IMPROVED ADHESION TO TPO AND OTHER HARD-TO-STICK SURFACES WITH WATERBORNE ACRYLIC RESINS

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Overview

• Adhesion is oftentimes a must-have for coatings formulations

• First noticeable sign of failure to a customer is often some form of adhesion failure

• Understanding the substrate is critical to formulating the correct type of paint
What’s in the Coating Formulation?

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Pounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>150</td>
</tr>
<tr>
<td>Dispersant</td>
<td>3</td>
</tr>
<tr>
<td>Ammonia</td>
<td>3</td>
</tr>
<tr>
<td>Defoamer</td>
<td>2</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>10</td>
</tr>
<tr>
<td>TiO2</td>
<td>60</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>400</td>
</tr>
<tr>
<td>Defoamer</td>
<td>2</td>
</tr>
<tr>
<td>Acrylic Latex (55% solids, 45% water)</td>
<td>500</td>
</tr>
<tr>
<td>Coalescent</td>
<td>7</td>
</tr>
<tr>
<td>Biocide/Fungicide</td>
<td>11</td>
</tr>
<tr>
<td>Glycol</td>
<td>11</td>
</tr>
<tr>
<td>Cellulose Thickener</td>
<td>3</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1162</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt% solids</td>
<td>65</td>
</tr>
<tr>
<td>Vol% solids</td>
<td>51</td>
</tr>
<tr>
<td>PVC</td>
<td>40</td>
</tr>
<tr>
<td>VOC, g /liter</td>
<td>41</td>
</tr>
<tr>
<td>wpg</td>
<td>11.6</td>
</tr>
</tbody>
</table>

33.5% Water

1.5% Solvent/glycol

2% Additives

24% Latex

39% Pigments/fillers
Overview

Basics of Challenging Substrates
- Metal
- Asphalt
- Low Surface Energy
  - Thermoplastic Olefin (TPO)
- Wood
- Cementitious
- Glass

Strategies to Adhere to Challenging Substrates
- Resin-based approach
- Coating Formulation
Overview

Basics of Challenging Substrates
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Strategies to Adhere to Challenging Substrates
• Resin-based approach
• Coating Formulation
Adhesion to Steel

- Provided sufficient wetting is present, acid/base interactions, ionic interactions and van der Waals forces considered of primary importance.
- Isoelectric point of steel difficult to pinpoint, but likely around pH ~8-9.
- As ammonia evaporates and pH drops, cationic sites arise allowing for electrostatic interactions.
- Mechanical interlocking also significant in blasted substrates.
Corrosion vs. Acid Content
Clear films, 1.2mil DFT, 300hrs B117

**Challenge:**
Adhesion cannot be obtained simply by increasing acid monomer content due to poor corrosion performance

Decreasing Acid Content = Improved Corrosion Resistance
Increasing Acid Content = Improved Adhesion
Formulation Impact on Adhesion Plasticizer and Dispersant

24 hr Adhesion

7 day Adhesion

Aluminum Substrate
## Adhesion to Multiple Substrates

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Metal</th>
<th>Asphalt</th>
<th>TPO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Substrate:</strong></td>
<td>Lewis acids/Lewis bases</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Adhesion Strategies:</strong></td>
<td>Use of acid monomer to improve adhesion</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dispersant choice</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Plasticizer did not impact</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Other Considerations:</strong></td>
<td>Impact on corrosion resistance</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Asphalt

- Also referred to as bitumen
- Composition
  - Naphthalenes
  - Polar Aromatics
  - Saturated hydrocarbons
  - Asphaltenes
- Widely varied in composition depending on location obtained
- Challenges with adhesion
  - Many small molecule organics (plasticize film)
  - Consideration of other properties (i.e., bleed-block)
## Design of Experiments for Asphalt Adhesion

<table>
<thead>
<tr>
<th>Design</th>
<th>Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Resin, Dispersants type, Extender type, PVC, Zinc</td>
</tr>
<tr>
<td>2</td>
<td>Resin, Dispersant type, Zinc, Wetting Aid</td>
</tr>
<tr>
<td>3</td>
<td>Resin, Dispersant Amount, PVC, Zinc</td>
</tr>
</tbody>
</table>
180° Peel Adhesion Testing

Coating Applied with Fabric Embedded

Water Soak

Strip Cut

Test Run
DOE 1 Results

- Adhesion: Significant effects from resin, hydrophilic dispersant imparts better adhesion
- Bleed Block: Hydrophilic dispersant detrimental, Large effect from latex, smaller effect from dispersant
DOE 2 Results

Adhesion affected by latex choice, dispersion type

Wetting aid had a surprising negative effect on adhesion

- Failure mode indicated aggregate pull out for all samples
- More aggregate removed with wetting aid present – interfering with previous bond?
DOE 3 Results

Main Effects Plot for Adhesion

<table>
<thead>
<tr>
<th>Latex</th>
<th>Disp (lbs)</th>
<th>ZnO (lbs)</th>
<th>PVC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Adhesion
## Adhesion to Multiple Substrates

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Adhesion Strategies</th>
<th>Other Considerations</th>
</tr>
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</table>
| **Metal** | • Lewis acids/Lewis bases  
• Use of acid monomer to improve adhesion  
• Dispersant choice  
• Plasticizer did not impact  
• Other Considerations:  
• Impact on corrosion resistance | |
| **Asphalt** | • Substrate:  
Small molecule hydrocarbons, Naphthalenes, polar aromatics  
• Adhesion Strategies:  
• Asphalt is a complex mixture  
• Resin choice  
• Many formulation options  
• Other Considerations  
• Impact on bleed black performance | |
| **TPO** | | |
Thermoplastic Olefin (TPO)

- Poly(olefins) are made from alkenes ($C_nH_{2n}$)
Thermoplastic Olefin (TPO)

- Unlike metal substrates, TPOs have no functionality that can be used to improve adhesion (i.e., acids, amines, hydroxyls, etc.)
- TPO membranes have other ingredients such as TiO$_2$, flame retardants, UV absorbers/stabilizers, processing aids

So how does one improve adhesion to TPO??
Methods to Improve TPO Adhesion: *Surface Roughening*

**TPO Substrate**

Surface roughening (i.e., sanding)

**Apply Coating**

**Drawback:** Requires modification of substrate
- As coating manufacturer, this is undesirable
- Also undesirable for coating applicator, as this requires time ($$$)
Methods to Improve TPO Adhesion: *Aging Substrate*

**TPO Substrate**

- Aging (Membrane Degradation)

**Drawback:** Requires time for TPO to age
  - Not useful for repair or in instances where virgin TPO is used
Methods to Improve TPO Adhesion: *Solvent-based*

**TPO Substrate**

- Apply solvent based coating system or wipe
- Allow solvent/polymer to penetrate into substrate and evaporate, leaving polymer

**Drawback:** High VOC, odor, may still not adhere (due to lack of functionality)
Methods to Improve TPO Adhesion: *Primer/Basecoat*

- **TPO Substrate**
  - Apply a primer/basecoat
  - Apply a topcoat

**Drawback:** High VOC, odor, may still not adhere (due to lack of functionality)
Methods to Improve TPO Adhesion: **Primer/Basecoat**

- Block copolymers with some component of functional PE/PP

**Drawback:** Difficult to make block copolymers in traditional emulsion polymerization
- Many of these primer/basecoat approaches are solvent-based
- Water-based approaches are not effective on virgin TPO
Methods to Improve TPO Adhesion: *Primer/Basecoat*

Typical emulsion polymer components

- Some components are necessary to make stable emulsion polymers
- Ethylene/propylene cannot be incorporated into emulsion polymerization
- Polarity of many common monomers not ideal

![Chemical structures of MMA, Styrene, BA, BMA, acrylic acid, methacrylic acid, and 2-EHA]
Methods to Improve TPO Adhesion: Primer/Basecoat

Typical emulsion polymer components
- Some components are necessary to make stable emulsion polymers
- Ethylene/propylene cannot be incorporated into emulsion polymerization

Emulsion polymers are random (not block-like)
- Difficult for “non-polar” regions to associate together

Drawback: Difficult to make block copolymers in traditional emulsion polymerization
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Methods to Improve TPO Adhesion: Primer/Basecoat

Emulsion polymers are random (not block-like)
- Difficult for “non-polar” regions to associate together

-AAAAA,BBBBBBBBBBAAAAAA-
-ABABABABABABBBABABABABA-

Drawback: Difficult to make block copolymers in traditional emulsion polymerization
- Many of these primer/basecoat approaches are solvent-based
- Water-based approaches are not effective on virgin TPO

Market Need: Obtain adhesion on virgin TPO in a waterborne acrylic emulsion
TPO Adhesion Experimental Design

Purpose

- Gain an understanding of the effect of various parameters on TPO primer formulation performance, namely, Adhesion, Tack, and Water Uptake

Variables tested

- Polymer Type (Conventional latex vs. Experimental latex)
- Dispersant ladder: 1 - 9 lbs
- Nonionic wetting aid: 0 - 1% on total pigment
- Filler particle size and PVC: Ladder from 20-60% by 5% using both 3 and 12 micron calcium carbonate (CC)
## TPO Primer Base Formula

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Pound</th>
<th>Gallon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>156.00</td>
<td>18.73</td>
</tr>
<tr>
<td>Dispersant</td>
<td>3.00</td>
<td>0.30</td>
</tr>
<tr>
<td>Ammonium Hydroxide</td>
<td>3.00</td>
<td>0.40</td>
</tr>
<tr>
<td>Defoamer</td>
<td>1.00</td>
<td>0.12</td>
</tr>
<tr>
<td>TiO₂</td>
<td>30.00</td>
<td>0.90</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>450.00</td>
<td>19.94</td>
</tr>
<tr>
<td>Defoamer</td>
<td>1.00</td>
<td>0.12</td>
</tr>
<tr>
<td>Polymer</td>
<td>450.00</td>
<td>52.63</td>
</tr>
<tr>
<td>Mildewcide/Fungicide</td>
<td>11.00</td>
<td>1.15</td>
</tr>
<tr>
<td>Propylene Glycol</td>
<td>11.00</td>
<td>1.27</td>
</tr>
<tr>
<td>Rheology Modifier</td>
<td>3.00</td>
<td>0.26</td>
</tr>
<tr>
<td>Water</td>
<td>34.90</td>
<td>4.18</td>
</tr>
<tr>
<td>Total</td>
<td>1153.9</td>
<td>100</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Weight Solids</td>
<td>65.91</td>
</tr>
<tr>
<td>Volume Solids</td>
<td>52.82</td>
</tr>
<tr>
<td>PVC</td>
<td>40.16</td>
</tr>
<tr>
<td>Weight/gal</td>
<td>11.54</td>
</tr>
<tr>
<td>VOC, g/L</td>
<td>24</td>
</tr>
</tbody>
</table>
Resin Impact on Peel Adhesion

Dramatic impact on resin choice…

45 mil new TPO

Dramatic impact on resin choice…
## Results - Adhesion

<table>
<thead>
<tr>
<th>Variable</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersant ladder</td>
<td>Little effect until 9 lbs then 25% drop</td>
</tr>
<tr>
<td>Nonionic wetting aid</td>
<td>Negative – 0.5% and 1% caused significant drop</td>
</tr>
<tr>
<td>Filler particle size and PVC</td>
<td>Negative - large drop above 40 PVC for 3m CC, 30 PVC for 12m CC</td>
</tr>
</tbody>
</table>

### Graphs

1. **Pigment Volume Concentration (PVC)**
   - Bars represent peel adhesion (pli) at different PVC levels.
   - Different colors indicate 3 micron CC and 12 micron CC.

2. **% Surfactant on Total Pigment**
   - Bars represent peel adhesion (pli) at different surfactant levels.
Roofing System Cross Section
180° Peel Membrane Adhesion Testing

Initial → 2 in/min pull rate → End of Test
Benchmarking - Adhesive

**Competitive Benchmark - 180° Peel Adhesion**

<table>
<thead>
<tr>
<th>Sample</th>
<th>24hr dwell @ RT</th>
<th>Mode of failure</th>
<th>7 day dwell @ RT</th>
<th>Mode of failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>WB Commercial Sample 1</td>
<td>4.1 pli</td>
<td>Adhesive</td>
<td>3.8 pli</td>
<td>Adhesive</td>
</tr>
<tr>
<td>WB Commercial Sample 2</td>
<td>6.9 pli</td>
<td>Adhesive</td>
<td>4.5 pli</td>
<td>Adhesive</td>
</tr>
<tr>
<td>WB Commercial Sample 3</td>
<td>5.3 pli</td>
<td>Cohesive</td>
<td>9.3 pli</td>
<td>Cohesive</td>
</tr>
<tr>
<td>EPS Experimental Polymer</td>
<td>9.5 pli</td>
<td>Cohesive</td>
<td>15.5 pli</td>
<td>Cohesive</td>
</tr>
<tr>
<td>Solvent-based Commercial Sample 1</td>
<td>2.2 pli</td>
<td>Cohesive</td>
<td>8.5 pli</td>
<td>Cohesive</td>
</tr>
<tr>
<td>Solvent-based Commercial Sample 2</td>
<td>2.5 pli</td>
<td>Cohesive</td>
<td>8.1 pli</td>
<td>Cohesive</td>
</tr>
<tr>
<td>Solvent-based Commercial Sample 3</td>
<td>1.9 pli</td>
<td>Cohesive</td>
<td>10.3 pli</td>
<td>Cohesive</td>
</tr>
</tbody>
</table>

**Testing Conditions - 180° Peel Adhesion**

- Crosshead Speed: 2 inches/minute
- Spread Rate: 9 lbs/100ft²
- GAF 45 mil TPO
- Substrate: Plywood

**Red: Adhesive failure, 24H**
- Pink: Adhesive failure, 7 day
- Blue: Cohesive failure, 24 H
- Lt. Blue: Cohesive failure, 7 day
# Adhesion to Multiple Substrates

## Metal
- **Substrate:**
  - Lewis acids/Lewis bases
- **Adhesion Strategies:**
  - Use of acid monomer to improve adhesion
  - Dispersant choice
  - Plasticizer did not impact
- **Other Considerations:**
  - Impact on corrosion resistance

## Asphalt
- **Substrate:**
  - Small molecule hydrocarbons, Naphthalenes, polar aromatics
- **Adhesion Strategies:**
  - Asphalt is a complex mixture
  - Resin choice
  - Many formulation options
- **Other Considerations:**
  - Impact on bleed black performance

## TPO
- **Substrate:**
  - Little to no Functionality
- **Adhesion Strategies:**
  - Use of primer/basecoat layer
  - Aged TPO
  - Resin strongly impacts adhesion
- **Other Considerations:**
  - Most WB emulsion polymers = poor adhesion
  - More unique chemistries needed to obtain adhesion in WB
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Summary

Obtaining adhesion to a substrate is a complex property, involving both resin and formulation

• Need to understand the substrate so that an appropriate coating can be designed

**Technical Contributors:**

• Brent Crenshaw, Glenn Frazee, Chris Fredrickson, Mary Jane Hibben, Chris LeFever, Ashley Rodgers, Edwin Rodriguez

The data in this presentation represent typical values. Because application variables are a major factor in product performance, this information should serve only as a general guide. EPS assumes no obligation or liability for use of this information.