Base Oil Fundamentals

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Canton STLE Chapter

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stle
Society of Tribologists and Lubrication Engineers

www.functionalproducts.com

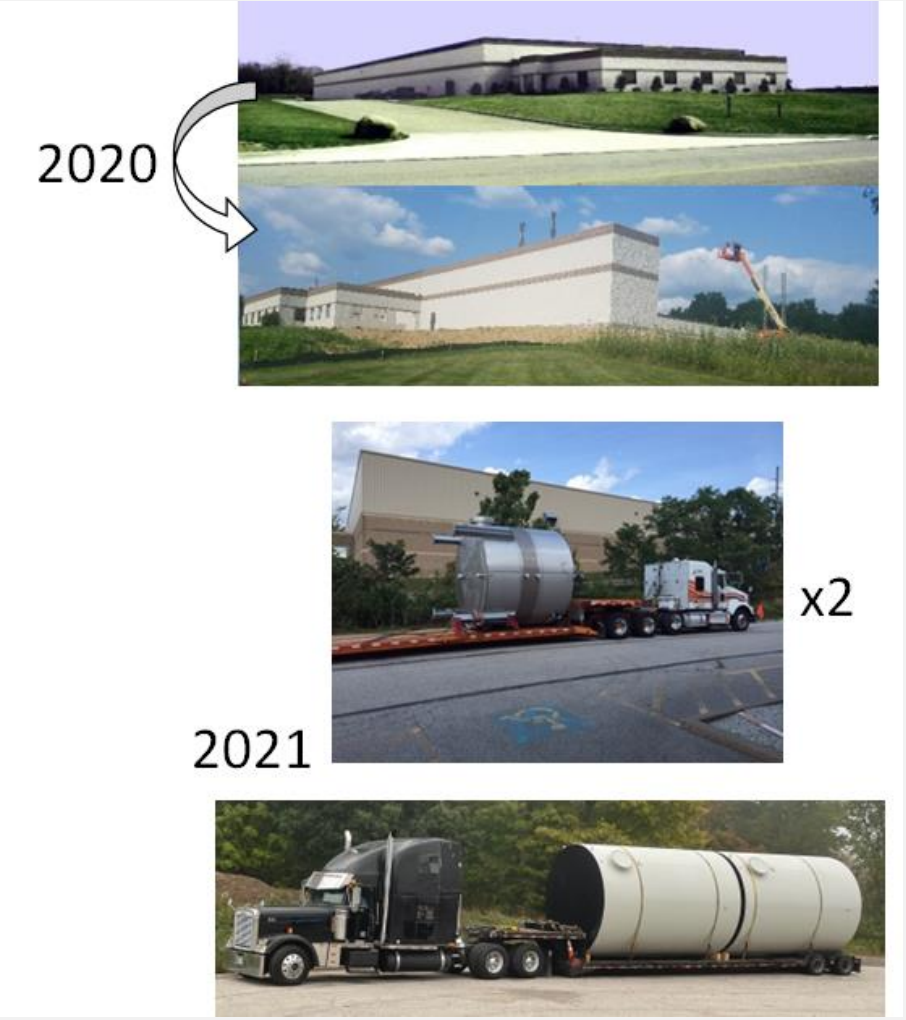
FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

Agenda

- Crude vs. refined oil
- The API Group system (and marketing terms)
- Refining technology for Group I/II/III
- Differences in basic properties (lubes, greases, MWF) and economics
- Group IV (PAO)
- Group V (other)

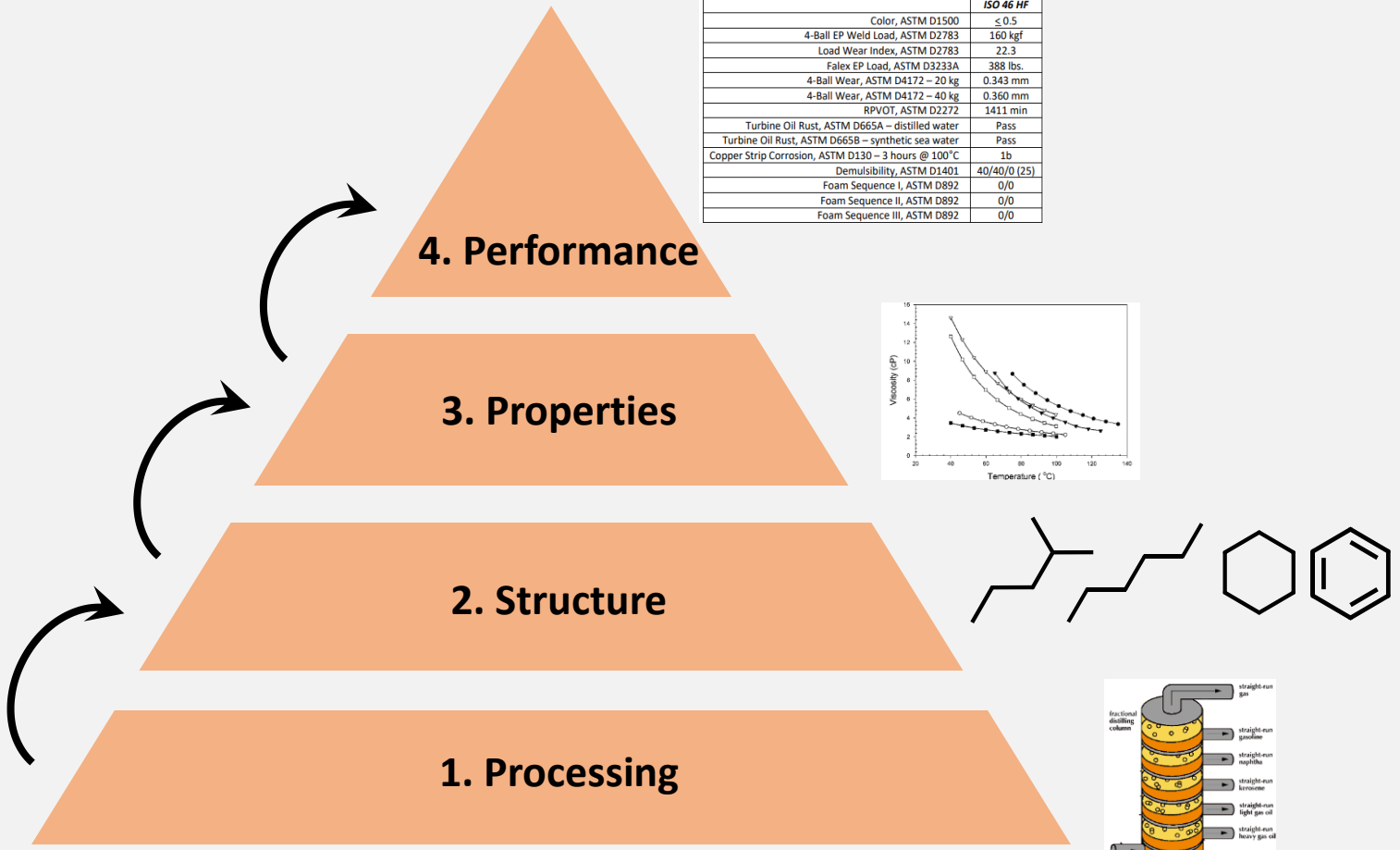
Functional Products Inc.

- Additive company specializing in polymer technology
- Based in Ohio, USA since 1985
- Focused on customer driven solutions
- ISO 9001 with Design
- Expansion completed 2020
- Lubes, greases, and starting to focus on MWF



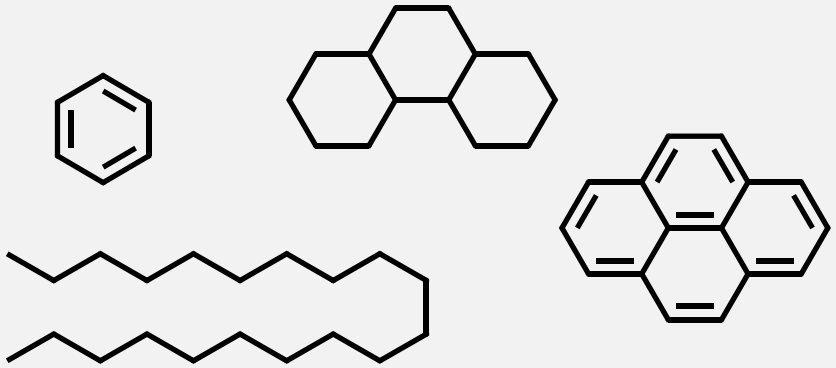
Material Science

Performance	
	ISO 46 HF
Color, ASTM D1500	≤ 0.5
4-Ball EP Weld Load, ASTM D2783	160 kgf
Load Wear Index, ASTM D2783	22.3
Falex EP Load, ASTM D3233A	388 lbs.
4-Ball Wear, ASTM D4172 – 20 kg	0.343 mm
4-Ball Wear, ASTM D4172 – 40 kg	0.360 mm
RPVOT, ASTM D2272	1411 min
Turbine Oil Rust, ASTM D665A – distilled water	Pass
Turbine Oil Rust, ASTM D665B – synthetic sea water	Pass
Copper Strip Corrosion, ASTM D130 – 3 hours @ 100°C	1b
Demulsibility, ASTM D1401	40/40/0 (25)
Foam Sequence I, ASTM D892	0/0
Foam Sequence II, ASTM D892	0/0
Foam Sequence III, ASTM D892	0/0




API Groups

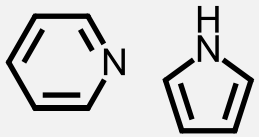
Crude Oil

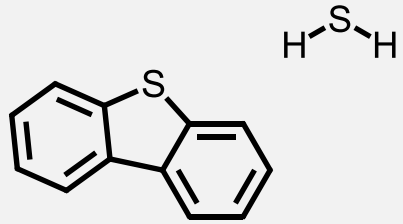


Hydrocarbons (80%+)

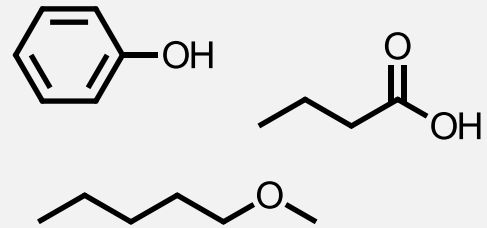
- 15-60% alkanes
- 30-60% naphthenes
- 3-30% aromatics
- 3-10% asphaltenes (C/H/N/O/S)

Nitrogen (0.1-2%)





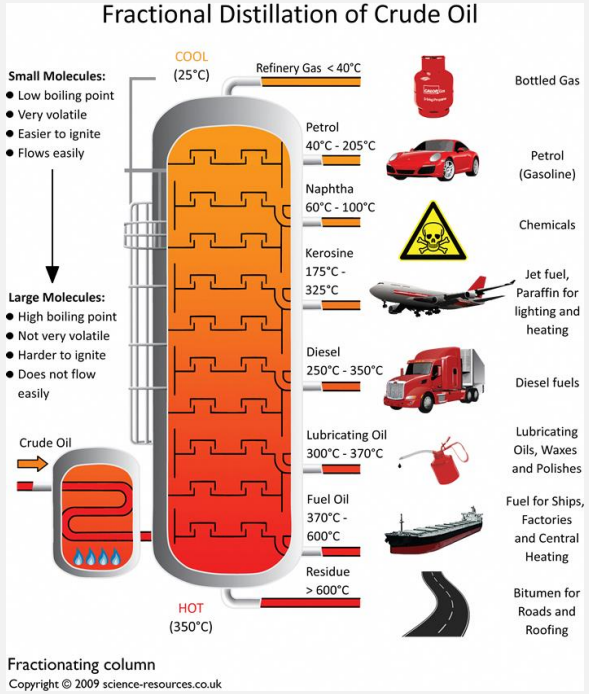
Sulfur (0.5-6%)



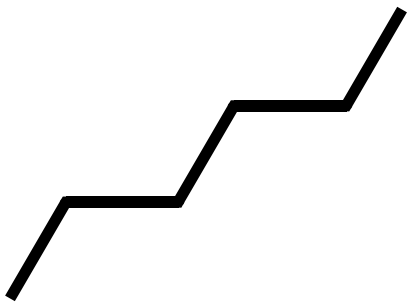
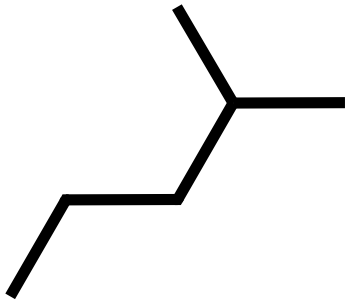
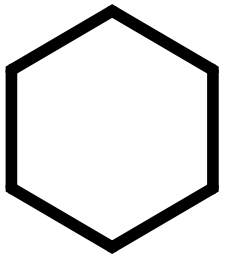
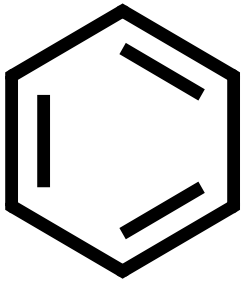
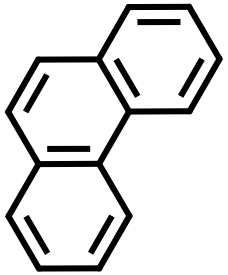
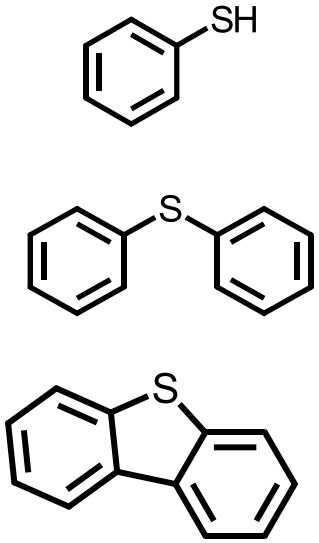
Oxygen (0.1-6%)

Refining

- Remove poisonous/caustic/corrosive elements (S/N/O)
- Break apart polycyclic aromatics
- Improve stability
  - Thermal stability
    - Oxidation / shelf life
    - Cold flow
- Deliver the right volatility or viscosity for fuels, lubes, etc.



Components of Refined Oil

Saturates			Unsaturates / Aromatics		
Alkanes (Wax)	Isoalkanes	Naphthenics	Aromatics	Polycyclic Aromatics	Sulfur Compounds
					
• Crystallize as solids • Limit low temperature	• Ideal		• Load carrying • Color	• EHS if >3wt% • Color	• Tribo-active sulfur (EP, corrosion) • Odor, color

API Group System

- Originally intended to spec-out **engine oils** and determine read across for interchangeability of base oil suppliers
    - When switching or upgrading base oil, this saves blenders $$$$ in having to retest for the big engine tests (Sequence I/II/III/etc.)
- Generally useful for the rest of us to set some basic expectations for the properties and quality of base oil from different plants / brands

Groups

- API Group system originally devised for engine oil quality and performance

	Viscosity Index	% Saturates	% Sulfur	Technology
Group I	80 - 120	< 90%	> 0.03%	Solvent extracted refined petroleum
Group II	80 - 120	≥ 90%	≤ 0.03%	Hydrocracked refined petroleum
Group III	≥ 120	≥ 90%	≤ 0.03%	Hydroisomerized refined petroleum; better crudes
Group IV	n/a	n/a	n/a	Polyalphaolefns (polymerization)
Group V	n/a	n/a	n/a	Everything else – naphthenic, synthetic, veg
** = not official; “+” is marketing				

"Plus"

- Qualitative improvements to VI, volatility, and sulfur but still in the API Group officially

	Viscosity Index	% Saturates	% Sulfur	Technology
Group I	80 - 120	< 90%	> 0.03%	Solvent extracted
Group I+ **	100+			
Group II	80 – 120	≥ 90%	≤ 0.03%	Hydrocracking
Group II+ **	110+			
Group III	≥ 120	≥ 90%	≤ 0.03%	Hydroisomerization
Group III+ **	130+			
Group IV	n/a	n/a	n/a	Olefin polymerization
Group V	n/a	n/a	n/a	Everything else – naphthenic, synthetic, veg
** = not official; "+" is marketing				

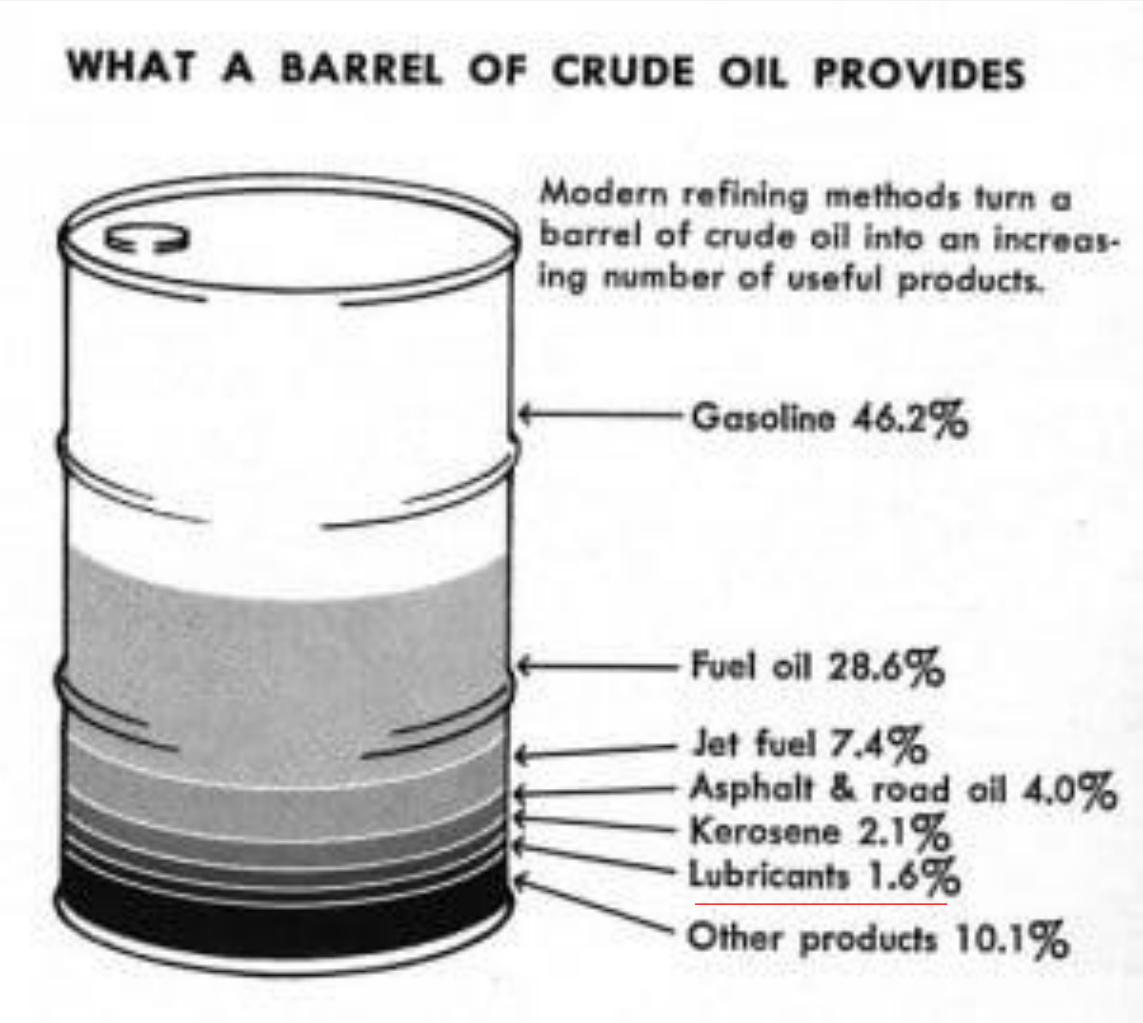
"Synthetic"

- US marketing term
- Group III can be marketed as "synthetic" for API licensed engine oil
  - Not synthetic in origin but giving synthetic-like performance (vs. PAO)
  - Mobil Oil vs. Castrol in 1999
- *Great conversation starter at networking receptions!*


Oil Processing

Lubricants and Petroleum

- Globally, we use a lot of petroleum
- 47M gallons/day of Group I/II/III
  - Only ~1% of the barrel
- ~50% of lube oil for engine oil
- 655K gallons/day of PAO



2022 Lubes 'n' Greases Base Oil Production Report

Refinery Processes (1/2)

- Distill
  - Separate different molecular weight fractions of oil by their volatility
- Extract impurities
  - Remove high polarity aromatics and S/N/O compounds with solvent
- Hydrogenate
  - Convert double bonds (unsaturation) to single bonds (saturates)

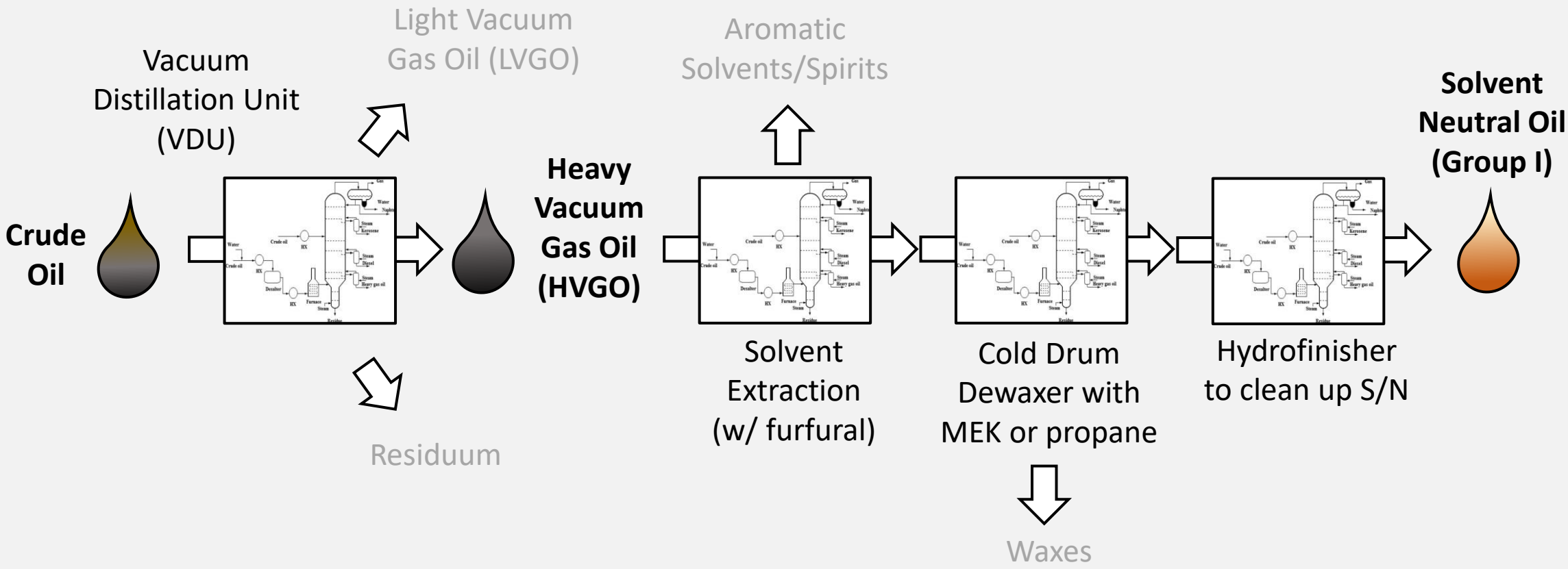
Refinery Processes (2/2)

- Hydrofinish / hydrotreat / desulfurize
  - Co/Ni/Mo catalyst reduces sulfides and amines to HS_2 / NH_3
  - Reduces residual color and odor

- Crack
  - Breaking hydrocarbon rings (naphthenes) into isoalkanes

- Isomerize
  - Rearranging linear alkanes (wax) into isoalkanes inside zeolite catalysts

Refining Group I



Variable time, temperature, pressure, and catalysts will output different quality levels ay varying cost

https://www.mckinseyenergyinsights.com/resources/refinery-reference-desk/

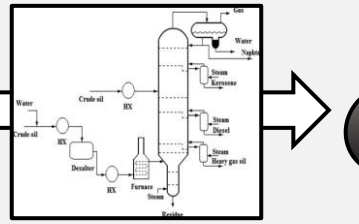
https://www.e-education.psu.edu/fsc432/

Plant and Process Unit – The Project Definition

Refining Group II

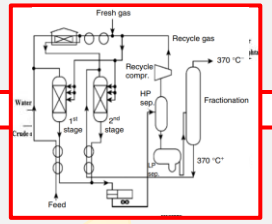
Paraffinic Crude Oil

Vacuum Distillation Unit (VDU)

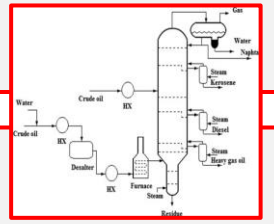


Heavy Vacuum Gas Oil (HVGO)

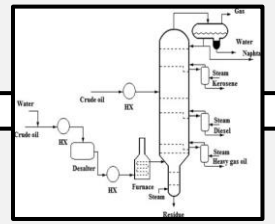
Hydrocracker



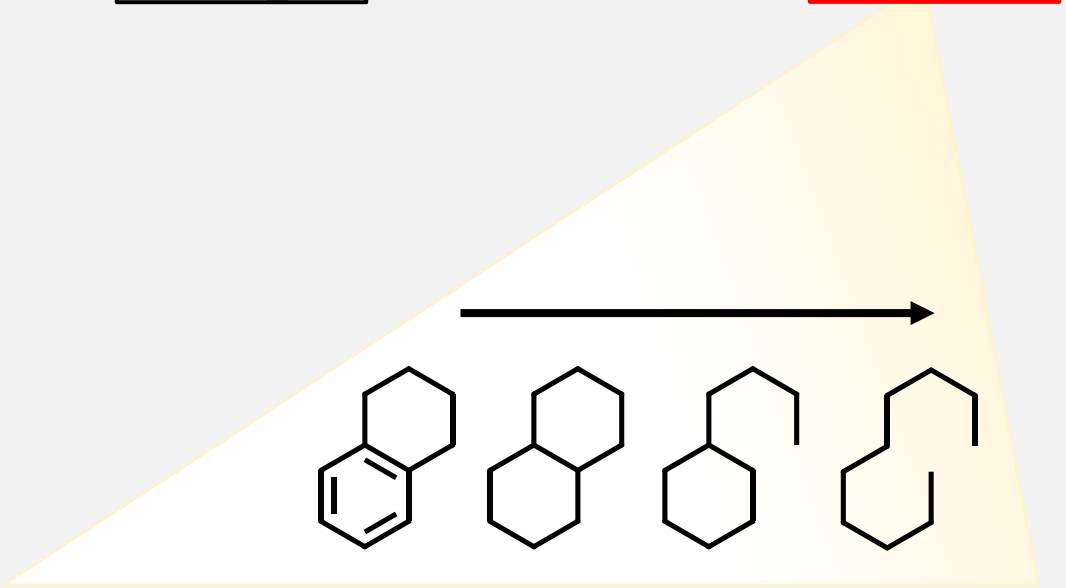
Catalytic Dewaxing



Hydrotreating (more severe hydrofinishing)



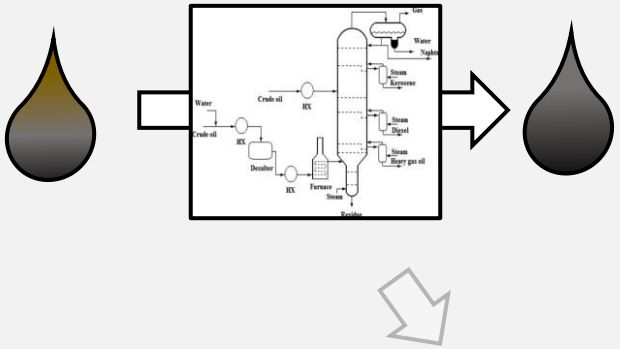
Neutral Oil (Group II)



Refining Group III

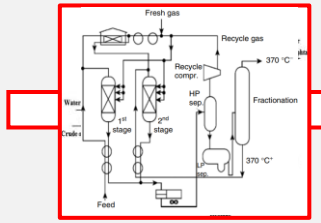
Higher VI Crude Oils and Waxes

Vacuum Distillation Unit (VDU)

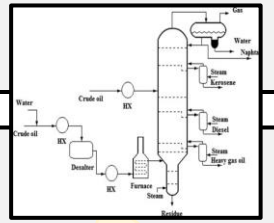


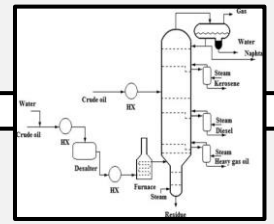
Heavy Vacuum Gas Oil (HVGO)

Increased Hydrocracker Severity



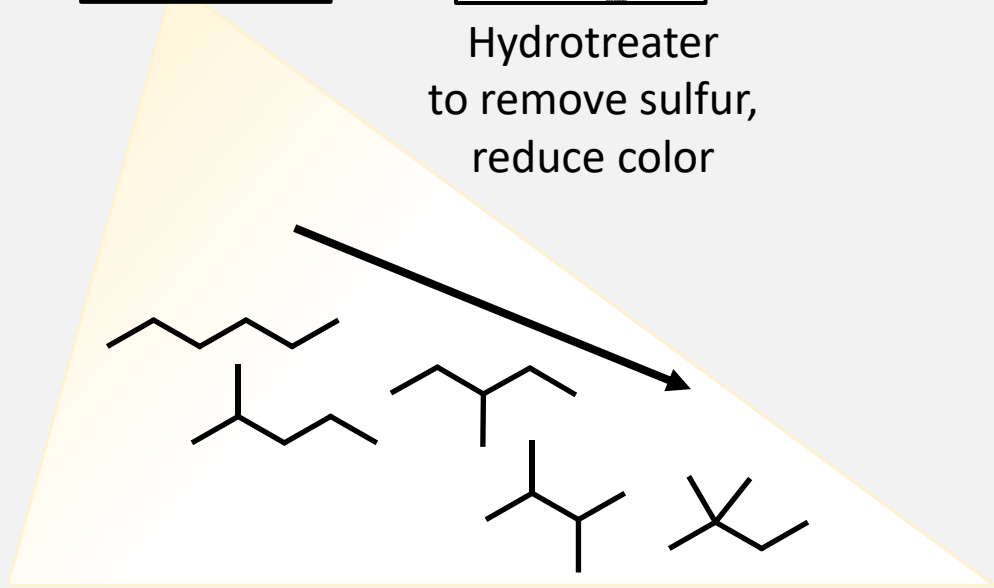
Catalytic Dewaxing





Hydrotreater to remove sulfur, reduce color

Group III Oil



Naphthenic Oils (Group V)

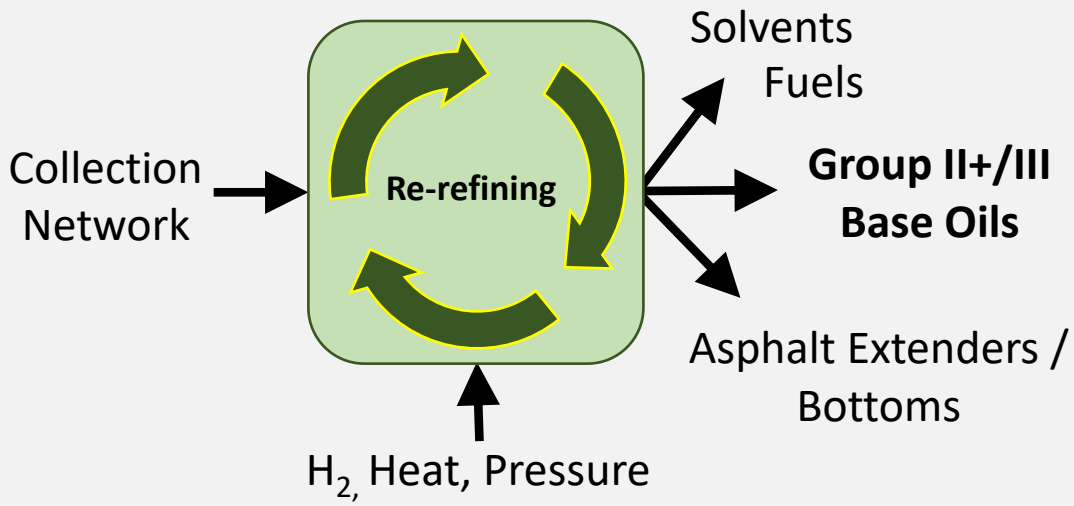
- Group I-III are paraffinic oils derived from paraffinic crude oils

- Naphthenic oils are high in aromatics and derived from naphthenic crude
  - Metalworking
  - Greases
  - Process oils (heat transfer)
  - Transformer oils

  - Lower cost, low viscosity index

Re-Refined Base Oils (RRBO)

- Group II process, reclaimed oil as crude
- Circular economy
  - Currently fed by engine oil
  - In future, EV coolants (if PAO)



- Has come a long way over the years – now have Group II+ and III options
  - Safety Kleen, Heritage Crystal Clear, Vertex, Avista, Puraglobe, etc.

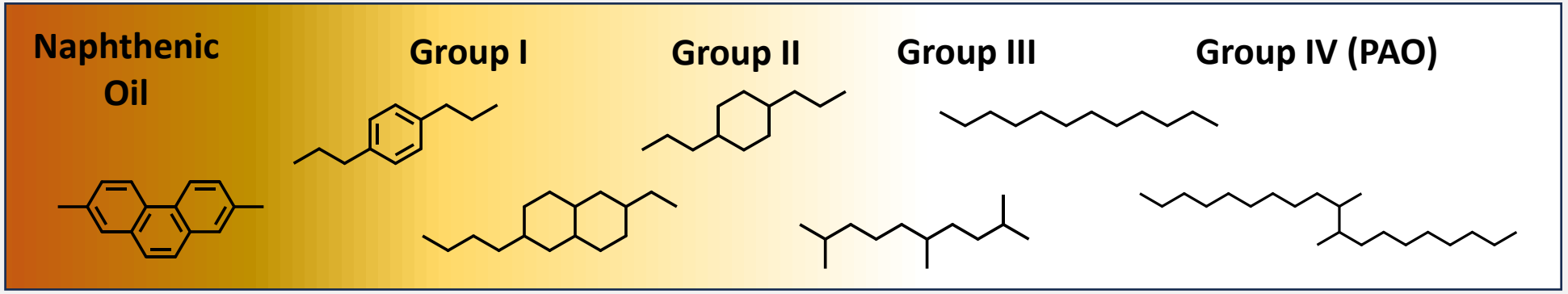
Working With Petroleum Oils

Key Things to Consider

- Composition vs. level of refining
- Price
- Basic datasheet information
  - Viscosity, Viscosity Index
  - Color
  - Impurities (Aromatics + Sulfur)
  - Volatility (Flash Point + NOACK)

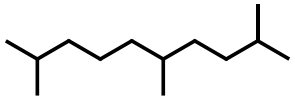
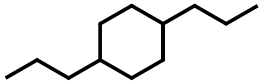
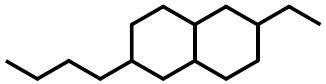
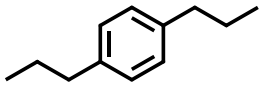
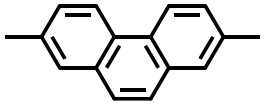
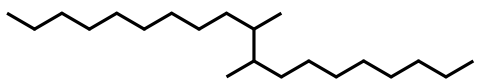
TEST DESCRIPTION	TEST METHOD	SPECIFICATIONS	
Physical Properties		MIN	MAX
Viscosity, SUS at 100°F (37.8°C)	ASTM D2161	300	330
Viscosity, SUS at 210°F (98.9°C)	ASTM D2161		
Viscosity, cSt at 40°C (104°F)	ASTM D445	58.1	63.8
Viscosity, cSt at 100°C (212°F)	ASTM D445		
API Gravity, 60°F (15.6°C)	ASTM D1250		
Specific Gravity, 60°F (15.6°C)	ASTM D4052		
Viscosity Index	ASTM D2270	95	
Viscosity-Gravity Constant	ASTM D2501		
Density, lbs/gal at 60°F	ASTM D1250		
Density at 15.6°C, g/cm³	ASTM D1250		
Molecular Weight	ASTM D2502		
Flash Point, COC, °F (°C)	ASTM D92	450 (232)	
Flash Point, PMCC, °F (°C)	ASTM D93		
Color, ASTM	ASTM D6045		2.0
Pour Point, °F (°C)	ASTM D5949		10 (-12)
Cloud Point, °F (°C)	ASTM D5773		
Noack Volatility, wt%	ASTM D5800		
Water Content	ASTM D7546M	PASS	
Appearance	ASTM D4176M	PASS	
Chemical Properties			
Acid Number, mg KOH/g	ASTM D664		
Aniline Point, °F (°C)	ASTM D611	235 (113)	255 (124)
Sulfur, ppm	ASTM D7220		
Health and Safety Properties			
Polycyclic Aromatic Compounds, wt%	IP 346		3
Modified Ames Assay, MI	ASTM E1687		1
FDA Regulation	21 CFR 178.3620 (C)	PASS	

Typical Distribution



	% Alkane Carbon	% Naphthenic Carbon	% Aromatic Carbon
Naphthenic Oil	50	40	10
Group I	60	35	5
Group II	65	34	1
Group III	80	20	0
PAO	100	0	0

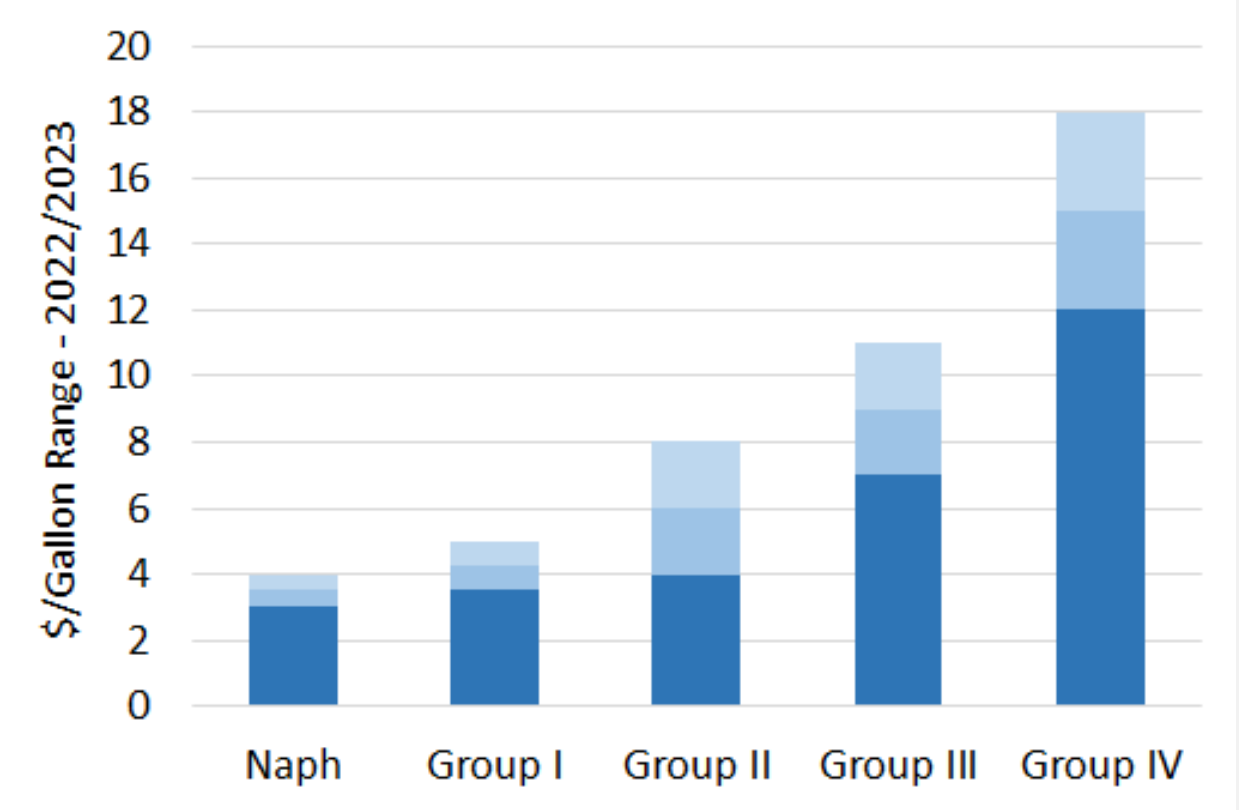
Relative Properties of Hydrocarbons

Molecule	Structure	VI	Pour Point	Oxidation	Solubility	Toxicity
N-Paraffin		5	1	5	1	5
Isoparaffin		4	3	5	3	5
Single-Ring Naphthenic		3	3	3	3	5
Multiring Naphthenic		2	5	3	5	5
Alkylbenzene		3	5	3	5	3
Polycyclic Aromatic		2	2	1	3	1
Polyalphaolefin		5	5	5	2	5

Reproduced from: Pirro, D. M., Webster, M. & Daschner, E. Lubrication Fundamentals, Revised and Expanded. (CRC Press, 2017), pg 19

Price

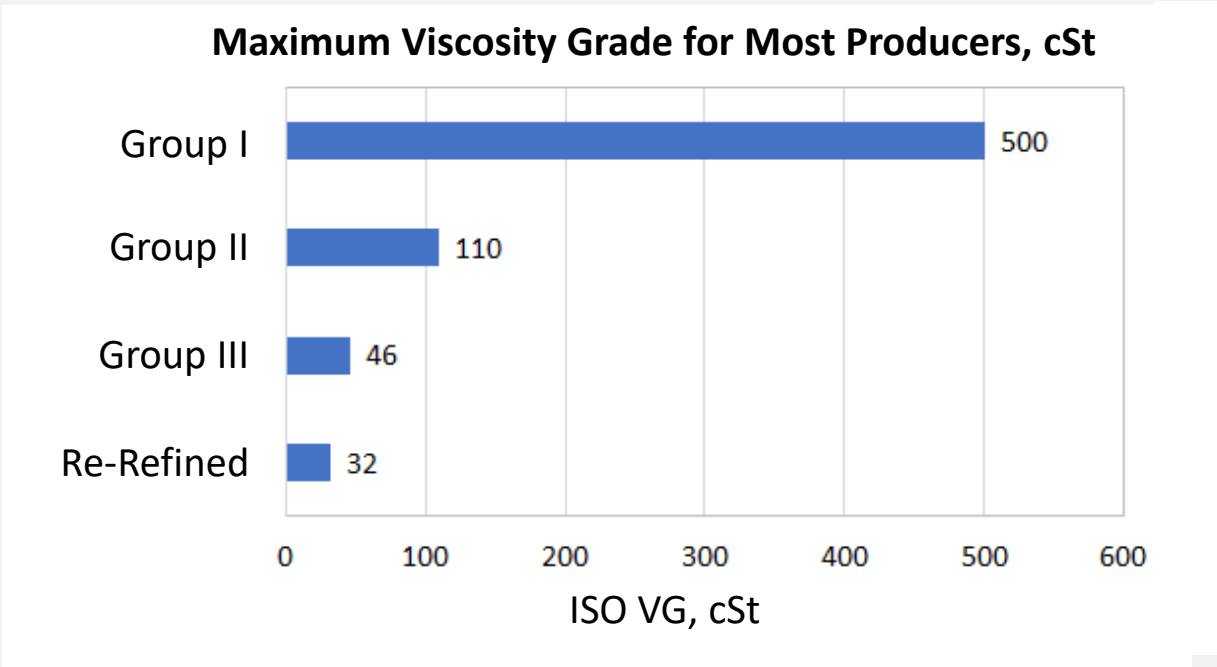
- Ultimately depends on:
  - Crude Oil
  - Supply
  - Packaging
    - Railcar
    - Tanker
    - Totes
  - Logistics, who's local?



Don't quote me on this…

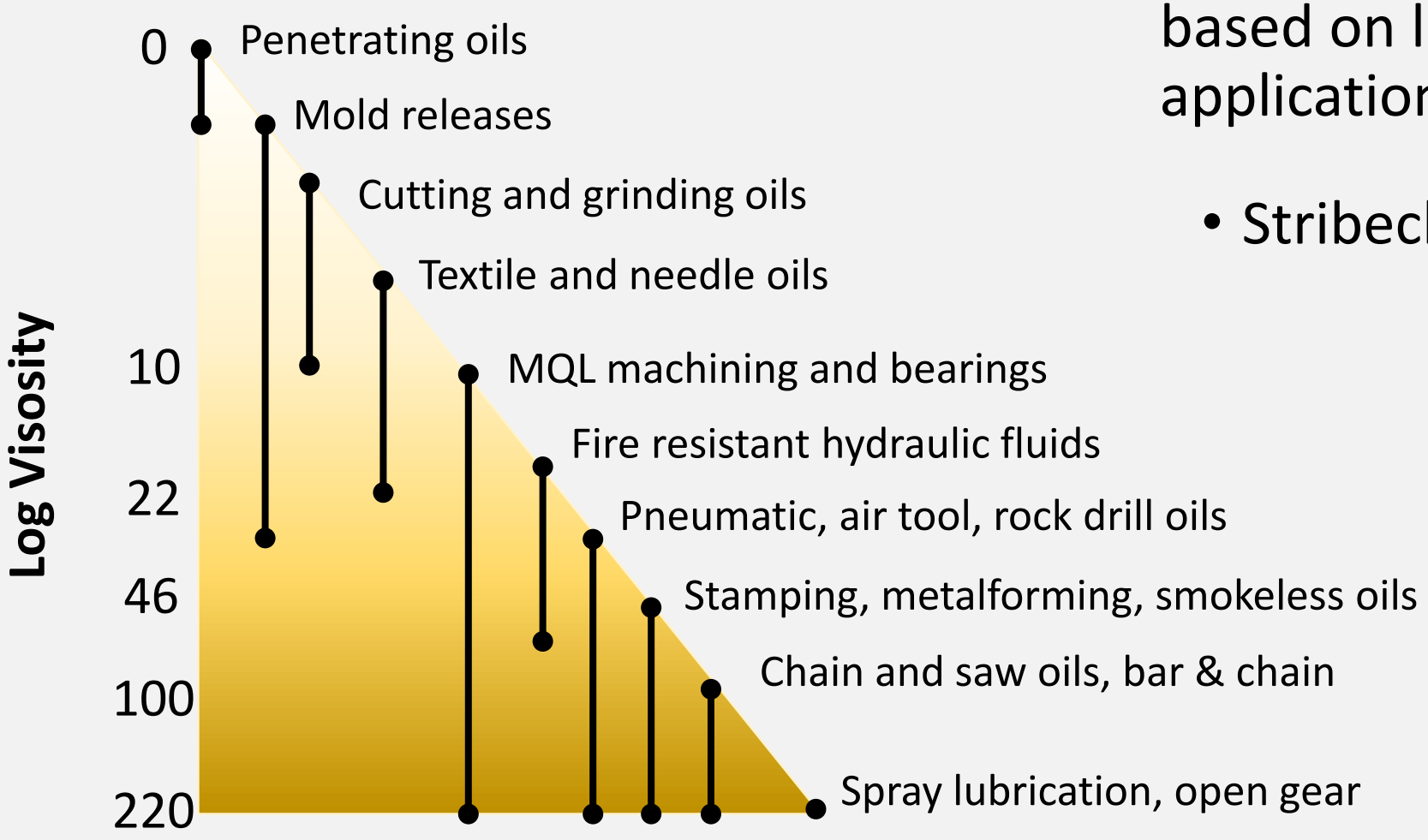
Viscosity by Group

- More severe refining = lower molecular weights = lower viscosity range



- Different refineries will only put out specific viscosity cuts depending on their priorities and market conditions (fuel vs. lubes vs. solvents)

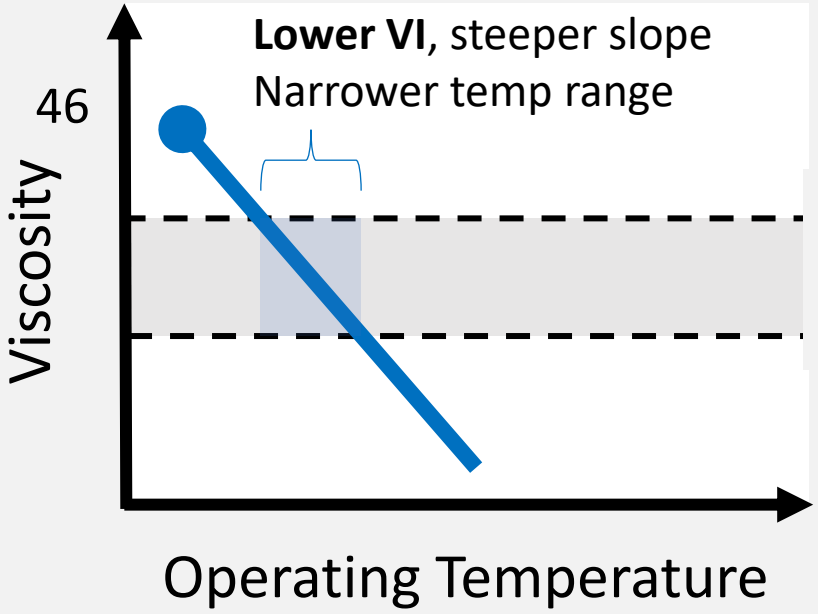
Viscosity by Application

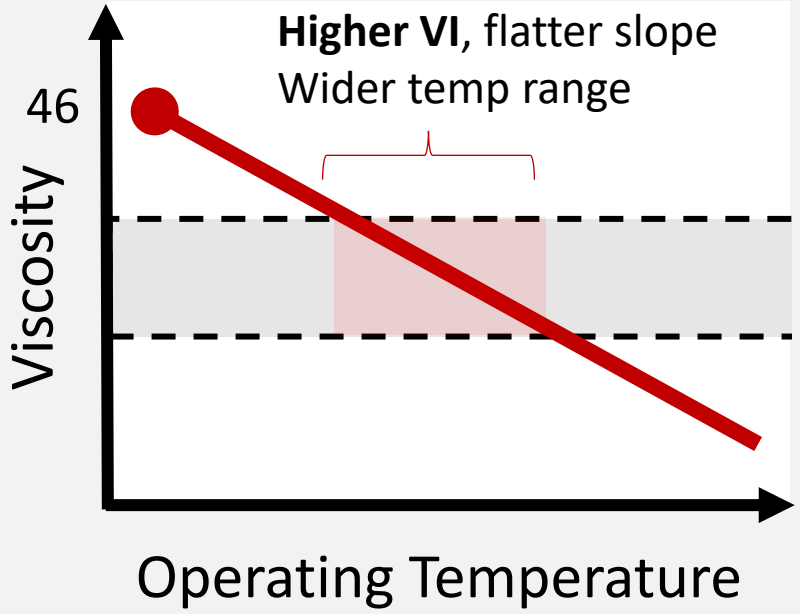


- Viscosity should be optimized based on load and speed of application
  - Stribeck Curve

Viscosity Index

- Lubricating a piece of equipment with speed S and load L
  - Viscosity, V, at operating temp is specified to optimize lubrication regime (Stribeck)
  - Higher VI, flatter temp-visc curve, wider 'operating window'



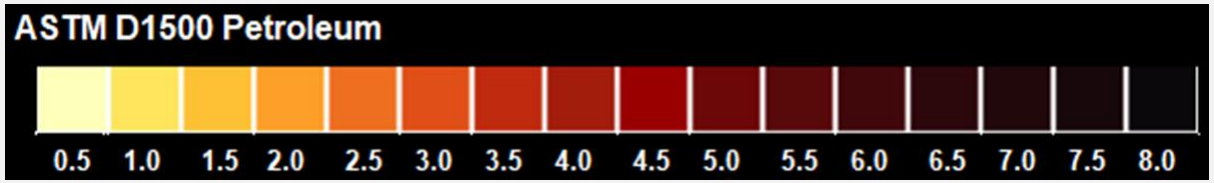


Color and Stability

- Aromatics, sulfur, color as reported by major base oil suppliers

	% Aromatics	% Sulfur	Color (D1500)
Group I	20.0%	0.10 – 0.20%	2 – 3
Group I+	10.0%	0.02 – 0.05%	1 – 2
Group II	5.0%	0.010%	0.5 – 1
Group II+	0.5%	0.003%	0.0
Group III	0.1%	0.001%	0.0
Group III+	0.0%	0.001%	0.0

0.0 color, aka "water white"

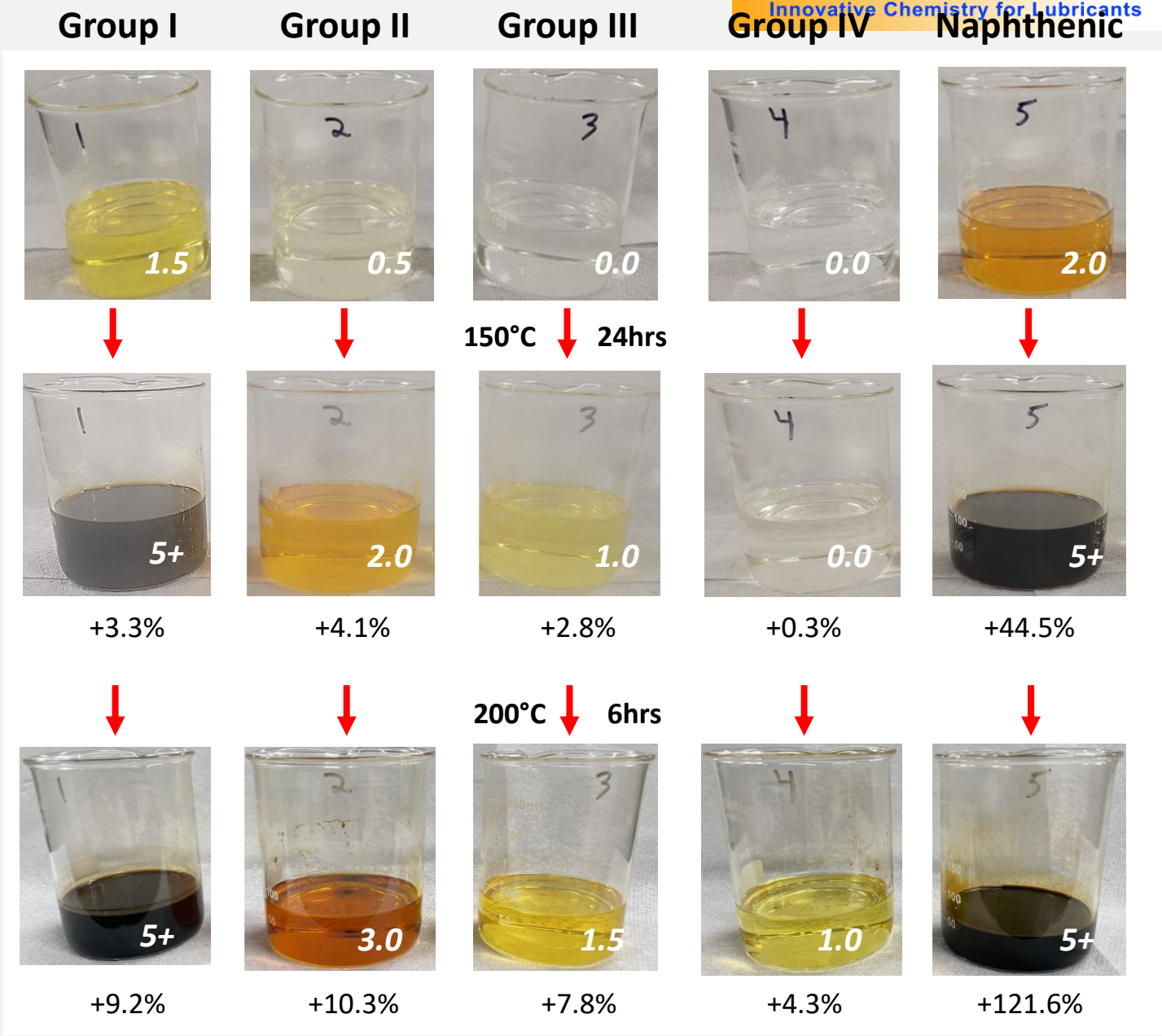


Oil in Oven Demo

- ISO 32
  - 0.05% phenolic AO
  - 0.05% aminic AO
- 24 hrs @ 150C
- 6 hrs @ 200C

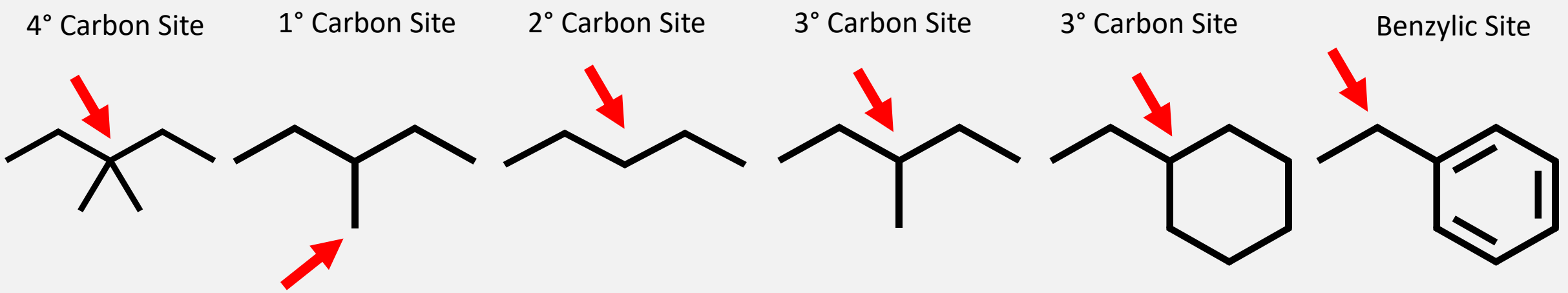
- Every 10C above 80C

  = 2x the rate of aging



Oxidation Rates of Hydrocarbon Sites

- Organic chemistry – different carbon sites react with oxygen differently
  - Alkanes > Naphthenes > Aromatics



Other Things to Consider

- Sometimes naphthenic or aromatic carbon is good – we still use Group I
  - Solvency and Emulsibility (Aniline Point)
  - Compressibility (i.e. Load Carrying Capability)
  - Waxes

Base Oil Solvency

- Aniline Point
  - Useful measure of solvency for the fuels/lubricants industry
  - Temperature at which the oil mixes with aniline (a polar agent)

	Aniline Point, °C	% Alkane Carbon	% Naphthenic Carbon	% Aromatic Carbon
Naphthenic Oil	70 - 90	50	40	10
Group I	90 - 110	60	35	5
Group II	110 - 120	65	34	1
Group III	120 - 130	80	20	0
PAO	130 - 140	100	0	0

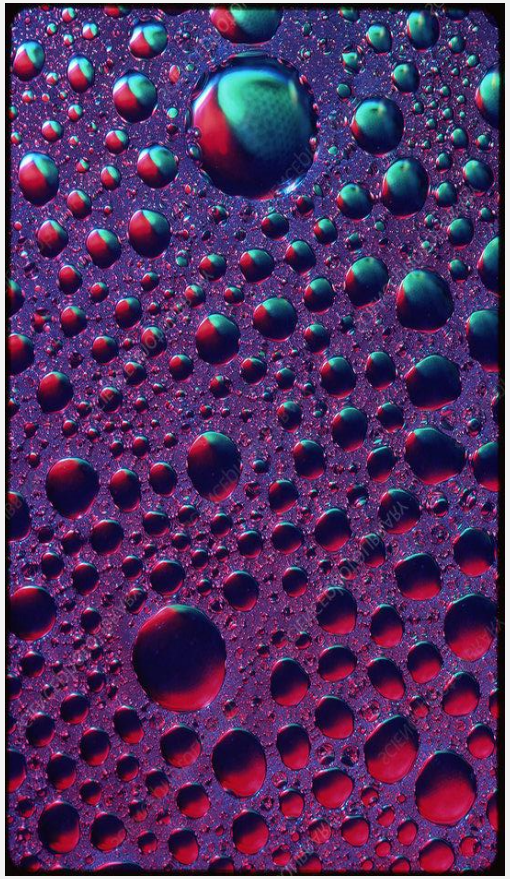
Solvency Issues

Emulsibility / Demulsibility

- ASTM D1401 – water separation test

- Higher aniline point -> greater tendency to emulsify (MWF)
- Lower aniline point -> better for demulsifying (lubricants)

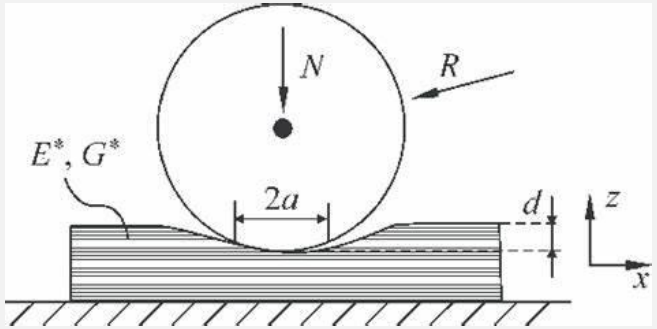
- Use emulsifier or demulsifier additive for best results
  - Ethoxylates
  - Fatty alcohols

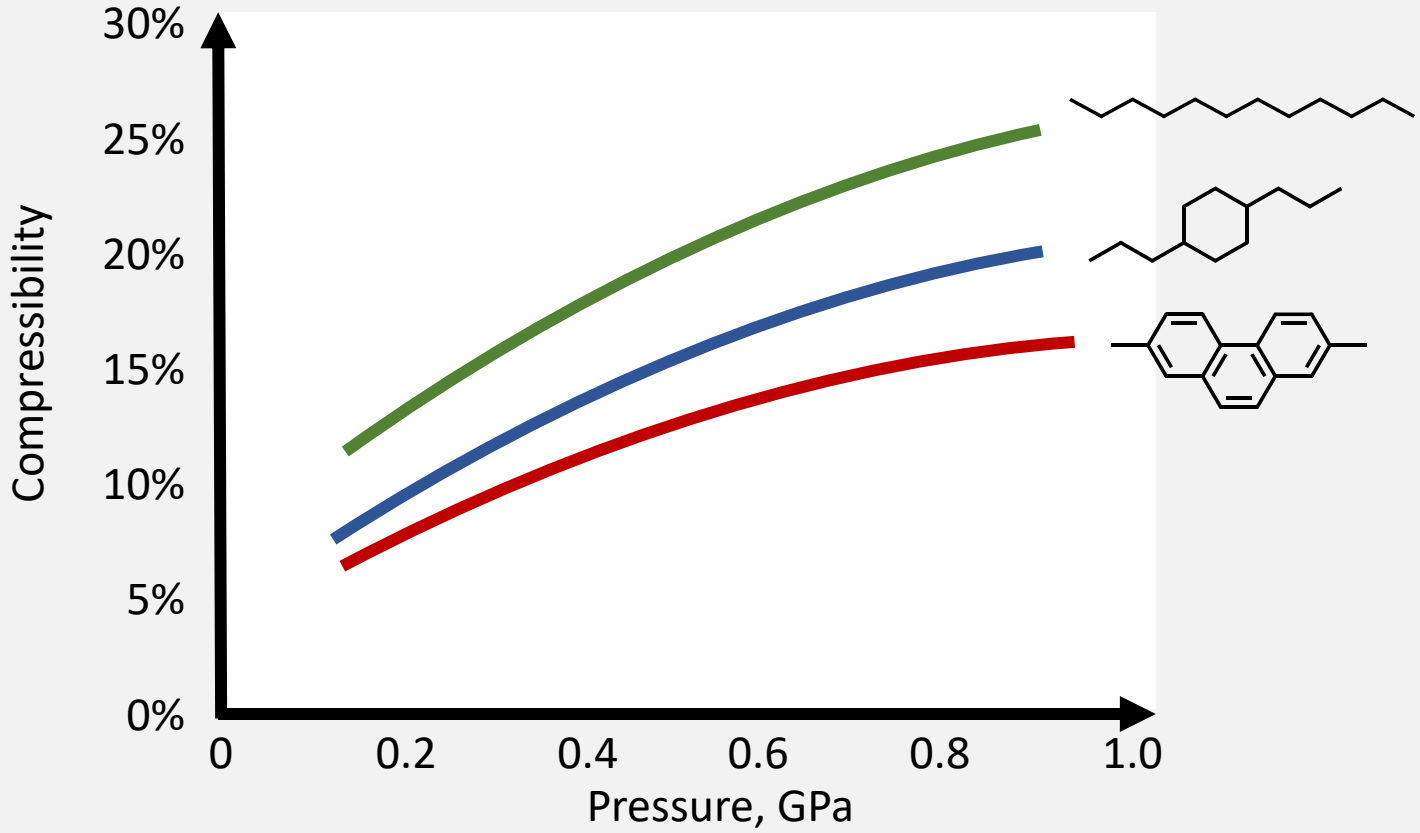


Great study - “BASE OIL AND EMULSIFIER SELECTION PRINCIPLES PART II - A METALWORKING FLUID EMULSION STABILITY STUDY” by Nynas

Compressibility

- Ring-like structures carry load and compress less than long paraffins
- Tribo-contacts up to 2 GPa pressure

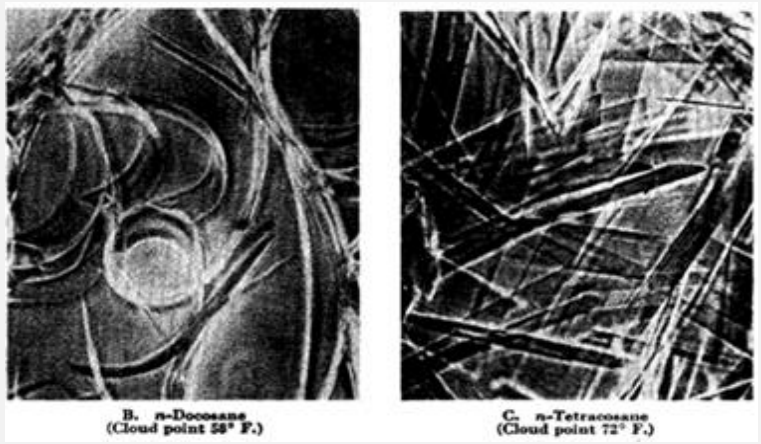




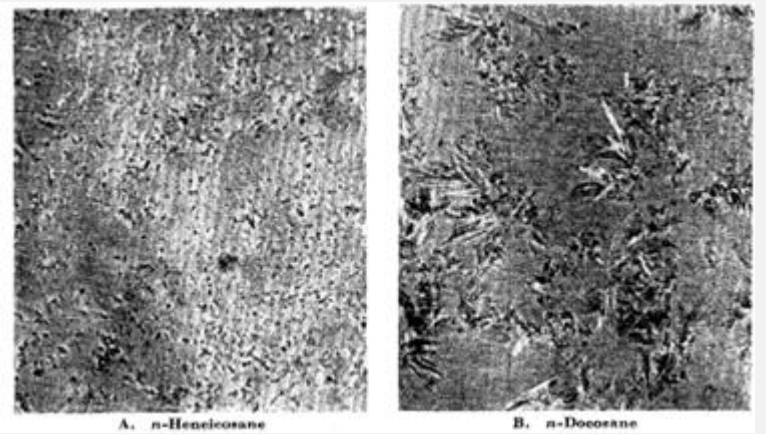
W. G. Cutler, R. H. McMickle, W. Webb, and R. W. Schiessler, 'Study of the Compressions of Several High Molecular Weight Hydrocarbons', *J Chem Phys*, vol. 29, no. 4, pp. 727–740, Oct. 1958.

Wax and Pour Point Depressants

- Paraffinic oils contain residual waxes from the refining process
- Wax can crystallize out at low T and temporarily gel the oil (“pour point”)
- Pour point depressants (PPD) counteract the gelation of waxes



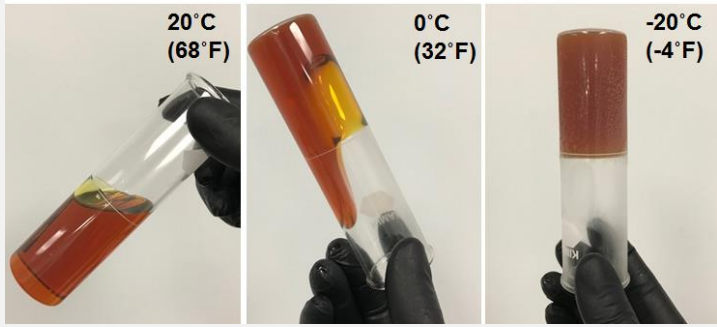
PPD

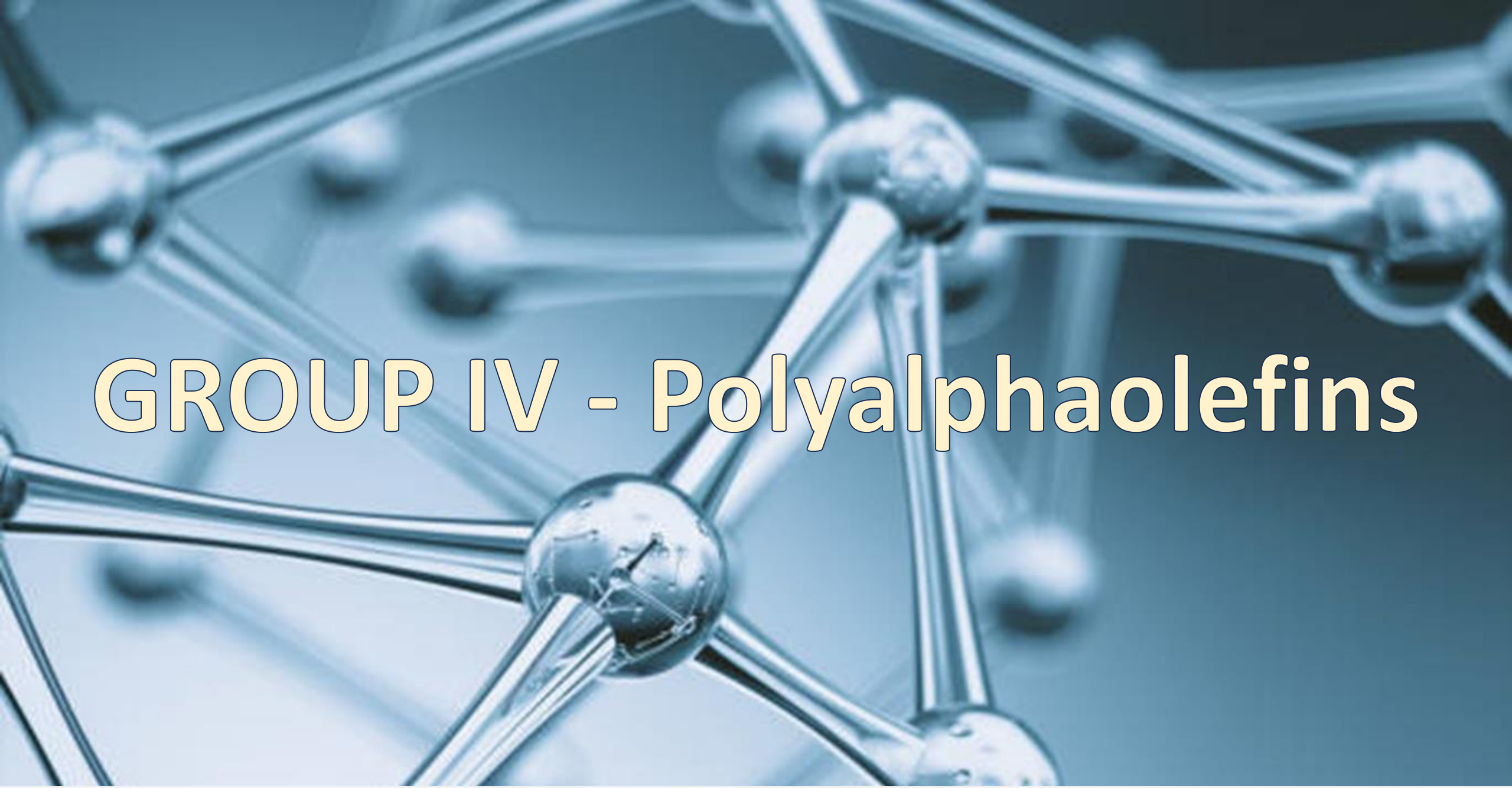


Cold Flow Improvement

- Typical PP of petroleum oils from -12 to -18°C
  - PPD can lower pour point to -30 to -51°C
- Also: CCS, TP-1 MRV, Brookfield
- Different PPDs for different types of oil
- Wax-free PAOs have inherent PP of -40 to -80°C

wt% PPD	ISO 32	ISO 150
0.0%	-18°C	-18°C
0.05%	-33°C	--
0.1%	-39°C	-21°C
0.2%	-42°C	-24°C
0.3%	-48°C	-30°C
0.5%	--	-33°C



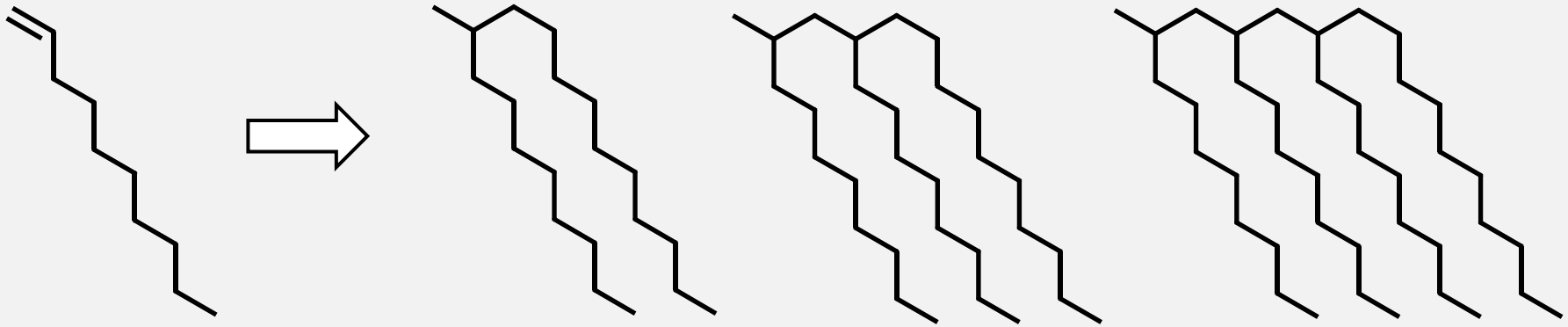


GROUP IV - Polyalphaolefins

Polyalphaolefins (PAO)

- Polymerization of alpha-olefins (octene, decene, dodecene, etc.)
  - Synthetic crude then distilled to obtain cuts of different viscosity

- No waxes or naphthenes; produces narrow cuts

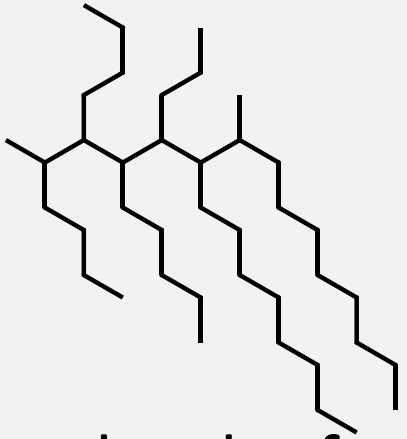


Decene (C10) Dimer (C20) Trimer (C30) Tetramer (C40)

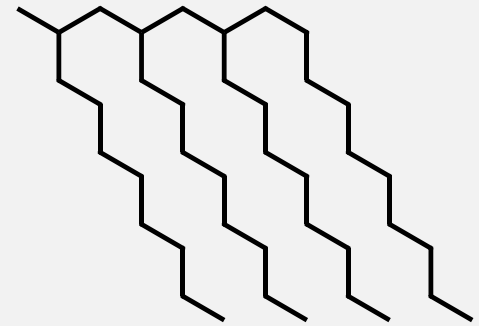
Ideal “comb-like” structures shown here

What is “mPAO”?

- PAO – synthetic ‘crude’ from radical polymerization of olefins; distilled off
  - Isomerization occurs, **many random branches**



- mPAO –synthesized using selective metallocene catalysts (molecular factory)
  - Closer to the ideal **‘comb-like’** structure
  - Greater uniformity and control



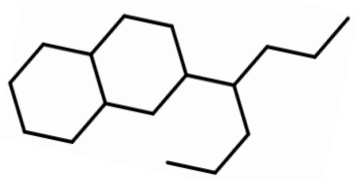
PAO Advantages

- Exceedingly low pour points due to no wax
- No rings or aromatics
  - Excellent thermal/oxidation stability
  - High resistance to emulsifying in wet applications
- NSF H1 for incidental food contact lubricants
- Improved or application-specific versions available
  - Dodecene PAO for higher temperature, lower volatility

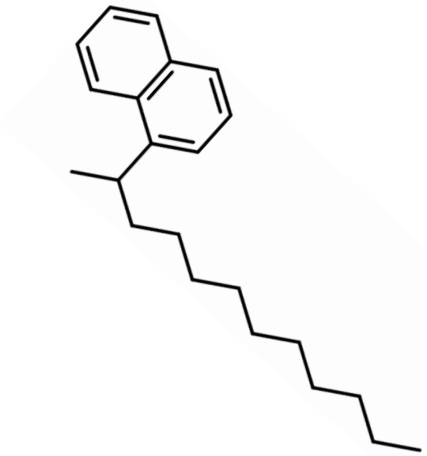
GROUP V – Everything Else

Group V – Everything Else

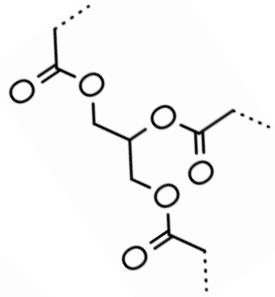
White Oil



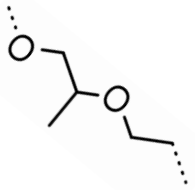
Alkylated Naphthalene



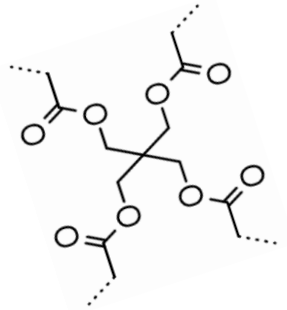
Vegetable/ Natural Oil



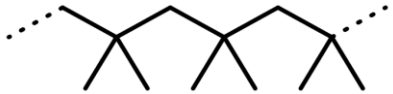
PAG



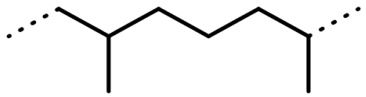
Synthetic Esters



Polybutenes (PIB / PB)



Ethylene Propylene Oligomer (EPO)



And more…

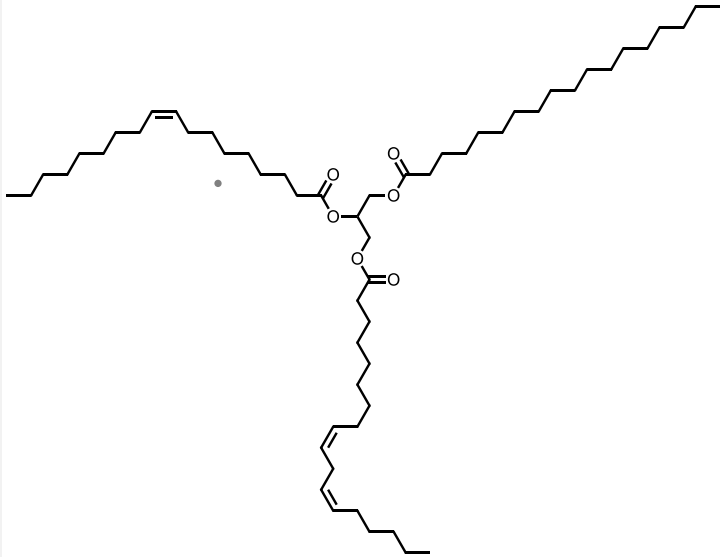
Biobased/Biodegradable Base Oils

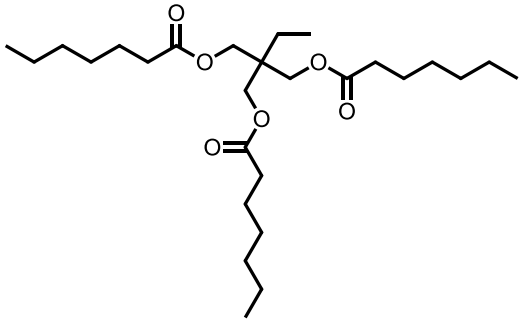
- Tend to have high solvency, great lubricity
- Additives might not work correctly (AW/EP)
- Vegetable oil = lowest cost
  - Issues with oxidation

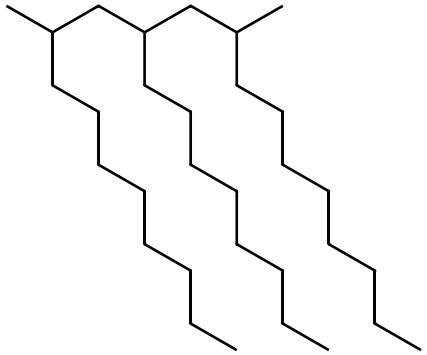
Biodegradable \ Biobased	No	Yes
Yes	PAO* Polyalkylene Glycol*	Vegetable Oil Synthetic Ester* Polymeric Esters*
No	Petroleum Oil Hydrocarbon Polymers	Commodities from Industrial Fermentation (Ethanol to Ethylene)

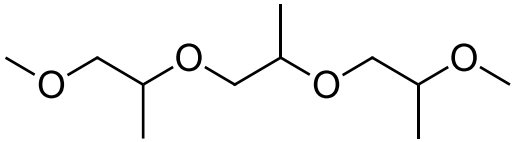
Environmentally Acceptable Base Oil Types

TG - Triglyceride	ES – Synthetic Ester	PR – PAO & Related	PG – Polyalkylene glycol









Base Stock	Biobased	Biodegradable
Triglyceride	Yes	Yes
Synthetic Ester	Maybe	Maybe
PAO & Related	Maybe	Maybe
PAG	No	Maybe


Conclusions

Summary

- A lot of work goes into producing massive quantities of high quality base oil
- Processing -> Structure -> Properties -> Performance
- Group I/II/III paraffinic oils present various benefits at increasing costs
  - The value is in performance relative to cost
  - Buy what you need, don't pay for what isn't used
- Synthetics like Group IV and V oils offer very unique properties due to high control over the raw materials