Fast Curing Polyurea Sealants: Controllable Reactivity with Commercially Available Secondary Amines

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Fast Curing Polyurea Sealants: Controllable Reactivity with Commercially Available Secondary Amines
Why Does the Market Use Polyurea Sealants?

• Fast reactivity
• Fast return to service – used on airports runways
• Can cut flush to surface within 5 to 20 minutes
• Insensitivity to atmospheric and substrate moisture
• Prevents spalling of concrete into joint
• Cures at low temperatures – used in refrigerators
• Tunable physical properties
• 1 to 1 volume ratios - easy to meter
• Reduced VOCs versus other sealants – no VOCs possible
• Good adhesion to most substrates – adhesion promoters
• Plasticizer free formulations
Target Physical Properties of Polyurea Sealants

- Gel time – 5 to 20 minutes – optimum 10 minutes
- Longer than 15 minutes the sealant may foam
- Hardness – Shore A 85 to 90 preferred
- Tensile strength – optimum 1500 psi – not stronger than concrete
- Maximum elongation – As high as possible
- Tear resistance – 250 pli or higher
- 100% modulus – as low as possible
- Low temperature cure
Current Polyurea Sealant Formulations

- Primary amines react too rapidly for static mix tube applications
- 4,4’-SBMDA developed as a slower reacting amine
- Secondary diamines react slowly – polyurea sealants possible
- Aromatic structure

\[
\text{H} \quad \text{H} \\
(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3) \quad (\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3) \\
(\text{C}_6\text{H}_4) \quad (\text{C}_6\text{H}_4) \\
\text{N} \quad \text{N} \\
\text{H} \quad \text{H}
\]

4,4’-SBMDA
## Typical Starting Point Formulation for Polyurea Sealant

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>JEFFAMINE® D-2000</td>
<td>40.25</td>
</tr>
<tr>
<td>4,4’-SBMDA</td>
<td>48.30</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>9.35</td>
</tr>
<tr>
<td>TINUVIN® 292</td>
<td>0.46</td>
</tr>
<tr>
<td>TINUVIN® 1130</td>
<td>0.46</td>
</tr>
<tr>
<td>IRGANOX® 1135</td>
<td>0.94</td>
</tr>
</tbody>
</table>

- Typically applied 1 to 1 by volume with a 14-16% NCO prepolymer

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¹Chemical Suppliers are on the last slide
Properties of 4,4’-SBMDA-based Sealants

- Used BAYTEC® MP-160 and a 14% NCO prepolymer
- 14% NCO prepolymer was blend of BAYTEC® MP-160 and DESMODUR® E 210
Gel Time of Polyurea Caulk

- **BAYTEC® MP-160**
  - Gel Time: 728B-16%
- **Blend**
  - Gel Time: 735A-14%
Hardness of Polyurea Caulk

Shore A Hardness

- BAYTEC® MP-160
- Blend

Values:
- 728B: 98
- 735A-14%: 92

Graph compares the hardness of Polyurea Caulk blends with BAYTEC® MP-160 and its blend.
Tensile Strength of Polyurea Caulk

- Too strong for most caulk applications
- Concrete will break before sealant

BAYTEC® MP-160

Strength is adequate

728B-16%

735A-14%

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Elongation of Polyurea Caulk

- BAYTEC® MP-160: 728B-16%
- Blend: 735A-14%

Good Elongation

Elongation (%)

- 728B-16%
- 735A-14%
Tear Resistance of Polyurea Caulk

- BAYTEC® MP-160 has good tear resistance.
- Blend has lower tear resistance compared to BAYTEC® MP-160.

Tear Resistance (pli):
- 728B-16%:
  - 600
- 735A-14%:
  - 400

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Evaluation of Aspartic Esters in Polyurea Sealant Formulations

• Objective – Evaluate aspartic ester amines in sealant formulations
• Reactivity of amines
  • DESMOPHEN® NH 1220 – very fast
  • DESMOPHEN® NH 1520 – very slow
  • DESMOPHEN® NH 1420 – close
• Blends of DESMOPHEN® NH 1520/DESMOPHEN® NH 1420 to adjust reactivity
# Polyaspartic Esters

<table>
<thead>
<tr>
<th>DESMOPHEN®</th>
<th>NH-1520</th>
<th>NH-1420</th>
<th>NH-1220</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Solids</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Eq Wt</td>
<td>291</td>
<td>277</td>
<td>229</td>
</tr>
<tr>
<td>η at 25°C (cps)</td>
<td>1500</td>
<td>1500</td>
<td>150</td>
</tr>
<tr>
<td>Reactivity</td>
<td>low</td>
<td>mid</td>
<td>high</td>
</tr>
<tr>
<td>Amine</td>
<td>cycloaliphatic</td>
<td>cycloaliphatic</td>
<td>linear</td>
</tr>
</tbody>
</table>

![Chemical structures](image-url)
Reactivity of Aspartic Ester Blends

![Graph showing gel time for different concentrations of Desmophen NH 1520.]

- **14 % NCO Prepolymer**
- **No JEFFAMINES® in B-side**

Gel Time (m):
- 0%
- 25%
- 50%
- 75%
- 100%

Desmophen NH 1520 (%):
- 0%
- 25%
- 50%
- 75%
- 100%
Effect of Jeffamine on Aspartic Ester Formulations

Technically possible to make ultra slow polyurea caulks, but…….. JEFFAMINE® Free hides the true reactivity of the aspartic esters.
Optimization of Properties and Process

Molecular sieves increases window

NH 1520 (%) vs. NCO (%) chart:
- Foamy
- Brittle
- Shorter Gel Times <5M
- Window

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Index Study

• Determine the effects of index on the physical properties of polyurea sealants.
• Base study on DESMODUR® E 210 (commercial product)
• Try to optimize properties with the commercial isocyanate
Gel Time of Polyurea Caulk

Good gel times

Gel Time (m)

<table>
<thead>
<tr>
<th>Gel Time</th>
<th>763H</th>
<th>763E</th>
<th>763F</th>
<th>763A</th>
<th>763G</th>
</tr>
</thead>
<tbody>
<tr>
<td>95</td>
<td></td>
<td>100</td>
<td>105</td>
<td>107</td>
<td>110</td>
</tr>
</tbody>
</table>

Good gel times: 95, 100, 105, 107
Tensile Strength of Polyurea Caulk

Adequate tensile strength

<table>
<thead>
<tr>
<th>Material</th>
<th>100%</th>
<th>200%</th>
<th>300%</th>
</tr>
</thead>
<tbody>
<tr>
<td>763H</td>
<td>95</td>
<td>100</td>
<td>105</td>
</tr>
<tr>
<td>763E</td>
<td>100</td>
<td>105</td>
<td>107</td>
</tr>
<tr>
<td>763F</td>
<td>100</td>
<td>105</td>
<td>107</td>
</tr>
<tr>
<td>763A</td>
<td>107</td>
<td></td>
<td></td>
</tr>
<tr>
<td>763G</td>
<td>110</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Elongation of Polyurea Caulk

Good elongations

Elongation (%)

763H: 95
763E: 100
763F: 105
763A: 107
763G: 110
Tear Resistance of Polyurea Caulk

![Bar chart showing tear resistance values for Polyurea Caulk samples 763H, 763E, 763F, 763A, and 763G. The values range from 95 to 110 pli.](image)
Properties of Optimized Desmodur® E 210 Polyurea Formulations

<table>
<thead>
<tr>
<th>Formulation</th>
<th>JEFFAMINE® D-2000*</th>
<th>DESMOPHEN® NH 1420</th>
<th>TINUVIN® 292</th>
<th>TINUVIN® 1130</th>
<th>IRGANOX® 1135</th>
<th>KRONOS®, TiO₂</th>
<th>Gel Time (m)</th>
<th>Shore A Hardness</th>
<th>Tensile Strength (psi)</th>
<th>100% Modulus (psi)</th>
<th>200 % Modulus (psi)</th>
<th>300 % Modulus (psi)</th>
<th>Maximum elongation (%)</th>
<th>Tear Resistance (pli)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41.28</td>
<td>47.67</td>
<td>0.24</td>
<td>0.24</td>
<td>0.49</td>
<td>9.82</td>
<td>6.1</td>
<td>91</td>
<td>1218</td>
<td>689</td>
<td>876</td>
<td>1091</td>
<td>352</td>
<td>341</td>
</tr>
<tr>
<td>2</td>
<td>38.00</td>
<td>51.75</td>
<td>0.25</td>
<td>0.25</td>
<td>0.50</td>
<td>5.00</td>
<td>9.5</td>
<td>91</td>
<td>914</td>
<td>502</td>
<td>611</td>
<td>720</td>
<td>450</td>
<td>288</td>
</tr>
</tbody>
</table>

*Blend reacted 1 to 1 with DESMODUR® E 210
UV Stability of Polyurea Caulks

• Compare standard polyurea sealant formulations with aspartic ester-based sealant formulations
• Tested using Xenon Arc weatherometer
• ASTM G 155*, cycle #1, 1000 h
  – 102 minute cycle no spray – 63 C black panel
  – 18 minute cycle with spray
  – 45 C conditioning water

*same as ASTM D6695 cycle #1 or ASTM D2565-99 cycle #1
500 H Xenon Arc
Aromatic Amine

930776A

500 H Xenon Arc
Aspartic Esters

930776B

OCT 19 2006
Low Temperature Performance

- Polyurea sealants are often used in low temperature applications
- Epoxies and polyurethanes do not cure as well as the temperature is lowered
- Polyurea sealants are often used in refrigerators
- Can be used in exterior applications where other sealants will not cure

Why Do Polyurea Sealants Cure at < 0 C?
Higher NCO content prepolymers evolve more energy
Lower NCO content evolves less energy
Aspartic ester amines react slower

Tested at 20 C
Polyurea Sealant Exotherm

Higher starting temperature – higher exotherm

Must keep resin warm before mixing
Increased Low Temperature Reactivity by Blending Amines

25% DESMOPHEN® NH 1220/
75% DESMOPHEN® NH 1420
Low Temperature Cure

• Higher NCO prepolymerers evolve more heat
• Higher NCO prepolymerers reach a higher exotherm temperature
• Aspartic ester-based formulations are designed to react slower
• Chemicals must be kept warm
• DESMOPHEN® NH 1220 can be used to speed up low temperature reactions
Advantages of Aspartic Esters in Polyurea Sealant Formulations

• Wide latitude in gel times
• Faster systems possible
• Slower systems possible
• Improved UV stability
• Improved color stability
• More economical formulations
• Plasticizer free formulations
Conclusions

• Aspartic ester can be used in polyurea sealants
• NCO content of the prepolymer must be lower with aspartic ester amine formulations
• UV stability is improved with aspartic ester b-side formulations
• Low temperature cure will still occur with aspartic ester technology
• Systems based on high NCO prepolymer will release more energy at low temperatures
• Keeping the B-side component warm is important in low temperature applications
• Plasticizer free formulations are possible
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