Polyalkylene Glycol Hydraulic Fluids: An Alternative for Environmentally Sensitive Areas

STLE Annual Meeting 2013 – Detroit
Synthetics & Hydraulics II
May 9th, 2013

Authors
Andrew Larson, The Dow Chemical Company
Dr. Martin Greaves, The Dow Chemical Company
Contents

• Current Trends
• Polyalkylene glycols – Introduction and Key Aspects
• Environmental vs. High Performance Lubricants
• Environmental & Performance Properties of PAGs
  – Including comparison to other hydraulic fluids
• Field Case Study
  – Involving PAG-based water soluble anhydrous hydraulic fluid
• Conclusions
Current Trends

• Increasing need for fluids in environmentally sensitive applications
  – Equipment with risk of spills and leaks into the environment including waterways
    • Dockside machinery
    • Tunnel boring machines
    • Hydro & coal burning power plants
    • Amusement parks
    • Forestry

• Regulatory bodies increasing coastal monitoring
  – Spill fines & clean-up costs increasing
  – EPA’s 2013 Vessel General Permit

• Companies now desire “green” image
  – Choosing products to support this

• Companies moving from conventional fluids to environmentally friendly fluids

• Applications are more demanding
  – Require improved performance
  – Still must minimize environmental impact
EPA’s 2013 Vessel General Permit (VGP)

• Effective Dec. 19, 2013
• Applies to commercial vessels ≥ 79 ft in length
  – Examples: cruise ships, barges, cargo ships
  – Excludes military & recreational vessels
• Final 2013 VGP
  – Excerpt from Section 2.2.9
    • “All vessels must use an EAL in all oil to sea interfaces, unless technically infeasible. ‘Environmentally acceptable lubricants’ means lubricants that are ‘biodegradable’ and ‘minimally-toxic’ and are ‘not bioaccumulative’….,”
Introduction to Polyalkylene Glycols (PAGs)

- High performance synthetic lubricants (Group V)
- First developed over 60 years ago
- Solve problems that mineral oils cannot
- Manufactured from ethylene oxide, propylene oxide, and/or butylene oxide
- Flexible chemistry – polymers can be designed and tailored to meet almost any requirement

\[
RO\left\{\begin{array}{c}
\text{CH}_3 \\
\text{CH}_2\text{CHO} \\
\text{CH}_2\text{CH}_2\text{O}
\end{array}\right\}_n\text{H}
\]

- Safe to use products with many environmental advantages over petroleum oils
- Increasingly used to offer environmental benefits and energy efficiency benefits
# Key Features of PAG-based Lubricants

<table>
<thead>
<tr>
<th>Feature</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Friction control &amp; anti-wear</td>
<td>Excellent lubrication and film forming properties. Mild extreme pressure performance.</td>
</tr>
<tr>
<td>Solubility</td>
<td>Possible to create PAG’s with solubility ranging from completely water soluble to completely oil soluble.</td>
</tr>
<tr>
<td>Deposit control</td>
<td>Excellent deposit control over all other base oils. Oxidation by-products are soluble in the base fluid.</td>
</tr>
<tr>
<td>Hydrolytic stability</td>
<td>PAG’s do not hydrolyze.</td>
</tr>
<tr>
<td>Oxidative stability</td>
<td>Good stability when protected with anti-oxidants up to 200 °C.</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>Typically superior to mineral oils allowing equipment to operate cooler.</td>
</tr>
</tbody>
</table>
## Typical Properties of PAG-based Water Soluble Anhydrous Hydraulic Fluid (ISO VG 32-68)

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Visual</td>
<td>Amber clear fluid</td>
</tr>
<tr>
<td>Viscosity @ 40 ºC, cSt</td>
<td>ASTM D445</td>
<td>32-68</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>ASTM D2270</td>
<td>190-220</td>
</tr>
<tr>
<td>Density @ 20 ºC, g/ml</td>
<td>ASTM D941</td>
<td>1.03</td>
</tr>
<tr>
<td>Pour Point, ºC</td>
<td>ASTM D97</td>
<td>&lt; -35</td>
</tr>
<tr>
<td>Vapor Pressure, mmHg, 20 ºC</td>
<td>ASTM E1719</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Vane pump wear, mg</td>
<td>ASTM D7043</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>RPVOT, min</td>
<td>ASTM D2272</td>
<td>&gt; 800</td>
</tr>
<tr>
<td>Deposit Control</td>
<td>ASTM D2893 (Mod)</td>
<td>Excellent</td>
</tr>
</tbody>
</table>
“Environmentally Friendly Lubricants”

What is an “Environmentally Friendly Lubricant”?  
- One definition is that an “Environmentally Friendly Lubricant” will have reduced environmental impact when compared to conventional lubricants (petroleum oils)

Key Environmental Performance Criteria
- Excellent biodegradation and reduced bio-accumulation
- Significantly lower eco-toxicity
- Water-solubility preferred
- Renewability preferred

Key Environmentally Friendly Lubricant Technologies
- Polyalkylene glycols
- Vegetable oils (e.g. rapeseed oils & other natural esters)
- Synthetic esters
“High Performance Lubricants”

What is a “High Performance Lubricant”?
• General consensus is that a “High Performance Lubricant” will possess the physical and tribological properties required to exhibit good, reliable and trouble-free performance in demanding conditions and applications

Key Lubricant Performance Criteria
• All season performance
• Friction control & anti-wear properties
• Deposit control properties
• Hydrolytic stability
• Oxidative stability
• Component compatibility (e.g. seals, multi-metals, etc.)

Key High Performance Lubricant Technologies
• Mineral oils
• Polyalkylene glycols
• Polyalphaolefins
• Synthetic esters
Ready Biodegradability of PAGs

- Ready (complete) biodegradability
  - Molecular cleavage
  - Removes all properties of original product
  - Forms CO₂ and water
  - > 70% removal after 28 days (per OECD 301 Methods, A-F)

<table>
<thead>
<tr>
<th>Product</th>
<th>% Biodegradation*</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO VG-32 PAG Formulation</td>
<td>81</td>
</tr>
<tr>
<td>ISO VG-46 PAG Formulation</td>
<td>72</td>
</tr>
<tr>
<td>ISO VG-68 PAG Formulation</td>
<td>80</td>
</tr>
</tbody>
</table>

*Tested via method OECD 301F 28-day test. Products were considered Readily Biodegradable.
Low Eco-Toxicity of PAGs

- U.S. Fish & Wildlife Classifications
  - Used to categorize or rank EL50/LL50 values
  - Compare test results & test species
    - EL vs. LL
    - Salt-water vs. fresh-water

<table>
<thead>
<tr>
<th>Relative Toxicity</th>
<th>Aquatic EL50 or LL50 (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Super Toxic</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Extremely Toxic</td>
<td>0.01 – 0.1</td>
</tr>
<tr>
<td>Highly Toxic</td>
<td>0.1 – 1.0</td>
</tr>
<tr>
<td>Moderately Toxic</td>
<td>1.0 – 10</td>
</tr>
<tr>
<td>Slightly Toxic</td>
<td>10 – 100</td>
</tr>
<tr>
<td>Practically Non-Toxic</td>
<td>100 – 1000</td>
</tr>
<tr>
<td>Relatively Harmless</td>
<td>&gt; 1000</td>
</tr>
</tbody>
</table>
Low Eco-Toxicity of PAGs

- Aquatic toxicity testing performed on PAG-based hydraulic fluids
- Salt & fresh water species observed

<table>
<thead>
<tr>
<th>Product</th>
<th>Fresh Water Species</th>
<th>Sea Water Species</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>48 h EL50 (mg/L) with water flea (Daphnia magna)*</td>
<td>96 h LL50 (mg/L) with Fathead minnow (Pimephales promelas)*</td>
</tr>
<tr>
<td>ISO VG-32 PAG</td>
<td>750</td>
<td>200</td>
</tr>
<tr>
<td>ISO VG-46 PAG</td>
<td>430</td>
<td>250</td>
</tr>
<tr>
<td>ISO VG-68 PAG</td>
<td>170</td>
<td>330</td>
</tr>
<tr>
<td></td>
<td>‡</td>
<td>&gt;1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>96 h LL50 (mg/L) with Mysid shrimp (Mysidopsis bahia)*</td>
<td>96 h EL50 (mg/L) Sheephead minnow (Cypronidon variegatus)*</td>
</tr>
<tr>
<td>ISO VG-32 PAG</td>
<td></td>
<td>200</td>
</tr>
<tr>
<td>ISO VG-46 PAG</td>
<td></td>
<td>250</td>
</tr>
<tr>
<td>ISO VG-68 PAG</td>
<td></td>
<td>330</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;1000</td>
</tr>
</tbody>
</table>

*All products are considered Practically Non-Toxic according to U.S. Fish & Wildlife Service Research Information Bulletin No. 84-78 (August, 1984). Testing of these formulations was performed according to U.S. EPA and OECD methods, and in compliance with their associated Good Laboratory Practice guidelines. Testing was performed after removal (membrane filtration) of insoluble components, with effects reported on the basis of nominal loading rate of the whole formulation.

‡Not tested. The ISO VG-32 and ISO VG-68 are expected to have fathead minnow LL50 values similar to that of ISO VG-46, based on similar results observed across these products for other species tested.

Green = Practically non-toxic
Red = Relatively harmless
Water Solubility of Common Lubricants

Common oils & their water solubility

Mineral Oil  White Oil  Vegetable Oil  Synthetic Ester

Oils added to water, then stirred and left to stand
Water Solubility of PAGs

Steady PAG Addition

After PAG Addition

• PAGs can be designed to be water soluble
  • They disperse and mix in water
  • They are denser than water
  • They avoid forming a sheen

Light stirring and the PAG lubricant becomes completely miscible to form a clear, homogeneous solution.
Testing for Sheening Tendency

• Determination using STATIC SHEEN TEST
  – US Environmental Protection Agency (EPA) method Appendix 1 to Subpart A of 40 CFR 435

• Samples are dispersed within a container and observed after one hour for:
  1. Sheen
  2. Increased reflectance
  3. Visual color
  4. Iridescence
  5. Oil slick
# Independent Test Results

## EPA Static Sheen Test

Static sheen test results of commercially available hydraulic fluid products

<table>
<thead>
<tr>
<th></th>
<th>PAG-based hydraulic fluid</th>
<th>Vegetable oil-based hydraulic fluid</th>
<th>Synthetic ester-based hydraulic fluid</th>
<th>White oil-based hydraulic fluid</th>
<th>Petroleum oil-based hydraulic fluid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silvery or metallic sheen</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td>Increased reflectivity</td>
<td>NO</td>
<td>NO</td>
<td>YES</td>
<td>YES</td>
<td>NO</td>
</tr>
<tr>
<td>Visual color</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td>Iridescence</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td>Oil slick exceeding 10% of surface area</td>
<td>NO</td>
<td>YES</td>
<td>YES</td>
<td>YES</td>
<td>YES</td>
</tr>
</tbody>
</table>

**Appendix 1 to sub-part A 40CFR435 – RESULT**

<table>
<thead>
<tr>
<th></th>
<th>PASS</th>
<th>FAIL</th>
<th>FAIL</th>
<th>FAIL</th>
<th>FAIL</th>
</tr>
</thead>
</table>

PASS | FAIL | FAIL | FAIL | FAIL
### Eaton (Vickers) Vane V-104C Performance Assessment

<table>
<thead>
<tr>
<th>Hydraulic Fluid Type</th>
<th>Ring Wear, mg</th>
<th>Vane Wear, mg</th>
<th>Total Ring &amp; Vane Weight Loss, mg</th>
<th>Initial KV40, cSt</th>
<th>Final KV40, cSt</th>
<th>KV40 % Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canola Oil</td>
<td>0.5</td>
<td>0.0</td>
<td>0.5</td>
<td>44.1</td>
<td>43.8</td>
<td>-1.4</td>
</tr>
<tr>
<td>Oleate-based Polyol Ester</td>
<td>1.0</td>
<td>2.4</td>
<td>3.4</td>
<td>48.4</td>
<td>41.3</td>
<td>-14.7</td>
</tr>
<tr>
<td>Saturated Polyol Ester</td>
<td>1.3</td>
<td>0.2</td>
<td>1.5</td>
<td>46.2</td>
<td>46.0</td>
<td>-0.4</td>
</tr>
<tr>
<td>PAG Fluid</td>
<td>3.1</td>
<td>0.2</td>
<td>3.3</td>
<td>46.1</td>
<td>45.5</td>
<td>-0.5</td>
</tr>
</tbody>
</table>

All 4 fluids have excellent low ring and vane wear.
RPVOT Results using ASTM D2272

- Canola Oil
- Oleate-based Polyol Ester
- Saturated Polyol Ester
- PAG Fluid
# Hydraulic Fluid Performance Matrix

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Petroleum Based</th>
<th>Vegetable Oils</th>
<th>Synthetic Esters</th>
<th>Polyalkylene Glycols**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ready biodegradation</td>
<td>Poor</td>
<td>Very Good</td>
<td>Very Good</td>
<td>Very Good</td>
</tr>
<tr>
<td>Eco-toxicity</td>
<td>Poor</td>
<td>Very Good</td>
<td>Very Good</td>
<td>Very Good</td>
</tr>
<tr>
<td>Water solubility</td>
<td>Poor</td>
<td>Poor</td>
<td>Poor</td>
<td>Very Good</td>
</tr>
<tr>
<td>Renewability</td>
<td>Low</td>
<td>High</td>
<td>*</td>
<td>Low</td>
</tr>
<tr>
<td>Oxidation Performance</td>
<td>Good</td>
<td>Poor</td>
<td>Good</td>
<td>Very Good</td>
</tr>
<tr>
<td>Wear Performance</td>
<td>Good</td>
<td>Very Good</td>
<td>Very Good</td>
<td>Very Good</td>
</tr>
<tr>
<td>Low Temperature Performance</td>
<td>Poor</td>
<td>Poor</td>
<td>Very Good</td>
<td>Very Good</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>Poor</td>
<td>Very Good</td>
<td>Good</td>
<td>Very Good</td>
</tr>
</tbody>
</table>

*Synthetic esters are derived from both petrochemical and oleochemical feedstocks

** Pertains to specially formulated water soluble PAG-based hydraulic fluids
PAGs in Environmentally Sensitive Applications
Tunnel Boring Machine

Fluid: PAG-based Hydraulic Fluid

Wisconsin’s Largest Construction Project

- Excavate 1.75 mi long, 27 ft dia. tunnel 200 ft below the bed of lake
- Water intake for transporting 1.8 billion gal of additional water for power plant

Pre-Trial Concerns

- Oil contamination: muck, gases, water, wear
- Environmental: leaks in waterways
- Toxicity: fish & other aquatic life
- Biodegradability, secondary waste water treatment complications

Technical Challenges

- Piston and gear pumps, servo valves
- 5000 psi, 100 °C
Conclusions

PAGs are an excellent choice for use in environmentally sensitive applications

1. Readily biodegradable
2. Low-toxicity
3. Non-sheening fluid
4. Fire resistance
5. Excellent lubricity
6. All season performance
7. Worker friendly
8. Long-life
9. Clean running
10. A good alternative to modern environmentally friendly natural and synthetic esters
Thank You

Andrew Larson
Lead Technical Service Representative
Ph: 989-638-4290
Email: arlarson@dow.com