Oil Soluble Polyalkylene Glycols and Aspects of Their Benefits for Hydraulic Fluids

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The Dow Chemical Company
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Presentation Objectives

- To review oil soluble PAGs – a new type of Group V base oil and performance additive
- To provide concepts that may be helpful in solving lubrication challenges using OSPs for hydraulic fluids
Contents

❖ Oil Soluble PAGs
  ▪ Chemistry & Physical properties
  ▪ Performance properties & Functional benefits

❖ Hydraulic Equipment & Fluids Trends
  ▪ Equipment design trends
  ▪ Impact of Fluids

❖ OSPs in Hydraulic Fluids
  ▪ Fully synthetic OSP hydraulic fluids
  ▪ OSPs as performance additives in hydrocarbon based hydraulic fluids
  ▪ OSPs as performance additives in ester based hydraulic fluids

❖ Conclusions
Oil soluble PAGs are new and build on 60 years of experience in using PAGs across many lubrication industries.

Aspects of the Chemistry of PAGs

Simplistic schematic of the types of oxides used in designing PAGs

- Ethylene oxide
- 1,2-Propylene oxide
- 1,2-Butylene oxide
- Higher oxides

Homo-polymers or Copolymers (random and block) are often used for lubricants.

Oil soluble PAGs

Water soluble PAGs

Water insoluble PAGs

Oil soluble PAGs

Oil soluble PAGs

Oil soluble PAGs
## New Oil Soluble PAGs – Typical Properties

<table>
<thead>
<tr>
<th>Grade</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>
</tr>
</thead>
<tbody>
<tr>
<td>OSP-18</td>
<td>18</td>
<td>4</td>
<td>123</td>
<td>n/d</td>
<td>-41</td>
<td>204</td>
<td>n/d</td>
</tr>
<tr>
<td>OSP-32</td>
<td>32</td>
<td>6.5</td>
<td>146</td>
<td>1750</td>
<td>-57</td>
<td>216</td>
<td>&lt;-30</td>
</tr>
<tr>
<td>OSP-46</td>
<td>46</td>
<td>8.5</td>
<td>164</td>
<td>2900</td>
<td>-57</td>
<td>210</td>
<td>&lt;-30</td>
</tr>
<tr>
<td>OSP-68</td>
<td>68</td>
<td>12</td>
<td>171</td>
<td>5400</td>
<td>-53</td>
<td>218</td>
<td>&lt;-30</td>
</tr>
<tr>
<td>OSP-150</td>
<td>150</td>
<td>23</td>
<td>186</td>
<td>17100</td>
<td>-37</td>
<td>228</td>
<td>&lt;-30</td>
</tr>
<tr>
<td>OSP-220</td>
<td>220</td>
<td>32</td>
<td>196</td>
<td>29100</td>
<td>-34</td>
<td>226</td>
<td>-22</td>
</tr>
<tr>
<td>OSP-320</td>
<td>320</td>
<td>36</td>
<td>163</td>
<td>n/d</td>
<td>-37</td>
<td>230</td>
<td>&lt;-30</td>
</tr>
<tr>
<td>OSP-460</td>
<td>460</td>
<td>52</td>
<td>177</td>
<td>n/d</td>
<td>-35</td>
<td>235</td>
<td>&lt;-30</td>
</tr>
<tr>
<td>OSP-680</td>
<td>680</td>
<td>77</td>
<td>196</td>
<td>n/d</td>
<td>-30</td>
<td>243</td>
<td>&lt;-30</td>
</tr>
</tbody>
</table>

Key grades for hydraulic applications
OSP attributes compared to traditional PAGs:

- Viscosity index
- Pour points
- Biodegradability
- Antiwear
- Hydrolytic stability
- Hygroscopicity
- Oxidation stability
- Deposit control
- Elastomer compatibility
- Oil miscibility

OSP benefits include:

- Retain many of the benefits of traditional PAGs
- Improve weaknesses

OSPs retain many of the benefits of traditional PAGs but improve their weaknesses.
Upgrading Hydrocarbon Oils with OSPs

Oil solubility of PAG increases for higher C/O ratios

Water soluble and water insoluble PAGs

Water based lubricants

Synthetics

Mineral oils

Traditional PAGs used in water based lubes and as primary base oils in synthetics

Oil soluble PAGs

Water based lubricants

Synthetics

Mineral oils

Oil soluble PAGs can open up the application envelope and solve problems with modern mineral oil lubricants
Examples of OSP Applications

- **Compressor Oils**
  - Deposit control & equipment reliability

- **Transmission Oils**
  - Fuel economy

- **Greases**
  - High temperature stability and friction control

- **Wind Turbine Lubricants**
  - Corrosion inhibitor boosters

- **Turbine Oil**
  - Deposit control

- **Engine Oils**
  - Fuel economy
Hydrocarbon based Hydraulic Fluids
- Treat levels of OSP of 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

Ester based hydraulic fluids containing OSP
- Treat levels of OSP 5-15%
- To improve hydrolytic stability
- To improve fluid cleanliness

Synthetic Mobile Hydraulic Fluids
- Outstanding air release
- Biodegradable
- Significantly more hydrolytically stable than conventional esters
- Deposit control

Fire Resistant Fluids (HF-D)
- OSPs have much lower heats of combustion than mineral oils (oxygen rich polymers)
Some Industry Trends on Hydraulics

- Higher system pressures
- Higher operating temperatures
- More compact with smaller reservoir sizes
- Tighter clearances and finer filter pores

### Performance Need

<table>
<thead>
<tr>
<th>Performance Need</th>
<th>Important Lubricant Feature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump reliability</td>
<td>Wear protection</td>
</tr>
<tr>
<td>Low compressibility</td>
<td>High bulk modulus</td>
</tr>
<tr>
<td>Operating temperature range</td>
<td>Viscosity index and low temperature properties</td>
</tr>
<tr>
<td>Deposit and varnish free</td>
<td>Oxidation stability and cleanliness</td>
</tr>
<tr>
<td>Water tolerance</td>
<td>Water separation and corrosion protection</td>
</tr>
<tr>
<td>Air tolerance</td>
<td>Air release and foam control</td>
</tr>
<tr>
<td>Particulate contamination</td>
<td>Filterability</td>
</tr>
</tbody>
</table>
Example 1
Synthetic OSP Hydraulic Fluid
Air Release Properties

Initial research showed very fast air release of OSP fluids

Importance of air release in hydraulic equipment
- Reduction in bulk modulus
- Erosion and cavitation
- Noise
- Spongy controls
- Faster ageing through oxidation
- Loss of system fluid (10% air ingress)

Air release, mins

Influence of viscosity on air release

Air release values generally increase as fluid viscosity increases (e.g. ISO-22 through to ISO-460)

Hydraulic Fluids with low air release values are highly desired
# Air Release Properties of Hydraulic Fluids

## Hydrocarbon Oils

<table>
<thead>
<tr>
<th>Type</th>
<th>Air Release Value, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral oil</td>
<td>7.5</td>
</tr>
<tr>
<td>PAO</td>
<td>3</td>
</tr>
</tbody>
</table>

## Esters and veg. oils

<table>
<thead>
<tr>
<th>Type</th>
<th>Air Release Value, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester 1 HEES</td>
<td>5</td>
</tr>
<tr>
<td>Ester 2 HEES</td>
<td>4.5</td>
</tr>
<tr>
<td>Vegetable oil HETG</td>
<td>8</td>
</tr>
<tr>
<td>Vegetable oil + ester HEES</td>
<td>6</td>
</tr>
<tr>
<td>Vegetable oil + PAG HETG</td>
<td>8.5</td>
</tr>
</tbody>
</table>

## Fire resistant Fluids

<table>
<thead>
<tr>
<th>Type</th>
<th>Air release, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water glycol HF-C</td>
<td>20</td>
</tr>
<tr>
<td>Polyol oleate HF-DU</td>
<td>7</td>
</tr>
<tr>
<td>PAG</td>
<td>9</td>
</tr>
<tr>
<td>PAG</td>
<td>7</td>
</tr>
<tr>
<td>Phosphate ester</td>
<td>1</td>
</tr>
</tbody>
</table>

All fluids are commercially available ISO-VG46 fluids.

Air release data is measured using ASTM D3427 at 50°C.

Data shared is reported on the manufacturers technical data sheets.

## New Dow OSP Formulated Hydraulic Fluid

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>OSP-46</td>
<td>98.15</td>
</tr>
<tr>
<td>Additive package</td>
<td>1.85%</td>
</tr>
</tbody>
</table>

## New OSP Hydraulic Fluid

<table>
<thead>
<tr>
<th>Component</th>
<th>ASTM Method</th>
<th>Typical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>KV40, cSt</td>
<td>ASTM D445</td>
<td>46</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>ASTM D2270</td>
<td>157</td>
</tr>
<tr>
<td>Pour point, oC</td>
<td>ASTM D97</td>
<td>-54</td>
</tr>
<tr>
<td>Air release, min</td>
<td>ASTM D3427</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>
Commercially Available Hydraulic Fluids – Air Release and Four Ball Data

Air release at 50°C using ASTM D3427

Four ball using ASTM D4172 (75°C, 1200 rpm, 40kg for 1 hour)
MTM helps screen additives and their friction control in the design of the optimum additive package.
### Performance Properties of Synthetic OSP Hydraulic Fluid

#### Synthetic OSP Hydraulic Fluid

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCON OSP-46</td>
<td>98.15</td>
</tr>
<tr>
<td>Additive package</td>
<td>1.85%</td>
</tr>
</tbody>
</table>

Additive package contains anti-oxidants, anti-wear and corrosion inhibitors

#### Typical Performance Properties

<table>
<thead>
<tr>
<th>Test</th>
<th>Method</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic viscosity at 40°C, cSt</td>
<td>ASTM D445</td>
<td>45.9</td>
</tr>
<tr>
<td>Kinematic viscosity at 100°C, cSt</td>
<td>ASTM D445</td>
<td>8.2</td>
</tr>
<tr>
<td>Kinematic viscosity at 0°C, cSt</td>
<td>ASTM D7042</td>
<td>463</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>ASTM D2272</td>
<td>157</td>
</tr>
<tr>
<td>Pour Point, °C</td>
<td>ASTM D97</td>
<td>-54</td>
</tr>
<tr>
<td>Density at 15°C, g/ml</td>
<td>ASTM D7042</td>
<td>0.968</td>
</tr>
<tr>
<td>Ferrous corrosion, 24 hours, de-ionised water/synthetic sea water</td>
<td>ASTM D665A/B</td>
<td>pass/pass</td>
</tr>
<tr>
<td>Copper corrosion,</td>
<td>ASTM D130</td>
<td>1a</td>
</tr>
<tr>
<td>Foam Sequence I, II and III, ml</td>
<td>ASTM D892</td>
<td>0/0</td>
</tr>
<tr>
<td>Four ball anti-wear, mm</td>
<td>ASTM D4172</td>
<td>0.31</td>
</tr>
<tr>
<td>Air release at 50°C, minutes</td>
<td>ASTM D3427</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Oxidation at 121°C, 70days KV40 change, %</td>
<td>ASTM D2893B – ext. time</td>
<td>1.3 Transl. no deposits</td>
</tr>
<tr>
<td>Visual appearance after 70d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermo-oxidative stability test at 95°C, TAN change after 1000 hours, mg KOH/g (wet conditions)</td>
<td>ASTM D943</td>
<td>+0.5</td>
</tr>
</tbody>
</table>
Hydraulic Vane Pump Testing

Hydraulic (V104C) Pump Test – ASTM D7043
- 100 hour duration
- 2000 psi, 1200 rpm & 65°C
- Measure weight loss of ring and vanes

<table>
<thead>
<tr>
<th>Commercial Hydraulic Product</th>
<th>Weight Loss of ring and vanes</th>
<th>KV40 change, %</th>
<th>AN Change mgKOH/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>High oleic canola oil</td>
<td>9.1</td>
<td>2.7</td>
<td>0.2</td>
</tr>
<tr>
<td>Polyol oleate</td>
<td>3.4</td>
<td>14.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Adipate ester</td>
<td>1.5</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>PAG</td>
<td>3.3</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>OSP-HF-46</td>
<td>0.4</td>
<td>0.5</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Oxidation Testing
ASTM D2893 at 95°C

<table>
<thead>
<tr>
<th>Commercial Hydraulic Product</th>
<th>% KV40 change after 13 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>High oleic canola oil</td>
<td>233</td>
</tr>
<tr>
<td>Polyol oleate</td>
<td>8</td>
</tr>
<tr>
<td>Adipate ester</td>
<td>0.2</td>
</tr>
<tr>
<td>PAG</td>
<td>0.2</td>
</tr>
<tr>
<td>OSP-HF-46</td>
<td>0.2</td>
</tr>
</tbody>
</table>

- All fluids are commercially available from different suppliers
- OSP-HF-46 is a new experimental OSP hydraulic fluid
Short Case Study and Trial on Synthetic OSP Hydraulic Fluid

Background

- Hydraulic fluid needed for moveable floors and booms of swimming pools

- Hydraulic system using food grade vegetable oil
  - caused seal degradation
  - fluid rapidly deteriorated resulting in deposit formation

- Critical fluid requirements included
  - Equipment reliability
  - Inert to swimming pool water ingress
  - Safe to use
  - Does not form deposits or varnish on ageing
  - Compatible with seals
  - Excellent corrosion protection
  - Longer fluid life than vegetable oil technology
Case Study Data

Corrosion Testing in Pool water

Above: ASTM D665 modified: Chlorine level of pool water was 179ppm. Test temp 50oC. No evidence of staining or corrosion after 7 days

Right: No evidence of fluid degradation or change after 90 days. Fe, Cr, Sn, Cu, S and Cl all below 10 ppm after 90 days
Example 2
Hydrocarbon Oil Based Hydraulic Fluids containing OSPs
Deposit Control Features of OSPs in Hydrocarbon Oils

**Simplistic Oxidation Process for Mineral Oils**

Mineral oil + $\text{O}_2$ → Large polar by-products

Insoluble in the parent base oil leading to deposit formation

**Simplistic Oxidation Process for PAGs**

PAG + $\text{O}_2$ → 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

Modified ASTM D2893B (extended test)

Inclusion of an OSP improves deposit control
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-additized)

OSPs may offer another choice to esters and other surface active additives
Benefits of an OSP in Hydrocarbon Hydraulic Fluids

Deposit Control
- Solubilize oxidation by-products of hydrocarbon oils
- Improve system cleanliness
- Eliminate or minimize blockages of servo-valves or filters
- Significantly extend fluid life and equipment reliability
- Recommended treat levels for deposit control is 1 to 20%

Friction Control
- OSPs act as friction reducers in hydrocarbon oils – improve energy efficiency
- Provide antiwear performance due to oxygen rich polymeric structures
- Recommended treat levels for friction control is 5-20%

Additional Benefits
- Can improve heat capacity and thermal conductivity
Example 3
OSPs & Environmentally Friendly Fluids
Environmentally Friendly Hydraulic Fluids Using OSPs

Biodegradability of Oil Soluble PAGs

Test Method OECD 301F – 28 day test

Key grades for hydraulic applications:
- OSP-32
- OSP-46
- OSP-68

Possible to develop environmentally friendly fluids (HEPG) that offer:

- biodegradability
- excellent air release
- excellent deposit control
- excellent wear performance
- suitable for operation in cold climates
Vegetable based hydraulic fluids (HETG)
- excellent wear performance
- biodegradable and renewable
- high viscosity indices

Synthetic esters (HEES) also used in more demanding applications
- good oxidation stability
- good low temperature properties
- excellent wear characteristics
- some are biodegradable and renewable

Limitation of Esters
- Natural and synthetic esters are prone to hydrolysis
- Impact can be a shorter fluid life and higher risk of equipment damage
### OSPs and Hydrolytic Stability

#### Improvements of Esters

#### Modified ASTM D2619 – Hydrolytic stability

<table>
<thead>
<tr>
<th></th>
<th>Vegetable Oil</th>
<th>Vegetable Oil + 10% OSP-46</th>
<th>Synthetic ester</th>
<th>Synthetic ester + 10% OSP-46</th>
</tr>
</thead>
<tbody>
<tr>
<td>KV40 cSt</td>
<td>32</td>
<td>34.5</td>
<td>22.9</td>
<td>23.9</td>
</tr>
<tr>
<td>Viscosity index</td>
<td>225</td>
<td>220</td>
<td>144</td>
<td>151</td>
</tr>
<tr>
<td>TAN change mg KOH/g</td>
<td>0.4</td>
<td>0.1</td>
<td>0.07</td>
<td>0.05</td>
</tr>
<tr>
<td>Total acidity of water layer mg KOH/g</td>
<td>7.3</td>
<td>1.2</td>
<td>3.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Copper appearance</td>
<td>3a</td>
<td>1b</td>
<td>2c</td>
<td>1b</td>
</tr>
</tbody>
</table>

Each formulation contains 0.75% of an additive package

**OSP acts as a polymeric sponge for water addition**
Environmentally Friendly Ester Based Hydraulic Fluids with OSPs

Accelerated oxidation test using modified ASTM D2893B at 121°C

Visual inspection of the tubes shows evidence for better deposit control and improved fluid cleanliness

OSP solubilizing oxidation by-products of esters

Conceptually it is possible to extend fluid life using OSPs as additives or co-base oils in vegetable oils
Conclusions

- Oil Soluble PAGs (OSP) offer formulators a new building block in developing synthetic or hydrocarbon based hydraulic fluids.
- Synthetic fluids based on OSPs offer exceptional air release properties, oxidation stability and wear properties.
- OSPs could enhance the deposit control and friction control aspects of hydrocarbon based hydraulic fluids.
- As additives in natural and synthetic esters, OSPs can improve their hydrolytic stability.
Thank you

Any questions please contact

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Email: mrgreaves@dow.com

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