Xiamen Pharmaceutical Stopper Seminar
November 2003
Phenolic Resins for Curing Elastomers
Presented by James Lamb
Global Business Manager – Performance Resin Division
Phenolic Resin Chemistry

Nomenclature

Functional Groups

(1) Aromatic Hydroxyl group
(2) ortho positions
(2) meta positions
(1) para position
Phenolic Resin Chemistry

**Functionality**

- Ortho and para directed reactions
- Tri-functional
- Capable of highly branched polymers
Phenolic Resin Chemistry

para-Alkylphenols

Para-substituted phenol is di-functional

Reactions produce linear polymers

Alkyl group affects solubility and compatibility
Phenolic Resin Chemistry

Monomers used in rubber

\[ \text{p-tert. Octyl Phenol} \]
\[ \text{p-tert. Butyl Phenol} \]
Phenolic Resin Chemistry

*Formaldehyde Reactions*

Monomers react with formaldehyde under different conditions to make different products.

Reacting under acid conditions yields thermoplastic resins (Novolaks).

Reacting under base conditions yields reactive resins (Resoles).

Resole resins can be used for curing of elastomers.
Phenolic Curing Resin

Description

- Complex polymer with multiple reactive sites (resole resin)
- Undergoes multiple reactions simultaneously
- Activated by halogens (resinous, elastomeric, or metallic salts)
- Requires zinc source for best results
Phenolic Resin Chemistry

*SP-1045 Curing Resin*

R' = --H or --CH₂OH

R = C₈H₁₇

Amorphous structure of various length chains

Multiple reactive sites, complex structure

Methylene or ether bridged monomeric units
Phenolic Resin Reactions

Unsaturated Elastomers

Chroman Ring Structure
R’ = -H, -CH₂H, or -CH₂Br

R = C₈H₁₇

Bromine can be added to resin

Increases rate of reaction with labile halogen

Increases complexity of cure mechanism
Phenolic Resin Reactions

Unsaturated Elastomers - \( Br \)

Chroman Ring Structure
Phenolic Curing Resin Characterization

- Capillary Melting Point – measure of crystalline nature of resin (related to Tg)

- Ball & Ring Softening Point – measure of melt viscosity of resin

- Methylol Content – measure of reactivity
  - Ortho- position required for desired reactions
  - Ether is counted as methylol by test method

- Bromine Content – Percent by weight
## Phenolic Curing Resin

### Available Grades

<table>
<thead>
<tr>
<th>Resin</th>
<th>Capillary Melt Point</th>
<th>Ball &amp; Ring Softening Point</th>
<th>Methylol, %</th>
<th>Bromine, %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SP-1044 (PTOP)</strong></td>
<td>135-150 °F</td>
<td>80 - 90 °C</td>
<td>7.5 - 9.5</td>
<td>None</td>
</tr>
<tr>
<td><strong>SP-1045 (PTOP)</strong></td>
<td>140-150 °F</td>
<td>80 - 95 °C</td>
<td>8.0 – 11.0</td>
<td>None</td>
</tr>
<tr>
<td><strong>HRJ-10518 (PTOP)</strong></td>
<td>140-150 °F</td>
<td>80 - 95 °C</td>
<td>6.0 – 9.0</td>
<td>None</td>
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<tr>
<td><strong>SP-1055 (PTOP)</strong></td>
<td>140-158 °F</td>
<td>85 – 95 °C</td>
<td>10.0 – 14.0</td>
<td>3.6 – 4.0</td>
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<tr>
<td><strong>SP-1056 (PTOP)</strong></td>
<td>140-158 °F</td>
<td>80 – 90 °C</td>
<td>9.0 – 11.0</td>
<td>6.0 – 7.5</td>
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<tr>
<td><strong>HRJ-1367 (PTBP)</strong></td>
<td>160 °F (typical)</td>
<td>92 - 100 °C</td>
<td>14.0 – 18.0</td>
<td>None</td>
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</tbody>
</table>
Phenolic Curing Resins

**Function**

- Phenolic resins can be used to vulcanize (crosslink) elastomers
- Methylol and hydroxyl groups of resin react with unsaturated sites of elastomer
- Properties of vulcanized elastomer changed
  - Reduced thermoplasticity
  - Improved abrasion resistance
  - Increased tensile strength
Phenolic Curing Resin

Benefits

- Forms covalent carbon-carbon bonds which are not easily broken
- Ideal for repeated heat cycles
- Acts as plasticizer until cure initiated
- Resin can be halogenated for rapid cure
Phenolic Curing Resin

More Benefits

- Does not require amine accelerators
- Can tolerate autoclave temperatures
- Low extractables compared to sulfur cure systems
Phenolic Curing Resin

Rubber Formulation

- Elastomer (butyl or halobutyl rubber)
- Reinforcing material (Clay, Carbon black)
- Modifiers (Wax, oils)
- Minerals (Zinc Oxide, Magnesium oxide)
- Phenolic Resin SP-1045 or SP-1055
Phenolic Curing Resin

Bladder Formulation 1

- Butyl 268 Elastomer 100
- HAF Carbon Black 50
- Castor Oil 5
- Zinc Oxide 5
- Curing Resin with Br 10
Phenolic Curing Resin

Bladder Formulation 2

- Butyl 268 Elastomer 100
- HAF Carbon Black 50
- Castor Oil 5
- Zinc Oxide 5
- Neoprene W 5
- Curing Resin without Br 10
SII Heat Reactive Resin Cure
Butyl Masterbatch
ODR 2000, 30' @ 300°F

<table>
<thead>
<tr>
<th></th>
<th>Brominated</th>
<th>Non Brominated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ML</td>
<td>MH</td>
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<tr>
<td>SP-1055, (Low BR)</td>
<td>7.13</td>
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<tr>
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<td>15.02</td>
<td>19.21</td>
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<td>SP-1056, (High BR)</td>
<td>6.96</td>
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<td>17.42</td>
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<td>SP-1044, (PTOP)</td>
<td>27.17</td>
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<td>7.86</td>
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<td>SP-1045, (PTOP)</td>
<td>11.55</td>
<td>5.75</td>
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<tr>
<td>HRJ-1367, (PTBP)</td>
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<td>HRJ-10518, (PTOP)</td>
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SII Heat Reactive Resin Cure
Butyl Masterbatch
ODR 2000, 30' @ 325°F

<table>
<thead>
<tr>
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<th>HRJ-1367, (PTBP)</th>
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SII Heat Reactive Resin Cure
Butyl Masterbatch
ODR 2000, 30' @ 350°F

ML  5.79  6.58  5.66  5.49  5.65  6.47
MH  23.64 23.70 21.53 22.59 20.51 24.80
L110 2.14 1.43  3.49  3.61  3.62  3.14
L150 4.60 3.03 12.26 12.88 13.57 10.66
L1S1 1.82 1.24  2.62  2.65  2.81  2.25
L1S2 2.22 1.50  4.13  4.01  4.52  3.31
SII Heat Reactive Resin Cure
Butyl Masterbatch
ODR 2000, 30’ @ 380 °F

<table>
<thead>
<tr>
<th></th>
<th>ML</th>
<th>SP-1056, (Low BR)</th>
<th>SP-1044, (PTOP)</th>
<th>SP-1045, (PTOP)</th>
<th>HRJ-1367, (PTBP)</th>
<th>HRJ-10518, (PTOP)</th>
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<td>t10</td>
<td>1.28</td>
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<td>2.31</td>
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<td>1.98</td>
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<tr>
<td>ML</td>
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<td>I10</td>
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<td>0.92</td>
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<tr>
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<td>2.34</td>
<td>2.62</td>
<td>1.98</td>
</tr>
</tbody>
</table>
Phenolic Curing Resin

Pharmaceutical Formulation

- Bromobutyl 2244 100.0
- Whitetex Clay 90.0
- AC 617A 3.0
- Zinc Oxide 0.5
- SP-1045 5.0

- Note low resin requirement
- Note no need for halogen donor
### Stress Press - 350°F

<table>
<thead>
<tr>
<th>SP-1045 - 3 phr, 0.5 phr ZnO</th>
<th>SP-1045 - 6 phr, 0.5 phr ZnO</th>
<th>SP-1045 - 9 phr, 0.5 phr ZnO</th>
<th>SP-1055 - 3 phr, 0.5 phr ZnO</th>
<th>SP-1055 - 6 phr, 0.5 phr ZnO</th>
<th>SP-1055 - 9 phr, 0.5 phr ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>stress @ 100%</td>
<td>154</td>
<td>291</td>
<td>371</td>
<td>144</td>
<td>256</td>
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<td>stress @ 300%</td>
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<td>654</td>
<td>757</td>
<td>342</td>
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<tr>
<td>stress @ break</td>
<td>706</td>
<td>811</td>
<td>800</td>
<td>650</td>
<td>774</td>
</tr>
</tbody>
</table>

- **SP-1045**
  - 3 phr, 0.5 phr ZnO
  - 6 phr, 0.5 phr ZnO
  - 9 phr, 0.5 phr ZnO

- **SP-1055**
  - 3 phr, 0.5 phr ZnO
  - 6 phr, 0.5 phr ZnO
  - 9 phr, 0.5 phr ZnO

**METR# 03-074**
Elongation, (Strain)/Hardness
Press - 350°F

% strain @ break
<table>
<thead>
<tr>
<th>Product</th>
<th>3 phr, 0.5 phr ZnO</th>
<th>6 phr, 0.5 phr ZnO</th>
<th>9 phr, 0.5 phr ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP-1045</td>
<td>667</td>
<td>448</td>
<td>337</td>
</tr>
<tr>
<td>SP-1055</td>
<td>682</td>
<td>451</td>
<td>373</td>
</tr>
</tbody>
</table>

Shore "A" Hardness
<table>
<thead>
<tr>
<th>Product</th>
<th>3 phr, 0.5 phr ZnO</th>
<th>6 phr, 0.5 phr ZnO</th>
<th>9 phr, 0.5 phr ZnO</th>
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</thead>
<tbody>
<tr>
<td>SP-1045</td>
<td>50</td>
<td>53</td>
<td>58</td>
</tr>
<tr>
<td>SP-1055</td>
<td>50</td>
<td>57</td>
<td>59</td>
</tr>
</tbody>
</table>
Phenolic Curing Resin

Regulatory Status

- Commonly used in approved products
- Compliant with CFR21 177.2410 (Durable goods for repeated use)
- Extraction studies run on products
Phenolic Curing Resins

*Market Analysis*

- Durable rubber goods
  - 20,000 MT estimated
- Thermoplastic Elastomers (TPV’s)
  - >200,000 MT finished goods
- Pharmaceutical Use
  - 6000 MT of products in North America
  - 4000 MT of products in Europe
  - Increased usage globally
References

- “The Mechanism of Phenolic Resin Vulcanization of Unsaturated Elastomers”
  Lattimer et al Paper No. 14, delivered at Dallas Meeting of ACS Rubber Division, April 19-22, 1988

- Helpful websites
  - www.fda.gov (US FDA website)
  - www.namsa.com (Evaluation of medical devices)
Thank you to the following for making this presentation possible:

- Schenectady International Inc.
- Schenectady International Shanghai, Ltd.
- ExxonMobil Chemical