FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

www.functionalproducts.com

Functional Products

CLGI Kunming of Yunnan

October 10-14, 2019

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Overview

- Grease polymers
  - What are they?
  - Structure
  - Mechanism of actions

- G.R.E.A.S.E.
  - Benefits
  - Test methods

- Forms available
- When/how to add to grease

- Quick picks (commercial products)

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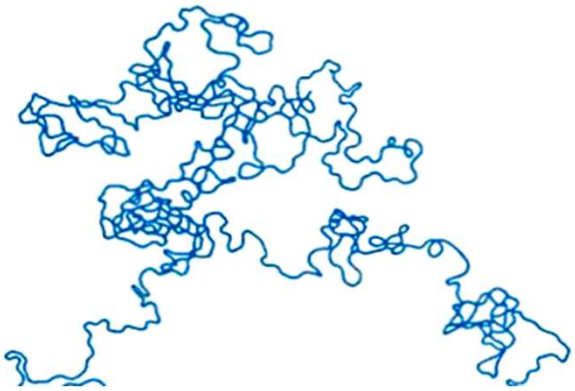
Polymers in Grease

- "Grease polymer"
  - To avoid confusion with grease thickeners: lithium complex, calcium, …
  - Provide tack, mechanical strength, water resistance, NLGI grade
  - Helps grease to perform its duties: lubricate, seal, deliver additives (AO/CI), stay in place

- Generally incompatible or poorly soluble in mineral oils
  - Different than lube oil (gear oil, HF) polymers like PIB, PMA, OCP



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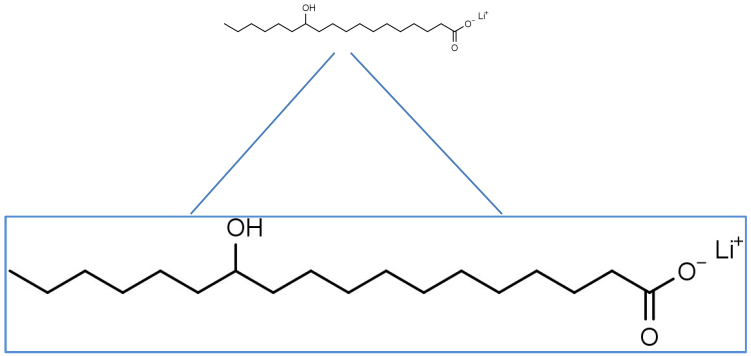
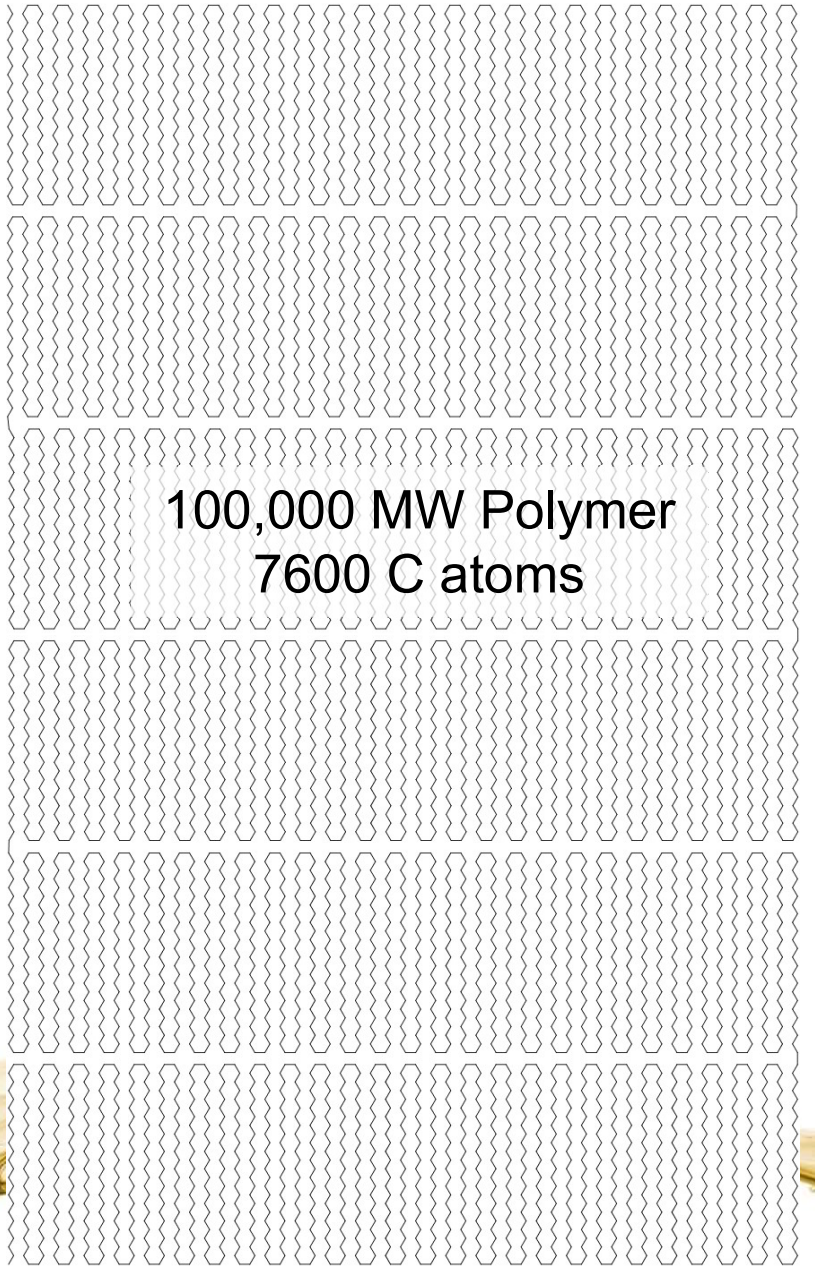
Sense of Scale

Li 12-HSA (361 g/mol) – 18 C atoms





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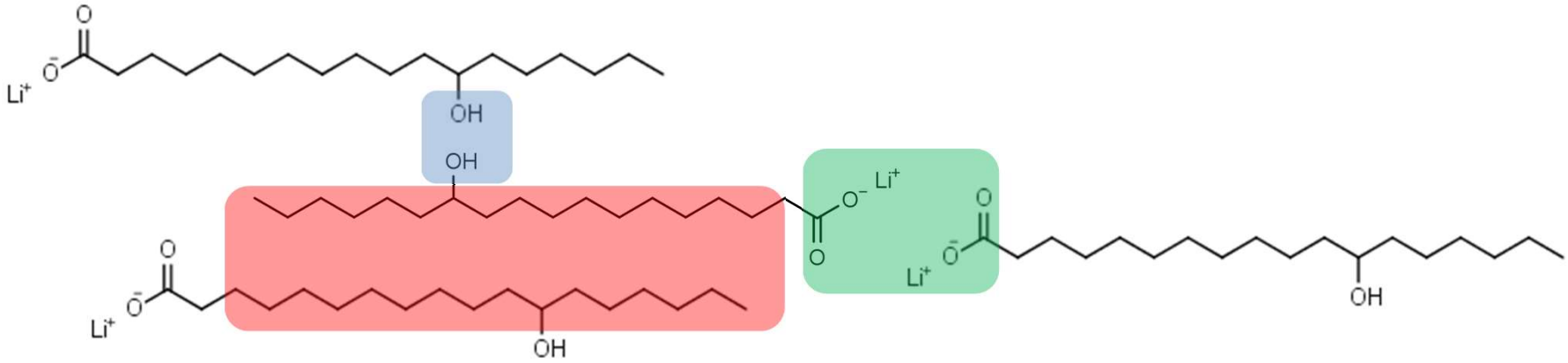
Short vs. Long Range

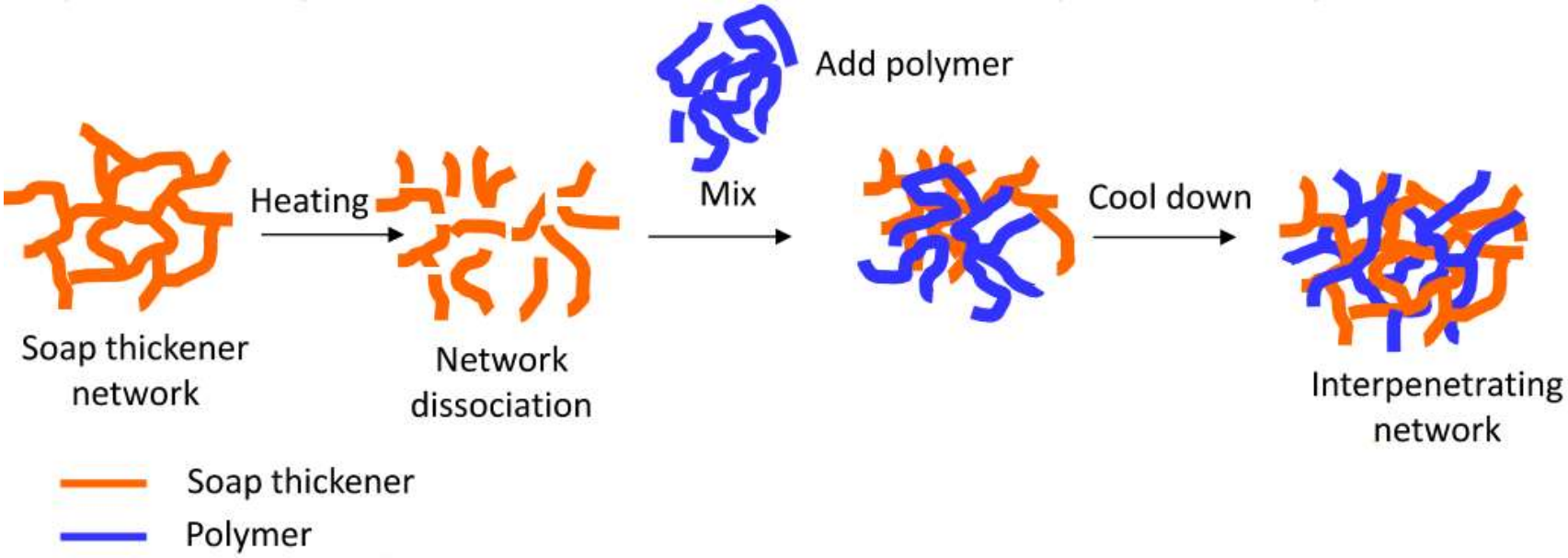
- Grease network - local, short range interactions
  - Ionic - R-COO$^-$ to Li$^+$, R-SO$_3^-$ to Ca^{2+}
  - Hydrogen bonding - R-OH to R-OH on 12-HSA
  - Waxy - interactions of stearic groups, tail of sulfonates, etc.



- Polymer network – covalent C-C bonds, long range

Interpenetrating Network

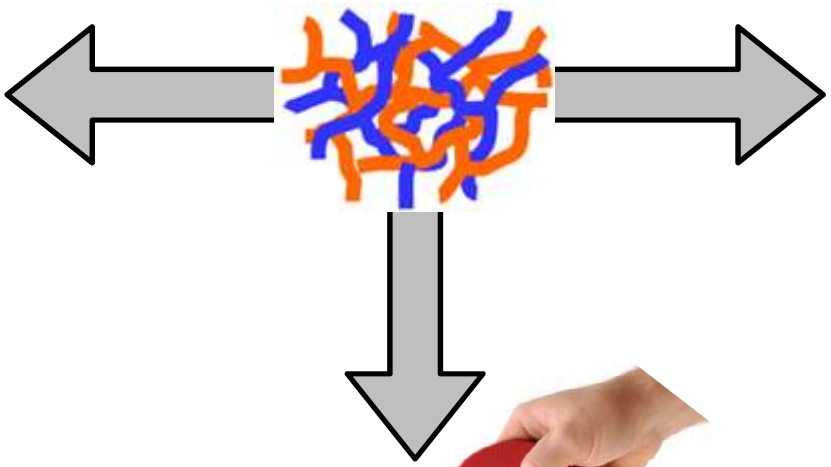
- Abbreviated “IPN”

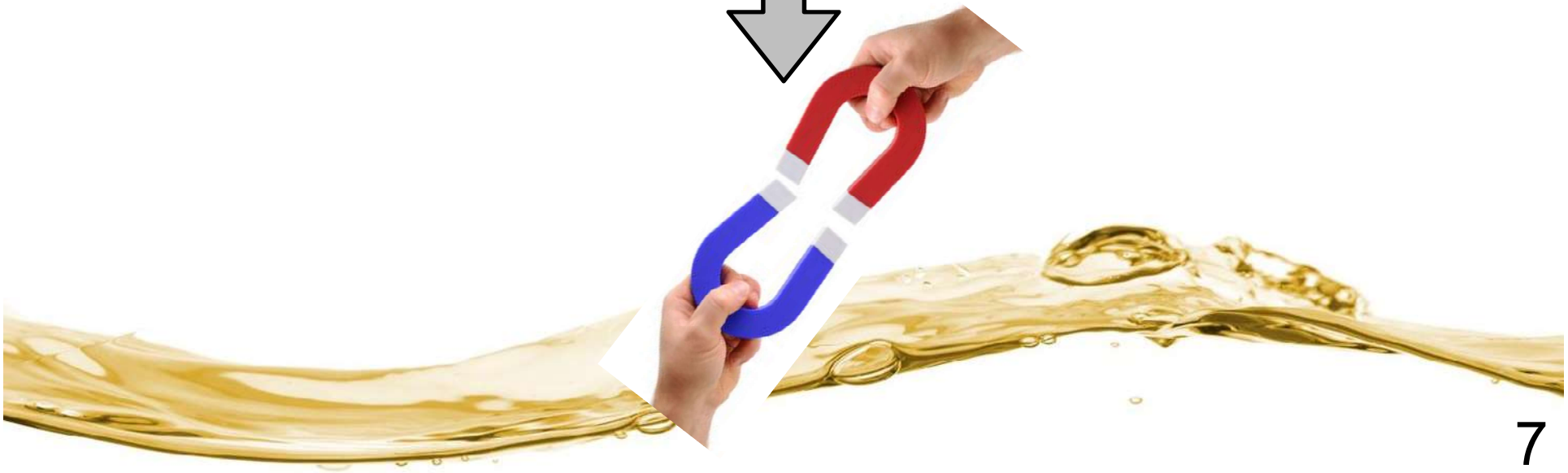


- Three mechanisms to form IPNs in grease
  - Polymer network needs a way to stay locked in around the thickener

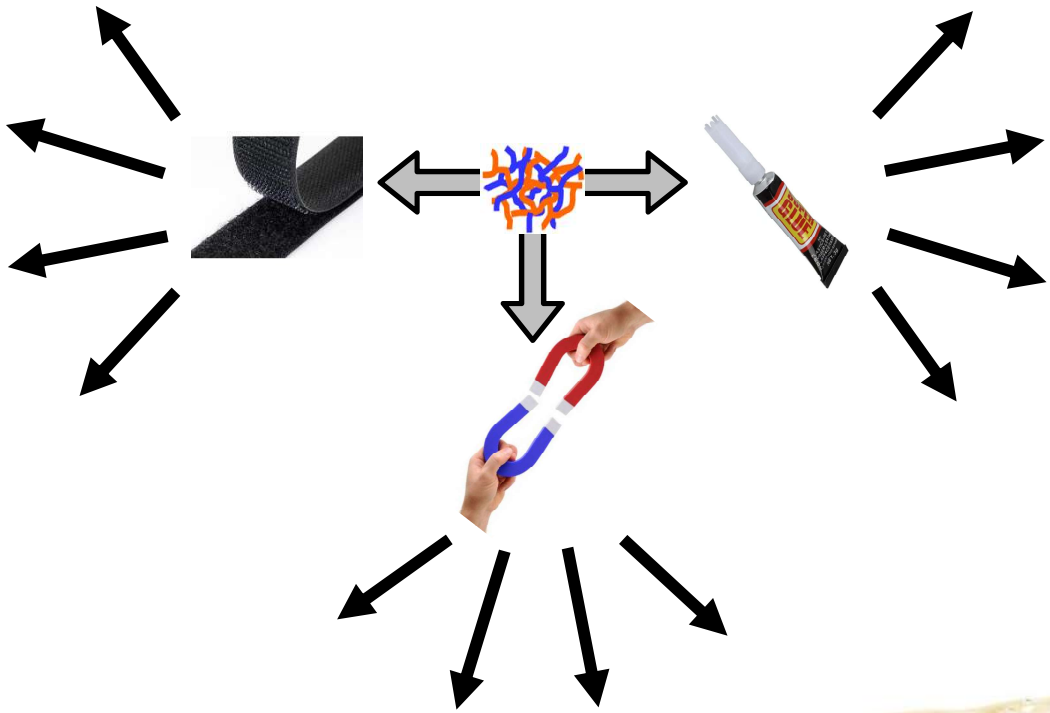
FPI Grease Portfolio

aligned along **three** mechanisms





- Each mechanism best targets specific grease chemistries
  - Branches out to products that fit different roles/performance



Roles:

- Pellet/Flake
- Low viscosity liquid
- High viscosity liquid
- Extra tacky
- Biobased
- HX1
- Etc.

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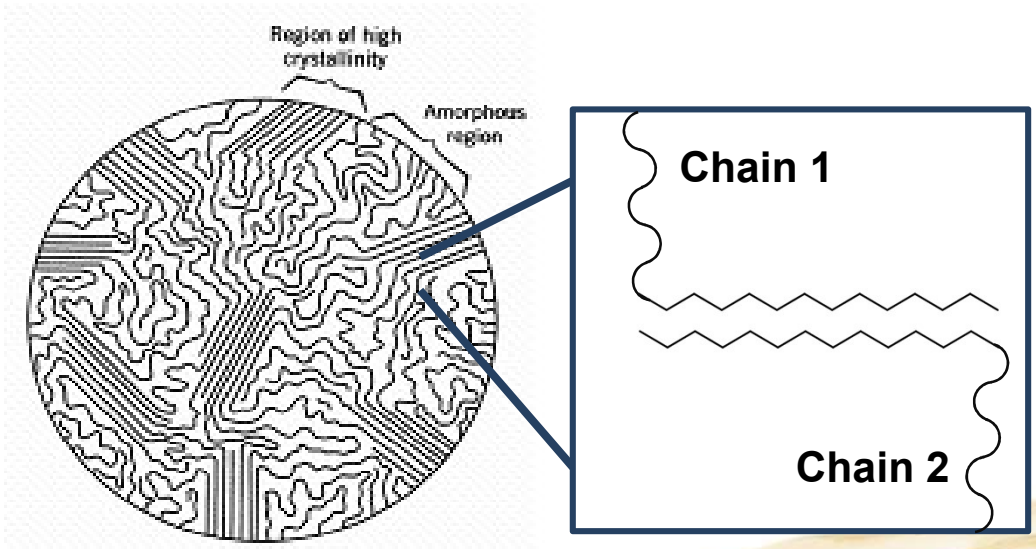
1. Temperature Sensitive

- Olefin copolymers (OCP)
  - High ethylene or styrene associate like Velcro (hook-and-loop) tape
    - “Semi-crystalline”

  - Heat temporarily melts the crystal sites
    - After cooling the sites reform around the grease network



Solid: V-207, V-211, V-4060

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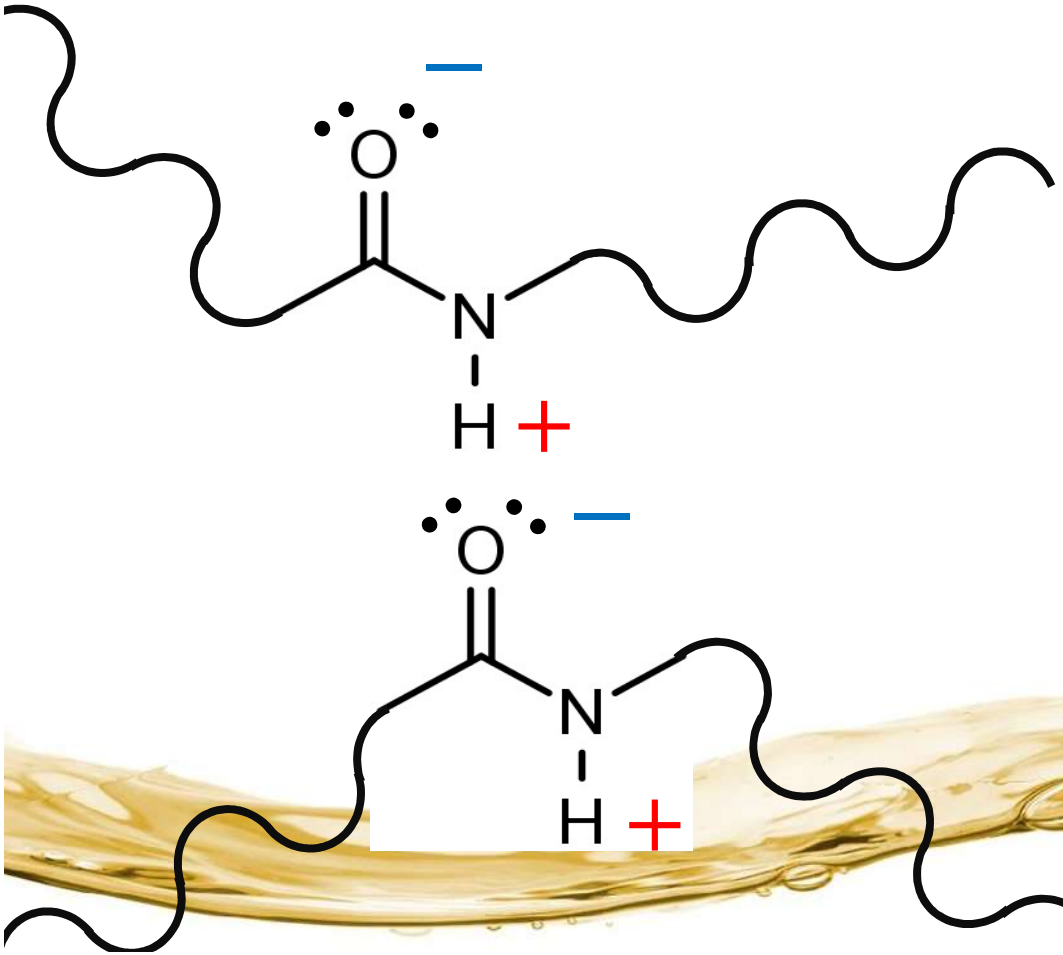
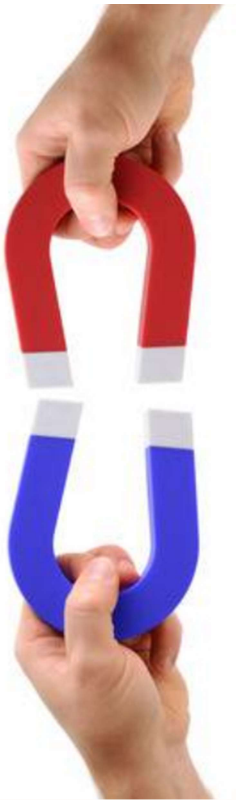
2. Hydrogen Bonding

- High MW ester-based polymers, amides, ureas, emulsions
  - Strong attraction between H and electrons on O or N sites
  - Most useful in biobased grease



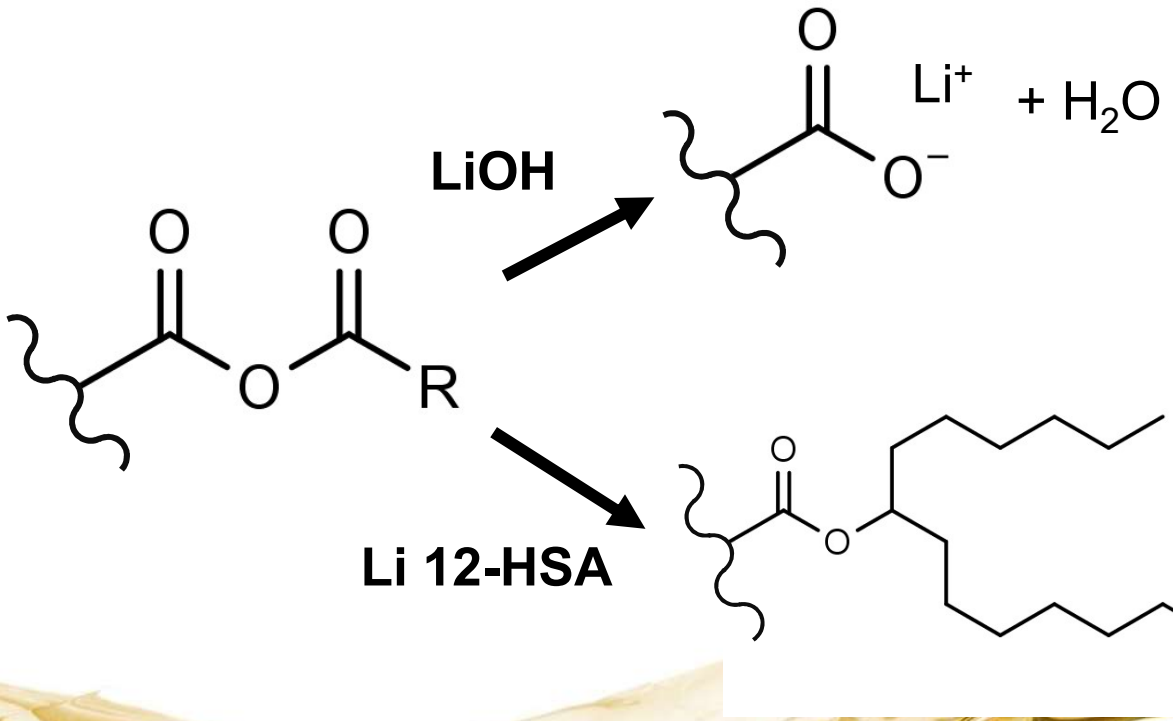
Liquid: V-508F, V-572, V-191
Solid: V-508S



3. Reactive

- Polymers grafted with reactive anhydride species
  - Coordinate with metal ion (Li^+, Ca^{2+}) like a diacid
  - Complex with –OH on hydroxystearate like a boron ester

    - Best in ionic greases like Li Complex, Ca Sulfonate



Liquid: V-4004A, V-4051
Solid: V-4020, V-4040P

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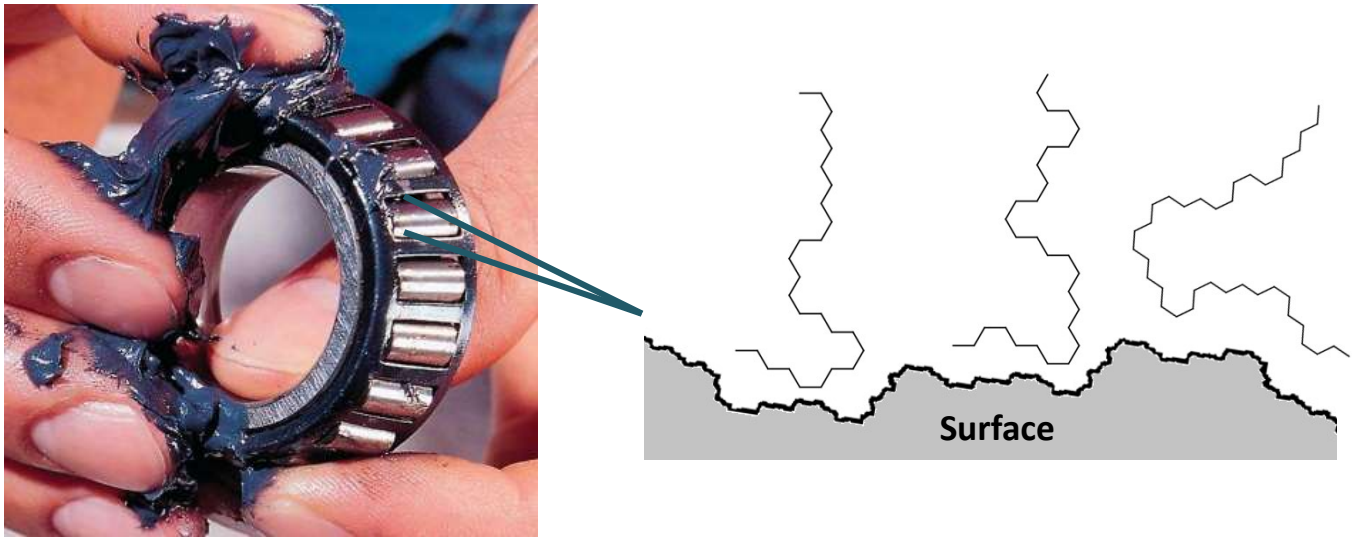
Benefits

Greater Adhesion
Reduced Bleeding
Elevated Tackiness
Added Yield
Superior Shear Resistance
Enhanced Water Resistance

Greater Adhesion

- **"Adhesive tack"**
  - Reinforcement of attachment between the grease and a surface

- *Lower MW polymers* which diffuse into asperities, act as anchors



- Test methods: pull-off force (FPI method), D3121 rolling ball tack, centrifugal fling-off (D4425 Koppers, Mobil method)

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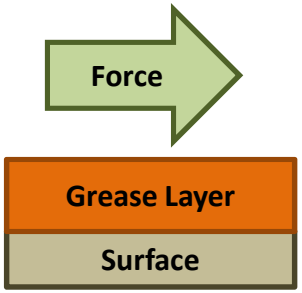
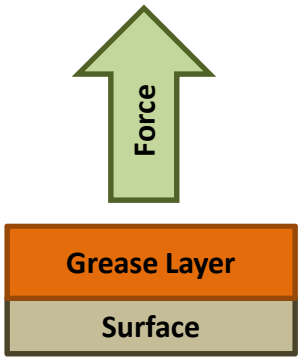
Adhesion Test Methods

D3121 – Rolling ball tack test

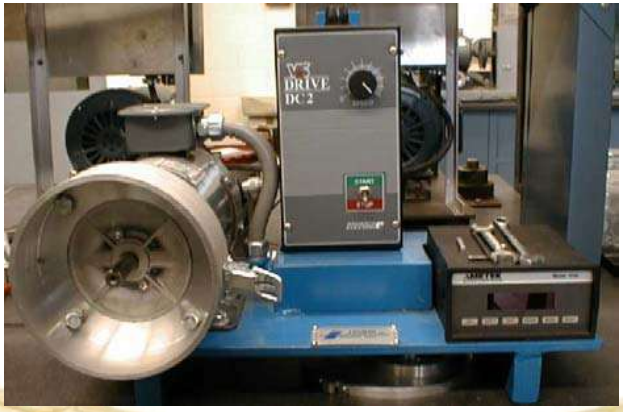
Animated: ChemInstruments, 2015

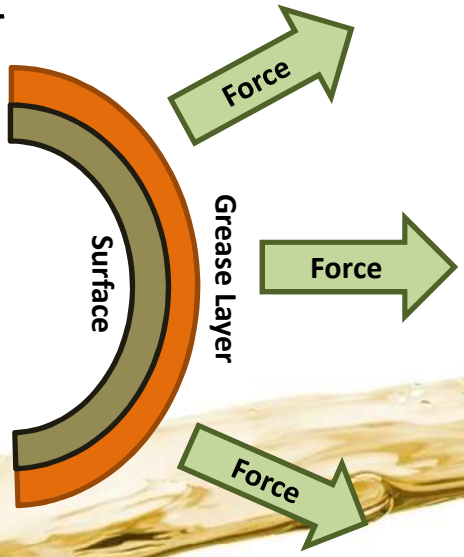


Pull-Off Force Test (2014, FPI)



Mobil Grease Fling-Off Test





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Reduced Bleeding

- Oil is about 80-90% of grease
  - Non-polar hydrocarbon dispersed into polar thickener (ionic salt)
    - Opposites repel - cause separation or “bleed” over time

- Bleed causes hardening, increase in NLGI grade, and customer complaints

Simple Lithium

Lithium Complex

Calcium Sulfonate

w/ Solid Particle

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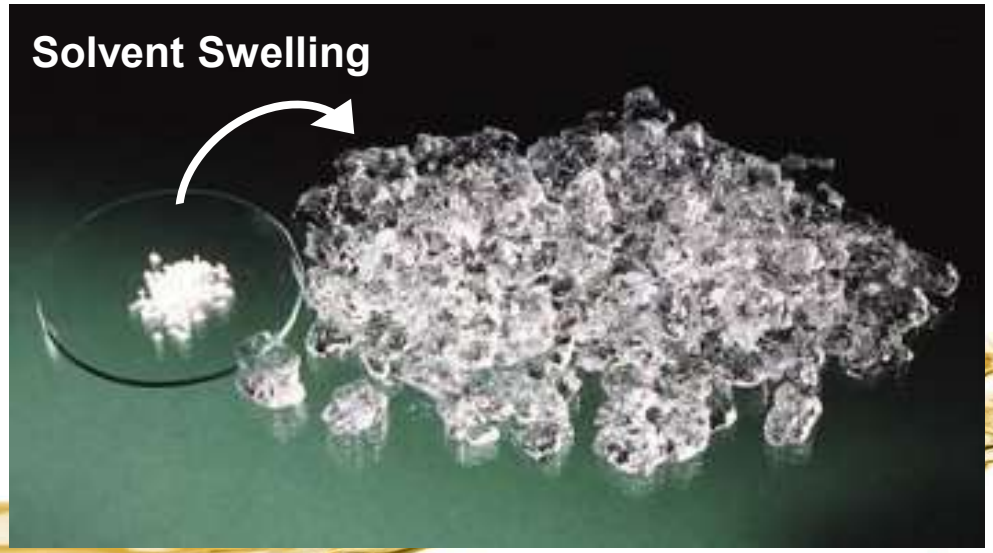
Polymers and Oil Bleed

- Polymers
  - Two ways they reduce oil bleed:

1. Like dissolves like
   - Hydrocarbon polymer is more compatible with oil than thickener
   - Greater compatibility and higher retained oil %

2. Osmotic pressure
   - Polymers spontaneously absorb solvents and swell



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Oil Bleed Performance

Treat	Oil Bleed D6184, 100°C, 30hrs
NLGI #2 Calcium Sulfonate	**3.30% initial**
1% V-188 liquid OCP tackifier	-24.6%
2% V-188 liquid OCP tackifier	-32.0%
1% V-211 styrene OCP flake (HX1)	-35.3%
1% V-207 semi-crystalline OCP flake	-49.3%
3% V-4004A liquid grafted-OCP	-52.2%
1% V-113 50 SSI OCP bale	-74.9%
1% V-4064 crystalline OCP flake (HX1)	-80.3%
1% V-191 emulsion	-86.0%

Hoskin Scientific 2019

- Best choice – very high MW OCP, high solids emulsion, or grafted-OCP
- Test method: Oil separation by conical sieve (D6184)

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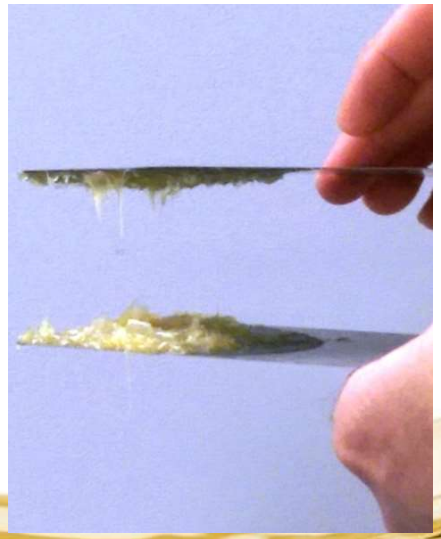
Elevated Tackiness

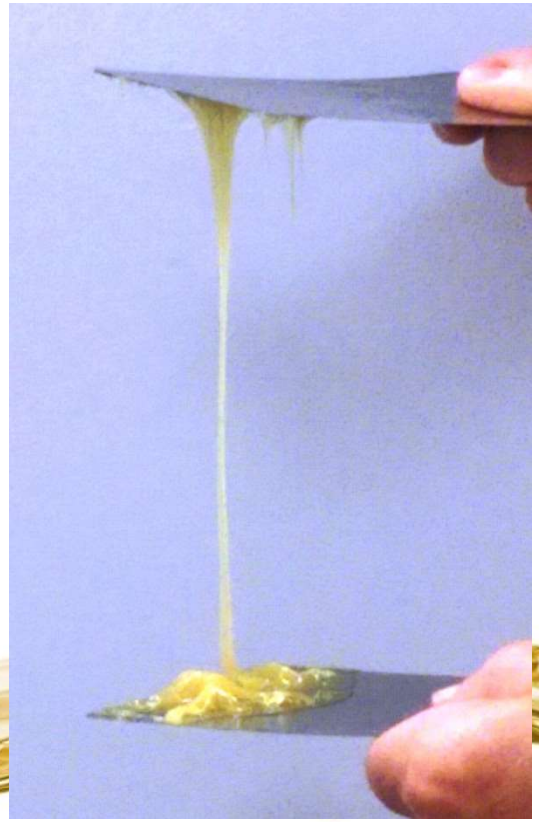
- **"Cohesive tack" -** Reinforcement of the internal structure of grease
  - Less prone to separating or breaking apart

- Cohesive tack contributes to performance in mechanical testing
  - No *standard* way to directly measure grease tack yet
    - i.e. ductless siphon for lube oil

- Functional V-176, V-188, etc.



No Polymer



2% PIB Tackifier

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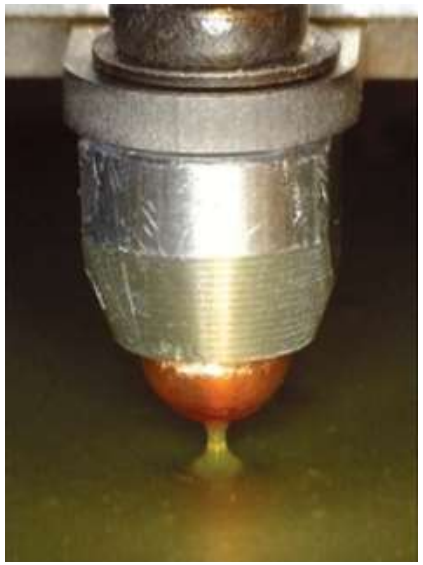
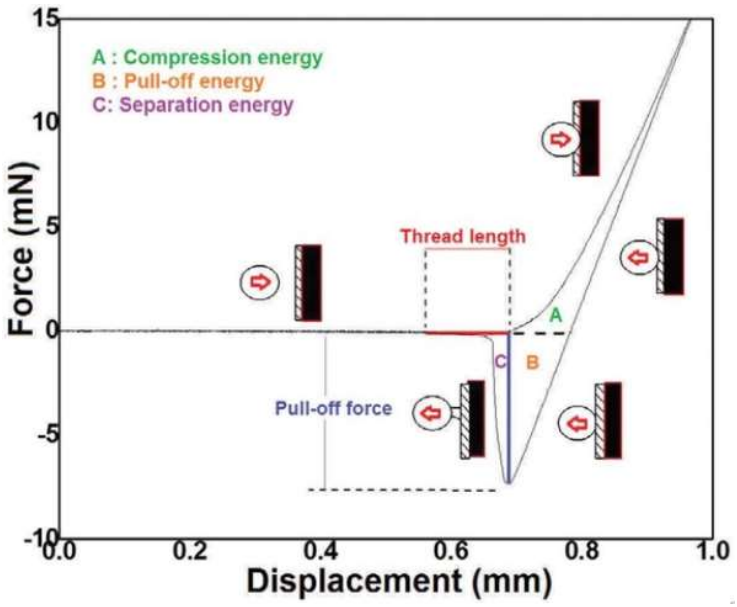
Tackiness Testing

- D2979 Probe Tack Test instrument for adhesives
- Modified pull-off force with gauge (FPI, 2014)

- Falex tack adhesion tester (Falex, 2018)
  - Force gauge on cantilevered copper probe



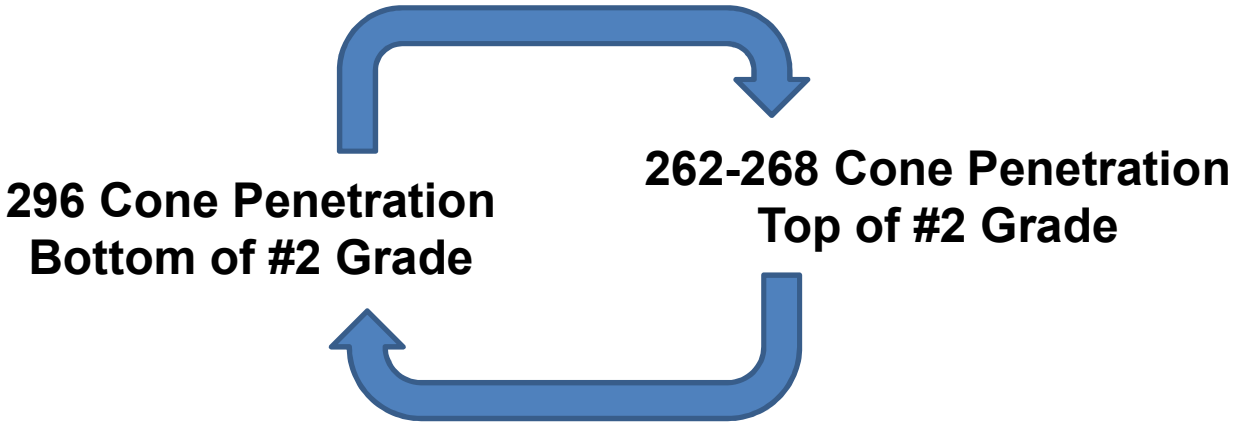


"Quantitative evaluation of tackiness...", D. Vargo, O.R. Serra, B. Lipowski, Lube Magazine, Feb. 2014
“On the Right Tack", M. Moon, Lubes n' Greases – Oct. 2018
Functional / Falex collaboration – ELGI 2019

Added Yield

- Polymers provide increased consistency and higher base oil viscosity
  - Lower cone penetration, higher NLGI grade
    - Cut-back thickener or add extra oil to produce intended grade
    - **More grease per kg of Li / Ca / Al / etc. thickener**

Add 1% V-207, 1% V-211, or +3wt% V-4004A



Reduce thickener by 15-20%

- Test method: D217 (cone penetration), D1403 (½-,¼-scale), worked cone

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Superior Shear Resistance

- Shearing forces on grease
  - Mechanical crushing between surfaces
  - EP / boundary lubrication
  - High pressure flow and depressurization
  - Milling

- Continuous use under heavy-duty demands can shear down grease
  - Loss of NLGI grade
  - Increase in cone penetration
  - Changes in mechanical properties or flow

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Networks Working Together

Grease is like concrete

Tough but brittle
Short-range structure
Small molecules (<500 g/mol)

Polymer is like rebar

Flexible
Long-range structure
Large molecule (100k – 1M)

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Worked Cone Shear

Treat	Worked Cone – 10,000 Strokes
	296 initial
NLGI #2 Lithium Complex, Mineral Oil	+8.1%
+0.75% V-207, OCP flake	+3.0%
+1.0% V-207, OCP flake	+1.7%
+0.5% V-211, styrene OCP flake	+2.4%
+1.0% V-211, styrene OCP flake	+1.3%
+2.0% V-211, styrene OCP flake	+1.0%
NLGI #2 Lithium Complex, Bio-Based	**+22%**
+1% V-572 liquid	**+15%**
+1% V-191 emulsion	**+11%**
+7% V-4004A grafted OCP	**+6.1%**
+1% biobased styrene copolymer, solid	**+5.7%**

Koehler 2009

88% reduction

74% reduction

- Test method: Worked cone penetration (D217/D1403) – 10,000 stroke

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Roll Stability Shear

Treat	% Change in Cone Pene. (D1831)
NLGI #2 Lithium Complex	+11%
+1% V-211 styrene OCP flake	+4.8%
+1% V-207 OCP flake	+4.4%
+3% V-4004A grafted-OCP liquid	+1.4%
+2% V-188, OCP tackifier liquid	+4.1%
+1% V-4060, OCP pellet	+0.5%
+2% V-178, PIB tackifier, liquid	-1.4%

95% reduction

Scavini
2019

- Test method: Roll stability (D1831) – lower % change is best

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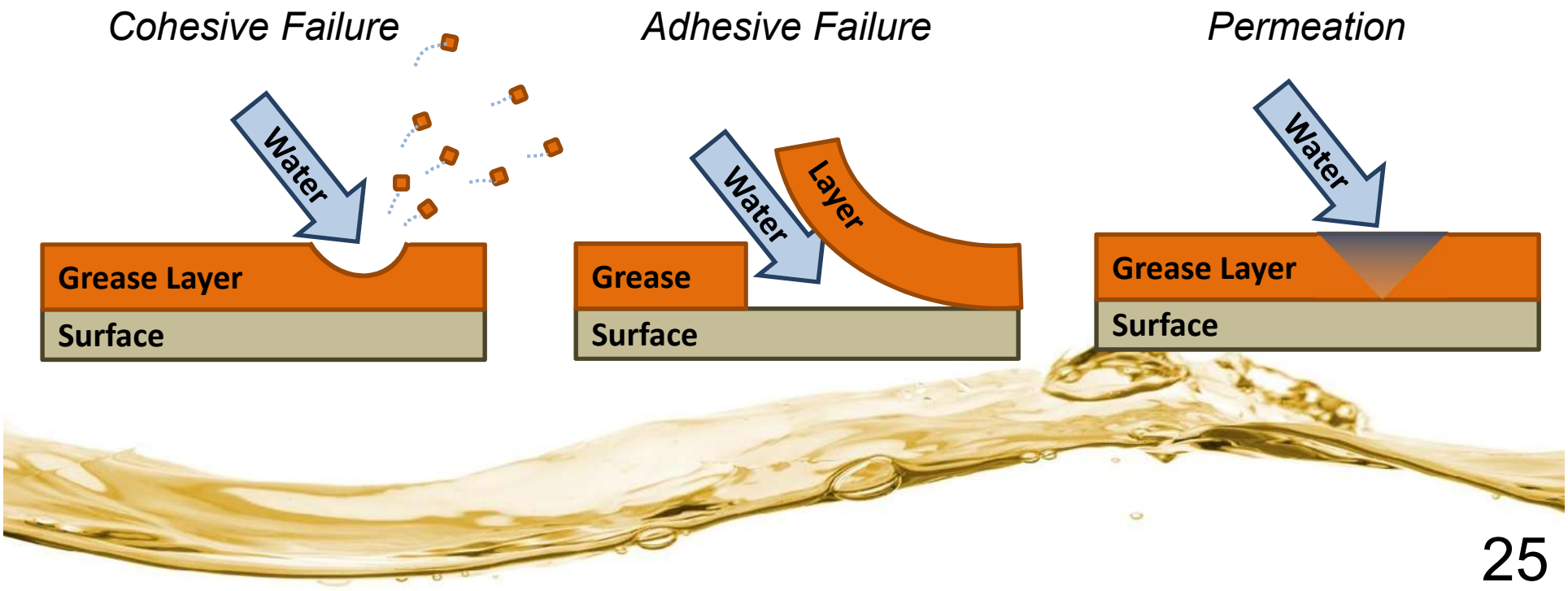
Enhanced Water Resistance

- Greatly improved water spray-off and wash-out resistance
  - Adhesive + cohesive tack resists physical removal of grease
  - Increased surface tension – less water absorbed into grease pores
    - Absorbed water can degrade grease over long term



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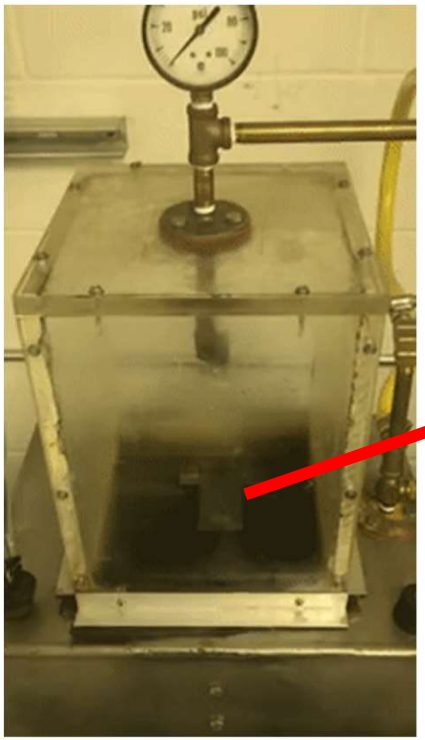
Water Resistance Testing

Water spray-off, WSO (D4049)



Grease plate after test

Water wash-out, WWO (D1264)

Stanhope-SETA 2015

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WSO/WWO Performance

Treat	WSO (D4049)	WWO (D1264)
NLGI #2 Lithium Complex	**52%**	**26%**
+1% V-207, OCP flake	24%	11%
+1% V-211 styrene OCP, flake	9%	12%
+1% V-4051 biobased grafted-OCP, liquid	23%	14%
+0.25% V-4020, grafted-OCP pellet	26%	25%
+4% V-4270 proprietary *blend* of liquids	7%	2%
NLGI #2 Calcium Sulfonate	**72%**	
+0.5% V-207, OCP flake	16%	
+1% V-207, OCP flake	7%	
+0.25% V-4020, grafted-OCP, pellet	47%	
+0.5% V-4020, grafted-OCP pellet	4%	
NLGI #2 Clay Grease	**49%**	
+5% V-114L, concentrated OCP liquid	48%	1.3%
+1% V-191, emulsion	10%	29%
+4% V-4004A, grafted-OCP liquid	12%	-2%

- Many polymers will favor either WSO **or** WWO performance
- Effectiveness depends on the match between polymer and grease

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What's Next?

- Now you've seen sample data on grease polymers in generic #2 greases
  - But performance varies from grease to grease depending on formula
    - We want to show **your data** on **your grease**
  - Grease projects
    - Supply 1 gallons to a pail of base grease without polymer
    - We begin by determining the most effective mechanism
      - Drills down into individual product selection or new prod. dev.

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Grease Testing at Functional

Common In-House and Contracted Grease Test Methods (complimentary):

- o Cone penetration for grease – 1⁄4 scale (ASTM D1403), full scale (ASTM D217)
- o Worked penetration (60 – 100k stroke)
- o Water spray-off (ASTM D4049)
- o Dropping point (ASTM D566)
- o Oil separation – up to 200°C (ASTM D6184)
- o Four-ball EP weld load for oil or grease (ASTM D2596)
- o Roll stability (ASTM D1863)
- o Dynamic/scanning viscosity with Brookfield viscometer

Ask for full test list including lube oil test methods

Functional will optimize grease additive treat/performance in your grease.

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Forms Available

- What forms can one buy grease polymers in?
  - Solids
    - Pellet – V-4020, V-4064, V-508S
    - Flake – easiest to solubilize solid, V-4040P, V-4064
    - Bale – uncommon but best shipping economics
  - Liquid (V-4004A, V-4270, V-4051)
    - Pre-dissolved polymer at 1 – 50wt%
    - Best convenience and speed of mixing
    - Dilute (400 cSt @ 100C) to concentrated (4000 cSt @ 100C)
  - Emulsion – liquid (V-191)
    - Very concentrated (30-50% solids) but easy handling
    - Carries over some water
    - Few options

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When/How to Add?

- Depends on the form/type of polymer
  - Use the least amount of heat necessary to get best stability

- Best practices / starting point for new blenders:

Mechanism	Form	When/How	
Temperature Sensitive	Solid Liquid	Add at end, with cooling oil Mix 1 – 3 hours @ 80-100°C / 176-212°F	V-207
Reactive	Liquid		
Hydrogen Bonding	Solid Liquid	Add at end, with cooling oil Mix 1 – 3 hours @ 100-120°C / 212-248°F	V-211 V-4060 V-4064
Temperature Sensitive (Styrene or High Melt)	Solid		
Reactive	Solid	Add at start, before alkali	
PIB/OCP Tackifiers	Liquid	Add after milling to avoid shear damage	

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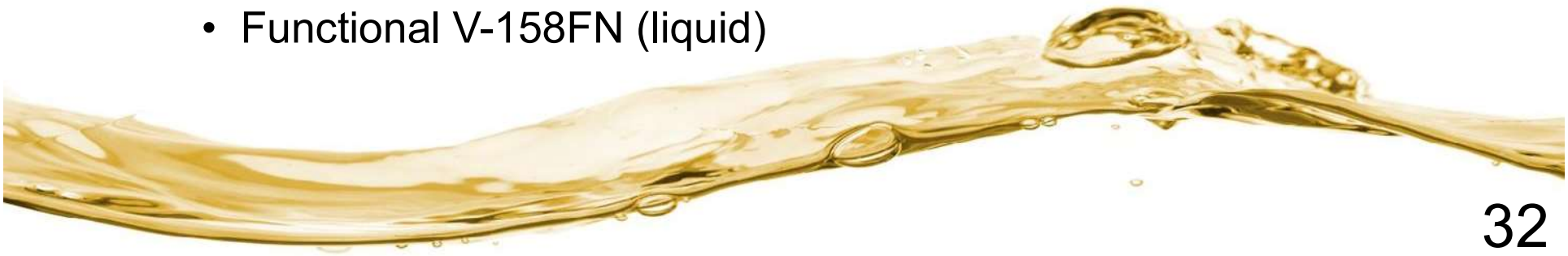
Odds and Ends

- Low temperature greases
  - Reduce base oil ISO VG, build up with polymer
    - Economically, use V-201
      - 60 SSI OCP and mid-level C2 content
      - Builds base oil VM **and** behaves like grease polymer
    - Or lower SSI VM but will need a grease polymer for G.R.E.A.S.E.
- Wireline grease
  - Not a true grease
  - 50 SSI OCP in light (60 SUS) naphthenic or paraffinic
    - Functional V-113 (solid)
    - Functional V-158FN (liquid)



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Quick Picks

Every grease is its own animal –
Different thickeners, oils, grades, additives, manufacturing processes.
We provide many options.

Lithium Complex
- Solid: V-4020 (0.25%), V-4040P (0.25%)
- Liquid: V-4004A (4%)

Calcium Sulfonate and Aluminum Complex
- Solid: V-207 (1%), V-211 (0.5%), V-4060 (1%)

Inorganic / Filled
- Liquid: V-191 (1%), V-4004A (4%)

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Quick Picks - Specialty

Bio-based Greases
- Liquid – V-4051 (1.5%), V-191 (1%), V-572 (5-10%),

Extra Tacky
- Liquid:
  V-178, V-188 (1-4%)

Water Resistant
- Liquid: V-4270 (4%)

Food Grade
- HX1 Solid: V-4064 (2%)
- HX2 Solid: V-207 (1%)

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Summary

- Polymers are used to influence the physical properties of grease
- IPN mechanisms define three branches of the grease portfolio
- Benefits include:
  - **G**reater Adhesion
  - **R**educed Bleeding
  - **E**levated Tackiness
  - **A**dded Yield
  - **S**uperior Shear Resistance
  - **E**nhanced Water Resistance
- Products to meet different performance targets
  - Variety of forms to suit handling and processing abilities