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

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

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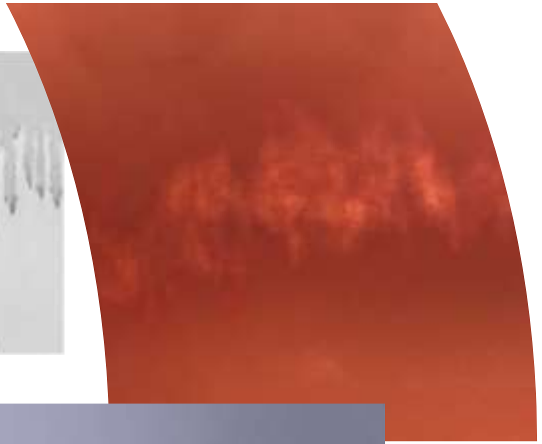
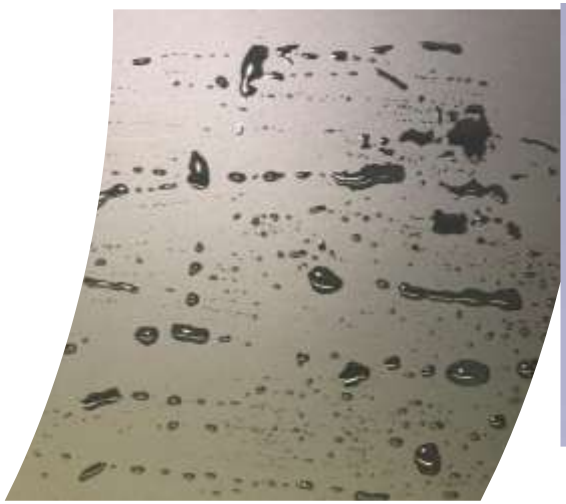
Agenda

- 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

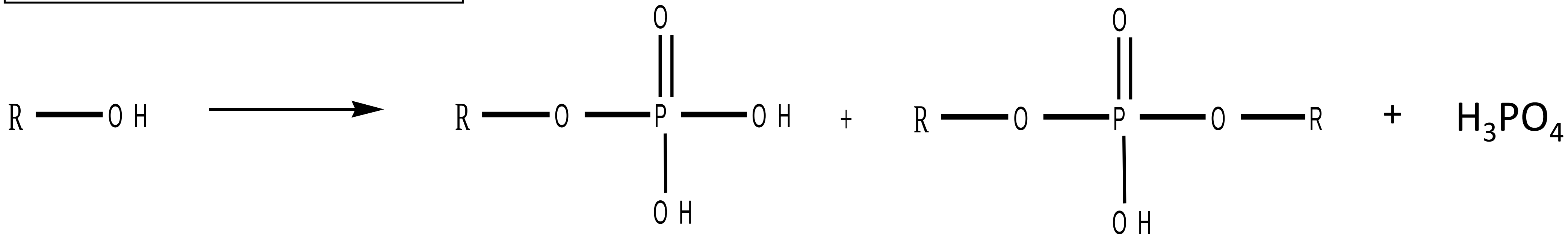
Phosphate Esters

Key Molecule Features:

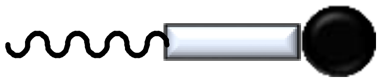
- Alkyl chain length and branching
- Alkoxylation degree
- Mono/Diester ratio

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:

- Mono/Diester ratio
- Formulation process

Test Formulation and Conditions

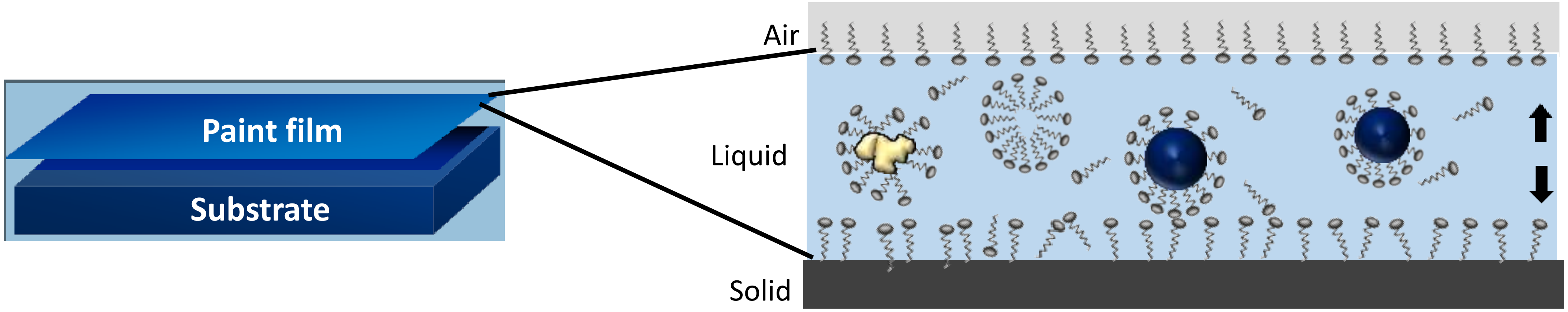
Paint Formulation

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_4OH	Neutralizing	0.57%
NEOLONE™ M-10	Biocide	0.10%
ACRYSOL™ SCT-275	Rheology modifier	0.39%
ACRYSOL™ RM-2020 NPR		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 <u>lubricating</u> mechanism:

Chemical structure and molecular packing →
- Migration speed
- Surface tension/energy
- Concentration at interface

→ **Block Resistance**

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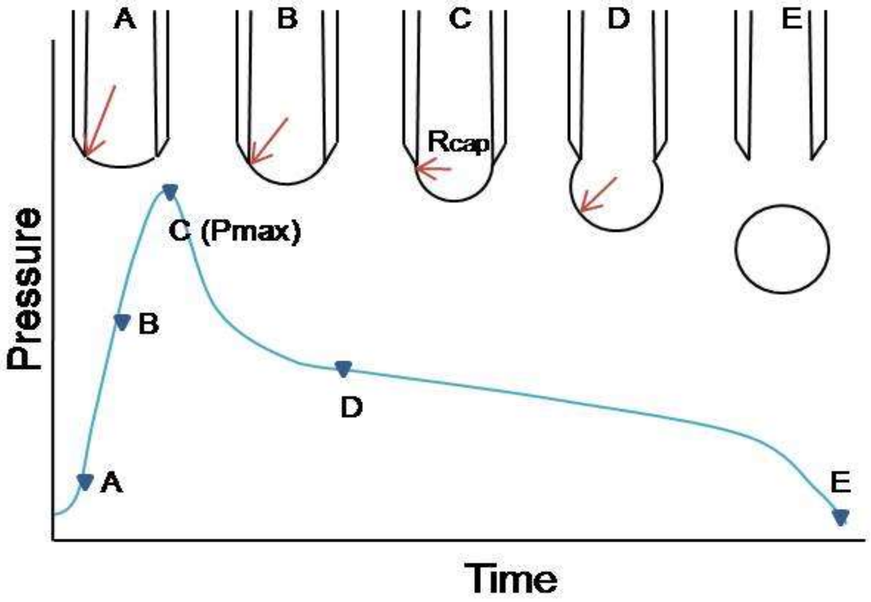
Dynamic Surface Tension



Bubble Pressure Tensiometer

Dynamic Surface Tension

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

Determines how quickly the additive moves to the interface

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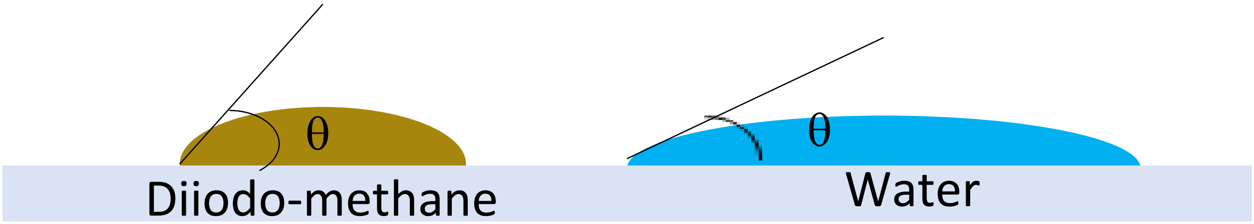
Contact Angle and Surface Energy



OWRK

Mobile Surface Analyzer (MSA)

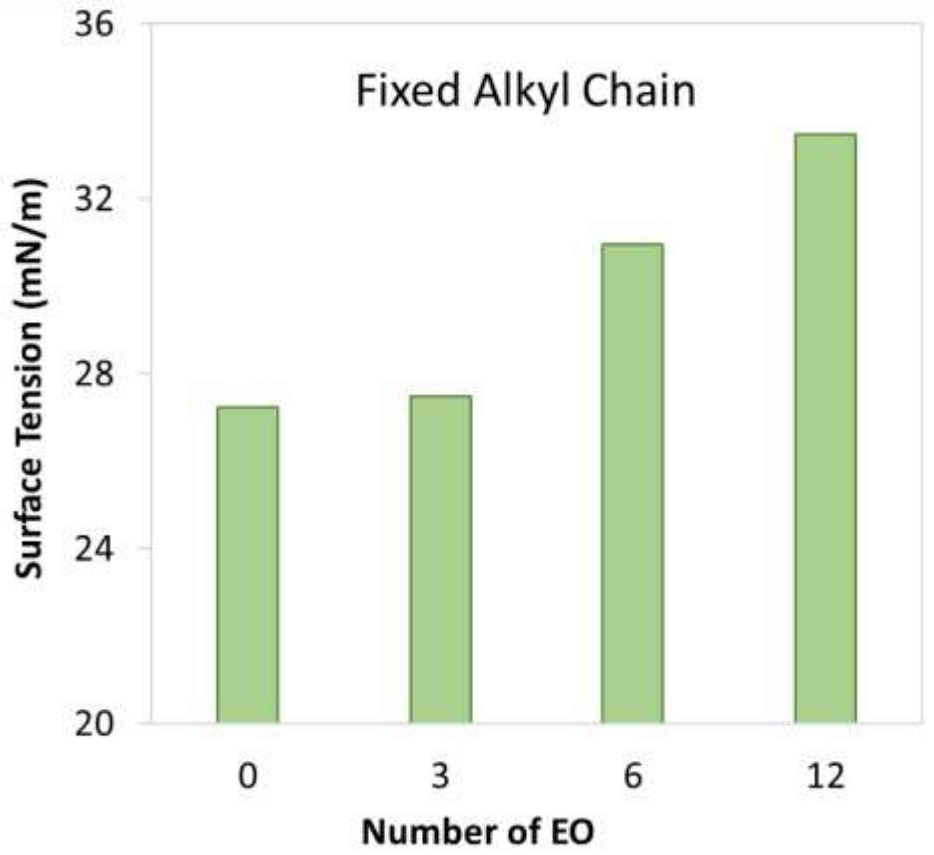
Surface Energy

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

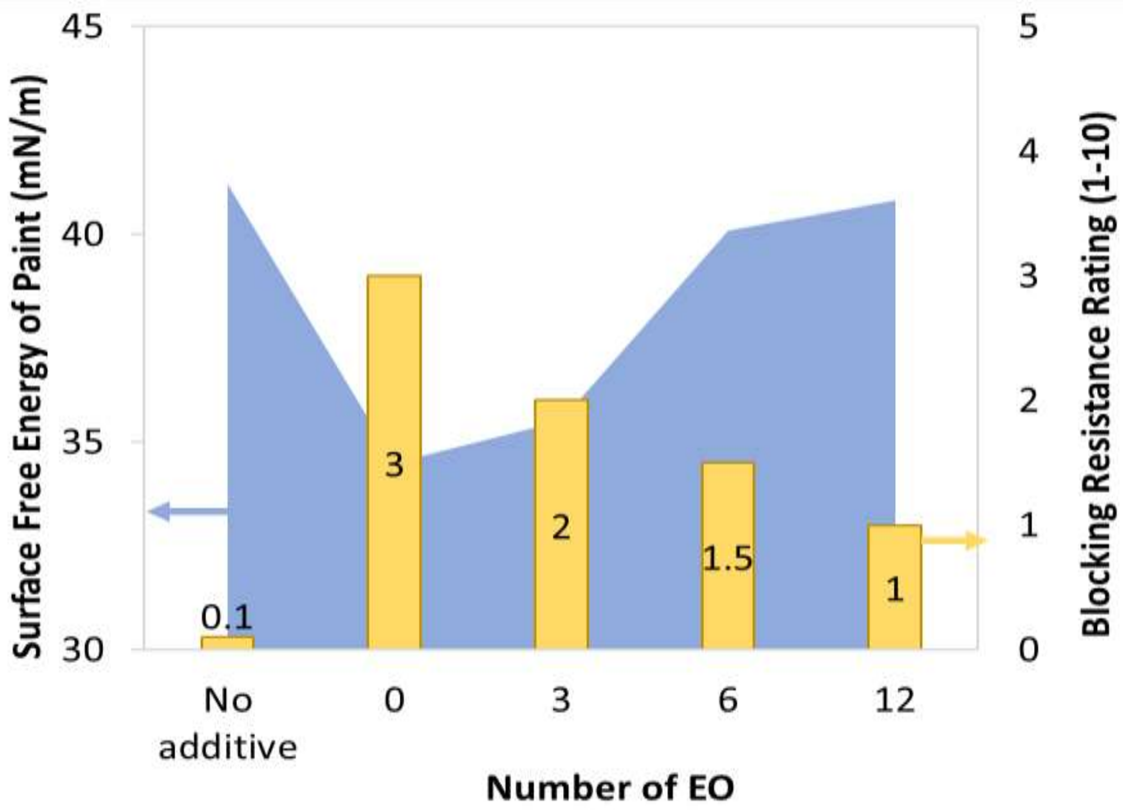
Determines the additive's impact on coating film surface

Chemistry Exploration: Impact of Ethoxylation

Surface Tension

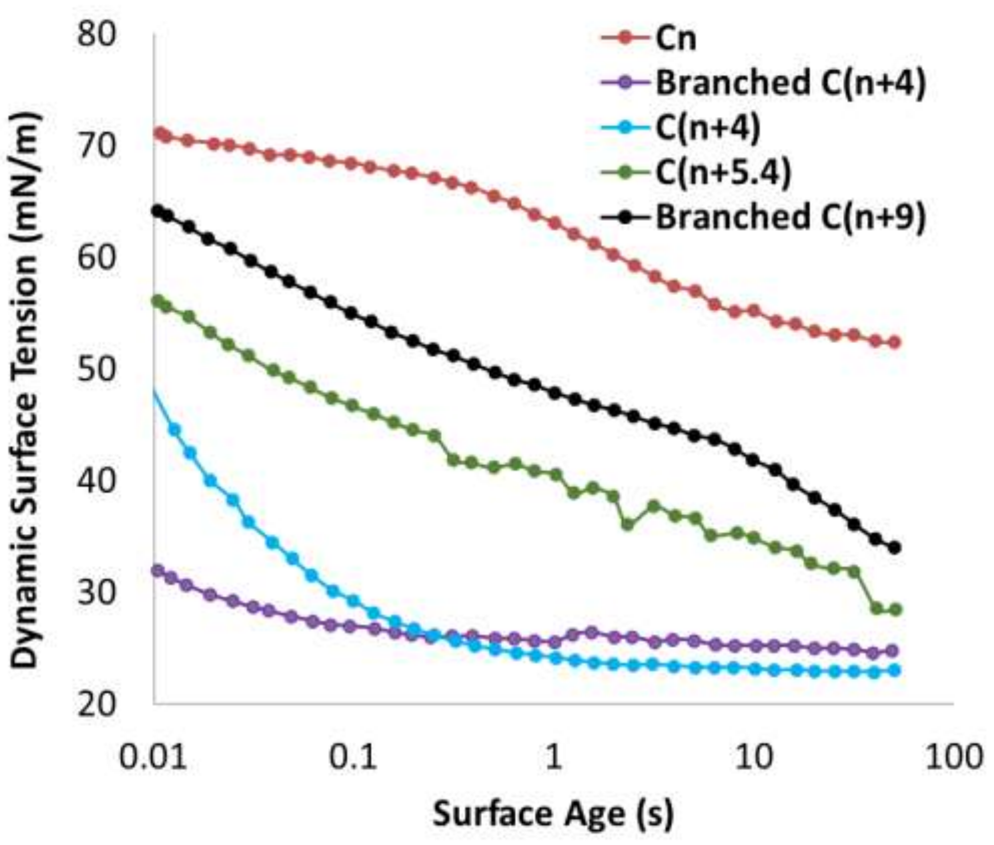


Surface Energy & Block Resistance

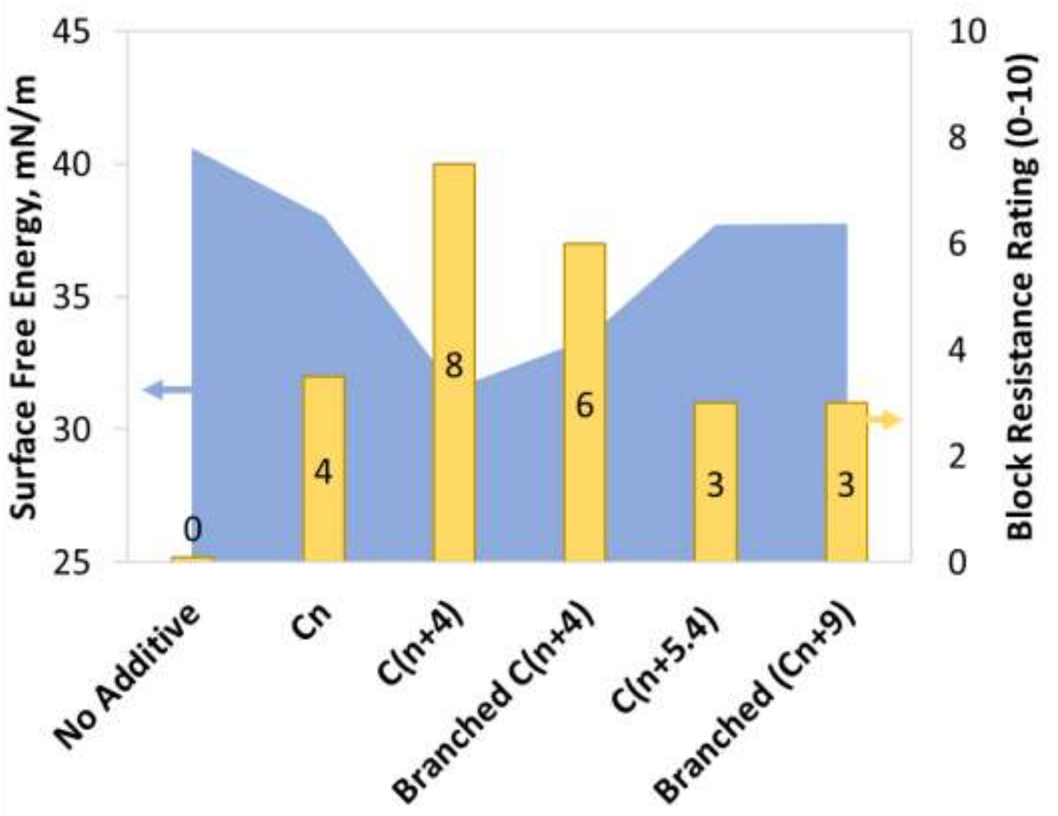


Chemistry Exploration: Impact of Alkyl Chain

Migration Speed & Surface Tension



Surface Energy & Block Resistance



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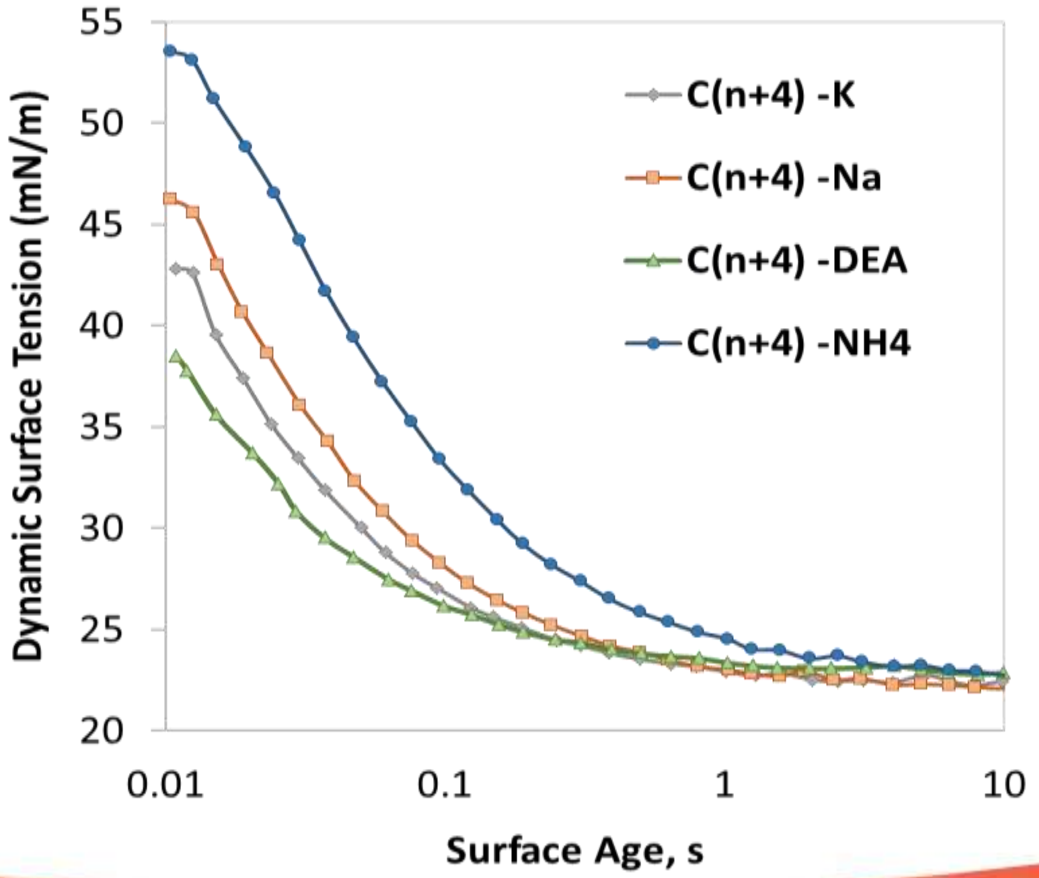
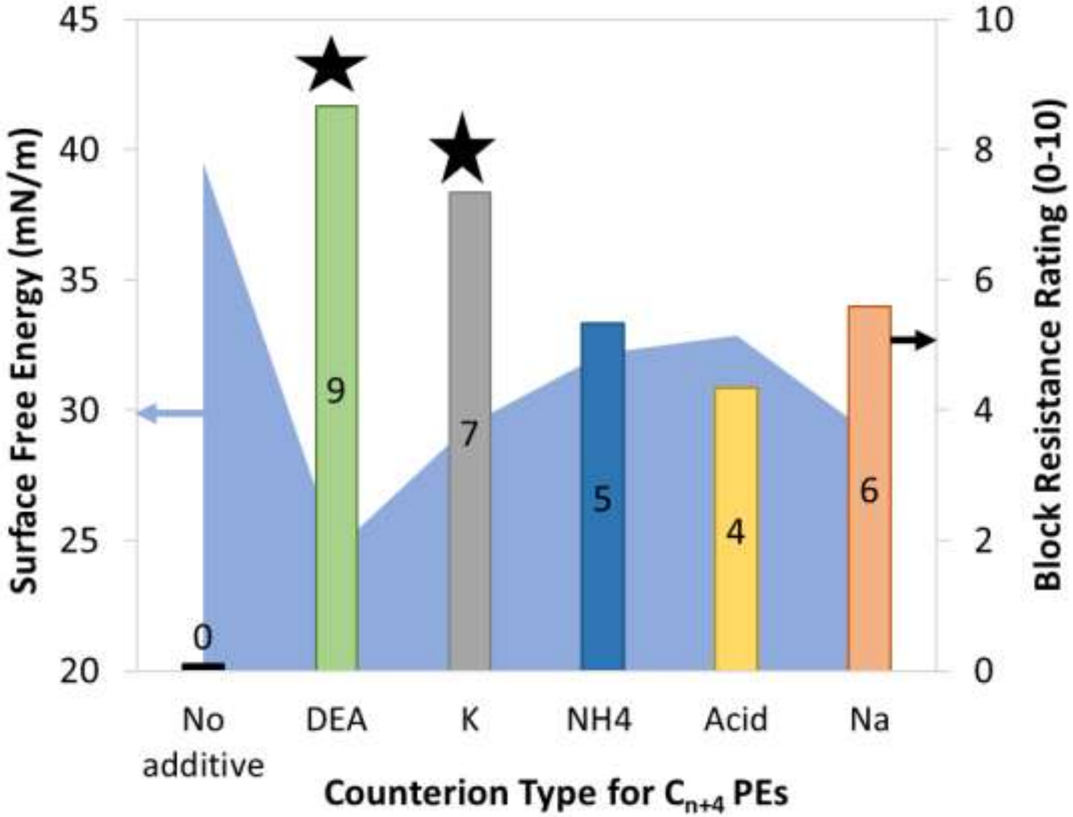
Chemistry Exploration: Impact of Counterions

Migration Speed & Surface Tension

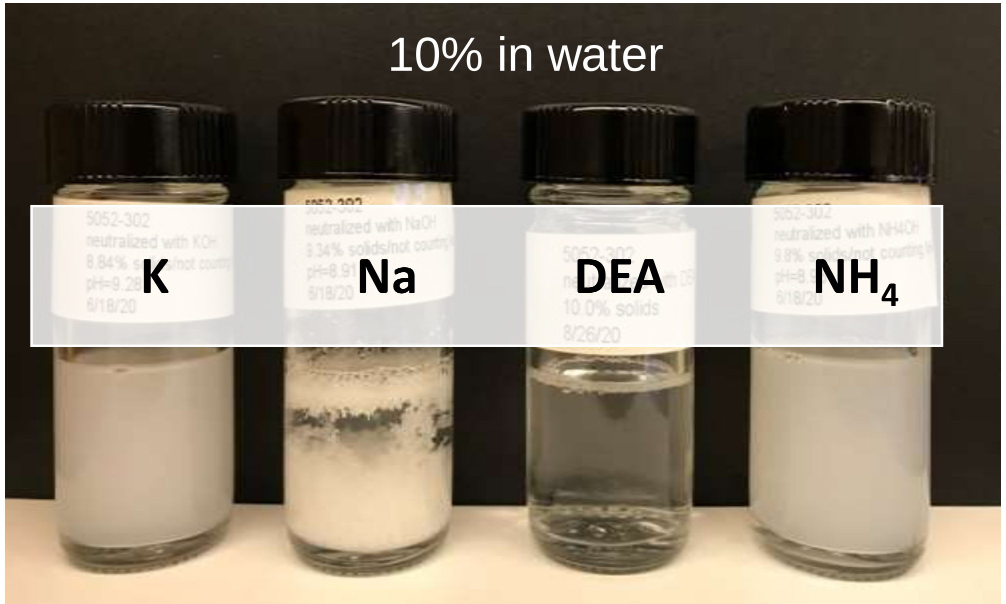


Surface Energy & Block Resistance



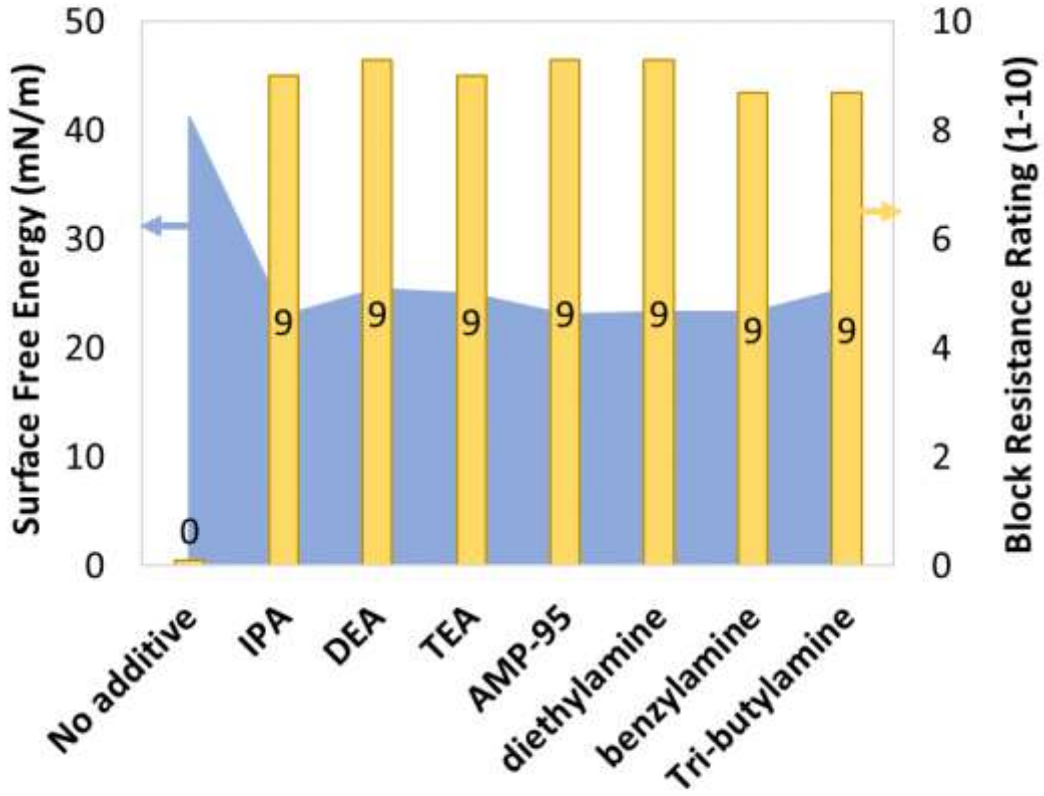
Advantages of Organic Counterions

Advantages of DEA Salt



Better water solubility for DEA Salt

More Counterion Choices



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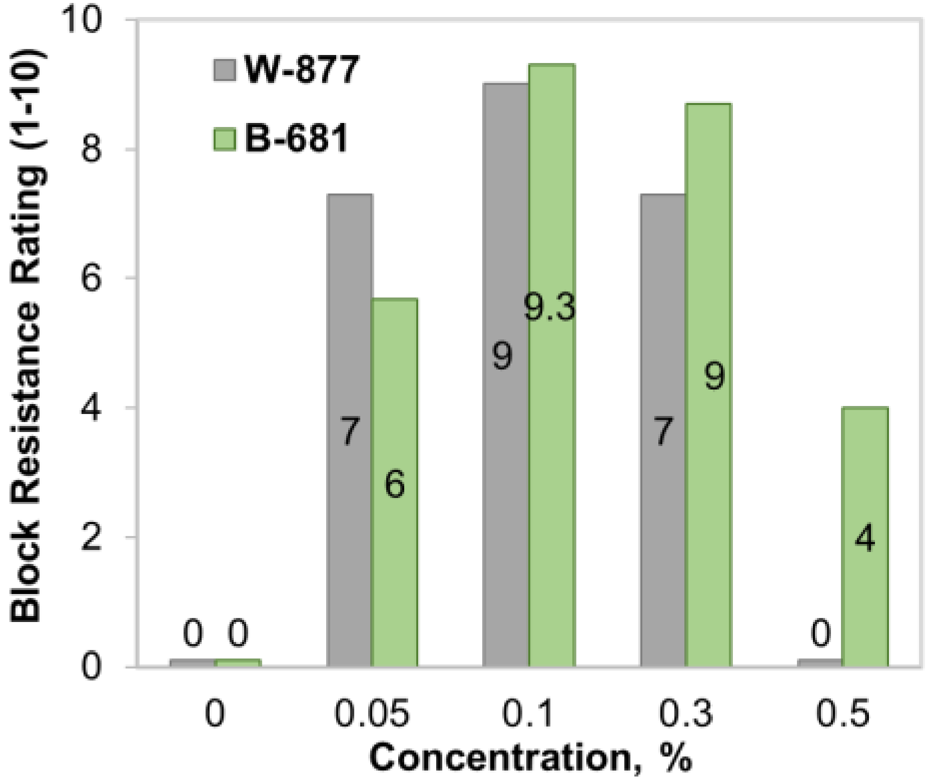
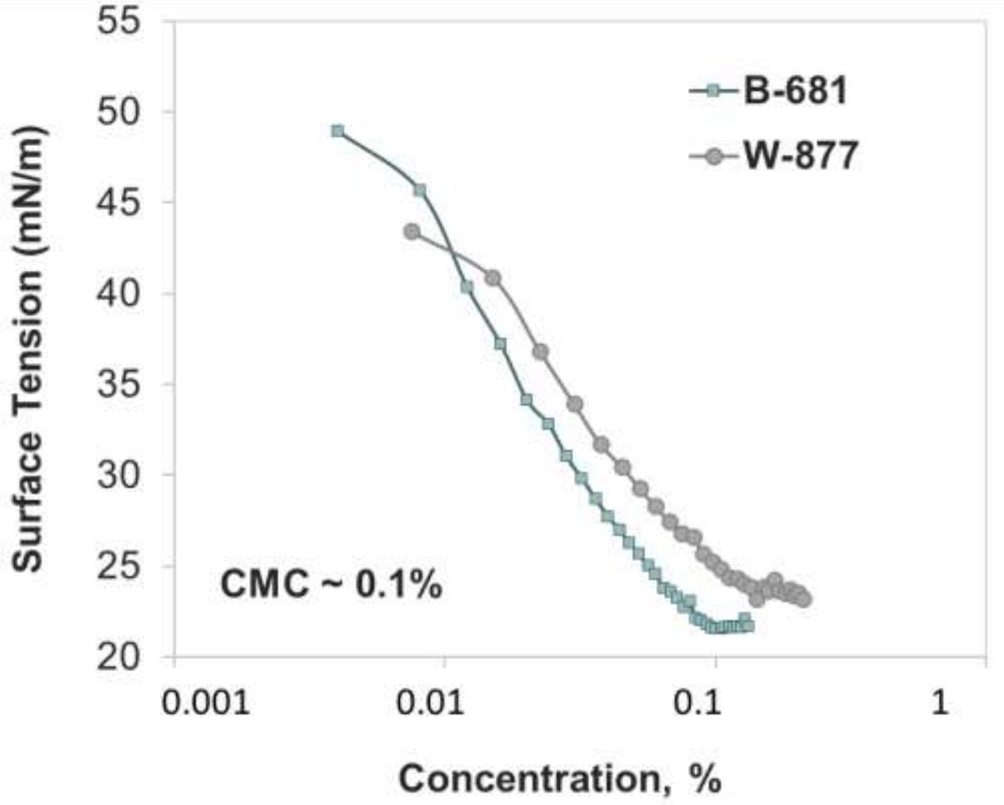
Dose Optimization

Block Resistance

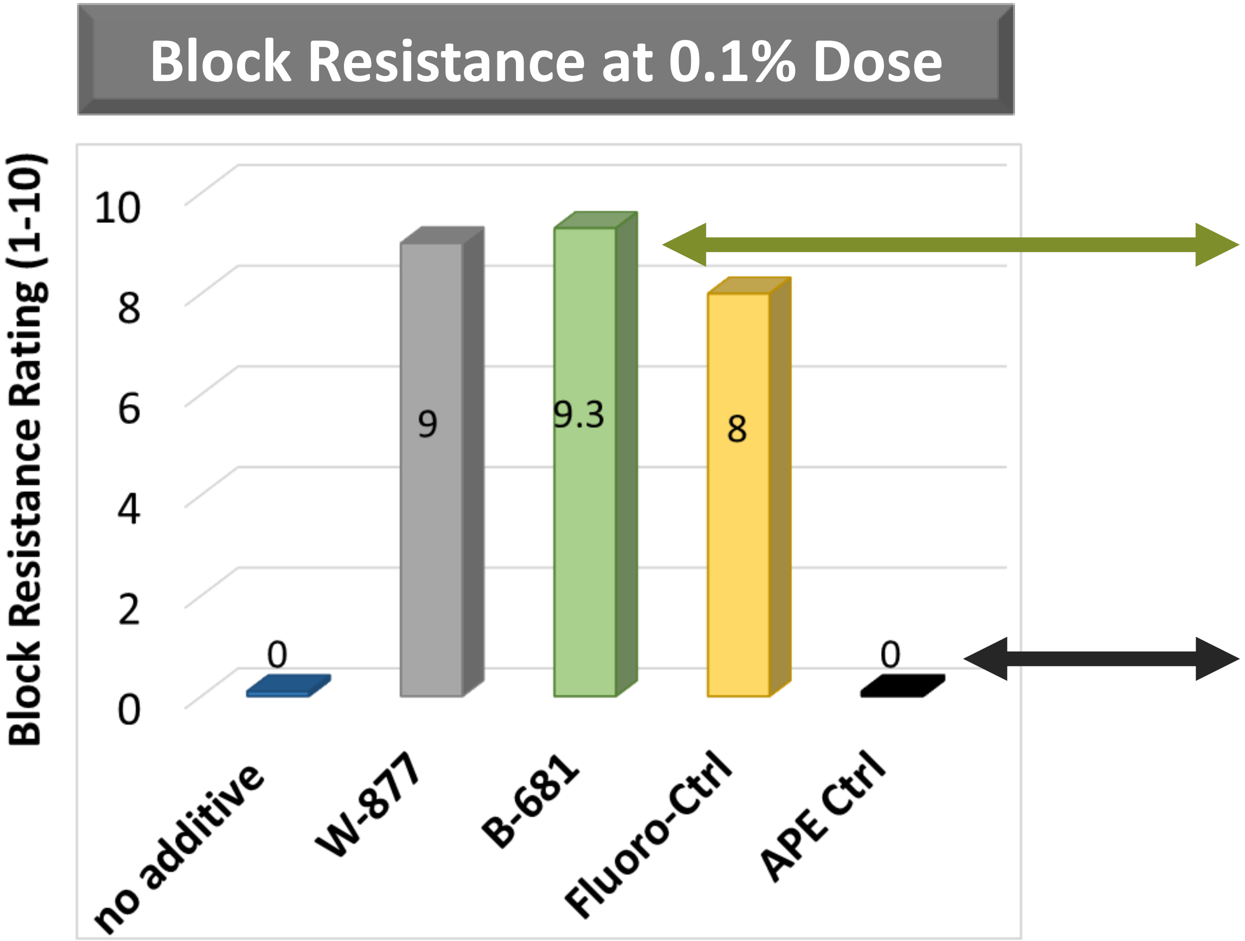


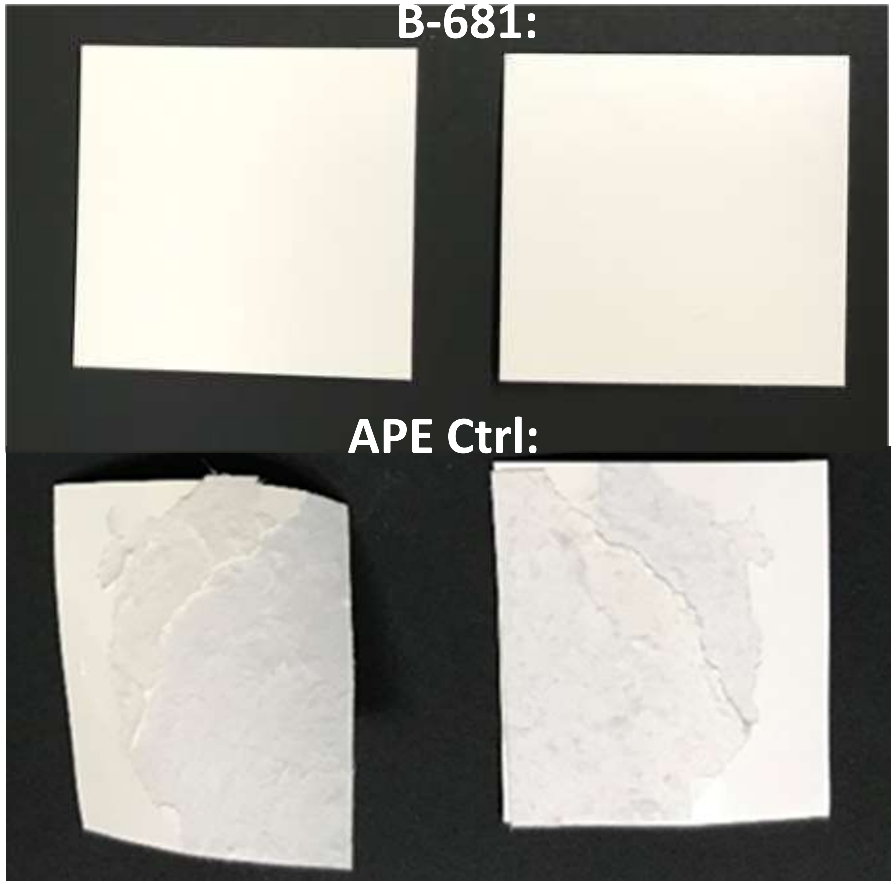
Critical Micelle Concentration



Optimum dose coincides with CMC

Performance Comparison at Equal Dose





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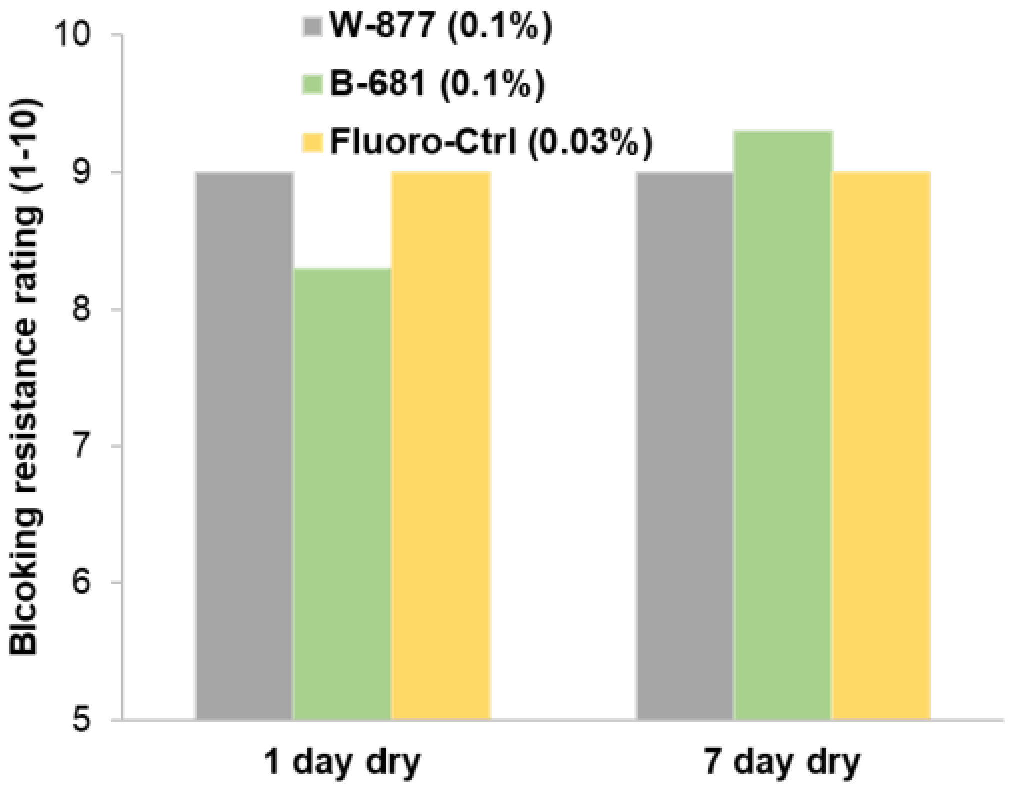
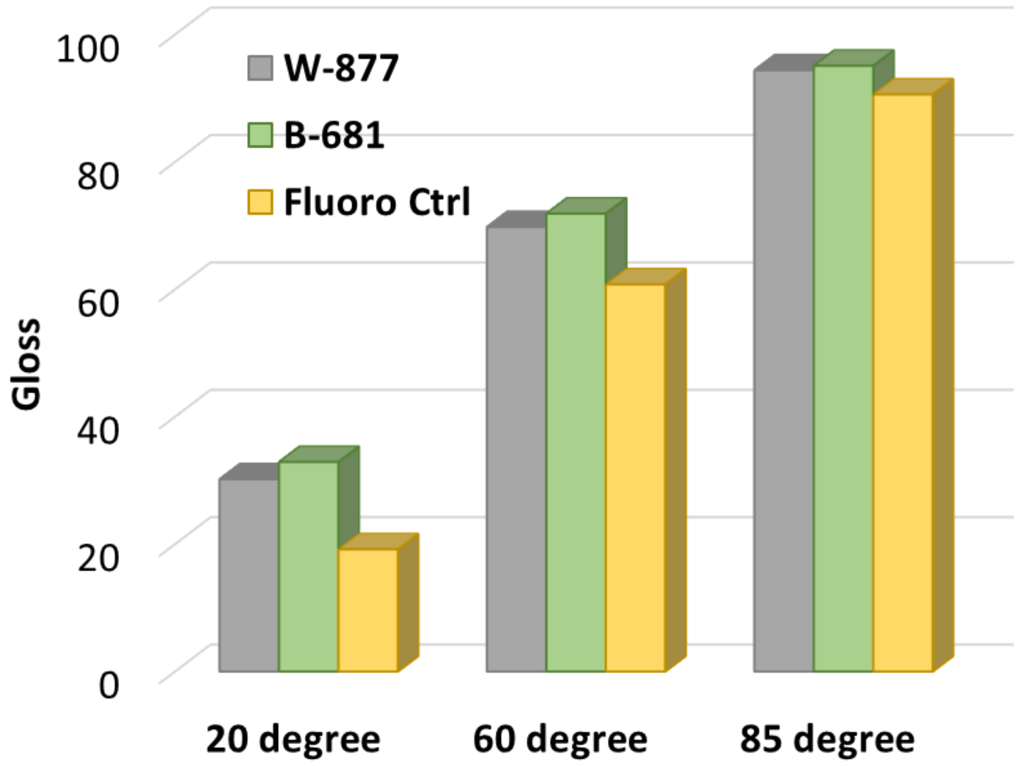
Performance Comparison at Optimum Dose

Equal/Better Blocking Resistance

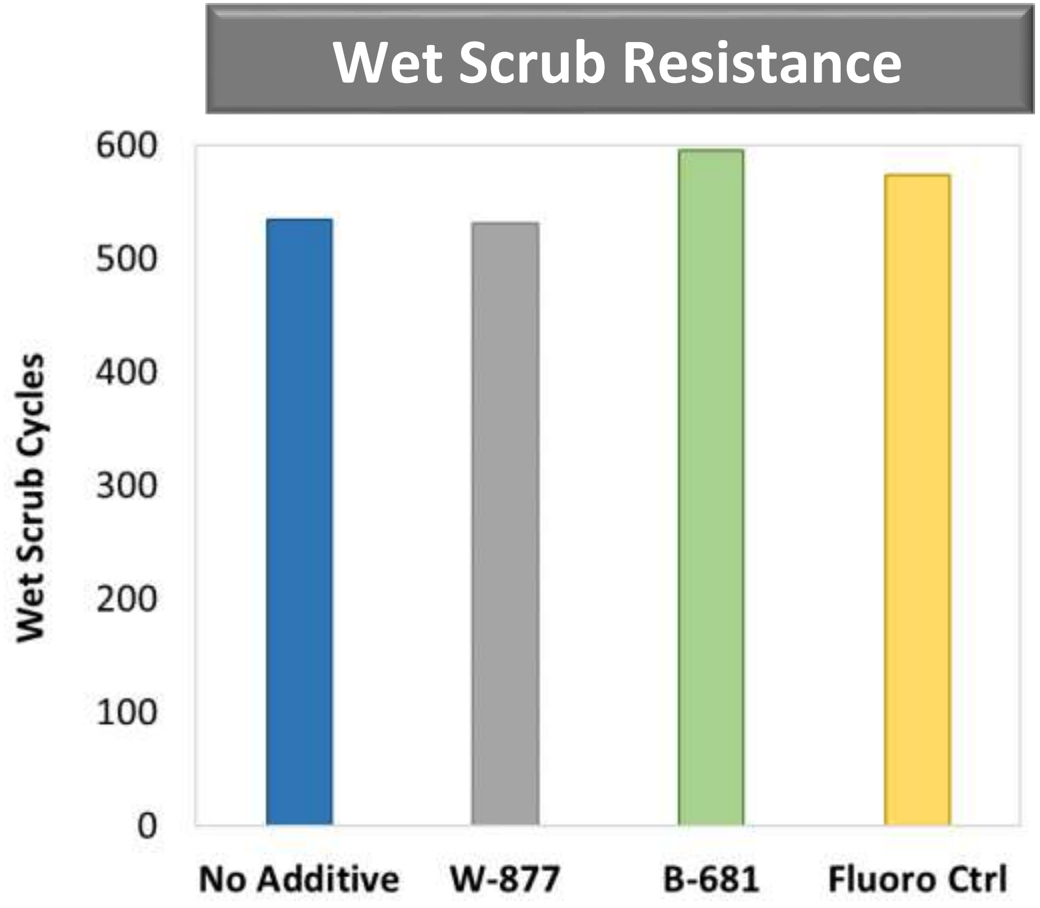


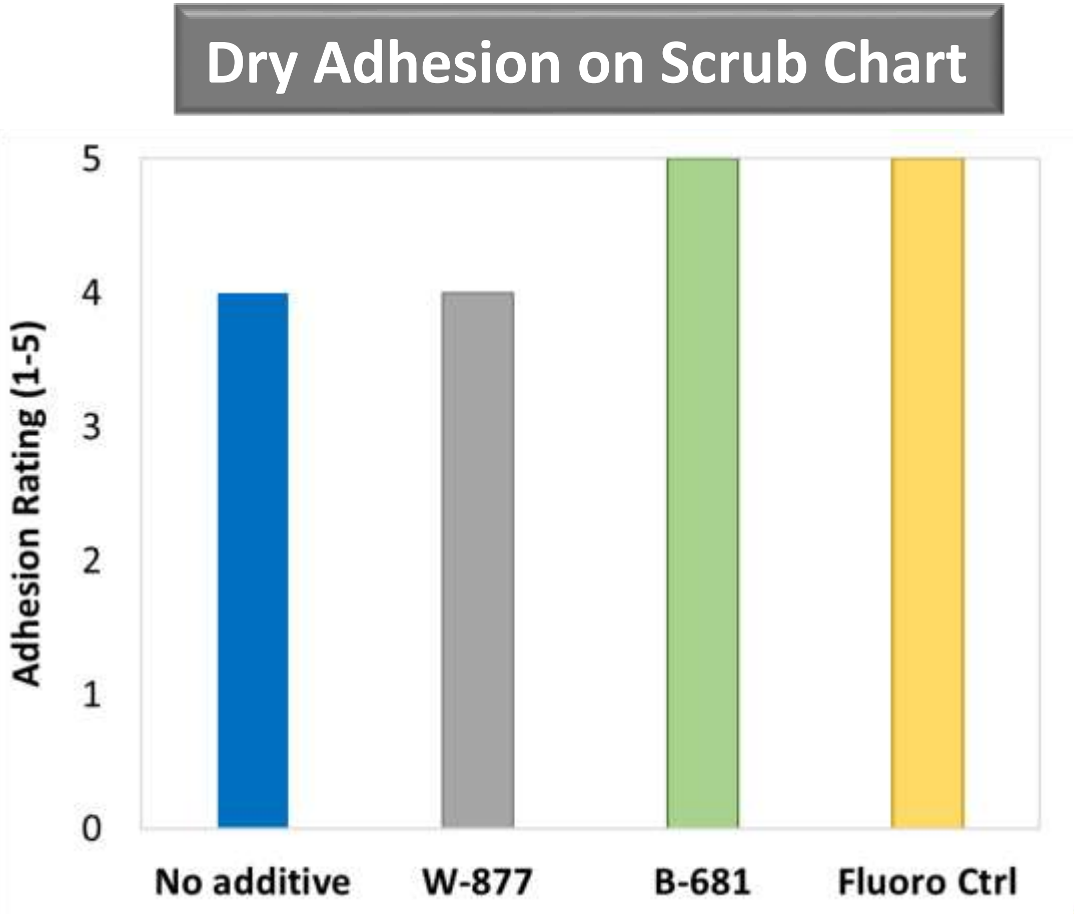
Improved Gloss



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

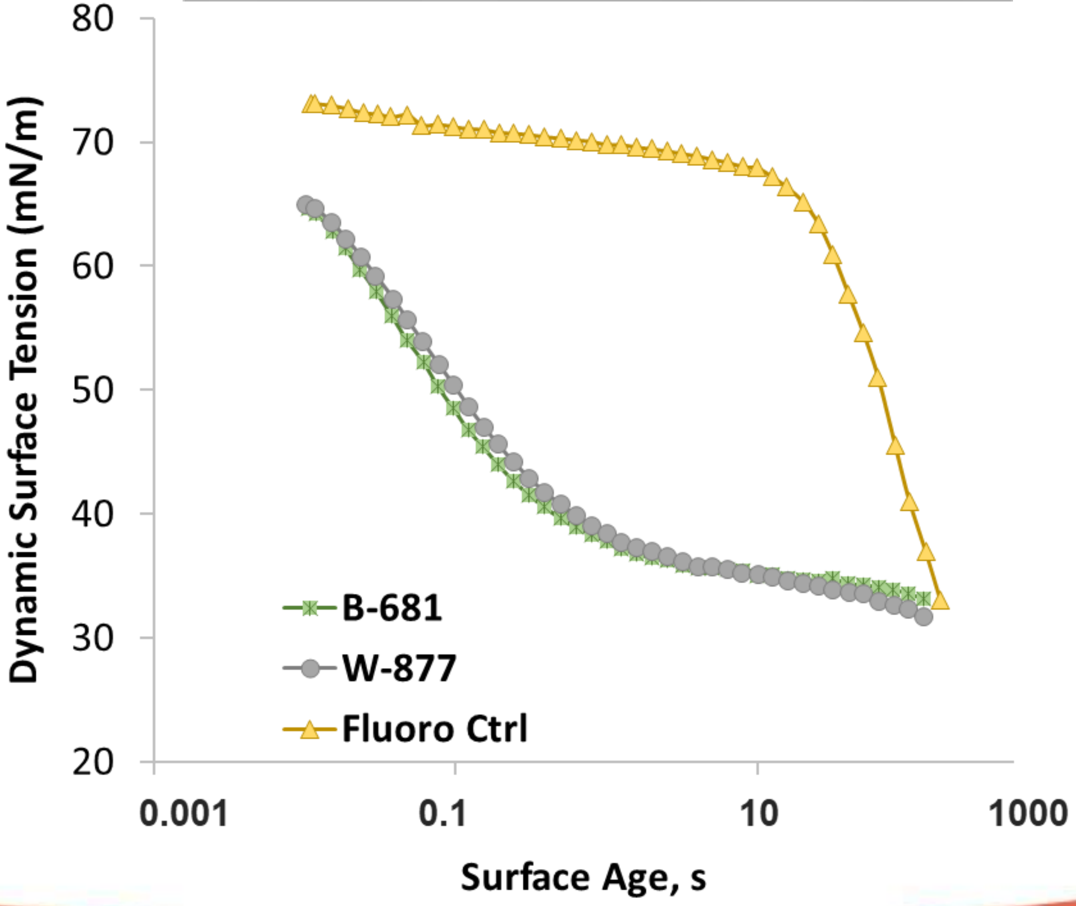
Multifunctional Benefits





Phosphate Esters vs. Fluorosurfactant Control

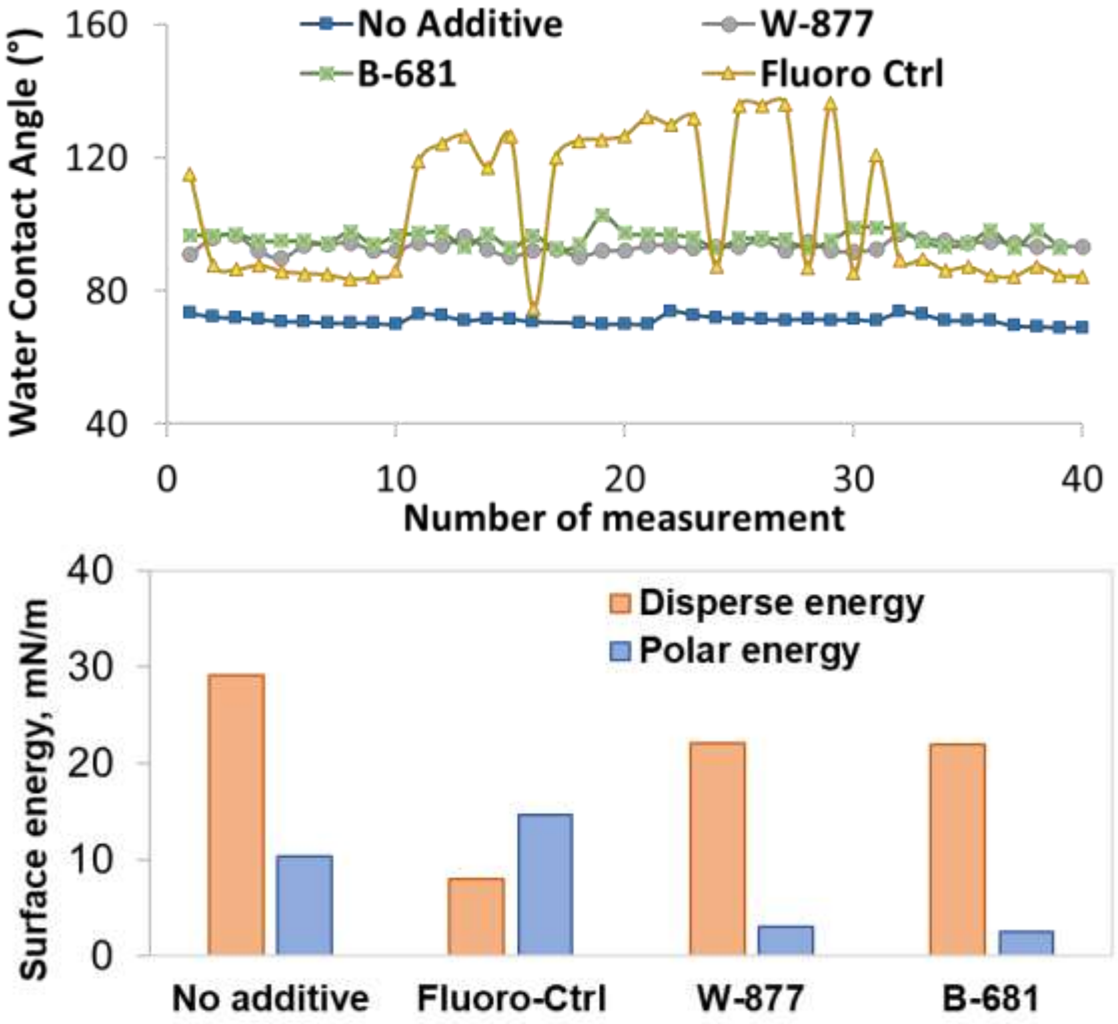
Dynamic Behavior

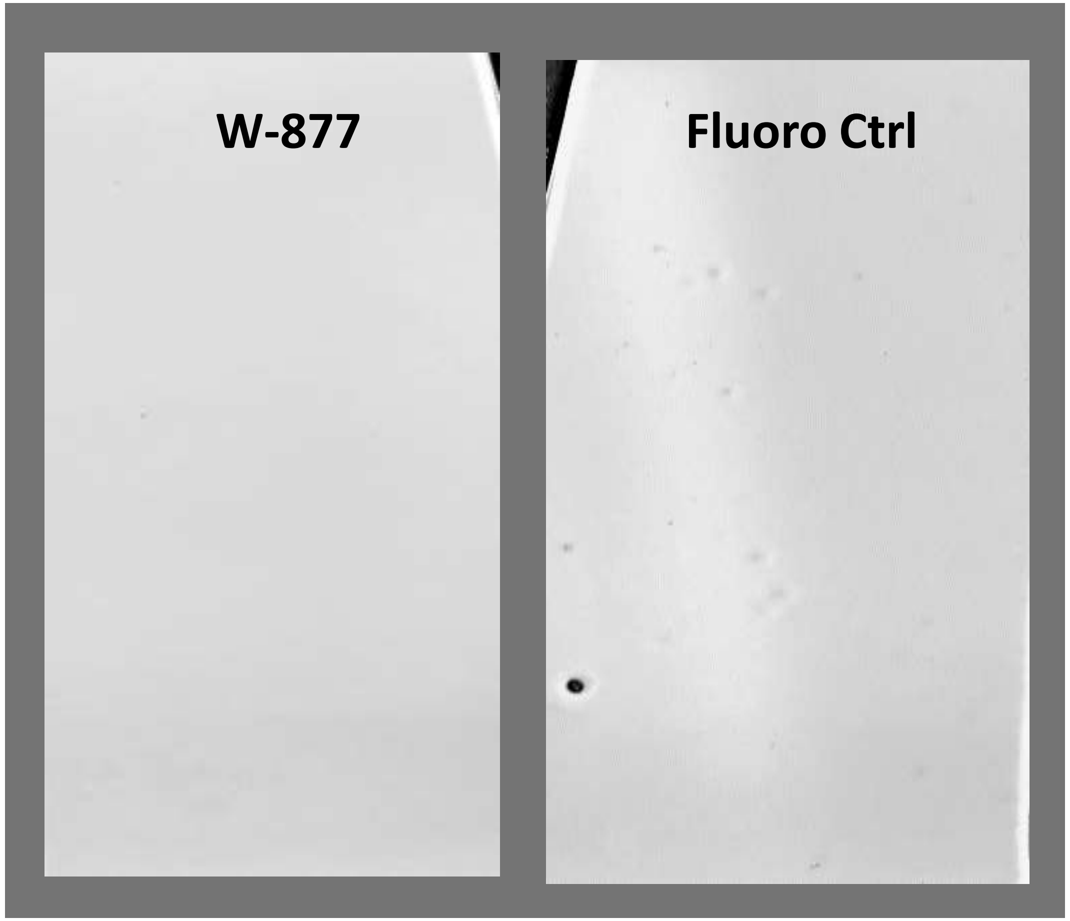


Basic Surfactant Properties

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





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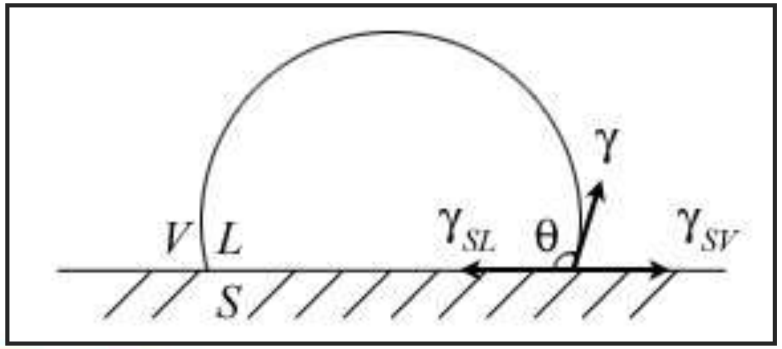
Phosphate Esters Reduce Water Sensitivity

Contact Angle (Water Repellency)

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



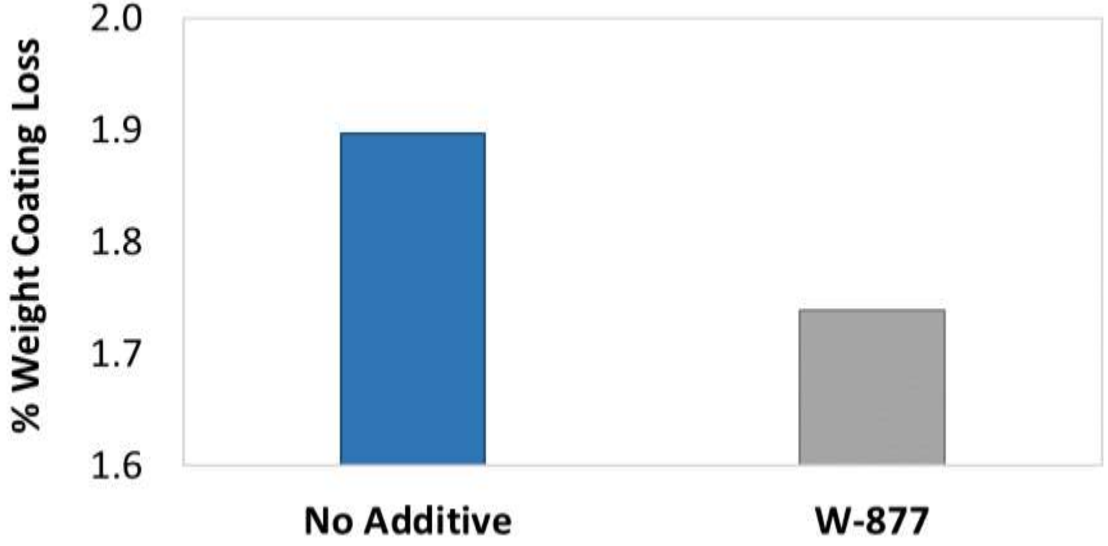
Wetting:

0° < θ <90°

Non-Wetting:

90° < θ <180°

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