Tire Durability
Importance of Innerliner Performance
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• Importance of Bromobutyl Rubber in Tire Innerliner

• Promix® 400 Homogenizing Agent Performance in Tire Innerliner Formulations
Tire Innerliner
Function and Performance
Tire Innerliner Functions and Performance

• Air inside the tire is 21% Oxygen, \( \text{O}_2 \). \( \text{O}_2 \) is the enemy of rubber as it causes degradation and loss in physical properties.

• The innerliner provides a barrier that helps prevent \( \text{O}_2 \) from entering the tire structure and degrading the tire rubber.

• When innerliner performance is not adequate, through appropriate compounding, oxidative degradation can be a primary cause of tire failure.
Tire Innerliner Functions and Performance

• Careful innerliner formulation can help ensure proper performance. Use of bromobutyl rubber provides the required O2 barrier properties while maintaining needed flexibility and adhesion.

• A poor innerliner formulation can result in higher levels of O2 and increased degradation of internal components.
Tire Innerliner and Belt-Edge Durability

- The tire belt-skim and wedge are subjected to very high interlaminar shear forces.

- A high O$_2$ level in the belt skim rubber from poor innerliner barrier performance can result in property degradation and a belt-to-belt separation.

- Low air pressure from poor innerliner performance can cause excessive tire deflection, higher heat generation and acceleration of oxidative property degradation.

Belt-Edge Separation from Property Degradation

**Belt-Edge separation caused by property degradation.**

Proper innerliner formulation can help prevent oxidative property degradation.
Importance of Bromobutyl Rubber in Tire Innerliner
Bromobutyl Rubber – Properties

- The performance of butyl rubber is driven by its structure. The Pendant methyl groups of polyisobutylene create a closely packed polymer structure that provides superior barrier to O₂.
- Halogenation of butyl rubber (i.e., bromobutyl) provides faster cure and improved adhesion to natural rubber.
- While butyl rubber is nearly 18 times less permeable to O₂ than natural rubber, it still has very good low temperature flexibility.

**Molecular Structure**

![Molecular Structures](image)

**O₂ Permeability and Diffusivity**

<table>
<thead>
<tr>
<th></th>
<th>Permeability (10⁻⁸ cm² s⁻¹ atm⁻¹)</th>
<th>Diffusivity (10⁻⁶ cm² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C</td>
<td>50°C</td>
</tr>
<tr>
<td>Natural Rubber</td>
<td>17.7</td>
<td>47</td>
</tr>
<tr>
<td>Butyl Rubber</td>
<td>0.99</td>
<td>4.03</td>
</tr>
</tbody>
</table>

*Journal of Polymer Science, vol. 5, issue 3, pp. 307-332*
The benefits of butyl rubber in innerliner were demonstrated by Waddell et. al. using the durability test method required by the United States Federal Motor Vehicle Safety Standard (FMVSS) 139.

While FMVSS 139 endurance is a passenger tire test, high O$_2$ level in the belt coat rubber are as much or more of a concern for commercial truck tires due to the higher inflation pressures and higher loads experienced by commercial tires in service.

The benefits of bromobutyl O$_2$ barrier properties are evident through tire endurance testing.
Bromobutyl – Barrier Properties and Tire Durability

- A 100% Bromobutyl polymer system provides the lowest O₂ permeability.

- Lower O₂ permeability leads to higher durability due to a reduction in oxidative property degradation.

- Addition of Natural Rubber results in higher O₂ permeability which negatively affects tire durability.

**Bromobutyl Affect on O₂ Permeability & Durability**

*Rubber World, Volume 234, Number 3, pp. 36-41 (June 2006)*
A 100% Bromobutyl polymer system provides the best Inflation Pressure Retention (IPR).

Better IPR leads to higher durability as excessive tire deflection and heat generation is avoided.

Addition of Natural Rubber results in higher Inflation Pressure loss rates which negatively affects tire durability.

Rubber World, Volume 234, Number 3, pp. 36-41 (June 2006)
A 100% Bromobutyl polymer system provides the lowest Intracarcass Pressure.

Lower Intracarcass Pressure leads to lower levels of dissolved \( \text{O}_2 \) and reduced oxidative property degradation.

Addition of Natural Rubber results in increased Intracarcass Pressure which negatively affects tire durability.

*Rubber World, Volume 234, Number 3, pp. 36-41 (June 2006)*
Bromobutyl Rubber – Summary

• High Bromobutyl content provides lower O₂ Permeability, better Inflation Pressure Retention and lower Intracarcass Pressure which result in better tire durability.

• Addition of Natural Rubber reduces the barrier performance of the Bromobutyl but provides improved physical properties and carcass adhesion.

• As with most polymer blends, homogenization of a mixed polymer system to a finer morphology can minimize challenges while maintaining or improving advantages.

• Promix® 400 is a homogenizer for the Bromobutyl/NR system!

### Bromobutyl Content Considerations

<table>
<thead>
<tr>
<th></th>
<th>100% Bromobutyl</th>
<th>80% Bromobutyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>300% Modulus (psi)</td>
<td>491</td>
<td>469</td>
</tr>
<tr>
<td>Tensile Strength (psi)</td>
<td>1337</td>
<td>1480</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>684</td>
<td>683</td>
</tr>
<tr>
<td>Carcass Adhesion (lbf/in)</td>
<td>187</td>
<td>212</td>
</tr>
<tr>
<td>Oxygen Transmission Rate (cc/100 in² day)</td>
<td>9.9</td>
<td>27.9</td>
</tr>
</tbody>
</table>

### Advantages to High Bromobutyl Content

- Improved barrier to O₂
- Improved Inflation Pressure Retention
- Reduced Intracarcass Pressure
- Improved Tire Durability

### Challenges of High Bromobutyl Content

- Reduced Tensile Strength
- Reduced Adhesion to Carcass
- Difficult processing
- Increased cost
Promix® 400 Homogenizing Agent
Performance in Tire Innerliner Formulations
Promix® 400 – Introduction

- **Increased Bromobutyl content provides better Inflation Pressure Retention, lowest Intracarcass Pressure and better durability.**

- **Addition of Natural Rubber reduces the barrier performance of the Bromobutyl but improves physical properties and carcass adhesion.**

- **As with most polymer blends homogenization can help minimize challenges and maintain advantages.**

- **Promix® 400 is a homogenizer for the Bromobutyl/NR system.**

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**Promix® 400 Features and Benefits**

**Features of Promix® 400**

- Copolymerized hydrocarbon resin
- Contains aromatic, naphthenic and aliphatic components
- Compatible with many elastomers
- Homogenizer for the Bromobutyl/NR polymer system
- Compliant with European PAH regulation

**Benefits of Promix® 400 in Tire Innerliner**

- Reduced O₂ Permeability
- Improved innerliner adhesion to carcass
- Improved fatigue properties
- Improved blending and processing
- Improved barrier even in 100% Bromobutyl systems
- Cost control through use of Bromobutyl with Natural Rubber and potential for gauge reduction.
Promix® 400 – Tire Innerliner Formulation

- Polymer system is typically 100% Bromobutyl or a blend of Bromobutyl (BIIR) and Natural Rubber (NR).
- Naphthenic oil is added for improved processability but decreases barrier properties.
- Promix® 400 Homogenizing Agent provides improved barrier properties, better adhesion, improved resistance to fatigue and improved processability.

Typical Tire Innerliner Formulations

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromobutyl</td>
<td>80 – 100 phr</td>
</tr>
<tr>
<td>Natural Rubber</td>
<td>0 – 20 phr</td>
</tr>
<tr>
<td>N660</td>
<td>60.00</td>
</tr>
<tr>
<td>Naphthenic Oil</td>
<td>0-15</td>
</tr>
<tr>
<td>Promix® 400</td>
<td>0-15</td>
</tr>
<tr>
<td>Tackifying Resin</td>
<td>4.00</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>2.00</td>
</tr>
<tr>
<td>Magnesium Oxide</td>
<td>0.15</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>1.00</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.50</td>
</tr>
<tr>
<td>MBTS</td>
<td>1.20</td>
</tr>
</tbody>
</table>
Example: BIIR/NR Innerliner

- Polymer system is 80phr Bromobutyl with 20phr Natural Rubber.
- Oil was reduced as Promix® 400 was added to maintain constant modulus.
- Addition of Natural Rubber made possible by Promix® 400 helps control cost.

### Bromobutyl/NR Innerliner Formulations

<table>
<thead>
<tr>
<th></th>
<th>No Promix® 400</th>
<th>7phr Promix® 400</th>
<th>14phr Promix® 400</th>
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</thead>
<tbody>
<tr>
<td>Bromobutyl</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Natural Rubber</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>N660</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Naphthenic Oil</td>
<td>16.5</td>
<td>8.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Promix® 400</td>
<td>0.0</td>
<td>7.0</td>
<td>14.0</td>
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<tr>
<td>Tackifying Resin</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
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<tr>
<td>Stearic Acid</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>MgO</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>ZnO</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>MBTS</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Example: BIIR/NR Innerliner

- Promix® 400 Homogenization

- In an innerliner formulation containing a 80% Bromobutyl, 20% Natural Rubber system, polymer phase morphology is clearly visible via microscopy.

- Use of Promix® 400 visibly improves polymer morphology and dramatically improves O2 barrier. Opportunity for improved performance and cost control through gauge reduction.
Promix® 400 in Bromobutyl/NR Innerliner

Example: BIIR/NR Innerliner

- Promix® 400 Homogenization
- Improved performance:
  - Equivalent tensile strength
  - ~20% improvement in De Mattia Crack Growth Rate
  - ~20% improved Carcass Adhesion with mode changed from smooth to cohesive
**Example: Full BIIR Innerliner**

- Polymer system is 100phr Bromobutyl without Natural Rubber.
- Promix® 400 in-place-of Naphthenic Oil
- Naphthenic oil was reduced as Promix® 400 was added to maintain constant modulus.

<table>
<thead>
<tr>
<th></th>
<th>No Promix® 400</th>
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<th>10phr Promix® 400</th>
<th>14phr Promix® 400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromobutyl</td>
<td>100</td>
<td>100</td>
<td>100</td>
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<tr>
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<td>1.0</td>
</tr>
<tr>
<td>Promix® 400</td>
<td>0.0</td>
<td>7.0</td>
<td>10</td>
<td>14.0</td>
</tr>
<tr>
<td>Tackifying Resin</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Stearic Acid</td>
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<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
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</table>
Promix® 400 in 100% Bromobutyl Innerliner

Example: Full BIIR Innerliner

- Promix® 400 in-place-of Naphthenic Oil
- Improved performance:
  - Equal tensile strength
  - Dramatic improvement in DeMattia Crack Growth Rate
  - 50%+ Improvement in Oxygen Barrier
  - ~20%+ improved Carcass Adhesion with mode changed from smooth to cohesive

** At 10phr and 14phr Promix® 400, DeMattia test stopped after 250k cycles with negligible crack growth rate.
Promix® 400 in Bromobutyl Innerliner

- Promix® 400 in Bromobutyl Innerliner
- Use of Promix® 400 in Bromobutyl innerliner in-place-of Naphthenic oil results in improved O$_2$ barrier.
- Improved barrier performance using Promix® 400 allows flexibility in use of Natural Rubber for enhanced physical properties and cost control.

** 80% Bromobutyl Innerliner with 14phr Promix® 400 has equivalent O2 barrier to Full Bromobutyl Innerliner. (MOCON OTR at 25°C)**
Promix® 400 in Innerliner – Summary

**Features of Promix® 400**
- Copolymerized hydrocarbon resin
- Contains aromatic, naphthenic and aliphatic components
- Compatible with many elastomers
- Homogenizer for the Bromobutyl/NR polymer system
- Compliant with European PAH regulation

**Benefits of Promix® 400 in Tire Innerliner**
- Reduced O₂ Permeability
- Improved innerliner adhesion to carcass
- Improved fatigue properties
- Improved blending and processing
- Improved barrier even in 100% Bromobutyl systems

*Promix® 400 provides opportunity to reduce tire oxidative degradation for improved tire durability.*