NOVEL RELIABLE TECHNOLOGIES Designing molecules for the future

February 2024

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Agenda:

- Viscometrics Basics
- PMAs History, Design, Properties
- Applications and Formulating
- PMA PPDs

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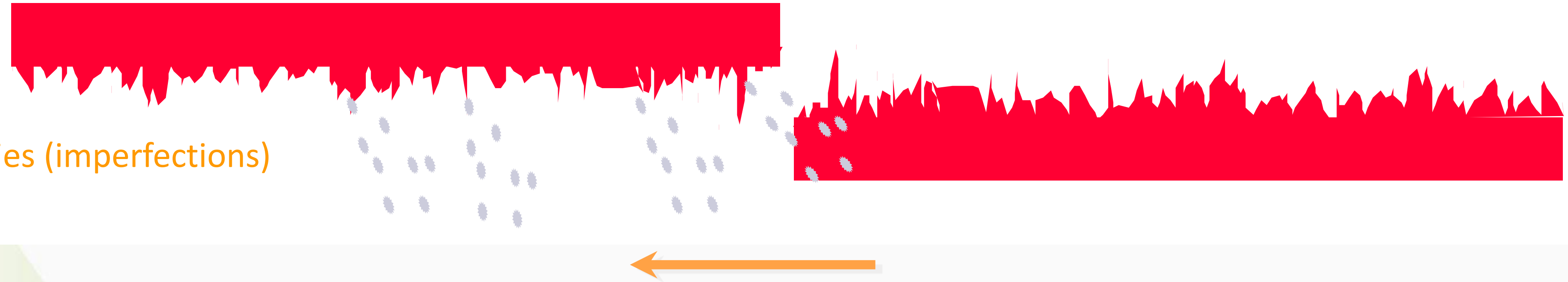
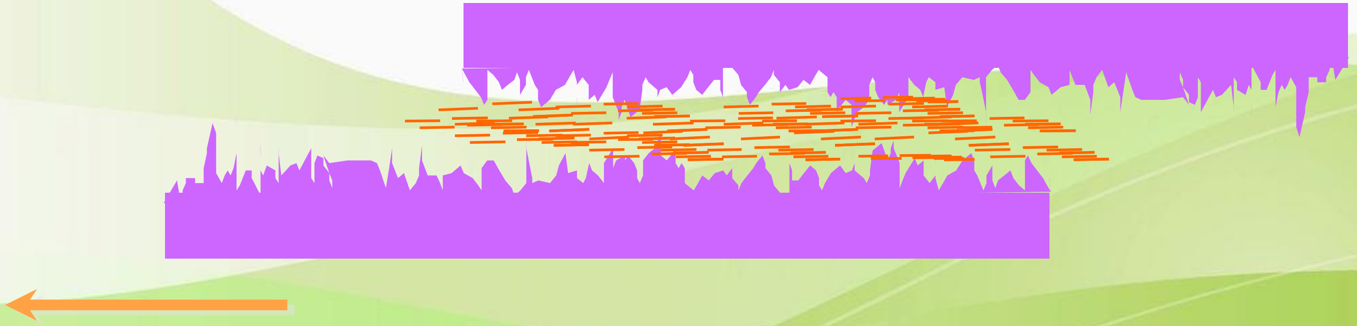
Friction and Lubrication



Asperities (imperfections)

Heat
Wear
Particles
Noise
Inefficient



Fluid Film Lubrication

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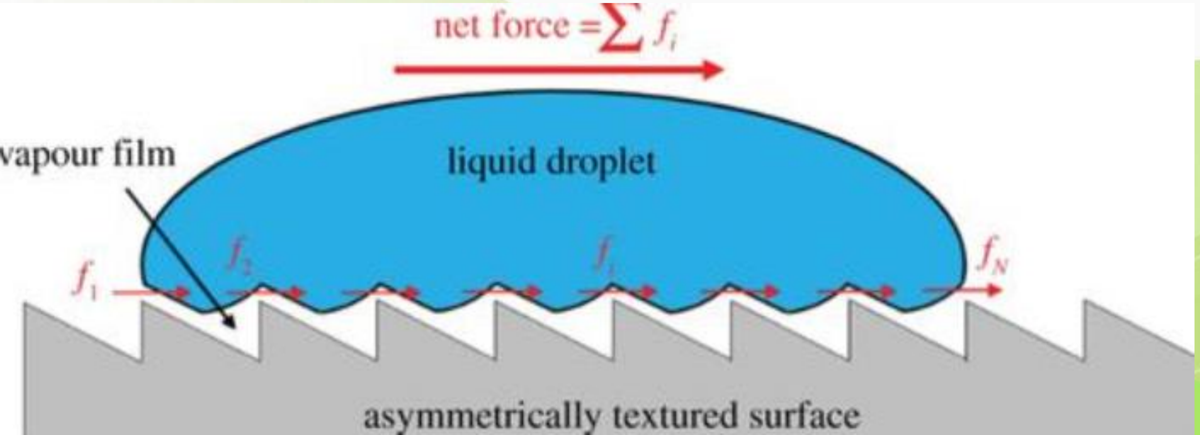
Hydrodynamic Lubrication

- Fluid Film
  - Fluid fills space between surfaces
    - Gas or liquid – usually liquid
  - Separates surfaces - oil film is sufficiently thick to separate the moving surfaces completely.

- Carries the load which would otherwise force the surfaces together
  - Viscous fluid media in motion generates pressure which supports the load
  - Strength of film depends primarily on geometry of device, speed, and viscosity



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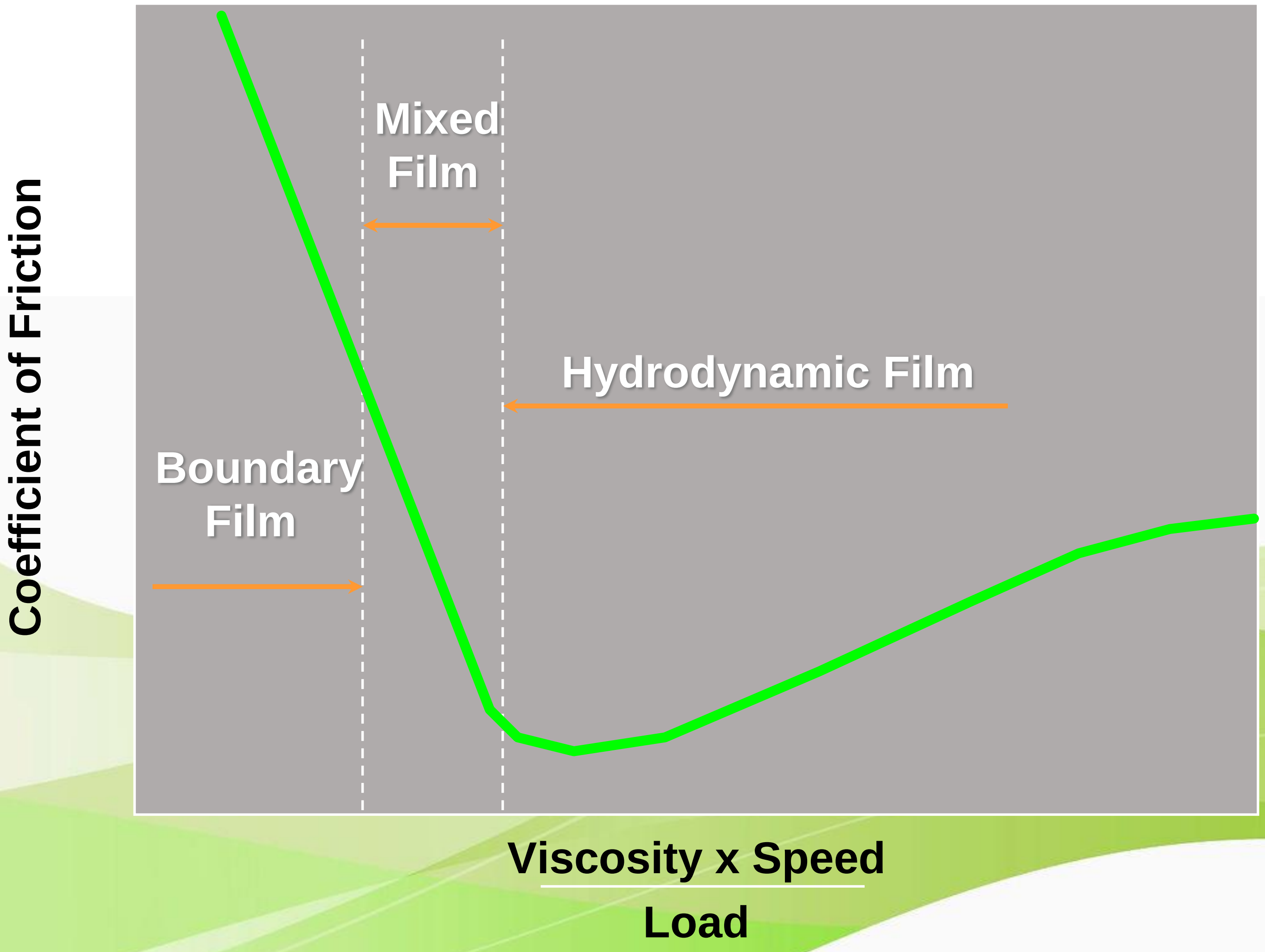
Stribeck Relationship



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“Viscosity”

- Thickness of a liquid
- Formal definition = resistance to flow
- Temperature dependent
    - Hotter = in general you see oil thinning
- Indicative of fluid film strength
    - Viscosity too low
        - Poor lubrication
        - Internal leakage
        - Noise
        - Heat
    - Viscosity too high
        - High power consumption
        - Sluggish operation
        - Poor flow (lubrication)
        - Heat

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VI Improvers Properties

- Thickening power (at high temperature)
  - The relative efficiency of a VI improver to impart viscosity to a fluid
  - A key economic question
  - Function of chemistry and molecular weight
- Shear stability
  - Ability to retain the viscosity imparted to the thickened fluid
  - Largely a function of molecular weight
- Viscosity index (or lack of thickening power at cold temperature)
  - VI improvers with relatively low viscosity index boost can be excluded from some applications
  - Function of chemistry and molecular weight

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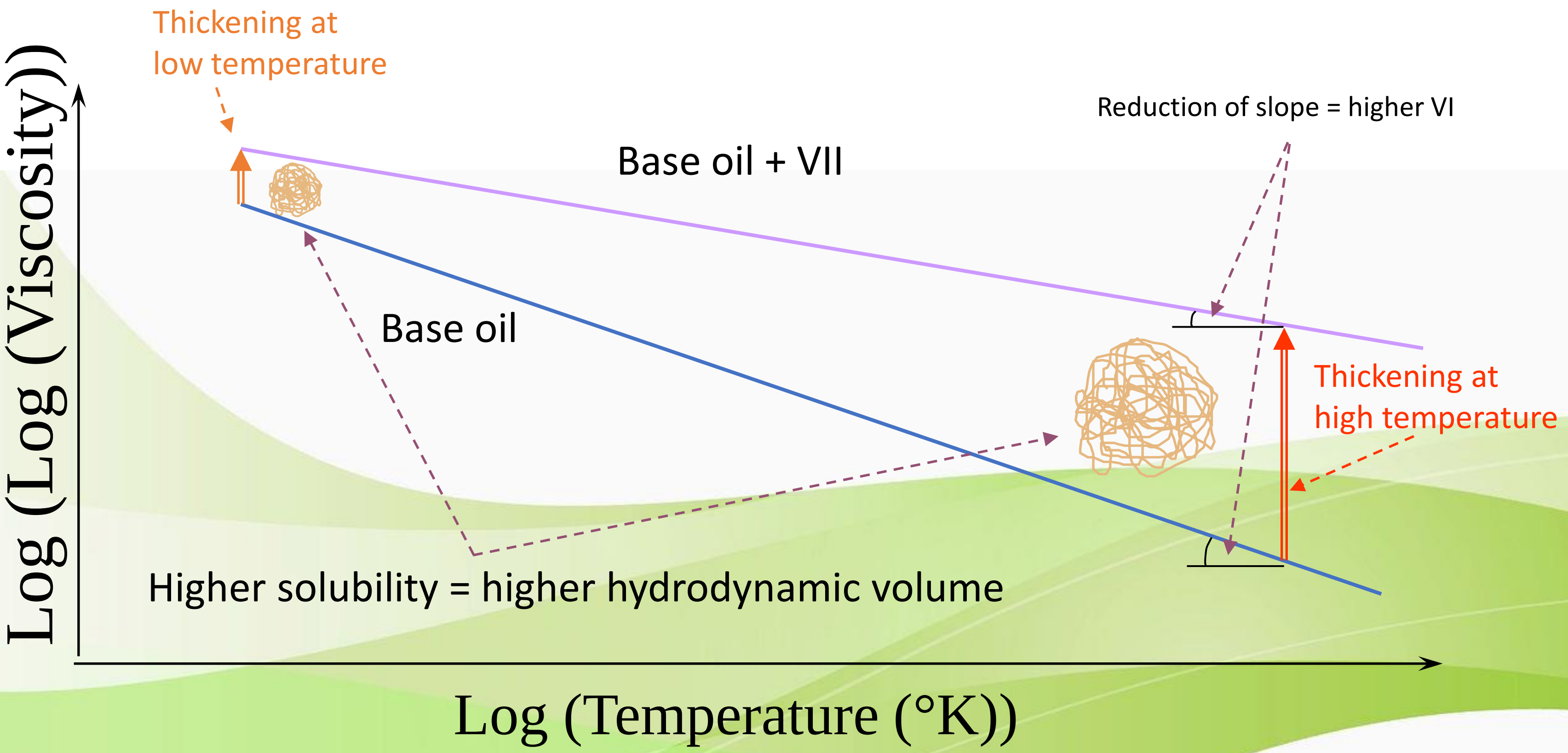
General benefits of VIIs.

- Wider Temperature Range: Lubricants with VIIs operate over a broader temperature span.
- Extended Service Life: VIIs reduce the need for frequent oil changes.
- Easier Processing: Lubricating oils with VIIs are easier to handle.
- Increased Machine Longevity: Lower energy consumption leads to cost savings.

Relationship of a polymer to temperature



Thickening efficiency related to Molecular Weight

Polymer size Smallest → Largest

VI Treat Rate, wt%	10	10	10
Kinematic Viscosity, cSt			
100C	7.4	10.5	13
40C	39	51.5	65
Viscosity Index	159	199	205
After Shear			
Kinematic Viscosity, cSt			
100C	6.808	7.14	7.15
40C	35.88	35.02	35.75
Viscosity Index	151	171	168

Note:

After shear Viscosity Index. Importance of picking the correct PMA for the application.

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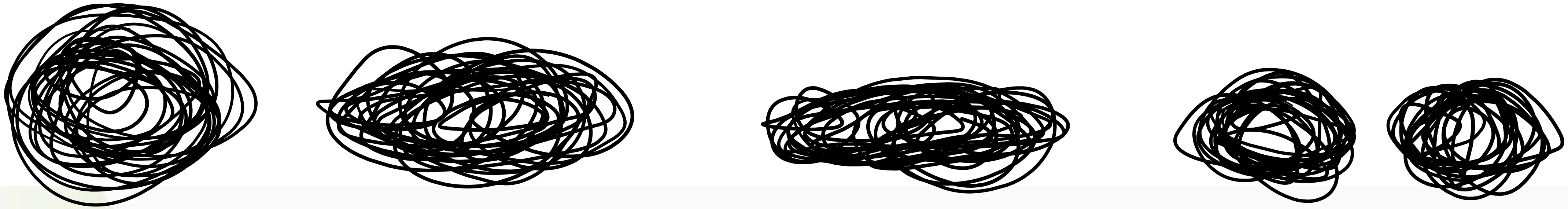
Shear on a polymer



Polymer

Stress applied

High Stress
(Temporary Shear)

Polymer Breakage
(Permanent Shear – SSI)

Note:

Polymer will deform under stress and will regain shape upon removal of stress
If permanent shear occurs, oil will lose viscosity build power.

**Some studies have indicated once a fluid (polymer) has been forced through clearances and placed under stress three times in lubricant system it will lose 95-98% of the permanent viscosity loss.

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SSI

% Overall Viscosity Loss =

$$\frac{\eta_i - \eta_s}{\eta_i}$$

Shear Stability Index (SSI) =

$$\frac{\eta_i - \eta_s}{\eta_i - \eta_o}$$

η_i = Viscosity before shear
η_s = Viscosity after shear
η_o = Viscosity of base stock and additives

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Molecular Weight

- MW rule of thumb
  - **Thickening Power**
    - **Higher MW ➡ Better Thickening**
  - **Shear Stability**
    - **Higher MW ➡ Worse Shear Stability**
  - **Handling Properties**
    - **Higher MW ➡ Higher Bulk Viscosity**

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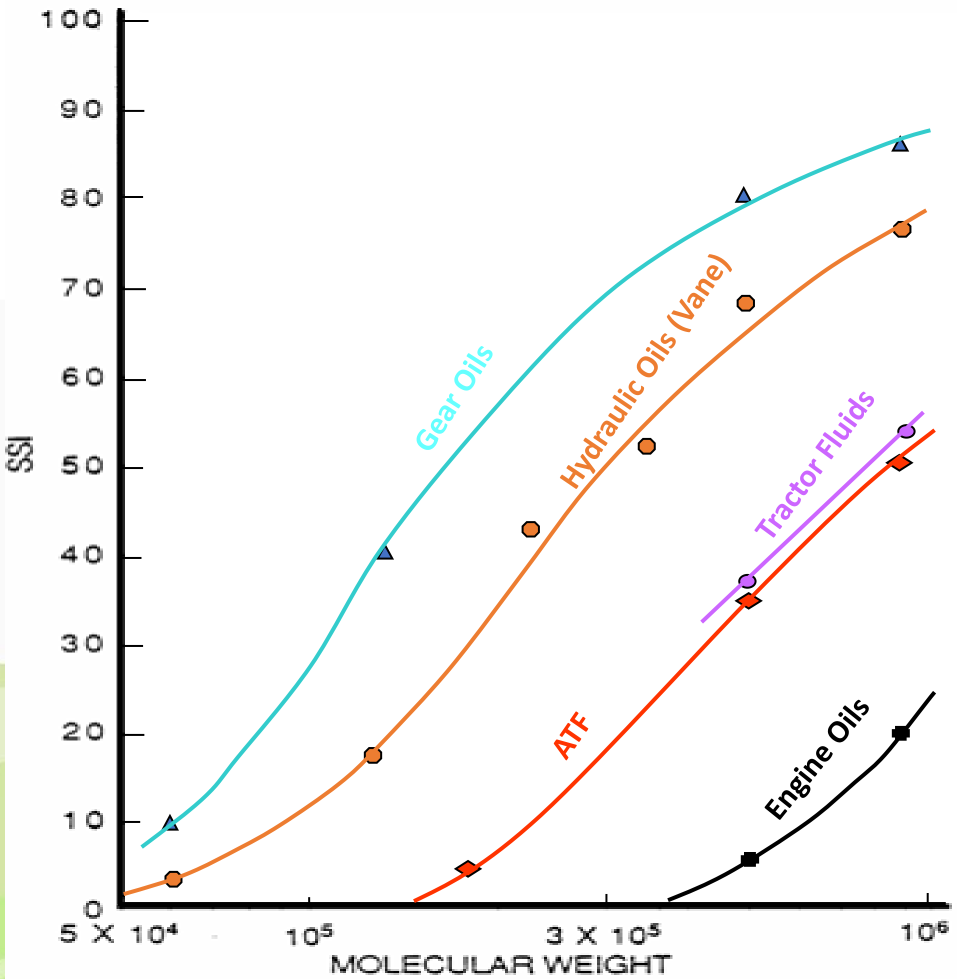
Molecular Weight – Shear Stability Index by Application



Viscosity Index

- The **viscosity index** (**VI**) is an arbitrary, unit-less measure of a fluid's change in viscosity relative to temperature change. It is mostly used to characterize the viscosity-temperature behavior of lubricating oils. The lower the VI, the more the viscosity is affected by changes in temperature. The higher the VI, the more stable the viscosity remains over some temperature range.
- The viscosity index was developed for this purpose (ASTM D2270) in 1929 based on benchmark based on Pennsylvania crude.

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History of PMAs

- Over 70 years of leading-edge lubricant additive development
  - Fundamental research in methacrylic chemistry by Dr. Otto Röhm in 1920’s

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PMA’s History of Applications

- Majority of the engine oil polymers until the early 1980’s.
- Aircraft Hydraulics
- Banana spray herbicide clingage medium
- Emergency generator fuel dispersant additive
- Bat, hockey stick, hammering tool damping promoter
- Military drone lubricant
- Bio-Based lubricants
- Cellular phone vibration lubricant
- Some 0W PCMO
- High VI hydraulic fluids – 160+ VI

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OCP (Olefin co-polymer)

Pros	Cons
-Great Thickener -Treat cost low -Good sourcing	-Poor Low Temperature Properties

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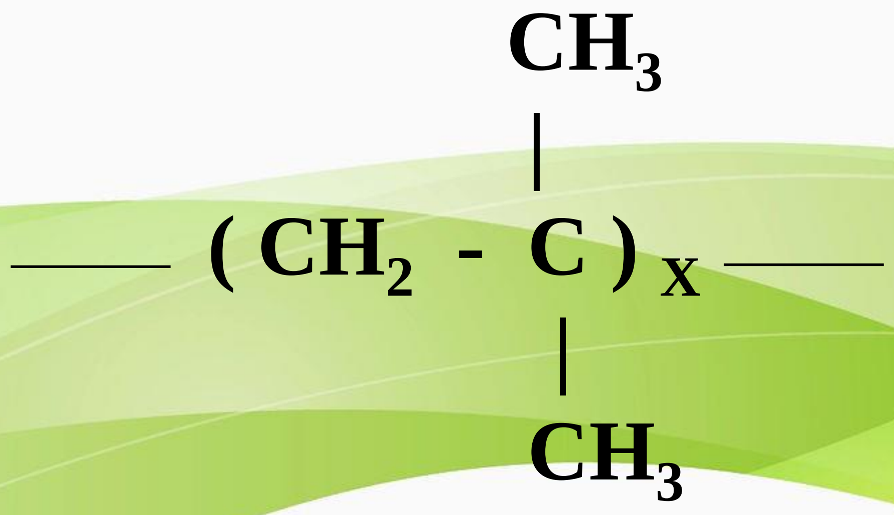
Polyisobutylene (PIB)

Pros	Cons
-Thermal Stability	-Poor Low Temperature Properties
-Relatively low treat cost	-Shear unstable
-Good sourcing	



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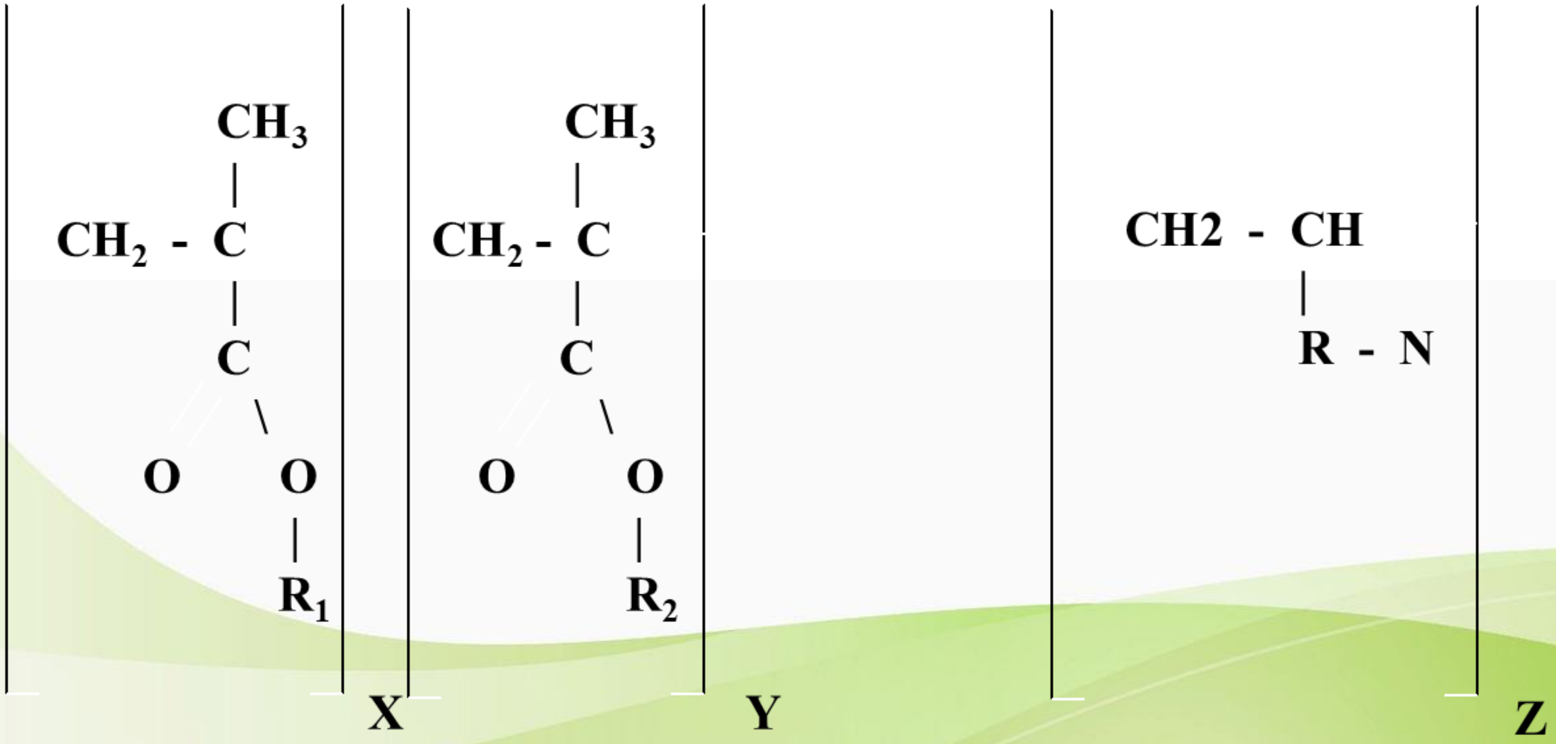
Polymethacrylate (PMA)



Non Dispersant

Dispersant

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PMA pro and cons

Pros

Versatile thickener

Promote formulation solubility

Inherit low temperature properties

Cons

Limited sourcing

Higher treat costs

Oxidization issues in limited applications

Manufacturing intensive

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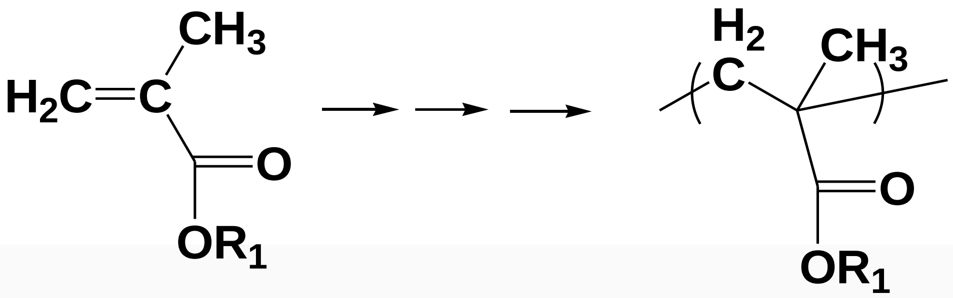
Design of PMA VI Improver



R_1 = CH_3 to $C_{22}H_{45}$

Average R typically ~C_9

Alkyl Size	Oil Solubility	Wax Interaction
LOW	NO	NO
MID-1	YES	NO
MID-2 Branched	YES	NO
MID-2 Linear	YES	MILD
HIGH (C_{14} and up)	YES	STRONG

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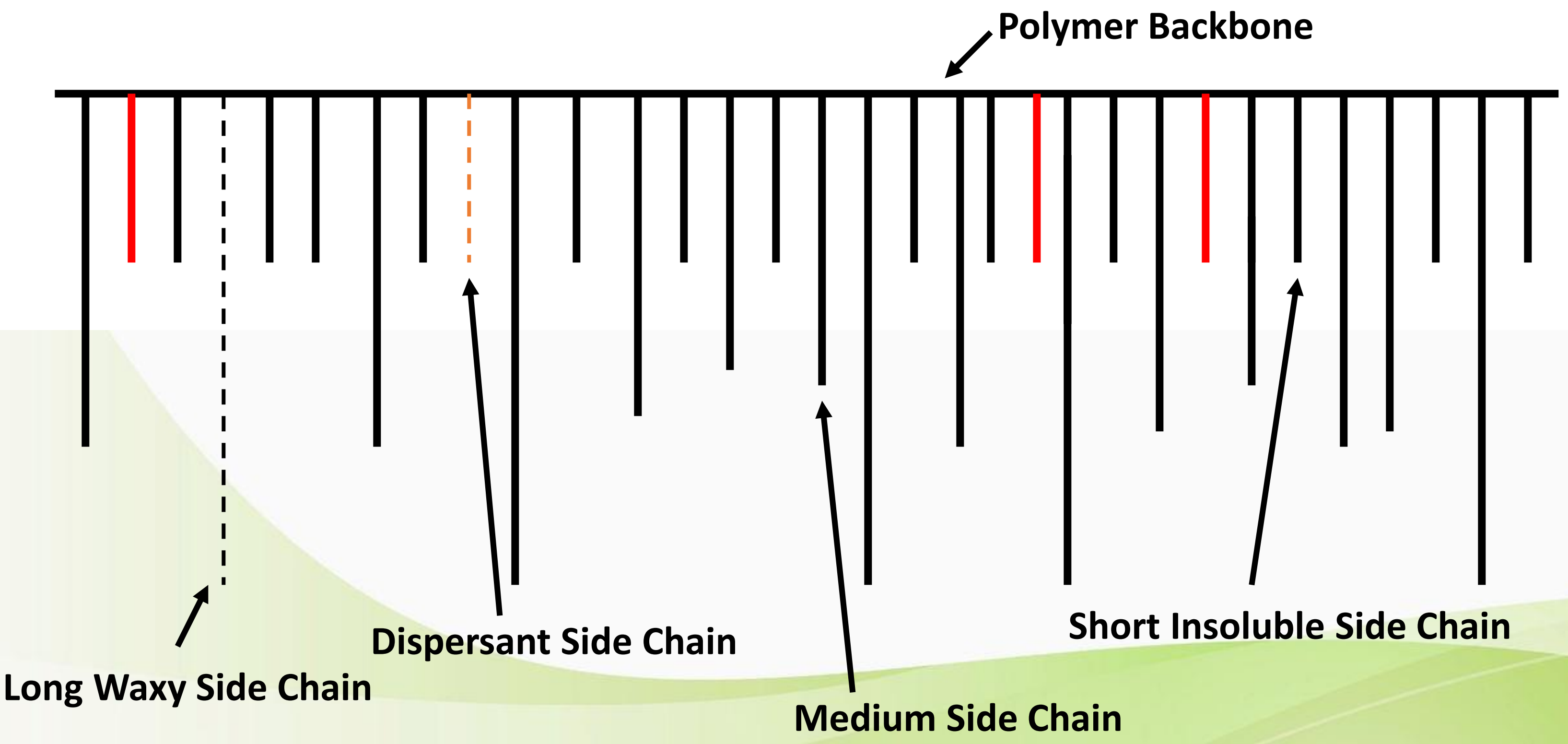
PMA VI Improver - *Composition*

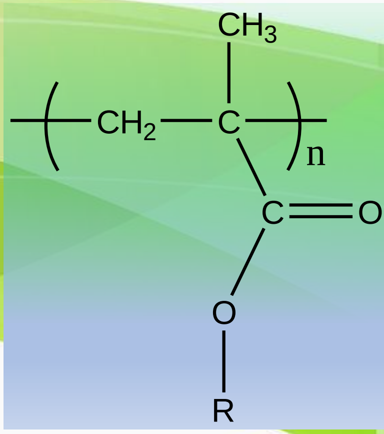


R1 Long Alkyl Chain
- Oil Soluble
- Wax Interaction

R2 Medium Alkyl Chain
- Oil Soluble
- "Neutral" Effect

R3 Very Short Alkyl Chain
- Oil Insoluble
- VI Effect

R4 Contains Hetroatom(s)
- Oil Insoluble
- Dispersancy Effect



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Dispersant PMA

- 2 ways to add additional chemistry to PMAs
  - Copolymerization
  - Grafted onto PAMA backbone - Addition of dispersant monomer

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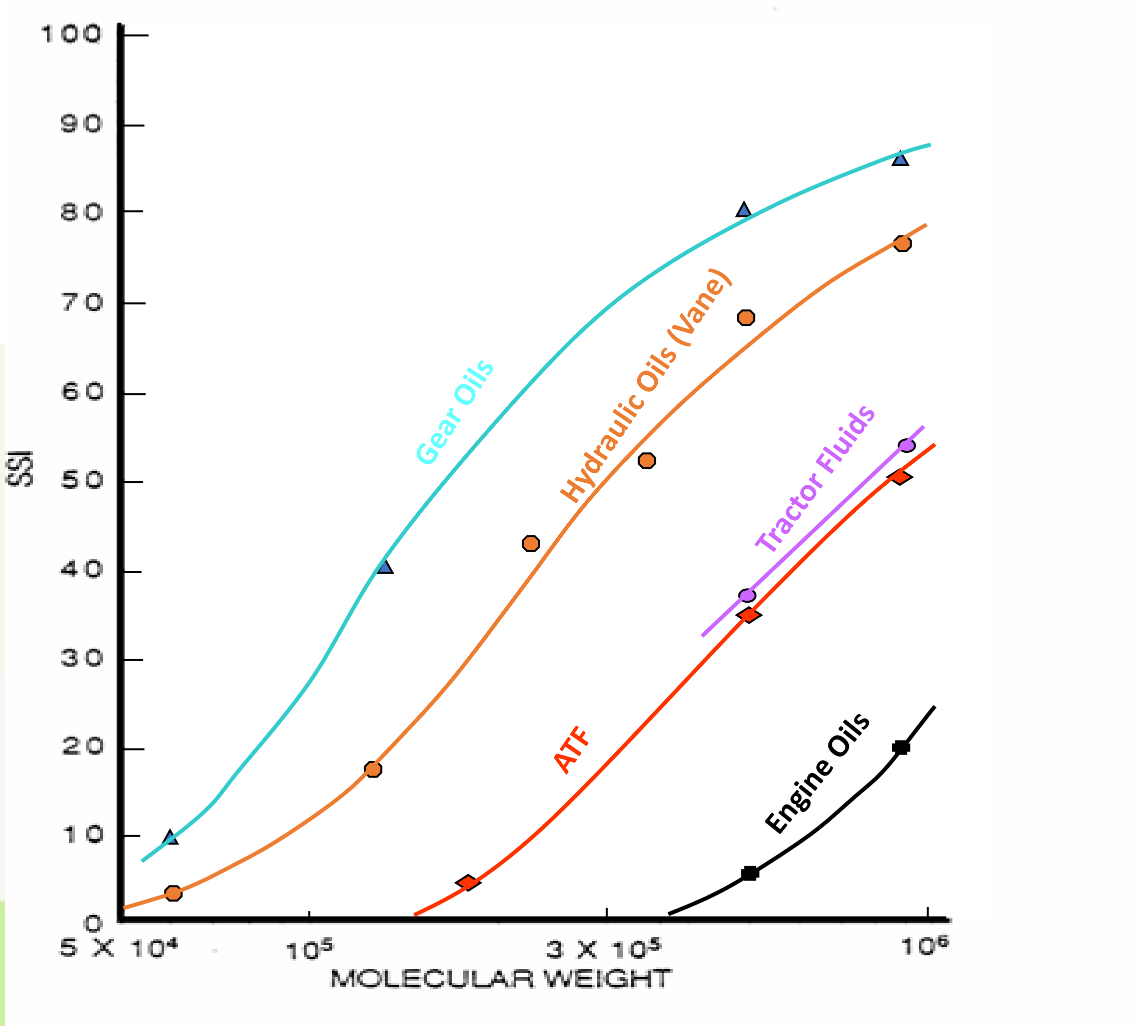
Selection PMA based on application



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Basics of Formulating with a PMA

- Consider Shear Stability needs. (K-O, sonic, KRL)
  - What is your shear in grade viscosity??

- What is the viscosity grade your trying to meet. (ISO 22, ISO 46, ISO 220, 75W90) or is there an OEM specification for viscosity.

- What are your treat cost requirements?

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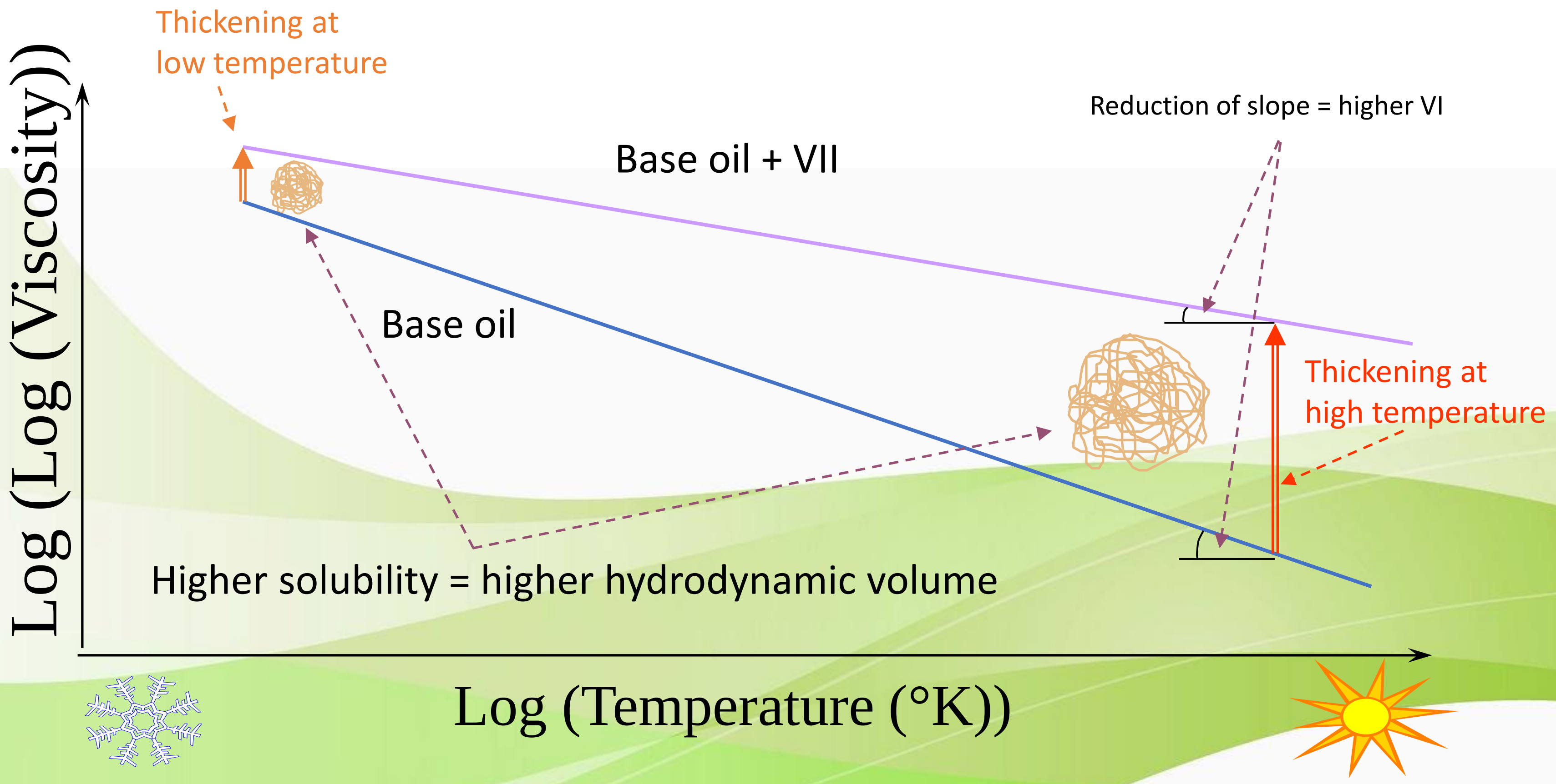
Basics of Formulating with a PMA – Cont.

- **What are the low temperature needs of your formulation (PP, Brookfield viscosity). Ie. -36 C PP, 2500 cst @ -54C and/or an OEM specification for low temperature. J20D, Mil-spec 5606**



Example of OEM specification (After Shear viscosity).

OEM	GM		Ford		
Specification	Dexron® III (expired)	Dexron® VI	Mercon® (expired)	Mercon® V	Mercon ® LV
KV100 [mm²/s]	Not defined (7.5 typ)	6.4 max	6.8 min	6.8 min	6.2 max
BF-40 [mPas]	<20,000	<15,000	<20,000	<13,000	<12,000
Shear Method	Cycling test 32,000	KRL40h	Cycling test 20,000	KRL20h	KRL20h
KV100 after shear [mm²/s]	>5.0	>5.5	>5.0	>6.0	>5.5
Recommended PMA (20 hour KRL)	~87-90%	39-41%	~87-90%	39-41%	8-12%

ATF – DEX III Package and d-PMA Polymer

Test	Test Method	Specification	Candidate Fluid Results
Color (with Red dye)	ASTM D-1500	6.0-8.0	7.5
Kinematic Viscosity at 100°C	ASTM D-445	6.8-7.2 cSt	7.05 cSt
Kinematic Viscosity at 40°C	ASTM-D445		34.36 cSt
Viscsoity Index		160 min	173
Brookfield Viscosity @-40°C	ASTM-D-2983	20,000 cP Max	17,825 cP
Foaming Characteristics	ASTM D-892, Seq I, II, III	50/0,50/0,50/0 ml	
Copper Corrossion	ASTM D-130 modified, 3 hours, 150oC	1b, max	
Rust prevention	ASTM 665A, 24 hours	pass	
Four Ball wear	ASTM, D4172, 600 RPM, 100oC, 40 Kg, 2 hour	0.61 mm (max)	
Vane Pump Testing	ASTM D7043, modified	10 mg loss (max)	
Oxidation testing	(CEC L-48-A-95) DKA, 160oC, 192 hours,		
	% change in KV@100oC	40% max	
	Change in IR-Absorbance at 1700 cm-1,40% max	40% max	
	Total insolubles, 1% max	1% max	
	No Sludge deposits	No sludge	

Formulation: 8.2 wt% (7.75 vol%) of Performance Package/PMA with 91.8 wt% 100 base oil

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Example formulations

- 75W90

	Ex 1	Ex 2
PMA	8%	8%
PIB	16	15
Gear Package	4	4
GIII 4 cst	72	72.5
GIII PPD	--	0.5
KV 100	18.3	17.7
KV 40	107.9	100.2
VI	189	195
Visual	Clear	Clear
Brookfield (-40C)	140,800 cP	118,400 cP

Note:

Combinations of different polymers chemistries can enhance properties and lower cost.

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HF and Mil-spec HF using PMA

ISO VG	15	46
Hydrocal 38	82.2	
100N paraffinic		87.5
Ad-Pac	2.3	2.3
Naphthenic PMA	15.5	10
PMA Pour Point		0.2
Pour Point (D97)	< -65C / -85F	-48C / -54
VI	300+	187

Note:

Naph PMA can be used with both paraffinic and naphthenic basestocks which makes it a very versatile polymer.

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HVI HF – Medium Shear Stable

ISO 22 HVI		
Component	Vol%	Weight%
Group 2, 80 N	94.64	94.13
Lubestervis 3454	4.7	5.1
AWHO additive	0.56	0.66
Lubesterflo 3485	0.1	0.11
Total	100	100
KV@40C	22.97	
KV@100C	5.54	
VI	195	

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THF Fluid and PMA vs. OCP

Components

Baseoil + Adco package		94.85	96.55	96.55
OCP		4.9		
PMA			3.2	
d-PMA				2.6
PMA PPD		0.25	0.25	0.25

Specifications

KV @ 100°C	9.1 cSt min.	9.4	9.8	9.9
BV @ -35°C, cP	70,000 cP max.	155,000 135,000	59,500	46,000
ASTM D97 °C	-36	-33	-45	-48

Note:

Formulating creativity help you meet the J20C BF viscosity, but if you had to meet the J20D BF (1,500 max at -20C) and KV the PMA would be an easy path forward.

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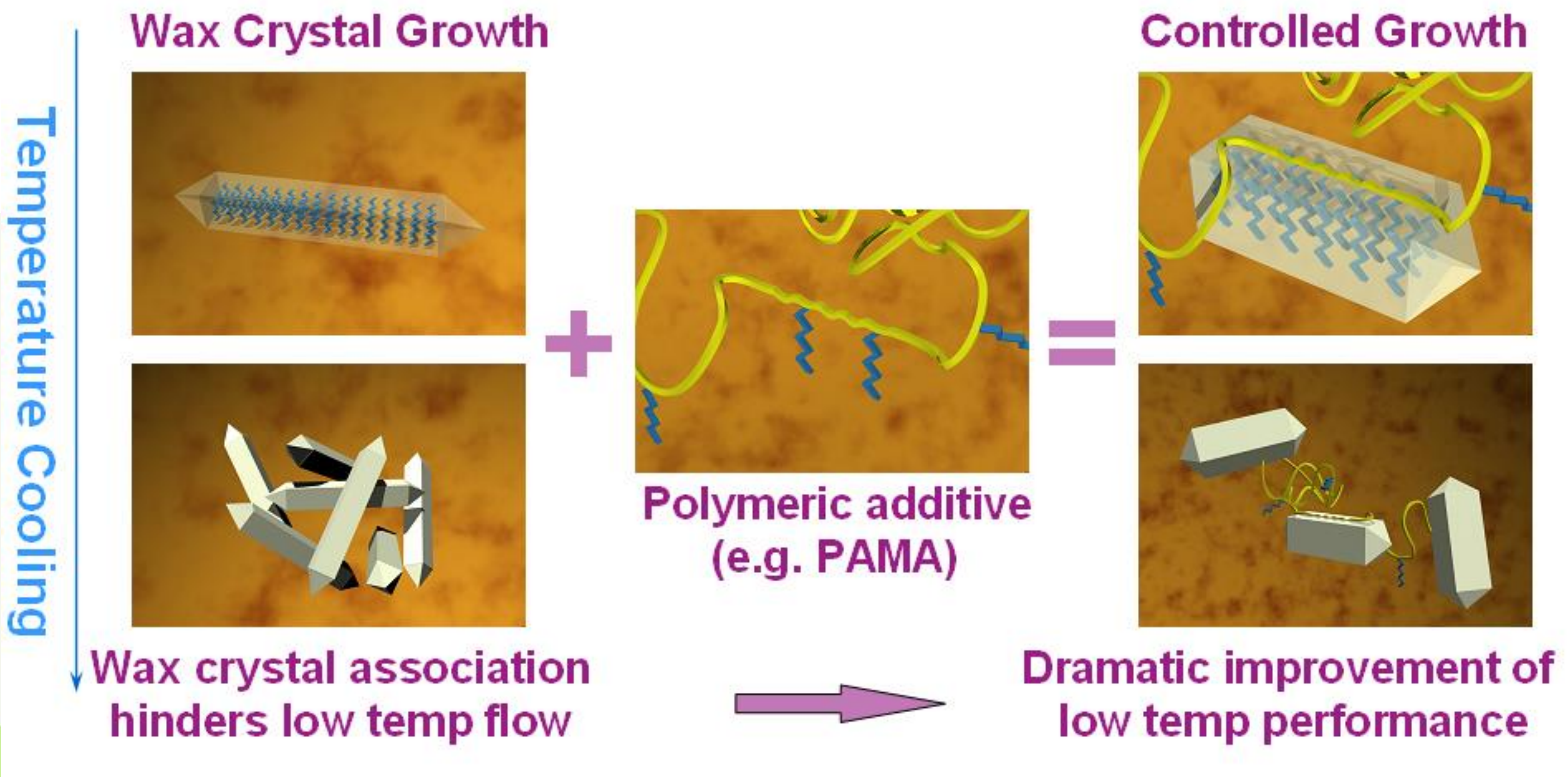
Don’t forget the Pour Point Depressant



Source: RohMax USA 2012

Lubrication Explained

https://youtu.be/ciPIplxjtvs?si=qH3SAUYgwtK8rhgr

Evonik

https://youtu.be/nuT6X5sw41w?si=hR7-AI_UTU16b2Qa

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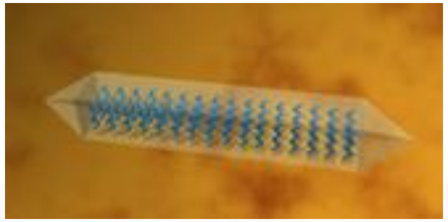
Consideration for PPD selection:

- Basestock selection
  - Generally Group I's have more of an appetite for wax control, where GIII basestocks need a narrow (monomer specific) PPD selection.



- Application and Low Temperature testing
  - D97 Pour Point is general us and industrial applications
  - Brookfield Viscosities run at different temperature from -20C to -54 C with varying viscosity maximums measured in cP.
  - MRV-TP1 – Measuring yield stress mainly for engine oils specs.
  - MRV - ASTM D3829 – Another mainly engine oil test to ensure pumpability of the oil at certain temperatures.

Note: Generally, the main different is measure oil flow based on cooling profile. Ie. Shock cooling vs. Slow cooling. CCS not a good source of low temp data due to high shear.

Other chemistries that affect PPDs

- Base Oil
  - Source
  - Refining Process
  - Catalyst type and age
  - Viscosity Grade
- Other Components that effective PPD performance
  - Detergents
  - Friction Modifiers
  - Type of thickeners

Note:

More is not always better. Over treat of the PPD can cause “reversion”. At higher treatrates of PPD the low temperature properties suffer.

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Not all PPDs are alike!

Brookfield data									
Formulation	1A	2A	3A	1B	2B	3B	1C	2C	3C
Motiva HVI 4							80	80	80
Motiva HVI 6							20	20	20
Yubase 4	90	90	90						
Yubase 6	10.00	10	10						
Motiva Star 12				80	80	80			
Bright Stock				20	20	20			
PMA PPD	0.1					0.5	0.1		
PMA PPD		0.1		0.5				0.1	
Non-PMA PPD			0.1		0.5				0.1
BF @ -26C, cP				96,500	102,300	114,300			
BF @ -40C, cP	164,400	89,888	92,588				19,960	14,080	21,270

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Additional PPD data

	Motiva Star 6	RHT 240	Motiva Star 12	Nexbase 3043	Yubase 6	Nexbase 3080
Know PMA PPD source	-42	-42	-36	-39	-36	-36
Know PMA PPD source	-42	-39	-33	-42	-33	-33
Unknown PMA PPD source	-39	-39	-30	-42	-42	-36

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Thank you - References

- Canter, N. (2011) ‘*Viscosity Index Improvers*’
- B. Kinker, 2006
- J. Soucik, 2012.
- *Encyclopedia Britannica*. June 2023
- RohMax USA 2012
- Champion Brands PPD study 2018
- PRI PPD study 2021

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Novel Reliable Technologies

- Manufacturer of Crankcase, driveline, and industrial additives packages
- Manufacturer of component chemistry including Pour point depressants, esters, gear oil polymer, tackifiers, dispersants, ZDDP, AW, AO, silicone materials
- Manufacturer of PMAs for automotive and industrial applications.

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