Do Polymers Affect the Mechanical Stability of Grease?

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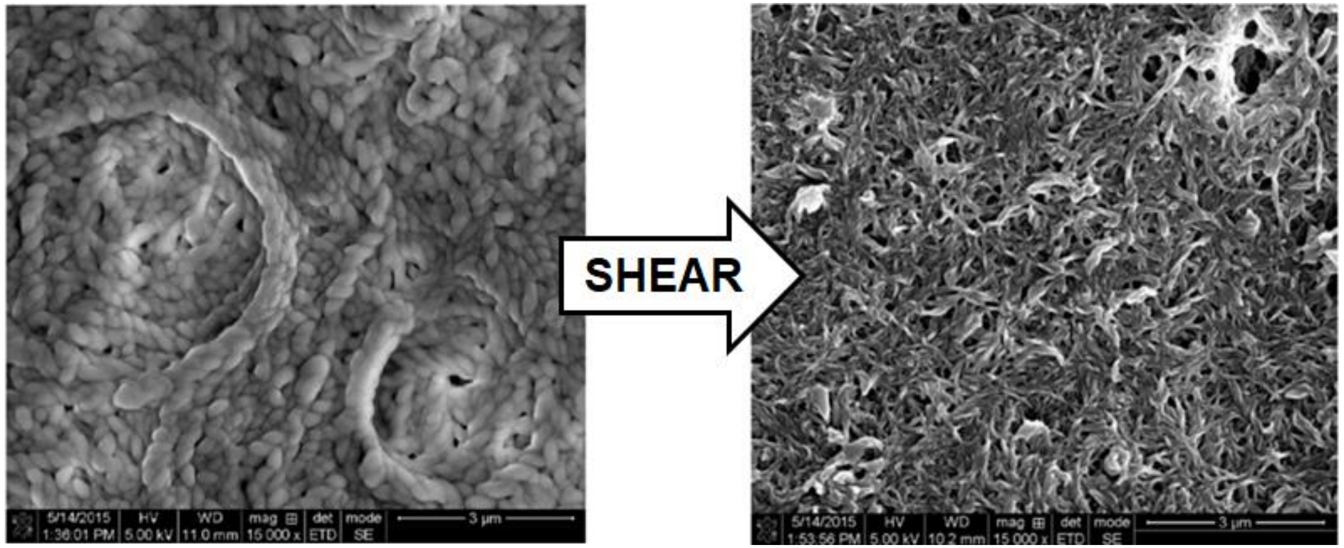
Outline

- Do polymers affect the mechanical stability of grease? *Yes, but…*

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

Motivation

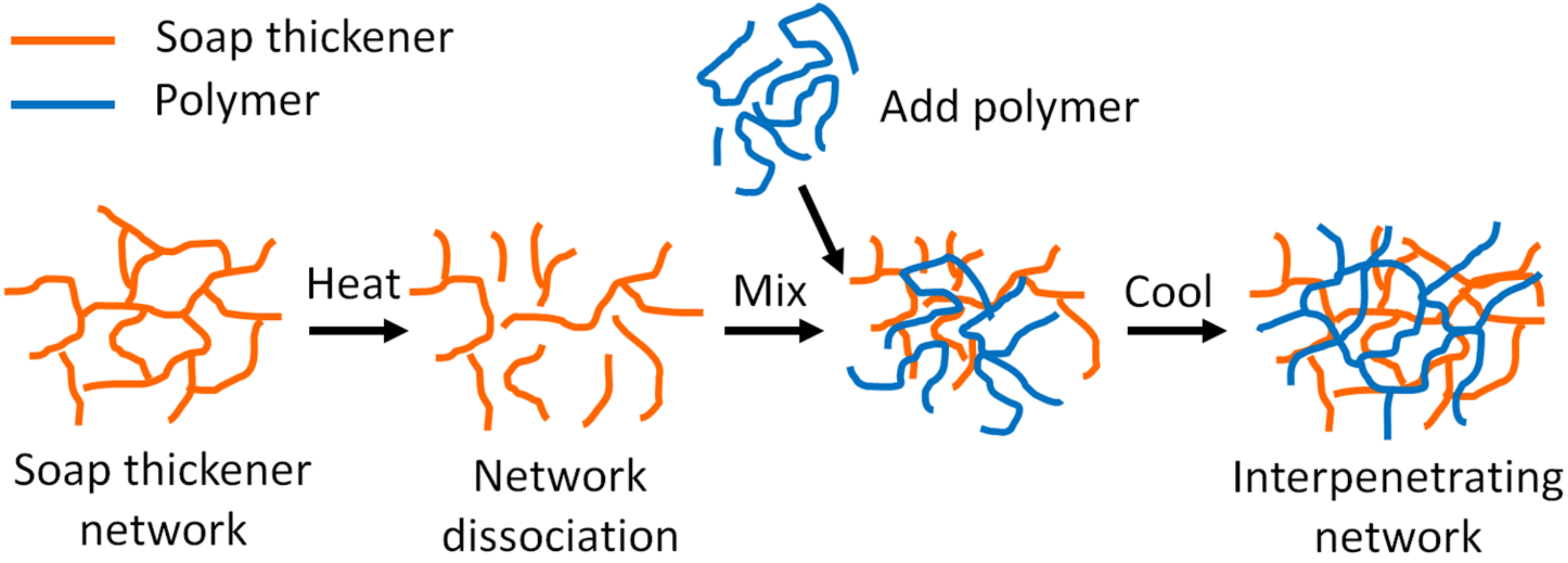
- Polymers will continue to play a role in emerging grease specs and applications
- HPM spec (water resistance, oil bleed), biobased grease, fill-for-life, EV market, etc.
- The ability to stay in grade and avoid consistency changes is critical to success



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

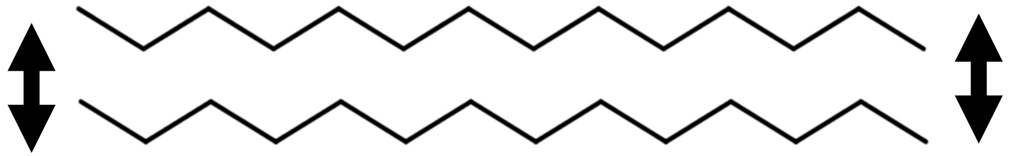
Grease Polymer

- Poorly soluble polymer which tends to mesh with the insoluble thickener rather than thicken oil
- Forms interpenetrating networks with grease thickener
- < 1wt% has significant effects on tackiness, water resistance, oil bleed, and rheology

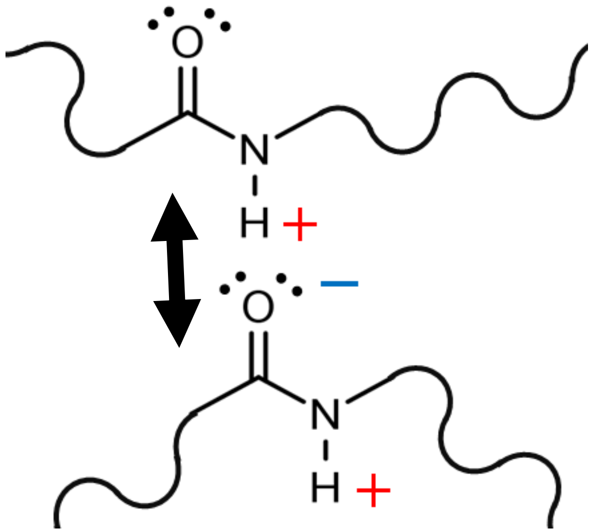


Grease Polymer Types

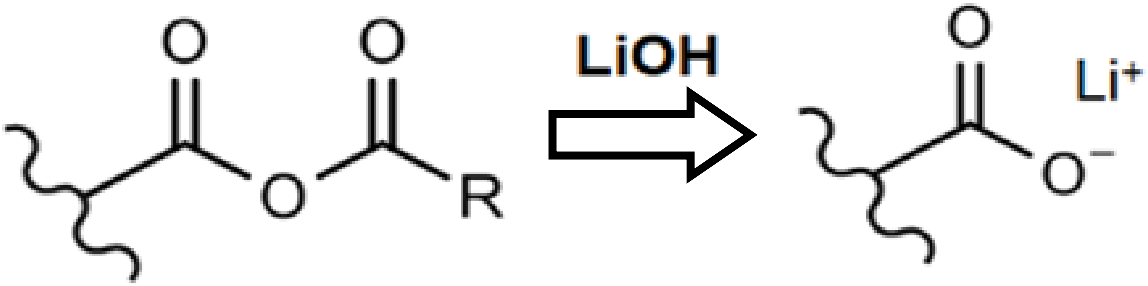
- **Temperature Sensitive** – long runs of ethylene or styrene form waxy linkages



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



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



Experimental Design

1. Screen a series of greases with different structures against different polymer chemistries

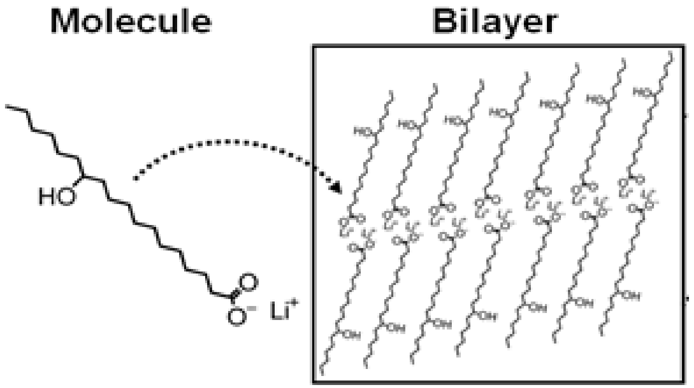
2. We assume an increase in consistency coincides with structuring b/w grease and polymer
    - i.e. formation of an Interpenetrating Network (IPN)

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 (60x worked)

The Greases

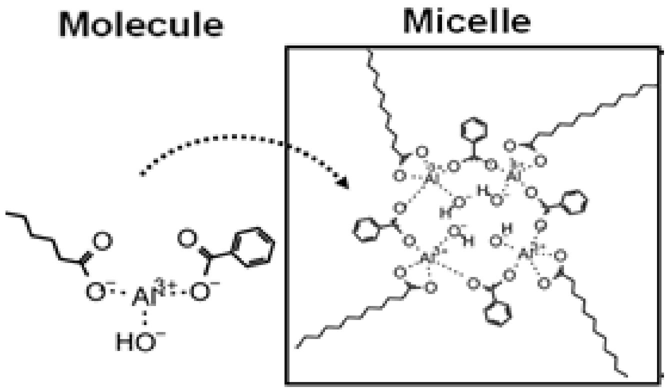
- Simple Lithium
- Lithium Complex

“FIBROUS”



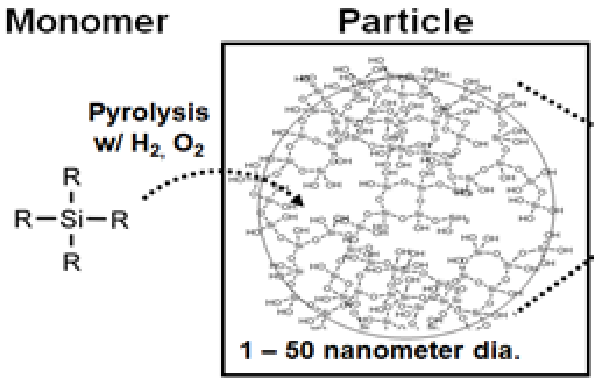
- Calcium Sulfonate
- Aluminum Complex

“GLOBULAR”



- Silica
- Bentonite Clay

“PARTICLE”



Grease Properties

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

Thickener	Cone Pen. (D1403)	NLGI Grade (D217)	Base Oil		Dropping Point (D2265)	Roll Stability (D1831)
			KV40	VI		
Simple Lithium	272	2	173	VI 98	391F / 199C	+1.2%
Lithium Complex	264	2.5	125	VI 113	518F / 270C	+36.1%
Calcium Sulfonate	242	3	86	VI 111	>752F / 400C	+3.1%
Aluminum Complex	253	2.5	159	VI 108	542F / 283C	+1.5%
Silica	309	1.5	118	VI 124	642F / 339C	+2.3%
Clay (Bentonite)	350	0.5	414	VI 101	>752F / 400C	+11.3%

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

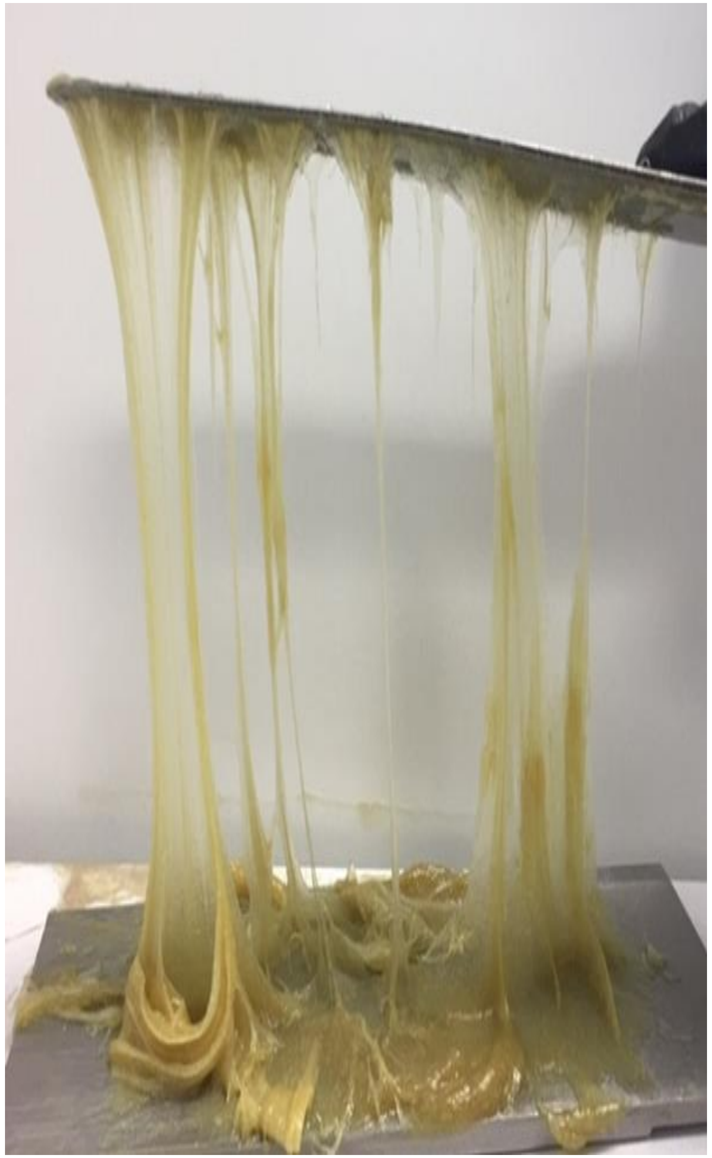
- Plus one dispersant PMA

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 alkyl and amine groups (0.1% N)



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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

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:

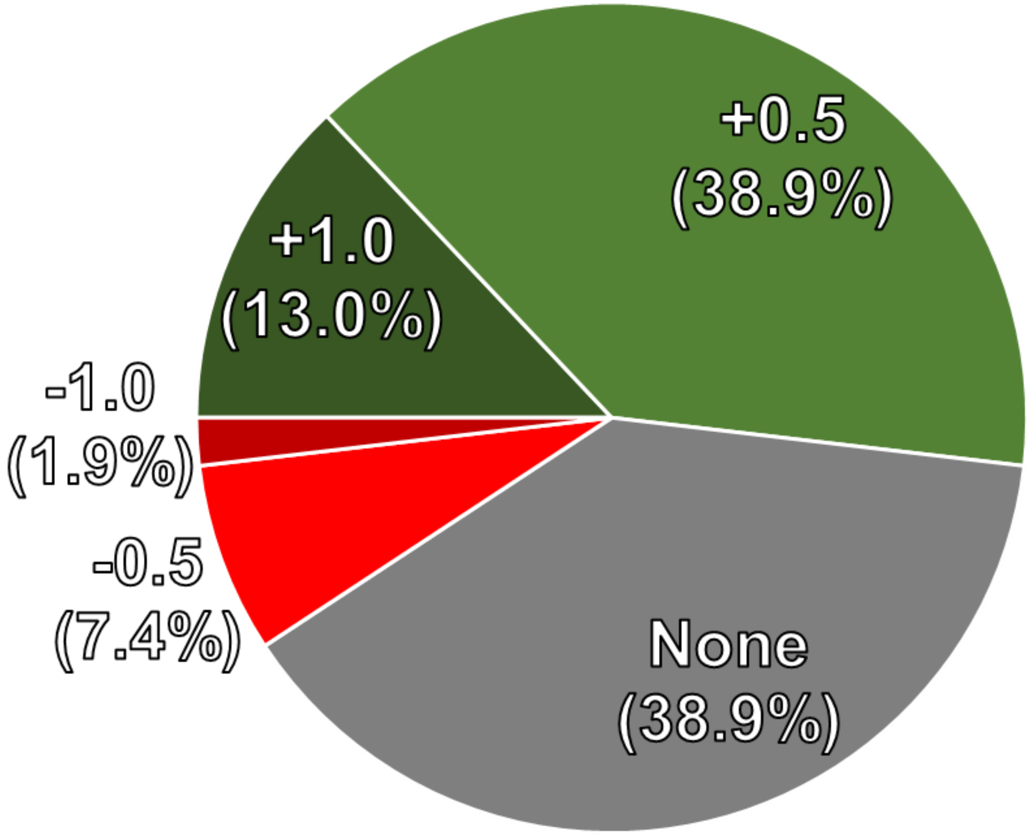
1. Changes to consistency with polymer are noted only if grade changes by 0.5 or more
   - Change from 280 to 270 is still NLGI #2
2. Changes to roll stability are significant only if larger than method error
   - 3.8% error based on ¼ cone and average consistency tested

Findings – Consistency

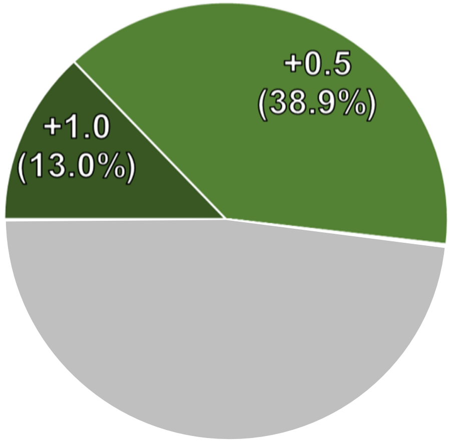
- 54 greases:
  - ~ 52% of cases show **grade increase**
  - ~ 39% show **no change**
  - ~ 9% show **grade loss**
- Change in grade vs. control (5wt% oil)
- 60x worked cone penetration

NLGI Grade Change

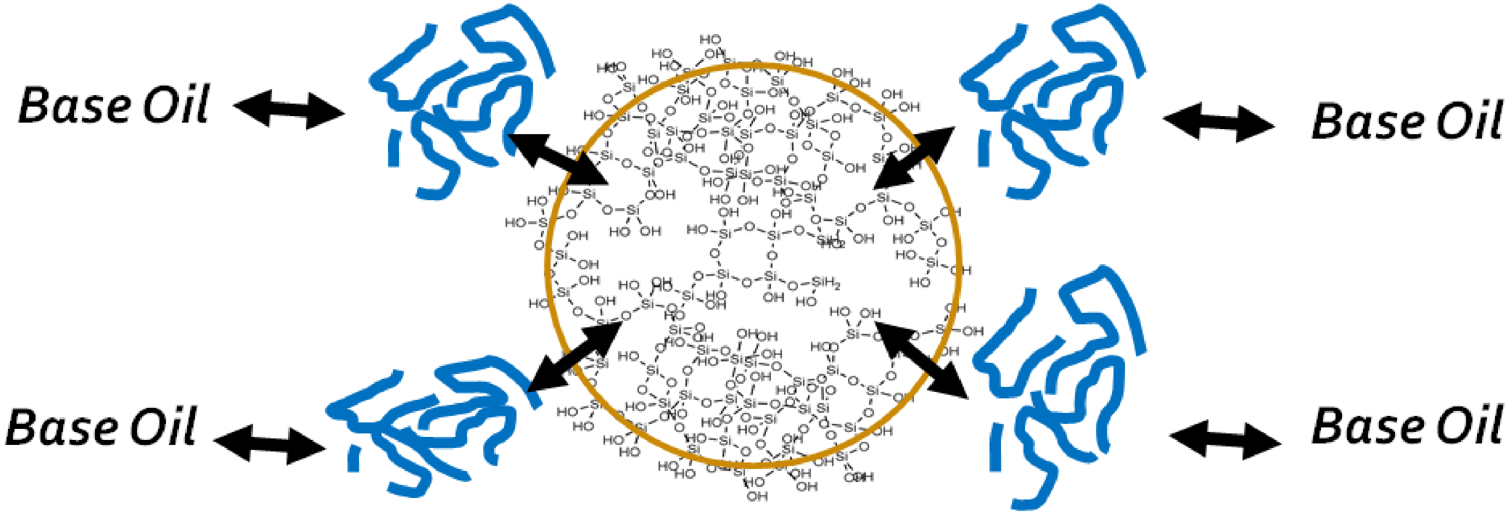
In Polymer-Modified Greases



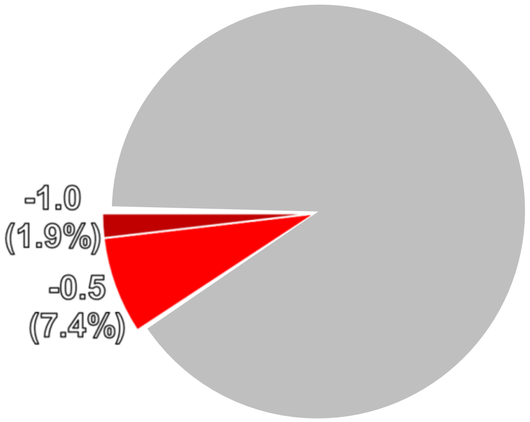
Consistency Gain



- 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

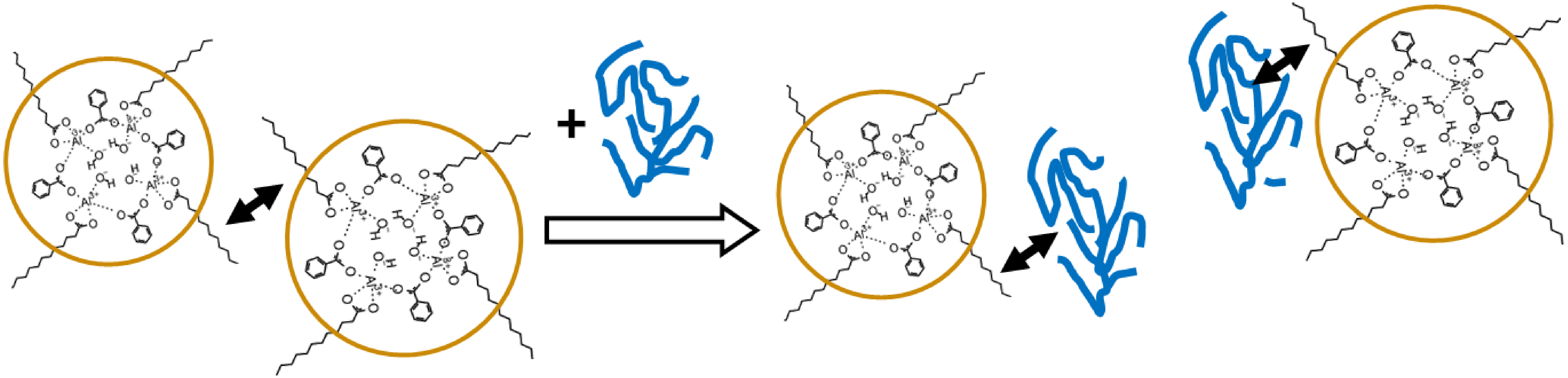


Consistency Loss

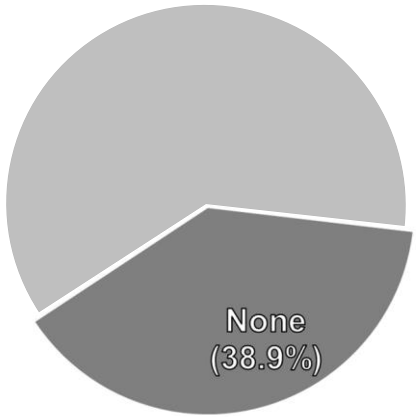


- Strange effect observed in calcium sulfonate and aluminum complex
- Most significant in stearate-based AlX w/ waxy high C2 polymers

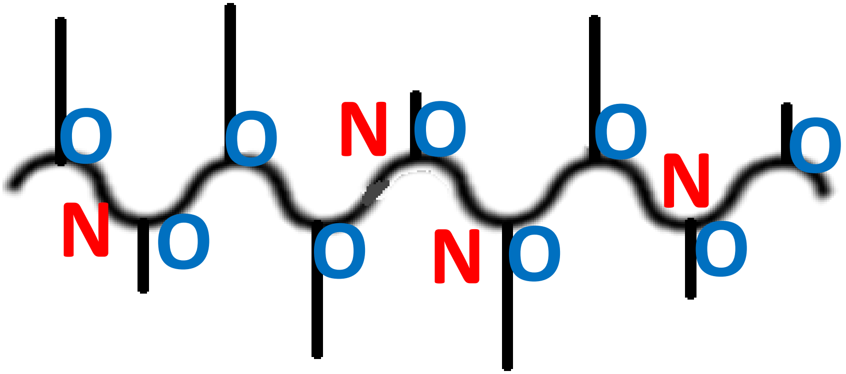
- Waxy polymers could disrupt waxy stearate-stearate interactions that make globules?



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



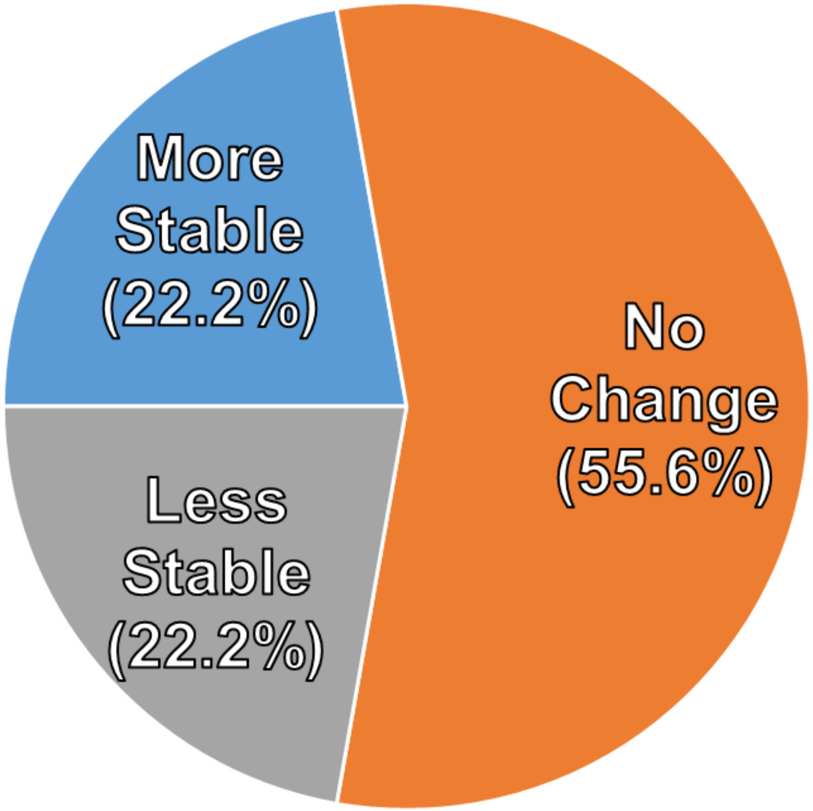
- Greases with low MW H-bonding polymer
  - Least effective grease polymer, too poorly soluble in paraffinic to perform correctly

Findings – Roll Stability

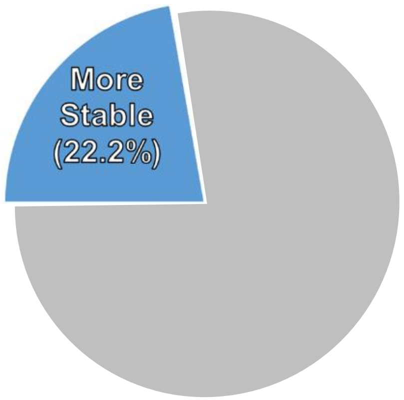
- D1831 on the 27 greases where NLGI grade increased:
  - 22.2% are **more stable** (lower penetration increase after D1831)
  - 22.2% are **less stable** (higher penetration increase after D1831)
  - 55.6% show **no change** within error
- ASTM D1831 roll stability – default 2hrs @ RT
  - Error +/- 3.8% based on method precision

Roll Stability Change

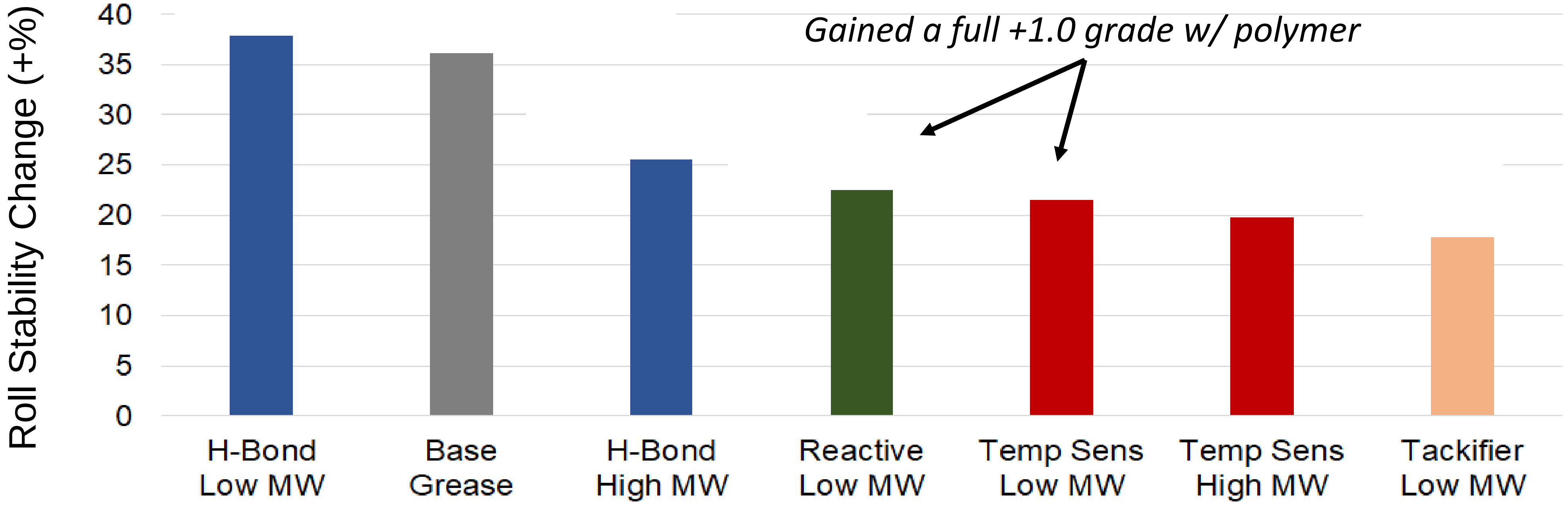
In Polymer-Modified Greases



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



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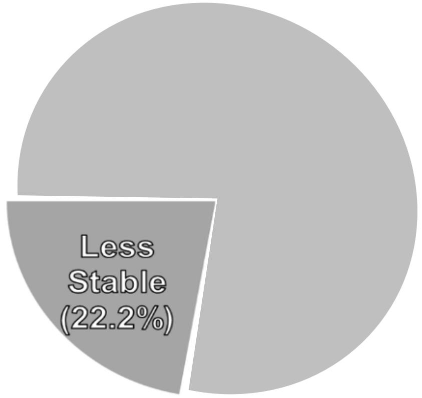
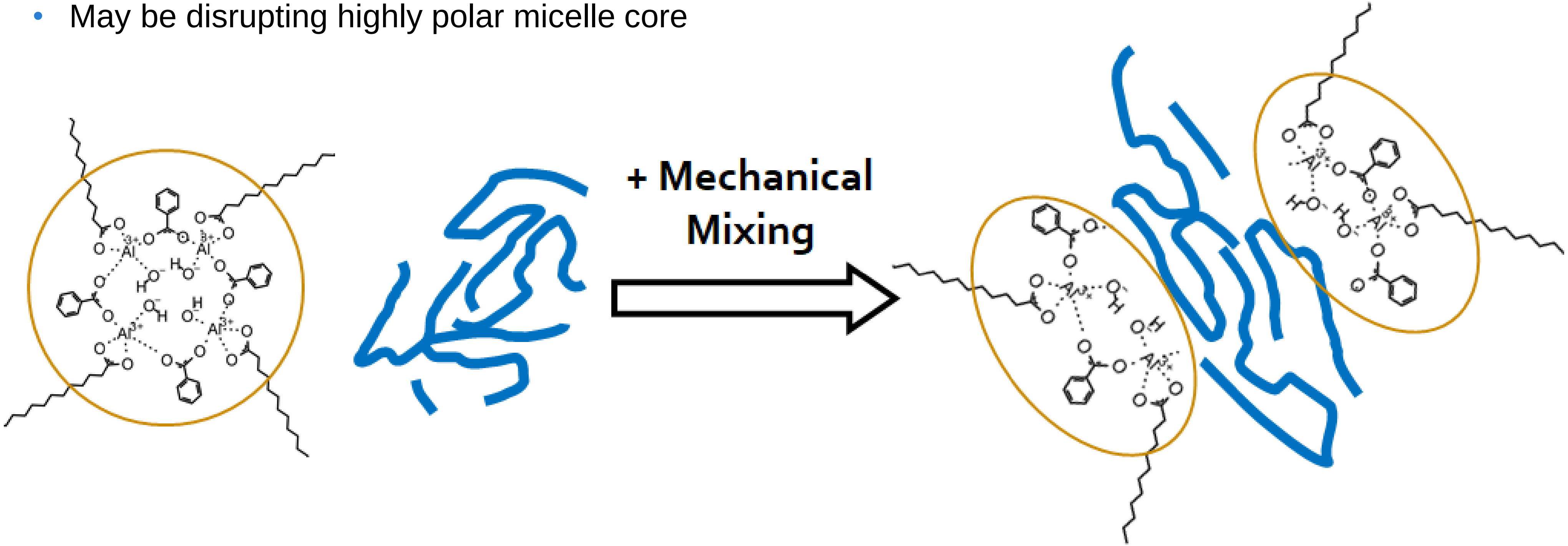
Roll Stability Worsens

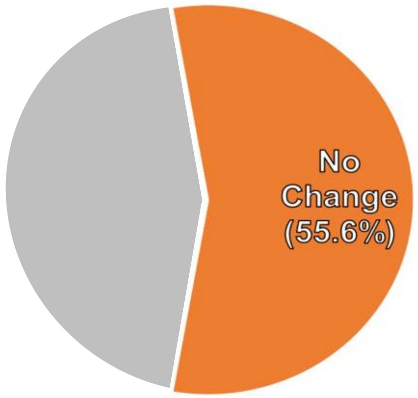


- Most common in calcium sulfonate and AlX
  - H-bonding and reactive polymers are antagonistic
    - May be disrupting highly polar micelle core



- May be artifact from not milling post-addition – but not systematic for any one grease or polymer

Roll Stability Unaffected



- Most common in simple lithium and clay

- May seem trivial but can 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…**

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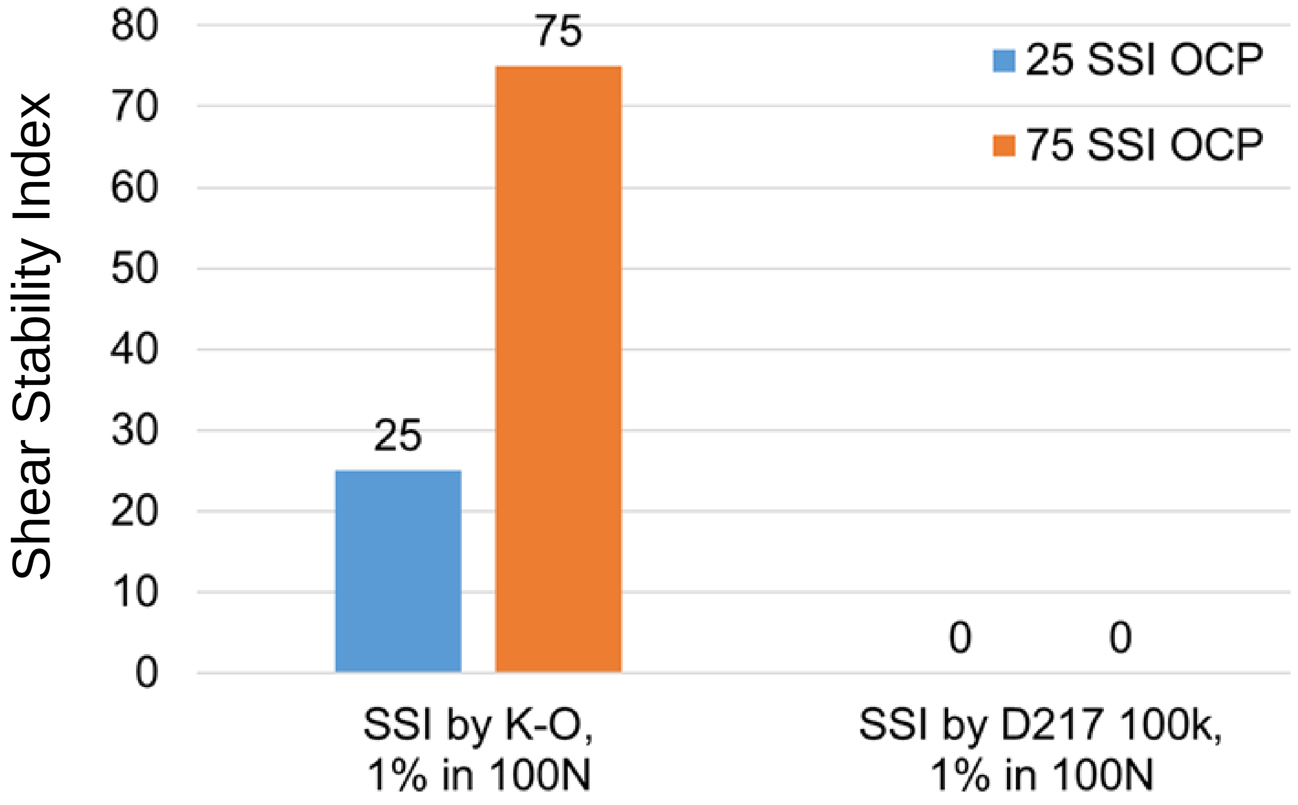
Mechanical Shearing Methods

- 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)

	Method	Nominal Speed	Load or Pressure	Temp	Hours
GREASE	ASTM D217 Worked Cone	0.133 m/s (60 up-down 2.625" strokes/min)	Undefined	25°C	2.8 to 28 (10K - 100K)
GREASE	ASTM D1831 Roll Stability	0.755 m/s (3 35/64" dia. roller weight @ 160 rpm)	5 kg weighted roller	25°C	2
LUBE OIL	ASTM D6278 Kurt Orbahn	111 m/s (170 mL/min, 0.18mm dia. nozzle)	2600 psi across 0.18mm dia.	35°C	0.5
LUBE OIL	ASTM D2603 Sonic Shear	6,000 – 20,000 oscillations/second	Ultrasonic cavitation (100 – 500W)	40°C	0.67
LUBE OIL	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

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



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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

Future Work

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

Thank you for your attention