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Innovative Chemistry for Lubricants

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Overcoming Obstacles in Water Resistant H1 and Biobased Specialty Greases Using Polymer

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Serving the grease industry since 1933
NLGI

Outline

- Motivation
- Calcium greasemaking
- Preliminary study in industrial oils
- Three approaches to water resistance in H1 calcium greases in:
  1. Medium solvency H1 petroleum ~40%
  2. Low solvency PAO ~20%
  3. High solvency vegetable oil ~40%
- Summary and Conclusions

Motivation

- Improving water resistance can be *painful*
  - Problem can occur inherently from base oil, thickener, low grade #
  - Far more complex and foundational to fix than adding AO or EP
- Common chokepoints
  1. Updating old greases to new specs without complete reformulation
  2. New greases formulated with limited options like NSF H1 and EAL

Materials and Methods

- NLGI #2 in ISO 150 blends of H1 base stocks
  - Hydrous calcium stearate for petroleum/PAO stocks
  - Calcium stearate-acetate complex (CaX) for veg oil to avoid water
    - St/Ac ratio <u>not</u> a simple 1:1
- ASTM D4049 water sprayoff to measure water resistance
- Observe deficiencies with water resistance and treat with grease polymer

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

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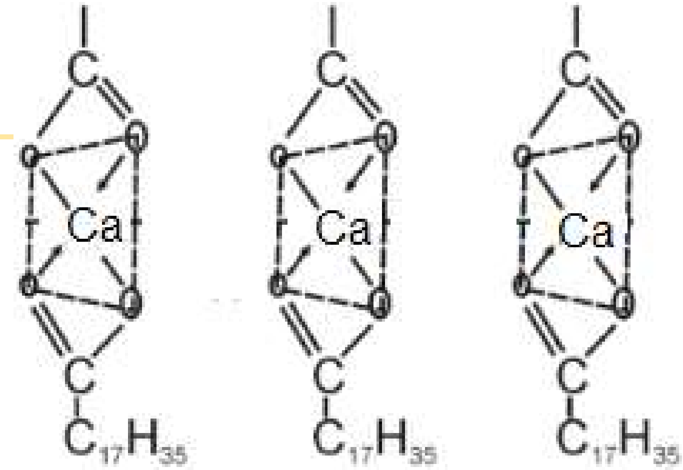
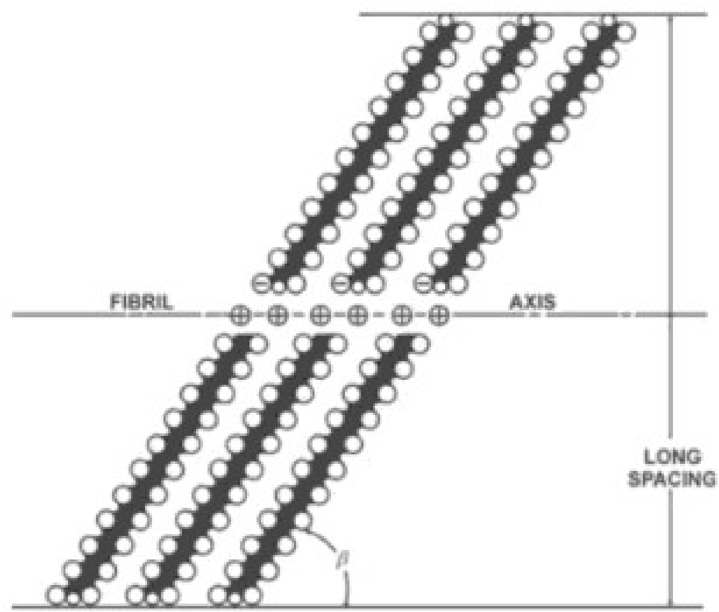
Calcium and CaX Grease

- Old but enduring technology
- GRAS, HX-1, EAL, MIL
- Robust supply chain
- 13.7% of global grease is Ca
    - Only 4% reported as CaSulf
    - 9.7% still hydrous/anhydrous/complex
        - 280 million pounds





2019 NLGI Production Survey
Modified from: Lubricating Oils, Greases and Petroleum Products Manufacturing Handbook

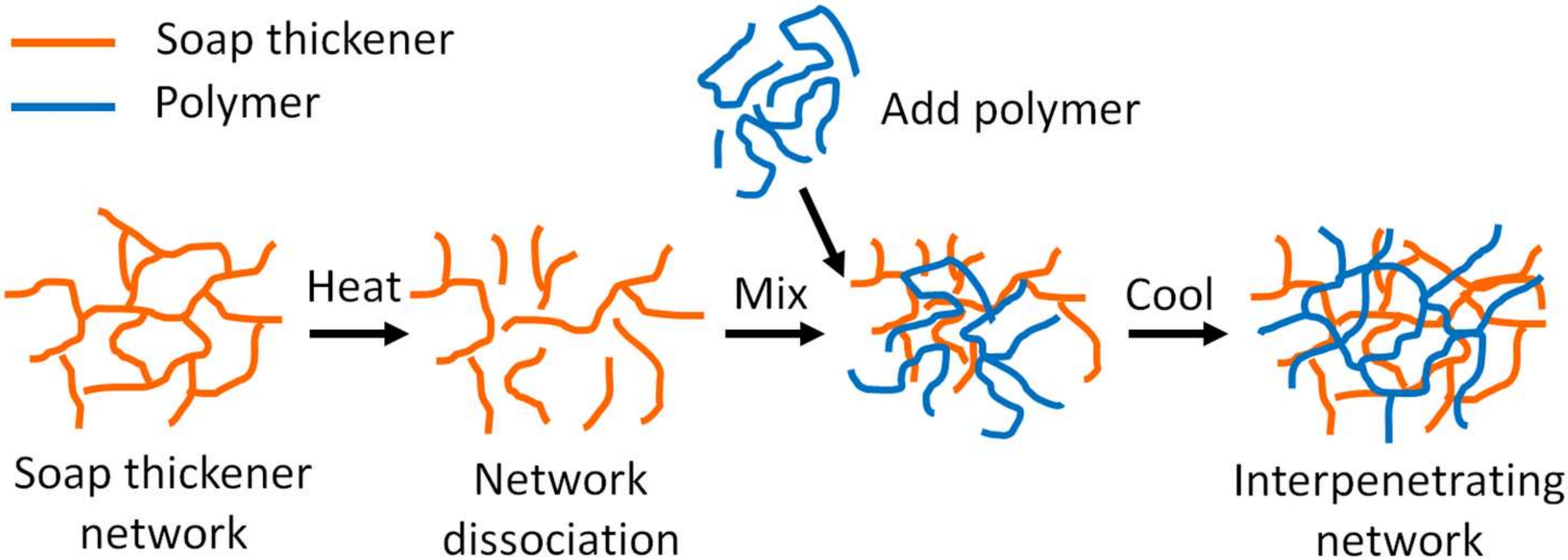
ASTM D4049 Water Sprayoff

- Static water spray test
  - 38°C/100°F water, 40 psi, 5 minutes
- HPM Water Resistant class
  - <40% WSO target
- Aggressive on soft, polar grease
  - 90%+ WSO in many Ca types
  - Polymer can fix this

Plate after test

ASTM D4049-: “Standard Test Method for Determining the Resistance of Lubricating Grease to Water Spray”

Grease + Polymer is like Concrete + Rebar



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

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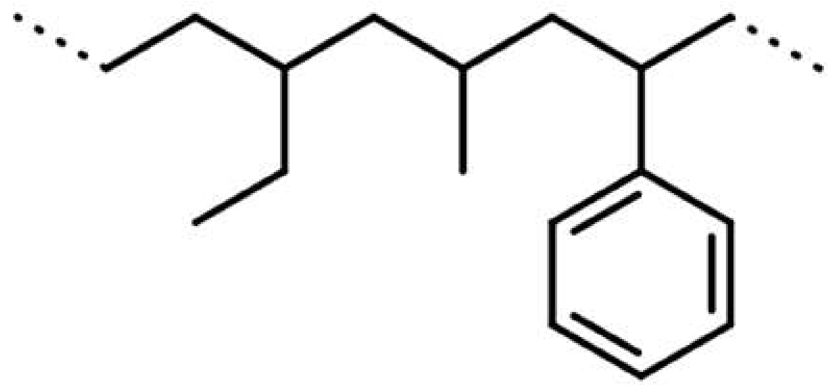
Starting from a Mystery

- This study begins with an industrial question
- Styrene copolymer grease polymer
  - Excellent WSO *for some*
    - Poor or no effect *for others*
      - Sometimes undesired rubberiness



Early Investigation into Styrene Selectivity

- Hydrous calcium stearate greases with ISO 150 blends of popular oils
    - Paraffinic = 600SN + 150BS
    - Naphthenic = 750 SUS
    - H1 PAO = PAO6 + mPAO100
    - H1 White Oil = 500WO + PIB2500
- Simulating different types of formulators favoring different base oils
- 1wt% styrene grease polymer in each blend + two controls w/o

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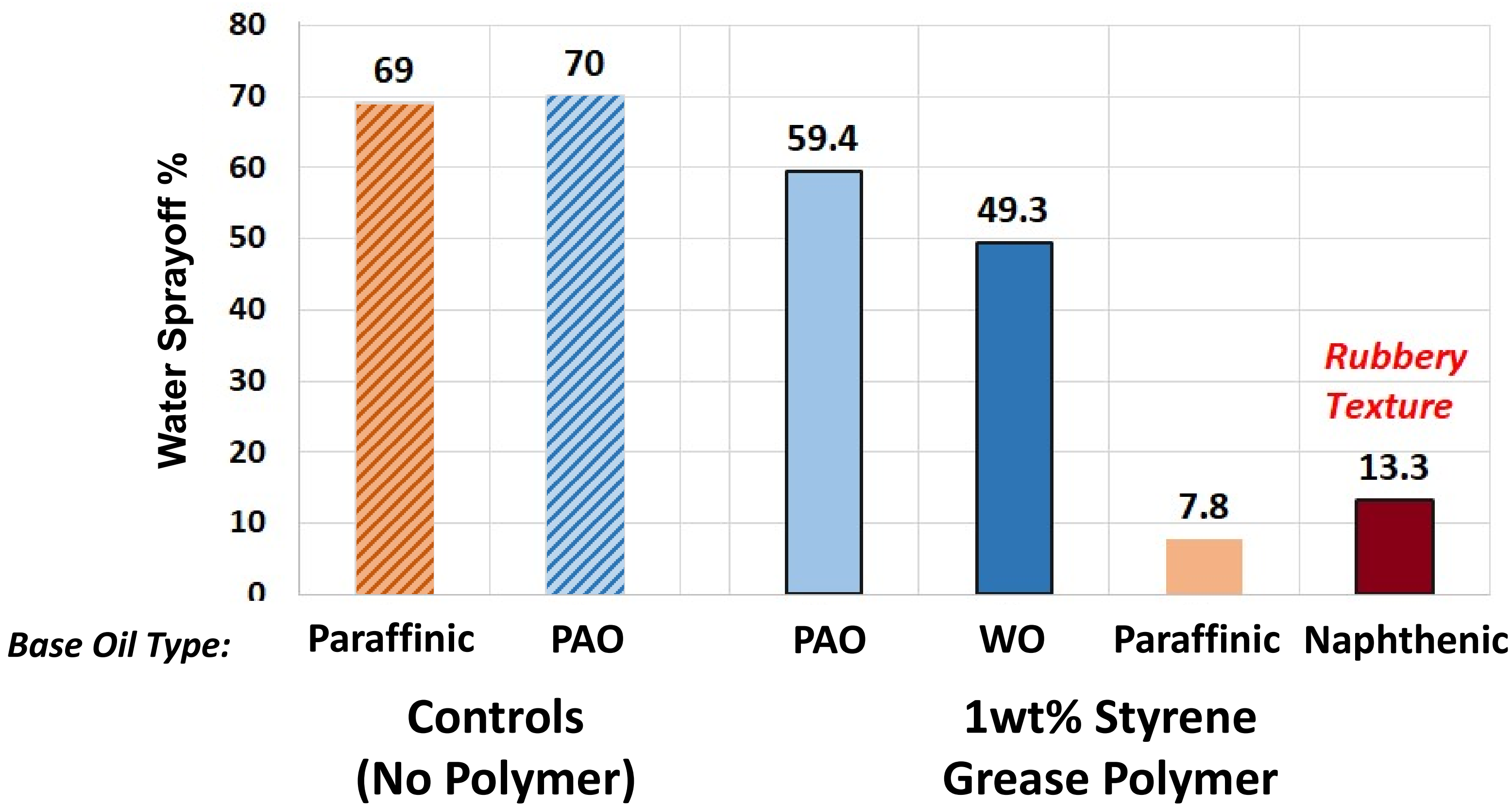
Preliminary Results

- Dataset was picked well and we captured the full range of outcomes



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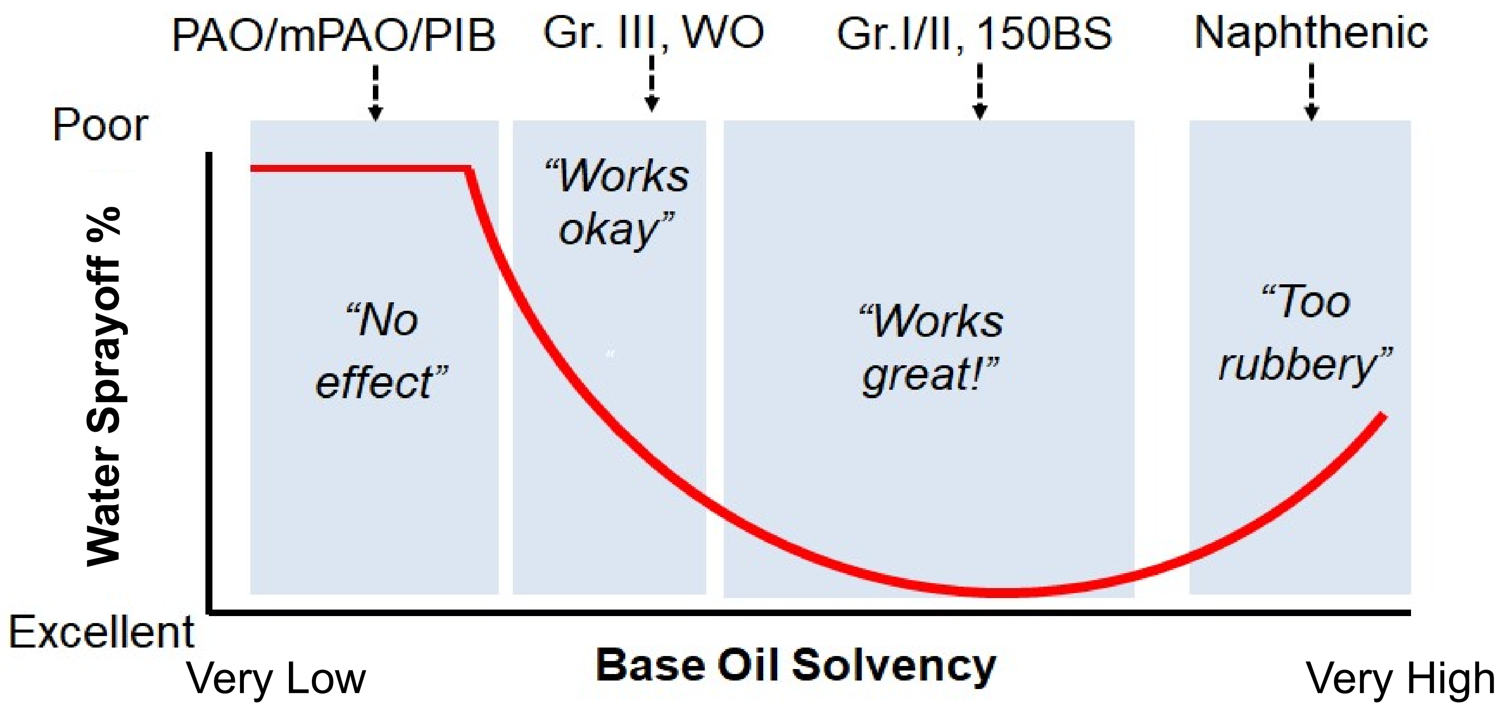
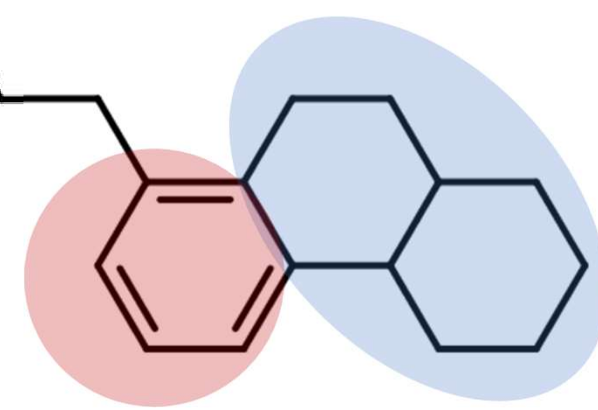
Styrene Polymer Selectivity

- We can map the range of experiences vs. base oil solvency



Qualitative "Solvency"

- Two lessons from comparing oil composition vs. WSO:



1. Naphthenic vs. Paraffinic Oil
   - **Aromatic carbon** is key (20% vs. 4%)

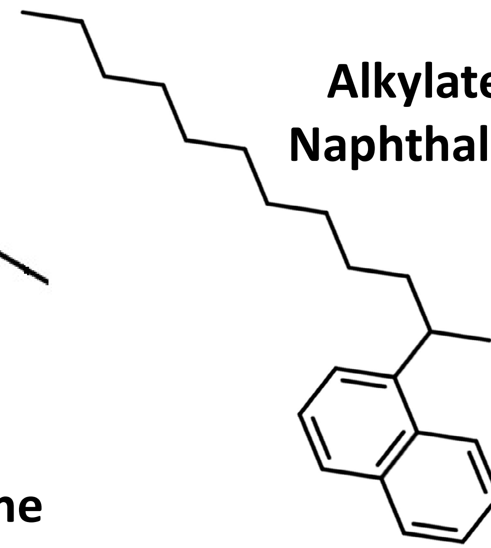
2. White Oil vs. PAO
   - **Naphthenic carbon** helps to lesser extent (30% vs. 0%)

Carbon type profile by ASTM D2140!

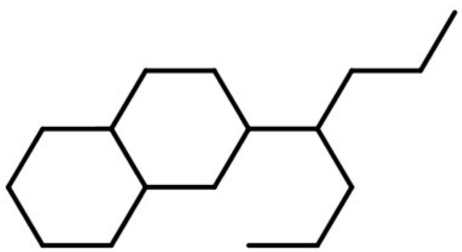
H1 Base Oils

- Ironically, the styrene polymer is now HX-1 listed
  - But H1 base oils are not known for their high solvency
    - Yet there's more to H1 than just PAO!

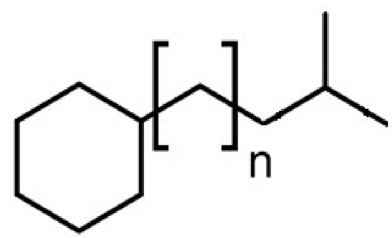
Alkylated Naphthalene



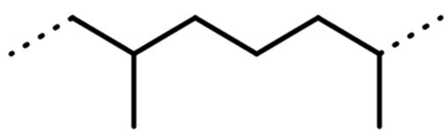
White Oil



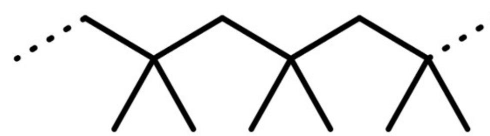
H1 Group III



Ethylene-Propylene Oligomer



H1 Polybutene



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Designing H1 "Solvency"

- Hypothesis: if we reproduce the "solvency" of Group I paraffinic oil using H1 oil blends then we will reproduce the high WSO improvement for H1 grease.
    - To test this we'll need to build from aromatics of alkylated naphthalenes, naphthenes of white oil or Group III, etc.
        - Likely the answer will be very specific so we need a measurable guide
- We know **% aromatic** and **% naphthenic carbon** are important – start there

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Modeling Solvency vs. WSO%

- We're going to capture and quantify "solvency" using two equations we'll feed with data

1. First equation relating important factors of base oil composition to **Solvency**
   - Linear equation adding up different factors multiplied by how important that factor is
     - **Solvency** = a[%aromatic carbon] + b[% naphthenic carbon] + …

2. Second equation that ties the calculated **Solvency** (x) to our measured **WSO%** (y)
   - Third order polynomial that roughly fits the curvature we saw in the preliminary study
     - **WSO% =** a**[Solvency]**^{3} + b**[Solvency]**^{2} + c**[Solvency]** + d

   - Use Excel trendline ("regression") to fit Solvency to WSO%

   - The R^2 of this regression is our compass to guide our equation optimizing

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Iterative Workflow

Start:

Use the model so far to design and test 3 - 5 base oils which **should** give low WSO%

WSO% will be **higher** than calculated – we're missing something

Add an extra term to **Solvency** equation to account for missing property of the oils

+ n[% Naphthenic Carbon]
-p[% PAO, mPAO, PB]
+v[% Viscosity Modifier]
....

Adjust the coefficient on that term up/down to improve fit of **WSO% regression** (R^2)

Try a different **WSO% regression** type to check for better fit (1°, 2°, 3°, log, etc.)

Re-analyze data from all previous oils/greases with the new **Solvency** and **WSO%** equations

Repeat Cycle

Details in the technical paper

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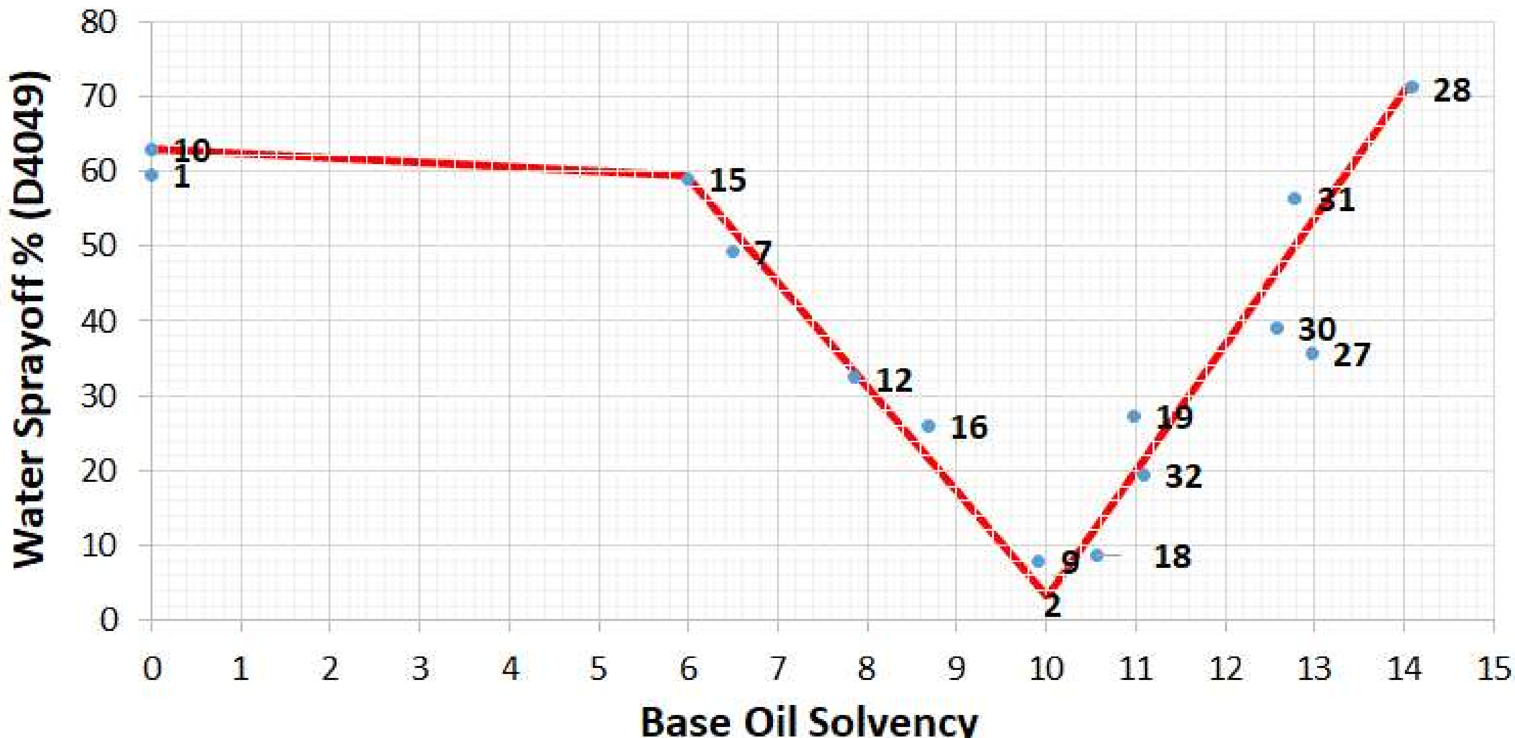
After Many Iterations…

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)

WSO% vs. **Solvency**:

- best fit by 3rd order polynomial in Excel
- (really more of a 'square-root' sign)

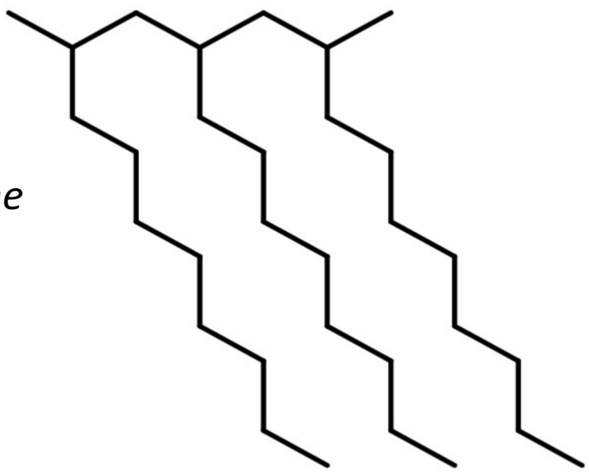


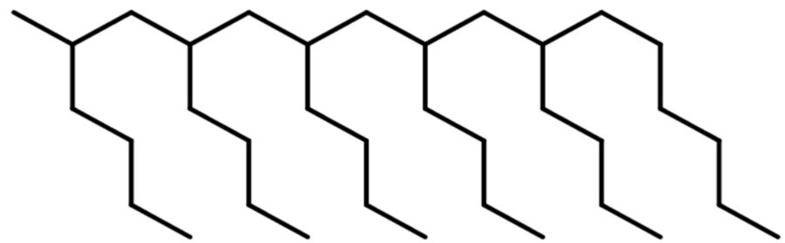
Details and exact blends in the technical paper

Low Solvency Case

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

polydecene



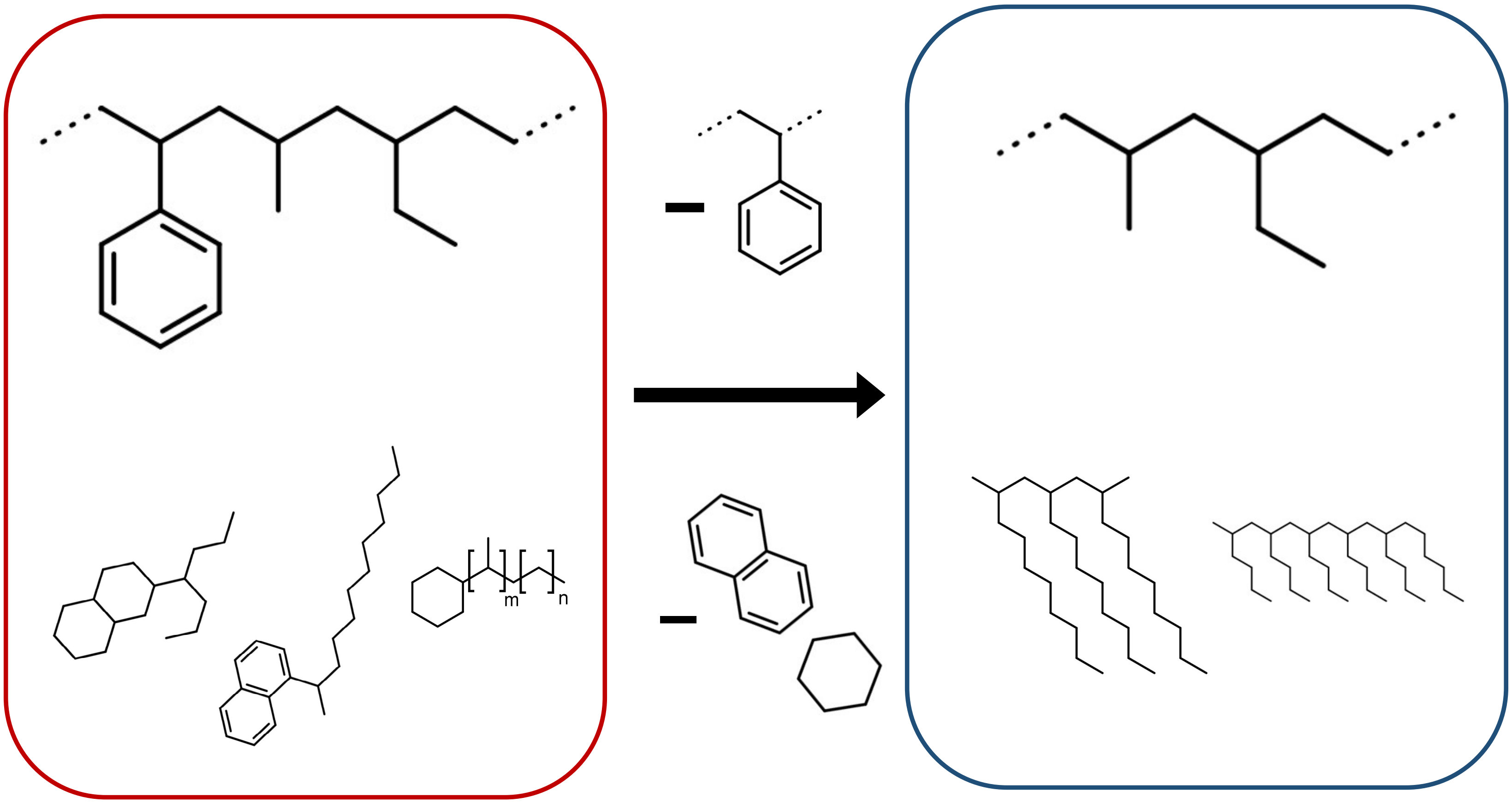


polyhexene

Tuning the Polymer for PAO

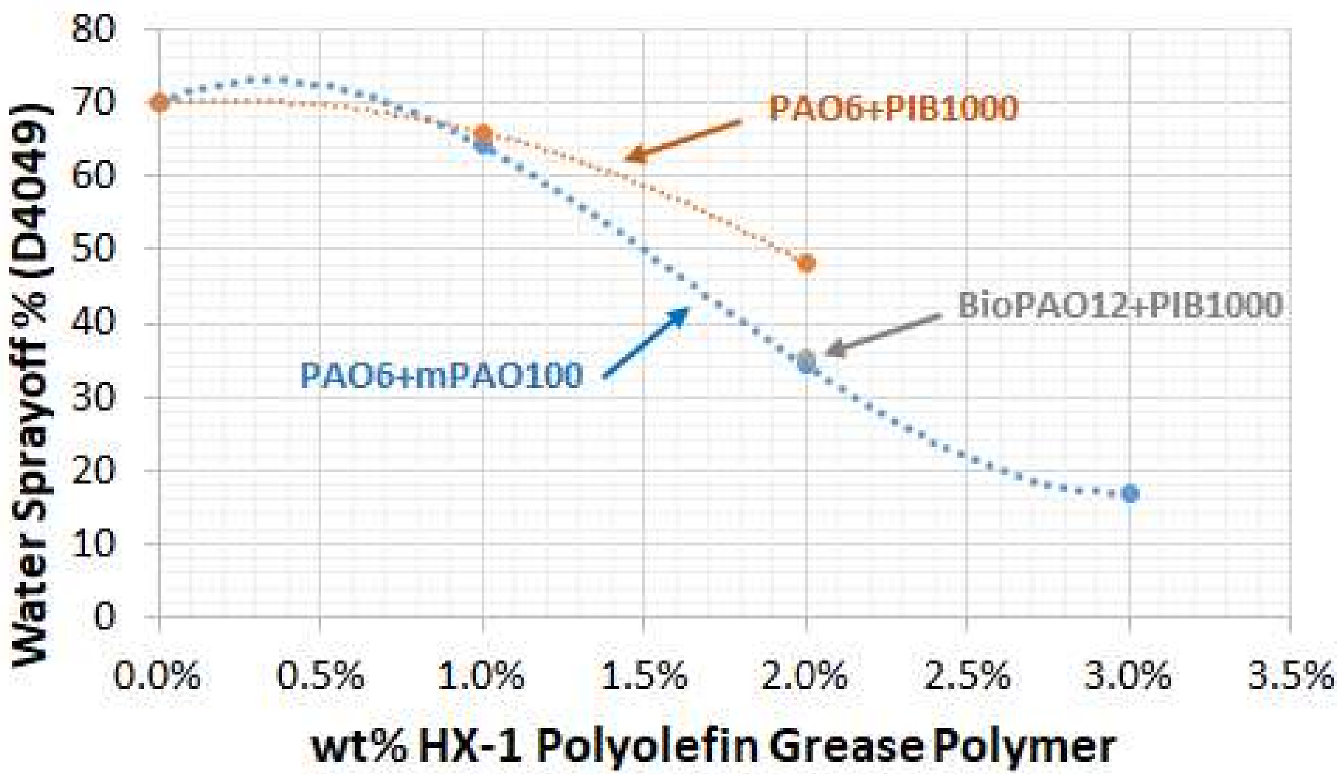
Grease Polymer

Preferred H1 Base Stocks



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

- Vegetable oils are an ideal EAL base stock in principle
    - 100% biobased/renewable/biodegradable
    - Typically $\leq$ 33% the price of synthetics
- First problem is viscosity
    - Limited to ISO ~32, no other “cuts”
    - Other problems too but viscosity is most glaring

Biobased Grease Approach

- We'll tackle vegetable based grease as a matter of low base oil viscosity
  - Three biobased viscosity modifiers on hand (one is HX-1)
    - We'll use each to build ISO 150 calcium complex greases
      - Does VM selection matter at same ISO VG and grade?
      - Which biobased VM chemistry works best?
      - Any other benefits?

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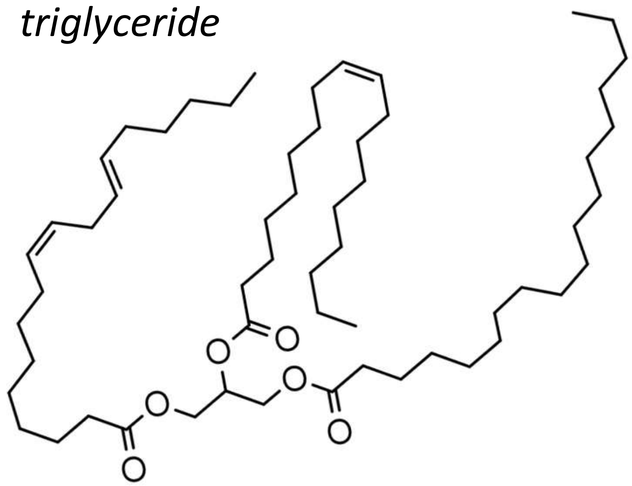
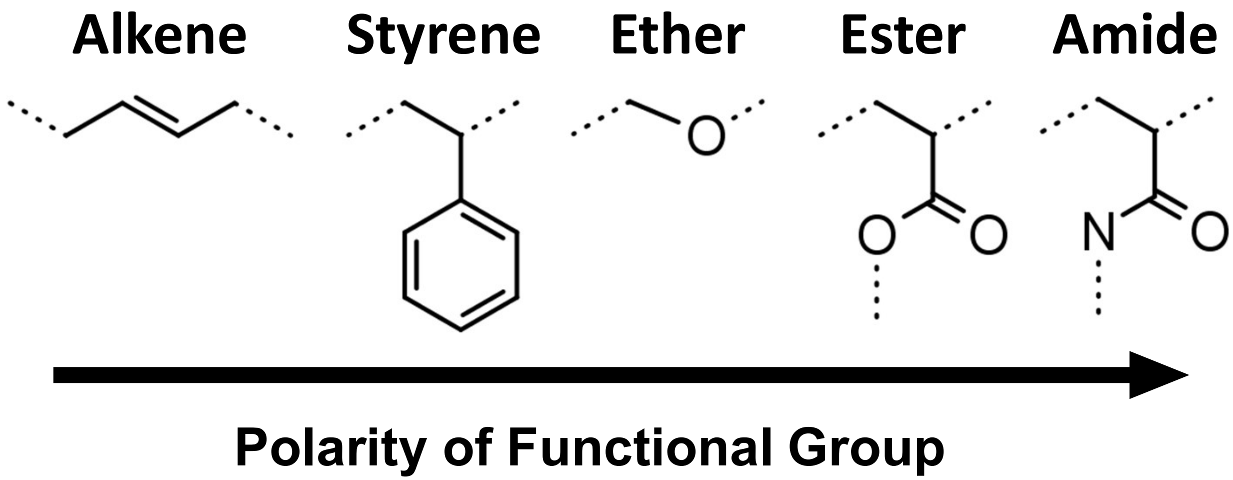
Biobased VMs

- Esters are highly discerning – ideally the VM 'looks' like the base fluid
  - Polarity, branching, MW, saturation determine fit

triglyceride





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

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Greasemaking with Liquid Bio VM's

- Three different biobased viscosity modifier chemistries tested
- Same ISO VG and grade, different yields and WSO

Grease Formulations by wt%	No VM Control	High MW Bio VM	Low Temp Bio VM	HX-1 Bio VM
Calcium Stearate/Acetate Powder	40.0	30.0	28.5	22.5
Antioxidant Blend	2.0	2.0	2.0	2.0
Biobased VM (various)	--	11.6	12.7	12.8
High Oleic Canola Oil	58.0	56.4	56.8	62.7
NLGI Grade	#2	#2	#2	#2
Base Oil Blend ISO VG	32	150	150	150
Water Sprayoff % (D4049)	99.0%	95.5%	74.8%	31.2%

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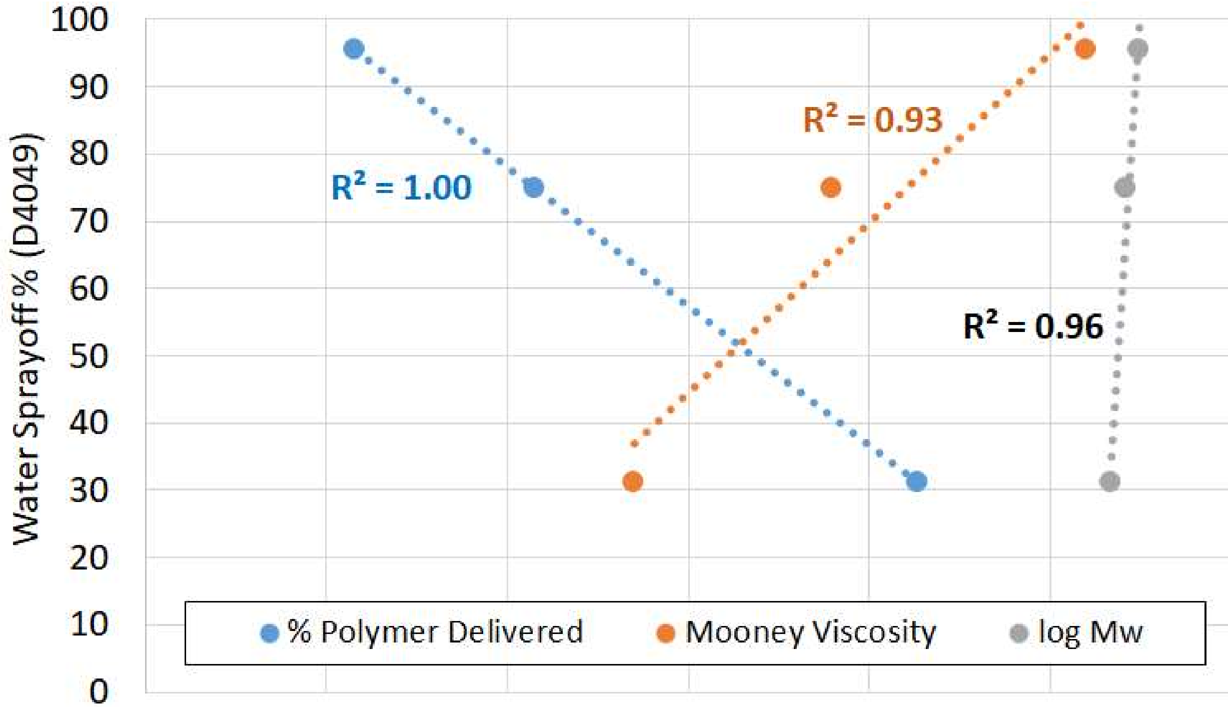
Bio VM Analysis

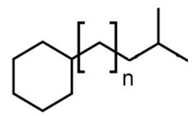
- What's driving the large difference in WSO?
- Amount of polymer delivered (solids content) appears most important



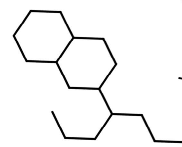
Putting It All Together (1/3)

H1 Grease Base Stock…

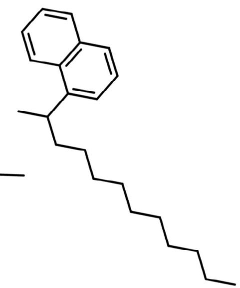
H1 Group III



White Oil



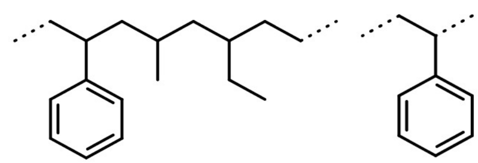
Alkyl. Naph.



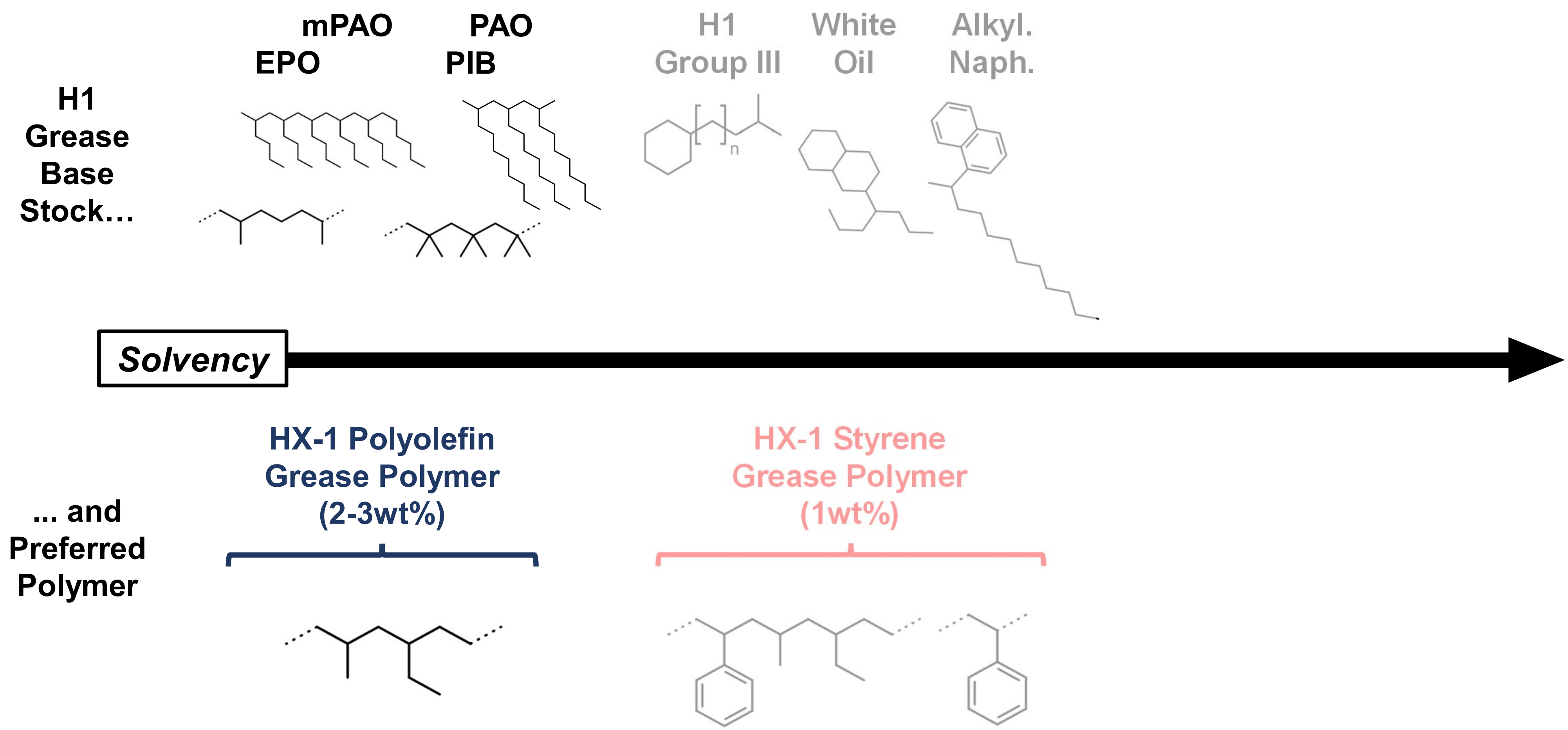
Solvency

... and Preferred Polymer

HX-1 Styrene Grease Polymer (1wt%)



Putting It All Together (2/3)



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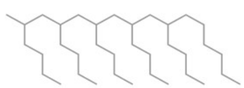
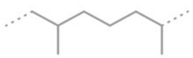
Putting It All Together (3/3)

H1 Grease Base Stock…

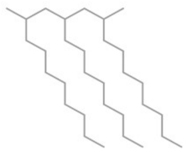
mPAO



EPO

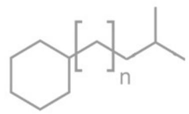


PAO



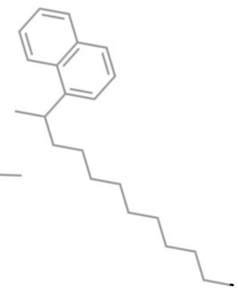
PIB

H1 Group III

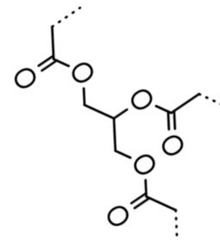


White Oil

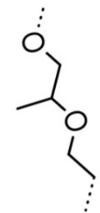
Alkyl. Naph.



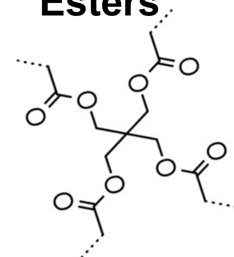
Vegetable Oil



PAG



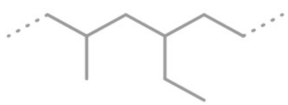
Polyol Esters



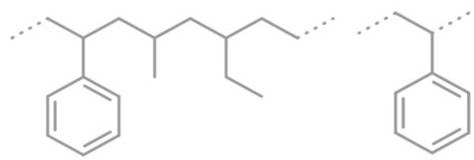
Solvency →

… and Preferred Polymer

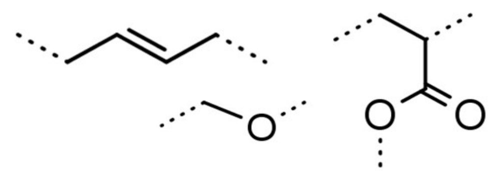
HX-1 Polyolefin Grease Polymer (2-3wt%)



HX-1 Styrene Grease Polymer (1wt%)



HX-1/Bio VMs (3-5wt%)



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Conclusions

- Worked the problem to define the parameters of an oil-selective high performance polymer
  - Able to translate from industrial to H1 stocks
- Developed math to engineer H1 blends with petroleum solvency
- Produced recommendations for H1 grease polymer selection based on base oil stock – low/medium/high solvency

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Future Work

- Extend biobased water resistance to <20% WSO – stuck at 31%
- Water washout (ASTM D1264) is still key to GC-LB and HPM
- Other H1 or EAL thickeners? CaSulf, AlX, Silica?

Thank you!

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