



**Coatings Trends
& Technologies**

Stepan 

Novel Fluoro-free and Silicone-Free Blocking Resistance Additives for Waterborne Coatings

S. Dong*, J. Zaug, G. Luebke, S.R. Kang and C. Vargas

September 9, 2021

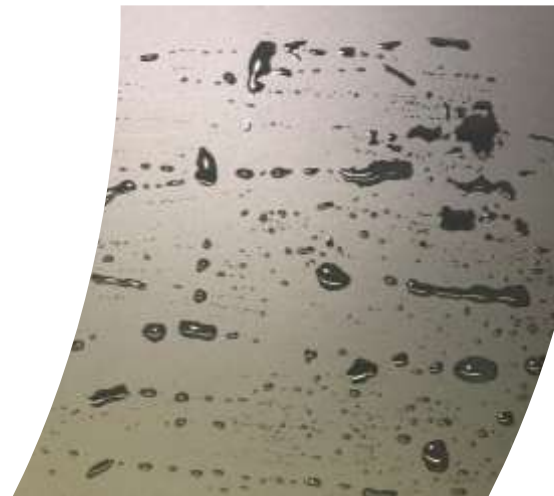
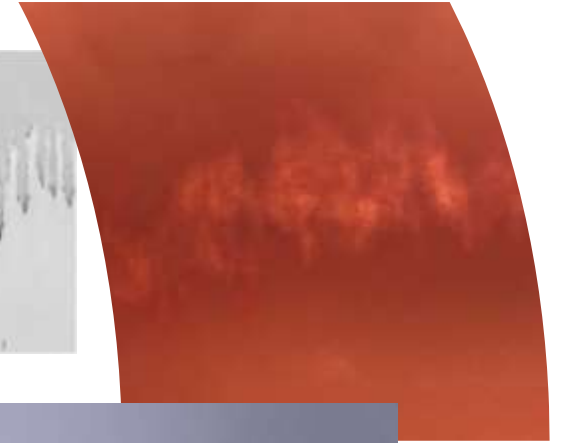
Agenda

- Background
- Experimental Details
- New High Temperature Blocking Resistance Additives
- Summary



Common Challenges In Waterborne Coatings

- Poor substrate wetting
- Dispersion/color issues
- Rheology problems
- Surface defects
- Foaming
- Poor film formation



Additives Improve Film Properties

Amphiphilic molecules enhance wetting and influence properties like:

- Gloss
- Color acceptance
- Hiding power
- **Block resistance**
- Corrosion resistance
- Scrub resistance
- Washability
- Adhesion
- Stability
- Open time
- Antifoaming
- Leaching
- Weathering
- Other ...

Block Issue (Example)



Tested according to ASTM D4946-89

Typical Solutions for Block Resistance

- Increase in PVC level of paint:



Not feasible for every paint system

- Use of silicone additives:



Incompatibility issues and lower efficacy

- Use of fluoro-based additives:



Environmental persistence and health concerns



Incompatibility issues leading to surface defects



Relatively expensive products

New Alternative to Improve Block Resistance

Phosphate Esters

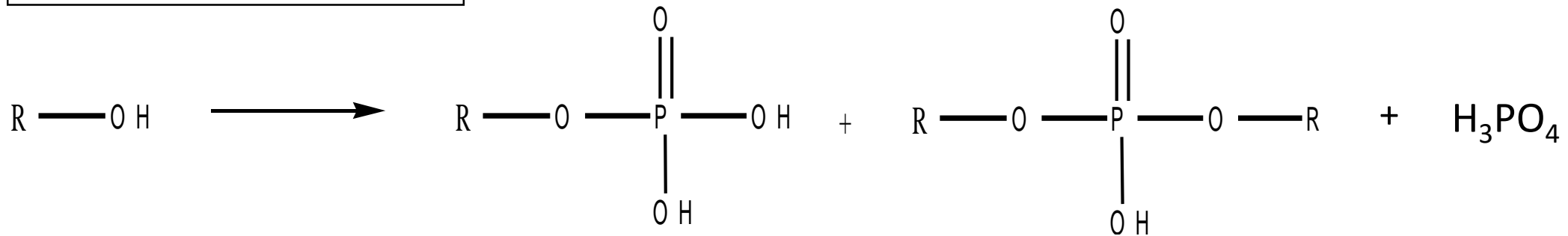
Alkyl chain - Alkoxyate - PE

Key Molecule Features:

- Alkyl chain length and branching
- Alkoxylation degree
- Mono/Diester ratio

Other Features:

- Nonionic content
- Free acid level
- Counterion, pH...



Monoester



Diester



Exploring New Additives Chemistry

Test Variable	Chemistry
Negative control	No additive
Degree of Ethoxylation	Rt-0EO
	Rt-3EO
	Rt-6EO
	Rt-12EO
Alkyl Chain Variation	Cn
	C(n+4)
	Branched-C(n+4)
	C(n+5.4)
	Branched C(n+9)

Test Variable	Chemistry
Positive Control	Fluorosurfactant
Counterion Type	NH ₄
	Na
	K
	DEA
	Other amines
Other Factors Screened:	
<ul style="list-style-type: none">• Mono/Diester ratio• Formulation process	

Test Formulation and Conditions

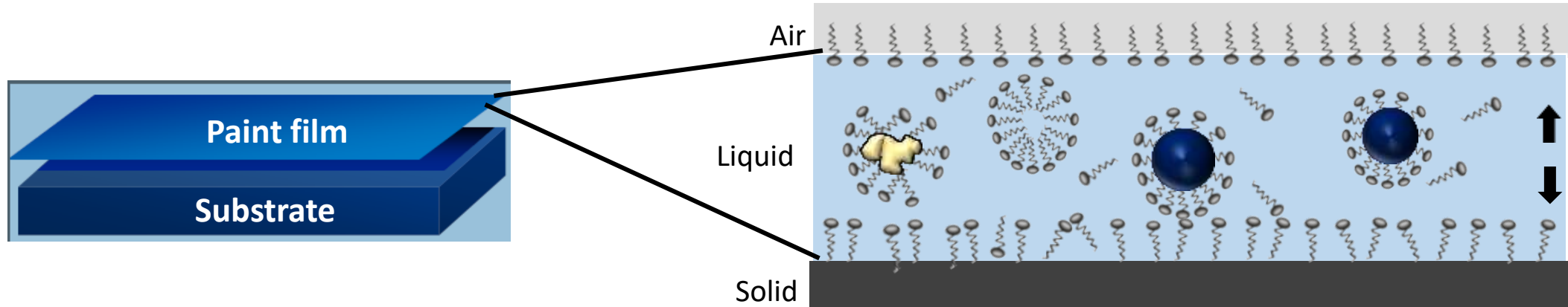
Paint Formulation

Component	Function	Dose
TRONOX® 826S-02	TiO ₂ pigment	34.74%
TAMOL™ 731A	Dispersant	0.39%
Propylene Glycol	Solvent	0.19%
BYK™-024	Defoamer	0.12%
Acrylic Latex (~45% act.)	Binder	45.79%
Texanol	Coalescing	0.62%
NH ₄ OH	Neutralizing	0.57%
NEOLONE™ M-10	Biocide	0.10%
ACRYSOL™ SCT-275	Rheology	0.39%
ACRYSOL™ RM-2020 NPR	modifier	3.19%
Water	Solvent	13.90%

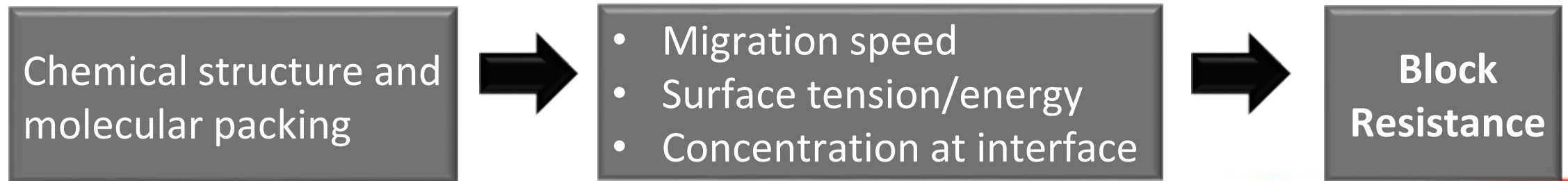
Performance Evaluation

- Paint PVC = 25.4% and pH = 9
- Additive added at 1~ 3 lb/100 gal to the final paint
- Block resistance: ASTM D4946-89; 6 mil wet film draw down
- Dynamic surface tension: Measured with bubble pressure tensiometer
- Surface energy & contact angle: Measured with MSA
- All other paint properties: According to ASTM methods

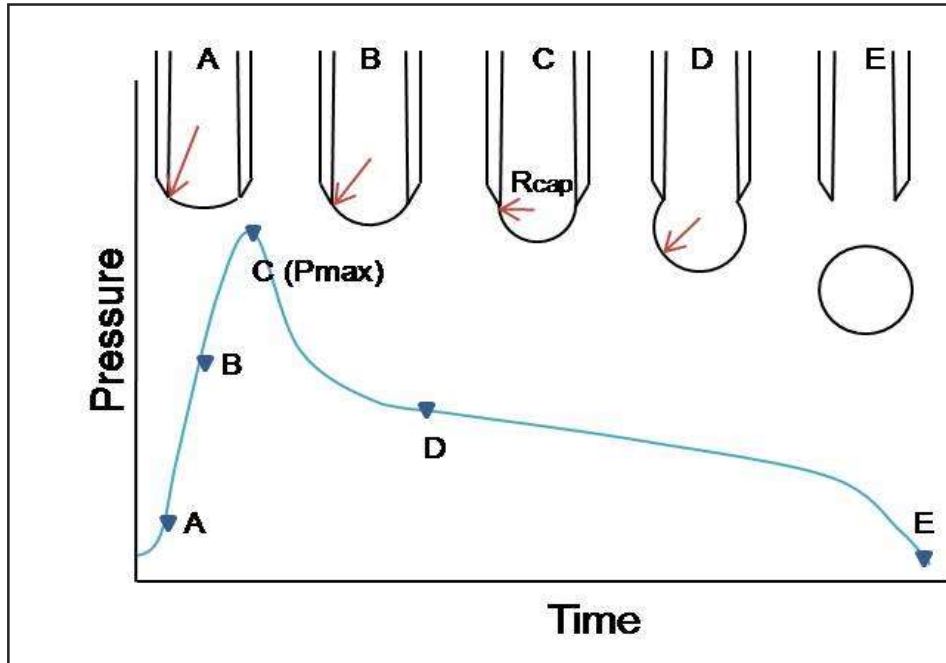
Role of Phosphate Esters in Surface Modification/Lubrication



Key factors that influence the lubricating mechanism:



Dynamic Surface Tension



**Bubble Pressure
Tensiometer**

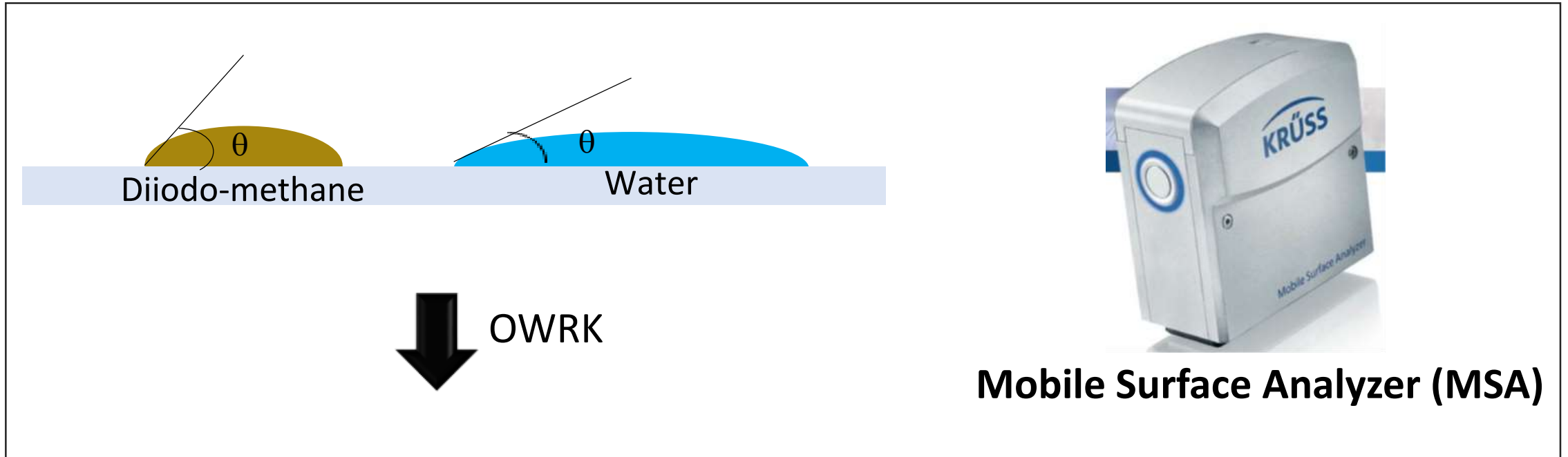
Dynamic Surface Tension

$$\sigma = \frac{\Delta P_{\max} \times R_{\text{cap}}}{2}$$



Determines how quickly the additive moves to the interface

Contact Angle and Surface Energy



Surface Energy

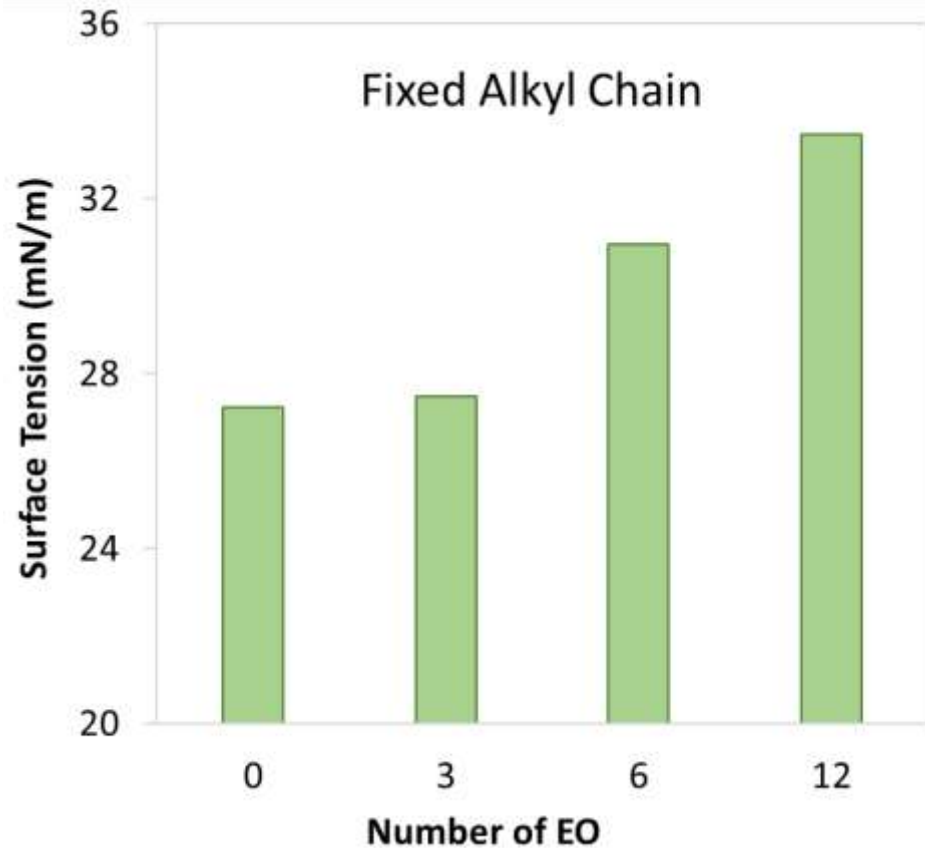
$$\sigma_S = \sigma_S^P + \sigma_S^D$$



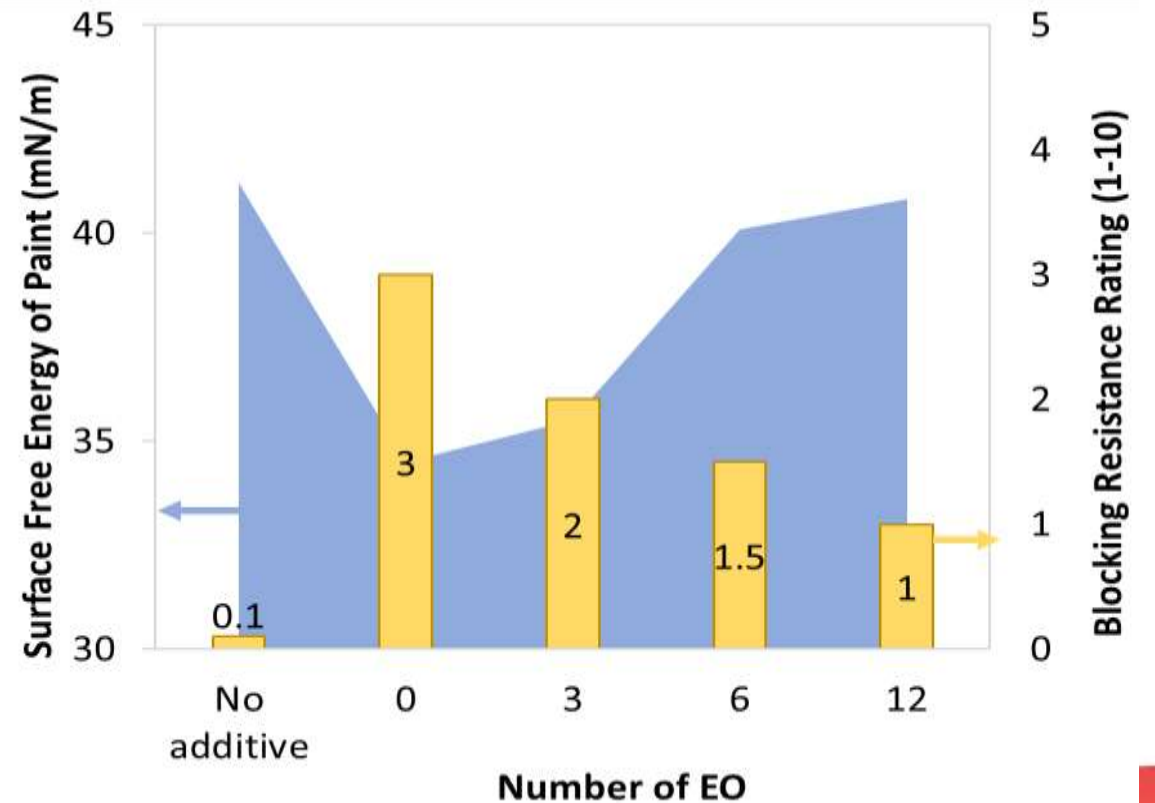
Determines the additive's impact on coating film surface

Chemistry Exploration: Impact of Ethoxylation

Surface Tension

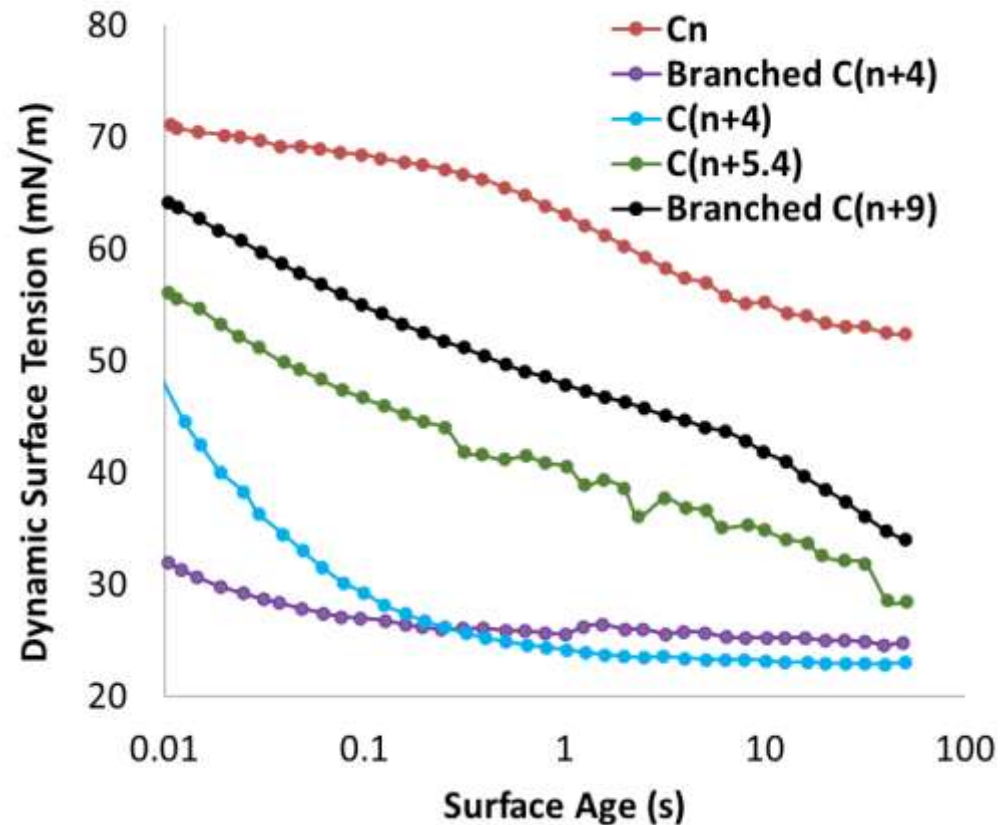


Surface Energy & Block Resistance

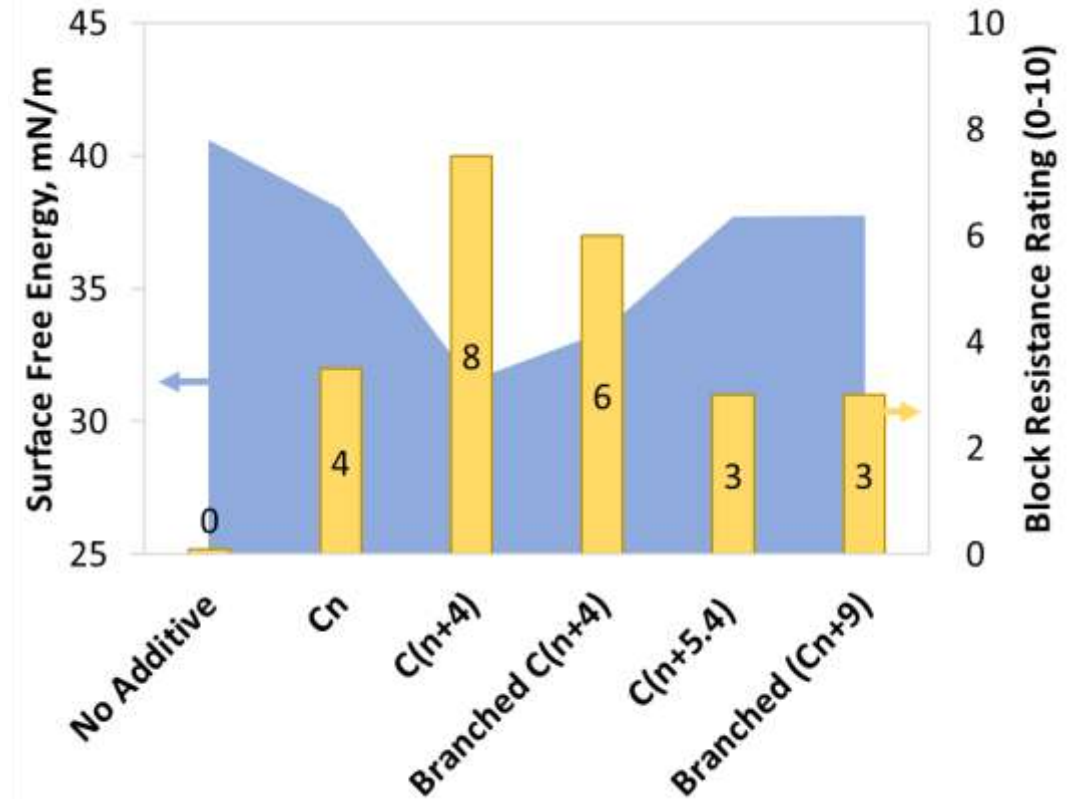


Chemistry Exploration: Impact of Alkyl Chain

Migration Speed & Surface Tension

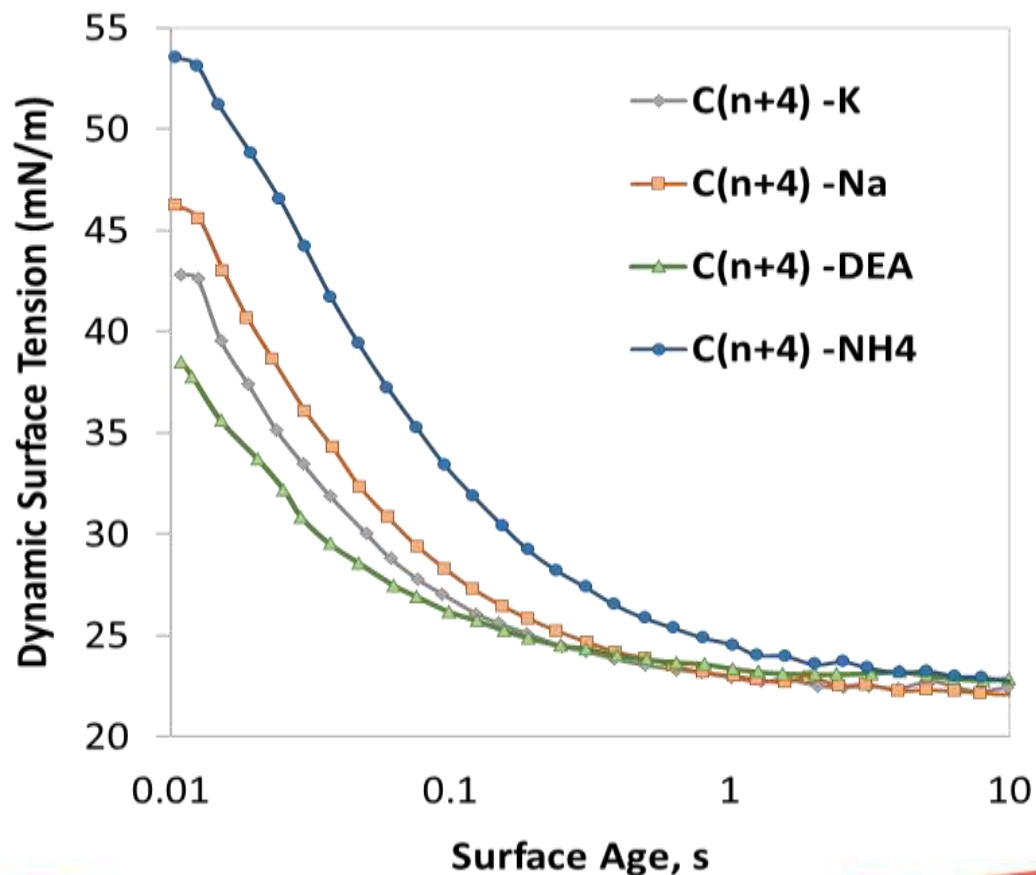


Surface Energy & Block Resistance

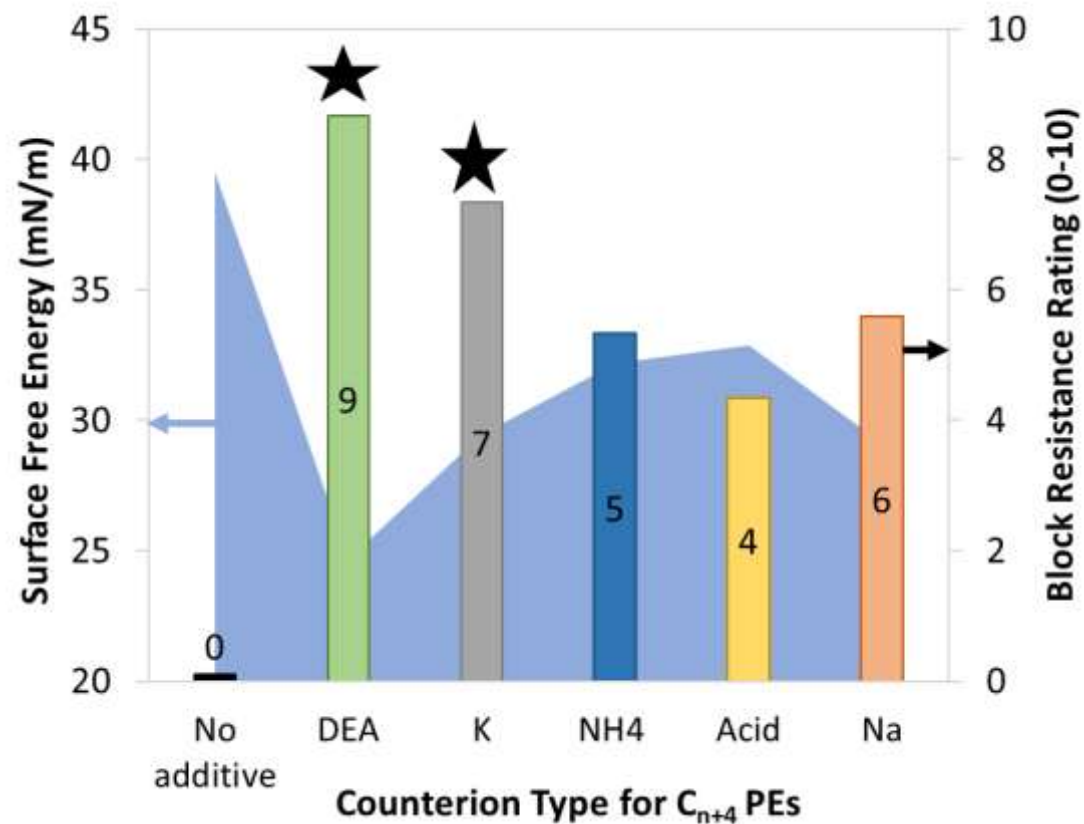


Chemistry Exploration: Impact of Counterions

Migration Speed & Surface Tension

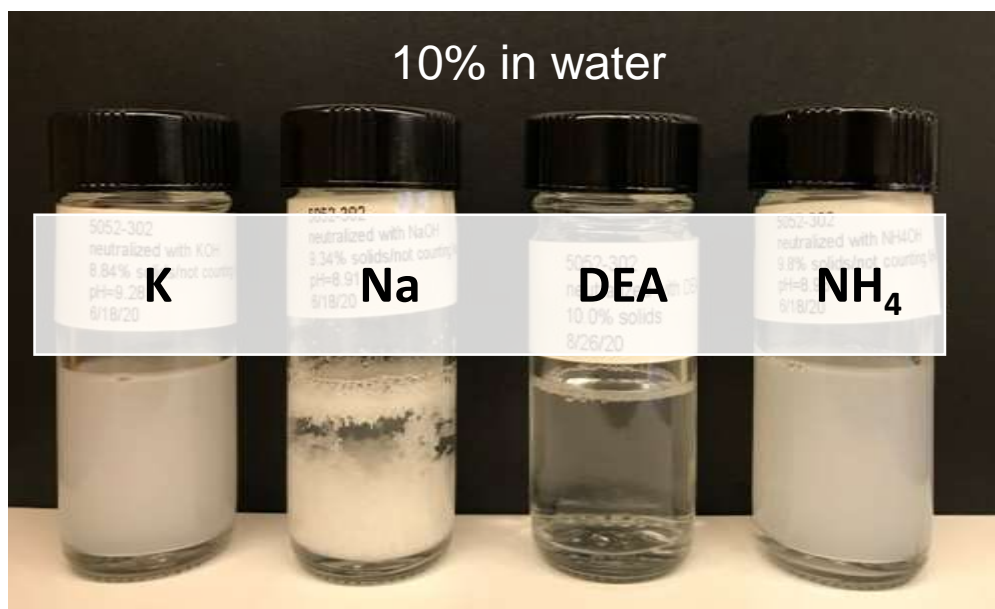


Surface Energy & Block Resistance



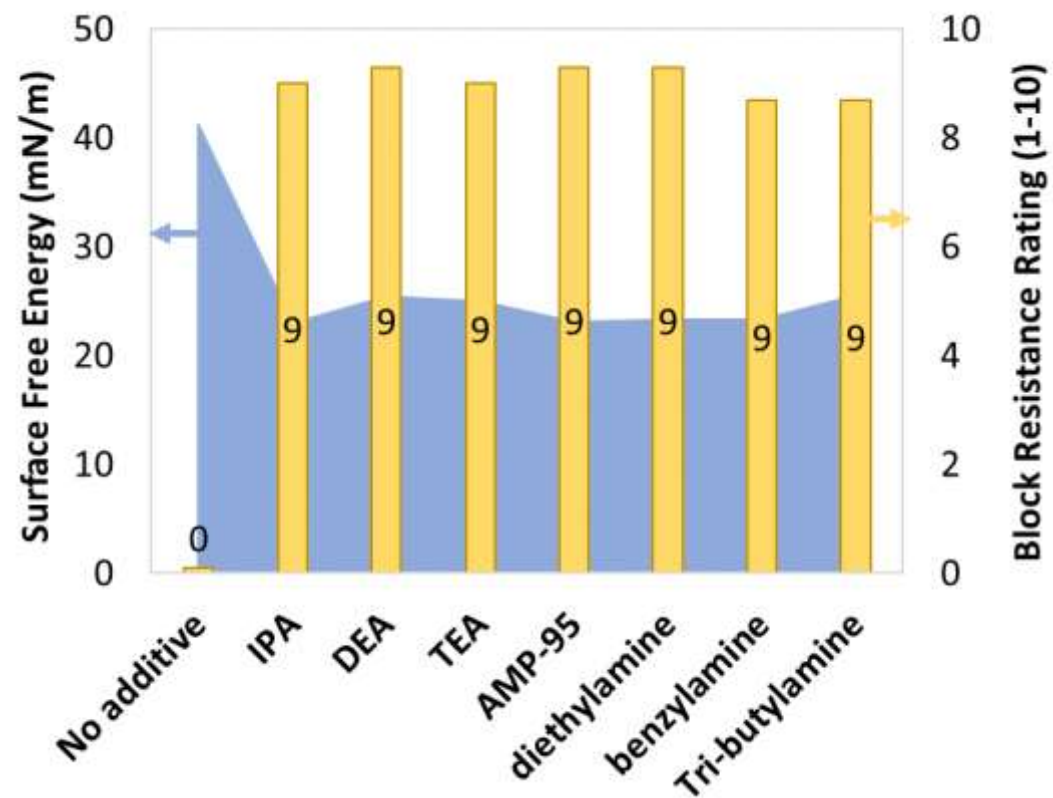
Advantages of Organic Counterions

Advantages of DEA Salt



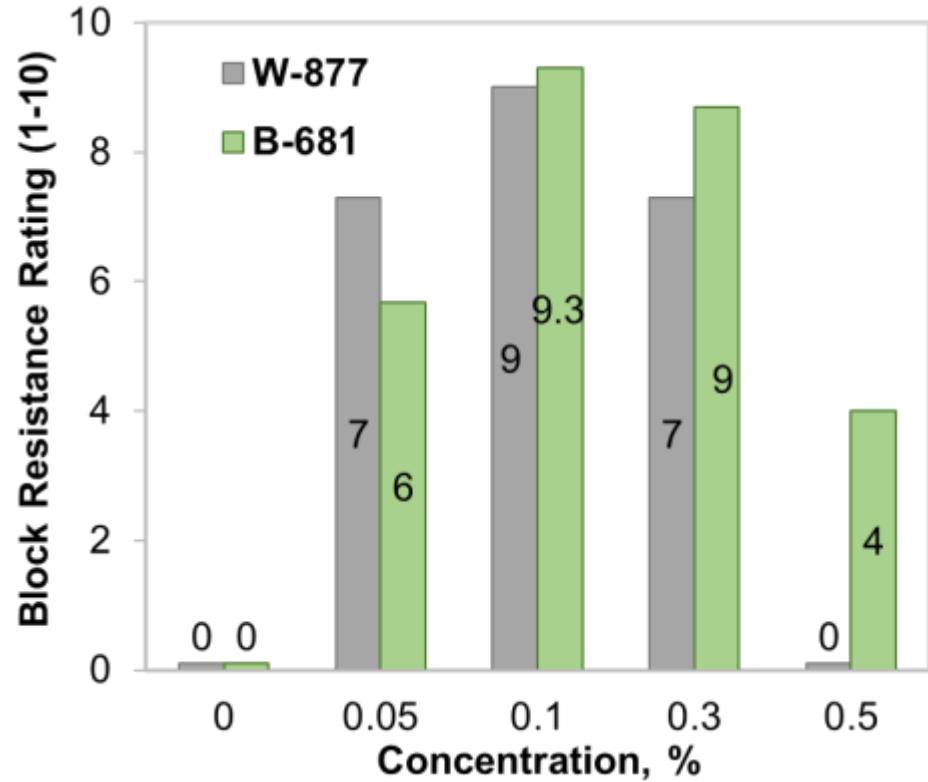
Better water solubility for DEA Salt

More Counterion Choices

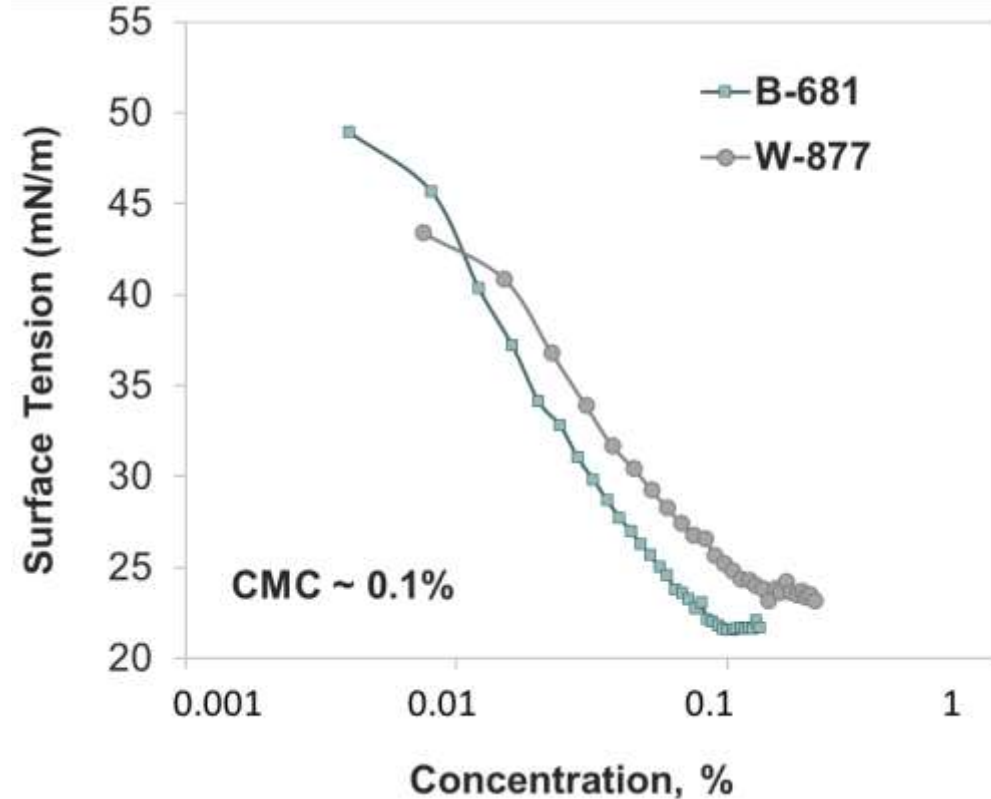


Dose Optimization

Block Resistance



Critical Micelle Concentration

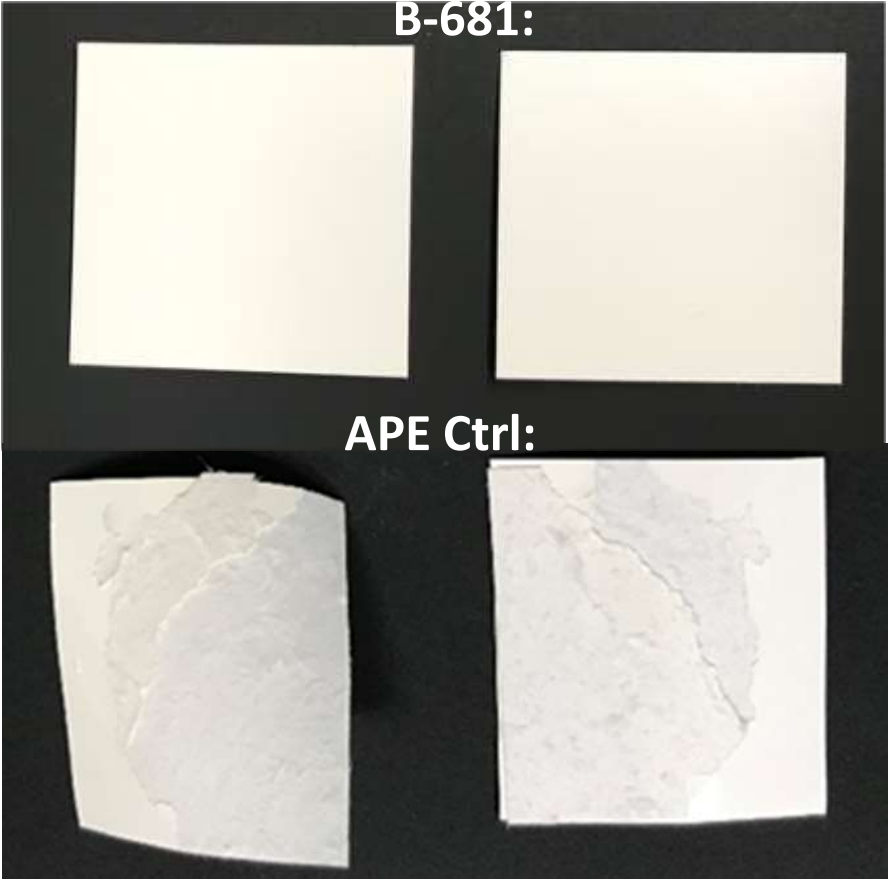
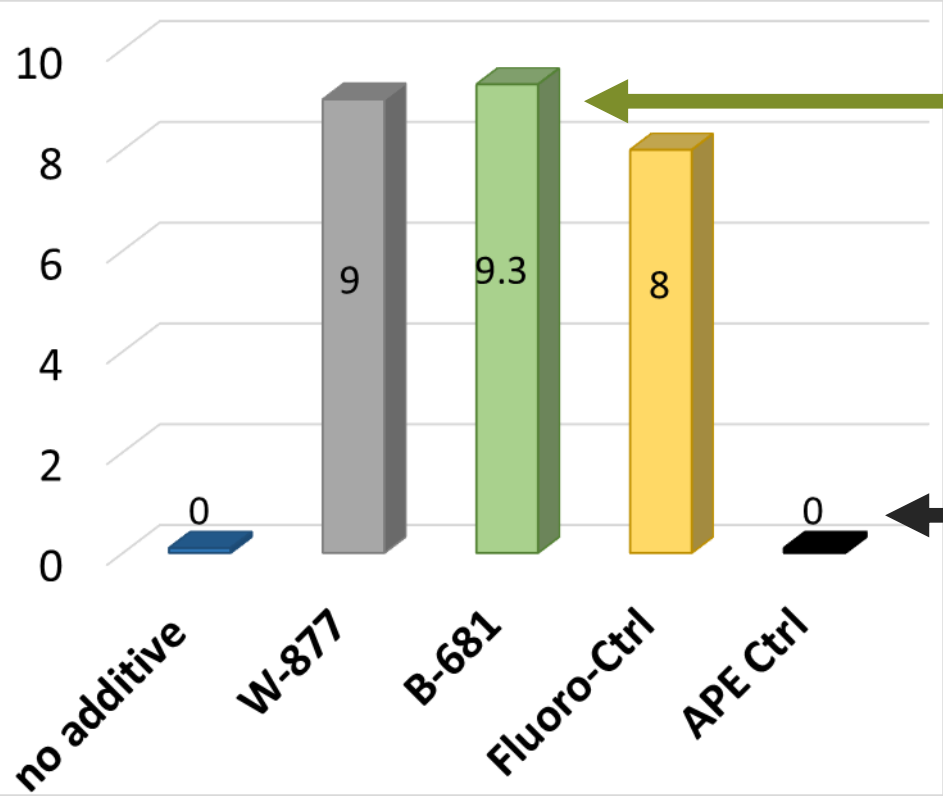


Optimum dose coincides with CMC

Performance Comparison at Equal Dose

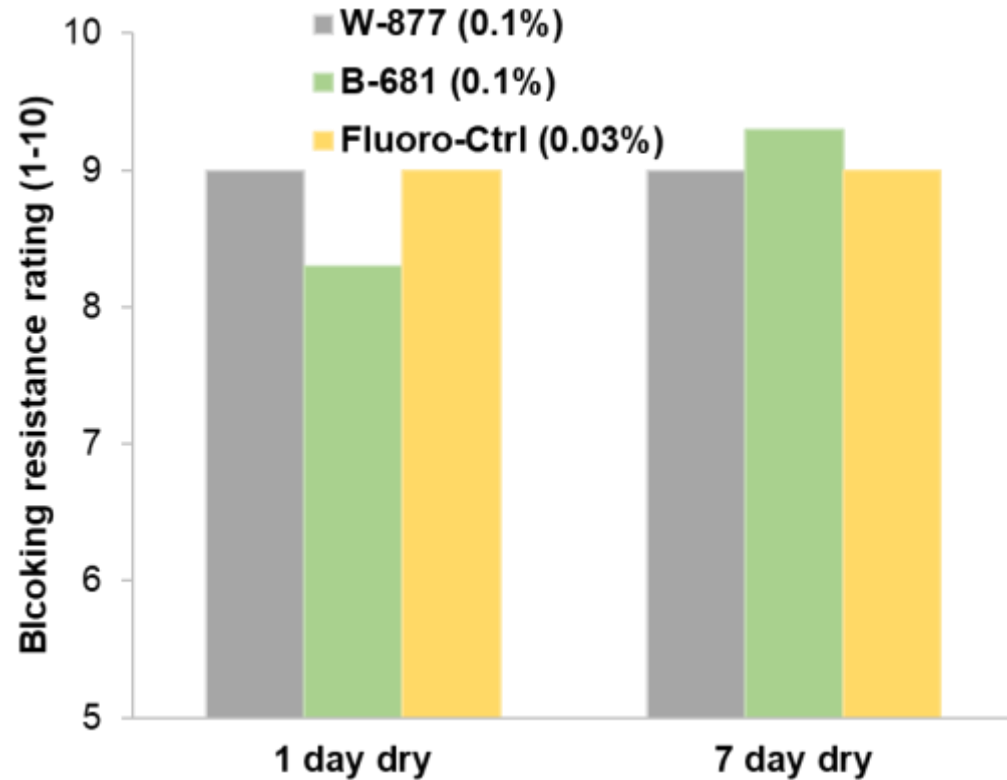
Block Resistance at 0.1% Dose

Block Resistance Rating (1-10)

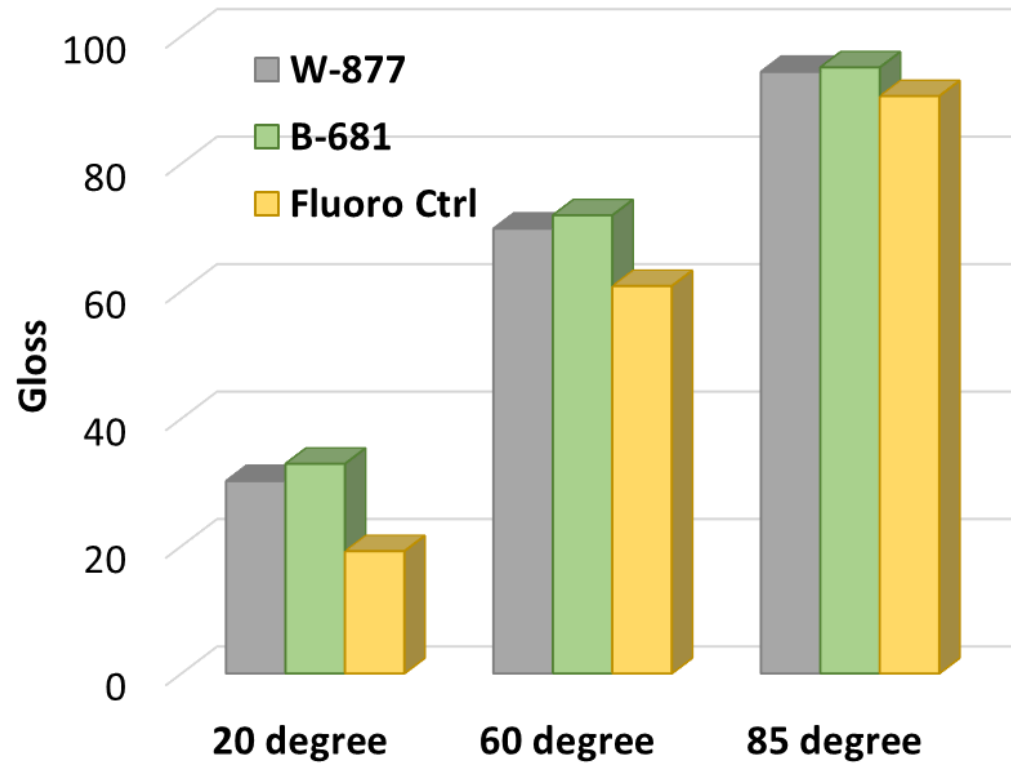


Performance Comparison at Optimum Dose

Equal/Better Blocking Resistance



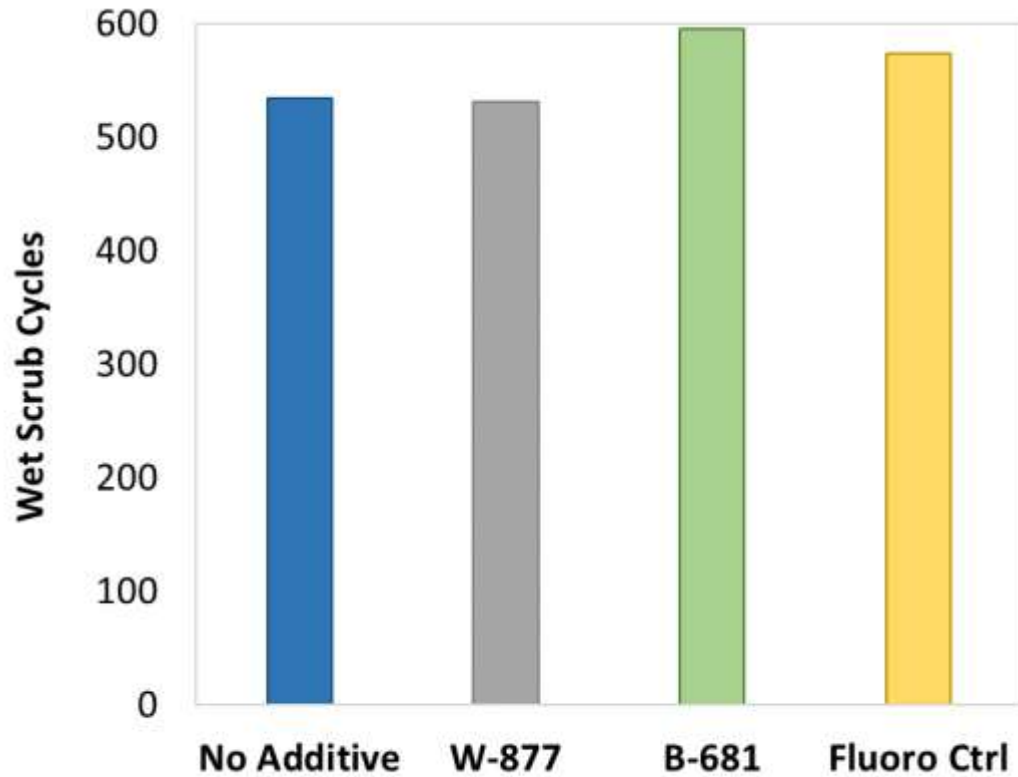
Improved Gloss



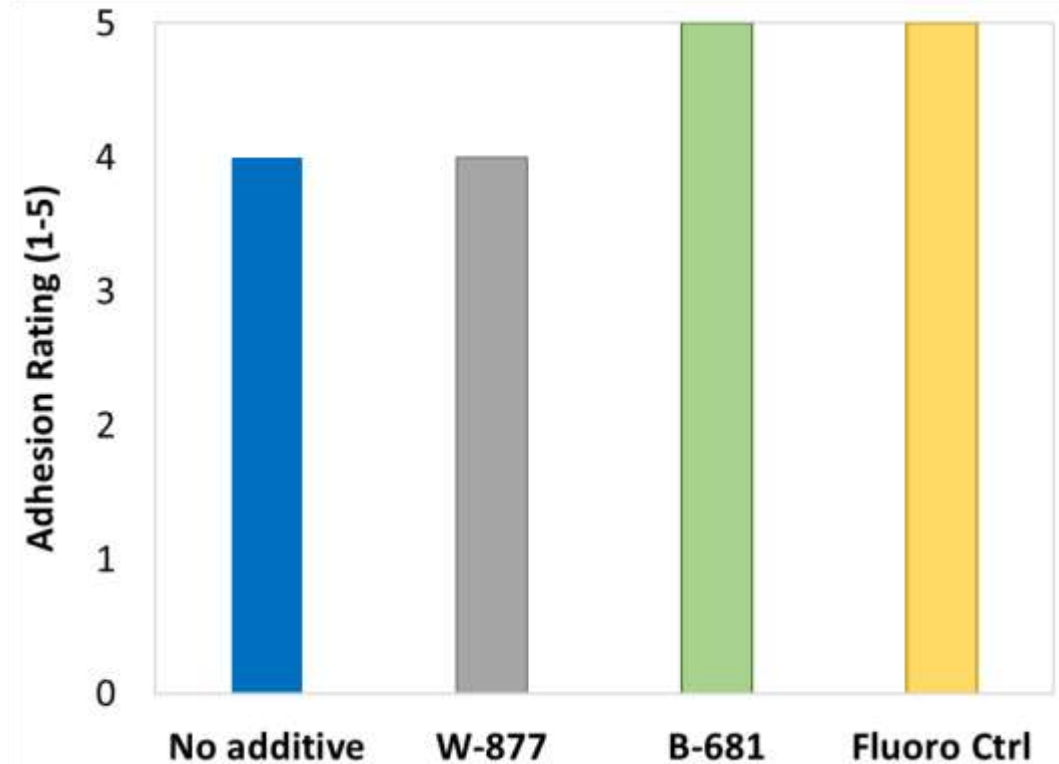
Optimum dose is ~ 2lb/100gal (as is). Fluoro Ctrl is more diluted

Multifunctional Benefits

Wet Scrub Resistance

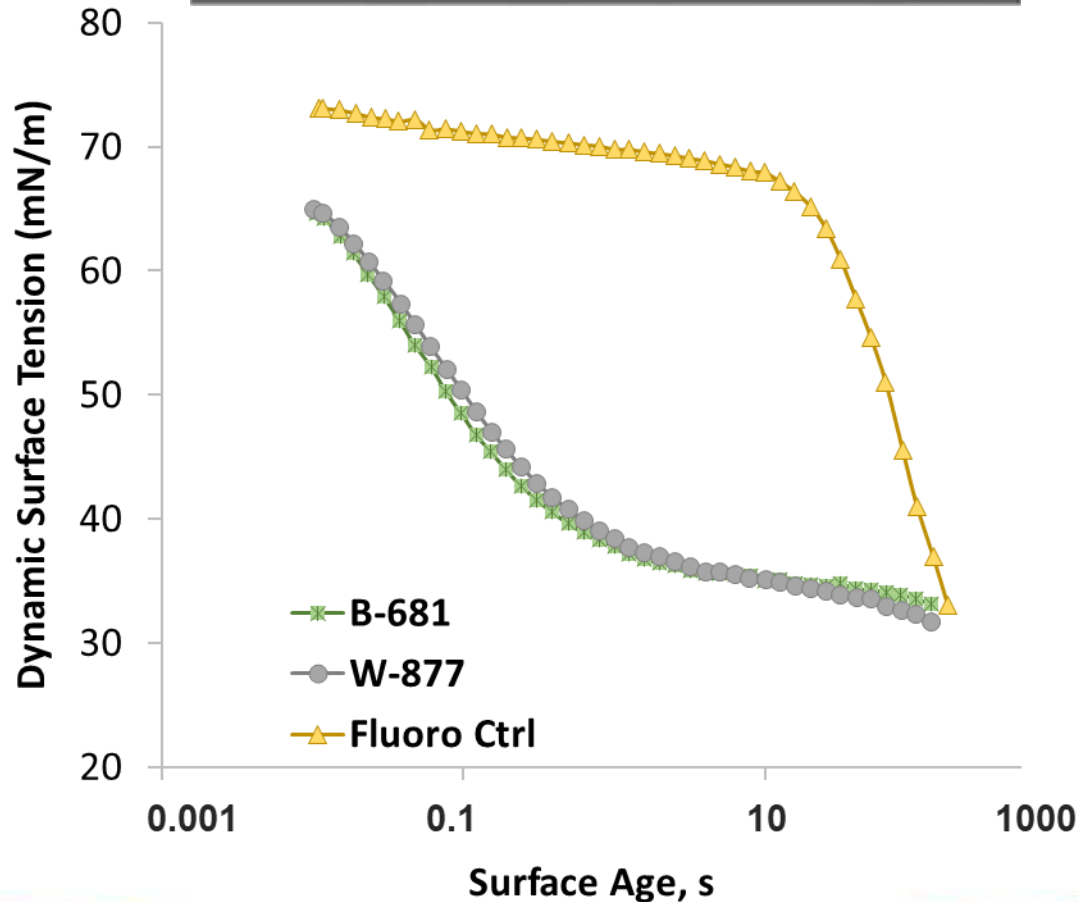


Dry Adhesion on Scrub Chart



Phosphate Esters vs. Fluorosurfactant Control

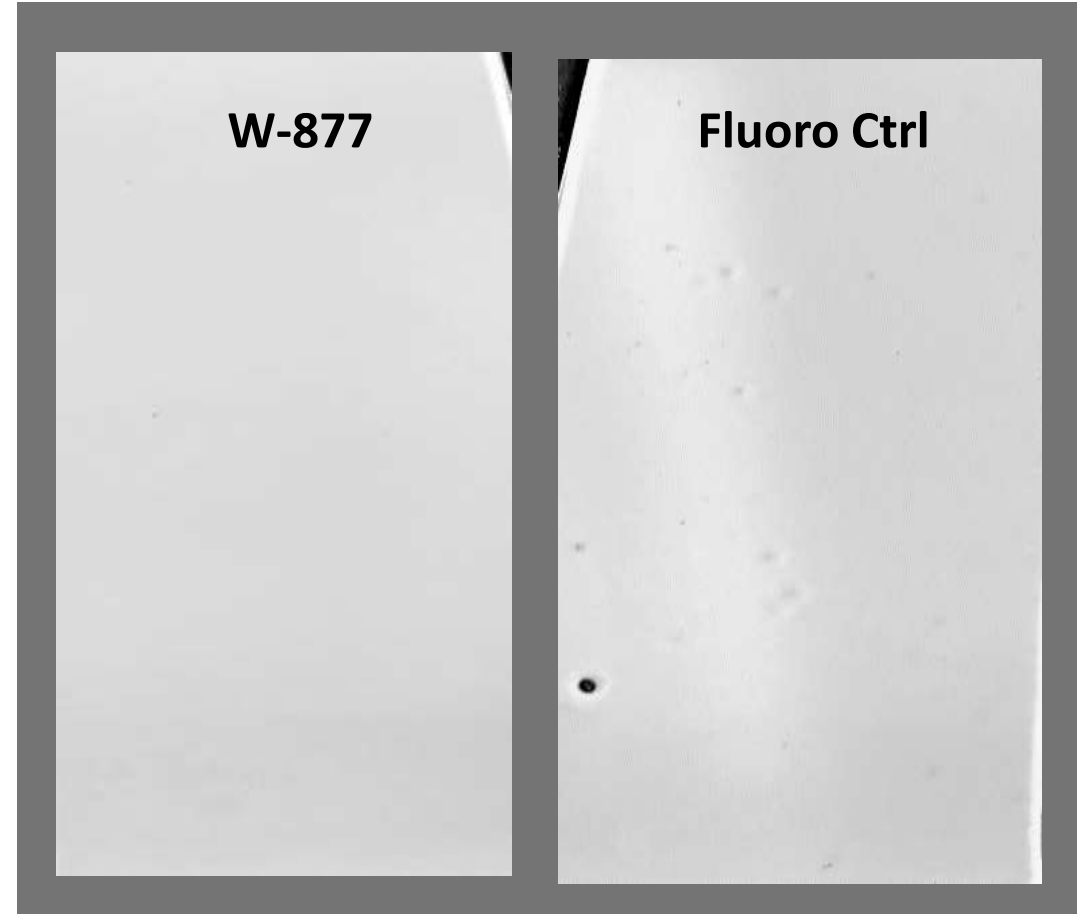
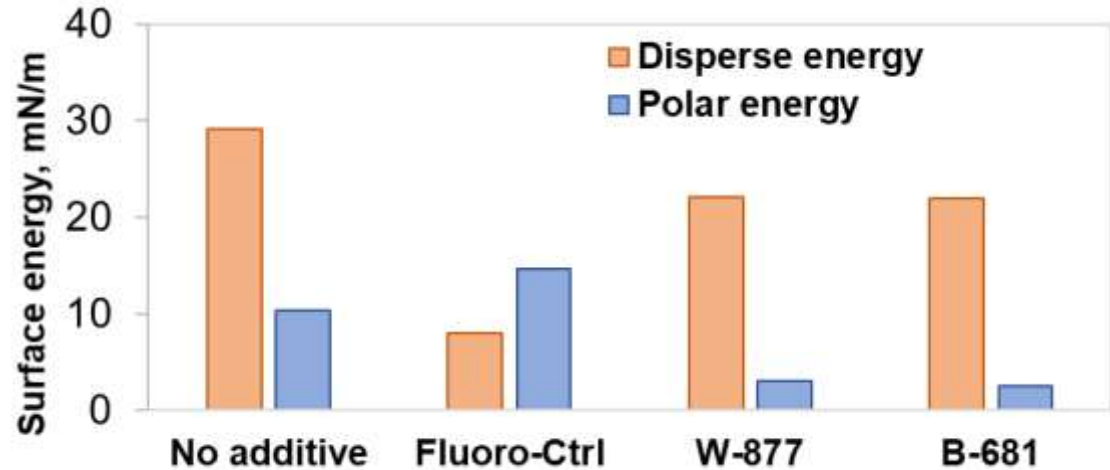
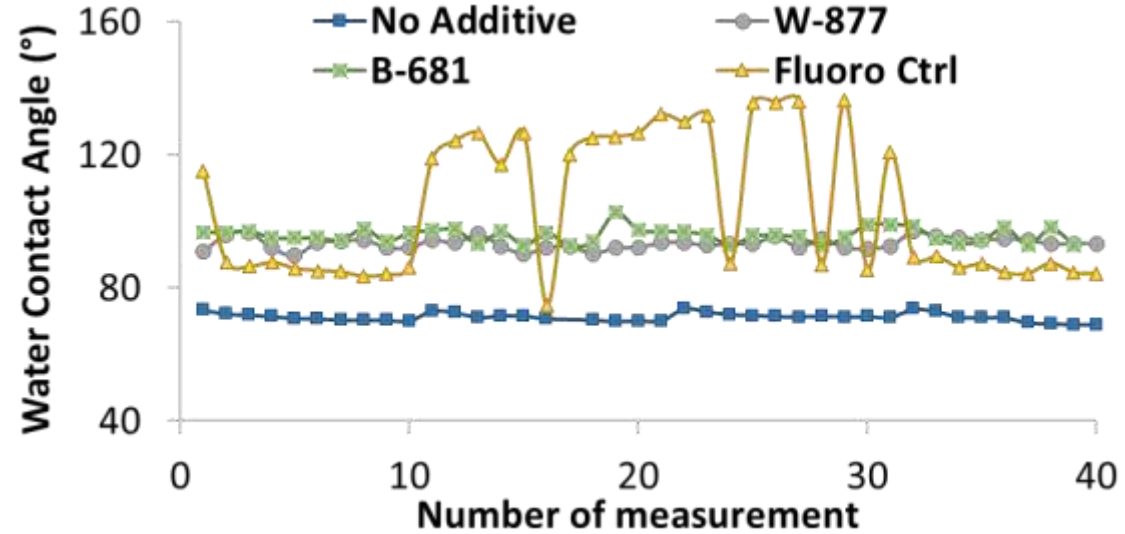
Dynamic Behavior



Basic Surfactant Properties

Additive	CMC	Minimum Surface Tension
B-681	~ 1000 mg/l	~ 21.5 mN/m
W-877	~ 1300 mg/l	~ 24 mN/m
Fluoro Ctrl	~ 75 mg/l	~ 16.5 mN/m

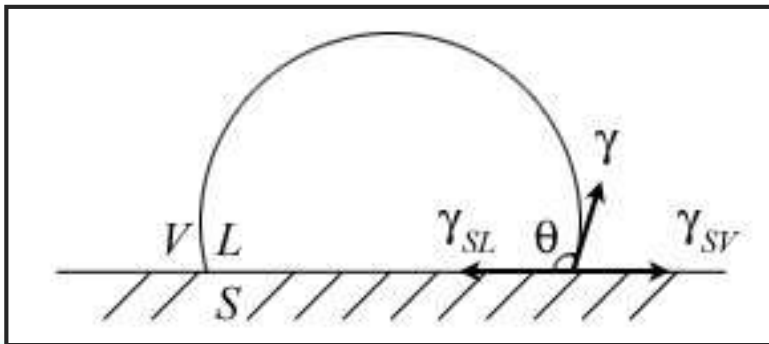
Additive Compatibility with Coatings



Phosphate Esters Reduce Water Sensitivity

Contact Angle (Water Repellency)

Paint with:	Water Contact Angle
B-681	95°
W-877	93°
Fluoro Ctrl	88°
No additive	71°



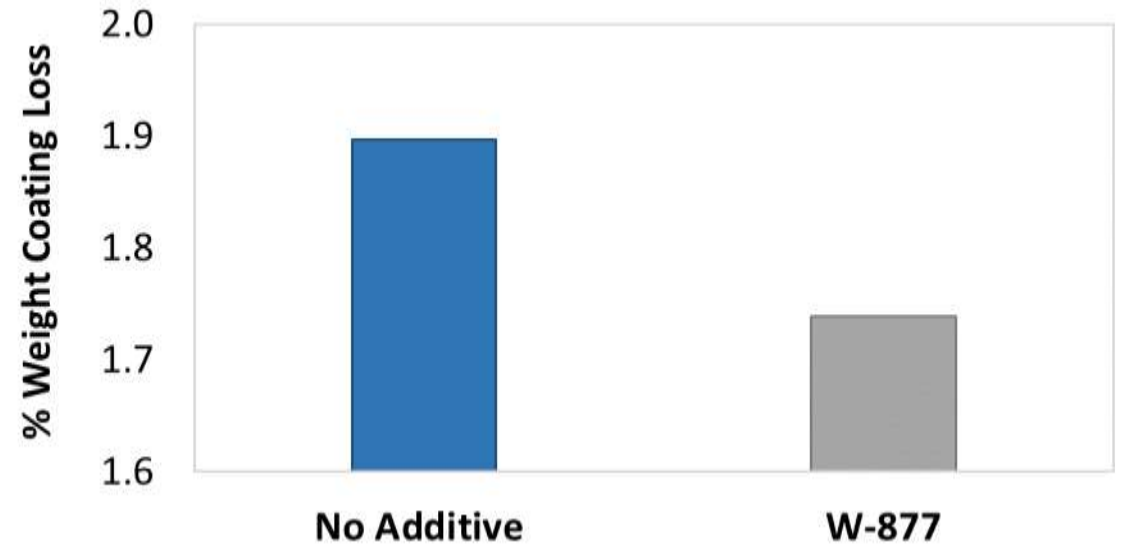
Wetting:

$$0^\circ < \theta < 90^\circ$$

Non-Wetting:


$$90^\circ < \theta < 180^\circ$$

Additive Leaching in High Humidity



Test done with architectural semi-gloss water-based acrylic latex paint at ambient T and 98% humidity for 6h

Fluoro-Free & Silicone-Free Block Resistance Additives



Additive	Benefit	Status	Water Solubility	Solids	TSCA	DSL	REACH
W-877	Excellent block resistance	Commercial product	Dispersible	~ 40%	√	Pending	-
B-681	Excellent block resistance	Proprietary samples available	Soluble	~ 45%	√	√	√

Summary

W-877 & B-681
specialty phosphate esters in paint deliver:

Improved
block
resistance

Improved
color
acceptance
and gloss

Reduced
water
sensitivity

Good
overall
properties

Stepan additives matched functionality of fluorosurfactants
in paint applications with better environmental profile



Contact info: sdong@stepan.com

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