THERBAN®/HNBR for the Energy Sector

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Overview

- HNBR Elastomer: Product & Properties

- Short term aging study:
  Fluid Aging: IRM903, DIESEL, STEAM
  H₂S Resistance
  Rapid Gas Decompression in CO₂ & N₂

- Summary
Polymer Structure

### NBR vs HNBR

**NBR** Poly(acrylonitrile-butadiene)

- Unsaturation in the main chain
  - \( \Rightarrow \) poor chemical and temperature stability

- ![NBR structure](image)

  - Oil resistance
  - Aging behavior

**HNBR** Hydrogenated Poly(acrylonitrile-butadiene)

- Hydrogenation required to reduce unsaturation.
  - \( \Rightarrow \) direct polymerization of C\(_2\) and ACN not possible!

- ![HNBR structure](image)

  - Oil resistance
  - Aging behavior
# THERBAN® Performance Features

<table>
<thead>
<tr>
<th>HNBR – Ideal polymer for oil field applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>➢ High strength</td>
</tr>
<tr>
<td>➢ Abrasion resistance</td>
</tr>
<tr>
<td>➢ Good mechanical properties at elevated temperature</td>
</tr>
<tr>
<td>➢ Very good heat resistance</td>
</tr>
<tr>
<td>➢ Good low temperature properties</td>
</tr>
<tr>
<td>➢ Excellent resistance to lubricating oils with chemically aggressive additives</td>
</tr>
<tr>
<td>➢ Low permeability to vapors &amp; gases</td>
</tr>
<tr>
<td>➢ Good resistance to ozone</td>
</tr>
<tr>
<td>➢ Good resistance to high energy radiation</td>
</tr>
<tr>
<td>➢ Low compression set</td>
</tr>
<tr>
<td>➢ Good resistance to crude oil even in the presence of hydrogen sulfide, amines, and corrosion inhibitors</td>
</tr>
</tbody>
</table>
## Typical properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Service Temperature, °C</td>
<td>- 40 to 165; &gt; 180/short term</td>
</tr>
<tr>
<td>Compound density, g/cc</td>
<td>1.1 – 1.4</td>
</tr>
<tr>
<td>Hardness, Shore A</td>
<td>30 – 90+</td>
</tr>
<tr>
<td>Ultimate Tensile, MPa</td>
<td>40</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>600</td>
</tr>
<tr>
<td>Compression set %, 70hrs/150C</td>
<td>&lt; 15</td>
</tr>
<tr>
<td>Tear Strength, kN/m</td>
<td>50</td>
</tr>
<tr>
<td>Rebound resilience, %</td>
<td>65</td>
</tr>
<tr>
<td>DIN Abrasion, mm³</td>
<td>35</td>
</tr>
</tbody>
</table>
## Effect of RDB (Residual Double bond) Level

<table>
<thead>
<tr>
<th>Fully Saturated Grades</th>
<th>Partially Saturated Grades</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peroxide Cure</td>
<td>Sulfur &amp; Peroxide Cure</td>
</tr>
</tbody>
</table>

- **Hot Air Resistance**
- **Ozone Resistance**
- **Lower Heat Build-up**
- **Modulus**
- **Ultimate Elongation**
- **Tear Strength**
### Effect of ACN Content

<table>
<thead>
<tr>
<th>ACN Content</th>
<th>Oil Resistance</th>
<th>Fuel Resistance</th>
<th>Hardness</th>
<th>Density</th>
<th>Lower Gas Permeability</th>
<th>Low Temp. Flexibility</th>
<th>Elasticity</th>
</tr>
</thead>
<tbody>
<tr>
<td>34 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39 %</td>
<td><strong>↑</strong></td>
<td><strong>↑</strong></td>
<td><strong>↑</strong></td>
<td><strong>↑</strong></td>
<td><strong>↑</strong></td>
<td><strong>↑</strong></td>
<td><strong>↑</strong></td>
</tr>
<tr>
<td>49 % ACN</td>
<td></td>
<td><strong>↑</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
# Outline of Compounds (H$_2$S and RGD Testing)

## Variation in ACN, RDB, ZnO, S vs P Cure and Hardness

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D / D'</th>
<th>E / E'</th>
<th>F / F'</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACN (%)</td>
<td>34</td>
<td>39</td>
<td>39</td>
<td>43</td>
<td>43</td>
<td>43</td>
</tr>
<tr>
<td>RDB (%)</td>
<td>0.9 max</td>
<td>0.9 max</td>
<td>0.9 max</td>
<td>0.9 max</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td>ZnO (phr)</td>
<td>--</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P: peroxide, S: sulfur</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>S</td>
</tr>
</tbody>
</table>

**Hardness:**
- Compounds A-F have ca. 90 Shore A
- Compounds D', E' and F' have ca. 70 Shore A.
Physical Properties (90 Shore A)

- A: 34% ACN
- B: 39% ACN
- C: 39% ACN (ZnO)
- D: 43% ACN
- E: 43% ACN
- F: 43% ACN (S-Cure)

- Tensile/10, PSI
- Young's Modulus/10, PSI
- M100/10, PSI
- Elongation, %

- < 1% RDB
- 5.5% RDB
Compression Set – Peroxide vs Sulfur

Improved Compression Set with Peroxide and Anaerobic Aging

Compound E’, @ 150 °C

- Air
- ASTM#1
- IRM903

43 % ACN, 5.5 % RDB, **Peroxide Cure**

- 168hrs
- 504hrs

Compound F’, @ 125 °C

- Air
- ASTM#1
- IRM903

43 % ACN, 5.5 % RDB, **Sulfur Cure**

**ASTM #1 and IRM 903 help to exclude air during testing**
Oil Resistance vs Low Temperature Properties

Higher ACN will lead to an increase in Tg but reduced swelling

Tg (°C) versus ACN

Volume Swell (%) vs ACN

Higher swelling in steam for the S-cured compound
Fluid Resistance (Immersion 3 days)

More hardening for S-Cured Compound with Steam

<table>
<thead>
<tr>
<th>Change in Hardness (pts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>8</td>
</tr>
</tbody>
</table>

High ACN reduces swelling/softening of compounds

- **IRM903, 72hrs/150C**
- **DIESEL, 72hrs/80C**
- **STEAM, 72hrs/175C**
Fluid Resistance (Immersion 3 days)

Change in Tensile, %

Change in Elongation, %
Hot air vs Nitrogen Aging Effects

Change in Properties of 70 Shore A Compounds

Reduced aging effects under N₂ atmosphere
H$_2$S Resistance

Chemical Reactions with C=C are Possible:

\[-\text{C} = \text{C} \quad \xrightarrow{\text{H}_2\text{S}} \quad \text{C} - \text{C} \quad + \quad \text{C} = \text{C} \quad \rightarrow \quad \text{C} - \text{C} - \text{S} - \text{C} - \text{C} -\]

Addition Reaction                   Crosslinking Reaction

Can extend lifetime and upper temperature limits with HNBR
H$_2$S Resistance

**Experimental Testing Procedure**

Five O-rings (214 type) of each compound were tested

Gas mixture composed of:
- 5% CO$_2$
- 10% H$_2$S
- 85% CH$_4$

No liquid phase was present in the vessel

The vessel was maintained at 150°C and 10 MPa for 72 hours

The pressure was then released at a very slow rate (avoid RGD)
less than 0.15 MPa/min
H₂S Resistance

High ACN and S-Cure shows reduced H₂S Resistance

- Chg in H, pts
- Chg in T, %
- Chg in EB, %
- Chg in Weight, %

P Cure, < 1% RDB
S Cure
Rapid Gas Decompression Resistance (CO$_2$)

Experimental Testing Procedure

Five O-rings of each of compounds A, D, and F were tested.

Vessel was filled with CO$_2$ at 100°C, 12 MPa for 24 hours.

The pressure was released at a rate of 3.7 MPa/min to simulate explosive decompression test conditions.

The O-rings of each compound were sectioned into two equal pieces and inspected under SEM with 50X magnification.
Rapid Gas Decompression Resistance (CO₂)

Good Results (no defects observable)

COMPOUND A
34 ACN, < 0.9 % RDB

COMPOUND D
43 ACN, < 0.9 % RDB
Rapid Gas Decompression Resistance ($\text{CO}_2$)

Good Results (no defects observable)

All compounds show no defects, cracks, or damage at these conditions - very good resistance to rapid gas decompression

COMPOUND F

43 ACN, sulfur cure
Rapid Gas Decompression Resistance (N₂)

### Experimental Testing Procedure / Results

ASTM dumbbells of compounds A (34 % ACN) and D (43 % ACN) were tested in N₂ at 100°C, 7 MPa for 24 hours.

The pressure was released at a rate of 3.7 MPa/min to simulate explosive decompression test conditions.

Both compounds showed no evidence of blisters, porosity or defects.

<table>
<thead>
<tr>
<th>Compound</th>
<th>A</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACN (%)</td>
<td>34</td>
<td>43</td>
</tr>
<tr>
<td>Chg in Hardness, pts</td>
<td>-1.8</td>
<td>-0.4</td>
</tr>
<tr>
<td>Chg in Tensile, %</td>
<td>-3</td>
<td>-1</td>
</tr>
<tr>
<td>Chg in Elongation, %</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Chg in volume, %</td>
<td>1</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Summary

Good Fluid Resistance and Rapid Gas Decompression Resistance

- Good high temperature aging properties for peroxide compounds
- Sulfur cured compounds show severe aging
- Reduced swelling with higher ACN, but reduced low T flexibility
- Improved high temperature stability under Nitrogen
- Peroxide cured HNBR compounds display good H$_2$S resistance: slight increase in aging (reduced EB) with higher ACN contents
- All compounds displayed very good RGD properties when tested under CO$_2$ and N$_2$
Thank you for your attention! Questions?

For more information please visit  
www.therban.com  
www.trp.lanxess.com

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