Lubricant base stocks
Outline

• What are base stocks?
  – Why are base stock important?
  – Key properties 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
Lubricant base stocks

• A lubricant component
  – Roughly 80-99+% of petroleum products
    • Usually doesn’t have all required properties
    • Additives are used to enhance and customize properties

• Mineral oil base stocks
  – Refined from crude oil
    • Petroleum = “Petra-oleum” = “Rock Oil”
  – Common processes
    • Solvent extraction
      – Separate “good” from “bad” molecules
    • Hydrocracking
      – Convert “bad” molecules into “good” molecules
    • Synthesis
      – “Built” from chemical reactions

• Animal and vegetable oils also used
Why are base stocks important?

1. They are the major component in lubricants

<table>
<thead>
<tr>
<th>Product Type</th>
<th>Base Stock Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial</td>
<td>~98 – 100% base stock</td>
</tr>
<tr>
<td>PCEO</td>
<td>~80 – 90% base stock</td>
</tr>
<tr>
<td>HDDO</td>
<td>~75 – 85% base stock</td>
</tr>
<tr>
<td>Marine</td>
<td>~65 – 80% base stock</td>
</tr>
</tbody>
</table>

Additives
Why are base stocks important?

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

- Gasoline Engine Oxidation Test
- Same PCEO Additive System in different base stocks
Why are base stocks important?

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

- Diesel Engine Soot Test (retarded timing for NO\textsubscript{X} control)
- Same HDDO Additive System in different base stocks

![Graph showing soot-induced thickening for different base stocks](image)
Lubricant properties affected by base stocks

- **Viscometrics**
  - SAE viscosity grade (e.g., SAE 5W-30)
  - Viscosity Index
  - 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
Key base stock properties

- **Viscosity**
  - Sometimes kinematic viscosity at 100°C: HC 4, HC 6, HC 12
  - Sometimes “Neutral Number”: S150N, S600N
  - ISO Grade for Industrial Oils – related to kinematic viscosity (mm²/s) at 40°C
  - Low temperature: CCS (D5293), MRV (D4684), SBV (D5133), Pour Point (D97)

- **Viscosity Index**
  - Rate of change of viscosity with temperature
  - Arbitrary scale defined by ASTM “Table Look-up”

- **Saturates**
  - Measure of “stable” vs. “reactive” molecules
  - Intended as an approximation of oxidative stability – Not perfect

- **Sulfur**
  - Corrosive and poison to exhaust catalysts

- **Volutility**
  - Evaporation

- **Chemical properties are also very important**
  - More difficult to measure and specify
Base stock refining
Refinery overview

Crude oil ➔ Refinery processes ➔ Petroleum products
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

• Using Refining processes:
  – 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

• Other processing steps involved
  – Not covered today
Major base stock refinery processes – 1

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

Diagram:
- Crude Oil
- Gases
- Heavy Bottoms
- # Carbons: 5 – 10 (30% yield), 11 – 13 (30% yield), 14 – 25 (10% yield), 26 – 40 (10% yield)
- Yield:
  - Diesel Fuel: 30%
  - Kerosene: 30%
  - Process Oils: 10%
  - Lubricating Oils: 10%
  - Heavy Fuel: 10%
  - Wax: 5%
  - Asphalt: 5%

Refinery Optimized for Base Stocks
U.S. refinery yields

Major base stock refinery processes – 2

• **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 \( \text{H}_2\text{S} \)
  – 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
Solvent extraction refinery process

- **Crude**
  - Gases
  - Gasoline
  - Kerosene
  - Diesel fuel
  - Atmospheric Distillation
  - Vacuum Distillation
  - Atmospheric residuum
  - Vacuum residuum
  - Deasphalting
  - Asphalt

- **Vacuum gas oil (VGO)**
  - Lube oil distillates
  - Solvent Extraction
  - Raffinates
  - Extract
  - Deasphalted resid

- **Naphtha**
  - S100N
  - S150N
  - S600N
  - Hydrofinishing
  - Base stocks
  - Bright stock
  - Dewaxed oil
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
Hydrocracking
Hydrocracking refinery process

Crude oil

Atmospheric Distillation

Vacuum Distillation

Atmospheric residuum

Hydrocracking

Naphtha

Hydrogen

Naphtha Naphtha

Catalytic Dewaxing

Hydrofinishing

Naphtha

Hydrogen

Vacuum Distillation

Atmospheric Distillation

Light

Medium

Heavy

VGO
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

![Chemical diagram showing the transformation of molecules through hydrocracking process.](attachment:image.png)
Synthetics
Synthetic process – PAO

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

![Diagram showing the synthetic process of PAO](image)

- Ethylene is used as the starting material.
- 1-decene is formed by building up from ethylene.
- Poly α-olefin PAO is created by further polymerizing the α-olefin.

**Chemical Structures:**
- Ethylene: $\text{H}_2\text{C}≡\text{C}\text{H}_2$
- 1-decene: $\text{H}_2\text{C}_9\text{H}_{16}$
- Poly α-olefin PAO: A polymer chain with multiple α-olefin units.
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”**
  - \( \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \)
  - \( \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \)
  - \( \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \)
  - Also other ways to make syngas

- Followed by Fischer-Tropsch synthesis
  - \( n\text{CO} + (2n+1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{(2n+2)} + n\text{H}_2\text{O} \)

- **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 supplying**
  - A large fuels plant could become largest source of base stock

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

Natural Gas → Synthesis Gas (CO + H₂) → Heavy Paraffin Synthesis → Hydroprocessing → Fischer-Tropsch Wax → Catalytic Isomerization → Dewaxing → GTL Base Stock

Source: RPS Energy, Lubes ‘n’ Greases, May 2014
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
API base oil classification
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
## API base oil classification

<table>
<thead>
<tr>
<th>Group</th>
<th>Vis. Index</th>
<th>Saturates</th>
<th>Sulfur</th>
<th>Other Properties</th>
</tr>
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<tbody>
<tr>
<td>I</td>
<td>$80 \leq x &lt; 120$</td>
<td>$&lt;90%$     and / or $&gt;0.03%$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>$80 \leq x &lt; 120$</td>
<td>$\geq90%$ and</td>
<td>$\leq0.03%$</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>$\geq120$</td>
<td>$\geq90%$ and</td>
<td>$\leq0.03%$</td>
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</tr>
<tr>
<td>IV</td>
<td></td>
<td></td>
<td></td>
<td>PAO (Poly Alpha Olefins)</td>
</tr>
<tr>
<td>V</td>
<td></td>
<td></td>
<td></td>
<td>Everything Else</td>
</tr>
</tbody>
</table>

- 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’
Volatileit

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

![Graph showing volatility vs. viscosity at 100°C](image)
Base stock names
Base stock names – API Group I

- Base stock names are brand names
  - These are some typical naming conventions:
- **Solvent xxx Neutral (SxxxxN, or SNxxx, or xxxSN, etc.)**
  - Solvent from “Solvent Extracted”
  - xxx = viscosity
    - Saybolt Universal Seconds at 100°F
    - Approximately 4.6 times mm²/s at 40°C
  - Neutral from “Neutralization after Acid Washing”
    - First base stock refining technique
- **HVI**
  - Redwood Number 1 Seconds at 140°F (European)
- **Descriptions**
  - Light, Medium, Heavy
- **Bright Stock**
  - Heaviest grade of base stock (~ S2500N)
  - xxx Bright Stock = SUS viscosity at 210°F
    - Approximately 4.6 times mm²/s at 100°C
  - “Bright” because heavy aromatics often fluorescent

<table>
<thead>
<tr>
<th>Base Stock Name</th>
<th>Viscosity at 100°C</th>
<th>Viscosity at 40°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>S150N</td>
<td>~32 mm²/s</td>
<td>~5 mm²/s</td>
</tr>
<tr>
<td>HVI 150</td>
<td>~11 mm²/s</td>
<td></td>
</tr>
<tr>
<td>150 Bright Stock</td>
<td>~32 mm²/s</td>
<td></td>
</tr>
</tbody>
</table>
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 mm²/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 mm²/s at 100°C
  – PAO 4  Usually 4 mm²/s at 100°C
  – PAO 45  Could be 4.5 or 45 mm²/s at 100°C
  – PAO 954  Could be 4 or 54 or 95.4 mm²/s at 100°C

S150N
~5 mm²/s at 100°C

HVI 150
~11 mm²/s at 100°C

150 Bright Stock
~32 mm²/s at 100°C

PAO 150
~150 mm²/s at 100°C
## Base stock grade equivalents

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

*SUS = Saybolt Universal Seconds  
#Approximate

150 SUS at 210°F
Base stock typical properties
Typical lube base stock properties (solvent neutrals – API Group I)*

<table>
<thead>
<tr>
<th></th>
<th>Light (S100N)</th>
<th>Medium (S150N)</th>
<th>Heavy (S600N)</th>
<th>Bright Stock (S2500N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity at 100°C, mm²/s</td>
<td>4</td>
<td>5</td>
<td>12</td>
<td>32</td>
</tr>
<tr>
<td>Viscosity at 40°C, mm²/s</td>
<td>20</td>
<td>30</td>
<td>110</td>
<td>490</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>95</td>
<td>95</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>Pour Point, °C</td>
<td>-18</td>
<td>-18</td>
<td>-9</td>
<td>-18</td>
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<tr>
<td>Volatility, GCD % off at 371°C</td>
<td>20</td>
<td>15</td>
<td>0</td>
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<tr>
<td>Volatility, NOACK</td>
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<td>2</td>
<td>1</td>
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<tr>
<td>Flash Point, °C</td>
<td>200</td>
<td>210</td>
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<tr>
<td>Saturates, mass percent</td>
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<td>70</td>
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<td>Sulfur, mass percent</td>
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<td>0.3</td>
<td>0.4</td>
<td>0.7</td>
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</tbody>
</table>

*Nominal, and not representative of any particular manufacturer.
## Typical lube base stock properties (hydrocracked – API Group II)*

<table>
<thead>
<tr>
<th>Property</th>
<th>Light (100N)</th>
<th>Medium (200N)</th>
<th>Heavy (600N)</th>
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</thead>
<tbody>
<tr>
<td>Viscosity at 100°C, mm²/s</td>
<td>4</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>Viscosity at 40°C, mm²/s</td>
<td>20</td>
<td>40</td>
<td>110</td>
</tr>
<tr>
<td>Viscosity Index</td>
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<td>100</td>
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<tr>
<td>Pour Point, °C</td>
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<td>-18</td>
<td>-18</td>
</tr>
<tr>
<td>Volatility, GCD % off at 371°C</td>
<td>16</td>
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<tr>
<td>Volatility, NOACK</td>
<td>23</td>
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<tr>
<td>Flash Point, °C</td>
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<td>Saturates, mass percent</td>
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<td>Sulfur, mass percent</td>
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<td>0.01</td>
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*Nominal, and not representative of any particular manufacturer
## Typical lube base stock properties (hydrocracked – API Group III)*

<table>
<thead>
<tr>
<th>Property</th>
<th>Light (100N)</th>
<th>Medium (150N)</th>
<th>Heavy (250N)</th>
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<tbody>
<tr>
<td>Viscosity at 100°C, mm²/s</td>
<td>4</td>
<td>6</td>
<td>8</td>
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<tr>
<td>Viscosity at 40°C, mm²/s</td>
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<td>33</td>
<td>50</td>
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<tr>
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<tr>
<td>Pour Point, °C</td>
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<td>-18</td>
<td>-12</td>
</tr>
<tr>
<td>Volatility, GCD % off at 371°C</td>
<td>13</td>
<td>6</td>
<td>4</td>
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<td>250</td>
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<tr>
<td>Sulfur, mass percent</td>
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*Nominal, and not representative of any particular manufacturer
## Typical lube base stock properties (GTL – API Group III)*

<table>
<thead>
<tr>
<th></th>
<th>Very Light (GTL 3)</th>
<th>Light (GTL 4)</th>
<th>Medium (GTL 6)</th>
<th>Heavy (GTL 8)</th>
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<tbody>
<tr>
<td>Viscosity at 100°C, mm²/s</td>
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<td>4</td>
<td>6</td>
<td>8</td>
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<tr>
<td>Viscosity at 40°C, mm²/s</td>
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<td>17</td>
<td>32</td>
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<td>Viscosity Index</td>
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<td>145</td>
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<td>-33</td>
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<tr>
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<td>1</td>
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*Nominal, and not representative of any particular manufacturer
## Typical lube base stock properties

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

<table>
<thead>
<tr>
<th></th>
<th>Light (PAO 4)</th>
<th>Medium (PAO 6)</th>
<th>Heavy (PAO 10)</th>
<th>Very Heavy (PAO 100)</th>
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<td>100</td>
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<tr>
<td>Viscosity at 40°C, mm²/s</td>
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<td>30</td>
<td>65</td>
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<td>Viscosity Index</td>
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<td>160</td>
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<td>-51</td>
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<td>Volatility, NOACK</td>
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<td>1</td>
<td>1</td>
</tr>
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<td>Flash Point, °C</td>
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<td>270</td>
<td>290</td>
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<td>96</td>
<td>96</td>
<td>94</td>
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<tr>
<td>Sulfur, mass percent</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Nominal, and not representative of any particular manufacturer
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
- Supply-Demand imbalance in many regions
- 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.)
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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