Lubricant Base Stocks
Outline

- Introduction
- Why are base stocks important?
- Basic chemistry
- Properties of base stocks
- Base stock classification
- Refinery processes
- Synthetic base stocks
- Drivers and Market Trends
Introduction

• Base stocks are the main component in lubricants

• Base stocks exhibit certain properties that impact how the lubricant performs in the engine
  – Base stocks are not all the same and these properties can vary enormously from base stock to base stock
  – Important when designing lubricant formulations but not always easy to understand and interpret

• Additives are used to enhance the performance of the base stock and to impart additional beneficial properties onto the lubricant
Why are Base Stocks Important?

- It is the major component in lubricants
- Amount varies from segment to segment

![Graph showing the component and additive ratio for different product types (Industrial, PCEO, HDDO, Marine).]
Why are Base Stocks Important?

- Base stocks can have a major effect on performance
- Some of these effects can be overcome by additive selection

Diagram:
- Base Stock
  - Sludge
  - Fuel Economy
  - Low Temperature Pumpability
  - Volatility
  - Deposits
  - Soot Handling
  - Wear Protection
  - Oxidation
## Basic Chemistry of Base Stocks

<table>
<thead>
<tr>
<th>Type</th>
<th>Example Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Saturates</strong></td>
<td></td>
</tr>
<tr>
<td>Paraffinic Straight Chain</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>Paraffinic Branched Chain</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>Naphthenic</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td><strong>Unsaturates</strong></td>
<td></td>
</tr>
<tr>
<td>Olefin</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>Aromatic</td>
<td><img src="image5" alt="Structure" /></td>
</tr>
<tr>
<td><strong>Polar Constituents</strong></td>
<td></td>
</tr>
<tr>
<td>Sulphur Containing</td>
<td><img src="image6" alt="Structure" /></td>
</tr>
<tr>
<td>Nitrogen Containing</td>
<td><img src="image7" alt="Structure" /></td>
</tr>
</tbody>
</table>
Properties of Base Stocks
Key Base Stock Properties

- Viscosity and Viscosity Index
- Pour Point
- NOACK Volatility
- Sulphur Content
- Saturates
- Nitrogen Content
- Other Properties

Key Base Stock Properties

Performance you can rely on.
Viscosity

- Dependent upon distillation conditions
- Different measures depending on temperature and amount of shear

<table>
<thead>
<tr>
<th>Cold Cranking Simulator (CCS)</th>
<th>High Temperature High Shear (HTHS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pumpability via Mini Rotary Viscometer (MRV)</td>
<td>Kinematic Viscosity (kV)</td>
</tr>
</tbody>
</table>

Impact on engine performance:
Fuel Economy
Wear
Viscosity Index (VI)

- Base stocks become thinner with increasing temperature
- The higher the VI the less the base stock thins
- Flexible molecules have high VI
  - Change configuration with temperature

![Graph showing viscosity index change with temperature](image-url)
NOACK Volatility

- Measures the evaporative loss
- Dependent on small molecule content of the base stock (“light ends”)

Impact on engine performance:
- Oil Consumption
- Deposits

Wider distribution means there are more small molecules and higher volatility
Pour Point

• Defined as the temperature at which the base stock becomes semi-solid and loses its flow characteristics
  – Related to melting point
  – Effect is seen in low temperature crystallisation
• Depends on the level of rings and branching relative to straight chain paraffins; base stocks with high levels of rings and branching tend to have lower pour points

Impact on engine performance: Low Temperature Pumpability
Saturates

- Dependent upon processing conditions
- Level of saturates impacts
  - Susceptibility of the base stock to undergo oxidation
  - Solvency and additive compatibility

Impact on engine performance:
- Oxidation
- Seals Compatibility
Sulphur and Nitrogen Content

- Dependent upon processing conditions
- Sulphur is a natural antioxidant
- Nitrogen is a natural pro-oxidant

Impact on engine performance:
- Oxidation
- Viscosity Increase
# Other Properties

<table>
<thead>
<tr>
<th>Test</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline point</td>
<td>Lowest T at which aniline and mineral base oil are miscible; indicator of base oil composition/solubility</td>
</tr>
<tr>
<td>Demulsibility</td>
<td>A measure of a fluid’s ability to separate from water</td>
</tr>
<tr>
<td>MRV</td>
<td>Mini-Rotary Viscosity – High shear viscosity test</td>
</tr>
<tr>
<td>kV</td>
<td>Kinematic Viscosity – Low shear viscosity test</td>
</tr>
<tr>
<td>End point</td>
<td>Highest vapour T during distillation</td>
</tr>
<tr>
<td>Flash point</td>
<td>Temperature at which vapors can ignite</td>
</tr>
<tr>
<td>Colour</td>
<td>Indicator of refining</td>
</tr>
<tr>
<td>Cloud Point</td>
<td>Temperature at which wax crystals precipitate</td>
</tr>
<tr>
<td>Carbon Residue</td>
<td>Coked material remaining after base oil has been exposed to high temperatures</td>
</tr>
<tr>
<td>Density</td>
<td>Indicator of base oil composition</td>
</tr>
</tbody>
</table>
Base Stock Classification
API Base Stock Classification

Base stocks are classified according to their properties and the saturate and sulphur content

<table>
<thead>
<tr>
<th>Group</th>
<th>Viscosity Index</th>
<th>Saturates</th>
<th>Sulphur</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$80 \leq x &lt; 120$</td>
<td>&lt; 90%</td>
<td>and/or</td>
<td>&gt; 0.03%</td>
</tr>
<tr>
<td>II</td>
<td>$80 \leq x &lt; 120$</td>
<td>≥ 90%</td>
<td>and</td>
<td>≤ 0.03%</td>
</tr>
<tr>
<td>III</td>
<td>≥ 120</td>
<td>≥ 90%</td>
<td>and</td>
<td>≤ 0.03%</td>
</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>
Group II+ and Group III+ Base Stocks

- Each of the API base stock Groups cover a broad range of properties

- Different base stocks within the same Group can have very different properties

- The terms Group II+ and Group III+ describe base stocks with a viscosity index that is higher in the range for their Group
  - This is a marketing term with no formal definition

- Generally:
  - For Group II+ base stocks: VI > 110
  - For Group III+ base stocks: VI > 130
## Comparison of Base Stock Groups

<table>
<thead>
<tr>
<th>Group</th>
<th>Saturates</th>
<th>Sulphur Content</th>
<th>Volatility</th>
<th>Oxidative Stability</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Low</td>
<td>High</td>
<td>High</td>
<td>Variable</td>
<td>Low</td>
</tr>
<tr>
<td>II</td>
<td>High</td>
<td>Low</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
</tr>
<tr>
<td>III*</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
<td>Medium</td>
</tr>
<tr>
<td>IV</td>
<td>Very High</td>
<td>Very Low</td>
<td>Very Low</td>
<td>Very High</td>
<td>High</td>
</tr>
<tr>
<td>V**</td>
<td>Very High</td>
<td>Very Low</td>
<td>Very Low</td>
<td>Variable</td>
<td>High</td>
</tr>
</tbody>
</table>

* Includes GTL
** Polyol ester used to improve polarity
Selecting a Base Stock

- When selecting a base stock for a formulation the properties and cost of the base stock need to be considered.
- Base stocks will be selected in order to meet viscometric and volatility requirements.

- Better high temperature viscometrics without low temperature viscosity increase.
- Thinner oils can be blended whilst maintaining volatility.
Refinery Processes
Refinery Overview

Crude oil → Refinery processes → Petroleum products
Crude Selection

- Each crude source has a different composition
  - Hydrocarbons
  - Sulphur compounds
  - Nitrogen compounds
  - Others

- Availability of various crudes
  - Determined by economics
    - Supply vs. demand
    - Fuel economics may be overriding
  - Political considerations may be important
Refining Process

Crude Oil

Vacuum Distillation

Solvent Extraction → Solvent Dewaxing → Hydro-finishing → Group I Base stocks

Hydro-cracking → Catalytic Dewaxing → Hydro-finishing → Distillation → Group II Base stocks

Hydro-isomerisation → Catalytic Dewaxing → Hydro-finishing → Distillation → Group III Base stocks
Vacuum Distillation

- Distillation
  - Separates lighter from heavier fractions
  - Selects viscosity “cut”
  - Controls volatility (evaporation)
Solvent Extraction

- Separation based on solubility
- Uses a polar solvent to remove less desirable molecules
  - Aromatics
- The more desirable molecules remain in the oil
  - Straight and branched chain paraffins
  - Naphthenes

![Diagram of solvent extraction process]

Less polar molecules end up here

More polar molecules end up here
Refining Process

Crude Oil → Vacuum Distillation → Hydro-cracking → Catalytic Dewaxing → Hydro-finishing

Group I Base stocks

Group II Base stocks

Group III Base stocks
Solvent Dewaxing and Hydrofinishing

Solvent Dewaxing

- Reduces the pour point and viscosity index of the base oil by removing wax
- Separation is based on solubility
- Wax is less soluble in solvent than oil
  - Oil and solvent mixture is chilled
  - Wax is filtered out at low temperature

Hydrofinishing

- Improves colour stability and acidity of the base oil
  - Sulphur, nitrogen, oxygen removed as H₂S, NH₃ and H₂O
  - Slight hydrogenation of unsaturated compounds
- Oil is contacted with hydrogen at about 600 psi and 250 – 320 °C
Refining Process

Crude Oil → Vacuum Distillation → Hydro-cracking → Solvent Extraction → Solvent Dewaxing → Hydro-finishing → Group I Base stocks

Hydro-isomerisation → Catalytic Dewaxing → Hydro-finishing → Distillation → Group II Base stocks

Hydro-finishing → Distillation → Group III Base stocks
Hydrocracking

• Conversion of unsaturated and aromatic molecules which are less desirable into more desirable saturated chains
  – ‘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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Hydroisomerisation

- Rearrangement of linear chains to branched chains
  - I.e. transforming wax to iso-paraffins
- Improves the VI of a base stock
- The process varies for each manufacturer and therefore the properties of Group III base stocks can also be quite different
Refining Process

Crude Oil → Vacuum Distillation → Hydro-cracking → Catalytic Dewaxing → Hydro-finishing → Group I Base stocks

Crude Oil → Vacuum Distillation → Hydro-isomerisation → Catalytic Dewaxing → Hydro-finishing → Distillation → Group II Base stocks

Crude Oil → Vacuum Distillation → Hydro-isomerisation → Catalytic Dewaxing → Hydro-finishing → Distillation → Group III Base stocks
Synthetic Base Stocks
Synthetic Base Stocks

- Group I, Group II and Group III base stocks that are manufactured by refining processes are referred to as ‘mineral’ base stocks.
- The term ‘synthetic’ is used to describe lubricants that have been processed.
  - This includes Group IV base stocks.
- ‘Synthetic’ is also used when marketing Group III base stocks that have been severely hydrocracked.
- ‘Semi-synthetic’ is a marketing term that does not necessarily reflect base stock quality.
Gas to Liquids (GTL)

- Processed from Natural Gas
- Performance Comparable to Group III / IV base stocks:
  - High VI (140+)
  - Low Noack volatility
  - Low pour point
  - Stable
  - High Saturates
  - No Sulphur or Nitrogen
- Classed as Group III by API definition
  - But it would be a “synthetic base oil” in all markets!
- First used by Shell from 1994
- Other oil companies now investing in GTL production
- Large initial investment but production cost comparable to Group II
Refinery Process for GTL

- GTL is produced by reacting the low molecular weight materials found in natural gas to form higher molecular weight materials.

  - Process is well controlled and can be adjusted to make different molecular structures with predictable properties.

  - Makes normal paraffins

  - Obtain desired molecular weight and structure

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Synthetic Process - PAO

- Poly alpha-olefins (PAO) are manufactured from linear alpha olefins (typically 1-decene)
- They have a branched paraffinic structure leading to desirable properties
  - High VI, low NOACK, good oxidative stability
- The process is very controlled leading to narrow properties
Group V Base Stocks

• Group V is defined as ‘Everything else’ not classified in the other API groups
• Versatile, custom made for specialised applications
• Examples of Group V Base Stocks are:
  • Di-Esters
    – Industrial applications are highest growth
    – Competitive with PAO in performance attributes
  • Polyol Esters
    – High-temperature applications
    – More costly than PAO, di-esters
  • Phosphoric Acid Esters
    – Used in fire resistant fluids
  • Silicone Oils
    – Used as heat transfer oils
Performance you can rely on.

Re-refining

- Used motor oil
- Used additives/contaminants

- Processing is very similar to conventional processes
  - Solvent Extraction
  - Hydrocracking

- Quality depends on
  - Starting material
  - Processes
  - Desired targets

  Just like conventional base stocks!

- Possible to make Group I and Group II base stocks with re-refining

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Drivers and Market Trends
Many of the main drivers for lubricant performance result in a need for improved base stock quality.

Drivers:
- Extended ODIs
- Aftertreatment Compatibility
- Fuel Economy
- Marketing Advantage

Improved Base Stock Quality

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Trend in Base Stock Demand

- Decline in demand for Group I base stocks
- Increase in demand for higher quality Group II and Group III base stocks

Source: Kline, 2013
Trends in Group III Base Stocks

- There has been an increase in Group III capacity from 2011 – 2017
- Largest proportion of Group III production is in Asia and Europe / Middle East
- There is potential for further investment in USA and Russia
Trends in Group IV Base Stocks

- The PAO market is < 2% of the total base stock market
- Main production capacity is in the US and Europe
- Global demand in PAO is increasing
- Increased capacity in PAO and LAO raw materials have been announced
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 sulphur 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
• General trend is move towards better quality base stocks
  – Drive for fuel economy
  – Move from Group I to higher quality base stocks
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