Compatibility of sealing materials with fuels and lubricants

Uniti Mineral Oil Technology Congress, Stuttgart, 4./5.April 2017
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Freudenberg Sealing Technologies

- World’s leading specialist in sealing technology
- Largest business group within the Freudenberg Group
- More than 15,000 employees worldwide and approx. 2.3 billion euros sales in 2015
- Annual production of 5 billion seals, about 400 million per month
- Global network with partner NOK in the U.S., Japan, China, India
- Decentralized structure
Revenue by sectors* (in %)

- Automotive: 54%
- General Industry: 32%
- Aftermarket: 14%

Revenue by region* (in %)

- Europe: 57%
- NAFTA: 33%
- China: 7%
- South America: 1%
- India, America: 1%
- South America, India: 1%
Part 1: Compatibility with Fuels
What is the role of the sealing material?

Similar solvents/fluids solve chemically identical materials:

- Polar substance in a polar fluid: Homogeneous solution
- Unpolar substance in polar fluid: Suspension
- (Un)polar material in (un)polar fluid causes high swelling

Optimum of the sealing function is achieved if the sealing material provides the **opposite polarity** to the fluid, which causes low swelling.
Exception: FFKM, FKM, FVMQ (VMQ)
Bascially, these materials can be used in polar fluids as well as in unpolar fluids.
Influence of the components to the sealing

Impact of the polarity of the fluid

<table>
<thead>
<tr>
<th>unpolar</th>
<th>polar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral Oil</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Fuels</td>
<td>Water</td>
</tr>
<tr>
<td>Biofuels</td>
<td>Methanol</td>
</tr>
</tbody>
</table>

Problem:

- Incompatible fluid – Sealing material combination causes swelling which can lead to deterioration -> leakage
- Higher polarity can also lead to increased miscibility with water. Chemical attack to the sealing material, even FKM
Biofuels in gasoline engine: Ethanol

Swelling of FKM rubbers (static applications)
- In different ethanol concentrations
- Different fluorine content

- Max. swelling in E20-E25
- Lowest swelling in E100
- Increasing fluorine content lowers the overall swelling level
Biofuels in gasoline engine: Methanol

Swelling of FKM rubbers (static applications)
- In different methanol concentrations
- Different fluorine content

1008 h/ 60 °C

<table>
<thead>
<tr>
<th>FKM 1</th>
<th>FKM 6</th>
<th>FKM 4</th>
<th>FKM 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP (66 %)</td>
<td>(64 %)</td>
<td>PO (67 %)</td>
<td>(71 %)</td>
</tr>
</tbody>
</table>

Basis: Fuel C

- Max. swelling in
- M75 for lower F content
- M15 for high F content
- Strong influence of the FKM polymer architecture
- Increasing fluorine content lowers the overall swelling level
Selective permeation

Test specimen

Permeation medium

Carrier gas: Argon

Mass spectrometer
Biodiesel

Possible reactions of fatty acid methyl esters

RME swelling after 1000h @ 100 and 125°C

No significant changes < 125 °C

Significant changes > 125 °C

Higher aggressivity with SME 20
Part 2: Compatibility with lubricants
Weak point analysis for seals in industrial transmissions

- **Main reason for short term leakage**
  - Shaft surface: 30%
  - Sealing environment: 10%
  - Assembly: 35%
  - Lubricant: 40%

- **Main reason for long term leakage**
  - Shaft surface: 5%
  - Operating conditions: 25%
  - Assembly: 10%
  - Sealing environment: 20%
  - Lubricant: 10%
Basic: Radial shaft seals
Tribology under the sealing / Pumping effect

Main influencing value for the sealing function
Rubber – Lubricant - Interaction

LUBRICANT

- anti aging agent
- corrosion protection additive
- extreme pressure additive
- swelling modifier
- base oil

physical interaction

chemical interaction

Elastomere

- anti aging agent
- network
- cross-linker
- softener
- filler
- polymer
Physical interaction: Polarity

molecule

polar groups nonpolar groups

Solubility

wettability
Composition of a Rubber compound

- Polymer
- fillers
  - Carbon black, silica, chalk, minerals
- Metal oxide
  - ZnO, MgO, CaO/Ca(OH)₂…
- Cross-linking agent
  - peroxide, sulfur, amines…
- Antioxidants
  - amines, phenols, carbodiimide …
- plasticizers
  - ethers, esters, thioethers, mineral oil
- Additive
  - Fatty acids

The properties of an elastomer depend strongly on composition, mixing procedure and processing!
Physical interaction: Polarity

Solubility

Additives used in Lubricants and in Rubber

Solubility of additives in lubricant and elastomer

=> swelling, shrinkage and material exchange without change in volume
Extraction of the swollen samples
analysing of extracts with GC-MS

storage in oil

extraction of the swollen samples

Oil

acetone / cyclohexane
Extraction of the swollen NBR samples
analysing of extracts with GC-MS

NBR without storing in oil

500h stored in pure PAO

Base Oil extract the NBR Material
=> strong volume change of NBR
Extraction of the swollen NBR samples analysing of extracts with GC-MS

500h stored in pure GR I

Base Oil extract the NBR Material
but diffusion of mineral oil into the NBR

500h stored in pure GR II

Base Oil extract the NBR Material
but diffusion of less mineral oil into the NBR
Extraction of the swollen samples with Cyclohexane / Acetone analysing of extracts with GC-MS

Real PAO with additive

Real mineral oil GP I with additive

high content of additive-package substances:
- sulphur-containing
- nitrogen-containing
- phosphorus-containing
Volume change of NBR with different mineral oils

Different behavior of different oils
Important to measure over longer time

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>168 h</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>336 h</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>512 h</td>
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<td></td>
<td></td>
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<tr>
<td>672 h</td>
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</table>
Rubber-Lubricant Interaction

Lubricant – rubber interaction in lab-tests (dynamic)

Lubricant – rubber interaction in lab-tests (static)

Lubricant – rubber interaction in a real tribological system
Influence of physical interaction on RSS properties

Example:
NBR materials with different PAOs
500h at 40°C
2mm test plate and RSS
Chemical interaction: Influence on crosslinking density

Crosslinked Polymer chains Rubber

Attacking medium (e.g. oxygen, additives...)

Chain degradation (loss of tension)

Additional crosslinking (increase of tension)

Reduction of crosslinking points (loss of tension)
Chemical interaction with sulfur cured rubber
e.g. NBR

Type of sulfur-linkage can change:
by temperature
by additives of the oil
Why is a dynamic test so important?
Results from the field
scanning electron microscope (SEM) analyses of the sealing lip

<table>
<thead>
<tr>
<th>Material</th>
<th>Description</th>
<th>Oil Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACM</td>
<td>engine seal</td>
<td>mineral based engine oil</td>
</tr>
<tr>
<td>FKM</td>
<td>hydraulic seal</td>
<td>mineral based hydraulic oil</td>
</tr>
<tr>
<td>NBR</td>
<td>gear box seal</td>
<td>PAG based gear box oil</td>
</tr>
</tbody>
</table>

Time:
- ACM: > 2000h
- FKM: 4000h
- NBR: 1000h
Results from the field
energy dispersive X-ray spectroscopy, EDX

ACM: engine seal
Oil: mineral based engine oil

FKM: hydraulic seal
Oil: mineral based hydraulic oil

NBR: gear box seal
Oil: PAG based gear box oil

Phosphor
Zinc
Sulfur

Strong chemical interaction at the sealing lip
Measurement of the change in mechanical properties at the sealing lip / New method

Strong change of stiffness in the surface near area
Interaction between elastomer and lubricant
Different types of interactions

- Dynamical application
  - The mechanical deformation of the elastomer at the shaft surface is a **surface effect** (20 µm)
  - The mechanical behavior of the elastomer in the area near the surface is influenced by the tribological behavior

Consequently:
Elastomer-lubricant combinations with little swelling can still show strong interactions in the dynamic test!
Rubber-Lubricant Interaction / conclusion:

Lubricant – rubber interaction in lab-tests (dynamic)

Very complex !!!

Lubricant – rubber interaction in lab-tests (static)

Lubricant – rubber interaction in a real tribological system
It is very important to do the right test!!!

For the characterization of the rubber - lubricant – compatibility the dynamic test is absolutely necessary!!!

Static test only for first evaluation!!!
Thank you very much for your attention!

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