Functional Polymethacrylates:
PMAs as thickeners and PPDs

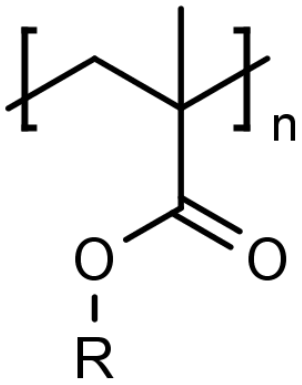
September 20, 2022

Agenda

- Intro to PMA
  - Why use PMAs?
  - What is PMA?
  - PPD Effect
- Choosing a PMA
  - Based on Shear
  - Based on Compatibility/Low Temperature
  - Based on Specialty Performance
- Formulating with PMA
  - Limits
  - Examples
- Review

Why PMA?

- Polymethacrylates in lubricants
  - Excellent Shear Stability
  - Excellent viscosity index improvement
  - Low wax formation and built-in pour point depression
  - Wide range of compatibility in paraffinic, veg, synthetic oils



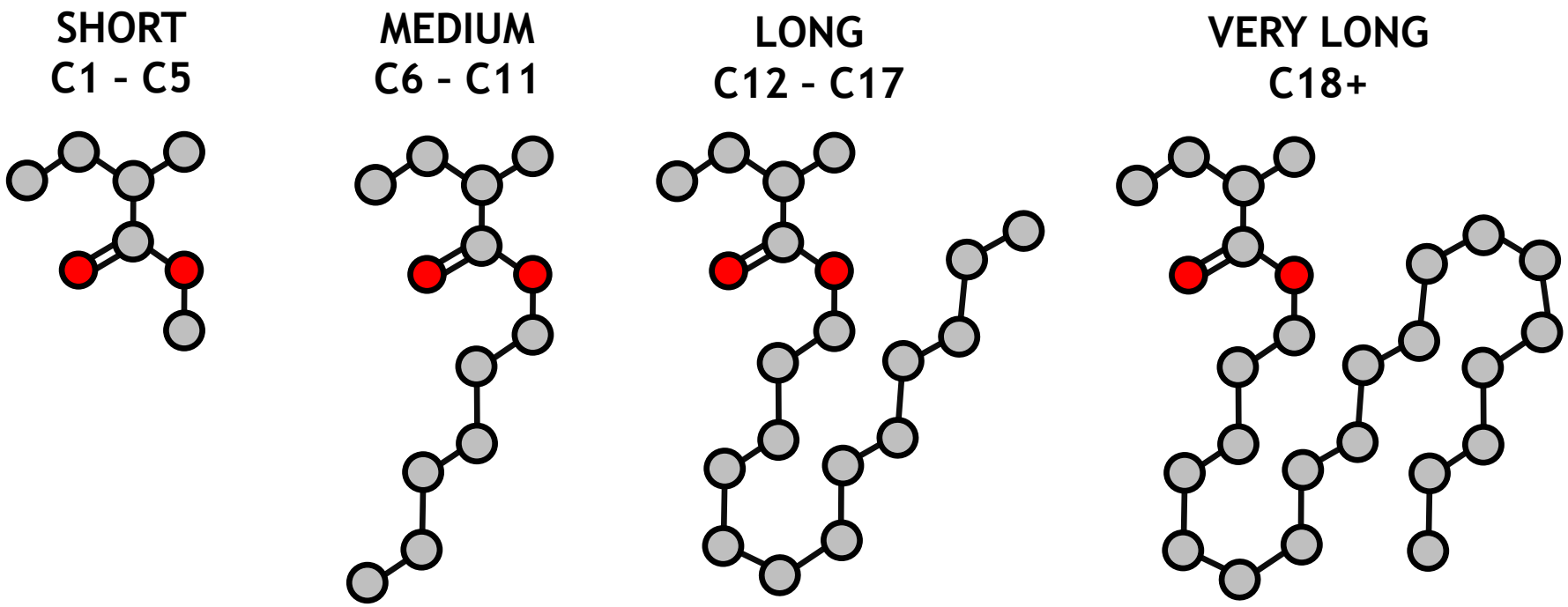
- Environmental benefits
  - Solvent-free synthesis at moderate temperatures
  - No byproducts to exhaust (high ‘atom economy’)
  - Bio-based feedstocks

- Easily customized

Tuning PMA

- Different alcohol chain lengths contribute different effects

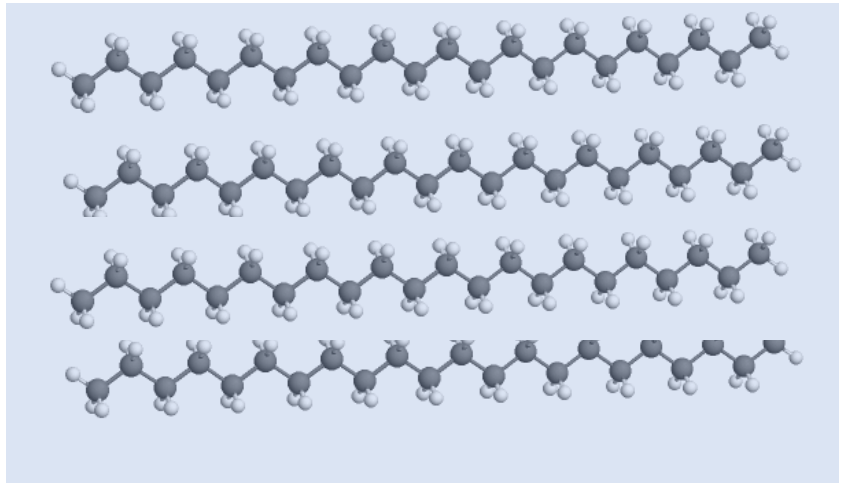
- Usually tune properties by looking at the average chain length



Florea, M., Catrinoiu, D., Luca, P. & Balliu, S. Lubr. Sci. 12, 31–44 (1999).

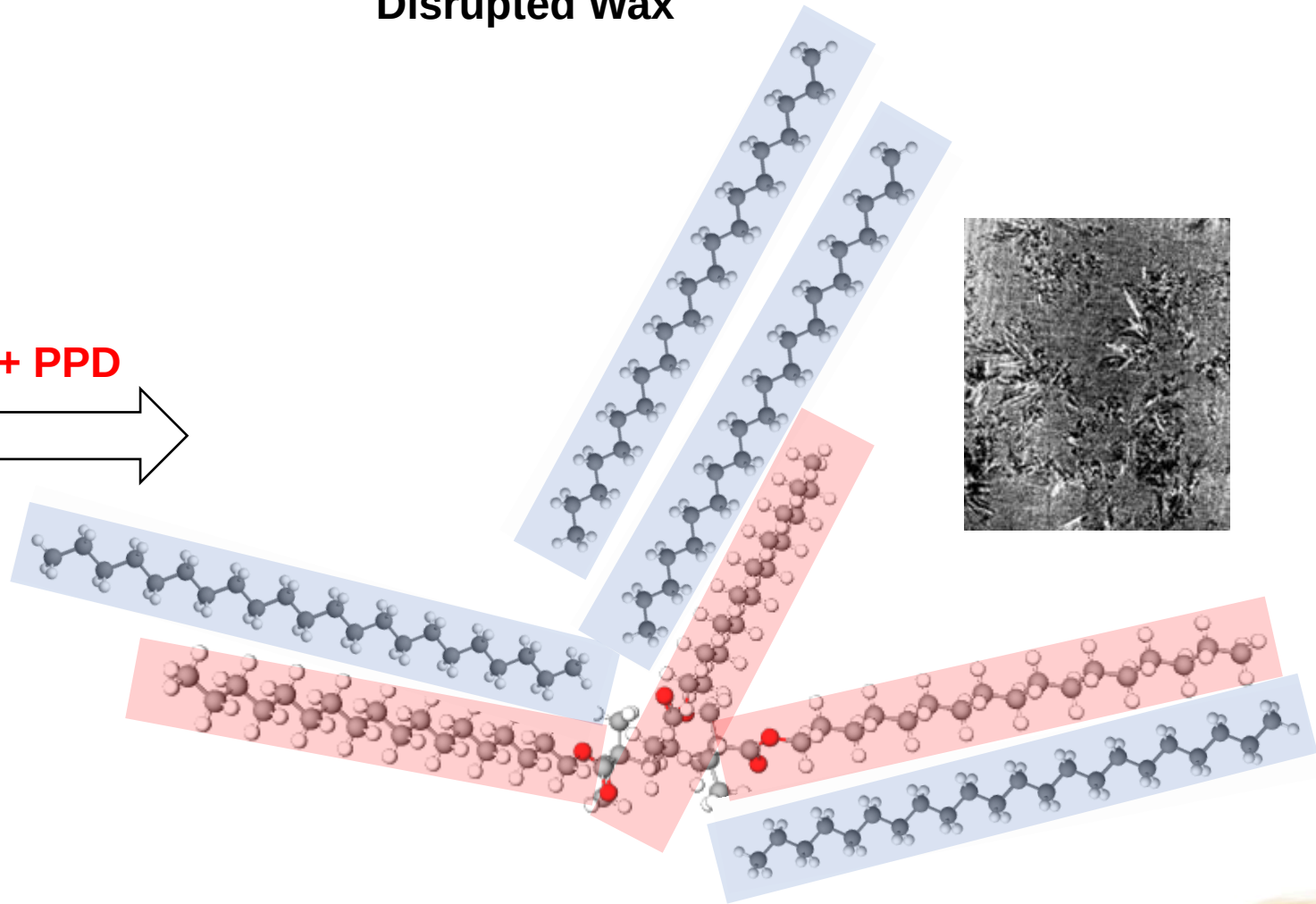
PPD Effect on Wax

Ordered Wax Crystal



+ PPD

Disrupted Wax



Functional PMAs

	Viscometrics		Shear Stability			Typical Applications											
	KV100, 10wt% (cSt*)	Treat Level (wt**)	K-O D6278	Sonic D5621	KRL 20 hr.	OEM Gear/HF/ Turbine	Auto. Gear 75W	High Visc. Ind.Gear	High Visc. HVI HF	Low Visc. Ind.Gear	HVI HF	Econ. HVI HF	Shock/ Susp.	Engine/ Crank	Racing Engine	Tractor	ATF
Industrial and Automotive Gear PMA																	
MG-1000	8.6	10%	0%	-	15%	X	PAO	X	X	X							
MG-3000	8.0	11%	0%	3%	20%	X	Gr.III	X	X	X	X					X	X
MG-1500	9.6	10%	0%	-	25%	X	Gr.III	X	X	X	X						
Hydraulic Fluid and Engine PMA																	
MH-2000	9.2	10%	1%	12%	35%	X	80W	X	X	X	X	X				X	X
MH-2500	11.1	8.6%	3%	29%	50%				X	X	X	X				X	X
MH-4000	11.3	7.5%	7%	33%	58%				X	X	X	X					
MH-4500	12.3	6.4%	15%	50%	65%							X	X	X	X		
MH-7000	15.0	3.7%	36%	71%	-							X	X	X	X		
Dispersant PMA																	
MD-2200	8.9	10%	3%	-	35%	X	X	X	X	X	X	X	X		X	X	X
MD-8000	16.0	4.8%	40%	74%	-								X	X	X	X	X
MD-8004	16.9	4.8%	40%	74%	-								X	X	X	X	X
MD-9000	20.0	3.0%	52%	81%	-								X	X	X	X	DEXIII
PAO Full Synthetic PMA																	
MG-1860	9.1	10%	0%	-	30%	X	X	X	X	X	X		X	X			X
Naphthenic PMA																	
MN-3500	12.0	5.7%	9%	-	-				X	X	5606	X	X				

Measuring Shear Stability

- Permanent Shear Stability Index (PSSI)
  - % viscosity permanently lost due to shear
  - Lower PSSI = better shear stability
- K-O Shear (ASTM D6278)
  - Diesel injector test, least harsh of the shear tests
  - Most relevant to engine oil, diesel, shock absorber, industrial applications
- Sonic Shear (ASTM D5621)
  - Intermediate severity shear test
  - Required for certain aviation fluids
- KRL Shear
  - Tapered Roller Bearing, typically run 20 hours
  - Harshest shear test required for most gear, shear stable HF, and ATF

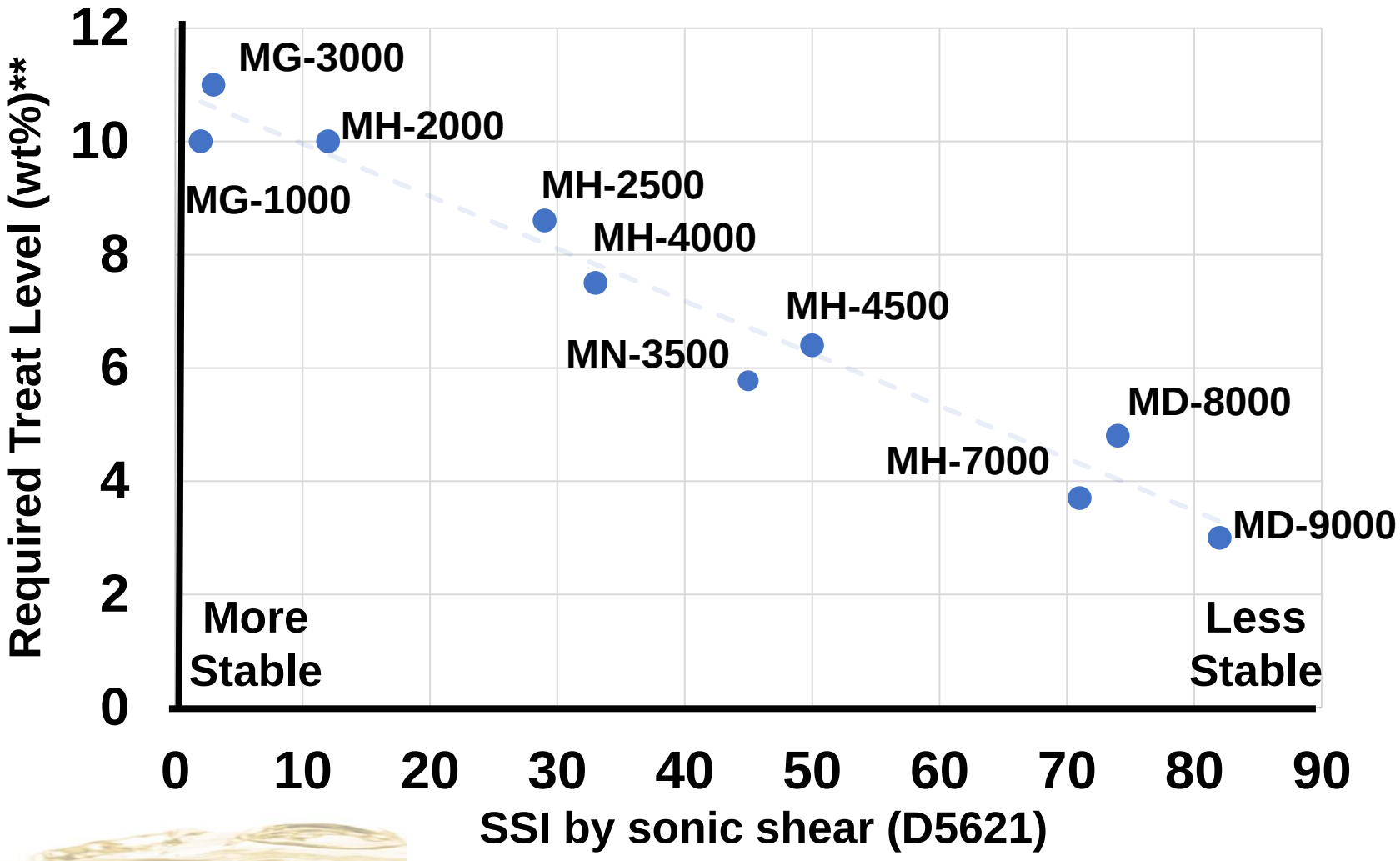
Matching Shear to Application

- MG-Series has the lowest shear of the PMAs
  - <25 PSSI by KRL
  - Suggested for gear oils, ATF, and other high shear applications
- MH-Series has intermediate shear
  - Suggested for hydraulic fluid applications
  - MH-2000 can be made to work for specific grades of gear
- MD-Series highest shear of Functional PMAs
  - Used when dispersancy is needed rather than just thickening
  - MD-2200 is available for low shear dispersancy

Matching Shear to Application

- Lower shear is not always better
- Less shear typically means less thickening efficiency
  - True within a specific chemistry
  - Less thickening efficiency = greater cost/treat
- Undercutting shear requirements can come at higher cost

Matching Shear to Application



Compatibility/Low Temperature (VM's)

- PMA is generally soluble
  - Depending on side chains some PMA/oil combinations have unique advantages
- MG-1000 -> Recommended for PAO based formulations
  - Maintains most solubility for additive package when combined with heavy mPAO basestocks
  - Minimal advantage in Gr. I-III from wax interactions
- MG-3000 -> Recommended for Gr. III based formulations
  - Strong affinity for Gr. III wax profile (may double as PPD)
- MG-1500 -> Optimized for both Gr. III and PAO
  - Higher thickening efficiency
  - Ideal for blend of oil types

Compatibility/Low Temperature (PPD's)

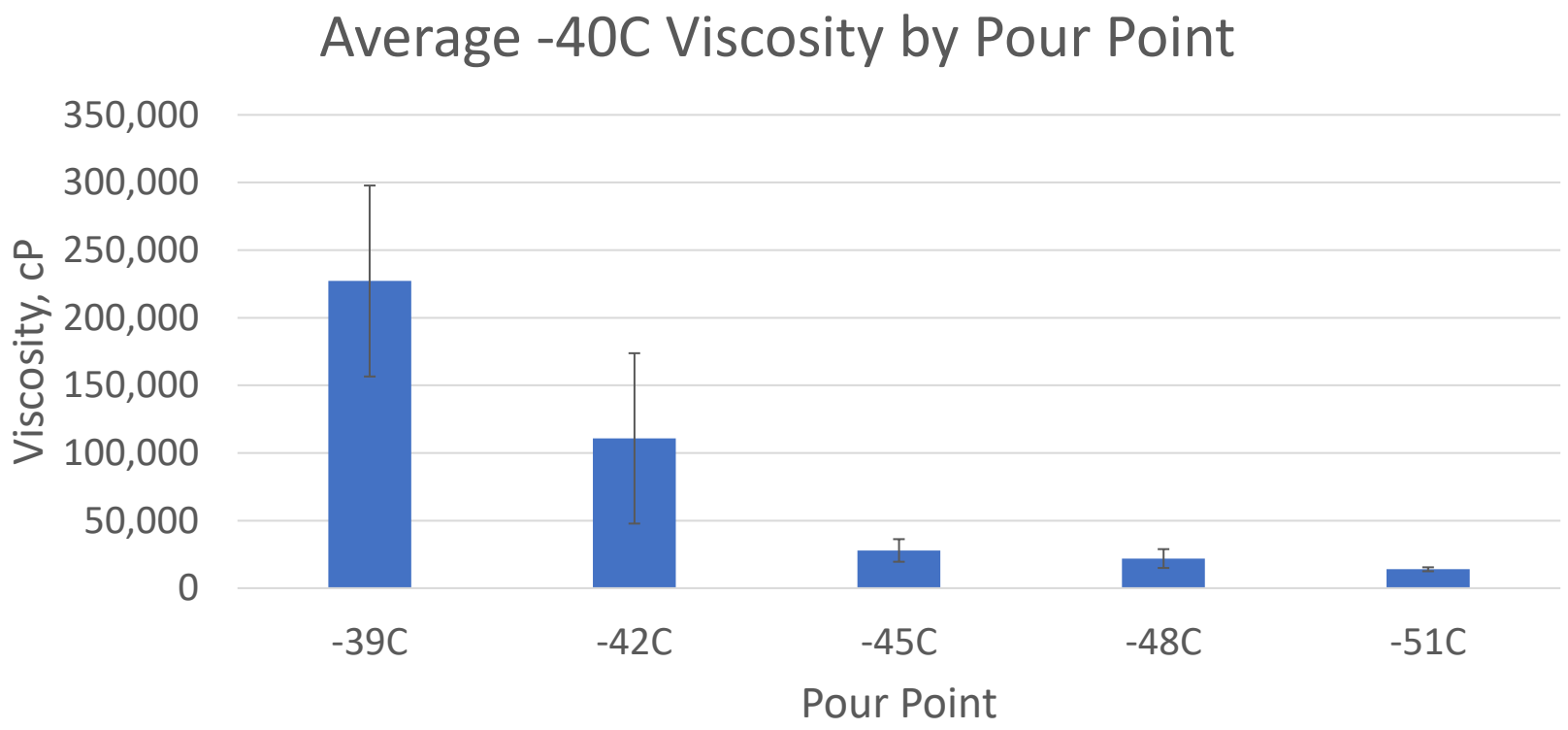
- Compatibility/matching a wax profile is most important for PPD
  - Typically too low treat to be concerned with shear or thickening
- PD-6XX series is designed for use in mineral oils

	Best Performance In…
Functional PD-610	High viscosity Gr. I / II (300N – 600N; Bright Stock)
Functional PD-620	Low viscosity Gr. I / II (70N – 220N; 4 cSt)
Functional PD-630	High viscosity Gr. III (6 and 8 cSt)

- PD-5XX series designed for use in vegetable oils

PPD Selection for Brookfield

- Proper selection and optimization of PPD important for other low temperature tests.
- Pour point acts as a good screen for Brookfield results



PPD Selection for Brookfield

- Results can vary within same pour point when looking at D2983 Brookfield Viscosity (spec for gear oils, tractor, etc):

Case 1: 80W90	Functional PD-610	Competitor PPD
Pour Point, D97	-36C w/ 0.5wt%	-36C w/ 0.5wt%
-26C BF Visc (D2983)	**49,700 cP**	139,000 cP

Case 2: Tractor HF	Functional PD-610	Competitor PPD
Pour Point, D97	-39C w/ 0.2wt%	-39C w/ 0.2wt%
-35C BF Visc (D2983)	**32,200 cP**	57,000 cP

Functional PPDs in Brookfield

- When properly matched to base oil, Functional PPDs tend to outperform competitors in Brookfield tests
- PD-630 designed for Gr. III/III+ base oils as shown

	Test	Yubase 4	Yubase 4+	Nexbase 3043	Motiva Star HVI 4	Adnoc 4	Ultra S-4
PD-630	Pour Point	-45C	-48C	-45C	-51C	-48C	-48C
	Brookfield*	17,915cP	10,140cP	13,130cP	10,113cP	11,328cP	9,513cP
PD-620	Pour Point	-42C	-48C	-39C	-51C	-42C	-42C
	Brookfield*	432,000cP	36,400cP	72,800cP	16,900cP	83,600cP	44,800cP
Comp. 1	Pour Point	-39C	-42C	-42C	-48C	-45C	-48C
	Brookfield*	216,400cP	82,000cP	47,100cP	32,400cP	77,800cP	41,100cP
Comp. 2	Pour Point	-45C	-45C	-45C	-48C	-48C	-45C
	Brookfield*	47,300cP	21,250cP	27,800cP	12,530cP	38,800cP	19,600cP
Comp. 3	Pour Point	-42C	-45C	-45C	-48C	-48C	-45C
	Brookfield*	136,800cP	43,500cP	38,000cP	21,000cP	39,400cP	28,450cP

Special Performance PMAs

- MD-Series PMAs are designed to act as dispersants
  - Choose for applications requiring a dispersant
  - Prevent soot build-up, carry away wear particles, etc.
- MD-Series performs several roles in one
  - Viscosity modifier
  - VI Improver
  - Dispersant
- MD-2200 -> For low shear applications requiring dispersant
- MD-9000 -> Provides great VI improvement at low treat

MD-8004 vs. MD-8000

- FUNCTIONAL MD-8004 offers greatly reduced handling viscosity
  - Same treat rates

Product (undiluted)	KV @ 100C	KV @ 40C	KV @ 25C
Functional MD-8000	2300	91,700	341,000
Functional MD-8004	1300	10,900	21,900

- Formulating for JDM 20 tractor fluid

Components (wt%)	No Pkg	No PPD	w/ PPD	*Spec*
Functional MD-8004	2.9%	2.9%	2.9%	
Functional PD-610	0.3%	0.0%	0.3%	
Tractor Package	0.0%	7.8%	7.8%	
6 cSt Group II	96.8%	89.3%	89.0%	
KV100, cSt	9.75	10.1	9.95	*9.1 – 10.5*
Brookfield D2983, -35C, cP		49,700	44,400	*< 70,000*
Brookfield D2983, -40C, cP	48,400			
20 hr KRL Sheared Visc.		7.6 cSt	7.6 cSt	*> 7.1 (JDQ-102)*

Special Performance PMAs

- MN-3500 is designed with naphthenic diluent for compatibility with light naphthenic oils
  - Designed for very high VI and use in very low temperature applications
  - Originally for use in MilSpec 5606 aviation hydraulic fluid

- V-766 recently designed as a non-PMA off-set to MN-3500
  - V-766 has high temperature ceiling
  - Cannot exceed 121C for extended periods

PMA Formulating

- Three different SSI values depending on application (K-O, sonic, KRL)
  - Typically formulating to shear in grade (“SIG”) by one of these methods
- A single PMA can’t make every ISO grade at every VI (140, 190, 240)
  - If you hit a wall, use a more stable PMA to increase wt% PMA
  - If VI still too low, use a lower viscosity base oil and increase wt% PMA
- Usually don’t have to add a PPD due to inherent effect of PMA VII

Limits of PMA

- Upper treat rate limit where Brookfield can no longer pass
  - Generally very good pour point and low temperature Brookfield performance
  - Above semi-dilute limit temperatures near glass transition no longer flow well
    - 10%-15% treat threshold where Brookfield viscosity is no longer controlled

- Only improves pour point in waxy oils
  - Will not improve pour point of PAO based fluids unless there is high wax carry-over from additive package

MH-7000 HF/Shock

- High SSI PMA useful for economic HF, shock absorber, misc. light duty
  - **MH-7000** (36 SSI)
    - Reaches VI 140 HF quickly but not much margin left for 190/240

Economic HVI HF, SIG by sonic

wt%	**ISO 32**	**ISO 46**	**ISO 68**
110N Gr. II	73.1	54.5	38.6
600N Gr. II	25.9	43.7	57.3
MH-7000	0.3	1.1	3.4
HF Pak	0.7	0.7	0.7
KV40	32.0	46.0	72.2
KV100	6.1	7.8	11.0
VI	141	140	143

Low Visc Shock Fluids

	ISO 15	**ISO 22**	**ISO 32**
65 SUS WO	93.25	89.35	85.35
MH-7000	5.0	8.9	12.9
WA-64	1.75	1.75	1.75
KV40	15.1	22	32.3
KV100	4.4	6.6	10
VI	227	288	319
Pour, D97	-48C	-48C	-48C

MH-2000 Industrial Gear

- Gear oils require extra stability - shear in grade by KRL; or <15% loss
- **MH-2000 -** 1 SSI; 35 SSI by KRL
  - Suitable for ISO 32–150 high VI fluids that shear in grade by KRL

VI 140 EP Gear Oils, SIG by KRL

wt%	ISO 32	ISO 46	ISO 68	ISO 100	ISO 150
110N Gr. II	77.7	60.9	43.6	29.4	10.1
600N Gr. II	18.8	33.6	47.4	57.4	74.1
MH-2000	1.5	3.5	7.0	11.2	13.8
GA-614	2.0	2.0	2.0	2.0	2.0
KV40	29.5	43.6	68	104.8	158.1
KV100	5.8	7.5	10.4	14.3	19.5
VI	141	140	140	140	141

GL-5 75W Automotive Gear

- Requires shear-in-grade by 20hr KRL and < 150,000 cP -40C Brookfield

Automotive Gear Oil Grade	75W90	75W90
Base Fluid	II+ / III+	Gr. III
Functional MG-3000	7	4.5
110N Group II+ (Phillips PP110N)	36.4	--
4 cSt Group III (Yubase 4)	--	74.7
4 cSt Group III+ (Adbase 4)	37.9	--
2500 MW Polybutene (Indopol H1900)	14.45	16.8
Functional PD-630	0.25	--
Functional GA	4.0	4.0
KV100, cSt	15.2	14.8
Viscosity Index	174	177
Brookfield Viscosity, -40C (D2983)	116,000	89,000

GL-5 75W Automotive Gear

- Requires shear-in-grade by 20hr KRL and < 150,000 cP -40C Brookfield

Automotive Gear Oil Grade	**75W90**
Base Fluid	Gr. III
Functional MG-3000	6.0
8 cSt Group III (Yubase 8)	73.05
950 MW Polybutene	16.70
Functional PD-630	0.25
Functional GA	4.0
KV100, cSt	14.9
Viscosity Index	99.2
Brookfield Viscosity, -40C (D2983)	138,400

GL-5 75W Automotive Gear

- Requires shear-in-grade by 20hr KRL and < 150,000 cP -40C Brookfield

Automotive Gear Oil Grade	75W90	75W90
Base Fluid	PAO4	PAO4
Functional MG-1000	15.0	15
PAO 4 (Durasyn 164)	60.5	69.6
mPAO 100 (Synfluid mPAO 100)	20.5	
mPAO 300 (Spectrasyn mPAO 300)		11.4
Functional GA	4.0	4.0
KV100, cSt	15.0	15
Viscosity Index	189	202
Brookfield Viscosity, -40C (D2983)	73,600	58,800

GL-5 75W Automotive Gear

- Requires shear-in-grade by 20hr KRL and < 150,000 cP -40C Brookfield

Automotive Gear Oil Grade	**75W140**	**75W140**
Base Fluid	PAO4	PAO4
Functional MG-1000	15.7	16.0
PAO 4 (Durasyn 164)	25.5	30.5
mPAO 100 (Synfluid mPAO 100)	39.8	
mPAO 150 (Spectrasyn mPAO 150)		29.5
Diisodecyl Adipate	15.0	5.0
Ditridecyl Adipate		15.0
Functional GA	4.0	4.0
KV100, cSt	27.0	27.1
Viscosity Index	189	177
Brookfield Viscosity, -40C (D2983)	80,700	122,200

Topics We Covered

1. Intro to PMAs
2. Choosing PMA Based on Application
3. Formulating with PMAs

Summary

- PMAs provide VI improvement, solubility, and improved low temperature with good shear stability using bio-feedstocks
- PMAs can be matched to an application based on
  - Shear requirements
  - Base oil compatibility
  - Low temperature improvement
  - Dispersancy requirements
- Formulation examples for shock, Hydraulic Fluid, Industrial/Automotive Gear

Thank you!