Polymer Technology in lubrication and approaches to reduce costs in formulations.

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On Behave of
IMCD Lubricants & Fuels

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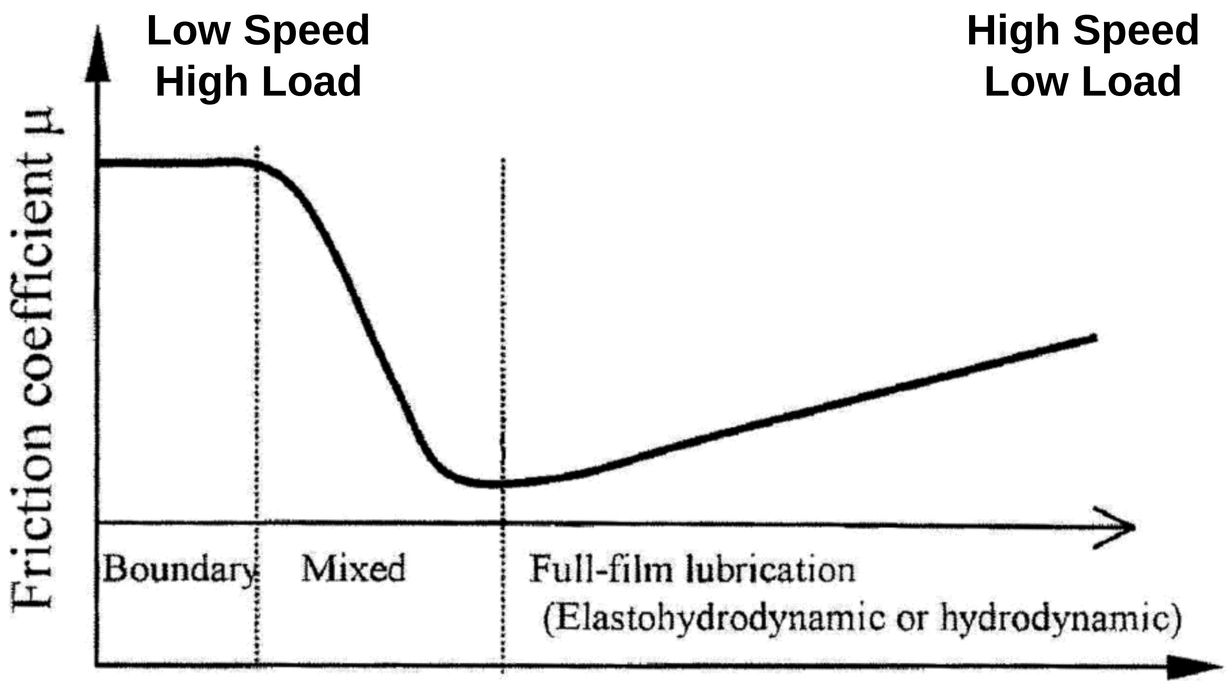
Polymer Technology (VM Fundamentals)

Motivation

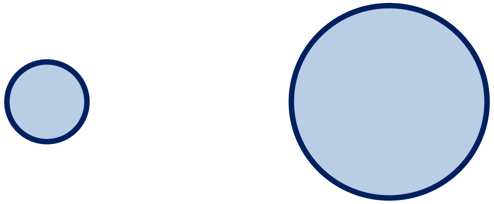
- Stribeck curve - three regimes of lubrication
  - **Viscosity** of lubricant vs. **Speed** / **Load** of application



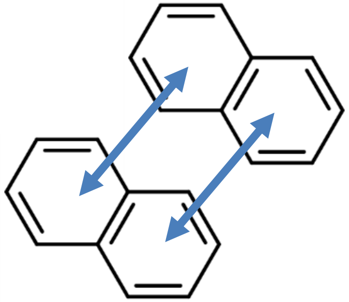
Viscosity x Speed / Load = Hersey Number

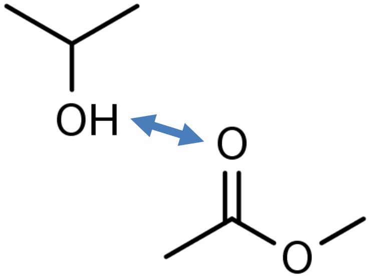
Viscosity

- **Viscosity** is a fluid’s resistance to flow
  - Size / MW of the fluid

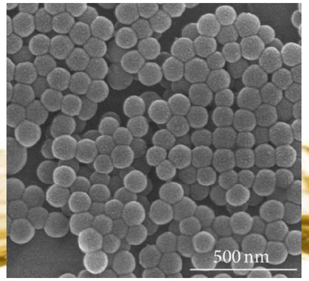


  - Attractions (aromatics, esters, hydroxyl)



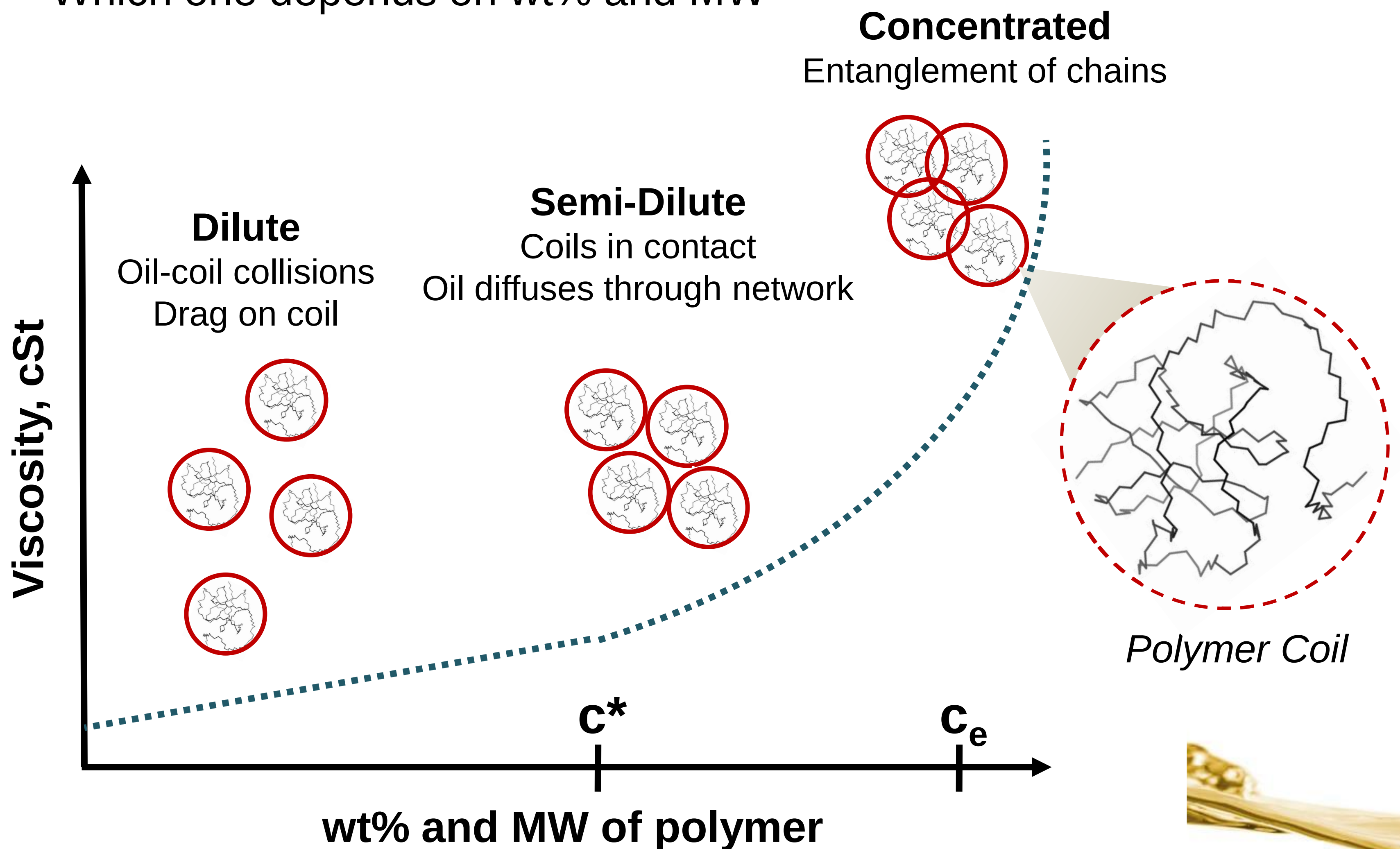


  - Physical obstructions (particles, **polymers**)



Viscosity from Polymers

- Three regimes of polymer solution behavior
  - Which one depends on wt% and MW



Willett, E; DeVore, A; Vargo, D. “Investigation of VI Improver Blends for Improved Low Temperature Lubricants” Functional Products Inc. 2018

Polymer VM Advantages

- Why use VM instead of blending oils?

1. Cheaper high VI
   - Gr.I and naphthenic with VI 140+
2. Higher viscosity grades
   - Gr. III, synthetic ester
3. Better low temperature
   - Polymer + light oil vs. heavy oil + light oil
4. Low visc, high VI formulations possible
   - Low visc base oils tend to be lower VI

What’s VI?

- **Viscosity index**
  - Standard Oil 1929
    - Needed a way to standardize visc-temp relationship of crude oils
      - Condense the logarithmic plot of visc-temp into one number
        - VI 100 = paraffinic Pennsylvania crude

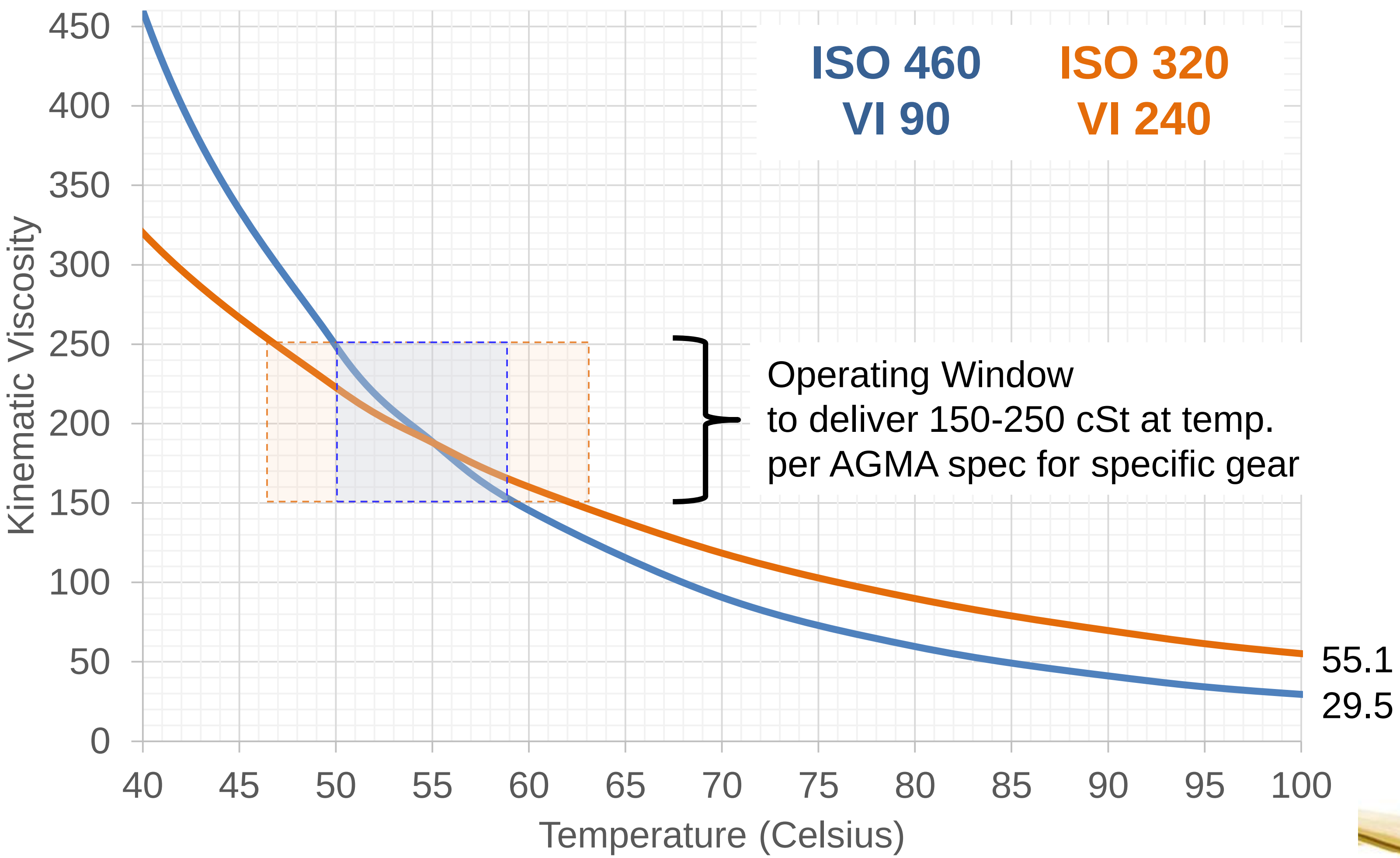
- The higher the VI, the lower the change in viscosity with temperature

- Wider operating temperature window for equipment
  - Oil may fall below or above grade with heating/cooling
  - “All Season” / “Multi-grade” / “High VI”

E.W. Dean, G.H.B. Davis, Chem. Met. Eng. 36 (**1929**) 618–619.
ASTM D2270, Standard Practice for Calculating Viscosity Index From Kinematic Viscosity at 40 and 100°C

VI Importance

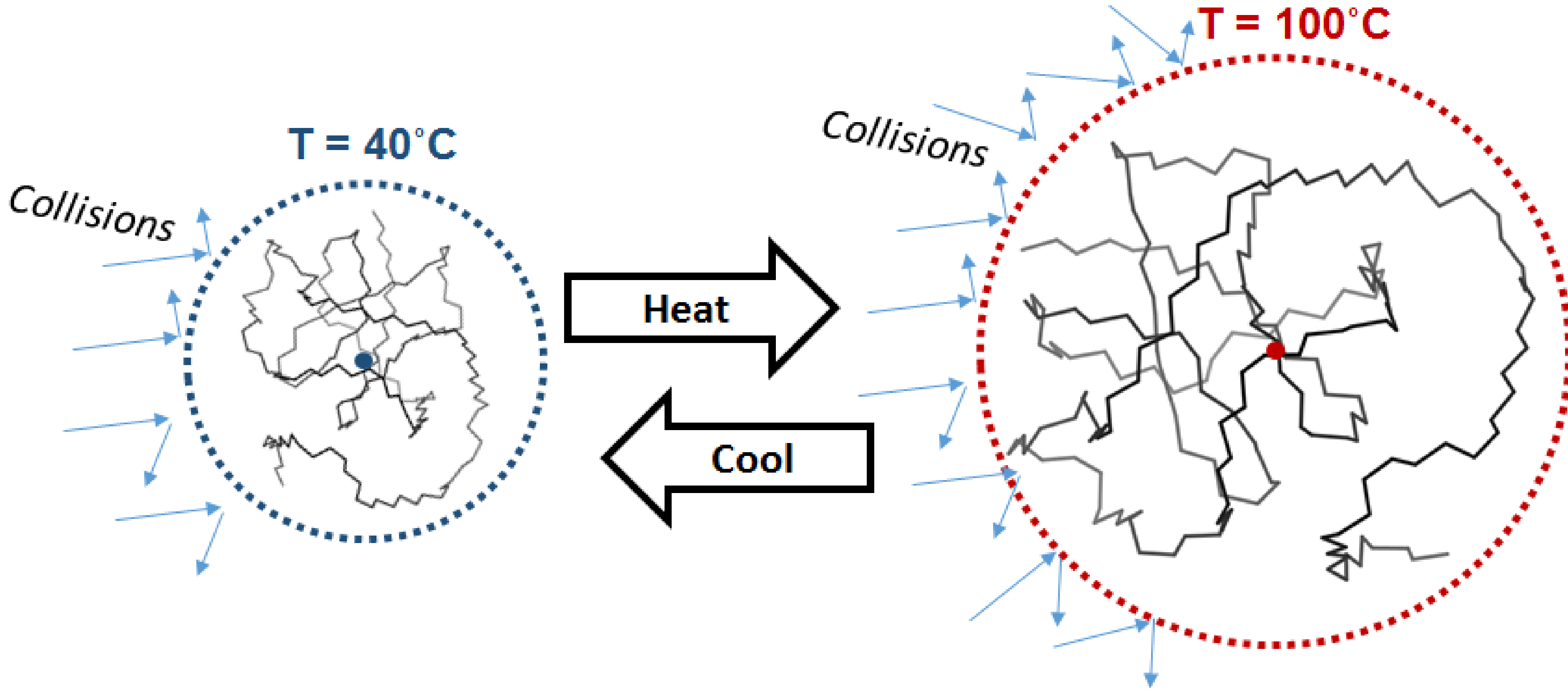
- Wider operating temperature window for equipment
  - “All Season”, “Multi-Grade”, “High VI”



ANSI/AGMA 9005-F16. Example: gear with pitchline velocity of 1.8 m/s (35mm dia. at 1000 rpm)

Polymer VI Improvers

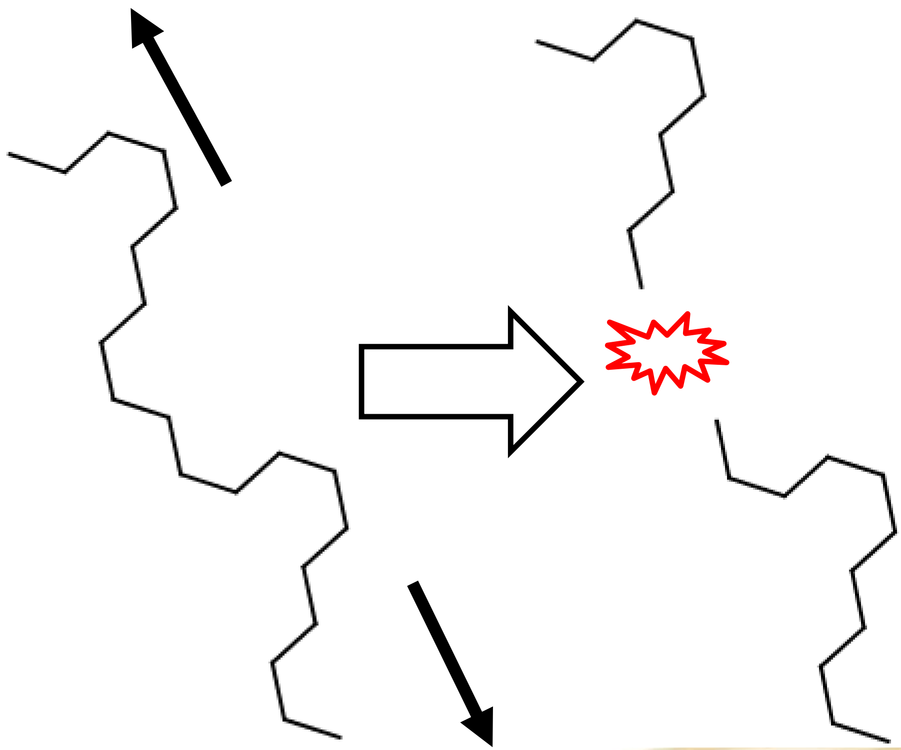
- Some polymers become more soluble at high temp and expand
- The greater the expansion, the larger the obstacle and resistance
  - Relatively higher KV100 = higher VI



Rudnick, L. R. Lubricant Additives: Chemistry and Applications, 3rd Ed. (CRC Press, 2017)

Polymers and Shear

- Mechanical stress on polymer from pressure, cavitation, boundary lub.
  - Carbon-carbon bond ruptures under high stress
    - MW decrease, permanent viscosity loss



C – C

Tensile Strength = 134 GPa

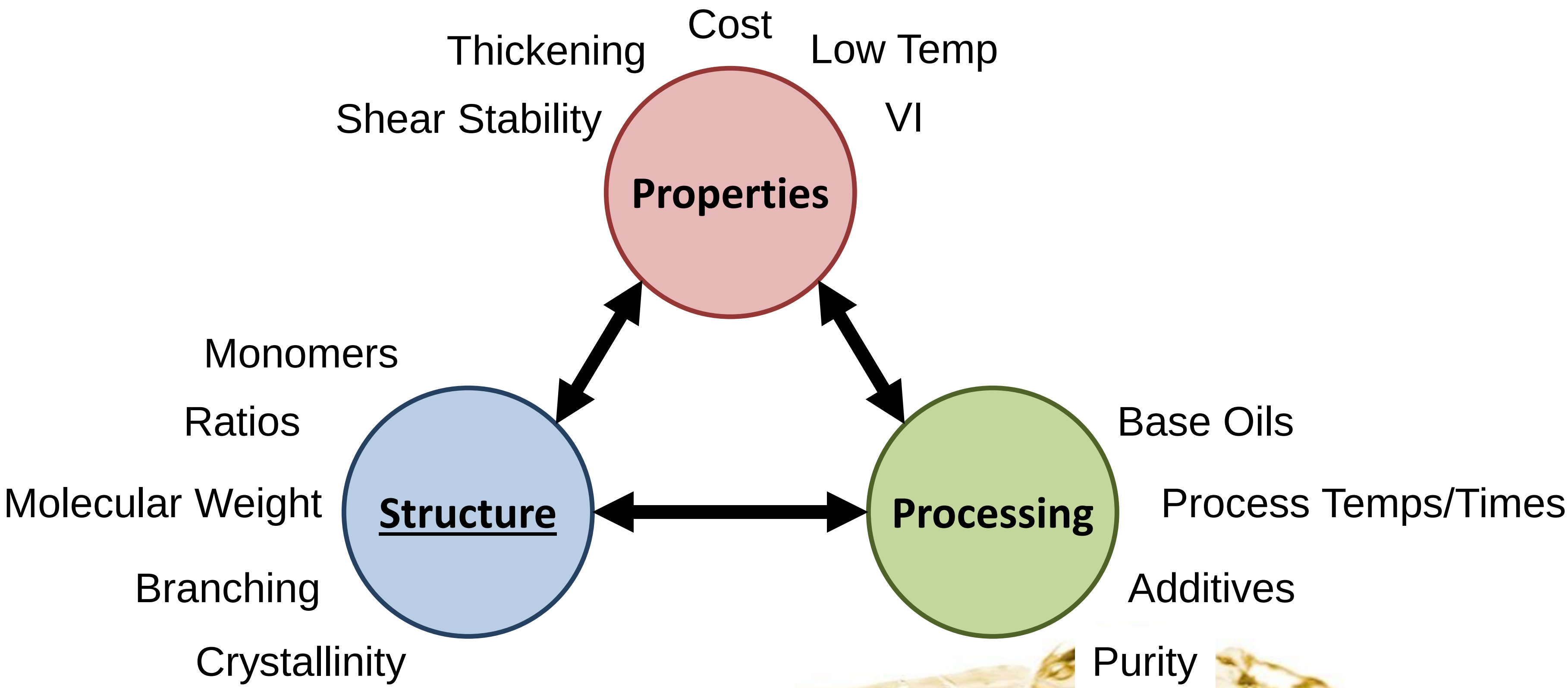
Hornyak, G. L., Dutta, J., Tibbals, H. F. & Rao, A. Introduction to Nanoscience. (CRC Press, 2008).

Testing for Shear Stability

- Three main tests of increasing severity:
  - **Engine oil** – ASTM D6278, Kurt-Orbahn / Bosch diesel injector
    - 30 – 250 cycles through diesel injector at 30°C (1min/cycle)
  - **Hydraulic fluids** – ASTM D5621 / D2603, sonic
    - 50W / 23 kHz sonic irradiation at 40˚C for 40min
  - **Gear oils** – CEC L-45-A, “20 hour KRL”
    - Tapered roller bearing, 1450 rpm, 5000N load; 60˚C for 20 hours

Material Science

- Why do polymers behave differently? Why are some VM or VII?
  - Material science of polymers

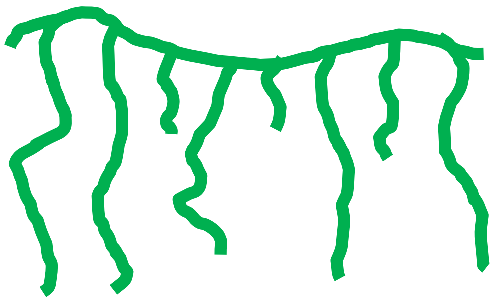


Architecture

Linear

Star

Comb / Brush

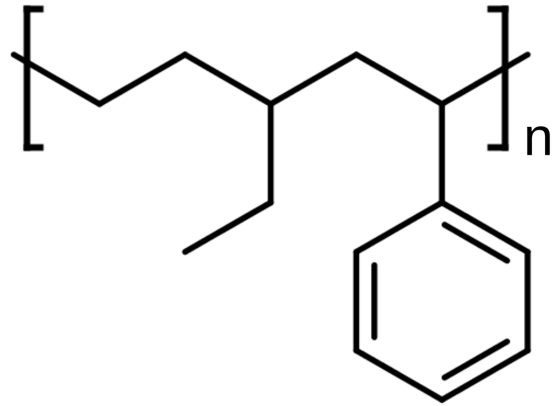


Polymers for Mineral Oil

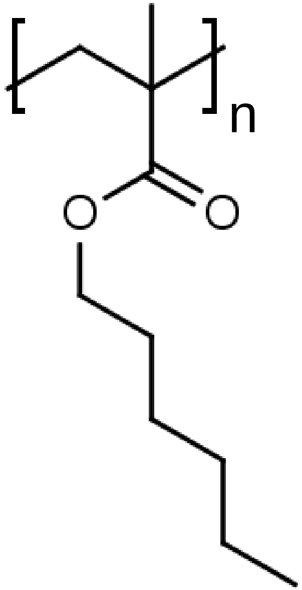
- Hydrocarbon polymers or very high C-H content (PMA)
- Low unsaturation / aromatics

Polyisobutylene (PIB)

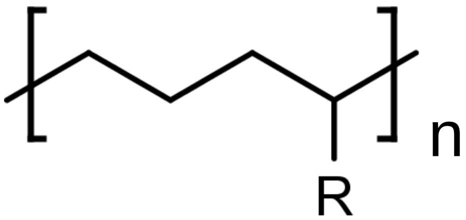
Styrene Copolymer



Polymethacrylates (PMA)



Olefin Copolymer (OCP)



Stambaugh, R. L. & Kinker, B. G. Viscosity Index Improvers and Thickeners. Chemistry and Technology of Lubricants: Third Edition (2010).

Mineral Oil Polymers

Chemistry	Application	Advantage	Disadvantage
PIB	Greases, gear, hydraulic fluids	Excellent tackifier Shear stable at low MW	Temperature sensitive Handling
OCP	Cost-sensitive, industrial gear	Excellent thickening efficiency Excellent economics Excellent variety and supply Good tackifier	Poor shear stability Poor low temperature
PMA	Gear oil, hydraulic, ATF	High VI improvement High shear stability Excellent pour point / Brookfield Optional built-in PPD or dispersant	Cost High treat
Styrene Copolymers	Gear oil, hydraulic	High VI improvement Excellent thickening efficiency Good pour point / Brookfield	Premium pricing Limited options

Picking a VM / VII

Picking a VM / VII for your application depends on several factors:

- **Severity**: EHL/boundary lubrication, high/low temperatures
- **Tier**: Premium vs. fighting grade
- **Use interval**: extended oil change vs. single-pass
- **Region**: Different requirements by country

- **Handling**: Solid or liquid VM, maximum viscosity

Biggest concern is **shear** which will be greatest influence on choice, cost

Rizvi, S. Q. A. Lubricant Chemistry, Technology, Selection, and Design. ASTM Int. Conshohocken (2009).
Rudnick, L. R. Lubricant Additives: Chemistry and Applications, 3rd Edition. (CRC Press, 2017)

Overview

- A few select tips, tricks, and theory:
  - Designing for shear and shear-in-grade
  - Haze in synthetics
  - Choosing base fluids for higher VI

Shear in Grade

- How to formulate a product that shears in grade or by a certain %?
  - Less intimidating than it seems to get very good estimates
  - Calculation on paper can save $$$ in shear testing ($250/per)

- Example:
  - We want to make an ISO 100 product with PAO4.
    - Our customer needs <15% viscosity by KRL shear method.
      - **What viscosity modifier should we use?**

Working with SSI

- Most VMs will have at least one SSI reported (Bosch, sonic, KRL)

- That SSI tends to be independent of base fluid, treat rate, or temp.
  - 50 SSI means we'll lose 50% of viscosity we add with that VM

- Knowing *that*, our KV, and **% viscosity from polymer**…
  - Then we can engineer % viscosity loss – quick, accurate, cheap

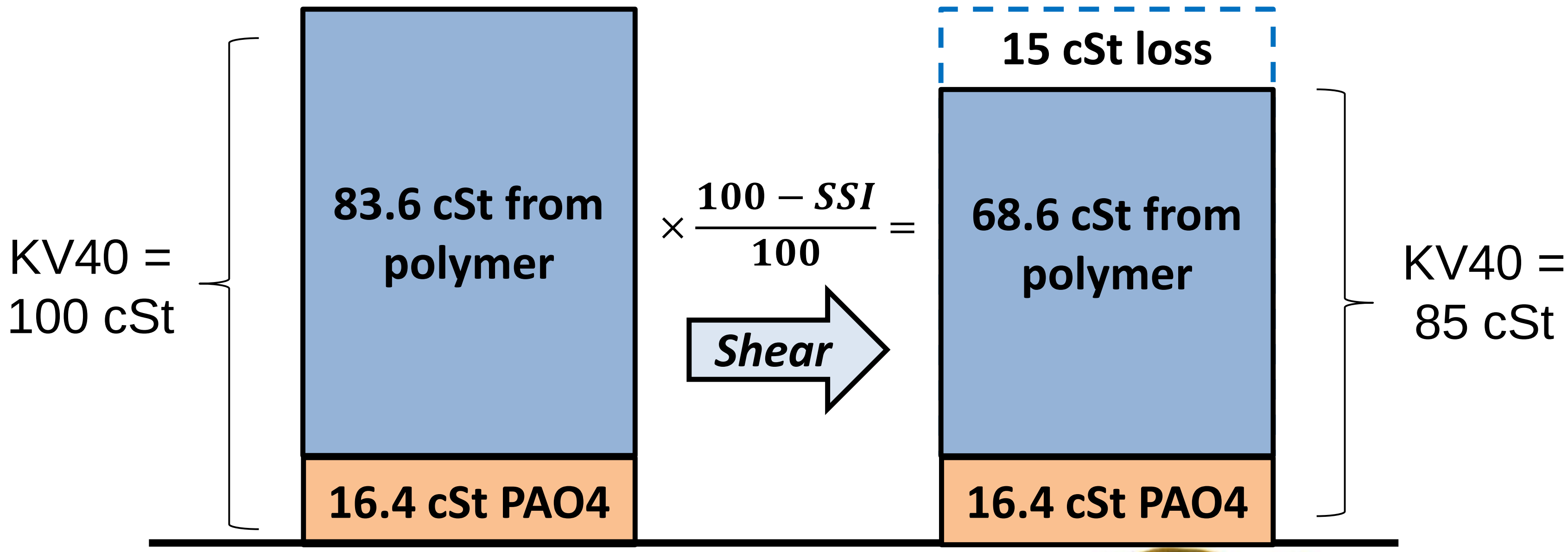
Viscosity from Polymer

- Let's say we have an ISO 100 formulation with VM
  - Viscosity of oils + ad paks + polybutene + PAO = "**Base Oil Viscosity**"
  - Product Viscosity – Base Oil Viscosity = "**Viscosity From Polymer"**
    - 100 cSt product – 16.4 cSt of oil = 83.6 cSt from polymer
      - 83.6 cSt / 100 cSt = 83.6 % viscosity from polymer

% Viscosity Loss

- Our product viscosity = 100 cSt
- Viscosity from Polymer = 83.6 cSt (83.6%)

- What SSI do need to get < 15% loss by KRL?

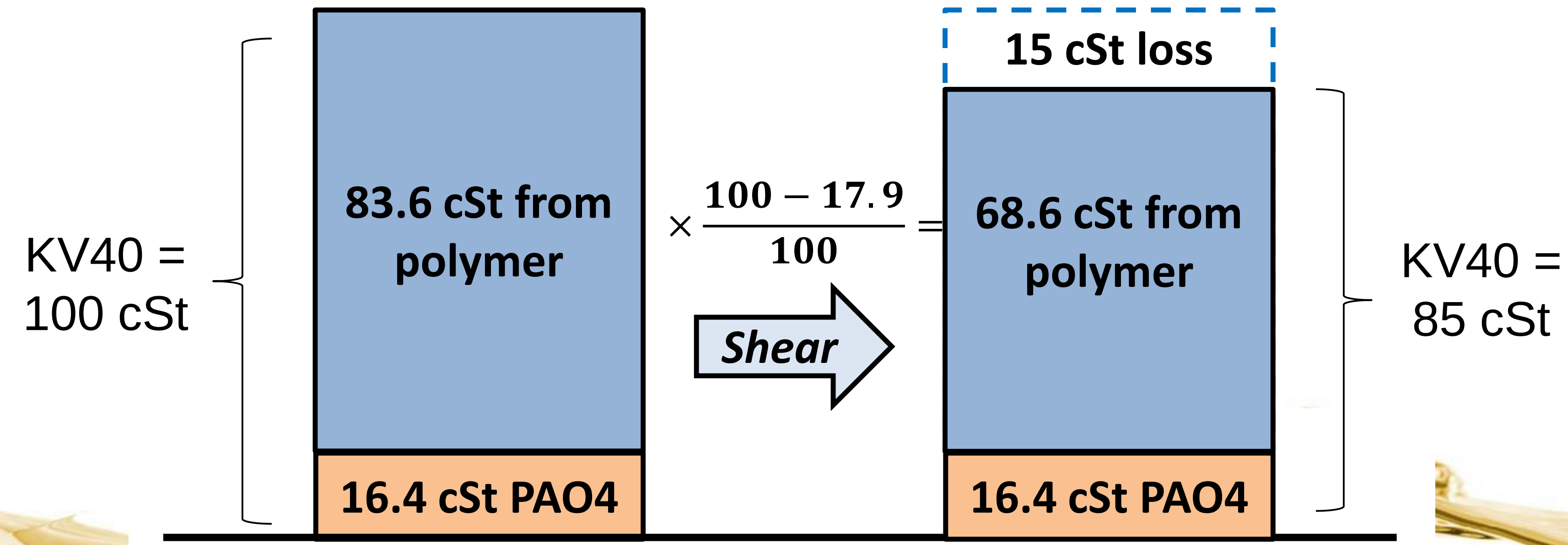


Calculating Required SSI

- What SSI do need to get < 15% loss by KRL?

$$\%\,Visc\ Loss = \%\,Visc\ from\ Polymer\ \times \frac{SSI}{100}$$

$$\boldsymbol{SSI\ Required} = \frac{100\ \times \%\,Visc\ Loss}{\%Visc\ from\ Polymer} = \frac{100\ \times 15}{83.6} = \mathbf{17.9}$$



Synthetic Troubles

- So we build the ISO 100
  - 31% SSI 15% KRL PMA, VI too high, small volume so PAO pricing not great…
    - Cut back some PMA with a polybutene to save some $

wt%	**ISO 100 PMA/PAO**	**ISO 100 PMA/PB/PAO**
PAO4	65.0	69.0
PMA 15% SSI	31.0	20.0
PB 2500 MW		7.0
Ad Pak	4.0	4.0
KV40	100.6	100
KV100	17.0	15.5
VI	184	164
$/lb, rough	$2.36	$2.07

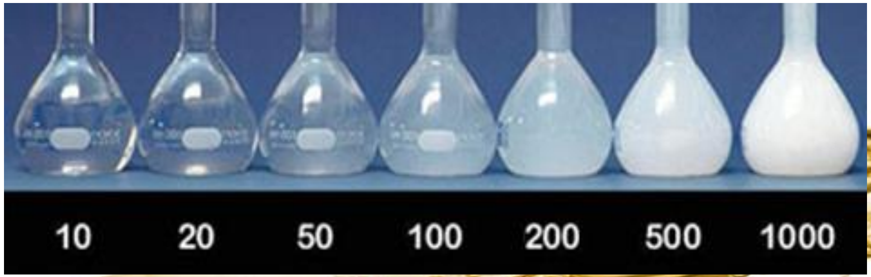
- Great! But now something changes…
  - We start seeing **haze** upon standing
  - Low temp viscosities and pour points got worse

Haze

- Common in semi/full synthetics with high wt% shear stable VM
  - Low solvency base oil made worse by replacing oil with polymer
    - Higher MW, worse solvency

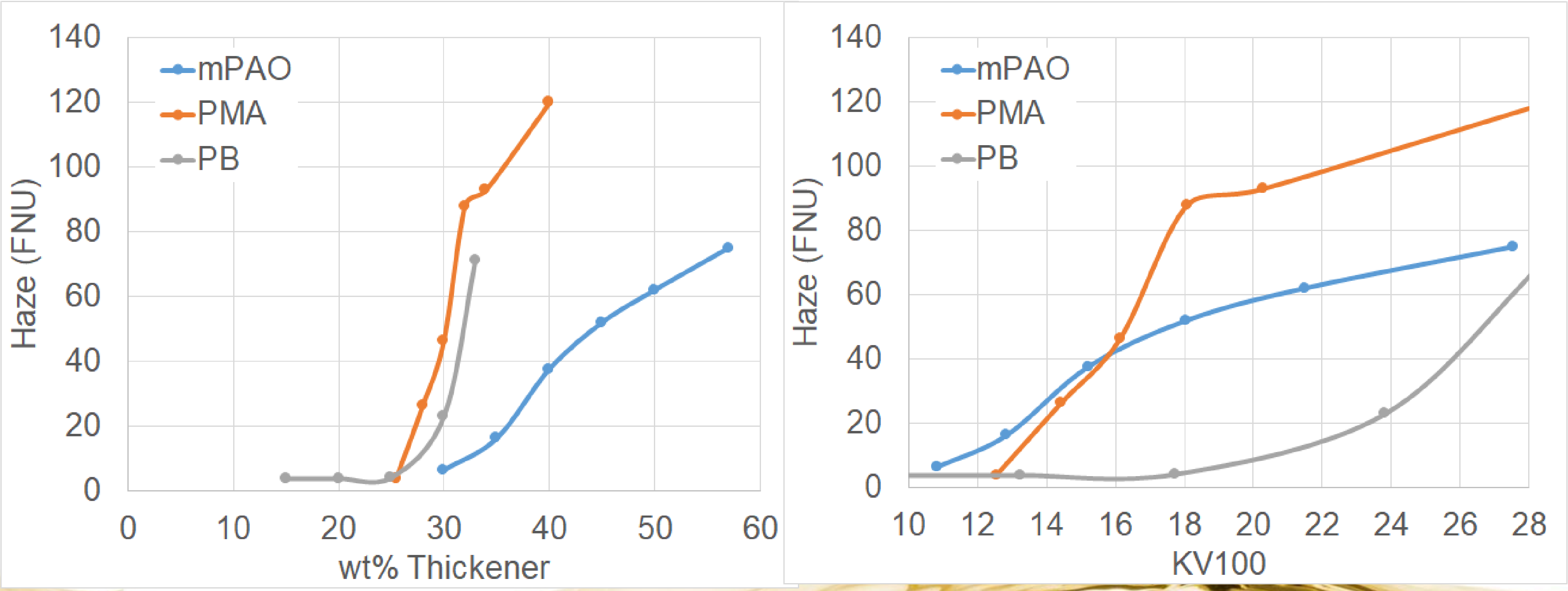
- *What are the conditions to cause haze?*
  - Study with turbidity meter
    - Haze measured for after -20C freeze/thaw
      - <10 FNU (Formazin Nephelometric Units) haze ideal; 20+ is visible to the eye

  - 0 – 60% PMA, PB, or mPAO in PAO4 with GL-5 ad pak



VM vs. Haze w/ Pak

- Best strategy
  - Limit PMA to < 25wt% and mPAO < 30wt% (likely 13-14 cSt)
  - Get the rest of your viscosity from PB
  - No ester required!



FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

What Is The Haze?

- Additive packages, as a whole, don’t haze
  - It may only be a few specific components that haze or precipitate
    - AW / EP / FM / CI / AO / dispersant / detergent / defoamer, etc.
      - Ionic or polar versus non-polar, low solvency PAO

- Functional performed another haze screening with individual components
  - PMA/PB/PAO blend at 75W140 visc, -54C freeze/thaw

Hazy Components

- 5 components found to cause haze/drop-out in the 75W140 test formula
  - Visual inspection didn’t always agree with turbidity meter

Trial	Chemistry	Treat	Role	FNU Haze	Visual
A	-control-	N/A	<control>	0	Clear
B	Alkyl triazole	0.1%	Corrosion inhibitor	10.6	Clear
C	Mb dithiocarbamate	3.0%	Friction modifier	2.92	Clear
D	Aromatic amine	1.0%	Antioxidant	1.43	**Haze**
E	Ashless dithiocarbamate	1.5%	Ashless friction modifier	1.62	Clear
F	Amine phosphate	1.0%	Corrosion inhibitor	4.55	Clear
G	Overbased calcium sulfonate	1.0%	Detergent	15.7	**Haze**
H	PIBSI	1.0%	Dispersant	0.8	**Haze**
I	Dialkyl pentasulfide	1.0%	Active sulfur EP	0	Clear
J	Sulfurized ester	1.0%	Inactive sulfur AW	1.15	Clear*
K	PAG defoamer	0.2%	PEG Defoamer	2.7	**Haze**
L	Acrylate defoamer	0.2%	Acrylate Defoamer	1.3	Clear

- Discrepancy between measured haze vs. visual inspection
- Worst haze: from D > G, H > K; delayed separation with J after one month

Thoughts on Haze

- The five components that hazed are quite standard in ad paks – what now?
    - Optimize PMA/PAO/PB blend for better solvency – previously discussed
    - Add ester (10-20wt) to solubilize the incompatibles
    - If you formulate ad pak from scratch, find lower polarity alternatives
    - If you buy ad pak, some ad paks available specific for synthetics

Very High VI

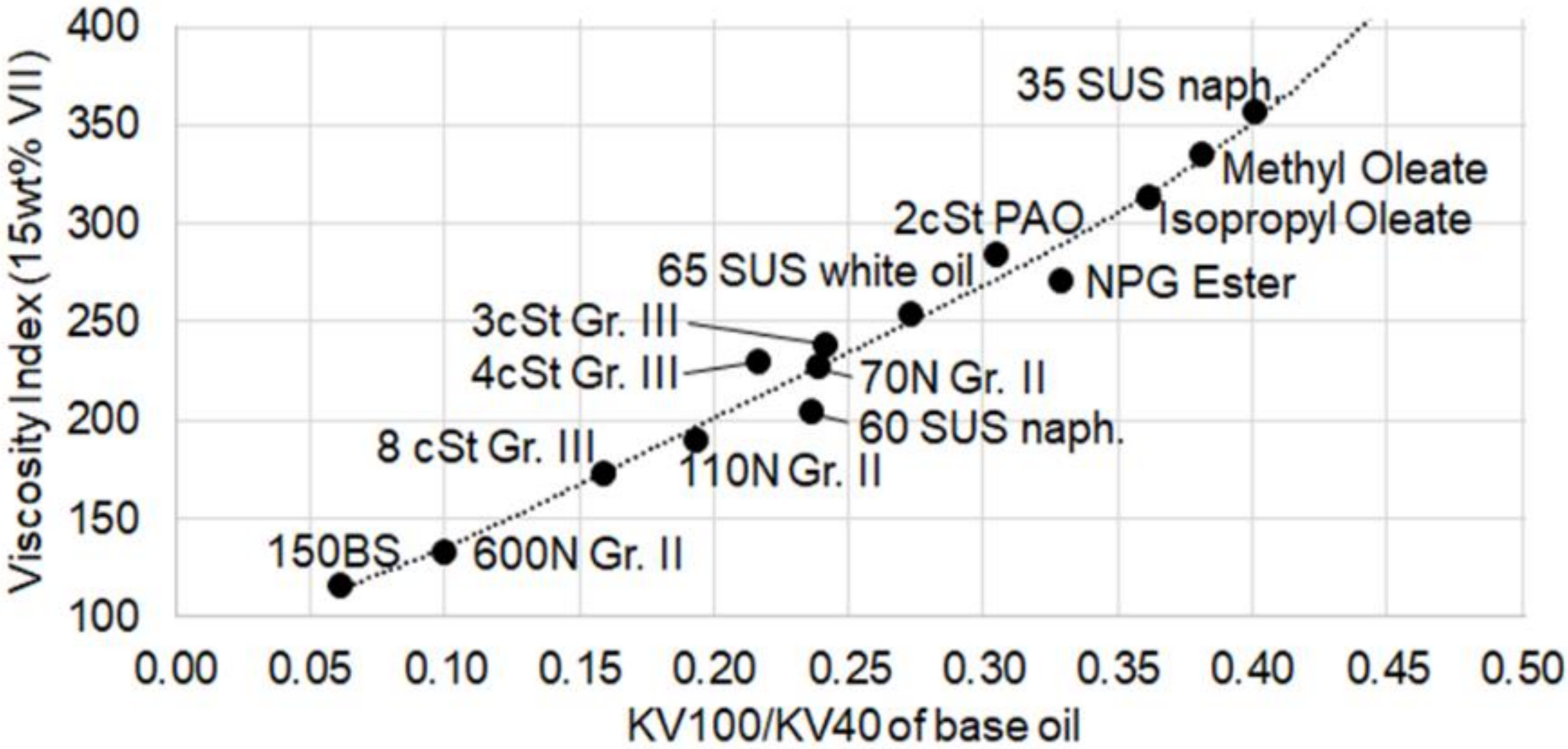
- At that rate, maybe the answer is to go back to higher solvency paraffinics
  - Can you still get high VI without synthetics? *Yes, with the right oil*

Base Fluid	Viscosity Index w/ 15% PMA SSI 35%
D-Limonene	572
35 SUS naph. oil	357
Methyl oleate	335
Isopropyl oleate	313
PAO2	284
C9 NPG Ester	271
65 SUS white oil	254
3 cSt Gr. III	238
4 cSt Gr. III	230
70N Gr. II	227
60 SUS naph. oil	204
110N Gr. II	190
8 cSt. Gr. III	173
600N Gr. II	133
150BS	116

What's the correlation here?
Is it high starting VI?
Low viscosity?
Synthetic status?

KV Ratio vs. VI Potential

- Best predictor is the KV100 to KV40 ratio
  - These fluids due to tend to be thinner oils requiring more stable VM



Summary

- Designing for shear
  - SSI is a key parameter in designing shear stable formulations
  - Back of envelope calculation is quite easy, accurate
  - Helps make decisions about base oil viscosity, VM, etc.

- Hazy synthetics
  - Low solvency oil + high wt% polymer + polar additives
  - Possible to optimize for clarity without ester

- Very high VI
  - Look at the KV100/KV40 ratio of your base oil blend when VI is low