Improving Surfactant Leaching and Exterior Performance of Architectural Flat Paints

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Engineered Polymer Solutions

eps

Surfactant Leaching

- Humidity and moisture causes water-soluble components in a paint formulation to leach out
  - Uneven appearance on painted surface – not desirable

Surfactant Leaching

- Humidity and moisture causes water-soluble components in a paint formulation to leach out
  - Uneven appearance on painted surface – not desirable

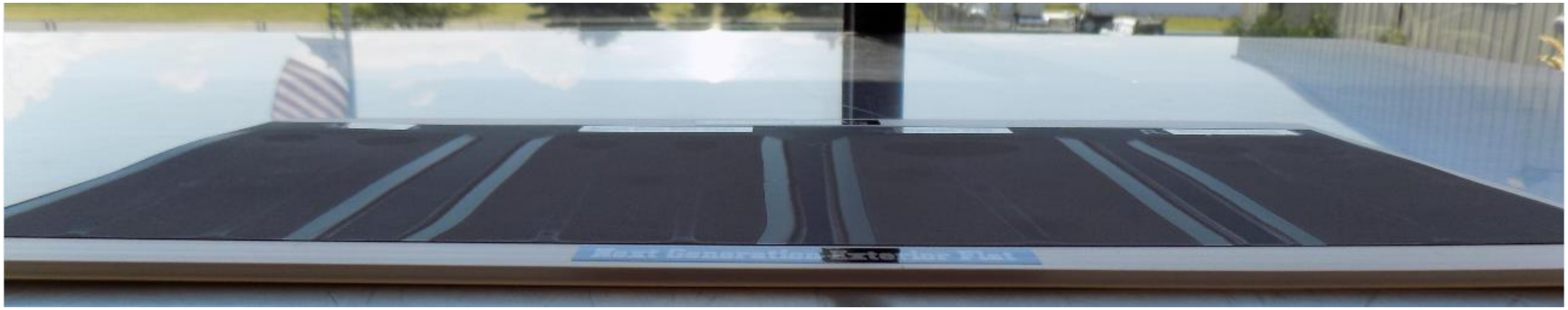
- Not necessarily a surfactant
- Testing methods typically involve application of water onto a panel and evaluating appearance

Surfactant Leaching

- Challenging to evaluate in accelerated/exposure testing
  - Moisture required during early drying time
  - Moisture/rain can rinse panel
  - Too much moisture will result in an even appearance – false negative
    - Will cause a change in sheen

Surfactant Leaching

- Challenging to evaluate in accelerated/exposure testing
  - Angle of observation and/or lighting may impact qualitative results



Overview

- Surfactant Leaching
  - Define
- Testing Protocols
- Design of Experiments
- Modelling to predict surfactant leaching
- Additional Exterior Performance
  - Dirt pick-up resistance
  - Highly alkaline substrate
  - Tannin stain blocking

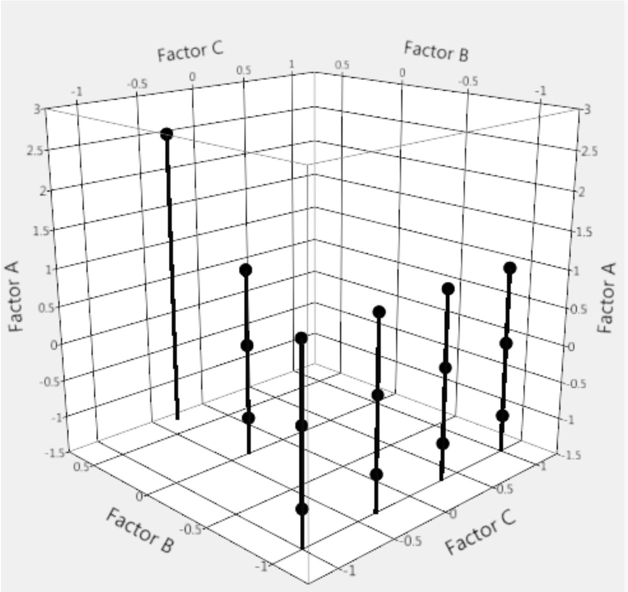
Surfactant Leaching Methods

- **Water Drop Method – (*ASTM D7190*)**
  - 5 water drops on panel – 30 min
  - Tip panel to remove water
  - Visual rating of surfactant leaching
  - High variability
- **EPS Analytical Method**
  - 5 g of water applied on panel after 4 hr dry
  - Water collected and analyzed (LC-MS) for extractables
  - Modeling of data to predict optimized compositions
- **Analyze by Weight**
  - Cannot determine composition
  - Need to accurately measure weight

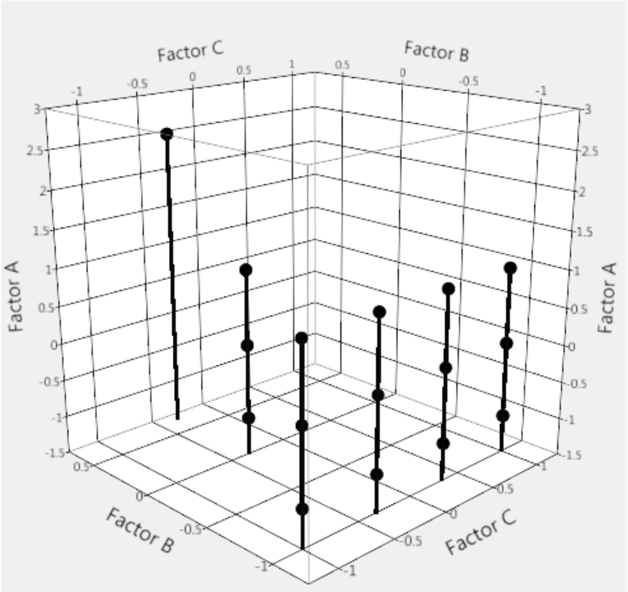
Drawdown Procedure:
6 mil straight drawdown bar
Black mylar chart
Dry 4 hours at RT

Design Space

4 Factor DoE – Factors A, B, C, and D



Factor D - Low



Factor D - Hi

A, B, D – hydrophobic functional factors
C - indifferent

32 Experimental Polymers
3 Internal Controls
2 Commercial Resin Controls

Design Space

Design:

Experimental Polymers: 32 polymers
Control Polymers: 5 samples

- 55 wt% solids
- APEO free
- All acrylic
- Not Prop. 65

Whites: (74 paints)
-DPUR
-Efflorescence (tinted red)
-Tannin

Neutral Base (Brown) : (37 paints)
-Surfactant Leeching

111 paints

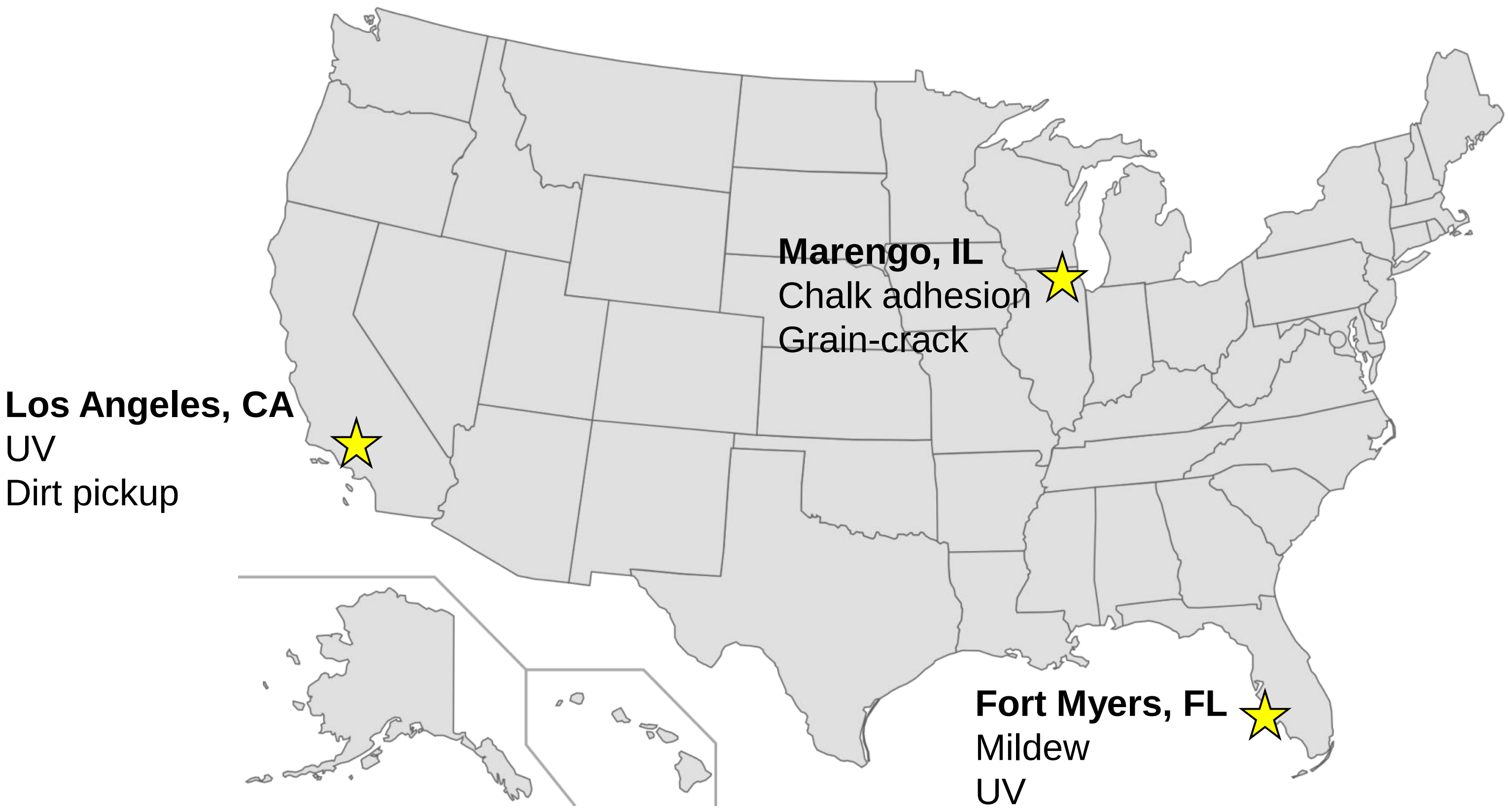
Exposures:

Los Angeles, CA
-Red (Skimcoat)
-White (New SYP)
-Brown (New SYP)

Marengo, IL
-Red (Skimcoat)
-White (W.SYP, Chalky)
-Brown (W.SYP, Chalky)

Fort Myers, FL
-Red (Skimcoat)
-White (New SYP)
-Brown (New SYP)

EPS Exterior Exposure Test Fence Sites



Multiple exterior exposure sites allow testing of different environments

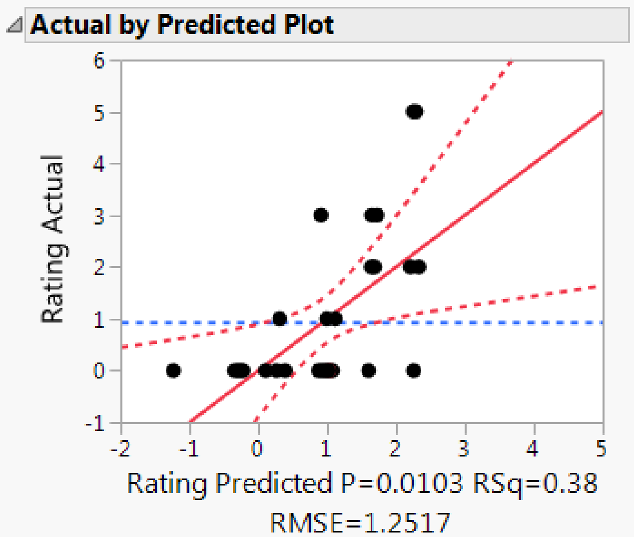
Exterior exposures in progress

Surfactant Leaching Methods

- **Water Drop Method – ASTM D7190**
  - 5 water drops on drawdown after 4 hr dry
    - – water on drawdown for 30 min
  - Tip panel vertically to remove water
  - Visual rating of surfactant leaching
  - High variability
- **EPS Analytical Method**
  - 5 g of water applied on drawdown after 4 hr dry
  - Water collected and analyzed (LC-MS) for extractables
  - Modeling of data to predict optimized compositions

Surfactant Leaching Model Comparison

Visual Observation Rating-based Model



Summary of Fit

RSquare	0.37681
RSquare Adj	0.284485
Root Mean Square Error	1.251651
Mean of Response	0.9375
Observations (or Sum Wgts)	32

R^2 = 0.38

- Visual observation results in poor model
    - Active factors – A, D

A, B, D – hydrophobic functional factors
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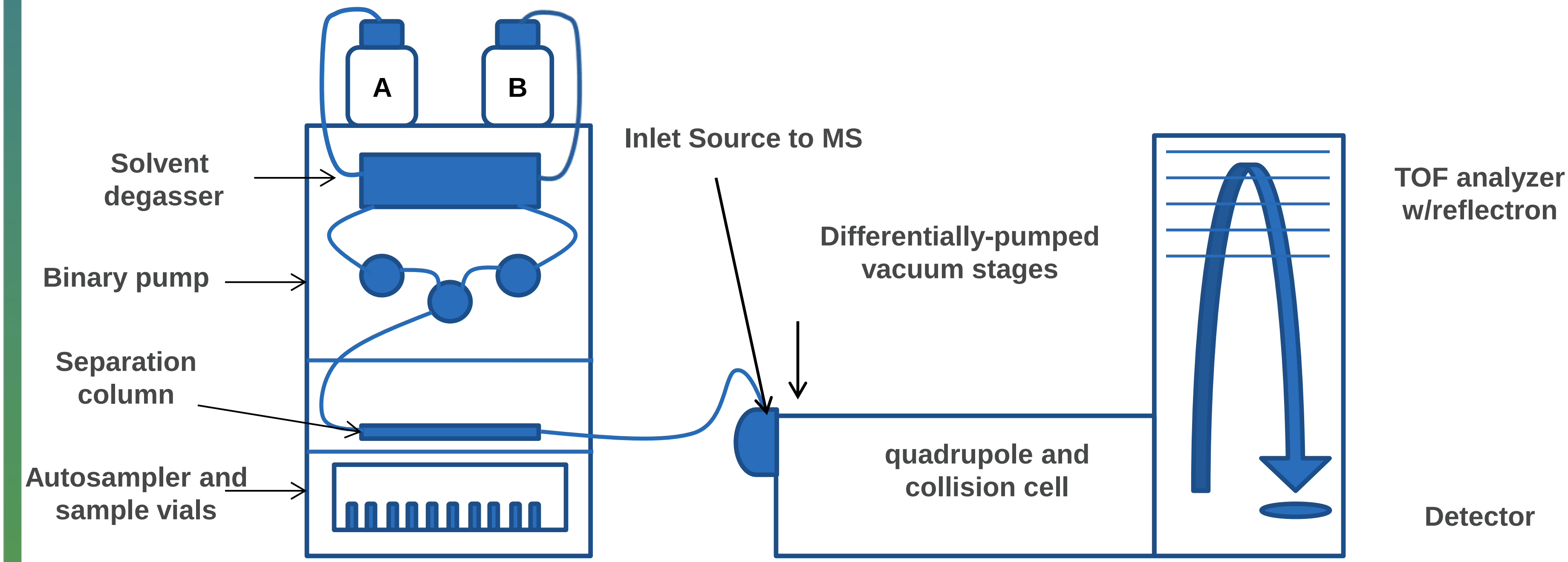
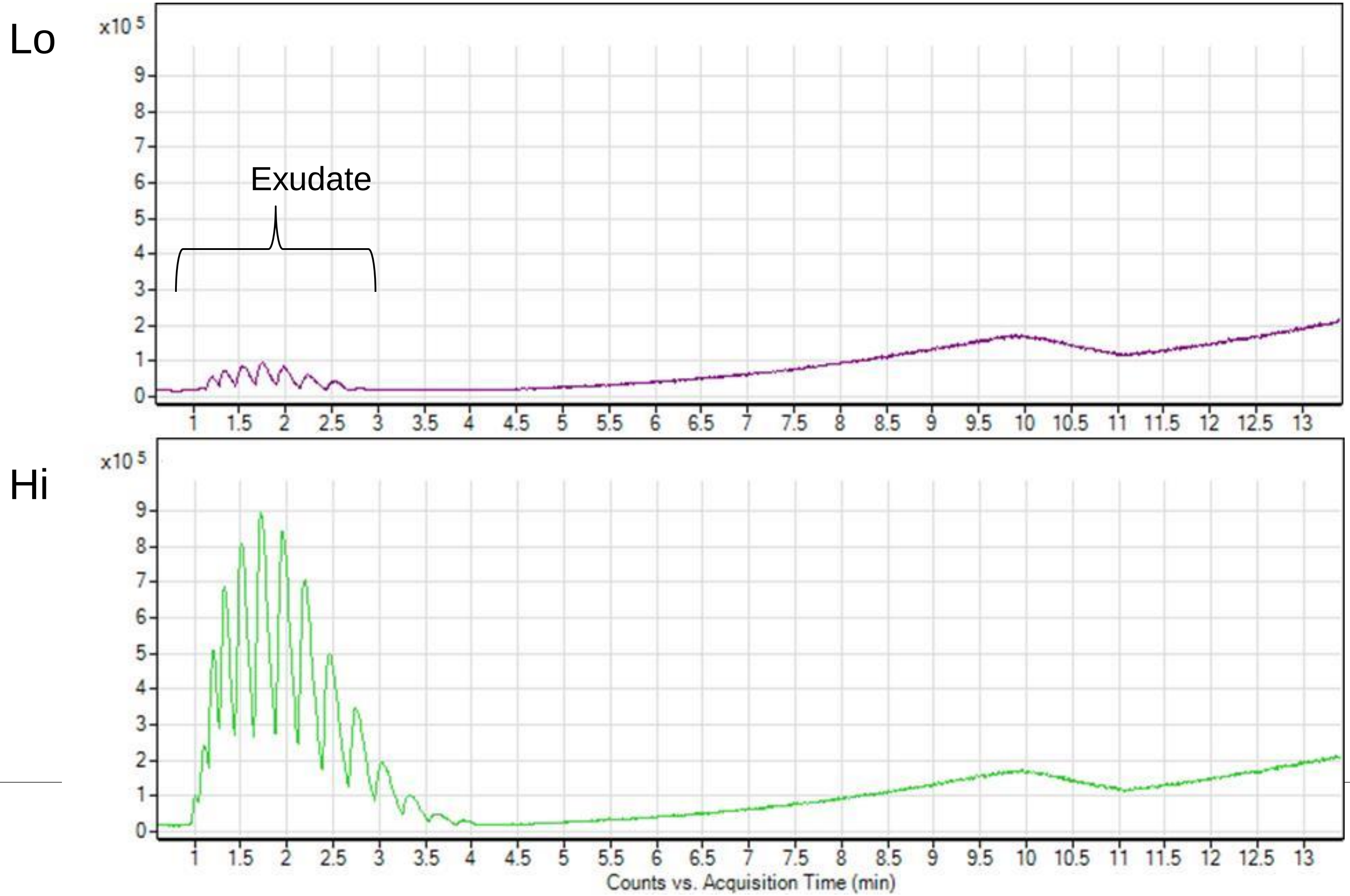
Surfactant Leaching Analysis – LC-MS

- LC-MS couples the condensed phase separation capabilities of Liquid Chromatography (HPLC) with the detection and mass analysis benefits of Mass Spectrometry (MS) to allow high specificity and sensitivity.



Surfactant Leaching Analysis – LC-MS

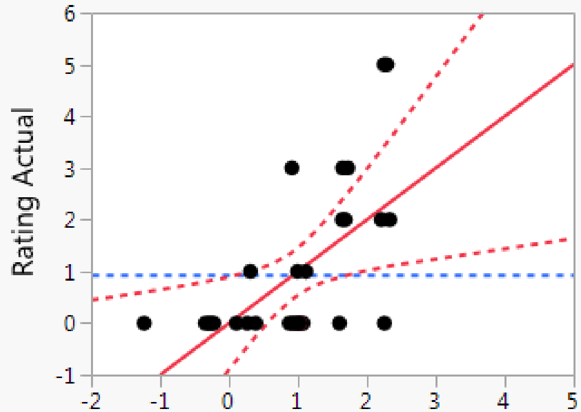
- At appropriate dilutions, the LC-MS response is linear to the concentration of exudate being analyzed. The concentration of leached exudate is calculated from this response using a calibration.



Surfactant Leaching Model Comparison

Visual Observation Rating-based Model

Actual by Predicted Plot



Rating Predicted P=0.0103 RSq=0.38
RMSE=1.2517

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Analytical Based Model

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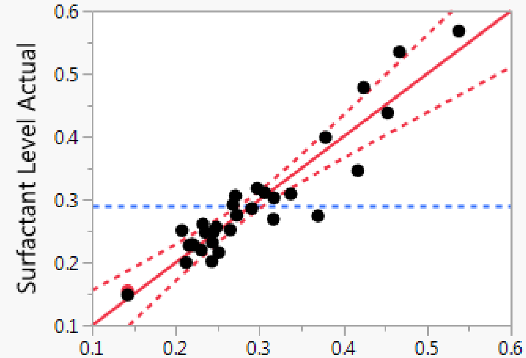


Surfactant Level Predicted P<.0001
RSq=0.88 RMSE=0.0378

Summary of Fit

RSquare	0.881124
RSquare Adj	0.852594
Root Mean Square Error	0.037796
Mean of Response	0.290016
Observations (or Sum Wgts)	32

R^2 = 0.88

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	6	0.26471115	0.044119	30.8840
Error	25	0.03571309	0.001429	Prob > F
C. Total	31	0.30042424		<.0001*

Lack Of Fit

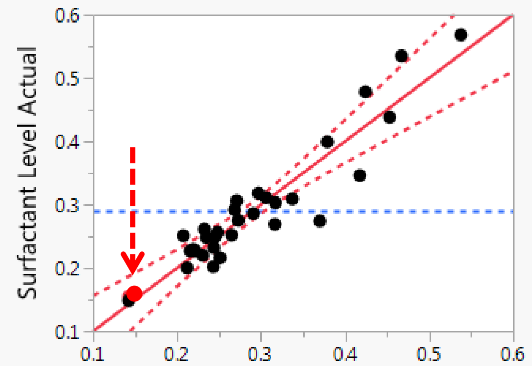
Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	24	0.03569196	0.001487	70.3984
Pure Error	1	0.00002113	0.000021	Prob > F
Total Error	25	0.03571309		0.0939
				Max RSq
				0.9999

- Visual observation results in poor model
  - Active factors – A, D

A, B, D – hydrophobic functional factors
C - indifferent

Design Space Modelling Summary

Actual by Predicted Plot



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Analytical Model:
6 Active Terms
A
B
C
D
BC
CD

Qualitative Visual Rating Model:
2 Active Terms
A
D

Qualitative analysis does not pick out key active terms

Additional data point not used to build model confirms model accuracy

Lo A
Lo B
Lo C
Lo D

Good Surfactant Leaching

Poor Dirt Pick-up Resistance

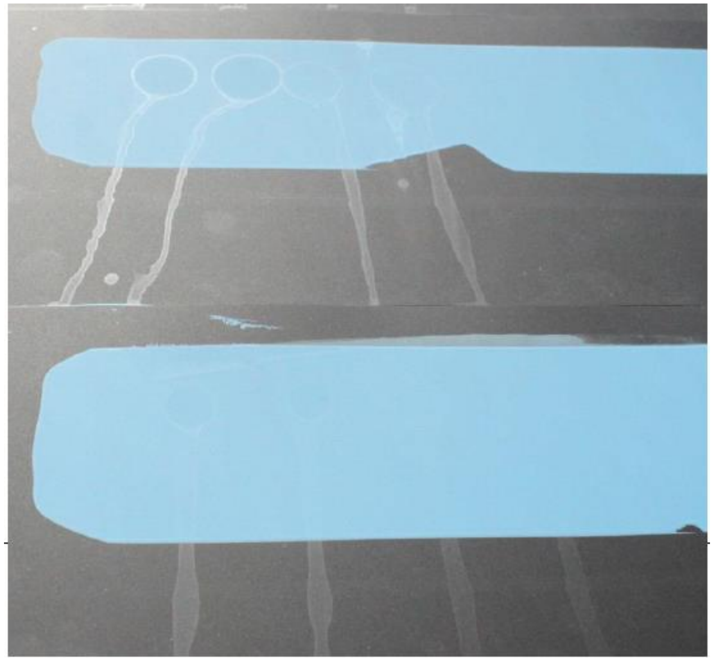
A, B, D – hydrophobic functional factors
C - indifferent

Surfactant Leaching in Alternate Formulas – Tinted Blue

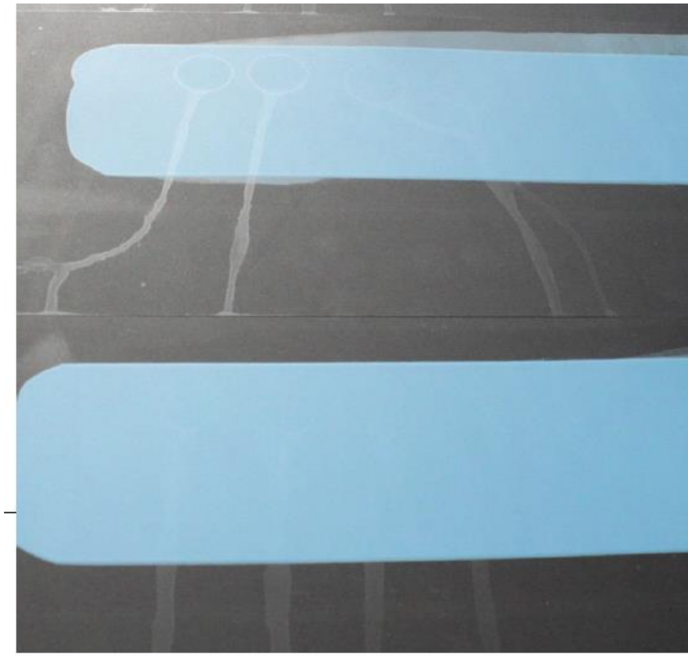
Formula A

Commercial Resin A

EPS Experimental Resin



Formula B



Resin	Formula A	Formula B
Commercial Benchmark Resin	0.2%	0.155%
EPS Experimental	0.182%	0.096%

Accelerated Lab Evaluations

Surfactant Leaching

- **Water Drop Method (ASTM D7190)**
  - 4 hours dry, 4 water drops on panel – tip panel to remove water
  - Visual rating of surfactant leaching
- **EPS Analytical Method**
  - 4 hours dry, 5 g of water applied on panel
  - Water collected and analyzed (LCMS) for extractables

Tannin Stain Resistance

- Redwood panels, 2 coats self-primed
- 5 days humidity cabinet

Alkaline Substrate Resistance

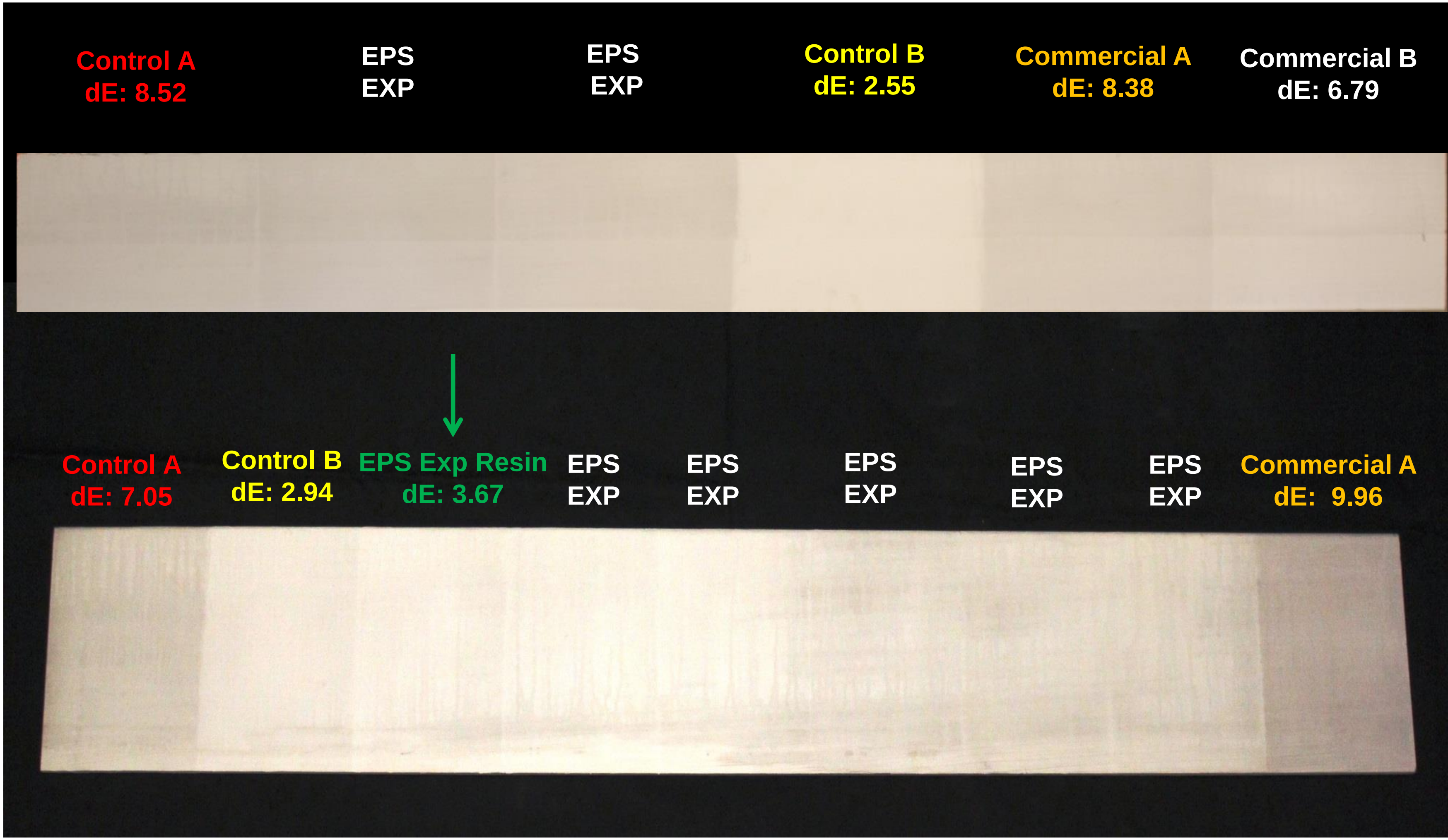
- Alkaline skimcoat over manufactured board substrate
- Placed outside on fence after 4 hours ambient cure (during damp weather)

Dirt Pickup Resistance

- ROX slurry method, dE
- Conditioned 7 days QUV-A / condensation cycle

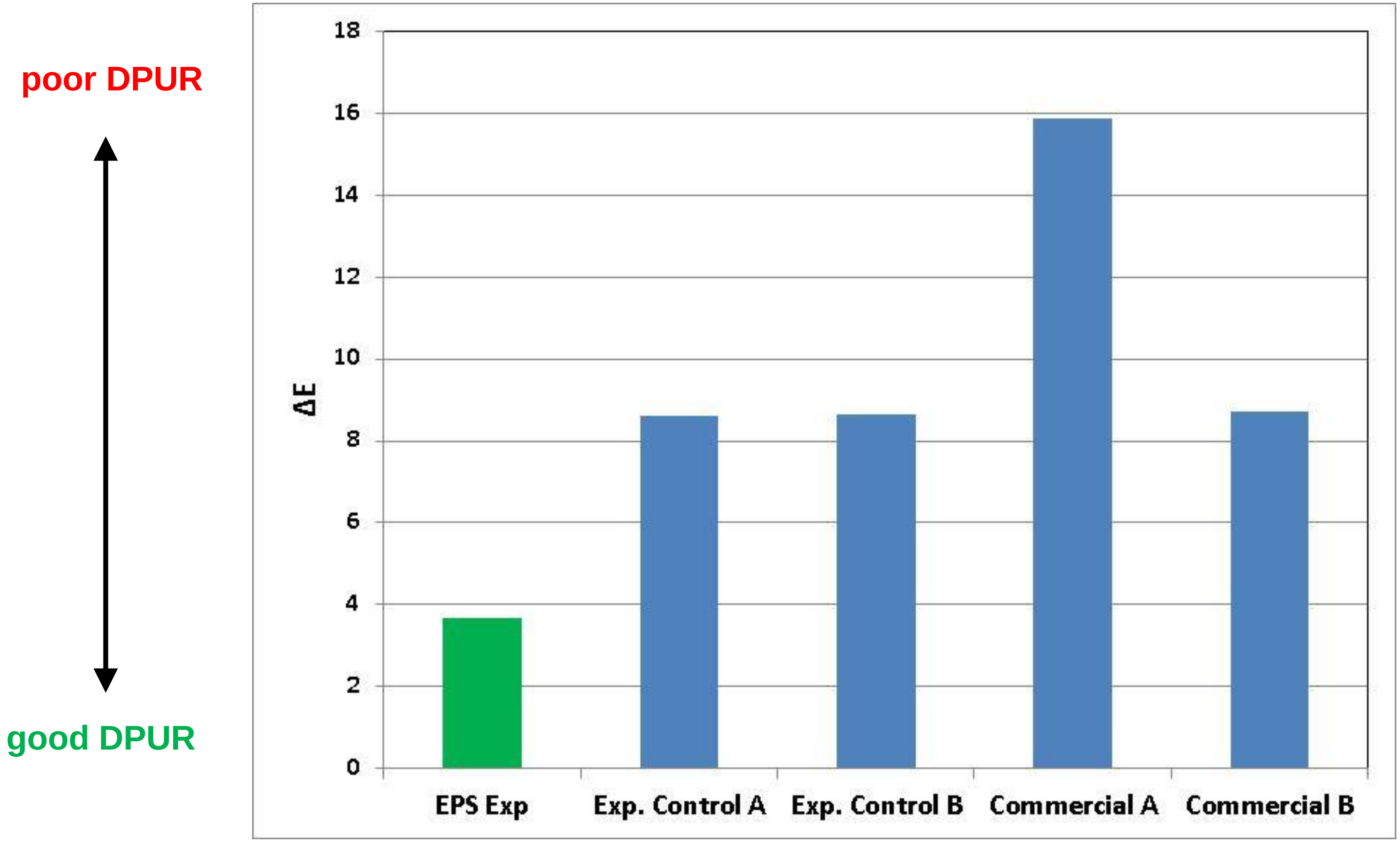
Accelerated lab evaluations also analyzed in context of DoE to determine best balance of properties

Tannin Stain Blocking
5 days humidity over redwood



Dirt Pick-up Resistance

Red-oxide slurry method



Los Angeles exterior exposures in progress

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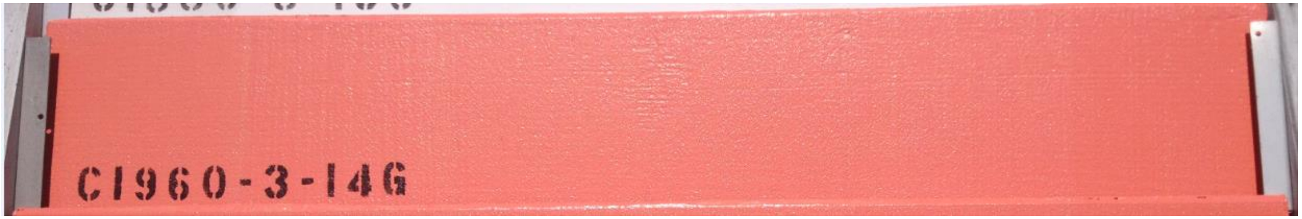
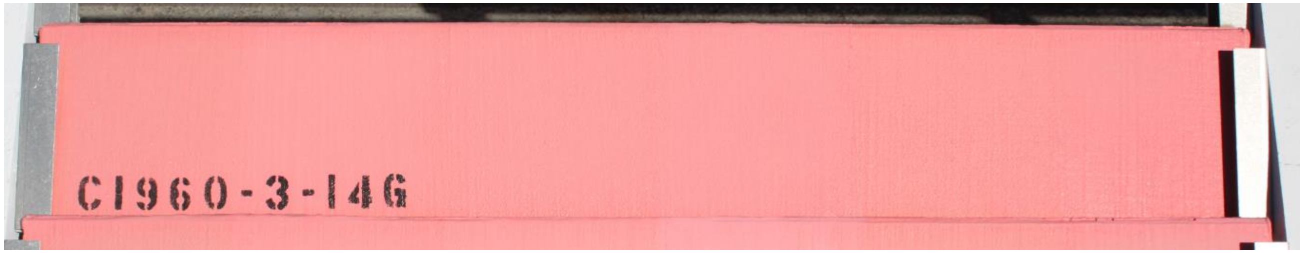
Performance on Highly Alkaline Substrate

Alkaline skimcoat over manufactured board substrate

Initial



18 months

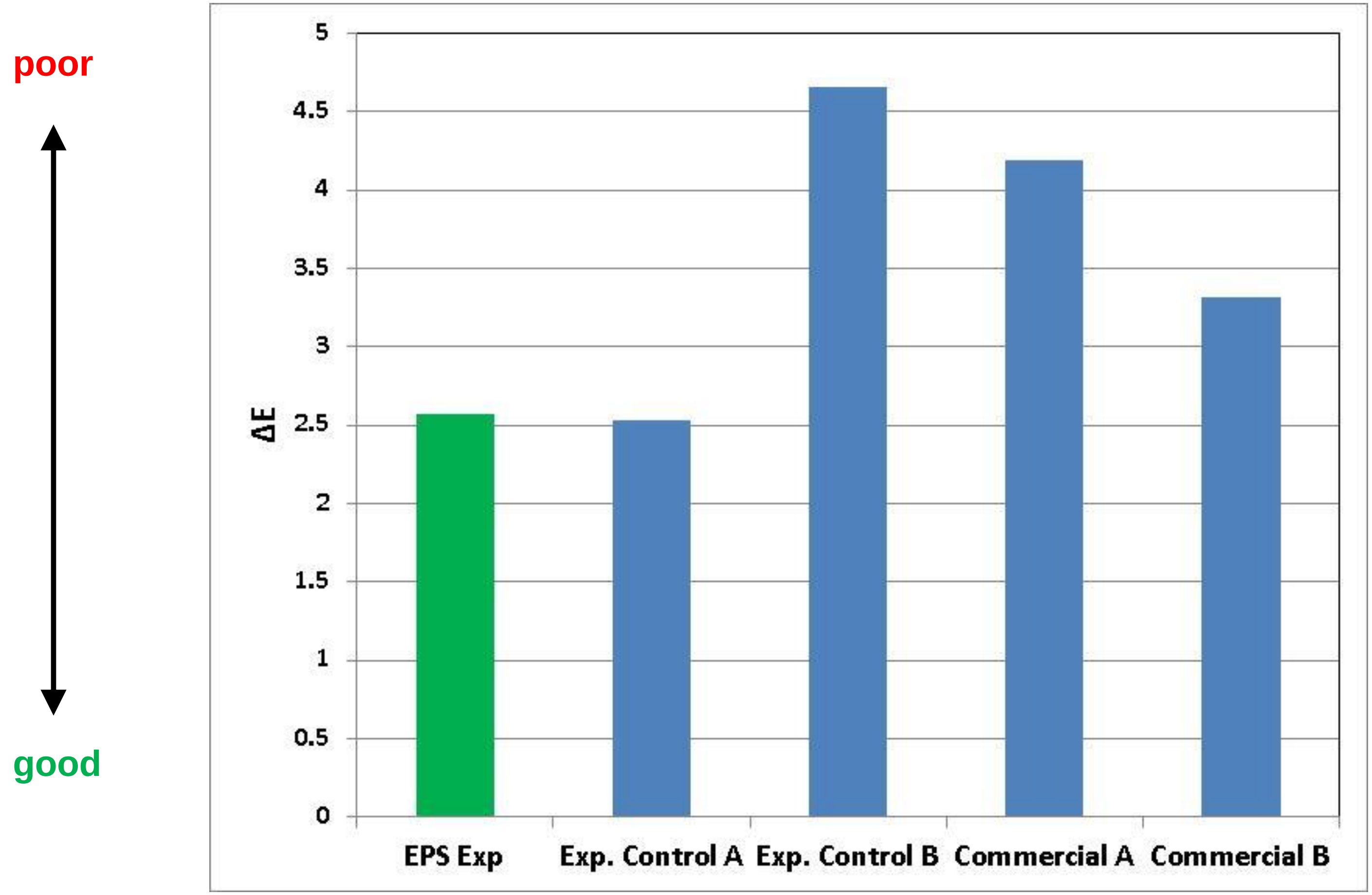


34 months

White paints tinted with quinacridone red and organic yellow

Performance on Highly Alkaline Substrate

Alkaline skimcoat over manufactured board substrate (14 day exterior exposure - IL)



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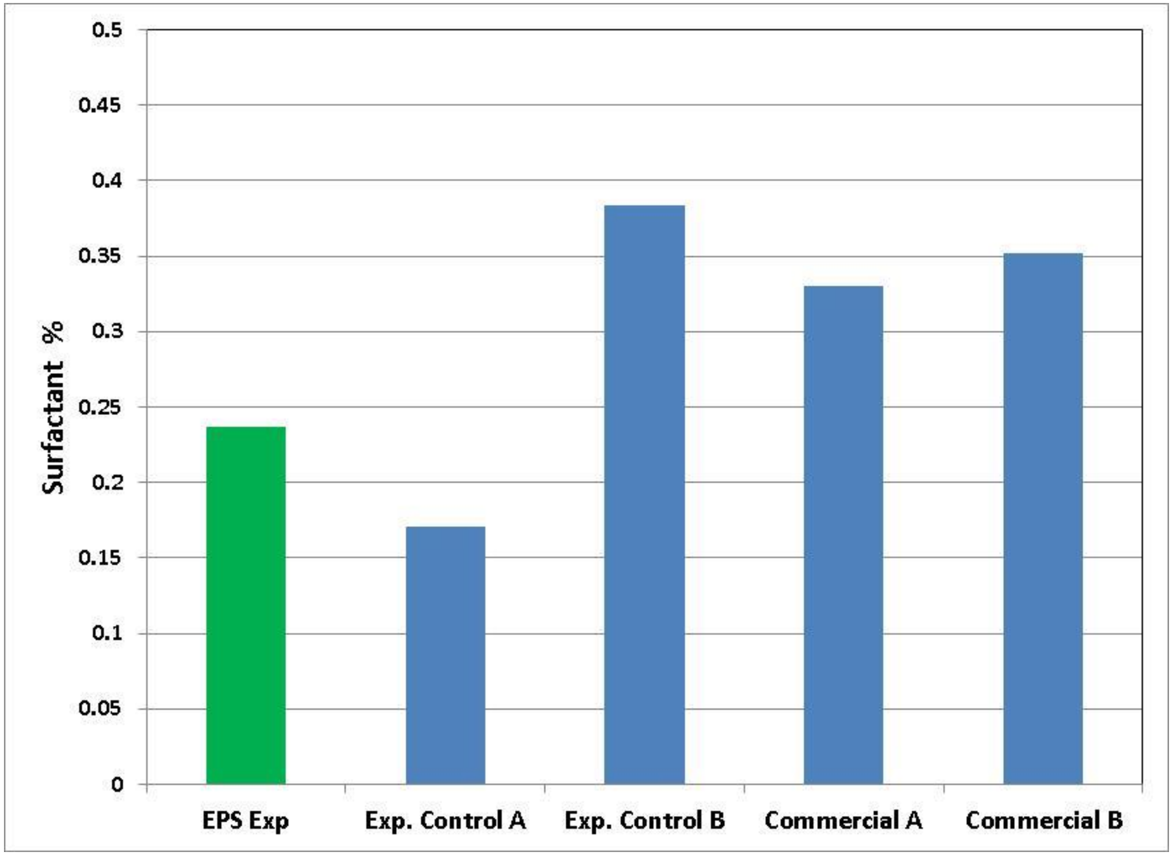
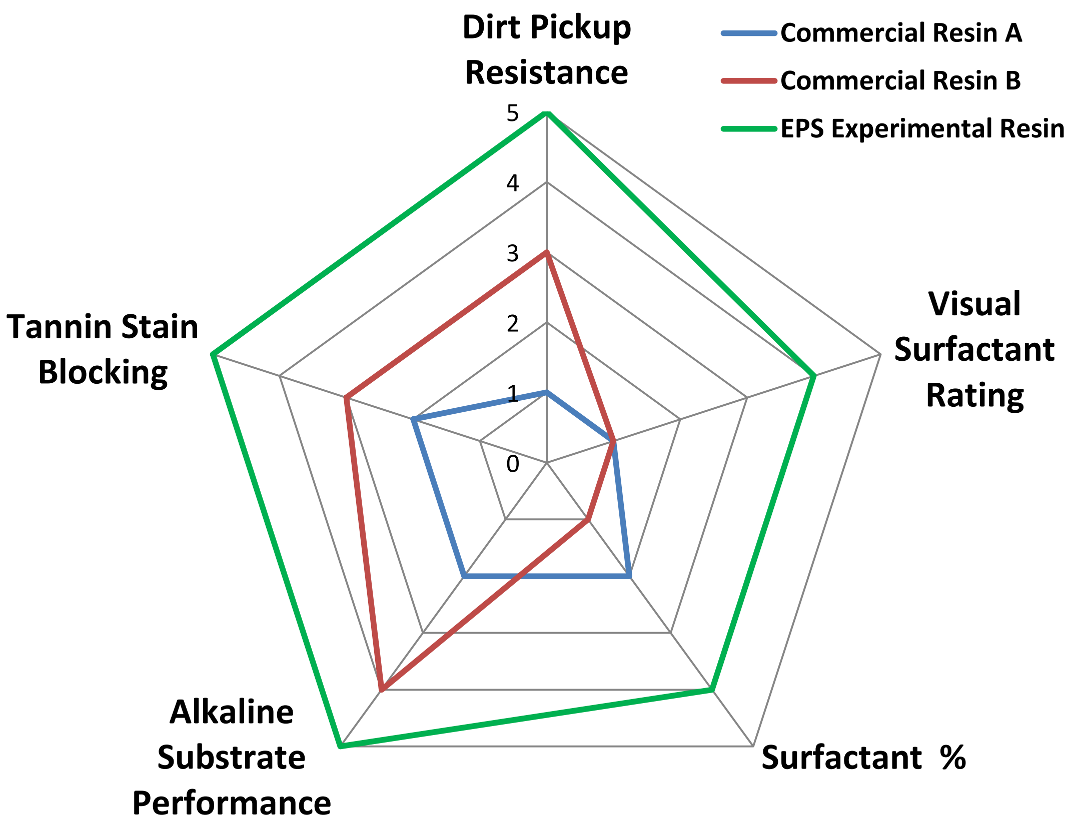
Surfactant Leaching
EPS Analytical Method

more leaching

less leaching



Summary


Dirt Pickup Resistance
Commercial Resin A
Commercial Resin B
EPS Experimental Resin
5
4
3
2
1
0
Visual Surfactant Rating
Surfactant %
Alkaline Substrate Performance
Tannin Stain Blocking

Summary

- Quantitative method for surfactant leaching allows for deeper understanding of structure/property relationships compared to qualitative visual analysis
- Hydrophobicity does not completely drive surfactant leaching
- Multiple resin composition factors impact surfactant leaching
- New resin developed with balance of improved
  - Surfactant leaching
  - Dirt pick-up resistance
  - Efflorescence
  - Tannin stain blocking