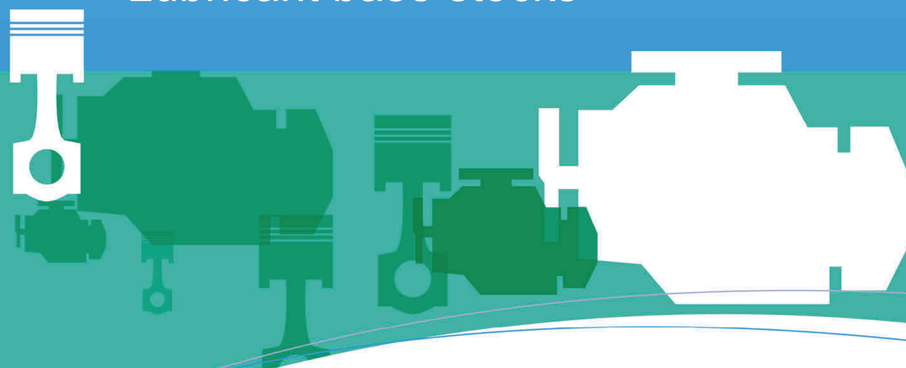
Performance you can rely on.

Lubricant base stocks



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Outline

- What are base stocks?
  - Why are base stock important?
  - Composition of base stocks
- Refining processes
  - Overview
  - Major base stock types
    - Solvent Extraction (SE)
    - Hydrocracking (HC)
    - Synthetics
    - Others
- API base oil groups
- Names and definitions
- Measurements and typical targets
- Recent trends

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Lubricant base stocks

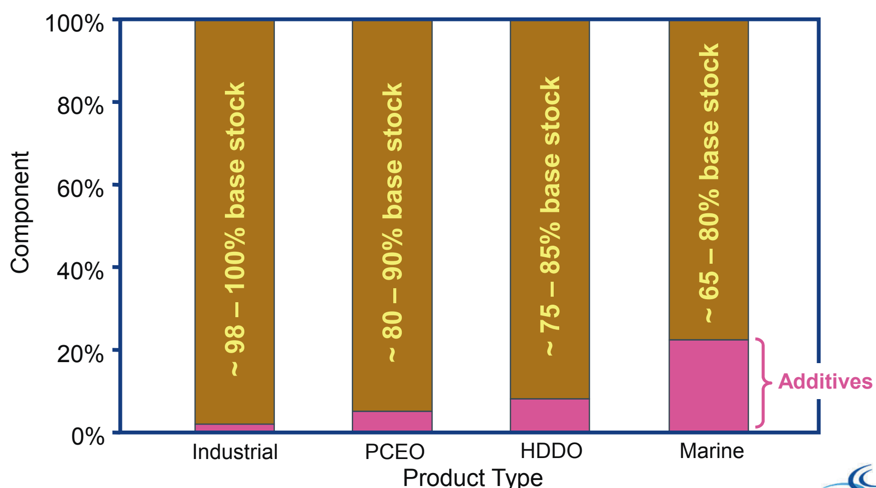
- A lubricant component
  - Roughly 80-99+% of petroleum products
    - Usually doesn't have all required properties – needs additive enhancement
- Mineral oil base stocks
  - Refined from crude oil
    - Petroleum = "Petra-oleum" = "Rock Oil"
  - Common processes
    - Solvent extraction
      - Separate "good" from "bad" molecules
    - Hydrocracking
      - Convent "bad" molecules into "good" molecules
    - Synthesis
      - "Built" from chemical reactions
- Animal and vegetable oils also used

Found in minerals, not made of minerals

Most of the starting materials come from crude oil

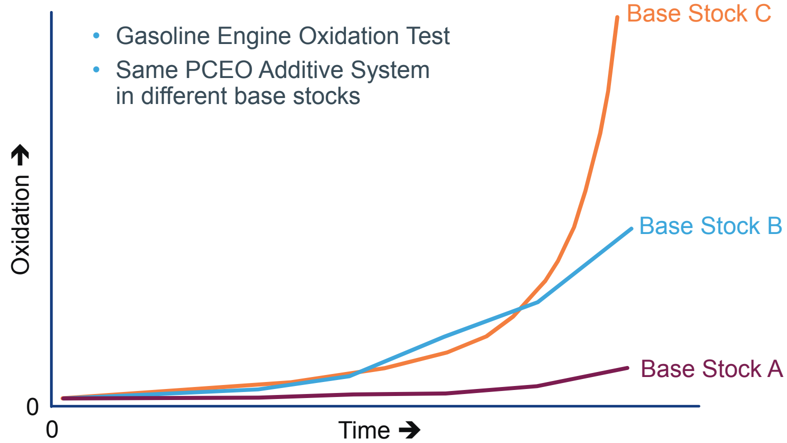
Why are base stocks important?

1. They are the major component in lubricants



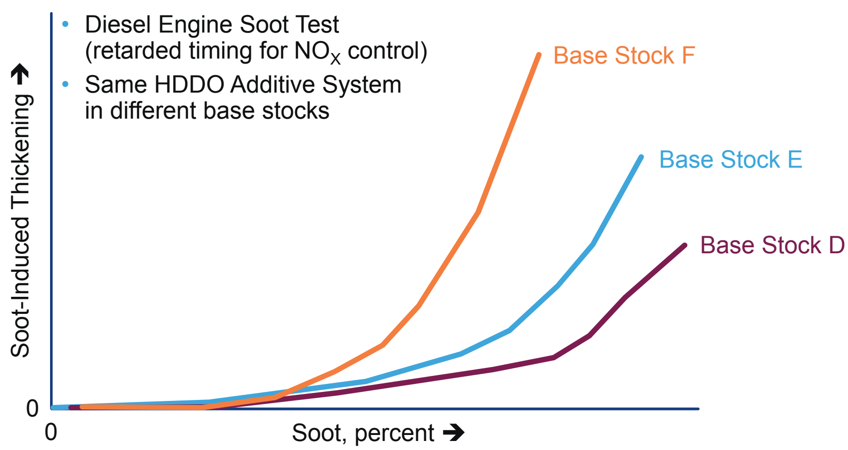
Why are base stocks important?

2. They have a major effect on performance (oxidation)



Why are base stocks important?

3. They have a major effect on performance (soot-handling)



Lubricant properties affected by base stocks

- Viscometrics
  - SAE viscosity grade (*e.g.*, SAE 5W-30)
  - Pour point and low temperature fluidity
  - Fuel economy
  - Wear protection
- Oxidation
  - Viscosity increase
  - Acid formation, that leads to corrosion
  - Deposit control
- Dispersancy and solvency
  - Soot control (HDD)
  - Viscosity increase and filter plugging
  - Sludge
  - Deposit control
- Foaming and air entrainment
- Volatility (evaporation)
  - Oil Consumption and Flash Point

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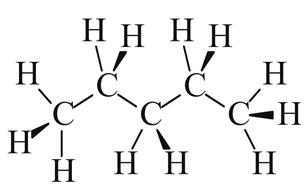
What are base stocks?

- Base stocks are primarily hydrocarbons
  - Hydrocarbon = molecule containing hydrogen and carbon
  - Sometimes generalized to molecules with other elements
- Equivalent chemical symbols:

C_5H_{12} =

(pentane)



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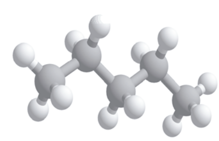

(three-dimensional)

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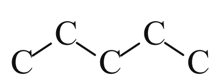

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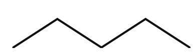

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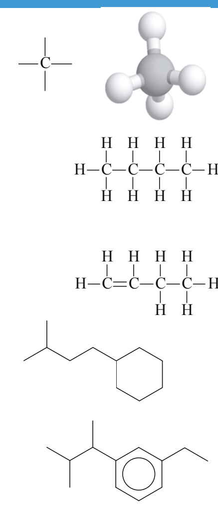
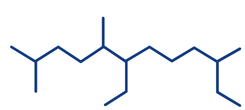
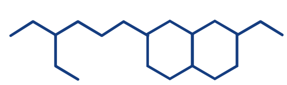
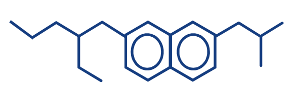
Chemical bonds and terminology

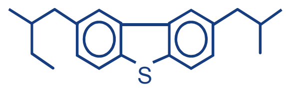
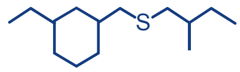
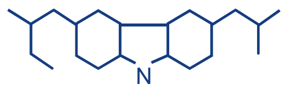
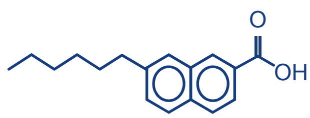
- Carbon likes to have four bonds
  - In three dimensions
- Carbon can form chains (straight or branched)
  - Hydrogen fills in the remaining four spaces
    - All positions filled → relatively unreactive
    - Saturated (paraffin)
- If there's a missing place, a double bond forms
  - Prefer to fill the spaces → more reactive; *e.g.*, oxidation
    - Unsaturated = missing spaces
- Ring structures (saturated)
  - Six-membered rings are common, but others are possible
    - Naphthene (cyclo-alkanes)
- Six-membered rings with three double bonds
  - Lots of empty space → reactive
    - Aromatic



Base stock molecules – hydrocarbons

Type	Structure	Properties
• Saturates		
• Paraffins (no rings) • Straight chain		Very high VI (~175) Excellent oxidation Very high pour point
Best lube molecules → • Branched chain		High VI (~100-150) Good oxidation Medium pour point
• Naphthenes (saturated rings)		Medium VI (~60-110) Poor oxidation Low pour point
• Aromatics (unsaturated rings)		Low VI (<60) Very poor oxidation Low pour point

Base stock molecules – polars

Type	Structure	Properties
• Sulfur		
– Dibenzothiophene		Antioxidant
– Dialkylsulfide		Corrosive
• Nitrogen		
– Alkylhydrocarbazole		Mild pro-oxidant
• Oxygen		
– β-naphthenoic acid		Usually not in base stock (formed during oxidation)

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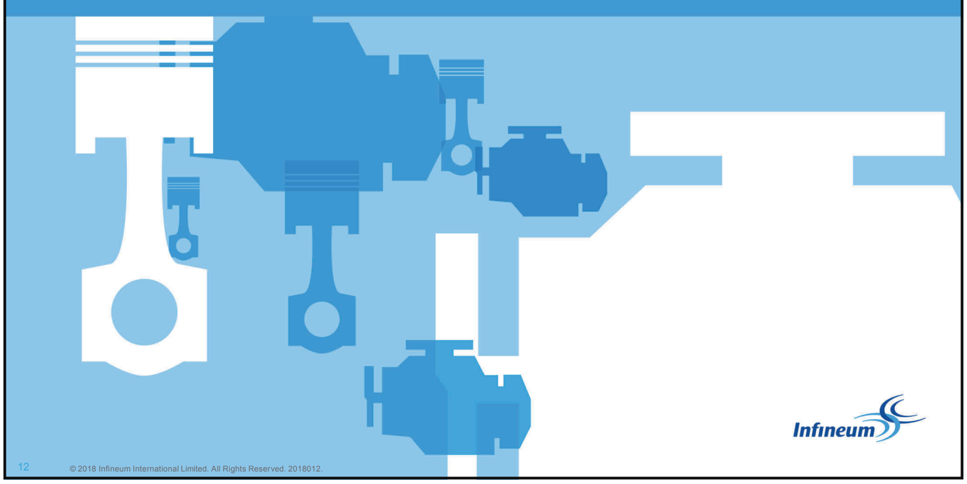
Base stock refining



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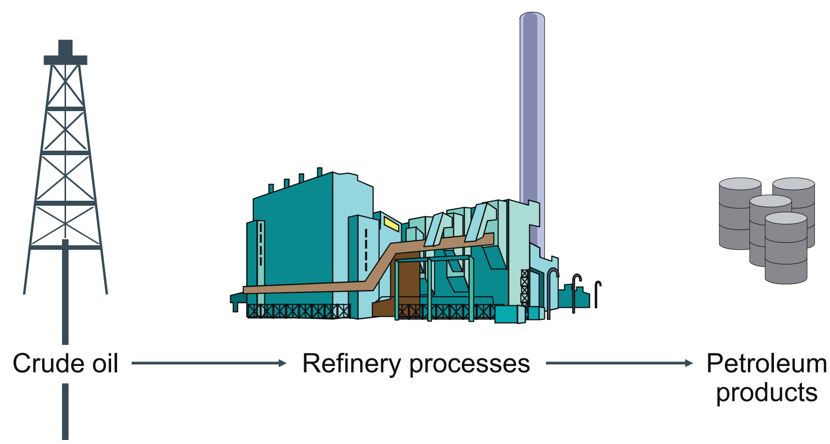
Refinery overview



Crude oil

- Crude oil is a mixture of thousands of different molecules
  - Some are **GOOD** for lubricants – some are **BAD** for lubricants
- Various classifications
  - "Light" *vs*. "Heavy"
  - "Sweet" *vs*. Sour"
  - Paraffinic *vs*. Naphthenic *vs*. Aromatic

Viscosity

Sulfur content

As defined on earlier pages

	Sweet	Sour
Light	West Texas Intermediate (WTI) Brent (North Sea)	Light-Sour Blend (Canada) Arabian Extra Light
Heavy	Cano Limon (Colombia) Minas (Indonesia)	Maya Heavy (Mexico) Merey (Venezuela)

Sources: Shell; Stratas Advisors; Sanford C. Bernstein

Refining in a nutshell

- Start
  - Crude oil
  - Mixtures of **GOOD** and **BAD** molecules
- Goal
  - **REDUCE** the Proportion of **BAD** molecules
  - **INCREASE** the Proportion of **GOOD** molecules
- How Do They Do That?
  - Refining
  - Separation
    - Remove the **BAD** molecules
      - Throw them away?
      - Use them for something else!
  - Conversion
    - Change **BAD** molecules into **GOOD** molecules
  - Synthesis
    - Build **GOOD** molecules from small ones

Solvent Extraction

Hydrocracking

Synthetics

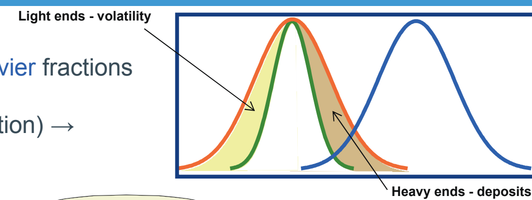
Performance you can rely on.

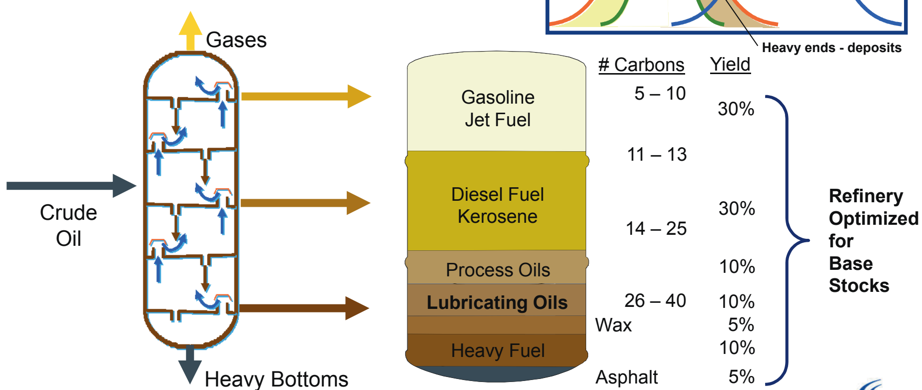
Base stock refinery process overview

- De-salting
  - To avoid corrosion in refinery units
- Distillation
  - Separates lighter from heavier fractions
  - Selects viscosity "cut" and controls volatility (evaporation)
  - Also used at end as a "clean-up" step
- Major Base Stock Refining Process
  - Solvent Extraction
  - Hydrocracking
- De-asphalting
  - Removes asphaltenes (heavy aromatics)
- Dewaxing
  - Removes wax and improves low temperature properties
  - Either solvent dewaxing or catalytic dewaxing or catalytic iso-dewaxing
- Processes are combined to create refinery 'schemes' ➔
  - Optimized based on crude source and refinery assets

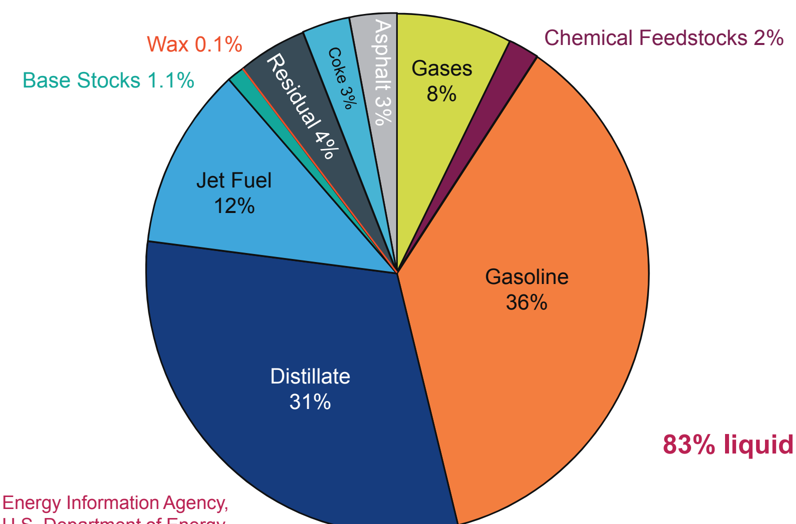
Major base stock refinery processes

- Distillation
  - Separates lighter from heavier fractions
  - Selects viscosity 'cut' →
  - Controls volatility (evaporation) →





U.S. refinery yields



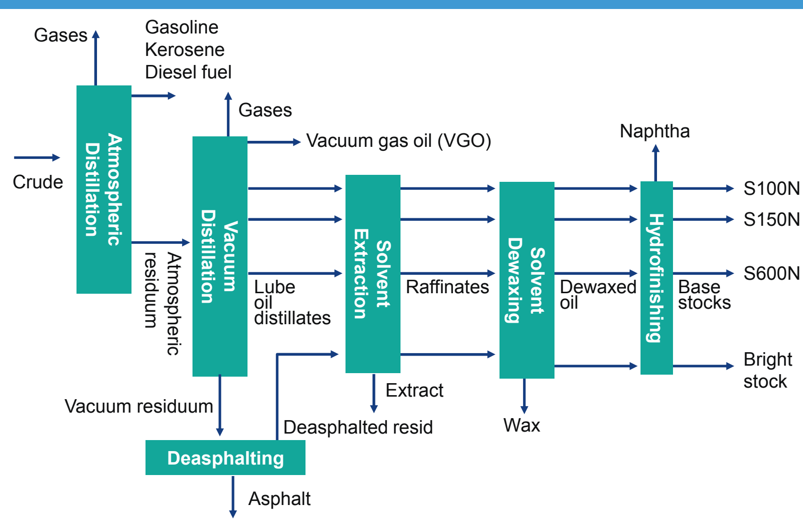
83% liquid fuels

Energy Information Agency, U.S. Department of Energy

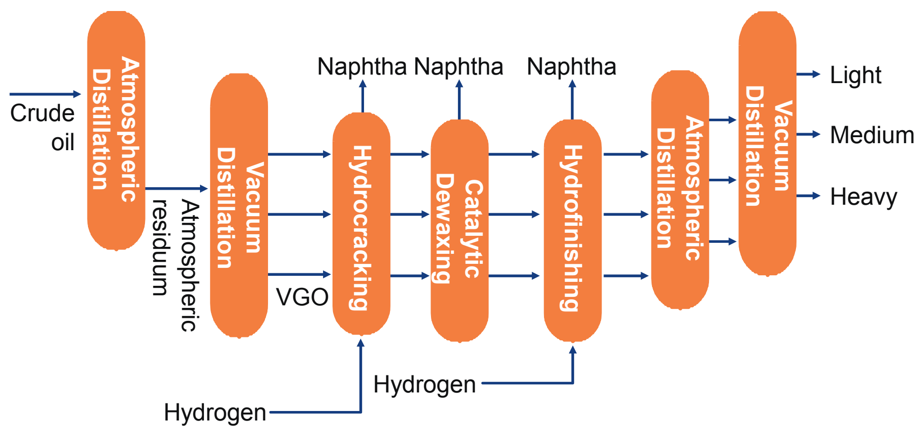
Major base stock refinery processes

- Solvent Extraction (Group I)
  - Separation technology
  - Polar solvent removes aromatics leaving good saturated molecules
  - Removes sulfur, which is predominantly in aromatic molecules
- Hydrocracking (Group II & III)
  - Conversion technology
  - Breaks chemical bonds and adds hydrogen
  - Increases saturates by adding hydrogen
  - Removes sulfur, converting to volatile H_2S
  - Group II *vs* III is a function of feedstock and hydrocracker severity
- Synthesis (Group III, IV, & V)
  - GTL – Gas to Liquid – combine methane (natural gas) into large hydrocarbons
  - PAO – PolyAlphaOlefin – combine small double-bond molecules
  - Esters – Build up specific molecules using various starting molecules

Solvent extraction refinery process



Hydrocracking refinery process



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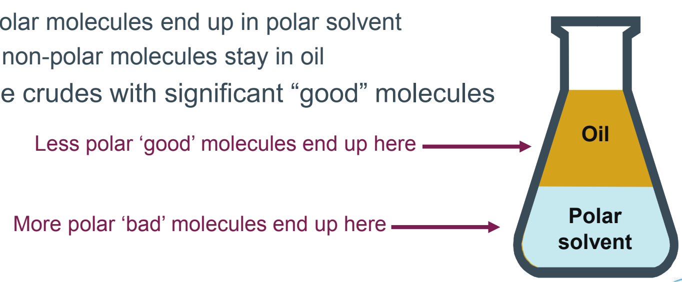
Solvent extraction

- Separation based on solubility
  - "Good" molecules are less polar
    - Straight and branched chain paraffins
    - Naphthenes
  - "Bad" molecules are more polar
    - Aromatics
- Use a polar solvent
  - "Bad" polar molecules end up in polar solvent
  - "Good" non-polar molecules stay in oil
- Must chose crudes with significant "good" molecules

Phenol
Furfural
N-methyl pyrrolidone



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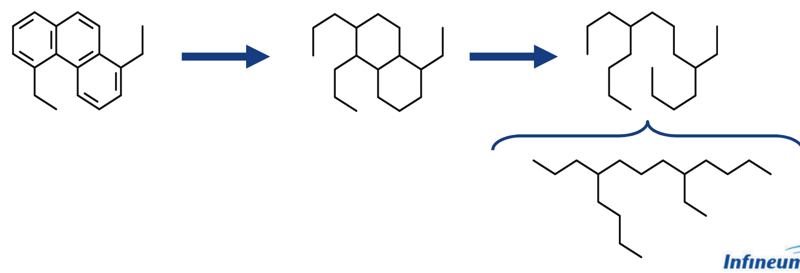
Hydrocracking

- Conversion of "bad" molecules into "good" molecules
  - "Cracking" means breaking apart
  - "Hydro" means adding hydrogen
  - "Hydrocracking" is breaking bonds and adding hydrogen
    - Hydrocracking usually implies high severity
    - Hydrofinishing usually implies low severity
    - Hydrotreatment can mean either



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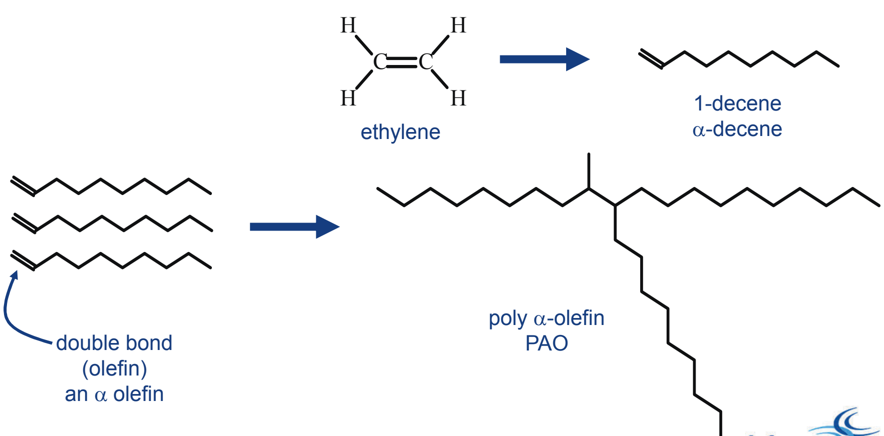
Synthetic process – PAO

- Select small molecules from other refinery streams
- Build up good molecules from the small ones



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Synthetic process – GTL*

- GTL = Gas-to-Liquids
  - Process of turning natural gas into liquid hydrocarbons
  - Primary focus is liquid fuel production, but base stocks can also be made
- Steam-Methane Reforming (SMR) to make "syngas" ← Also other ways to make syngas

$CH_4 + H_2O \rightarrow CO + 3H_2$

$CO + H_2O \rightarrow CO_2 + H_2$

$CH_4 + CO_2 \rightarrow 2CO + 2H_2$

Net Reaction:
$CH_4 + H_2O \rightarrow 2CO + 3H_2$
"Syngas"

- Followed by Fischer-Tropsch synthesis

$nCO + (2n+1)H_2 \rightarrow C_nH_{(2n+2)} + nH_2O$

- GTL base stocks have:
  - Very high saturates and Viscosity Index
  - Essentially no sulfur, nitrogen, aromatics, or olefins
- GTL's meet the chemical and physical definition of API Group III
- A few GTL plants started-up recently
  - A large fuels plant could become largest source of base stock

*"Chemistry and Technology of Lubricants," 3ed., Mortier, Fox, and Orszulik (Eds.), Springer, 2010

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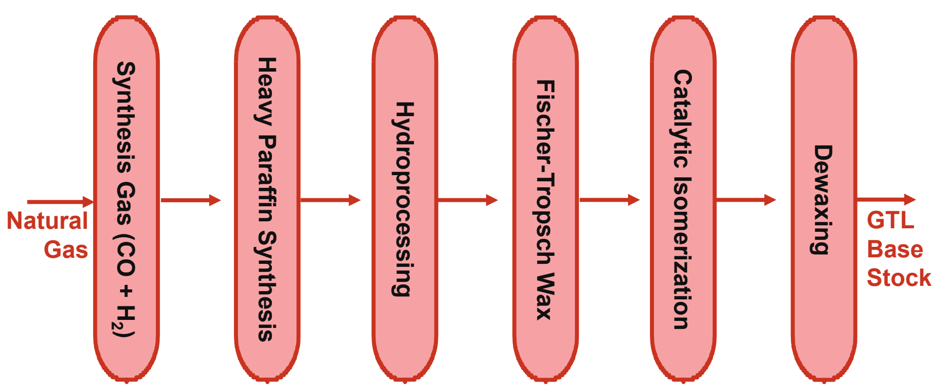
Gas-to-liquids



Source: RPS Energy, Lubes 'n' Greases, May 2014

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Other base stock types (reference)

- Esters
  - Diesters
  - Polyol esters
  - Phosphate esters
- PolyAlkylene Glycol (PAG)
- Alkylated naphthene (AN)
- Polyphenyl ether
- Silicones
- Bio-based
  - Natural oils
  - Chemically-functionalized vegetable oils
  - Biotechnology renewable oils (*e.g.*, from plant sugars *via* algae)
- Many others

Ref: "Synthetics, Mineral Oils, and Bio-Based Lubricants, Chemistry and Technology"
L. R. Rudnick (ed.), CRC Taylor and Francis, 2006

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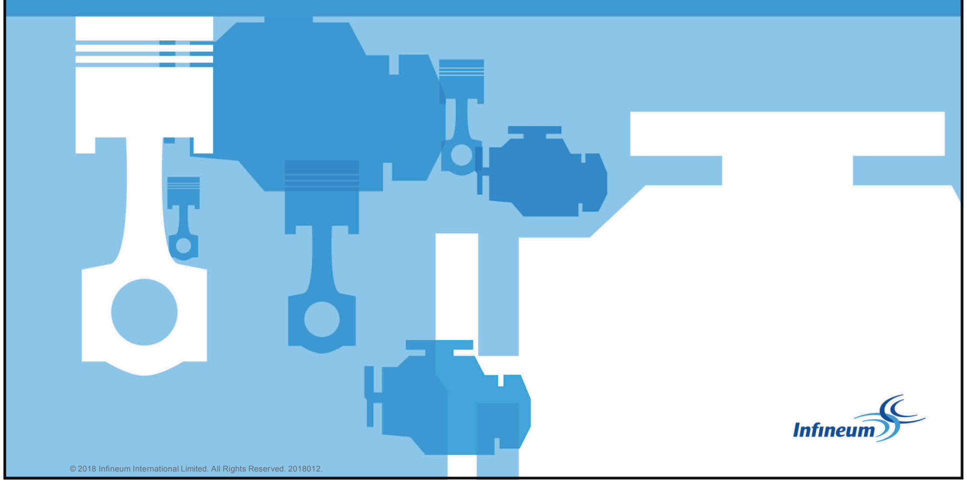
Base stock key inspections



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Key base stock properties – overview

- Viscosity (D445)
  - Sometimes kinematic viscosity at 100°C
    - Examples: HC4, HC6, HC12
  - Sometimes "Neutral Number" – approx. 4.6 times kinematic viscosity at 40°C
    - Examples: S100N, S150N, S600N
  - ISO Grade for Industrial Oils – related to kinematic viscosity (mm^2/s) at 40°C
- Viscosity Index (D2270)
  - Rate of change of viscosity with temperature
- Low temperature properties
  - CCS (D5293), MRV (D4684), SBV (D5133), or Pour point (D97)
- Saturates (D2007)
  - Measure of "stable" vs. "reactive" molecules
  - Intended as an approximation of oxidative stability – Not perfect
- Sulfur (D4294)
  - Corrosive and poison to exhaust catalysts
- Volatility (D5800)
  - Evaporation
- Chemical properties are also very important

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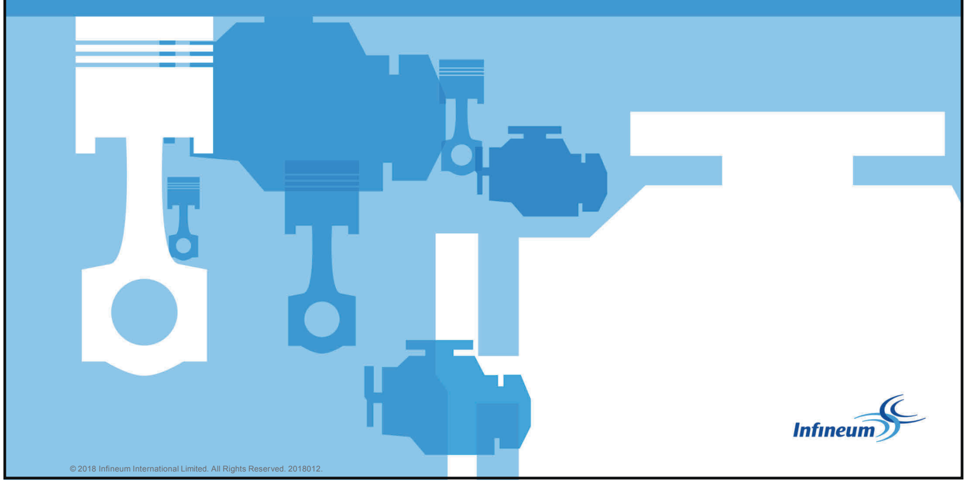
API base oil classification



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Base oil classification

- American Petroleum Institute (API)
  - Trade association of oil companies
- Wanted a way to classify base oils
  - Base oil is a mixture of (one or more) base stocks
- Intended for Base Oil Interchange Guidelines (BOIG)
  - To approve an additive package previously approved in another base oil
    - Using Read-Across
    - More detail in the Specifications and Passenger Car sections
- Now used for marketing, lobbying, and other commercial activities

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API base oil classification

Group	Vis. Index	Saturates		Sulfur	Other
I	80≤ x <120	<90%	and / or	>0.03%	
II	80≤ x <120	≥90%	and	≤0.03%	
II Plus	>about 110				
III	≥120	≥90%	and	≤0.03%	
III Plus	>about 135				
IV					PAO (Poly Alpha Olefins)
V					Everything Else
VI		Europe Only (ATIEL)			PIO (Poly Internal Olefins)

- Companies started using their own (unofficial) marketing phrases
  - “Group II Plus” and “Group III Plus”
  - Now used generally to mean “towards the high end of the group”
- Note: The word ‘Synthetic’ is not part of the API Classification
  - “Synthetic” is a marketing term, not a technical term
  - “Group III” can legally be labeled ‘synthetic’

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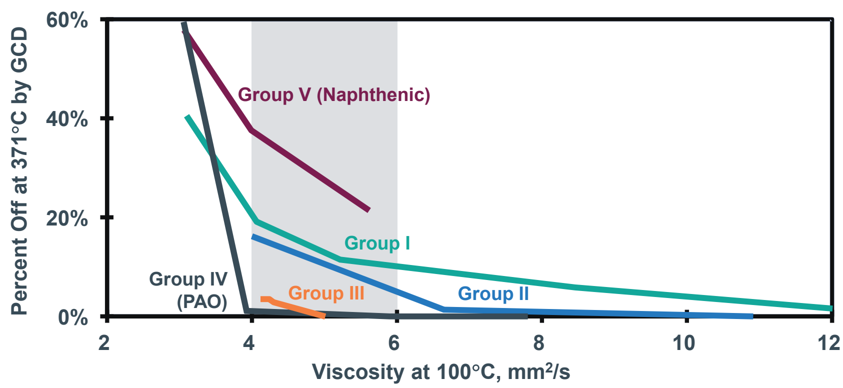
Volatility

- Volatility depends on viscosity and molecular structure
  - Advantages for Group III and Group IV at low viscosity



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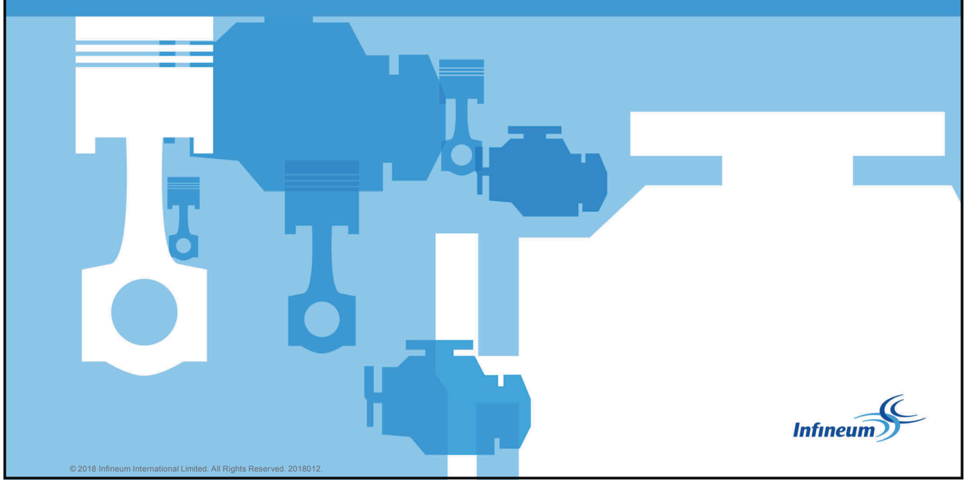
Base stock names and viscosity scales



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Base stock names – API Group I

- Base stock names are brand names
  - Specific to each producing company
  - These are typical naming conventions:
- Solvent xxx Neutral (SxxxN, or SNxxx, or xxxSN, *etc.*)
  - Solvent from "Solvent Extracted"
  - xxx = viscosity
    - Saybolt Universal Seconds at 100°F
    - Approximately 4.6 times mm^2/s at 210F (~100C)
  - Neutral from "Neutralization after Acid Washing"
    - First base stock refining technique
- HVI
  - Redwood Number 1 Seconds at 140°F (European)
- Bright Stock
  - Heaviest grade of base stock (~ S2500N ≈ 650 Redwood)
  - xxx Bright Stock = SUS viscosity at 210°F (*e.g.*, 150 Bright Stock)
    - Approximately 4.6 times mm2/s at 100°F (~40°C)
    - "Bright" because heavy aromatics often fluorescent

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Base stock names – API Groups II, III, IV, & V

- Base stock names are brand names
  - Specific to each producing company
  - These are typical naming conventions:
- HC xxx
  - HydroCracked xxx
    - xxx viscosity usually mm^2/s at 100°C
      - HC4
    - Sometimes equivalent "Neutral Number"
      - HC100
- MVI, HVI, VHVI and XHVI

– Medium Viscosity Index	Naphthenic	(Group V)
– High Viscosity Index	Paraffinic	(Group I)
– Very High Viscosity Index	Hydrocracked	(Group II)
– eXtra High Viscosity Index	Hydrocracked	(Group III)

- PAO x = usually some number related to mm^2/s at 100°C

– PAO 4	4 mm^2/s at 100°C
– PAO 45	4 mm^2/s at 100°C
– PAO 284	4 mm^2/s at 100°C

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Base stock grade equivalents

Grade	SUS* at 100°F	Redwood# at 140°F	mm²/s at 100°C	mm²/s at 40°C
S 75N	75	-	3.1	13
S100N	105	-	4.1	20
S150N	155	-	5.1	30
S325N	330	-	8.5	65
S600N	590	160	12.1	115
150 Bright Stock	2500	650	31.5	5000

150 SUS at 210°F (refers to 31.5 mm²/s at 100°C)

*SUS = Saybolt Universal Seconds
#Approximate

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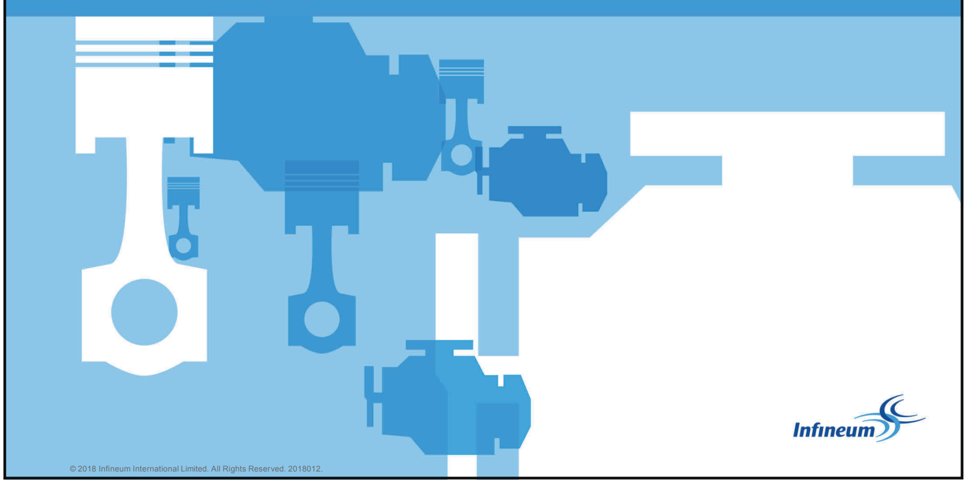
Base stock typical properties



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Typical lube base stock properties (solvent neutrals – API Group I)*

	Light (S100N)	Medium (S150N)	Heavy (S600N)	Bright Stock (S2500N)
Viscosity at 100°C, mm^2/s	4	5	12	32
Viscosity at 40C, mm^2/s	20	30	110	490
Viscosity Index	95	95	95	95
Pour Point, °C	-18	-18	-9	-18
Volatility, GCD % off at 371°C	20	15	0	0
Volatility, NOACK	24	18	2	1
Flash Point, °C	200	210	250	280
Saturates, mass percent	75	75	70	60
Sulfur, mass percent	0.3	0.3	0.4	0.7

*Nominal, and not representative of any particular manufacturer

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Typical lube base stock properties (hydrocracked – API Group II)*

	Light (100N)	Medium (200N)	Heavy (600N)
Viscosity at 100°C, mm^2/s	4	6	12
Viscosity at 40C, mm^2/s	20	40	110
Viscosity Index	100	100	100
Pour Point, °C	-18	-18	-18
Volatility, GCD % off at 371°C	16	2	0
Volatility, NOACK	23	11	2
Flash Point, °C	200	220	250
Saturates, mass percent	95	95	95
Sulfur, mass percent	0.01	0.01	0.01

*Nominal, and not representative of any particular manufacturer

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Performance you can rely on.

Typical lube base stock properties (hydrocracked – API Group III)*

	Light (100N)	Medium (150N)	Heavy (250N)
Viscosity at 100°C, mm^2/s	4	6	8
Viscosity at 40C, mm^2/s	17	33	50
Viscosity Index	130	130	130
Pour Point, °C	-18	-18	-12
Volatility, GCD % off at 371°C			
Volatility, NOACK	13	6	4
Flash Point, °C	240	250	260
Saturates, mass percent	97	97	97
Sulfur, mass percent	0	0	0

*Nominal, and not representative of any particular manufacturer

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Performance you can rely on.

Typical lube base stock properties (GTL – API Group III)*

	Very Light (GTL 3)	Light (GTL 4)	Medium (GTL 6)	Heavy (GTL 8)
Viscosity at 100°C, mm^2/s	3	4	6	8
Viscosity at 40C, mm^2/s	11	17	32	46
Viscosity Index	120	130	135	145
Pour Point, °C	-42	-33		-24
Volatility, GCD % off at 371°C		3	0.6	0
Volatility, NOACK	34	9	3	1
Flash Point, °C	200	230	240	270
Saturates, mass percent	98	97	97	96
Sulfur, mass percent	0	0	0	0

*Nominal, and not representative of any particular manufacturer

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Typical lube base stock properties (PAO – API Group IV)*

	Light (PAO 4)	Medium (PAO 6)	Heavy (PAO 10)	Very Heavy (PAO 100)
Viscosity at 100°C, mm^2/s	4	6	10	100
Viscosity at 40C, mm^2/s	18	30	65	1300
Viscosity Index	130	135	130	160
Pour Point, °C	-63	-63	-51	-30
Volatility, GCD % off at 371°C	1	0	0	0
Volatility, NOACK	12	2	1	1
Flash Point, °C	200	240	270	290
Saturates, mass percent	96	96	96	94
Sulfur, mass percent	0	0	0	0

*Nominal, and not representative of any particular manufacturer

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Performance you can rely on.

Base stock recent trends

- Transition from API Group I to Group II continuing
  - Demand for higher quality (oxidation, dispersancy, *etc.*)
  - Specifications with sulfur restrictions
  - Demand for lower volatility in lower viscosity grades
- API Group I base stocks still have uses
  - Higher viscosity: Marine, railroad, gear oils
  - Lower viscosity: Transformer oils, process oils, spray oils
- Demand for API Group III (and Group III Plus) will increase
  - Growth of SAE 0W-xx and 5W-xx grades
- PAO capacity expected to increase
- Green base stocks are niche for now
  - Re-refined (derived from used oil re-cycling)
  - Bio-lubricants (derived from sugarcane, algae, *etc.*)

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Base stock summary

- Base stocks are the main component in lubricants
  - Have a significant effect on performance
- Base stocks are complex mixtures of molecules
  - Derived from crude oil by refinery processes
- Chemical composition determines performance
  - Saturates and sulfur usually most important, but not the whole story
- Physical properties are also important
  - Viscosity, Viscosity Index, pour point, volatility
- Performance testing of products still required
  - Compositional effects not well enough known
  - Additives are a major factor in finished products
  - API BOIG's are used to read-across testing
- Base stock research continuing
  - Develop better analytical test methods
  - Improve performance predictions
  - Demand for higher quality expected to continue

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