A Family of Waterbased Acrylics based on a Unique Self-Crosslinking Mechanism
Overview of the Presentation

- History of Interpolymer Acrylic Development
- Self-Crosslinking Theory, Monomers, Backbone & Mechanism
- Film Formation Overview
- Acrylics & Starting Point Formulation Details
- Application Information
- Physical Testing Results
- Summary
- Thank You & Questions
Timeline of Acrylic Development at Interpolymer

- **1960’s**  Styrenated Acrylics
- **1980’s**  Olefin Grafted Acrylics
- **1990’s**  Cationic Acrylics
- **2000’s**  Bimodal Acrylics
- **2010’s**  Self-Crosslinking Acrylics

Interpolymer – A company of Zschimmer & Schwarz
Developmental Model for the Self-Crosslinking Acrylic

Development Theory (what potential product should have)
- Ease of use (1K instead of 2K system potential).
- Health and Safety benefits.
- Improved economics of coating.
- Properties need to be similar to traditional post-addition crosslinkers.

Development Target (what Interpolymer wants beyond Theory)
- Crosslinking needs to react at room temperature.
- Stability profile needs to be same as traditional acrylic technology.
- Robust enough to be usable in multiple technologies & markets.
- Needs to be “Unique” mechanism that adds value to our product line.
Monomers used in Self-Crosslinking Acrylics

MAA = Methacrylic Acid Monomer, $\text{H}_2\text{C}=\text{C(CH}_3\text{-COOH}$

$X = \text{Schiff Monomer blend, H}_2\text{C}=\text{CH-R-Z} \& \text{H}_2\text{C}=\text{CH-R’-Z’}$

STY = Styrene Monomer, $\text{H}_2\text{C}=\text{CH-C}_6\text{H}_5$

MMA = Methyl Methacrylate Monomer, $\text{H}_2\text{C}=\text{C(CH}_3\text{-CO-O-CH}_3$

$Y = \text{Self-Condensing Monomer, H}_2\text{C}=\text{CH-R’’-Z’’}$

BA = Butyl Acrylate Monomer, $\text{H}_2\text{C}=\text{CH-CO-O-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$
Backbone Formation of Self-Crosslinking Acrylics

Acrylic Emulsion Polymerization

Interpolymer – A company of Zschimmer & Schwarz
Mechanism of Self-Crosslinking Acrylates

1. Apply formulated polymer to substrate
2. Remove the Water & Coalescing Solvents
3. Crosslinking network develops during film formation.

Aqueous Emulsion

Self-Crosslinked Polymer Film
**Film Formation of Waterbased Polymers**

*MFFT* = Minimum Film Formation Temperature

- No film formation
- Film formation

**Factors that Influence the Film Formation:**
- Backbone configuration and composition
- Atmospheric conditions
- Ingredients of the formula
- Substrate porosity and composition

**Water evaporation**

- Aqueous emulsion
- Closest particle packing
- Deformed particles
- Polymer film

Film formation

*T°C > MFFT*
### Information on Acrylics used in this Presentation

<table>
<thead>
<tr>
<th>Code</th>
<th>% NV</th>
<th>Calc. Tg</th>
<th>Actual MFFT</th>
<th>X/Y Ratio</th>
<th>% X+Y of Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>SX Tg 5</td>
<td>42%</td>
<td>5°C (41°F)</td>
<td>15°C (59°F)</td>
<td>55/45</td>
<td>4.5%</td>
</tr>
<tr>
<td>Tg 5</td>
<td>42%</td>
<td>5°C (41°F)</td>
<td>10°C (50°F)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SX Tg 35</td>
<td>42%</td>
<td>35°C (95°F)</td>
<td>45°C (113°F)</td>
<td>55/45</td>
<td>5.2%</td>
</tr>
<tr>
<td>Tg 35</td>
<td>42%</td>
<td>35°C (95°F)</td>
<td>40°C (104°F)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SX Tg 65</td>
<td>40%</td>
<td>65°C (149°F)</td>
<td>75°C (167°F)</td>
<td>64/36</td>
<td>4.0%</td>
</tr>
<tr>
<td>Tg 65</td>
<td>40%</td>
<td>65°C (149°F)</td>
<td>68°C (155°F)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: all of the above acrylic backbones are the same, ratio’s adjusted to hit targeted Tg. X & Y levels chosen to optimize Tg and physical property targets.
### Information on Application Formulas used in this Presentation

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Tg 5 Polymers</th>
<th>Tg 35 Polymers</th>
<th>Tg 65 Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>27.60%</td>
<td>28.99%</td>
<td>29.22%</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>-</td>
<td>2.89%</td>
<td>5.67%</td>
</tr>
<tr>
<td>Coalescing Solvent</td>
<td>-</td>
<td>2.71%</td>
<td>3.24%</td>
</tr>
<tr>
<td>Leveler</td>
<td>0.90%</td>
<td>0.90%</td>
<td>0.90%</td>
</tr>
<tr>
<td>Acrylic Resin</td>
<td>71.50%</td>
<td>64.51%</td>
<td>60.97%</td>
</tr>
<tr>
<td>Total Solids</td>
<td>30%</td>
<td>30%</td>
<td>30%</td>
</tr>
<tr>
<td>pH</td>
<td>7-9</td>
<td>7-9</td>
<td>7-9</td>
</tr>
<tr>
<td>Viscosity</td>
<td>&lt; 100 cps</td>
<td>&lt; 100 cps</td>
<td>&lt; 100 cps</td>
</tr>
<tr>
<td>VOC Content</td>
<td>&lt; 10 g/L</td>
<td>79.5 g/L</td>
<td>94.3 g/L</td>
</tr>
</tbody>
</table>

*Note: all of the above formulas were designed for room temperature film formation.*

*This slide does not include the white paint formula based on Tg 5 polymers used in some examples.*
Information on Application Data used in this Presentation

• This Evaluation took place over a 10 month period (February 2016 – December 2016).

• The purpose was to evaluate our Self-Crosslinking Mechanism over multiple substrates targeting multiple markets.

• 14 Substrate types used during evaluation (Concrete, Oak, Maple, Pine, Poplar, Red & Grey Quarry Tiles, PVC, VCT, Glass, Steel, Aluminum and Coated & non-Coated Leneta Cards)

• 6 Markets were targeted during evaluation (Flooring, Furniture, OPV for Labels, OPV for non-FDA Packaging, Paints and Kitchen Cabinets).

• All evaluations were repeated by the multiple members of Interpolymer’s Massachusetts Laboratory Staff.

• The following is only the highlights of all the data & photographs recorded during the Self-Crosslinking Acrylic Study.
Physical Testing - Bench Testing Results

<table>
<thead>
<tr>
<th></th>
<th>Tg 5</th>
<th>SX Tg 5</th>
<th>Tg 35</th>
<th>SX Tg 35</th>
<th>Tg 65</th>
<th>SX Tg 65</th>
</tr>
</thead>
<tbody>
<tr>
<td>60° Gloss</td>
<td>86</td>
<td>88</td>
<td>84</td>
<td>86</td>
<td>84</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>71</td>
<td>72</td>
<td>73</td>
<td>74</td>
<td>74</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>76</td>
<td>78</td>
<td>65</td>
<td>80</td>
<td>67</td>
<td>75</td>
</tr>
<tr>
<td>Recoatablety</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>(ASTM D 3153)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sward Hardness</td>
<td>18</td>
<td>24</td>
<td>28</td>
<td>30</td>
<td>30</td>
<td>34</td>
</tr>
<tr>
<td>(ASTM D 2134)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pencil Hardness</td>
<td>3B</td>
<td>2B</td>
<td>2B</td>
<td>HB</td>
<td>B</td>
<td>F</td>
</tr>
<tr>
<td>(ASTM D 3363)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wear Index</td>
<td>48</td>
<td>46</td>
<td>60</td>
<td>62</td>
<td>64</td>
<td>65</td>
</tr>
<tr>
<td>(ASTM D 4060)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Pencil Hardness Scale (softer to harder): 6B-5B-4B-3B-2B-B-HB-F-H-2H-3H-4H-5H-6H
Wear Index based on 1000 cycles using CX-17 wheels with 500 g weight
### Physical Testing – Chemical Spot (ASTM D 1308) Testing Results

<table>
<thead>
<tr>
<th></th>
<th>Tg 5</th>
<th>SX Tg 5</th>
<th>Tg 35</th>
<th>SX Tg 35</th>
<th>Tg 65</th>
<th>SX Tg 65</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubbing Alcohol</td>
<td>4</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>100% Ethanol</td>
<td>4</td>
<td>1</td>
<td>5</td>
<td>0</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Skydrol Fluid</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>Mustard</td>
<td>3</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Red Wine</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Betadine</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>4</td>
<td>3</td>
</tr>
</tbody>
</table>

*Note: Chemical resistance is reported subjectively on a scale from 0 to 5 where “0” indicates no change to the film and “5” indicates complete film removal.*
Physical Testing – Water Submersion Test (Internal Method)

Tg 5

SX Tg 5

Tg 35

SX Tg 35

Tg 65

SX Tg 65

Note: Coated Red Quarry Tiles dried at room temp for 4 hours, then submerged in water for 1 week.
Physical Testing – Stain Resistance Test (ASTM D-1308)

Tg 5

SX Tg 5

Tg 35

SX Tg 35

Tg 65

SX Tg 65

Mustard
(Clear over Oak)

Betadine
(Clear over VCT Tile)

Skydrol Fluid
(Clear over Concrete)
**Physical Testing – Alcohol Resistance Test (AATCC, ASTM, KCMA)**

- **Tg 5**
  - SX Tg 5

- **Tg 35**
  - SX Tg 35

- **Tg 65**
  - SX Tg 65

**Alcohol Rubs**
(Paint over PVC)

**Hand Sanitizer Gel**
(Clear over Concrete)

**100 Proof Alcohol**
(Clear over Oak)
**Physical Testing – Alkali Submerged Test (Internal Method)**

- **Tg 5**
- **Tg 35**
- **Tg 65**

- **SX Tg 5**
- **SX Tg 35**
- **SX Tg 65**

*Note: Coated glass panel dried at room temp for 48 hours, then submerged in 2.5% Sodium Hydroxide Solution for 1 hour at 80°C.*
Physical Testing – Hot Tire Resistance Test (Internal Method)

Note: Coated panel dried at room temp for 48 hours, then 60°C tire strip pressed on surface for 15 minutes at 1000 psi.
Physical Testing – Adhesion Test (ASTM D-3359 & D-7234)

- SX Tg 5: Paint over PVC
- SX Tg 35: Clear over CRS
- SX Tg 65: Clear over Oak

- Clear Primer over Concrete
- Clear Primer over Concrete
- Clear Primer over Concrete

*Note: Concrete tested with P.A.T.T.I. Pneumatic Adhesion Pull-off Tester.*
Summary of the Self-Crosslinking Presentation

• Developed a room temperature waterbased self-crosslinking mechanism.
• Self-crosslinking mechanism based on unique dual chemistries.
• Dual chemistries allow for ability to “dial-in” property improvements.
• Improvement on stain, chemical and water resistances over uncrosslinked acrylics (similar to expected results with post-added crosslinkers).
• Easy transition from standard acrylic to self-crosslinking acrylic of same Tg, due to same stability / compatibility profile and formulation requirements.
• Better economics & EHS profile using self-crosslinking acrylics.
• Like all of our Technologies (Bimodal, Wax Graft, etc), can be manufactured at any Interpolymer facility.
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