High performance Polyimide SP and SCP parts & Perfluoroelastomer parts for valves applications ranging from cryogenics (eg LNG) to high temperatures

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DuPont International Operations sarl
Agenda

• Polyimide “S” and “SCP” family which can perform from – 273°C up to 300°C
  – LNG valve seats
  – High temperature valve seats
  – Backup rings

• Perfluoroelastomer parts (FFKM) combine chemical resistance similar to PTFE, thermal stability up to 327°C, extrusion resistance and excellent Rapid Gas Decompression (RGD) performance
  – Sealing of valve seat
  – Improving control valve emissions and hysteresis
What are Polyimide SP and SCP?

• **SP:**
  SP grades offer cost-effective combinations of physical, low wear and electrical properties, for lubricated and un-lubricated sealing and low wear in vacuum and dry environments. SP grades have no glass transition (melting point), and are softer than SCP grades, leading to excellent wear characteristics against soft materials.

• **SCP:**
  SCP is a DuPont polymer that extends the continual operating performance of polyimide resins to 370°C. SCP grades offer the highest performance of imidized polymers in terms of wear and friction with high PV limits and low coefficient of friction in unlubricated conditions, compressive strength (similar to carbon steel), and thermal oxidation resistance at very high temperatures.
Compressive Modulus (ASTM D695)

- Constant Compressive Modulus between 2500 and 4200 MPa of the tested polyimide parts and shapes within the operating temperature range.

<table>
<thead>
<tr>
<th>Compressive Modulus</th>
<th>Polyimide SP-21 ISO</th>
<th>Polyimide SP-21 DF</th>
<th>Polyimide SP-211 ISO</th>
<th>Polyimide SP-211 DF</th>
</tr>
</thead>
<tbody>
<tr>
<td>-196°C</td>
<td>3654</td>
<td>2940</td>
<td>3516</td>
<td>2620</td>
</tr>
<tr>
<td>23°C</td>
<td>4200</td>
<td>2813</td>
<td>3550</td>
<td>2454</td>
</tr>
</tbody>
</table>

Compressive Modulus

Temperature (°C)

Compressive Modulus (MPa)

SP-21 ISO
SP-21 DF
SP-211 ISO
SP-211 DF

CREEP (ASTM D695 - Deformation Under Load)

• **Deformation under load, 14 MPa, 48 hrs** (DuPont proprietary method)
  - Less than 0.52 % at room temperature.
  - Negligible at -196 °C

<table>
<thead>
<tr>
<th>Creep, 14 MPa, 48 hrs, %</th>
<th>-196 °C</th>
<th>23 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyimide SP-21 ISO</td>
<td>0.025 %</td>
<td>0.46 %</td>
</tr>
<tr>
<td>Polyimide SP-211 ISO</td>
<td>0.006 (*) %</td>
<td>0.52 %</td>
</tr>
</tbody>
</table>

(*) should be verified as dispersion of results

• **Deformation under load, 30 MPa, One week** (DuPont proprietary method)
  - Less than 1.5% at higher pressure and longer time at room temperature,
  - Less than 0.03 % at -196 °C

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<tr>
<th>Creep, 30 MPa, One Week, %</th>
<th>-196 °C</th>
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<td>1.45 %</td>
</tr>
</tbody>
</table>
LNG Valve Seats

• Outstanding properties
  – No significant modulus change between Ambient and -196°C
  – Small to negligible creep at cryogenic temperature
  – Low coefficient of friction

• BENEFITS
  – Reduction of the actuator size
    • No significant modulus change between Ambient and -196°C
      No need to increase the force applied on the seat to ensure sealing
    • Low coefficient of friction
  – Extended service life
    • Small to negligible creep at cryogenic temperature
Polyimide SCP-5000 & SCP-5050 - High Temperature High Strength Properties

Flexural Strength (left) and Compressive Strength (right) of Polyimide SCP-5000 and SCP-5050 at 23°C and 260°C (73°F and 500°F)
Polyimide SCP-5050 - Chemical Resistance In Diesel Fuel

- Compressive properties after ageing in Diesel fuel at 343°C (650°F) [ASTM D-695]
Polyimide SCP-5000 and SCP-5050 - Extrusion Resistance Versus Unfilled

Test conditions

- $T = 288^\circ C$ (550°F)
- $P = 200MPa$ (29 ksi)
- Extrusion gap on diameter = 1 mm
- Samples dimensions OD 12.4mm x h 6mm

Maximum extrusion height of PI SCP-5000, PI SCP-5050 and PEEK unfilled in function of time at 288°C under 200MPa
Polyimide SCP High Temperature Valve Seat

• Outstanding properties
  – Excellent properties stability between RT and 300°C (ie. Compressive modulus)
  – Low creep even at temperature up to 288°C. Higher temperatures being tested
  – Low coefficient of friction
  – Coefficient of thermal expansion 23°C - 300°C:
    • PI SCP-5050 16 um/m/°C (x-y plane – radial direction for valve seat)
    • PI SCP-5000 47 um/m/°C (Isotropic)

• BENEFITS
  – Use of polymeric valve seat at temperature above other thermoplastics
  – Lower coefficient of friction for Polyimide/metal compared to a metal/metal solution
  – Ease of sealing due to the compliance of polymer/metal vs metal/metal
  – Coefficient of thermal expansion can match stainless steels for selected filled grades – like SS316, simplifying design.
Polyimide SCP Backup Ring

• Outstanding properties
  – Improved chemical resistance achieved through a differentiated chemical structure, still within polyimide family
  – Low creep even at temperature up to 288°C

• BENEFITS
  – Use of a polymeric solution in backup-rings for short to moderate term exposures to aggressive environments
What Are Perfluoroelastomers Parts

• Perfluoroelastomer (FFKM) were invented by DuPont in 1969, this is a high performance elastomer.
• Fully fluorinated elastomer which provides
  – High temperature resistance up to 327ºC
  – Chemical resistance, inertness and cleanliness of PTFE, together with resilience and associated benefits of elastomers
    • Excellent resistance to H2S, up to very high concentration (65% to 100%).
Extrusion Resistance
AS568-329 O-Ring (*)

* James Walker & Co proprietary test method

100°C = 212°F
150°C = 302°F

600 bar = 8700 PSI / 1400 bar = 20305 PSI
Low Temperature Performance of FFKM-0090 Parts

• The low temperature capabilities depends on the application conditions.
• Based on our test results, increasing the pressure improves the low temperature sealing.
• Low temperature sealing performance does not correlate with measured values such as Tg, TR-10.

<table>
<thead>
<tr>
<th>AS568 size</th>
<th>Leak Detection</th>
<th>Gas</th>
<th>Compression</th>
<th>Pressure (MPa)</th>
<th>Low Temp. Sealing (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>214</td>
<td>3.0 ccm</td>
<td>Air</td>
<td>16% radial</td>
<td>0.4 (Before cooling)</td>
<td>- 21 °C</td>
</tr>
<tr>
<td>312</td>
<td>0.1 ccm</td>
<td>Nitrogen</td>
<td>14% vertical</td>
<td>10 (Before cooling)</td>
<td>- 40 °C</td>
</tr>
<tr>
<td>312</td>
<td>0.1 ccm</td>
<td>Nitrogen</td>
<td>14% vertical</td>
<td>10 (After cooling)</td>
<td>- 25 °C</td>
</tr>
</tbody>
</table>

* DuPont proprietary test method  
** James Walker & Co proprietary test method
Elastomeric sealing for valve seats

• Outstanding properties
  – Certified by MERL to meet Norsok M-710 rev.2 annex A & B
  – Qualified by CETIM under TOTAL GS EP PVV 142 rev.5 to CSD=6.99mm
  – Extrusion resistance without backup rings

• BENEFITS
  – Use of perfluoroelastomer (FFKM) up to large cross sections under RGD conditions
  – Avoiding the use of backup rings lead to improved low temperature properties (Assuming pressure is applied first)
  – Avoiding the use of backup rings helps reducing the groove size and overall cost of the application
What is Valve Stem Packing?

Combination of
- FFKM-3035 V-rings
- Fibre reinforced fluoropolymer CR-6100 backup components

The FFKM V-rings have very low friction characteristics requiring low loading forces to activate and seal, the backup components are undercut for a non-interference fit.
Leak test: Helium versus Methane

- For Valve Stem Packing Helium shows higher leak rate than Methane, Argon and Nitrogen due to diffusion. Real VOC leakage is therefore better than the Helium lab test.

- Measured by independent test lab on 1.2mm thick slab FFKM-3035.

EPA method 21: methane concentration

Permeation coefficient
\( \text{cm}^3(\text{NTP}) \times \text{mm}/(\text{m}^2 \times \text{h} \times \text{bar}) \)

Elastomeric sealing for valve seats

• Outstanding properties
  – Low coefficient of friction
  – Chemical resistance of perfluoroelastomers

• BENEFITS
  – Low loading force required
  – Low hysteresis
  – Excellent permeation properties (save Helium)
Conclusion

• Valve seat upgrade using Polyimide SP or SCP
  – For cryogenic application
  – For high temperature application

• Valve sealing using perfluoroelastomers
  – For valve exposed to Rapid Gas Decompression, FFKM-0090 has proven to withstand TOTAL GS EP PVV 142 rev.5 up to CSD=6.99
  – Avoiding the use of backup rings because of its excellent extrusion resistance
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