Using Polymers to Improve Water Resistance in H1 or Biobased Greases

STLE Virtual Annual Meeting 2021 – Session 8A – Grease III
May 20th 2021 – 4pm

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Outline

- Motivation
- Calcium Grease
- Preliminary study in industrial oils
- Three approaches to water resistance in H1 calcium greases in:
  1. Medium solvency white oils and Gr. III
  2. Low solvency PAO
  3. High solvency vegetable oil
- Summary and Conclusions

Motivation

- Improving water resistance can be difficult late in a project
  - Often see up 70-100% WSO need to come down to <10%
  - Can reformulate and delay but a few % grease polymer may fix
- Two main cases
  1. Updating old greases to new specs
  2. Specialties like NSF H1 incidental food contact, EAL biobased

#1 - Old Greases, New HPM-WR

- ASTM D4049 WSO is new test to NLGI grease specs adding in the water resistant subcategory of High Performance Multiuse grease spec

- Already seeing formulators updated old formulas to HPM-WR in 2020/2021

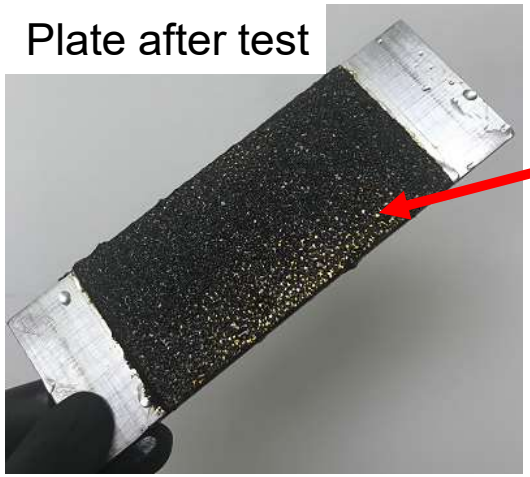
Grease Specification (Year)	NLGI Category	ASTM D4049 (WSO) Limit	ASTM D1264 (WWO) Limit
Automotive Service Greases - ASTM D4950 (1989)	GB	--	<15% @ 79°C
	GC	--	<15% @ 79°C
	GC-LB	--	<15% @ 79°C
NLGI High Performance Multiuse Grease (2020)	HPM	--	<10% @ 79°C
	HPM-WR	**<40% @ 38°C**	<5% @ 79°C

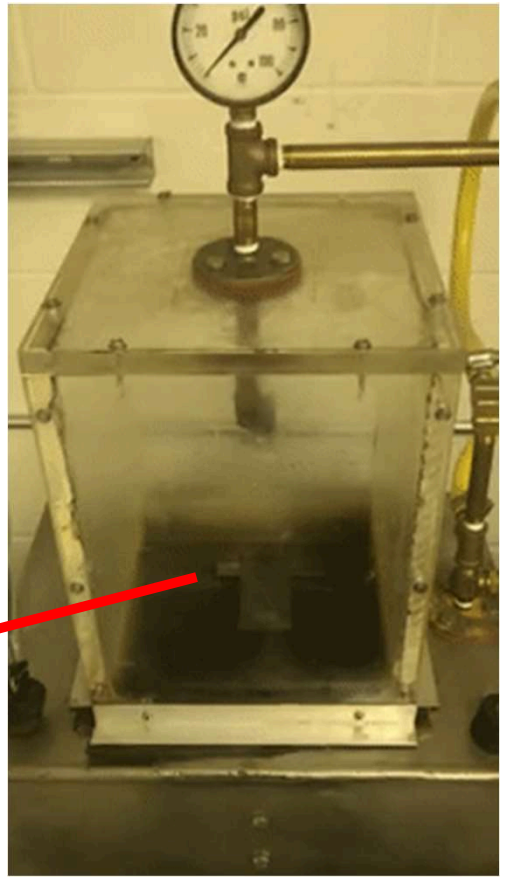
ASTM D4049

- Water Spray Off
  - 40 psi spray of water at 38°C for 5 minutes
  - Static grease-on-plate test

- Grease pushed off (cohesive fail)
- Grease lifted off (adhesive fail)

Plate after test





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#2 - New Greases, New Interests

- Most grease and grease knowledge is based on petroleum / lithium grease
  - 70% is Li/LiX, 86% is mineral oil based

- Industrial greases use anything available, what works best

- “Specialty” greases often use a narrow selection of approved components from whitelists (NSF HX-1, Ecolabel LuSC, US SCIL etc.)

- This work seeks to expand the knowledge for H1 and biobased

Chuck Coe. NLGI 2020 Grease Production Survey. (2020).

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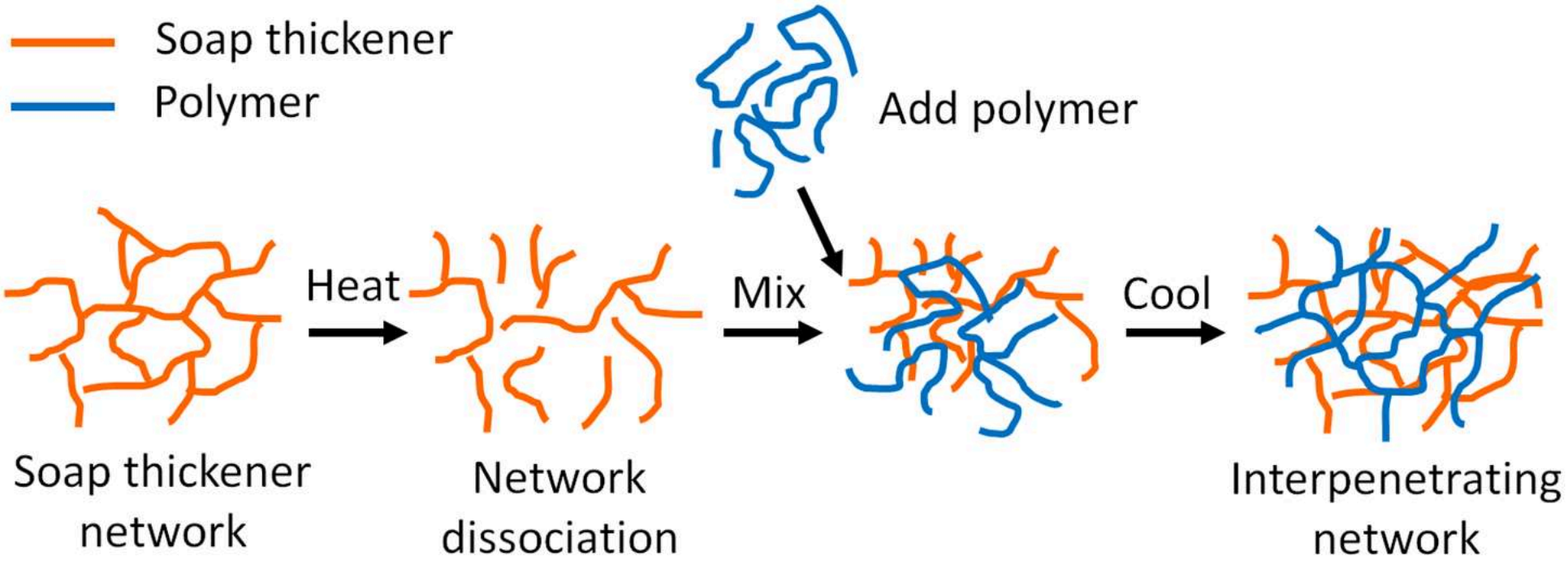
Grease Polymers

- **Grease + grease polymer** is like **concrete + rebar**



Willett, E. "The Mechanical Stability of Polymer-Modified Greases", Functional Products Inc. (2020)

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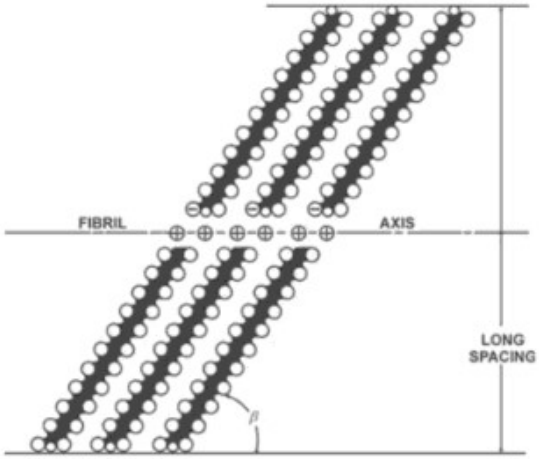
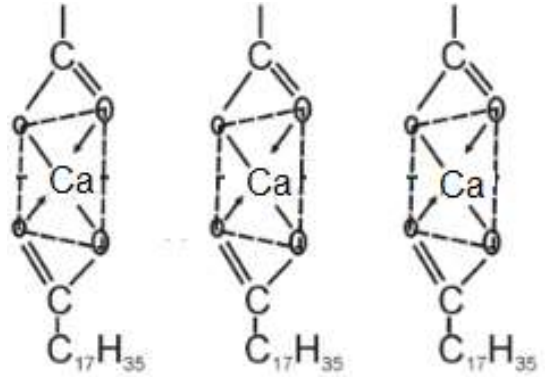
Calcium Greases

- Calcium stearate/acetate – not high technology but…
  - GRAS and NSF H1
  - Biobased feedstocks
  - More commodity, metal stearates easier to source (2020's proof?)
  - And timely - HPM promotes more non-Li grease





Modified from: Lubricating Oils, Greases and Petroleum Products Manufacturing Handbook

Materials and Methods

- Calcium stearate and stearate-acetate greases from preformed powders

- H1 hydrocarbon solvency work
  - #2 Hydrated Calcium Stearate grease in ISO 150 base oil blends
    - 160°C preparation

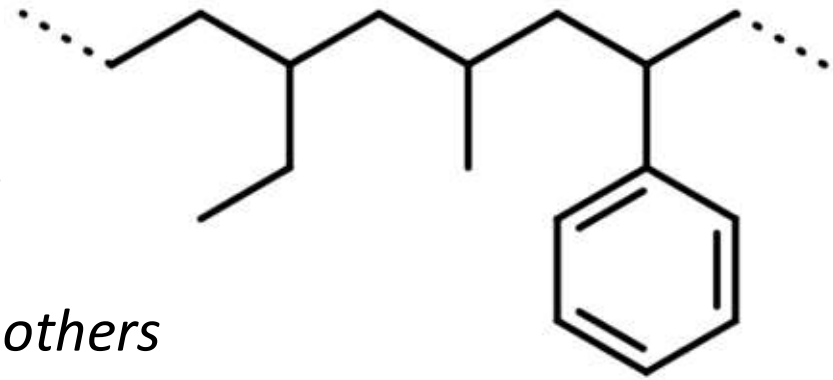
- H1 vegetable oil grease work
  - #2 Calcium Stearate-Acetate complex grease in HO canola
    - HO canola thickened up to ISO 12000 by bio VM
    - 200°C preparation, extra antioxidant

Watanabe, K. Tribology Online 11, 639–645 (2016)
Neumann, E. & Vámos, E. Periodica Polytechnica Chemical Engineering 19, 75–89 (1975)

First, A Mystery

- This H1 study has roots in a long issue with an industrial grease polymer

- Styrene copolymer grease polymer
  - Excellent WSO performance *for some*
    - Poor or no WSO improvement *for others*
      - Undesired rubberiness in some cases

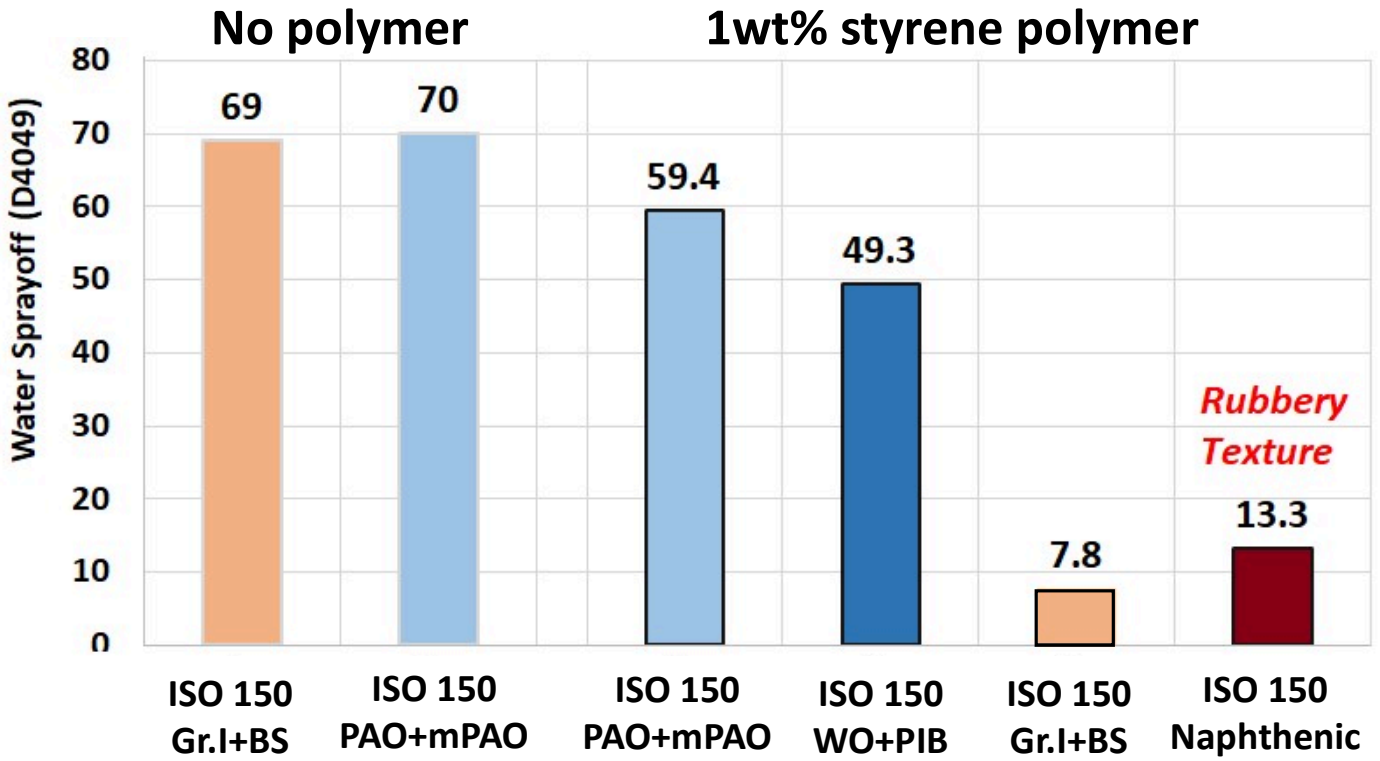


Early Investigation into Styrene Selectivity

- Formulated #2 calcium stearate greases with popular base oils at ISO 150
  - Paraffinic (600SN + 150BS)
  - Naphthenic (750 SUS)
  - H1 PAO (PAO6 + mPAO100)
  - H1 White Oil + PIB (500WO + PIB2500)
- Simulating different types of formulators favoring different base oils
- 1wt% styrene polymer and two controls w/o polymer

Preliminary Results

- Dataset was well picked and we captured a range of outcomes



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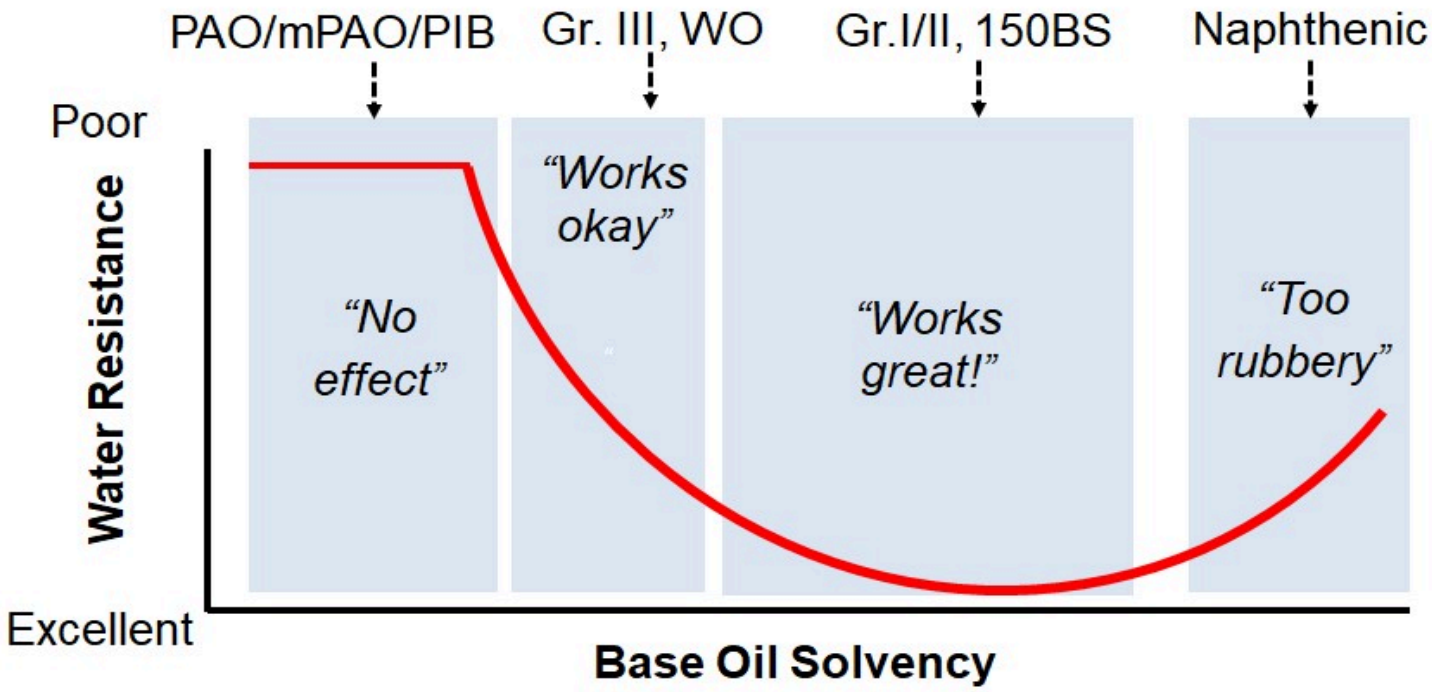
Styrene Polymer Selectivity

- The different experiences trend along one axis – base oil solvency

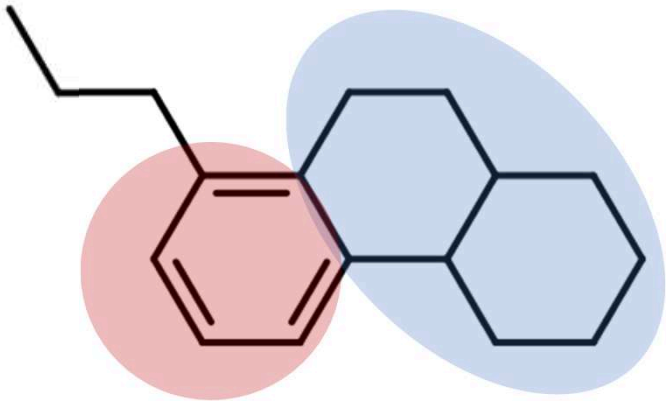


Qualitative “Solvency”

- Two lessons learned from first four blends

1. Naphthenic vs. Paraffinic Oil – **aromatic carbon** is key (20% vs. 4%)

2. White Oil vs. PAO – **naphthenes** help to lesser extent (30% vs. 0%)

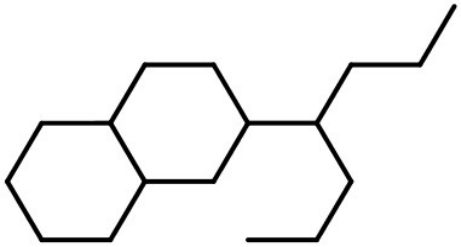


H1 Base Oils

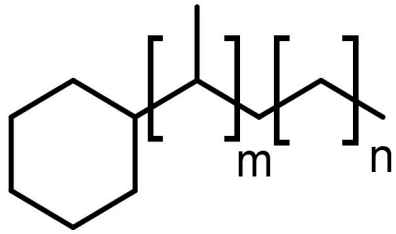
- Ironically, the styrene polymer is now HX-1 listed
  - But H1 base oils are not known for their high solvency
    - We need a certain range of 'medium' solvency for the polymer

  - Yet there's more to H1 than just PAO!

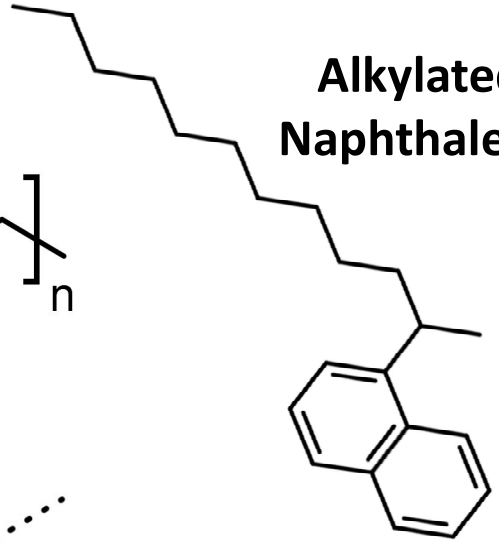
White Oil



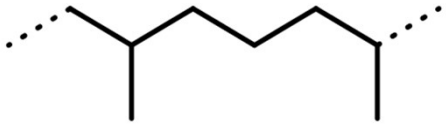
H1 Group III



Alkylated Naphthalene



EPO



H1 PIB

Putting Numbers on H1 “Solvency”

- We hypothesis that if we build H1 base oil blends using WO + Gr.III + AN with the same solvency as the Gr. I + 150BS then we’ll reproduce low WSO

- Likely the answer will be very specific and we need a metric to guide us
  - Other quantitative solvency methods: Hildebrand, Hansen, HLB, etc.

- We know **% aromatic** and **% naphthenic carbon** are important

Workflow in Quantifying Solvency

- Iterative process to measuring solvency and its relationship to WSO

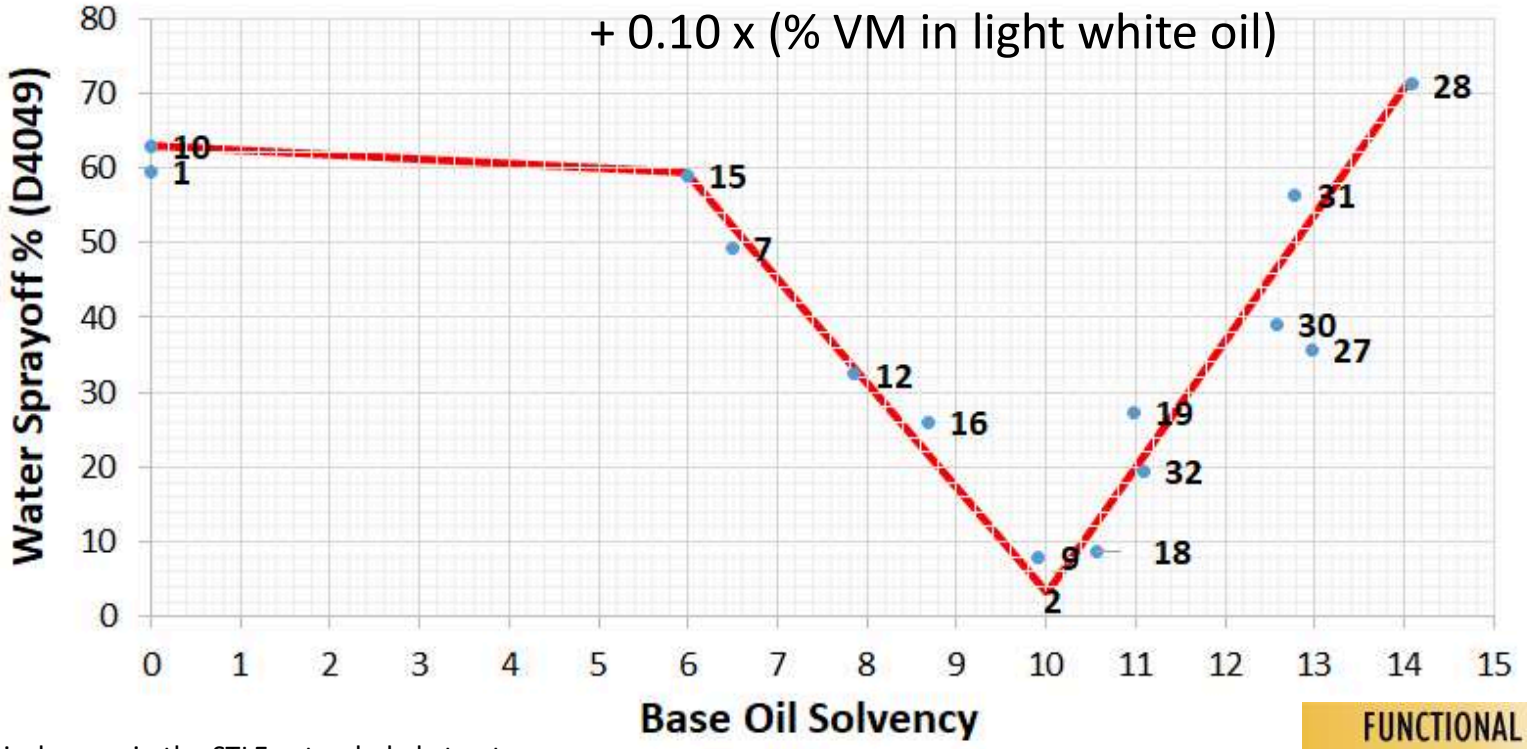
1. Start with an equation for **Solvency = (% Aromatic Carbon)**
2. Create a polynomial regression for **WSO = f(Solvency)** in an Excel plot

3. Use the regression to design a few blends that should give 10% WSO
4. Obtain 10 – 70% WSO
5. Hypothesize what part of the oil-polymer interaction we've left out
6. Add a term to the solvency equation encompassing that factor
7. Refit the regression with all prior data to test the hypothesis
8. Repeat

Details in the technical paper in the STLE extended abstract.

After Many Iterations with H1 Base Oil Blends…

Base Oil Solvency = 1.00 x (% Aromatic Carbon)
+ 0.24 x (% Naphthenic Carbon)
- 0.07 x (% PAO + mPAO + PIB)
+ 0.10 x (% VM in light white oil)



Details in the technical paper in the STLE extended abstract.

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Optimized H1 Blends

- Base oil solvency of 9 – 11 is great, 10 is ideal

- H1 base oil blends with same range of WSO as Gr.I + 150BS:

	ISO 150 Base Oil Blend:	30	27	12	19	16	32	18	9
Base Oil	8 cSt Group III	68.1	70.0		75.0				
	500 SUS White Oil			68.0		69.0		86.0	82.5
	PAO 10						57.4		
Thickener/VM	75 SSI H1 OCP VM	17.0					14.3		
	22 SSI H1 OCP VM		12.6		12.5			6.7	
	mPAO 100			22.0					
	PIB 2500 MW					16.0			7.5
AN (as solvent)	5 cSt Alkylated Naph.	14.9	17.4	10.0	12.5	15.0	28.3	7.3	10.0
	Base Oil Solvency	12.6	13.0	7.9	11.0	8.7	11.1	10.6	9.9
	WSO % (D4049, 38C)	**39.0%**	**35.6%**	**32.4%**	**27.3%**	**26.0%**	**19.5%**	**8.7%**	**8.0%**

Formula #'s are page numbers in lab notebook, not order of attempts.
Details in the technical paper in the STLE extended abstract.

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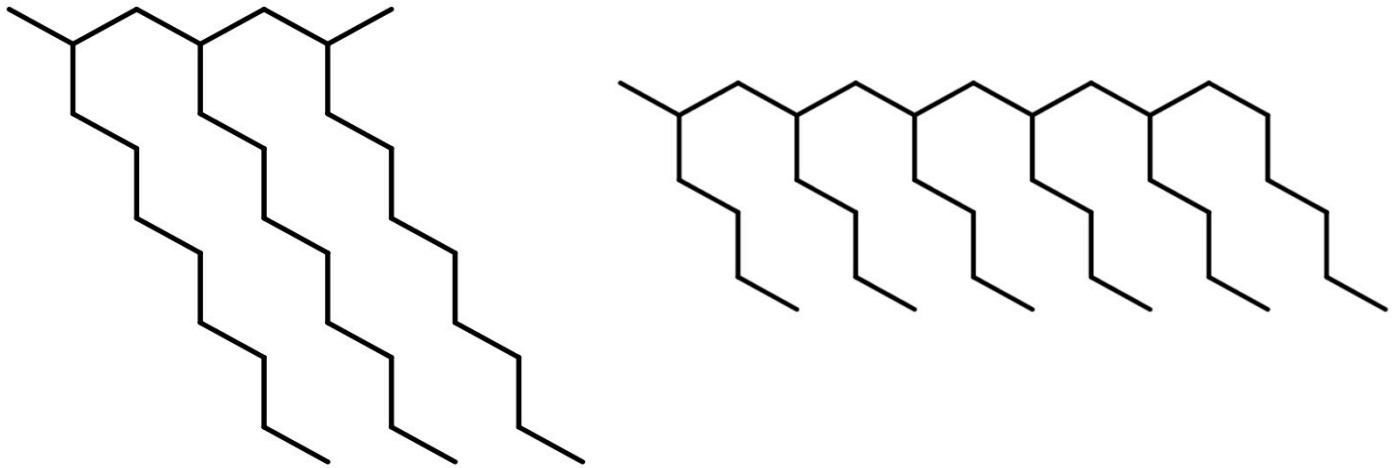
Low Solvency Case

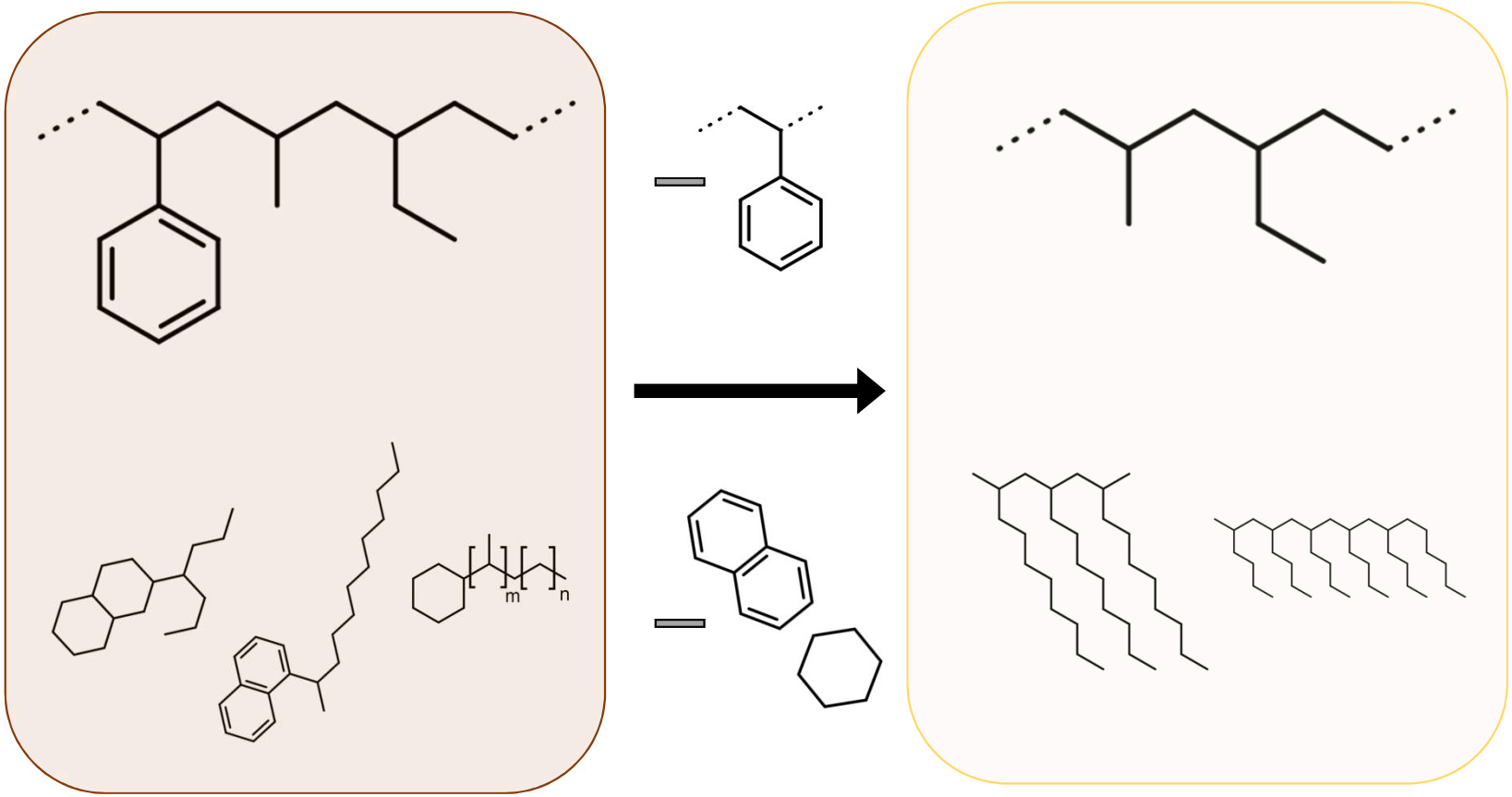
- What if we want to use full PAO/mPAO?
  - No naphthenes or aromatics for solvency



Tuning the Polymer for PAO

HX-1 Grease Polymer

H1 Base Fluid For The Grease



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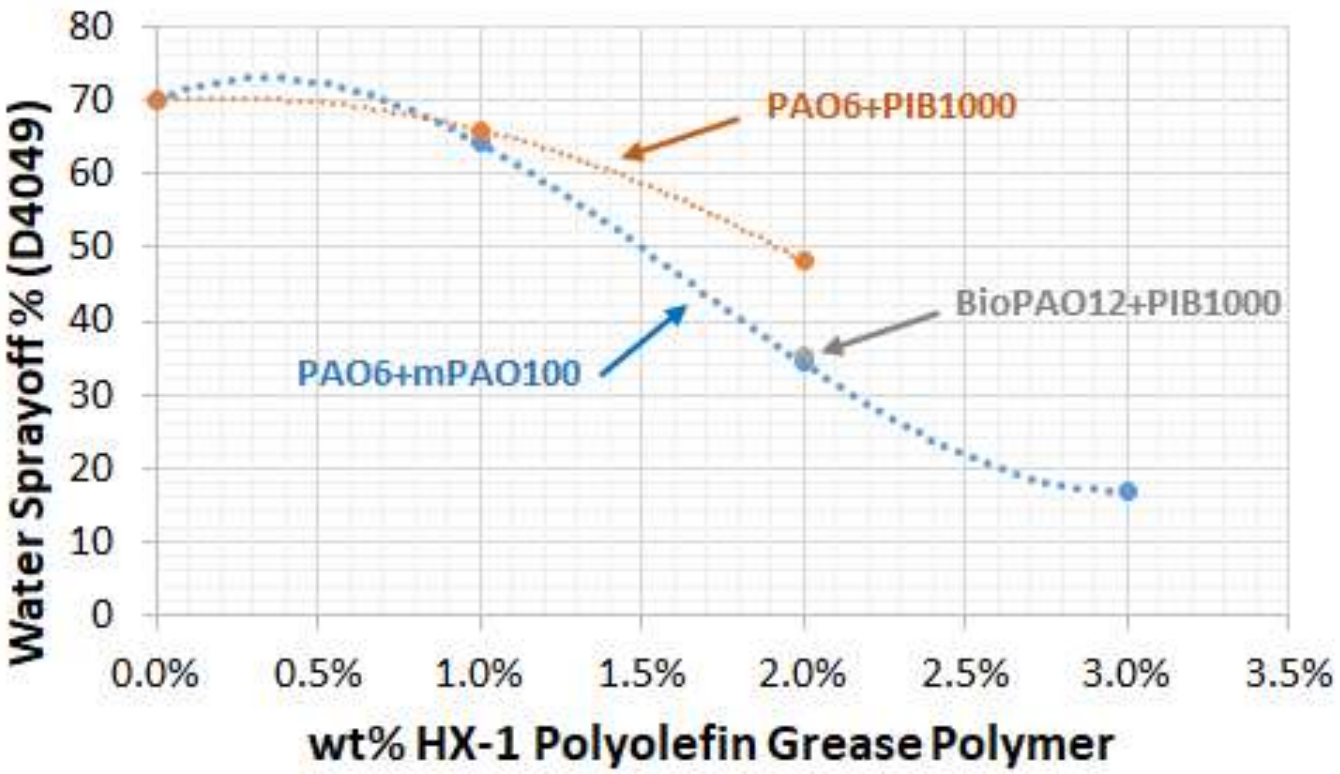
HX-1 Polyolefin

- HX-1 polyolefin isn't effective at 1wt% vs. HX-1 styrene polymer
- Yet at lower cost, we can uptreat - sometimes the solution is that simple



1.75wt% for 40% WSO

2.50wt% for 20% WSO

Environmentally Acceptable Grease (w/ H1)

- Vegetable oils are generally NSF H1 base stocks
  - 100% biobased and exceedingly biodegradable

- On paper, biggest difference in veg oil vs. other fluids is viscosity
  - Limited to ISO 32-36, no other “cuts”
    - Other problems too but viscosity is most glaring

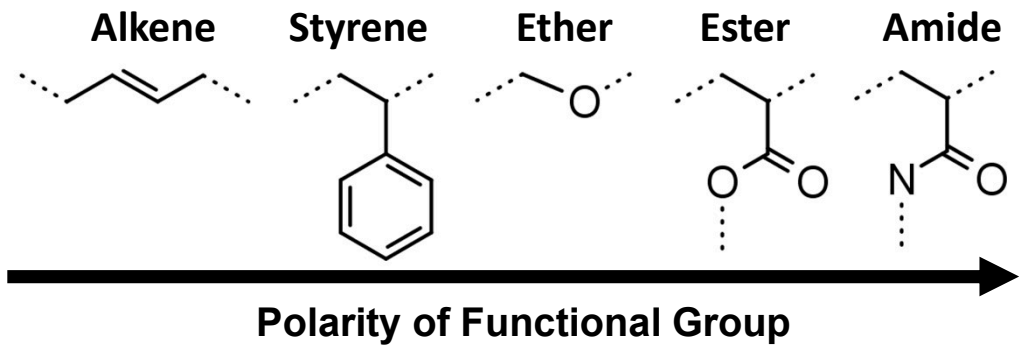
Biobased Grease Approach

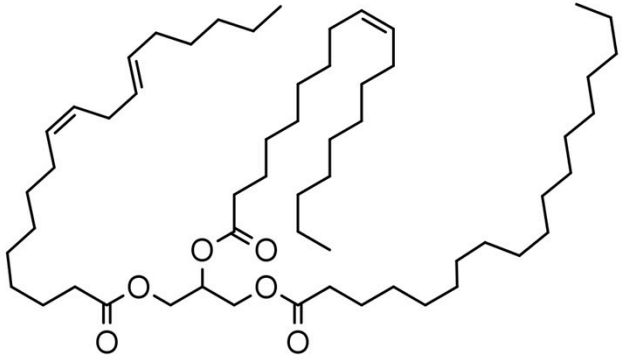
- We'll tackle vegetable based grease as a matter of base oil viscosity
  - How high should it be?
    - How do we get there?

- Using three commercial biobased viscosity modifiers which are EAL (Ecolabel LuSC listed), one of which is NSF HX-1

Biobased VMs

- Different than the styrene / polyolefin chemistries
- Esters are polar and high MW polymers need sufficiently close polarity to remain dissolved under a wide range of conditions

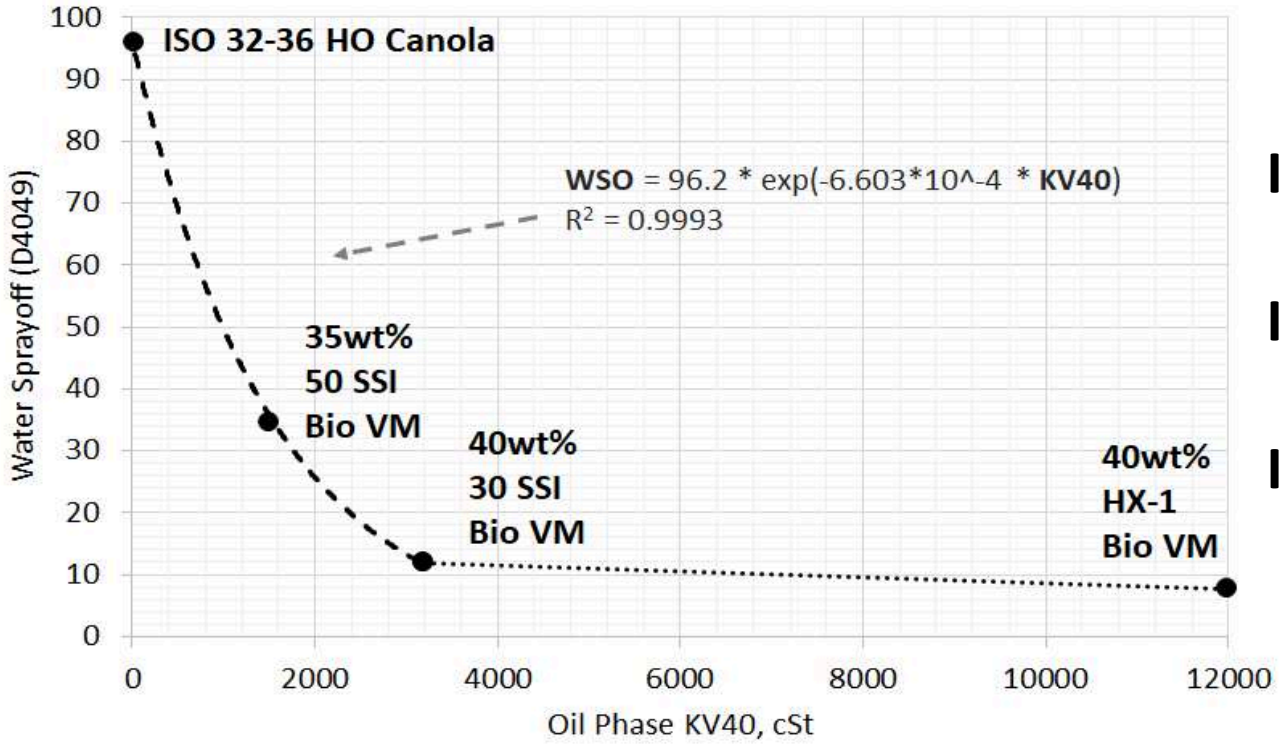




Wang, S. & DeVore, D. A study of polymer additives in mineral oil and vegetable oil-based greases. ELGI 2011 (2011).

Critical ISO VG for Good WSO

- #2 calcium stearate-acetate grease made to avoid adding water
- #3 diluted to #2 with bio VM and checked for WSO, base oil VG calculated



ISO VG 1500 for 40% WSO

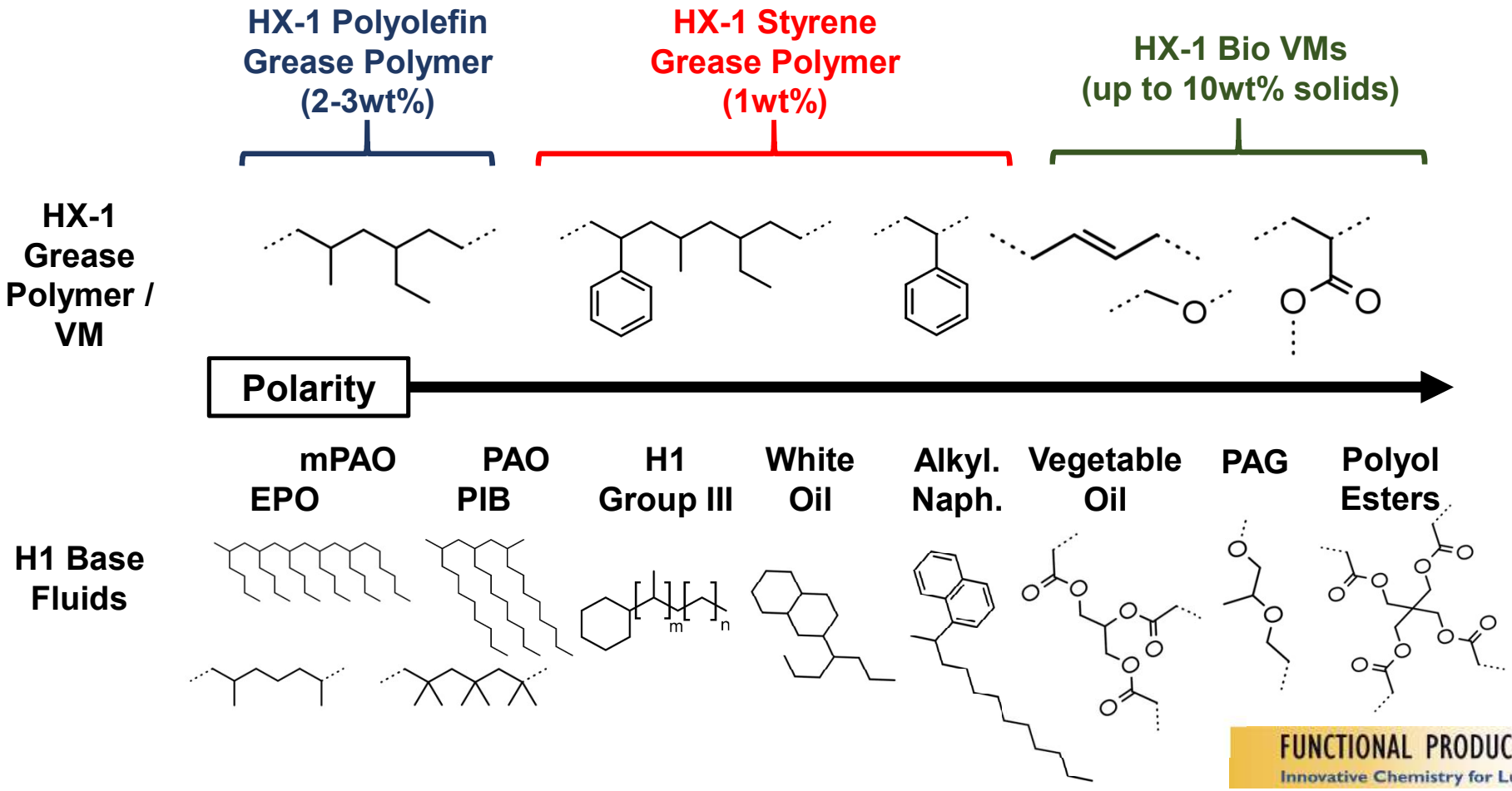
ISO VG 2200 for 20% WSO

ISO VG 3200 for 10% WSO

Summary

- For specialty grease, a few approaches to boosting water resistance
  - **1st case** – a well-tuned match between base oil solvency and polymer polarity to optimize water resistance at low treat
  - **2nd case** – uptreat a less effective polymer to 2-3wt% where usually 0.5-1% is customary in petroleum greases
  - **3rd case** – build up base oil viscosity using VMs (H1 or bio) that complement the type of product

Putting It All Together



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Conclusions

- We solved a mystery on varying results with the styrene polymer
  - Base oil selectivity and way to quantify it

- HX-1 styrene grease polymer is excellent in medium solvency white oil / Group III with alkylated naphthalene

- Polyolefin grease polymer chemistry better suited to PAO/mPAO grease

- Vegetable based greases should be boosted to ISO 1500 – 3200 to start off with excellent water resistance

Future Work

- Water washout (ASTM D1264) is still key to HPM and GC-LB
- H1 calcium sulfonate and aluminum complex thickeners

Thank you for your attention

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