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

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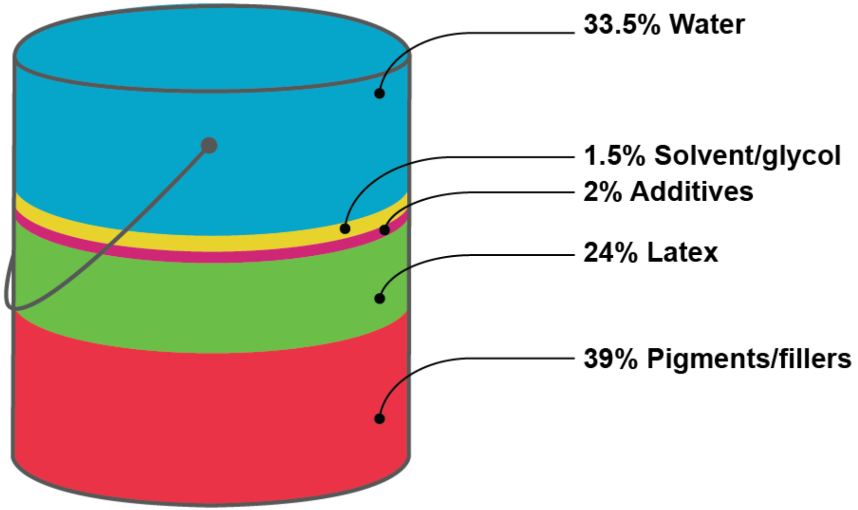
What's in the Coating Formulation?

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

Parameter	Value
Wt% solids	65
Vol% solids	51
PVC	40
VOC, g /liter	41
wpg	11.6



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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

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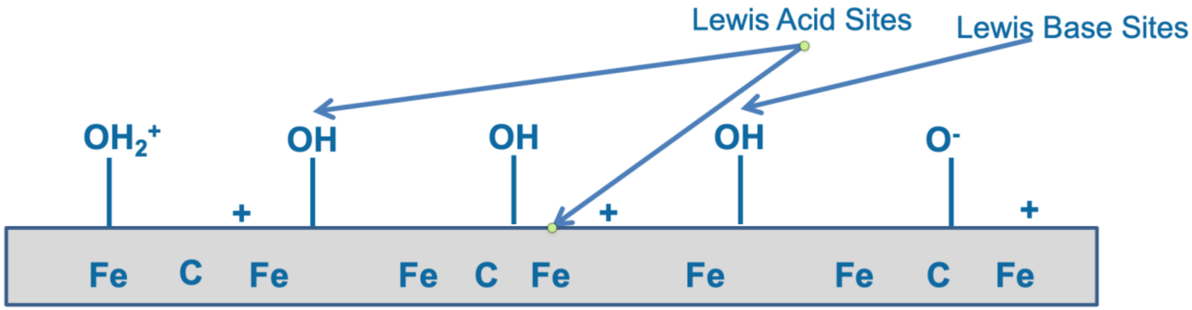
Adhesion to Steel

- Provided sufficient wetting is present, acid/base interactions, ionic interactions and van der Waals forces considered of primary importance[1]
- 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



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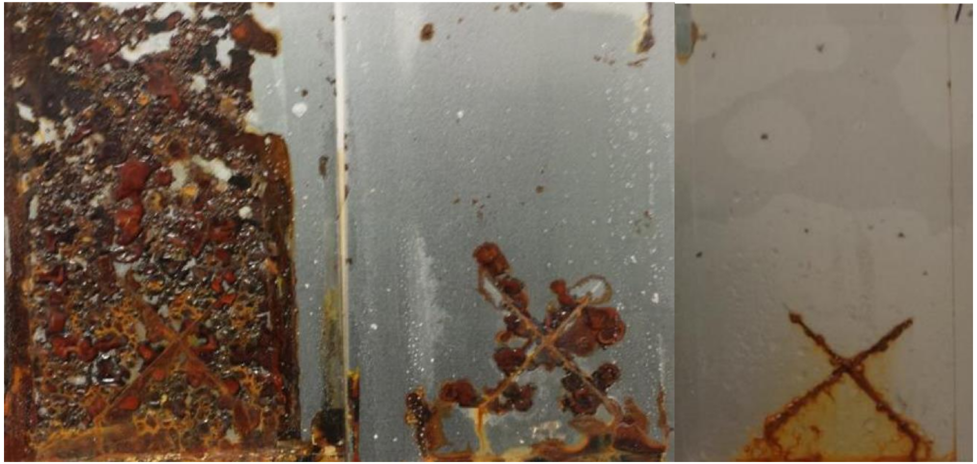
Corrosion vs. Acid Content

Clear films, 1.2mil DFT, 300hrs B117

Decreasing Acid Content = Improved Corrosion Resistance

Increasing Acid Content = Improved Adhesion

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



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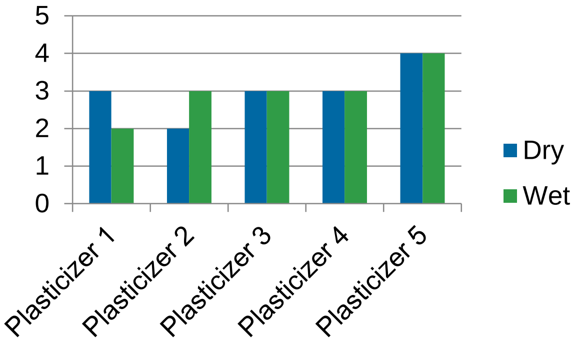
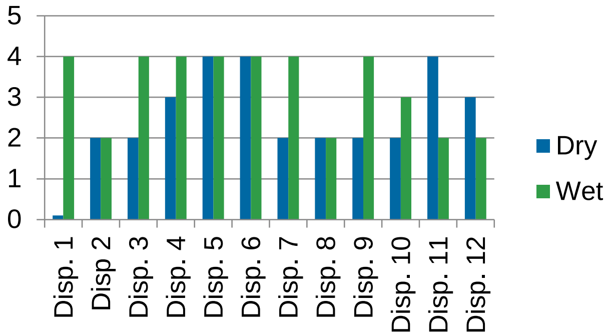
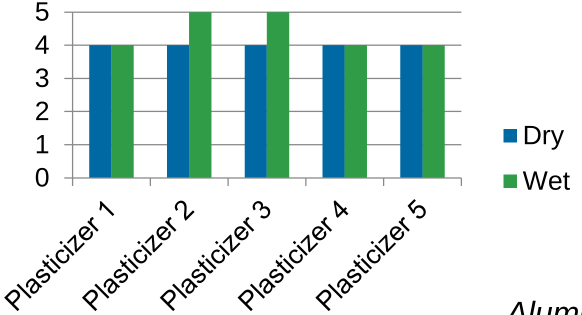
Formulation Impact on Adhesion Plasticizer and Dispersant

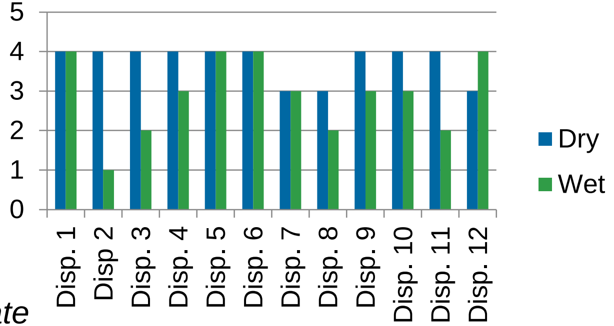
24 hr Adhesion





7 day Adhesion





Aluminum Substrate

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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

TPO

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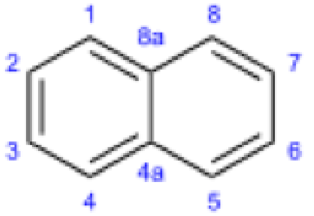
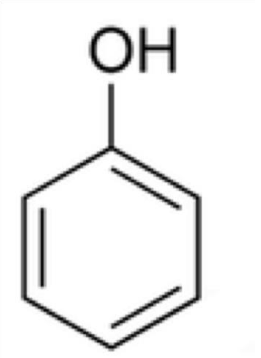
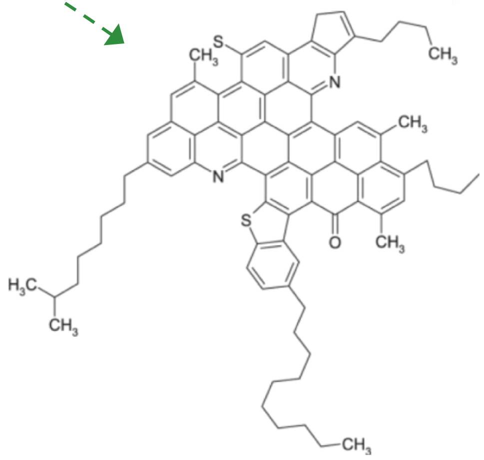
Asphalt

- 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

Design	Factors
1	Resin, Dispersants type, Extender type, PVC, Zinc
2	Resin, Dispersant type, Zinc, Wetting Aid
3	Resin, Dispersant Amount, PVC, Zinc

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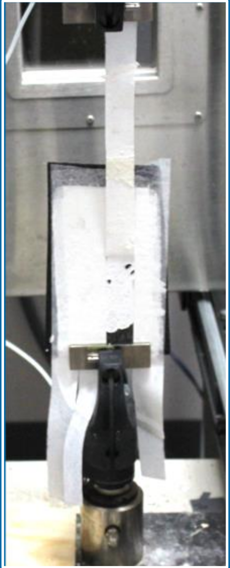
180° Peel Adhesion Testing

Coating Applied with Fabric Embedded

Water Soak

Strip Cut

Test Run



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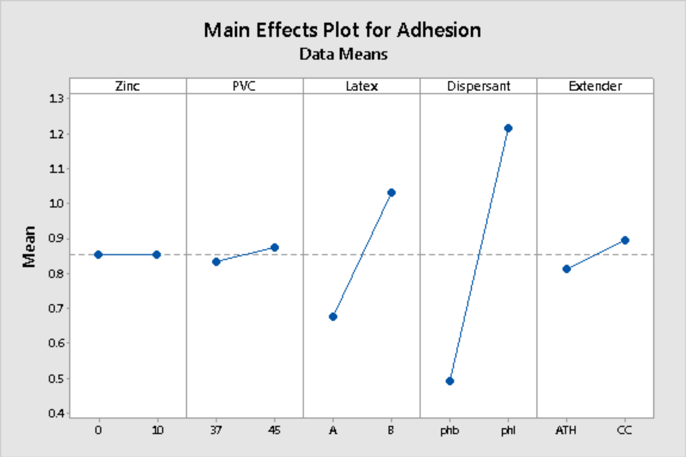
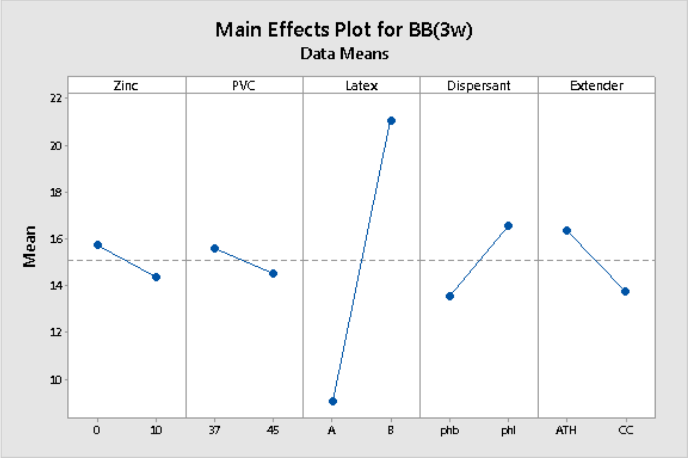
DOE 1 Results



Adhesion



Bleed Block

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

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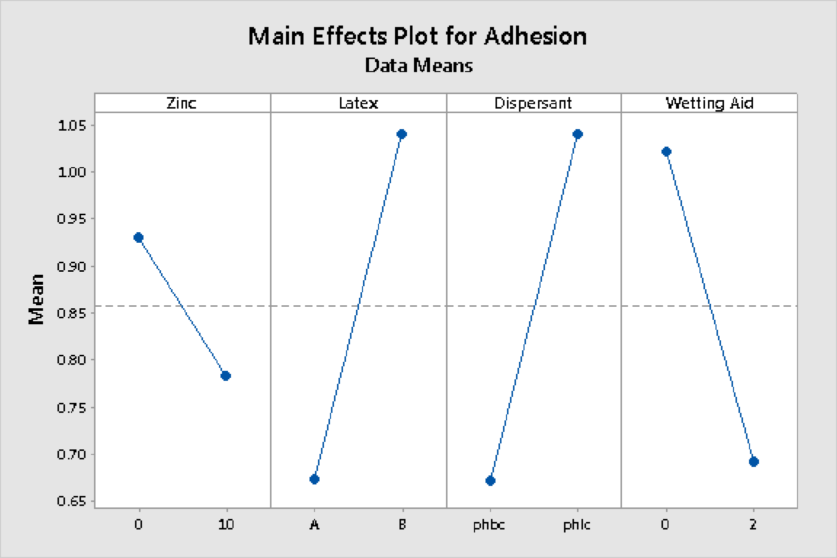
DOE 2 Results

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?



Adhesion

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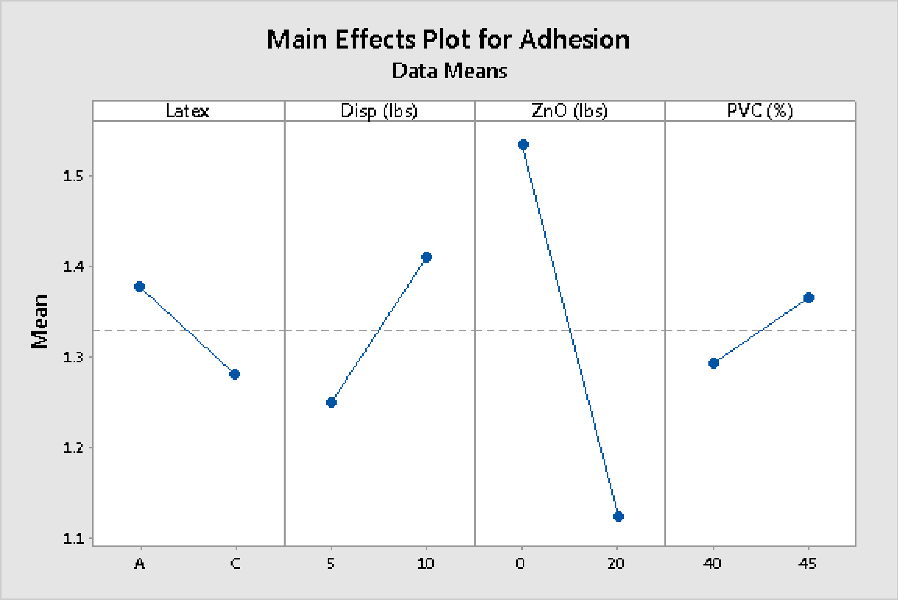
DOE 3 Results



Adhesion

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Adhesion to Multiple Substrates

Metal

- **Substrate:**
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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

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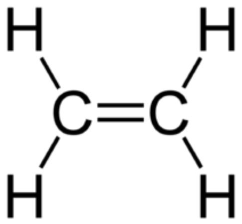
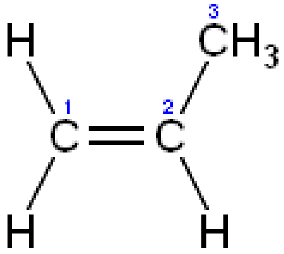
Thermoplastic Olefin (TPO)

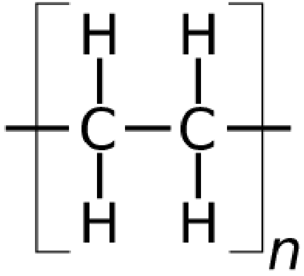
- Poly(olefins) are made from alkenes (C_nH_{2n})



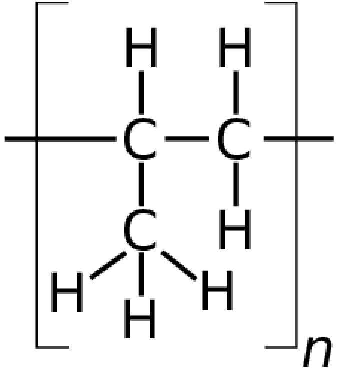
Ethylene



Propylene



Polyethylene



Polypropylene

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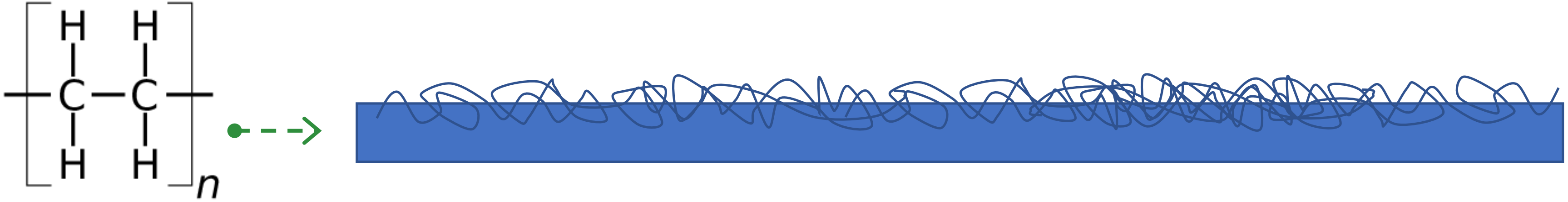
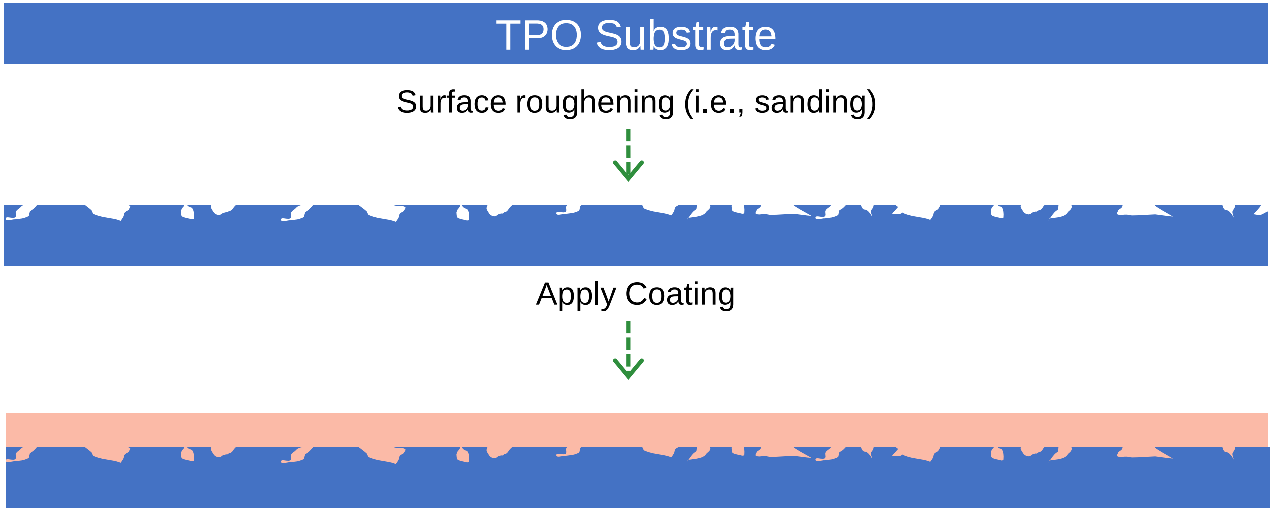
Thermoplastic Olefin (TPO)

- 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??



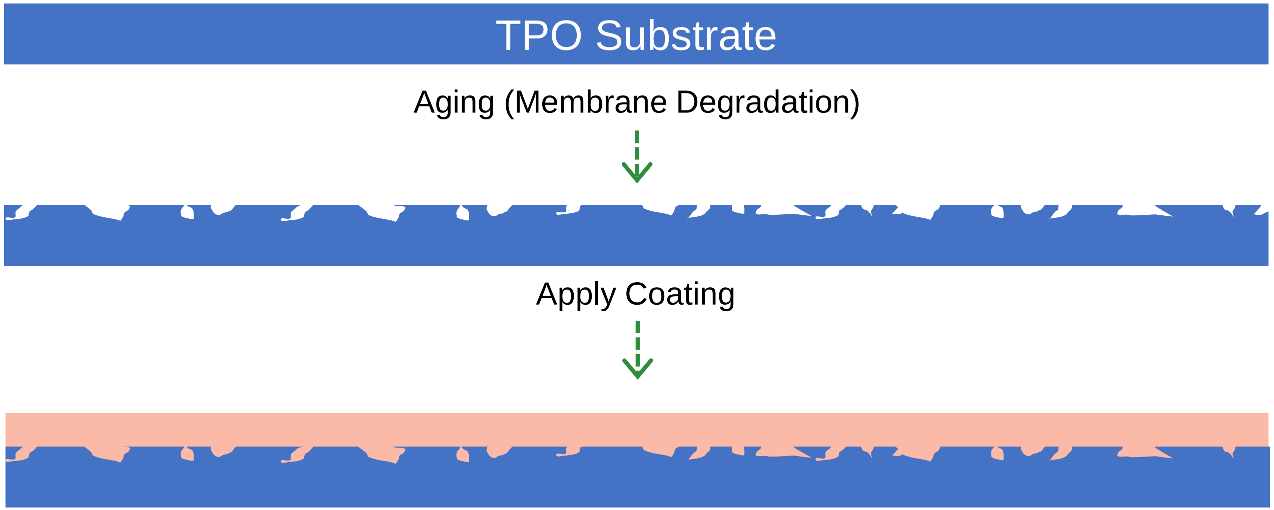
Methods to Improve TPO Adhesion: *Surface Roughening*



Drawback: Requires modification of substrate

- As coating manufacturer, this is undesirable
- Also undesirable for coating applicator, as this requires time ($$$)

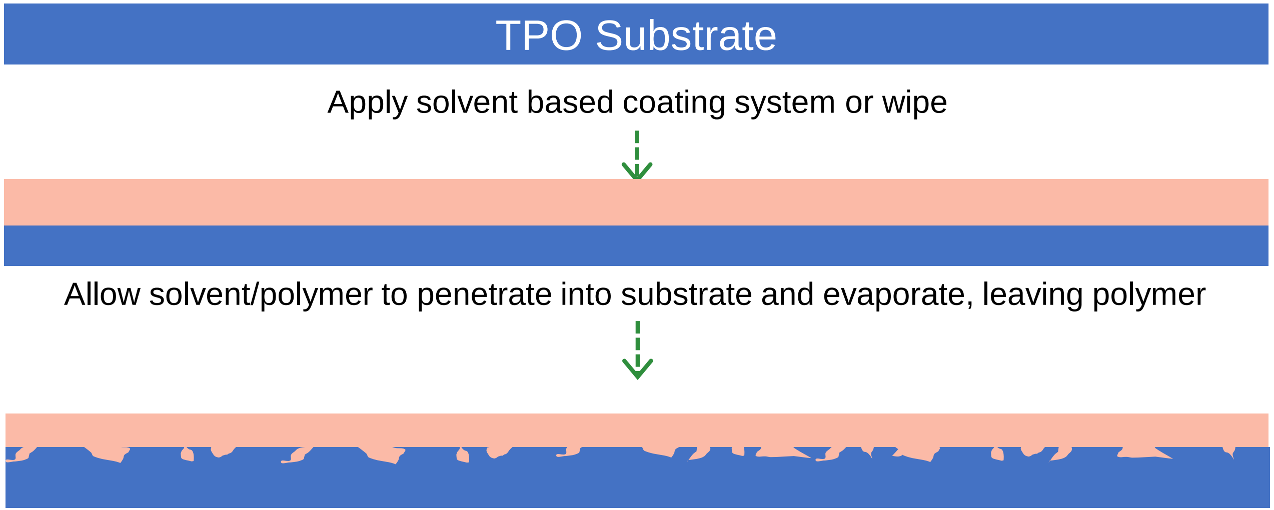
Methods to Improve TPO Adhesion: *Aging Substrate*



Drawback: Requires time for TPO to age

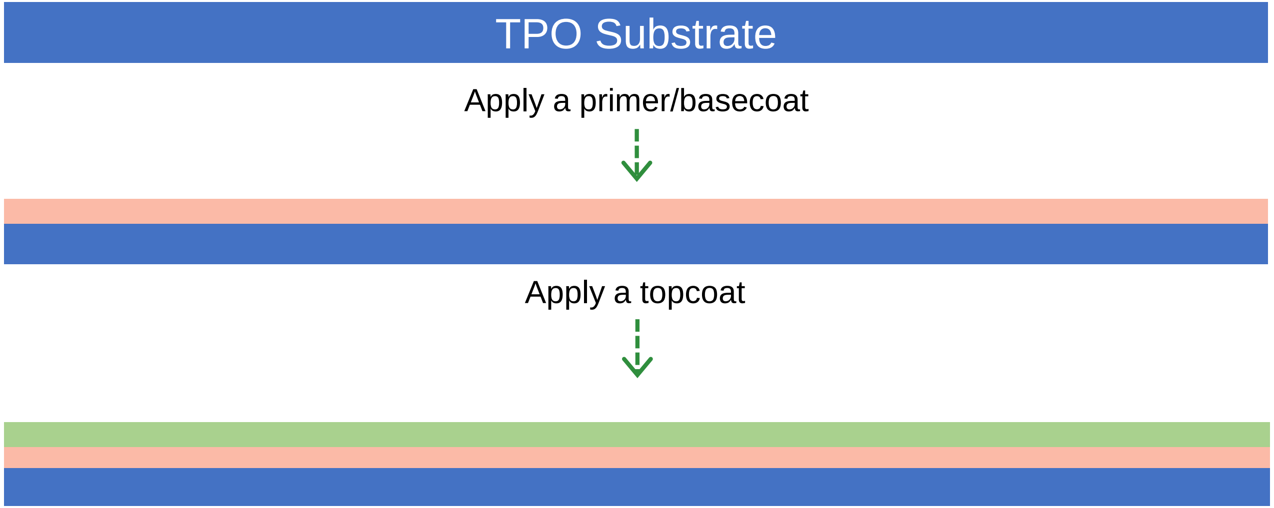
- Not useful for repair or in instances where virgin TPO is used

Methods to Improve TPO Adhesion: *Solvent-based*



Drawback: High VOC, odor, may still not adhere (due to lack of functionality)

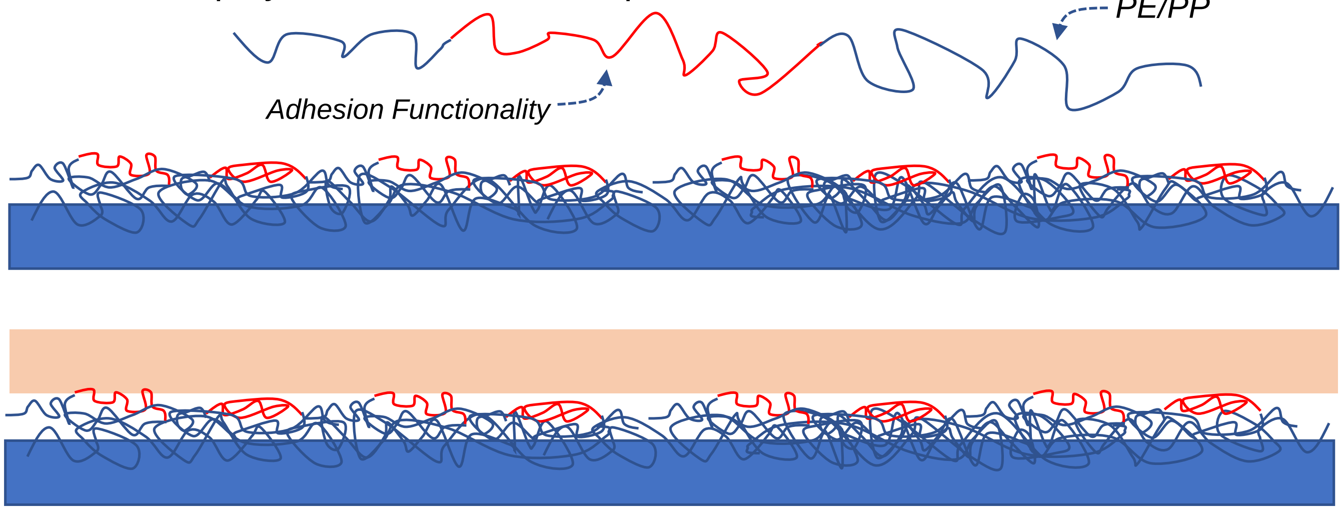
Methods to Improve TPO Adhesion: *Primer/Basecoat*



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



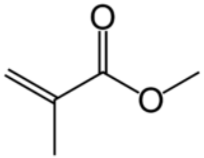
Drawback: Difficult to make block copolymers in traditional emulsion polymerization

- Many of these primer/basecoat approaches are solvent-based
- Water-based approaches are not effective on virgin TPO

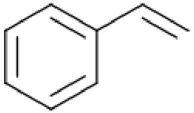
Methods to Improve TPO Adhesion: *Primer/Basecoat*

Typical emulsion polymer components

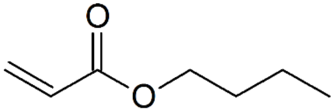
- Some components are necessary to make stable emulsion polymers
- Ethylene/propylene cannot be incorporated into emulsion polymerization
- Polarity of many common monomers not ideal



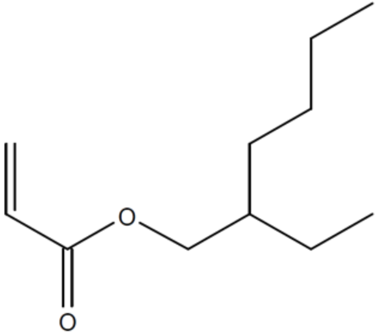
MMA



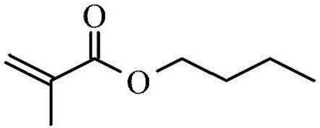
Styrene



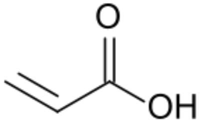
BA



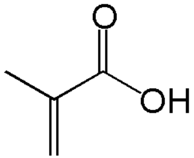
2-EHA



BMA



Acrylic acid



Methacrylic acid

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

-AAAAABBBBBBBBAAAAA-

-AABBABAAABABBBAABABABA-

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

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Market Need: *Obtain adhesion on virgin TPO in a waterborne acrylic emulsion*

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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)

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TPO Primer Base Formula

Pounds	Gallons	Raw Material
156.00	18.73	Water
3.00	0.30	Dispersant
3.00	0.40	Ammonium Hydroxide
1.00	0.12	Defoamer
30.00	0.90	TiO_2
450.00	19.94	Calcium Carbonate
1.00	0.12	Defoamer
450.00	52.63	Polymer
11.00	1.15	Mildewcide/Fungicide
11.00	1.27	Propylene Glycol
3.00	0.26	Rheology Modifier
34.90	4.18	Water
1153.9	100	Total

Parameter	Value
Weight Solids	65.91
Volume Solids	52.82
PVC	40.16
Weight/gal	11.54
VOC, g/L	24

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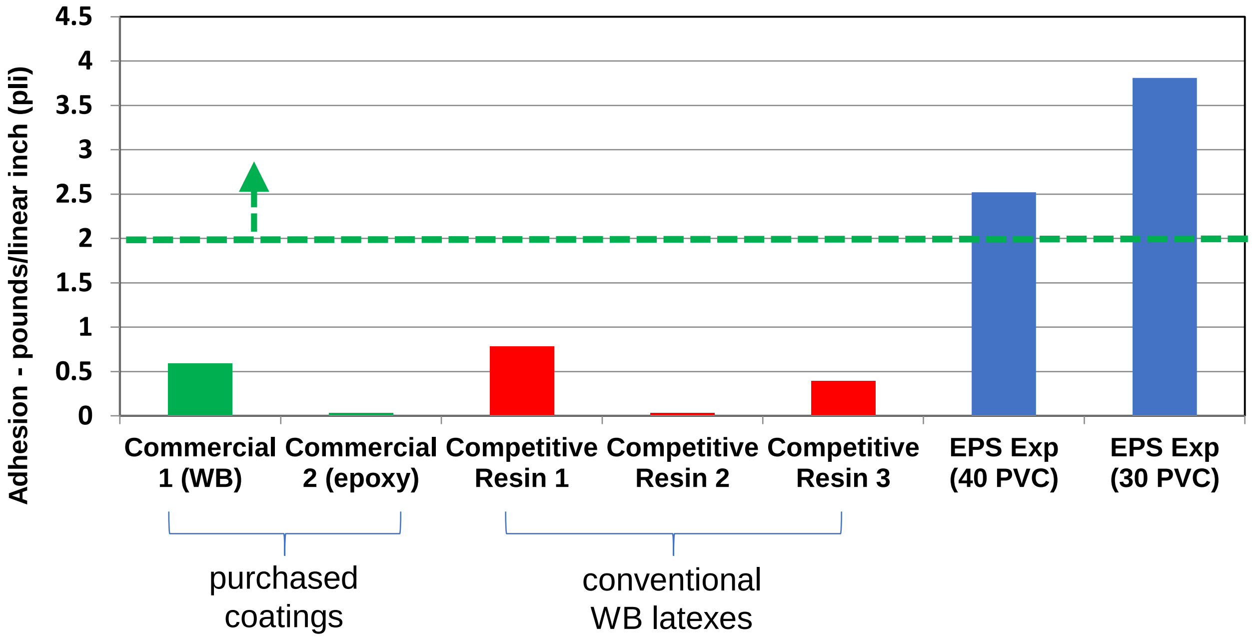
Resin Impact on Peel Adhesion

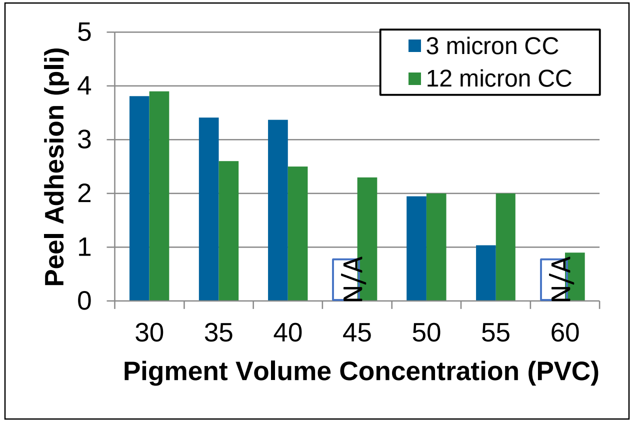


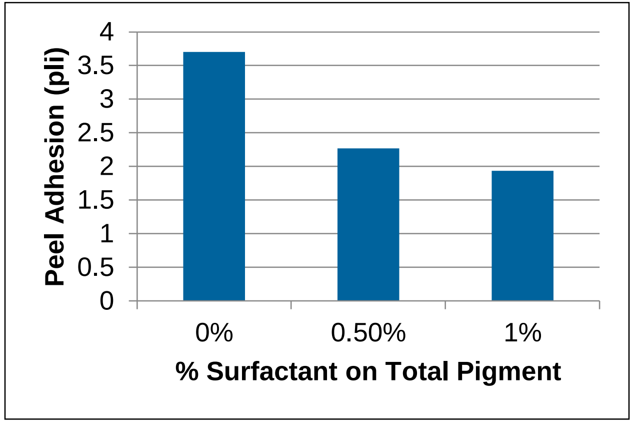
45 mil new TPO

Dramatic impact on resin choice…

Results - *Adhesion*

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





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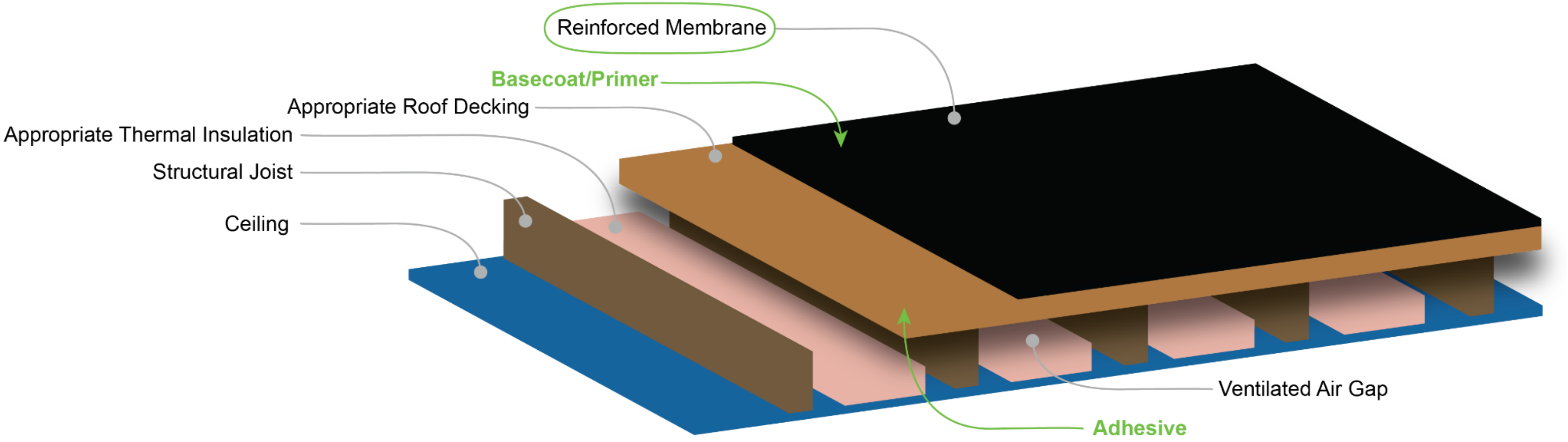
Roofing System Cross Section



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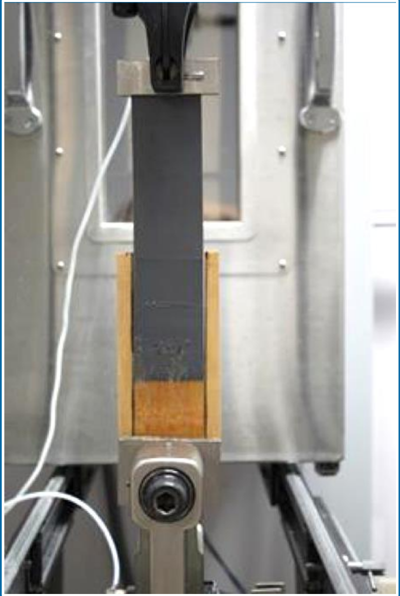
180° Peel Membrane Adhesion Testing

Initial



End of Test

2 in/min pull rate

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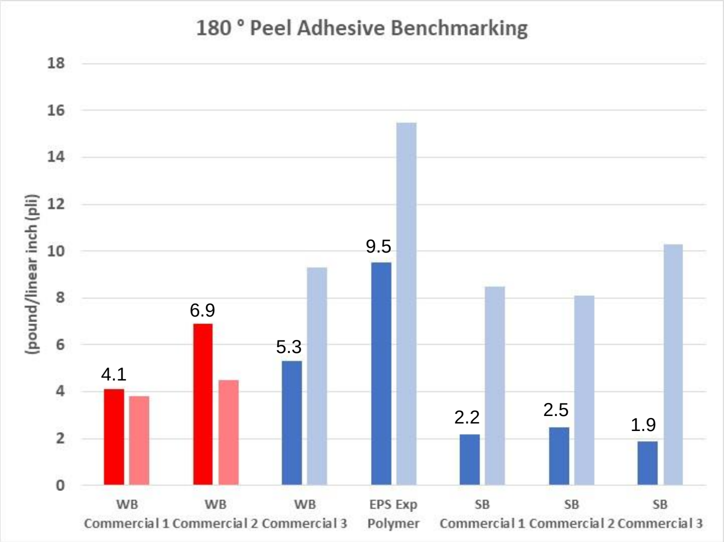
Benchmarking - *Adhesive*



Red: Adhesive failure, 24H
Pink: Adhesive failure, 7 day
Blue: Cohesive failure, 24 H
Lt. Blue: Cohesive failure, 7 day

Competitive Benchmark - 180° Peel Adhesion

Sample	24hr dwell @ RT	Mode of failure	7 day dwell @ RT	Mode of failure
WB Commercial Sample 1	4.1 pli	Adhesive	3.8 pli	Adhesive
WB Commercial Sample 2	6.9 pli	Adhesive	4.5 pli	Adhesive
WB Commercial Sample 3	5.3 pli	Cohesive	9.3 pli	Cohesive
EPS Experimental Polymer WB	**9.5 pli**	**Cohesive**	**15.5 pli**	**Cohesive**
Solvent-based Commercial Sample 1	2.2 pli	Cohesive	8.5 pli	Cohesive
Solvent-based Commercial Sample 2	2.5 pli	Cohesive	8.1 pli	Cohesive
Solvent-based Commercial Sample 3	1.9 pli	Cohesive	10.3 pli	Cohesive

Testing Conditions - 180° Peel Adhesion-Crosshead Speed 2 inches/minute

Spread Rate - 9 lbs/100ft^2

GAF 45 mil TPO

Substrate - Plywood

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Adhesion to Multiple Substrates

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  - 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*