Aromatic Polycarbodiimides: Crosslinkers for Water Based Adhesives

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Crosslinkers in PSAs

- Lower peel strength
- Lower peel build
- Increase shear
- Increase anchorage
- Increase water & chemical resistance
- Impart clean removability
Applications Using Crosslinkers

- Protective masking films
- Mounting tapes
- Carpet tapes
- Vinlys for graphic arts, lettering
- Removable labels
Aromatic pCDI

Made by polymerizing di-functional isocyanates
Reaction of pCDI with Carboxylic Acid

\[ \text{N} = \text{C} = \text{N} \quad + \quad \text{COH} \quad \rightarrow \quad \text{H}_2\text{N} - \text{C} - \text{N} - \text{C} = \text{O} \]

Reaction occurs in wet emulsion, added just prior to coating
Main absorption band at 2135 cm$^{-1}$, well separated from any polymer bands
Toxicity of pCDI

- Studies
  - Ames test: negative (test for mutagenic/carcinogenic potential)
  - Ingestion LD$_{50}$: no effects up to highest dosage level tested (5g/Kg)
- HMIS – 1,2,0 (Toxicity, Flammability, Reactivity)
- Supplied as a 50% solution in propylene glycol methyl ether acetate
Test Conditions

- Samples direct coated to 2 mil treated LDPE film
- Coatweight target 0.3 mils dry
- Samples covered with silicone release liner, conditioned at least overnight at 72°F, 50% rH (PSTC conditions) before testing
- Peel measured using PSTC-1
- All failure modes adhesive unless otherwise noted
- Crosslinker percentages calculated solid on solid
Potlife of pCDI Crosslinker: Peel Reduction

Peel level of un-crosslinked emulsion

0.5% pCDI in PSA-1
Potlife of pCDI Crosslinker: 
Anchorage

<table>
<thead>
<tr>
<th></th>
<th>none</th>
<th>init.</th>
<th>1 hr</th>
<th>4 hr</th>
<th>8 hr</th>
<th>16 hr</th>
<th>24 hr</th>
<th>5 day</th>
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</thead>
<tbody>
<tr>
<td>1 hr</td>
<td>fail</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
<td>fail</td>
</tr>
<tr>
<td>24 hr</td>
<td>fail</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
<td>fail</td>
</tr>
</tbody>
</table>

0.5% pCDI in PSA-1

Test Method:
Immerse test strips in water for specified time, test anchorage by rubbing the exposed adhesive side with the intent to remove it.
Peel Force with Different Levels of pCDI Crosslinker

![Bar chart showing peel force with different levels of pCDI crosslinker.](chart.png)

PSA-1.
Typical Crosslinkers Used in Water Based PSAs

- Polyaziridine
- Polyisocyanates
- Metal Ions – Zinc, Zirconium, etc.

- Crosslinkers available for use in water based polymers are limited compared to solvent based counterparts.
Polyaziridine Reaction with Polymer

\[
\text{Polymer} - \text{CO}_2\text{CH}_2\text{CH}_2\text{NHR} + \text{Polymer} - \text{COH} \rightarrow \text{Polymer} - \text{CO}_2\text{CH}_2\text{CH}_2\text{NHR} - \text{N}_2
\]
Polyaziridine Crosslinker Data

PSA-1.
Polyisocyanate Reactions with Polymer

\[
\text{Polymer—CO}_2\text{H} + \text{R—NCO} \rightarrow \text{Polymer—CONH—R} + \text{CO}_2
\]

competing reaction – produces urea

\[
\text{H}_2\text{O} + \text{R—NCO} \rightarrow \text{R—N—C—N—R}
\]
Polyisocyanate Crosslinker Data

- PSA-1.
Metal Ion Reaction with Polymer

Polymer—CO$_2$H + M$^{++}$ →

Polymer—CO$_2$—M—O$_2$C—Polymer
Metal Ion Crosslinker Data

- Peel (oz/in)
  - PSA-4: 0% 0.3%
  - PSA-2: 0% 0.3%

- Percent Zinc Crosslinker: 1 hour, 1 week
- Cohesive
- Mixed
- Delamination

Graph illustrates the peel strength data for different crosslinker percentages and times.
Peel Force Comparison of pCDI to Other Crosslinkers

Peel (oz/in)

- none
- Zn (0.3)
- NCO (4.0)
- AZ (0.25)
- pCDI (0.5)

1 hour, 1 week, 7d@70°C

Delamination

PSA-2.
Peel Force Comparison of pCDI to Other Crosslinkers

Peel (oz/in)

- none
- Zn (0.3)
- NCO (4.0)
- AZ (0.25)
- pCDI (0.5)

- 1 hour
- 1 week
- 7d@70°C

Delamination

PSA-3.
**Wet Anchorage Test: Comparison of pCDI to Other Crosslinkers**

<table>
<thead>
<tr>
<th></th>
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<th>Zn</th>
<th>NCO</th>
<th>AZ</th>
<th>pCDI</th>
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</thead>
<tbody>
<tr>
<td>1 hour</td>
<td>fail</td>
<td>fail</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
</tr>
<tr>
<td>24 hours</td>
<td>fail</td>
<td>fail</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
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0.5% pCDI in PSA-1

**Test Method:**
Immerse test strips in water for specified time, test anchorage by rubbing the exposed adhesive side with the intent to remove it.
## Comparison of Crosslinkers

<table>
<thead>
<tr>
<th></th>
<th>None</th>
<th>Metal ion</th>
<th>NCO</th>
<th>AZ</th>
<th>pCDI</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Potlife</strong></td>
<td>good</td>
<td>good</td>
<td>2 – 8 hr</td>
<td>8+ hr</td>
<td>8+ hr</td>
</tr>
<tr>
<td><strong>Peel reduction</strong></td>
<td>none</td>
<td>high</td>
<td>high</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td><strong>Peel build</strong></td>
<td>high</td>
<td>low</td>
<td>low</td>
<td>low</td>
<td>low</td>
</tr>
<tr>
<td><strong>Anchorage</strong></td>
<td>poor</td>
<td>poor</td>
<td>good</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td><strong>Water sensitivity</strong></td>
<td>high</td>
<td>high</td>
<td>low</td>
<td>low</td>
<td>low</td>
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<tr>
<td><strong>Toxicity</strong></td>
<td>low</td>
<td>low</td>
<td>high</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td><strong>Cost in use</strong></td>
<td>--</td>
<td>low</td>
<td>high</td>
<td>low</td>
<td>mod</td>
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</tbody>
</table>
Conclusions

• Polycarbodiimides show performance characteristics similar to traditional crosslinkers commonly used in PSA’s

• Benefits:
  – Peel reduction
  – Improved anchorage to film
  – Useful potlife
  – Low toxicity