benzoate. In fact, the behavior of these bands is to a degree independent, as can be seen in Figures 24a and 24b. These are spectra of a complex aluminum grease before and after oxidation, in which the sharp decrease of the fatty acid band predominates, whereas the benzoate bands do not undergo any noteworthy alteration.

Figure 25 follows the process of the grease formation and permits an analysis of the possibilities of using IR for composition readjustments. Figure 25a shows the product after addition of the acids to the trimer and heating to 85°C. Soap formation is shown by the predominance of benzoate bands and the start of the rupture of the trimer ring when both phases of the reaction are intermingled. No trimer band is observed and the free acid band predominates.

Figure 25b shows the reaction is completed after heating to

190°C. The fatty acid is present to a higher degree in the soap band. The presence of residual excess acid is detected from the characteristic bands.

An attempt was made to neutralize the excess acid by adding an additional quantity of trimer. This trimer was added in excess in order to determine whether the excess was detectable. The reaction at 50°C was immediate, and the acid band disappeared (Figure 25c). The excess trimer is not detectable, and the soap band is not altered appreciably. After heating at 185°C, it can be observed in Figure 25d that the fatty soap band is reinforced with respect to the benzoate bands. Upon adding a fresh quantity of fatty acid at 185°C and quickly recording a spectrum, the presence of this acid could be detected (Figure 25e). Three minutes later, the free acid was no longer detectable Figure 25f. This confirms the existence of non-reacting trimer or its intermediate product. The incorporation of this acid is reflected in the spectrum by the new increase in relative intensity of the soap band corresponding to the fatty acid.
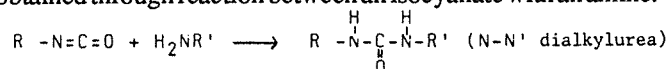
In conclusion, it seems clear that in the case of complex aluminum greases as with complex calcium greases, IR allows the monitoring of the various reaction phases. The formation of by-products can be determined, as can the relative proportions of both long and short chain acid components. Excess acid is detectable, and its neutralization by means of alcoholates can be monitored. However, it is not possible to detect the presence of excess alcoholate other than by its property to neutralize new acid additions. In these cases, the volatility of the benzoic acid at high temperature must be taken into account, as well as the risk of reducing the dropping point and other properties of the finished product. Such would occur if the originally selected ratio is imbalanced through the introduction of new quantities of fatty acid exclusively.
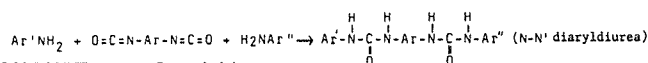
Substituted Urea Greases

Substituted urea greases are fundamentally different from those discussed up to now. Nevertheless, they are worth consideration as unlike other non-soap thickeners, (such as bentones, phthalocyanines, silicas, hydrocarbon polymers, etc.), *in situ* formation of polyureas implies a chemical reaction which may be monitored by IR.

The basic chemical structure of these thickening agents is substituted N-N' urea, having the general formula

The possibility of R and R (prime symbol) containing active substitution groups permits repetition of the structure leading to the formation of polymers with many possible variations. Such would depend on whether the substituted agents are aliphatic or aromatic, the length of the chains linked to the functional groups, and the presence of other substituents such as halogens.

In practice, a substituted N-N (prime symbol) urea can be obtained through reaction between an isocyanate with an amine:

$$R -N=C=O + H_2NR' \longrightarrow R -\overset{\overset{H}{|}}{N}-\overset{\overset{}{\underset{\underset{O}{||}}{C}}}-\overset{\overset{H}{|}}{N}-R' \quad (N-N' \text{ dialkylurea})$$

If as mentioned before, R' contains another isocyanate group, the basic structure is repeated through reaction with other amine molecules, thus yielding diureas:

$$Ar'NH_2 + O=C=N-Ar-N=C=O + H_2NAr'' \longrightarrow Ar'-\overset{\overset{H}{|}}{N}-\overset{\overset{H}{|}}{\underset{\underset{O}{||}}{C}}-\overset{\overset{H}{|}}{N}-Ar-\overset{\overset{H}{|}}{N}-\overset{\overset{}{\underset{\underset{O}{||}}{C}}}-\overset{\overset{H}{|}}{N}-Ar'' \quad (N-N' \text{ diaryldiurea})$$

If diamines are used, the molecule polymerizes by reacting with another diisocyanate molecule, and the reaction continues. The addition of a monoamine will stop polymerization. In practice, monoamines are mixed with the diamines, from which tetraureas, predominantly, are obtained. The isocyanate group is often introduced into the reaction with toluenediisocyanates.

The various types of substituted-urea thickeners can be identified with IR [15]. For monitoring the formation of the thickeners, however, the presence of the isocyanate group is of interest because of its strong band at approximately 2250 cm⁻¹ that corresponds to the asymmetrical stretching frequency of the isocyanate group (-N=C=0). The corresponding symmetrical stretching band, between 1415 and 1350 cm⁻¹, is much weaker with no practical usefulness.

Amines, the other components of the reaction, have NH stretching bands between 3500 and 3200 cm⁻¹, two in the case of primary amines and one with secondary amines. There are other distinctive amine absorptions the in plane NH deformation near 1600 cm⁻¹; deformation of the C-N link between 1360 and 1020 cm⁻¹ (higher frequencies belonging to the aromatic amines); wide band of out-of-plane deformation of the NH between 900-650 cm⁻¹.

Figure 26 shows the development of a polyurea grease by reaction between toluenediisocyanate (TDI) and amines in mineral oil. The absence of aromatic amines simplifies the spectrum. Albeit unusual, the fact that the amines have been added to the isocyanate in portions allows a progressive monitoring of the formation of the urea and the disappearance of the isocyanate. Were it not for the partial additions, following the reaction would not otherwise be easy due to the high reactivity of the components.

In Figure 26a, the spectrum of 2,4-and 2,6-toluenediisocyanate in mineral oil shows the very strong stretching band of the isocyanate group at 2250 cm⁻¹. In Figure 26b the effect of the addition of a small amine portion can be seen. No diminution of the 2250 cm⁻¹ band is evident (the slightly more intense absorption is due to small differences in film thicknesses). The band at 3300 cm⁻¹ (stretching of NH), and the intensity of absorption at 1600 cm⁻¹ and 1560 cm⁻¹ indicate the formation of the Amide I (stretching of C=0) and the Amide II (deformation of the NH and C-N) bands.

As the amine concentration is increased, the diminution of the stretching isocyanate band becomes clearly noticeable (Figure 26c). The disappearance of other, less important, bands is also detected. Simultaneously, the amide bands I and II develop strongly, and the amide III band at 1240 cm⁻¹ (CN stretching) appears. At this state, the spectrum resembles that of the finished grease except for the remaining isocyanate band. From this point on, the reaction is monitored by the disappearance of this band.

Figure 26d corresponds to a finished grease containing only traces of residual isocyanate, although its band is still faintly visible at 2250 cm⁻¹. This spectrum somewhat resembles that of sodium terephthalamate (Figure 20f) due to the amide groups present in both.

For comparative purposes, Figure 27 shows the monitoring of

the previous reaction through the inverse procedure of adding TDI to the amines. The spectrum of the amine solution in mineral oil (Figure 27a) shows the following bands: Stretching double NH band between 3400-3200 cm^{-1} due to primary amines, in-plane deformation NH band at 1590 cm^{-1}, stretching C-N band at approximately 1060 cm^{-1}, and wide, strong out-of-plane deformation NH band at 800 cm^{-1}.

After the addition of mineral oil solution containing approximately 10 percent of the total TDI to the amine solution the spectrum changed somewhat as seen in Figure 27b. The stretching NH band is increased and shows a tendency to become a single band, whereas the absorption of the deformation in plane at approximately 1590 cm^{-1} is changing into what will become the Amides I and II bands. The CN stretching and the out-of-plane NH deformation bands at 800 cm^{-1} decrease in intensity. The Amide III band starts to appear at approximately 1240 cm^{-1}.

After 75 percent TDI was added, the spectrum (Figure 27c) strongly resembles that of a finished grease. The NH stretching band has become a single band although it still overlaps traces of the wide band between 3700-3500 cm^{-1}. This indicates that the reaction is not yet complete. The Amide I and II bands are now clear and strong at approximately 1620 and 1575 cm^{-1}. The Amide III band at 1250 cm^{-1} is still weak but fully defined. Traces of the amine deformation band at 800 cm^{-1} can be still observed. After the complete addition of TDI, the spectrum (Figure 27d) of the finished grease is essentially identical to that of Figure 26d.

Monitoring the reaction of the addition of TDI to amines is not as clear-cut as when the reverse if the case. When adding TDI to the amines, the evolution of the spectra shows that the most suitable monitoring criteria are the change in shape of the wide stretching band at 3700-3400 cm^{-1} and the disappearance of the inflection at 800 cm^{-1}, both due to amine NH bands. The usefulness of the latter band, only present in primary amines, is of doubtful utility when aromatic bands are present. These spectra also show the progressive development of the Amide I, II, and III bands, respectively at 1620, 1575, and 1220 cm^{-1}.

Because isocyanates and amines are both volatile and toxic, processing of these products is normally carried out under stringent safety conditions making it difficult to obtain the samples. In any case, IR provides an effective method for the study and quality control of processes involving these type products.

Conclusion

We have examined several examples of the thickener formation phase in various lubricating greases to demonstrate the usefulness of process monitoring with IR. The primary advantage of IR lies in its speed and in the fact that a spectrum is a faithful, graphic reflection of the condition of the system at that time. With this, it is possible to follow the development of reactions with respect to time by comparing the successive spectra obtained in different phases of a process. This implies the possibility of modifying the reaction conditions of the system with a view toward optimization.

With regard to the determination of the neutralization point, compared with the volumetric monitoring techniques, IR has the basic advantage of not altering the sample during handling. Although less accurate in determining the excess of a component, the information provided by IR, in the case of incomplete reactions, is more reliable than that obtained by titration. This is because, with titration volumetry, there is a risk of the reaction continuing during the sample preparation with the result that the measurement does not reflect the true initial condition of the sample in which case IR is better suited. Also, titration is not suitable in some cases, as for instance in the case of free esters which are not detected by this method. On the other hand, in some instances IR may not prove effective because some basic products have exceedingly weak bands for interpretation. Fortunately, both extremes do not occur at the same time, and the determination generally can be effected with one technique or the other. Thus, titrimetry and IR analysis may be considered as complementary to each other.

Some of the cases presented herein have been studied in depth. From which we can conclude that, in research and more specifically in development of new products and improvement of existing products, IR has increased its value. IR will point to new avenues of research, based on more rational premises, it can detect aspects which otherwise would have passed unnoticed, and it will aid in the interpretation of observations obtained with other techniques. An example illustrating this point is the section devoted to calcium greases, in which the existence of a generally similar nature is proven through the analysis of the evolution of their most characteristic bands. These very significant similarities reflect common origin which could not have been presumed from the external appearance of the products or by their physical properties.

An attempt has been made to provide a general picture with examples of products from various bases, such as calcium, lithium, sodium, aluminum and polyurea. Although the less common types (such as barium, potassium and strontium) were not discussed, it should be pointed out that these monitoring techniques are similarly applicable. Mixed base greases and their high number of possible combinations [29] have not been discussed here, although their study with IR offers interesting possibilities.

Spectral interpretations should be made with reservations, as IR of itself does not provide a base solid enough to inspire definitive conclusions. Thus, the technique of considering the soap and short chain component bands of complex calcium and aluminum greases as if they formed and developed independently is no more than a practical method of simplifying the monitoring of the reaction. It does not take into account the strong relationships between the components which have been described by others [30,31].

At any rate, in the spectrum of a grease many other secondary bands exist as a result of the physical state and surroundings of the molecules. For one who is familiar with his products and knows their precise composition, these secondary bands are highly significant. Their consideration suggests the use of IR in the later stages of grease production phases which are just as

important as that discussed here, and yet more delicate, without which it would not be possible to obtain a product with the required properties. The type of help offered by IR is more specific and is the result of a very subjective interpretation, consequently it may not be readily transferred to other cases as it is often tied to small details specific to the process, the equipment, and the nature of minor components in the formulation.

Under these conditions, it is evident that we approach a field of application for IR which may appear more suited to research work in the field of structure, transition temperatures from the crystalline to the liquid state, and formation of complexes and polymorphous stages of soaps[32-39]. In this borderline circumstance between application work and a more theoretical research program, the user of the technique must decide whether the usefulness of the technique justifies his efforts in this field.

Currently, many tons of excellent quality lubricating greases are produced every day in the world without recourse to IR, and there are many experienced manufacturers quite convinced than the achievement of this quality is a bigger challenge today to manufacturing techniques that to the chemical composition of the product.

However, one must consider that the implementation of reproducible processes to achieve consistent quality, is the result of prior research which required more than one test with readjustments during production. In these stages of perfecting the production stream, IR is a tool of unquestionable value. Its usefulness extends to the study of anomalies observed during routine production.

The empirical use of IR is a main reason for its wide application. Despite its empirism, the application of IR to the technology of development and production of lubricating greases undoubtedly will bring scientific insights to an industry which has been for many years qualified as an art rather than a science.

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About the Author

A. Izcue G.
graduated from Saria Chemical Institute, Barcelona, Spain, as a chemist engineer. In 1965, after a year as analytical chemistry laboratory assistant at the Institute, he joined Krafft, S.A. a Spanish company for automotive and industrial products as a research chemist in the area of lubricating greases. Also in charge for some years of grease manufacture, he is presently director of Lubricants Research & Development. He is a recipient of the NLGI Authors' Award.

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