Oil Soluble Polyalkylene Glycols
A New Type of Group V Base Oil

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Presentation Objectives

- To introduce oil soluble PAGs – a new type of Group V base oil and performance additive
- To provide concepts to allow formulators to solve some of their lubrication challenges
- To provide guidance on using OSPs in specific industrial and automotive applications
- Global supplier of synthetic base fluids and fully formulated lubricants
- Primary chemistry is Polyalkylene Glycol (PAG) – Global leader
- Multiple Channels-to-Market but primarily:
  - Formulators & Original Equipment Manufacturers
- Innovator – Recent technology introductions: PAG Gas Turbine Fluids, Wind Turbine Oils, Fire Resistant Hydraulic Fluids, Renewable Base Oils
Recent Innovations in API Group IV and V Base Oils

**Polyalphaolefins**
- High viscosity PAOs manufactured from new catalysis routes
- Applications include gear and wind turbine lubricants

**Esters**
- High performance esters from renewable feed stocks
- Applications include Bio-hydraulic Fluids

**Oil Soluble PAGs**
- New range of ISO viscosity grade base oils and performance enhancing additives
- Broad range of industrial and automotive formulation options

The Chemical Industry continues to innovate to bring advanced solutions to emerging market needs
Introduction to Polyalkylene Glycols (PAG)

- High performance **synthetic lubricants**
- First developed over 60 years ago
- Solve problems that mineral oils can not
- Manufactured from ethylene oxide and propylene oxide with global infrastructure in place to supply
- Flexible chemistry – polymers can be tailor designed to almost any requirement

\[
\text{RO} \left\{ \text{CH}_2\text{CHO} \right\}_n \left\{ \text{CH}_2\text{CH}_2\text{O} \right\}_m \text{H}
\]

- Safe to use products with many environmental advantages over petroleum oils
- **Increasingly used to offer environmental benefits and energy efficiency benefits**
Supply of PAGs – Manufacturing Aspects

Huge global infra-structure existing today for manufacturing polyglycols for a wide variety of applications and industries:

Applications
- Polyurethanes
- Fuel additives
- Surfactants
- Pharmaceuticals
- Personal care
- Drilling fluids as well as ..... 
- Lubricants

European PAG Base Oil Manufacturing Plants

4-5 major suppliers of PAGs in Europe for lubricants
Only two are back integrated into key oxides (EO, PO and BO)
Traditional Polyalkylene Glycol Technology

Typical Synthesis Route to Polyalkylene Glycols

\[ \text{Initiator, ROH} \]

Ethylene oxide (EO)  Propylene oxide (PO)

- High performance synthetic lubricants
- Solve problems that mineral oils can not.
- Synthesized from ethylene oxide and propylene oxide
- Flexible chemistry – polymers can be tailor designed to meet many requirements
- Extensively researched to provide energy efficient solutions

CLASSICAL POLYMER STRUCTURES BASED ON EO & PO

Initiators are typically monols, diols or triols (for example butanol, propylene glycol, glycerol).

PAGs can be designed to have a wide range of molecular weights, viscosities and functional performance.
PAG Application Expansion

**PAG Synthetic Precursors**

- Ethylene oxide
- Propylene oxide

More than 100 PAG polymer products used in lubricant applications

**Historical application development**

- **1960s**
  - Fire resistant hydraulic fluids (HF-C)
  - Quenchants

- **1970s**
  - Textile oils
  - Metalworking fluids

- **1980s**
  - Gear oils
  - Refrigeration oils

- **1990-today**
  - Hydraulic fluids (HF-D)
  - Compressor fluids
  - Gas turbine fluids

**PAG chemistry and functional use**

<table>
<thead>
<tr>
<th>EO/PO</th>
<th>EO/PO</th>
<th>EO/PO</th>
<th>PO</th>
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</thead>
<tbody>
<tr>
<td>Additive Viscosity builder</td>
<td>Additive Lubricity aid</td>
<td>Primary Base oil</td>
<td>Primary Base oil</td>
</tr>
</tbody>
</table>
Benefits of Traditional PAGs

Typical values

- KV 40 range: 10 to 50,000cSt
- Viscosity Index: 160–250
- Pour points: -30 to -45oC
- Biodegradability: 20-80%

Design of new PAGs should retain the benefits of traditional PAGs but improve their inherent weaknesses.
Upgrading Hydrocarbon Oils with OSPs

- **Oil soluble PAGs**
  - Ethylene oxide
  - 1,2-Propylene oxide
  - 1,2-Butylene oxide
  - Higher alkoxides

- **Water soluble and water insoluble PAGs**
  - Traditional PAGs used in water based lubes and as primary base oils in synthetics

- **Water soluble PAGs**
  - Oil soluble PAGs can open up the application envelope and solve problems with modern mineral oil lubricants

- **Water based lubricants**
  - Water soluble and water insoluble PAGs
  - Traditional PAGs used in water based lubes and as primary base oils in synthetics

- **Synthetics**
  - Oil soluble PAGs
  - Water soluble PAGs

- **Mineral oils**
  - Ethylene oxide
  - 1,2-Propylene oxide
  - 1,2-Butylene oxide
  - Higher alkoxides
PAG Polymer Design Principles

Conventional rules for designing new PAG polymer structures
# New Oil Soluble PAGs – Typical Properties

Polymers derived from downstream derivatives of butylene oxide

<table>
<thead>
<tr>
<th></th>
<th>KV40 cSt</th>
<th>KV100 cSt</th>
<th>Viscosity Index</th>
<th>CCS viscosity at -20°C mPa.s</th>
<th>Pour Point oC</th>
<th>Flash Point, oC</th>
<th>Aniline Point, oC</th>
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<tr>
<td>OSP-18</td>
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<td>243</td>
<td>&lt;-30</td>
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</table>
Typical Group I-IV Hydrocarbon Oil Solubility

Solubility of OSPs at up to 10% in hydrocarbon oils

Group I Mineral Oils

Solubility

Group II and III Mineral Oils

Solubility

Group IV PAO – Low viscosity

Solubility

Solubility is typically good in other base oils such as
- Diesters
- Polyol esters
- Vegetable oils
- PAGs (PO homo-polymers)
Oxidation Performance of OSPs

**RPVOT – ASTM D2272**

- EO/PO
- OSP
- EO/PO + 2% AO
- OSP + 2% AO

**ASTM D2893B – 121°C, 312 hours**

- EO/PO
- OSP
- EO/PO + 2% AO
- OSP + 2% AO

**Thermo-gravimetric Analysis**

- Heating rate 10°C/min, in air
- Onset temp = 2% weight loss

AO = alkylated diphenylamine
EO/PO is ISOVG-46 PAG base oil

**Oxidation performance indicates:**
- Similar performance to conventional EO/PO PAGs
- Good response to conventional aminic anti-oxidants
Friction Performance of OSPs as Additives in PAO

Mini-traction machine, steel ball on steel disc, temperature 80°C, speed 15 mm/sec, Slide roll ratio = 10%, Pressure = 0.9GPa

Polyalphaolefin is a PAO-8 base oil (un-addititized)

OSPs may offer another choice to esters and other surface active additives
NOACK Volatilities of OSPs

Method CEC-L-40

Virgin base oil
1% Anti-oxidant
2% Anti-oxidant

Volatility of OSP base oils is suppressed with anti-oxidants

Virgin PAO base oil
PAO + 1% AO
PAO + 1% AO + OSP-32
Attributes of OSPs & Traditional PAGs

PAG polymer design space is significant
Changes in polymer chemistry can target improvements in functional performance
# Hydrocarbon Base Oil Compositions

<table>
<thead>
<tr>
<th>Classification</th>
<th>Sulphur content</th>
<th>Saturates</th>
<th>Viscosity Index</th>
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</thead>
<tbody>
<tr>
<td>Group I</td>
<td>&gt;0.03% and/or</td>
<td>&lt;90%</td>
<td>80 &lt; VI &lt;120</td>
</tr>
<tr>
<td>Group II</td>
<td>&lt;0.03% and</td>
<td>&gt;90%</td>
<td>80 &lt; VI &lt;120</td>
</tr>
<tr>
<td>Group III</td>
<td>&lt;0.03% and</td>
<td>&gt;90%</td>
<td>VI &gt; 120</td>
</tr>
<tr>
<td>Group IV</td>
<td>Polyalphaolefins (PAO)</td>
<td>140 (typical)</td>
<td></td>
</tr>
</tbody>
</table>

Base oil hydro-processing, hydro-treating, catalytic de-waxing and hydro-cracking techniques leading to higher performance base oils with improved viscometric and volatility properties.

## Group II, III and IV base oils
- Higher iso-paraffinic content
- Low or no aromatic content
- Provide more challenges in formulating with modern performance boosting additives due to lower solubility of these additives
Comparison of Aniline Points

Typical values - Aniline points using ASTM D611-01

Additive technologies used to boost solvency in hydrocarbon oils

Base oil solvency (polarity) typically decreases from Group I-IV

Oil Soluble PAGs can provide formulators another option for adding back solvency power to Group II, III and IV base oils
Headlines - Deposit Control in Lubricant Equipment

SOLVING VARNISH PROBLEMS IN GAS TURBINE LUBRICANTS
By Linda Bay
Contributing Editor

TLT Magazine Jan 2008

Identifying varnish and oxidation precursors in lubricant sumps

TLT Magazine, April 2011
Engine oils specifications continue to move to tighter deposit control and cleanliness specifications.

ILSAC GF-4 versus GF-5 specifications: Minor and Major changes

- Fuel economy
- Corrosion protection
- Volatility
- Engine sludge protection
- Piston cleanliness
- Oxidative thickening
- Wear protection
- Emission system durability
- Turbo charger protection
- Seal compatibility
Deposit Control Field Experience with PAGs

Thousands of rotary screw air compressors and turbo-machinery use conventional PAG technology.

Problems with deposit formation in some gas turbines are being solved today using conventional PAG technology.

Simplistic Oxidation Process for Mineral Oils

Mineral oil $\xrightarrow{O_2}$ Large polar by-products

Insoluble in the parent base oil leading to deposit formation

Simplistic Oxidation Process for PAGs

PAG $\xrightarrow{O_2}$ Small polar by-products

Soluble in the parent base oil and no deposit formation

Conceptually – OSPs as components of mineral oils may improve deposit control and extend fluid life.
Deposit Control Study – OSP Concentration Effect

Group I Mineral Oil

Group I Mineral Oil + OSP-46 (10%)

Deposit formation

Deposit free

Group I Mineral Oil + OSP-46 (5%)

Group I Mineral Oil + OSP-46 (1%)

Deposit free

Minor deposit

Modified ASTM D2893B at 120°C
OSP versus Esters and Alkylated Naphthalenes

Group I Mineral Oil

Group I Mineral Oil + OSP-46 (10%)

Deposit formation

Deposit free

Group I Mineral Oil + Synthetic Ester (10%)

Group I Mineral Oil + Alkylated Naphthalene (10%)

0 14d 50d

Deposit formation

Deposit formation
Concepts for OSPs for Hydraulic Fluids

Hydrocarbon based Anti-wear Hydraulic Fluids

- OSPs to upgrade current technology
- Treat levels 1-20%
- Inherent film forming properties of OSPs to deliver improved wear rates
- Deposit control to minimize varnish formation and filter and servo valve blockages

Fire Resistant Hydraulic Fluids

- OSPs have much lower heats of combustion than mineral oils (oxygen rich polymers)
- Significantly more hydrolytically stable than conventional esters
- Provide excellent deposit control
- Offer a high level of biodegradability
Concepts for OSPs for Gas and Air Compressors

Compressor types
- Centrifugal
- Rotary screw
- Reciprocating

Function of OSPs
- Primary base oil or additive in hydrocarbon oils
- Deposit control
- Heat removal – higher high capacities
Utilize OSPs as a component additive or co-base oil in Group II and III mineral oils

- Improve deposit control
- Reduce risk of varnish formation
- Reduce risk of equipment failure or turbine shut down
Concepts for OSPs in Gear and Transmission Fluids

Industrial Gear & Transmission Lubricants
Hydrocarbon oils containing OSPs

- Improved friction control through excellent film forming behaviour of OSPs
- Better energy efficiency
- Good deposit control
- Extended lubricant and equipment life
Concepts for OSPs in Wind Turbine Lubricants

- PAGs (OSPs) can generate much thicker EHD films than mineral oils and PAOs under higher contact pressures
  - 10-25% thicker EHD films at 60-100°C
  - Predicted to yield longer gear life
- PAGs have higher heat capacities than hydrocarbon oils
  - Potentially lower oxidation rates
Recent research observations

- Excellent friction control
- High dropping points
- Reduced thickener concentration in blend preparations (e.g. Li complex)
- Formulation flexibility (excellent additive solvating power)
Concepts for OSPs in Engine Oils

Formulation Component of Engine Oil
- OSP friction control and film forming behaviour (fuel economy benefit)
- Deposit control and engine cleanliness (reduced wear)
- Heat capacity improvement (improved oxidation stability)
Concepts for OSPs for Metalworking Fluids

Oxygen rich polymers providing surface activity and film forming behaviour

Metal Deformation & Metal Cutting
- Lubricity (AW/EP) booster for neat hydrocarbon oils
- Metal deformation applications (stamping, drawing, rolling etc) and metal removal (cutting, drilling)
- Detergent additive – to maintain machine cleanliness and prevent swarf build-up (validated by customers in machine trials).
Future PAG Application Expansion

Historical application development

1960s
Fire resistant hydraulic Fluids (HF-C)
Quenchants

1970s
Textile oils
Metalworking Fluids

1980s
Gear oils
Refrigeration oils

1990-today
Hydraulic Fluids (HF-D)
Compressor Fluids
Gas Turbine Fluids

PAG chemistry and functional use

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<td>Lubricity aid</td>
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<td>builder</td>
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FUTURE
PAG Expansion Through Innovation

PAGs from alternative oxides

PAGs to upgrade mineral oils

OIL SOLUBLE PAGs

OSPAs as performance enhancing additives for
- Deposit control
- Friction control
- Viscosity builders
- Corrosion inhibitors
- Base oil solvency booster
Conclusions

- Oil Soluble PAGs (OSP) extend the versatility and use of polyalkylene glycols
- OSPs will open up the application envelope for PAGs
- OSPs offer formulators an additional tool for upgrading hydrocarbon oils
- The flexibility of PAG chemistry provides huge scope for innovation in developing solutions to address many of today’s technical challenges within our industry
- Dow Chemical continues to innovate to provide solutions to industry needs
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