August 27th 2020
1:40-2:25 pm EST
NLGI Technical Week

THE MECHANICAL STABILITY OF POLYMER-MODIFIED GREASES

Erik Willett – Technical Director

Functional Products Inc.

Presenter Bio:

Erik Willett
Technical Director
Functional Products Inc.

Professional Background:

Material scientist focused on using polymers to solve problems in lubrication; develops additives and formulates conventional and specialty lubes/greases

- PhD Polymer Science (U. of Akron)
- BS Chemistry, Polymer Focus (U. of Connecticut)
- 2018 NLGI Development Author Award
- Articles in NLGI Spokesman, LnG, TLT

FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

NLGI Serving the grease industry since 1933

Outline

"Do polymers affect the mechanical stability of grease?"

- Motivation
- Grease Polymer Theory
- Experimental Design
- Interpretation of Results
- Key Points

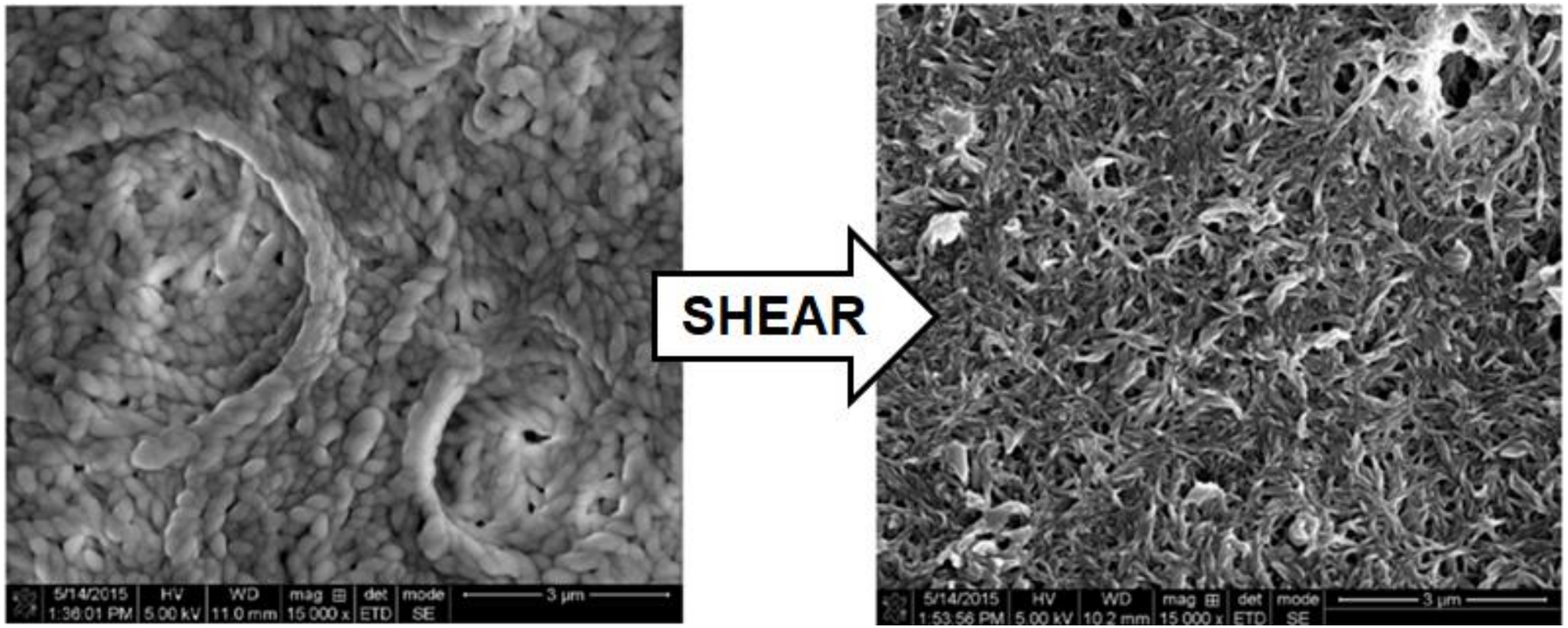
"Yes, but…"

FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

NLGI Serving the grease industry since 1933

Motivation

- Polymers will continue to play a role in emerging grease specs and applications
  - HPM spec (water resistance, oil bleed), biobased grease, fill-for-life, EV market, etc.
- The ability to stay in grade and avoid consistency changes is critical to success



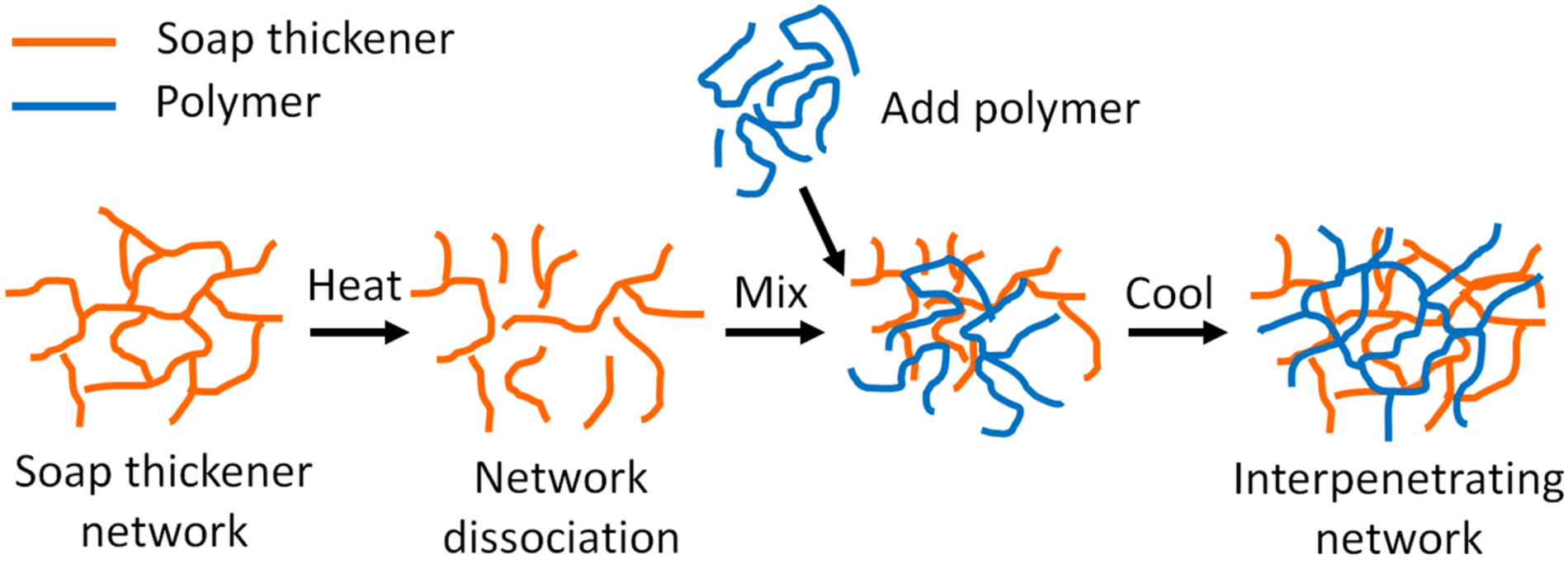
Rezasoltani, A. & Khonsari, M. M. Lubricants 4, (2016).

FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

NLGI Serving the grease industry since 1933

Grease Polymers

- Grease polymers form interpenetrating networks with grease thickener
- < 1wt% has significant effects on tackiness, water resistance, oil bleed, and rheology
  - **Does using polymers for one purpose have consequences on mechanical stability?**

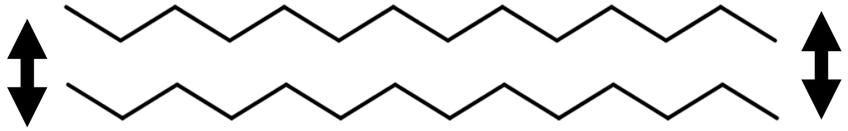


FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

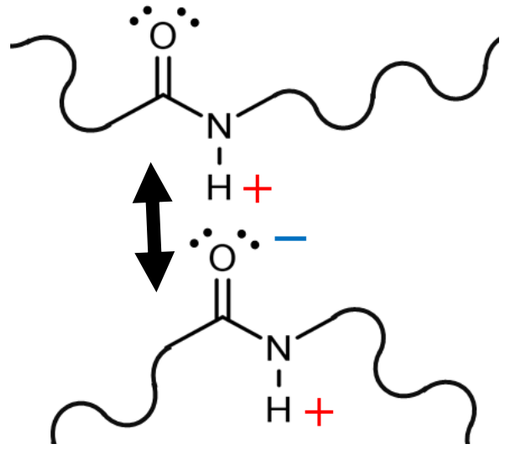
NLGI Serving the grease industry since 1933

Grease Polymer Types

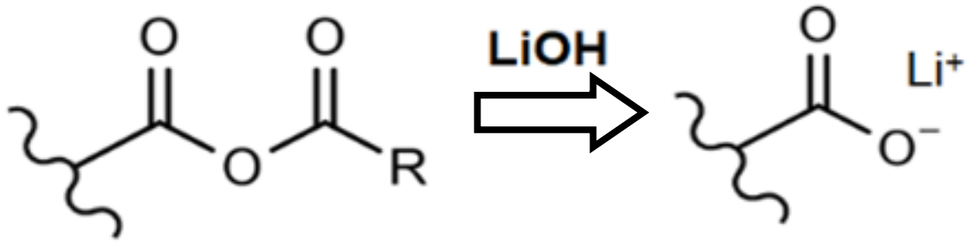
- **Temperature Sensitive** – long runs of ethylene or styrene form waxy linkages



- **Hydrogen Bonding** – interactions between polar Lewis acid (+) and base (-) sites



- **Reactive** – reaction between –OH or M^+ with acid anhydrides



FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

NLGI Serving the grease industry since 1933

Experimental Design

1. Screen a variety of greases with different structures against several different types of grease polymers to find positive or negative interactions

2. We assume an increase in consistency coincides with structuring b/w grease and polymer
   - i.e. formation of an Interpenetrating Network (IPN)

3. We then proceed with roll stability only on the positive grease + polymer combinations to evaluate if consistency from polymer is shear stable
   - We assume negative combos have already shown mechanical instability (6ox worked)

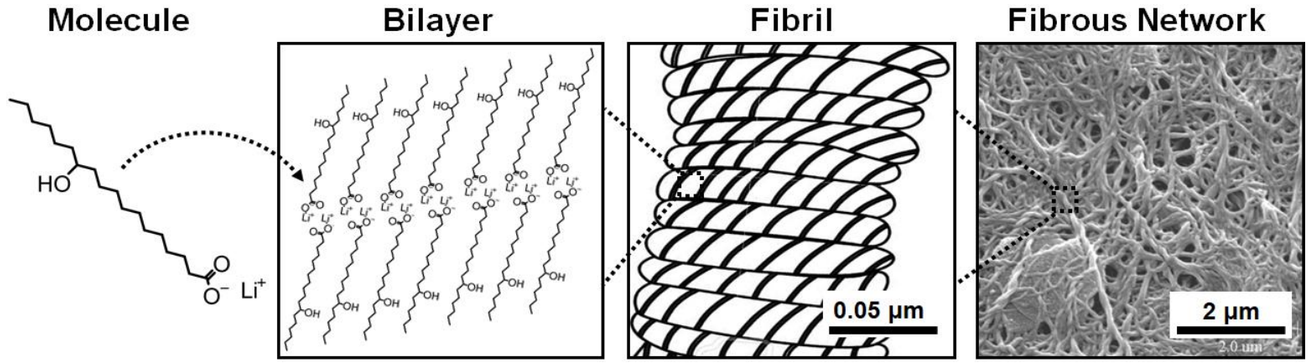
FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

Serving the grease industry since 1933 NLGI

The Greases

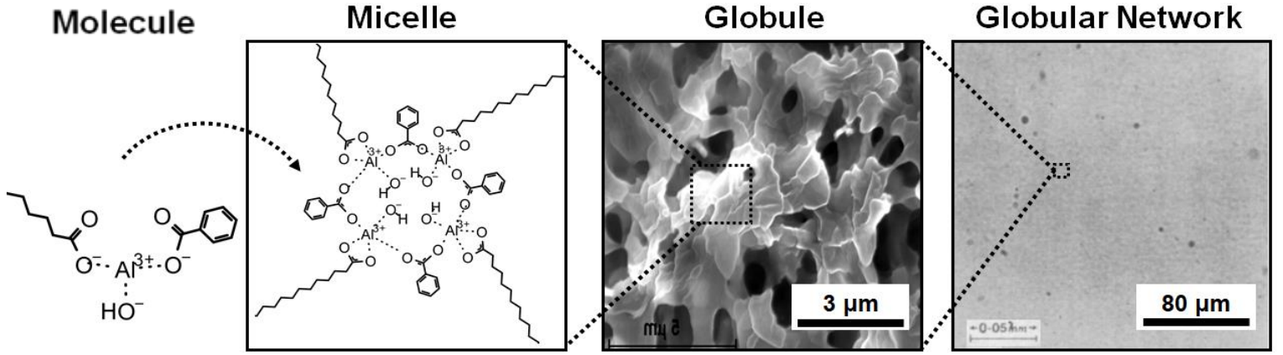
- Simple Lithium
- Lithium Complex

"FIBROUS"



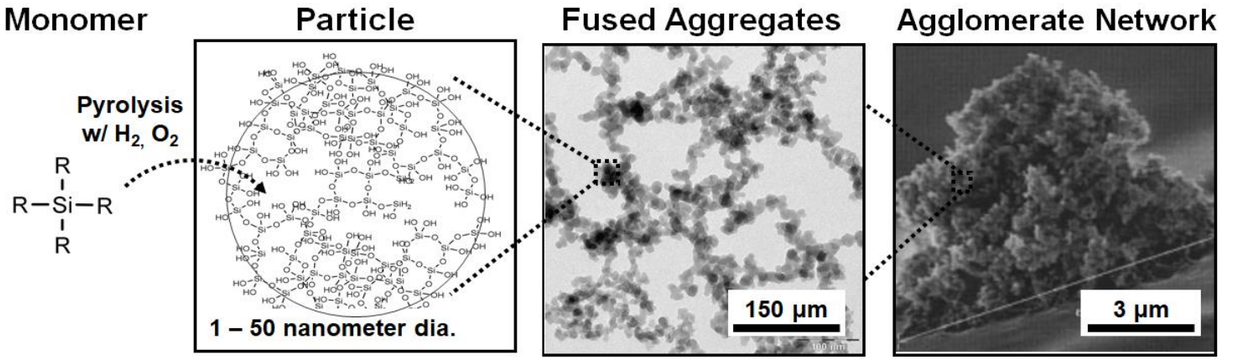
- Calcium Sulfonate
- Aluminum Complex

"GLOBULAR"



- Silica
- Bentonite Clay

"PARTICLE"



FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

Microscopy and structures based on Refs 3-13 in paper

NLGI Serving the grease industry since 1933

Grease Properties

Thickener	Cone Pen. (D1403)	NLGI Grade (D217)	Base Oil (D445, D2270)	Dropping Point (D2265)	Roll Stability (D1831)
Simple Lithium	272	2	ISO 150 VI 98	391F / 199C	+1.2%
Lithium Complex	264	2.5	600N VI 113	518F / 270C	+36.1%
Calcium Sulfonate	242	3	ISO 100 VI 111	>752F / 400C	+3.1%
Aluminum Complex	253	2.5	ISO 150 VI 108	542F / 283C	+1.5%
Silica	309	1.5	600N VI 124	642F / 339C	+2.3%
Clay (Bentonite)	350	0.5	ISO 460 VI 101	>752F / 400C	+11.3%

- Milled commercial greases minus polymer
- Base oil sampled from oil bleed

FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

NLGI Serving the grease industry since 1933

The Polymers

- We know:
  - Certain grease thickeners favor specific types of grease polymers
  - MW dependencies exist for parameters such as water resistance and tack

- **Nine** polymers selected:
  - A low and a high MW example each from four categories:
    - Temperature sensitive grease polymer
    - Hydrogen bonding grease polymer
    - Reactive grease polymer
    - Tackifier

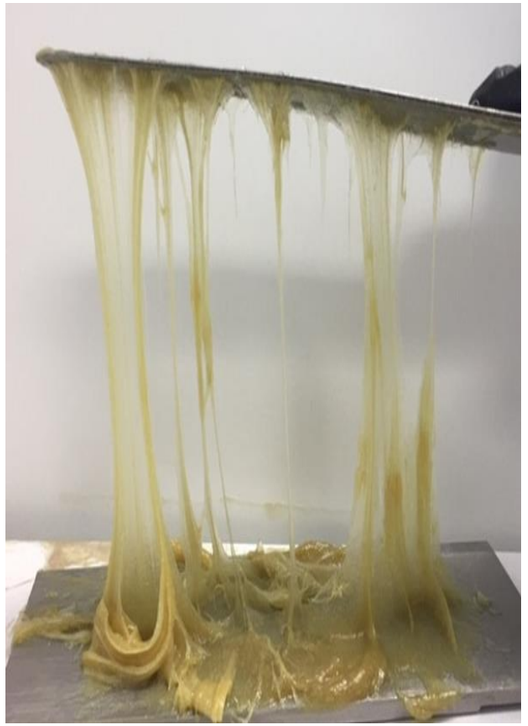
  - Plus one dispersant PMA

FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

Serving the grease industry since 1933 NLGI

Polymer Details

- Low MW grease polymers = 100,000 – 200,000 Mw
- High MW grease polymers = 300,000 – 600,000 Mw



- Low MW tackifier was olefin copolymer
- High MW tackifier was an ultrahigh MW PIB

- Dispersant PMA with short/long alkyl groups and amine functionality (0.1% N)

FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

Serving the grease industry since 1933

Sample Prep

- Polymers added to pre-made greases from liquid concentrate to standardize the addition between different greases and expedite the preparation of 60 samples

1. Each polymer diluted to 8-10wt% in 100N with mixing at 100-120°C for 24 hrs
2. Filtered then added at 5wt% to each base grease
3. Greases mixed at 80-100°C for 2 hours
4. Allowed to rest at room temperature for 24 hours before testing

- Control samples prepared by adding 5wt% of 100N
- Did not mill post-addition

FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

Serving the grease industry since 1933 NLGI

Data Handling

- Our goal is to cast a wide net and establish a high level study to look at **trends**
    - Many data points: 6 greases x (9 polymers + 2 controls) x multiple measurements…
- Two simplifications to data analysis:
    1. Changes to consistency with polymer are noted only if grade changes by 0.5 or more
        - Change from 280 to 270 is still NLGI #2
    2. Changes to roll stability are significant only if larger than method error
        - 3.8% error based on ¼ cone and average consistency tested

FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

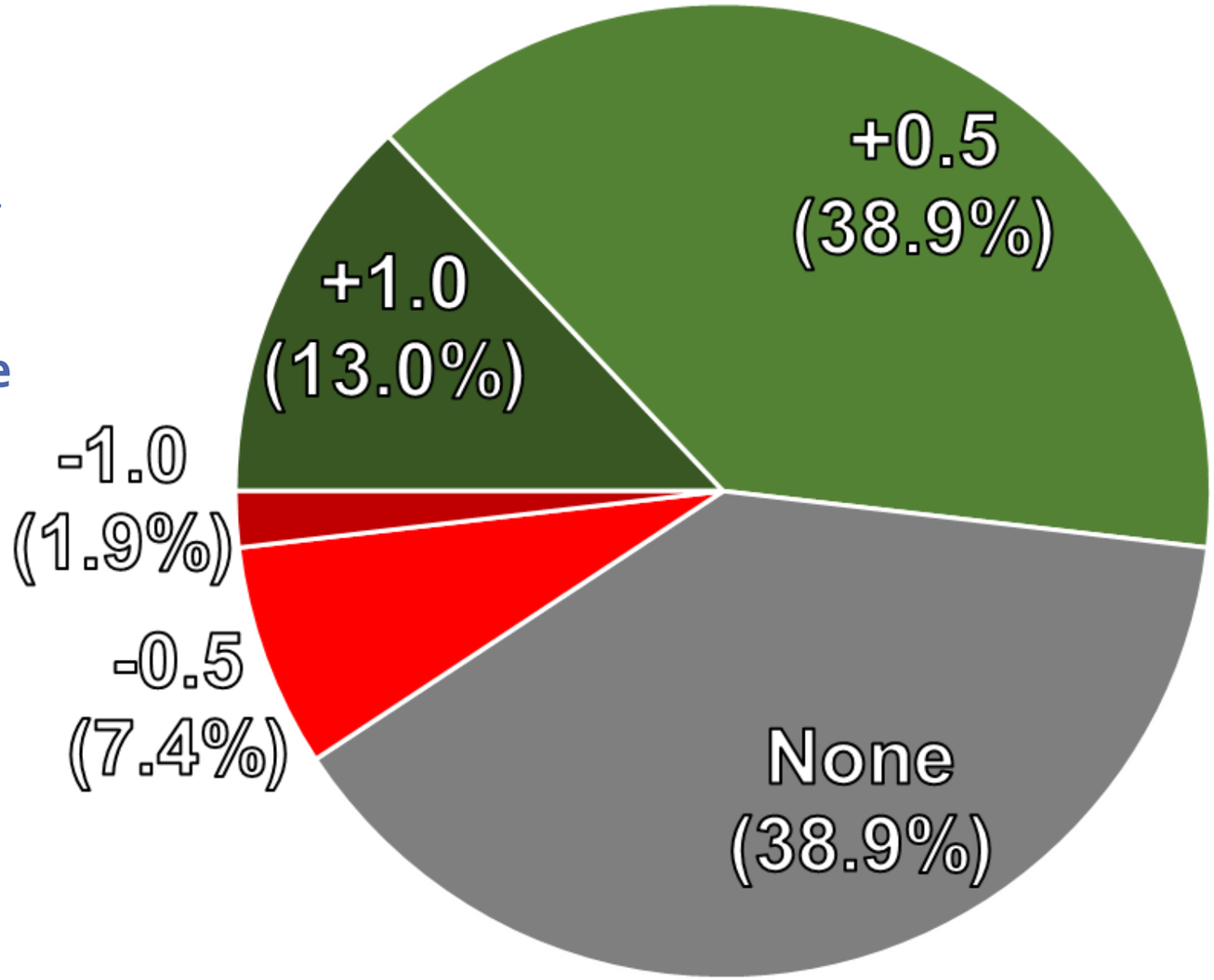
NLGI Serving the grease industry since 1933

Findings – Consistency

54 greases; control = grease w/ 5% oil

- ~ 52% of cases show **grade increase**
- ~ 39% show **no grade change**
- ~ 9% show **grade loss**

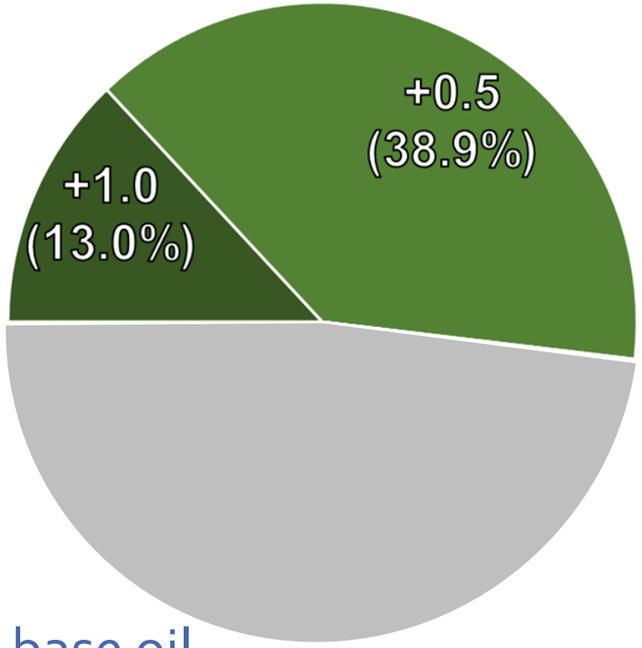
NLGI Grade Change In Polymer-Modified Grease



FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

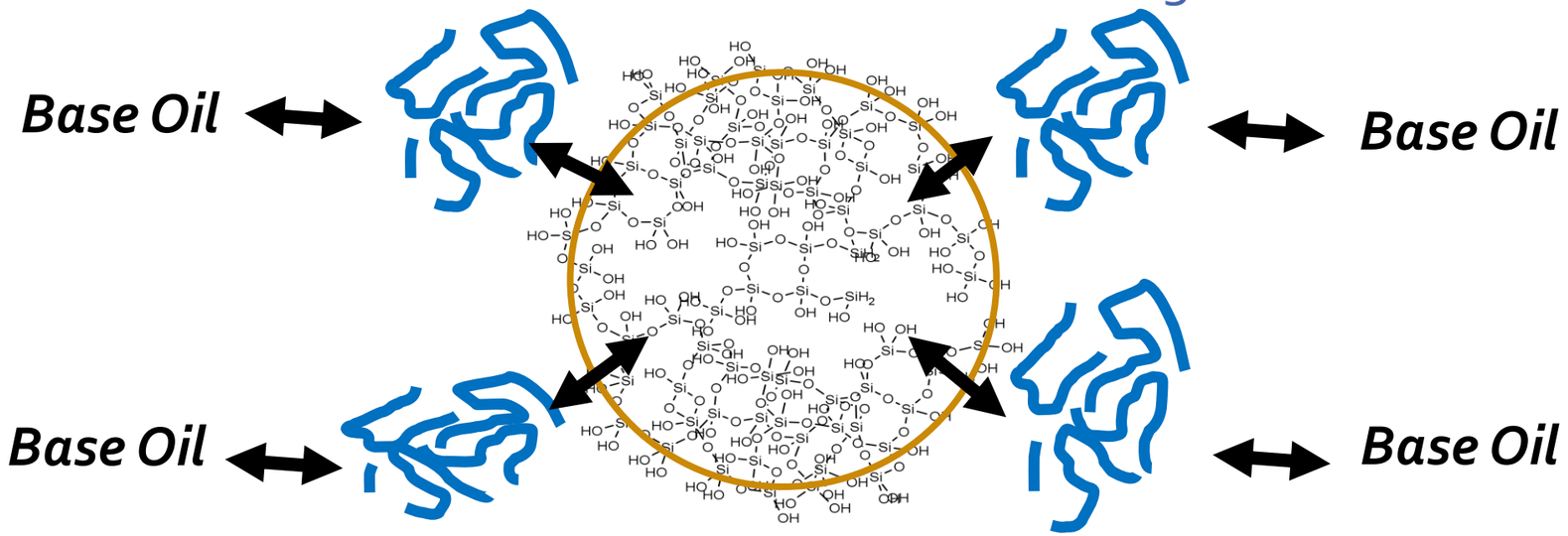
NLGI Serving the grease industry since 1933

Consistency **Gain**



- Lithium and lithium complex greases with most polymers
- Calcium sulfonate with lube oil tackifiers

- Clay with hydrogen bonding or reactive polymers
  - Polymer likely associating with surface sites and coupling clay to base oil
    - We see less effect on the more surface inactive silica grease

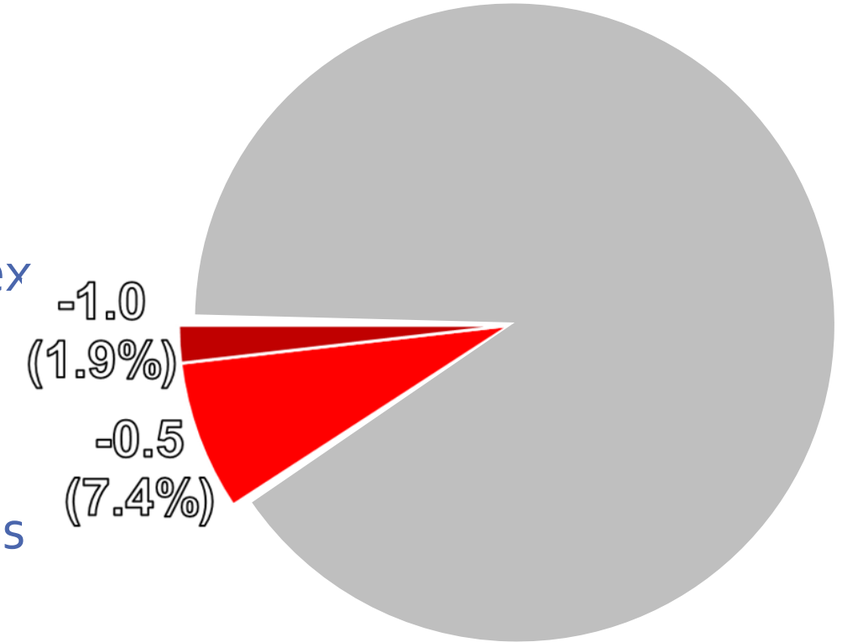


FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

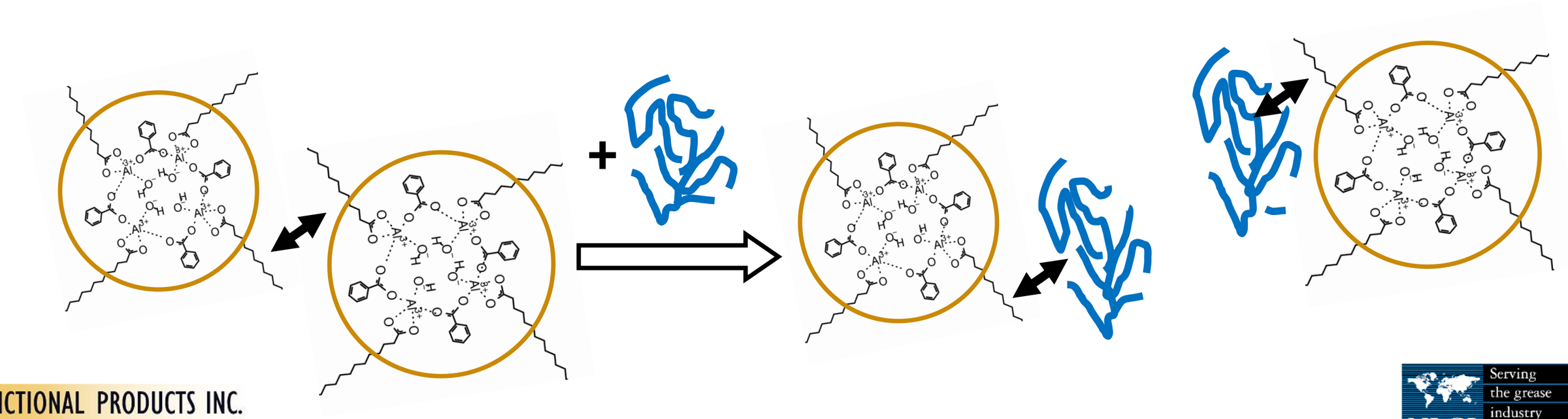
Serving the grease industry since 1933 NLGI

Consistency **Loss**

- Only observed in calcium sulfonate and aluminum complex
  - Significant in stearate-based AlX w/ waxy polymers



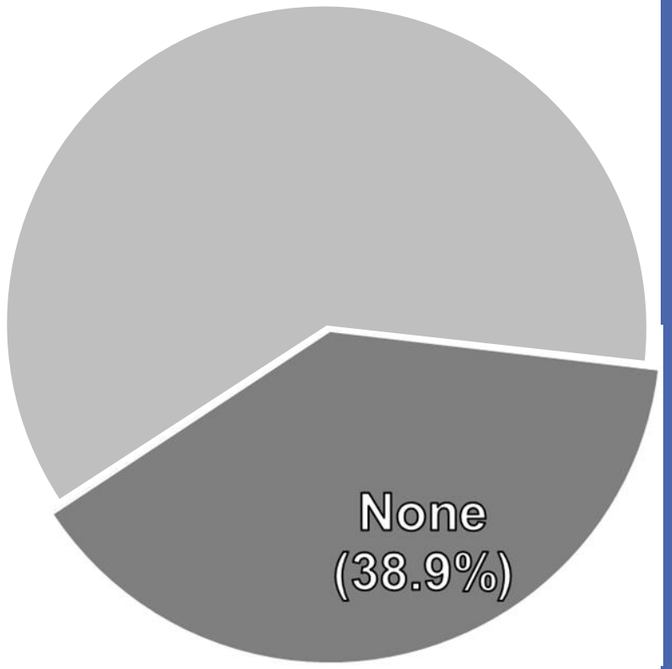
- 'Globular' grease network of stearate-stearate interactions
  - Waxy polymers can disrupt wax networks (aka PPDs)



FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

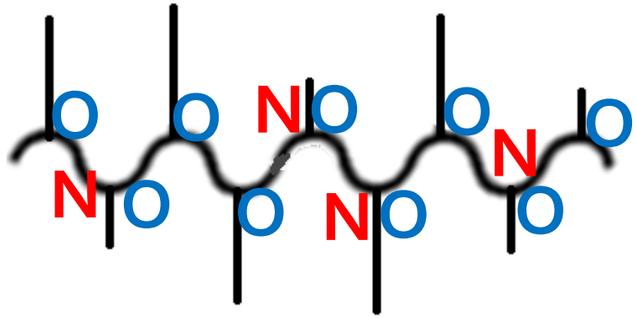
Serving the grease industry since 1933 NLGI

Consistency **Unaffected**



- Silica grease
  - Fumed silica, lower surface functionality than clay, more inert

- Greases with dispersant PMA
  - Polar sites in low concentration, protected by long alkyl groups
    - Low interaction w/ thickener



- Greases with low MW H-bonding polymer
  - Least effective grease polymer, too poorly soluble in paraffinic to perform correctly

FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

NLGI Serving the grease industry since 1933

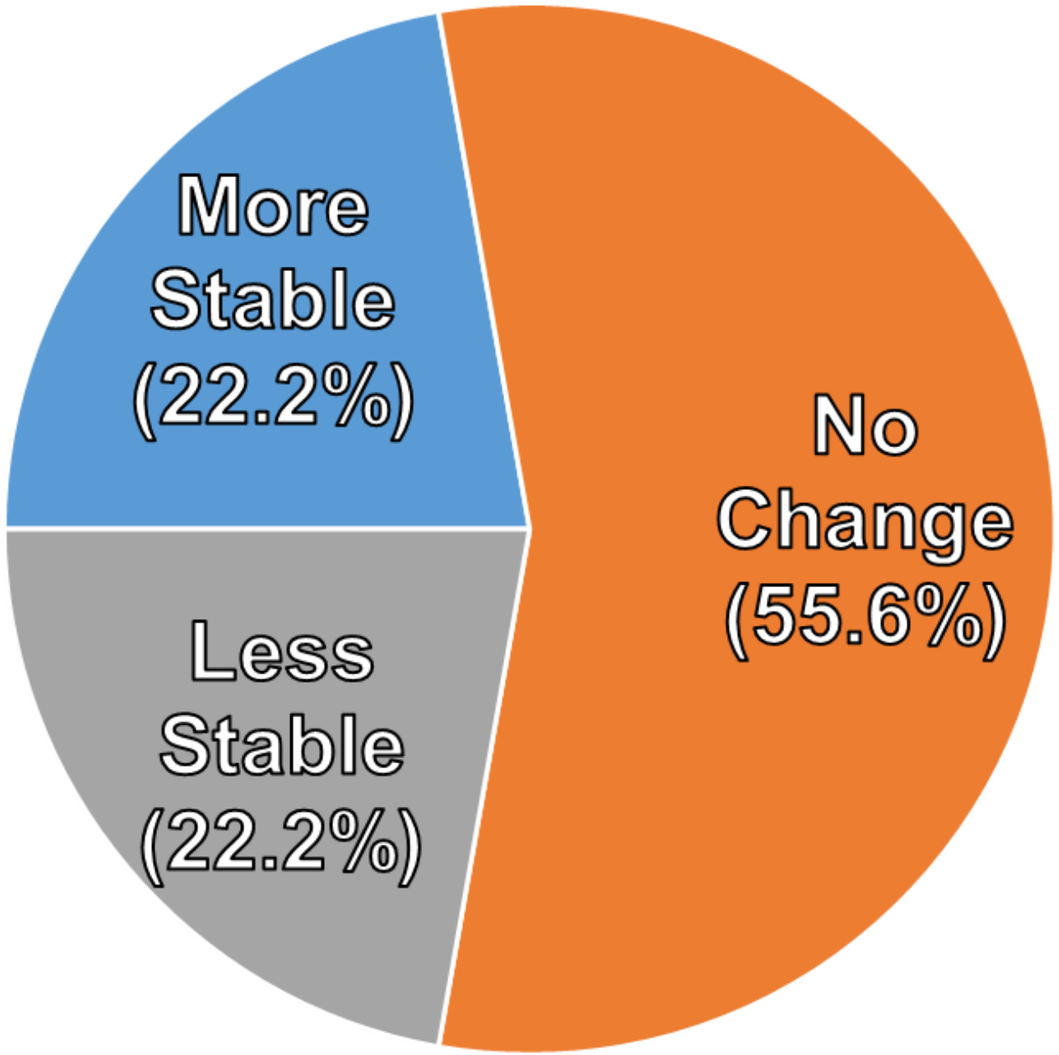
Findings – Roll Stability

27 greases, control = base grease:

Only measured for greases with grade gain

- ~ 22.2% show **more roll stability**
- ~ 22.2% show **less roll stability**
- ~ 55.6% show **no change within error**

Roll Stability Change In Polymer-Modified Grease

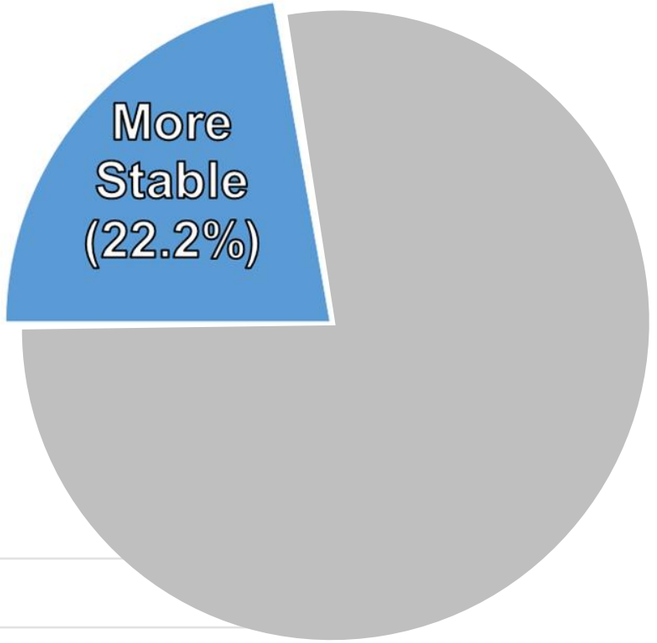


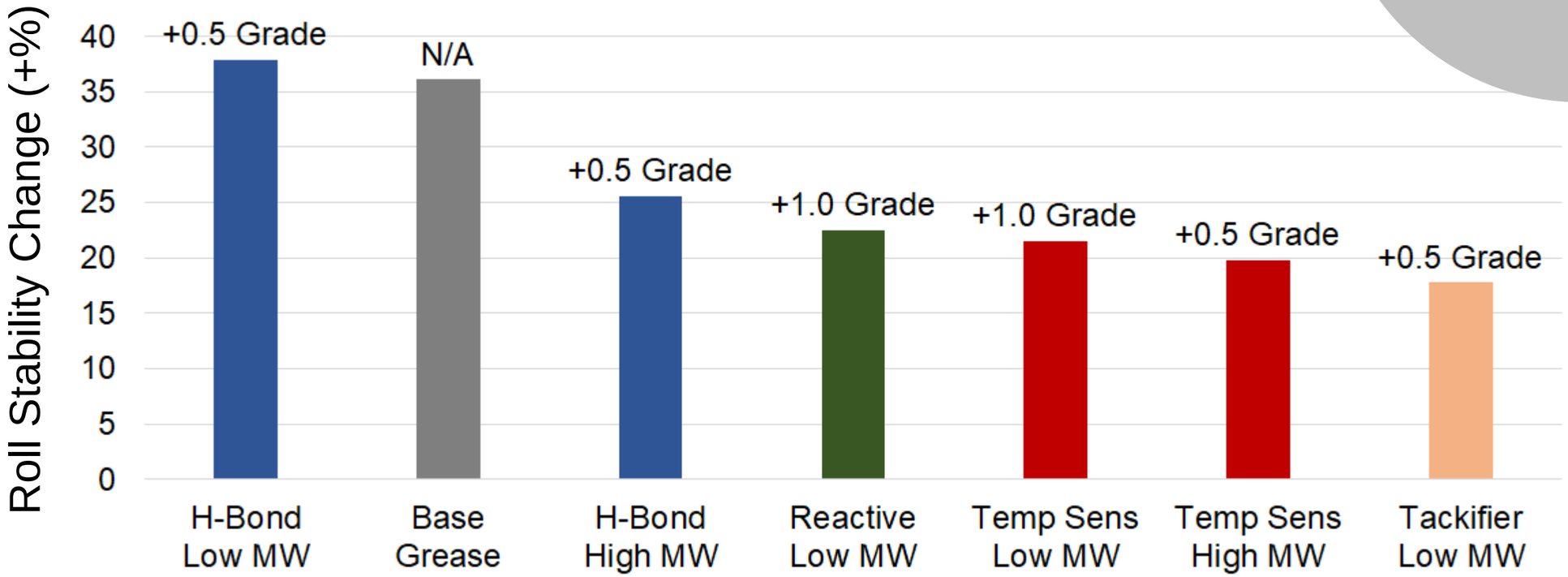
FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

NLGI Serving the grease industry since 1933

Roll Stability Improves

- Almost exclusively in lithium complex grease
  - Best stability from the non-polar high MW polymer
  - Similar stability whether +0.5 or +1.0 grade

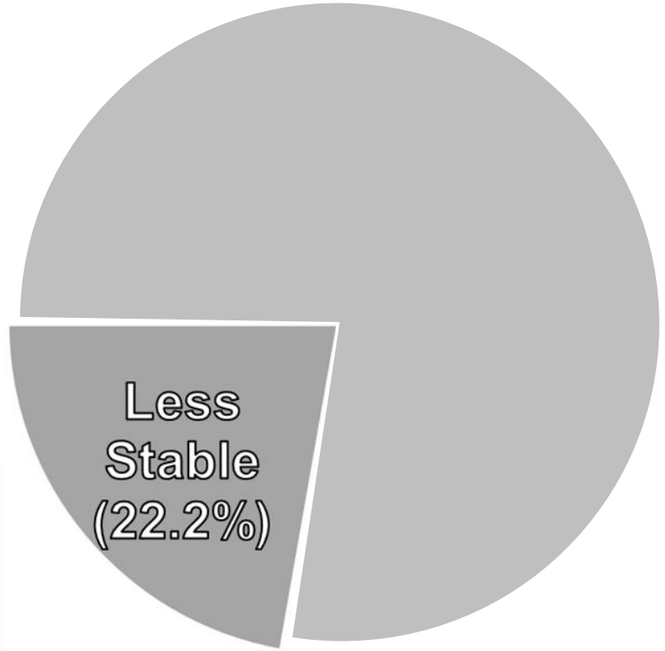




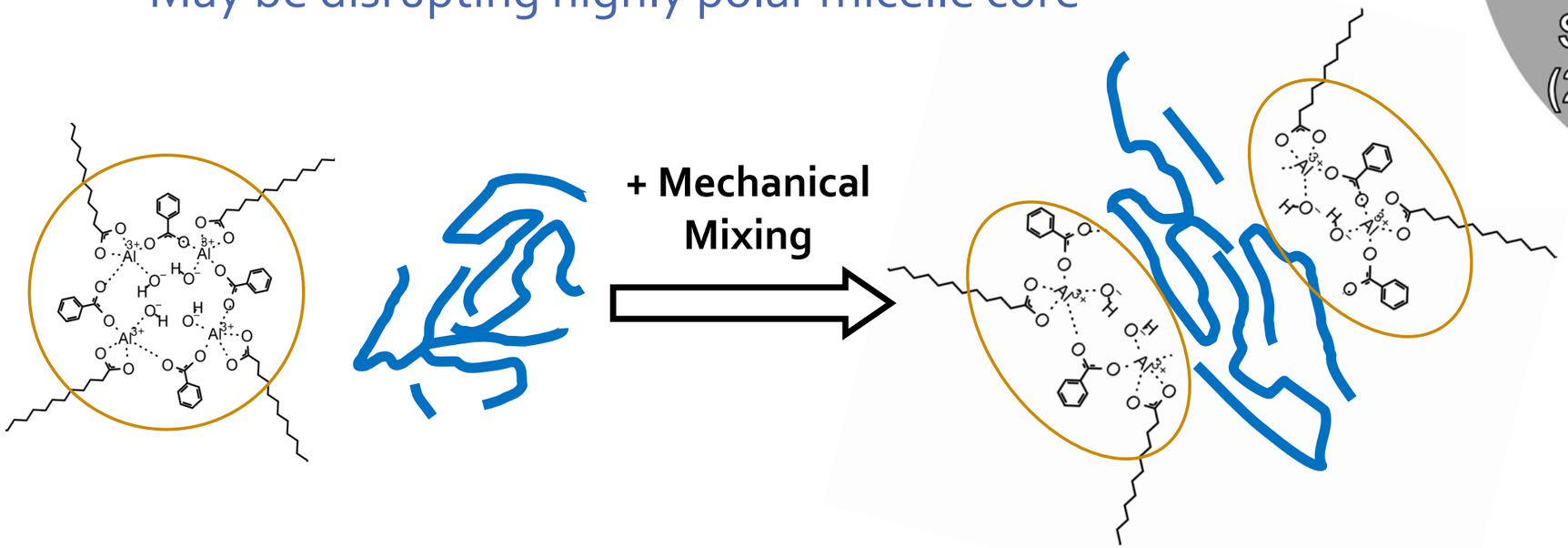
FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

Serving the grease industry since 1933 NLGI

Roll Stability Worsens



- Most common in calcium sulfonate and AlX
  - H-bonding and reactive polymers are antagonistic
    - May be disrupting highly polar micelle core

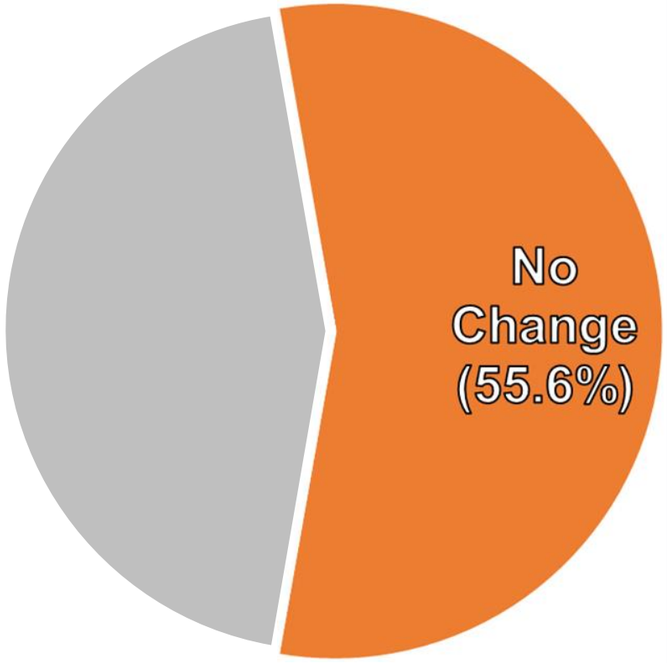


- May be an artifact from not milling post-addition
  - But did not happen consistently for same greases or polymers

FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

Serving the grease industry since 1933 NLGI

Roll Stability Unaffected



- Most common in simple lithium and clay
- May still be considered a 'win' for grease polymers
- Thickener content reduced but net gain in grade from polymer
  - Implies a considerable amount of consistency now from polymer but no loss in stability
- *Let's consider D1831 vs. other lubricant shear methods…*

FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

NLGI Serving the grease industry since 1933

Mechanical Shearing Methods

- Compare magnitude of conditions at work in D217 and D1831 versus lube shear methods
- Most grease polymers fall in MW range of engine oil polymers (25-60 SSI by K-O)

LUBE OIL GREASE

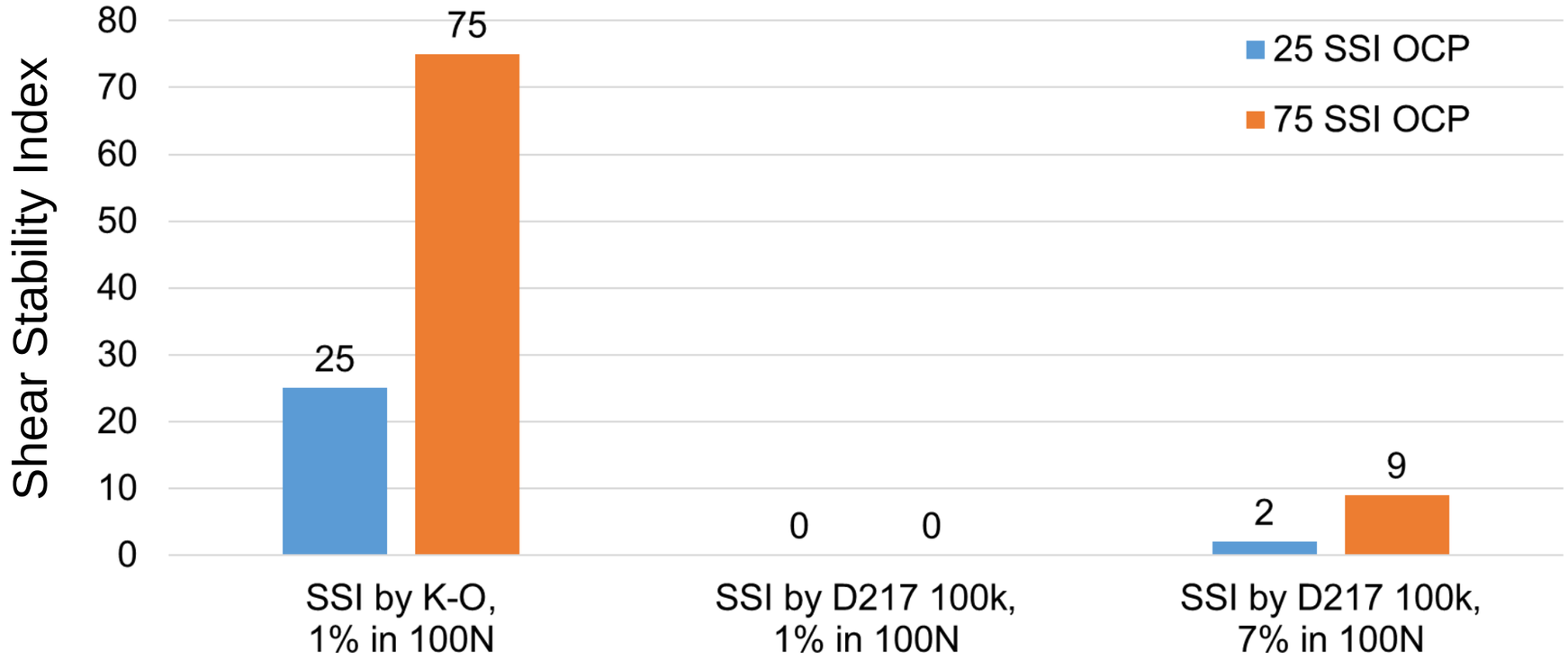
Method	Nominal Speed	Load or Pressure	Temp	Hours
ASTM D217 Worked Cone	0.133 m/s (60 up-down 2.625” strokes/min)	Undefined	25°C	27.8 (100K)
ASTM D1831 Roll Stability	0.755 m/s (3 35/64” dia. roller weight @ 160 rpm)	5 kg weighted roller	25°C	2
ASTM D6278 Kurt Orbahn	111 m/s (170 mL/min, 0.18mm dia. nozzle)	2600 psi across 0.18mm dia.	35°C	0.5
ASTM D2603 Sonic Shear	6,000 – 20,000 oscillations/second	Ultrasonic cavitation (100 – 500W)	40°C	0.67
CEC L-45-99-A 20 Hour KRL	4.15 m/s (54.7mm race dia. @ 1450 rpm)	509.9 kg (5000 N)	60°C	20

FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

NLGI Serving the grease industry since 1933

Final Look at Shear

- Two olefin copolymers at 1wt% and 7wt% in 100N, sheared by D217 100K stroke
- ~90% less shear than D6278 K-O, the least aggressive lube shear method



FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

Serving the grease industry since 1933 NLGI

Conclusions

- Grease polymers can often provide increased consistency (yield) to a variety of greases
- Increased consistency from grease polymer is generally stable and does not shear

- Different thickeners responded differently to grease polymers
  - Fibrous grease (Li and LiX) are compatible with a wide range of polymer chemistries
  - Globular grease (CaSulf and AlX) are highly selective and can often lose grade
  - Particle greases (Silica and Clay) are best with H-bonding and reactive polymers

FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

NLGI Serving the grease industry since 1933

Future Work

- Test hypotheses generated from high level analysis of consistency and shear data
- Microscopy on grease structures w/ and w/o polymer after shear?
- Evaluate greases that did not change in grade – are they more shear stable?
- Can we pick better polymers to improve roll stability?

Improvements

- Wider range of initial roll stability for base grease – most were < 5% change to start
- Use 'base grease + 5% oil' as control for roll stability to probe if % thickener affects stability
- Mill greases post-addition
- 1/2 cone measurements on roll stability

FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

NLGI Serving the grease industry since 1933

Thanks to:
Daniel Vargo, Functional Products – grease discussion
Pat Stockton, Clark Testing – advice on D1831

Thank you!

Erik Willett
ewillett@functionalproducts.com
330-963-3060

FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants