New Prepolymer Developments for Polyurea Applications

Servaas Holvoet
Krakow, November 2014
Differentiated isocyanates: helping formulators to close the gap …

PUA specifications

- $-30 \, ^\circ C < T_g$
  
  weak acids, spills
  secondary containment

  dry adhesion
  gen. steel protection

  SBI E (B2)
  cold use
  potable water: repair
  std hybrids

- $T_g << -40 \, ^\circ C$
  
  strong acids, fuel resistance, ctu exposure
  primary containment

  high wet adhesion, minimal WV & $O_2$ T
  anti-corrosive coats

  SBI D (B1)
  domestic use
  fittings

  SBI C (B1)
  specific use
  tank
  pipe

  amine availability low
  functional hybrids

Molecules

SUPRASEC® 2008
SUPRASEC® 2054
SUPRASEC® 2067

Standard prepolymer

SUPRASEC® 2154

New isocyanates

higher end applications

stringency

Tg << - 40 °C
low T flexibility

strong acids, fuel resistance, ctu exposure
primary containment

high wet adhesion, minimal WV & $O_2$ T
anti-corrosive coats

SBI C (B1)
high FR performance coating

specific use
pipe

differentiating

amine availability low
functional hybrids

PDA Europe 2014 Annual Conference - Krakow, 5-7 November
Investing in PUA: new reactor assets
Outline

- Novel PUA prepolymer
  - Hydrophobic prepolymer
  - Slower prepolymer

- Flexible PUA primer technology
Novel hydrophobic PUA prepolymer
Minimal impact on spray conditions

<table>
<thead>
<tr>
<th>Prepolymer</th>
<th>EID10093</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>yellow liquid</td>
</tr>
<tr>
<td>NCO (%)</td>
<td>15</td>
</tr>
<tr>
<td>Viscosity at 25 °C (mPa.s)</td>
<td>2900</td>
</tr>
<tr>
<td>Solvent</td>
<td>free</td>
</tr>
<tr>
<td>Functionality (av.)</td>
<td>2.05</td>
</tr>
<tr>
<td>Compatibility backbone</td>
<td>compatible with major polyether &amp; polyester polyols</td>
</tr>
</tbody>
</table>

- Excellent hydrophobicity
- Adhesion to a variety of substrates
- Hydrolytic stability
  - Resistance to aqueous acids and bases
  - Low-temperature flexibility
  - Low moisture vapor transmission rates

![Graph showing viscosity vs. temperature for EID10093 and S2054]
Graco air purge spray gun with AF2020 mix chamber in combination with a 438 spray tip.
Target thickness of films ~ 1.5 mm.

### Formulations & Application parameters

<table>
<thead>
<tr>
<th></th>
<th>Full PO prepolymer</th>
<th>PO-EO prepolymer</th>
<th>Hydrophobic prepolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2000</td>
<td>63</td>
<td>63</td>
<td>63</td>
</tr>
<tr>
<td>DEDTA</td>
<td>22</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>Unilink 4200</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Pigment paste</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Prepolymer</td>
<td>100</td>
<td>100</td>
<td>100</td>
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<tr>
<td>Index</td>
<td>110</td>
<td>110</td>
<td>110</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Full PO prepolymer</th>
<th>PO-EO prepolymer</th>
<th>Hydrophobic prepolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (A&amp;B, hose) (°C)</td>
<td>~ 80</td>
<td>~ 80</td>
<td>~ 80</td>
</tr>
<tr>
<td>Mixing Pressure (bar)</td>
<td>~ 185</td>
<td>~ 185</td>
<td>~ 185</td>
</tr>
<tr>
<td>Gel time (s)</td>
<td>5</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Tack free time (s)</td>
<td>9</td>
<td>9</td>
<td>9</td>
</tr>
</tbody>
</table>
Reduced water uptake characteristics

Gravimetric assessment, 25 deg C
Reduced water vapour transmission

Gravimetric assessment, 25 deg C
Mechanical properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Full PO prepolymer</th>
<th>Hydrophobic prepolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shore A</td>
<td>90</td>
<td>91</td>
</tr>
<tr>
<td>Shore D</td>
<td>31</td>
<td>37</td>
</tr>
<tr>
<td>Abrasion (Taber H18 1000 cycles)</td>
<td>60.6</td>
<td>83.5</td>
</tr>
<tr>
<td>Tensile strength at break</td>
<td>21.1</td>
<td>13.8</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>376</td>
<td>334</td>
</tr>
<tr>
<td>Trouser Tear</td>
<td>33.4</td>
<td>20.8</td>
</tr>
</tbody>
</table>
Slower prepolymers towards more cost efficient PUA systems
Need for slower PUA systems

- Typically, PUA reacts upon contact

  Comp A: isocyanate
  SUPRASEC® 2054 100,-

  Comp B: resin blend
  JEFFAMINE® T5000 8.8,-
  JEFFAMINE® D2000 52.8,-
  DEDTA 23.2,-
  Colour paste 0.2,-
  TiO2 15,-

- Prolonged gel times could bring benefits in terms of
  - Performance: adhesion
  - Application: overspray

- State of the art:
  - Primary aromatic amine CE
  - Secondary amine CE
  - Secondary amine polyols
  - (reactive) Diluents / Flexibilisers
  - Hybrids
  - …

Gel time: 3 sec.

For adhesion to occur, the substrate must be well wetted

Variable spray distance & fast gel time -> overspray

<table>
<thead>
<tr>
<th>TYPICAL STRUCTURE</th>
<th>RELATIVE REACTION RATE*</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-NH₂</td>
<td>100,000</td>
</tr>
<tr>
<td>RR’NH</td>
<td>20,000 – 50,000</td>
</tr>
<tr>
<td>Ar-NH₂</td>
<td>200 – 300</td>
</tr>
<tr>
<td>RCH₂-OH</td>
<td>100</td>
</tr>
<tr>
<td>HOH</td>
<td>100</td>
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</tbody>
</table>
A new isocyanate based raw material enables formulation with lower amine additives

**Standard resin / hardener system**

- **hardener**
- **PREPOLYMER**
- **+ resin**
- **Amines**
  - **DEDTA**
  - **3-4 sec.**
- **slower**
- **Gel time**
  - **7-8 sec.**
- **High CE content, €**

**Our Offer**

- **hardener**
- **UNIQUE PREPOLYMER**
- **+ resin**
- **Amines**
  - **DEDTA**
  - **7-8 sec.**
- **Gel time**
  - **7-8 sec.**
- **Reduced CE content**
While slower, performance is in line with std PUA systems

Std resin blend: D2000 + DEDTA + pigment

<table>
<thead>
<tr>
<th>NCOv (%)</th>
<th>15</th>
<th>13</th>
<th>13</th>
<th>13</th>
<th>13</th>
<th>13</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength a.b. (MPa)</td>
<td>23</td>
<td>15</td>
<td>11</td>
<td>21</td>
<td>19</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>Elongation a.b. (%)</td>
<td>416</td>
<td>412</td>
<td>236</td>
<td>376</td>
<td>407</td>
<td>461</td>
<td></td>
</tr>
<tr>
<td>Angle Tear (N/mm)</td>
<td>71</td>
<td>66</td>
<td>41</td>
<td>89</td>
<td>65</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>Abrasion (taber H18, 1000 cycles) (mg)</td>
<td>70</td>
<td>150</td>
<td>100</td>
<td>61</td>
<td>72</td>
<td>75</td>
<td></td>
</tr>
</tbody>
</table>

Slow CE free!
Flexible primer technology
Substrates can dimensionally vary in time…

Metallic  Wood  Asphalt

Ceramics  Overlap zones concrete with rubber, asphalt etc.

Expansion & shrinkage through heat/cold, Δ moisture, load etc.

Need for flexible coating technologies to accommodate these
1K PU primers

- **Product characteristics**
  - light brown colour, transparent
  - ± 250 - 425 mPa.s @ 25 ºC
  - 100% solids

- **Product features** (under adequate surface preparation conditions)
  - 1K moisture cure at low temperature
  - low consumption (150 g/m²/layer or lower)
  - fast/broad overcoat window
  - low viscosity which allows good penetration in porous substrates
  - good wetting of broad range of substrates

<table>
<thead>
<tr>
<th>Primer</th>
<th>Reactivity to moisture</th>
<th>Tensile strength (MPa)</th>
<th>Elongation (%)</th>
<th>Viscosity (mPa.s) (*)</th>
<th>NCOv (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUPRASEC® 2413</td>
<td>Slow</td>
<td>too brittle</td>
<td></td>
<td>250</td>
<td>24</td>
</tr>
<tr>
<td>SUPRASEC® 2416</td>
<td>Fast</td>
<td>too brittle</td>
<td></td>
<td>250</td>
<td>24</td>
</tr>
<tr>
<td><strong>SUPRASEC® 2451</strong></td>
<td><strong>Slow</strong></td>
<td><strong>65</strong></td>
<td><strong>35</strong></td>
<td><strong>425</strong></td>
<td><strong>12</strong></td>
</tr>
</tbody>
</table>

(*) measured at 25 ºC
Cylindrical bend test demonstrates high flexibility

CuSO₄/HCl test -> defect free!
**Priming concrete for Polyurea: flex primer**

- **Cohesive strength concrete**: 5.8 MPa
- **25 °C, 50 % relative humidity**

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Graph showing:
- Fast strength build-up
- Recommended overcoat window: 30 min. - 48 hours
- Mode of failure: mainly concrete failure
Priming **concrete** for Polyurea

25 °C, 50 % relative humidity

Cohesive strength concrete = 5.8 MPa

<table>
<thead>
<tr>
<th>Primer</th>
<th>Recommended overcoat window</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2413</td>
<td>2 – 72 hrs</td>
</tr>
<tr>
<td>S2416</td>
<td>0.5 – 48 hrs</td>
</tr>
<tr>
<td>S2451</td>
<td>0.5 – 48 hrs</td>
</tr>
</tbody>
</table>
Priming **steel** for Polyurea: flex primer

25 ºC, 50 % relative humidity

Cohesive strength concrete = 5.8 MPa

- recommended overcoat window: 4 – 48 hrs
- catalysis allows for a faster window
- recommended loading: 50 - 150 g/m²
**Priming steel for Polyurea**

25 ºC, 50% relative humidity

Cohesive strength concrete = 5.8 MPa

<table>
<thead>
<tr>
<th>Primer</th>
<th>Recommended Overcoat Window</th>
<th>Recommended Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2413</td>
<td>2 – 24 hrs</td>
<td>50-150 g/m²</td>
</tr>
<tr>
<td>S2416</td>
<td>0.5 – 8 hrs</td>
<td>50-150 g/m²</td>
</tr>
<tr>
<td>S2451</td>
<td>8 – 48 hrs</td>
<td>50-150 g/m²</td>
</tr>
</tbody>
</table>

Graph showing adhesion over time for different primers, with recommended overcoat windows and loading.
Conclusions & Acknowledgements

- Huntsman continues to innovate and provide solutions for the PUA market through differentiated isocyanates
  - hydrophobic prepolymerms enabling water repellent systems
  - slower, easier applicable prepolymerms enabling more cost-efficient formulating
  - a novel 1K flexible primer technology

- Huntsman is committed to develop these with formulators in the Polyurea market.

- All credits for the coating team: Stijn Roeckaerts, Sylvie Cochet, Stefan Priemen, Maren Ryckeboer and Marc Broekaert

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