



Bridging the Development Gap with Low VOC DTM

Emulsions



Presented by: Dr. Allen Bulick

Agenda

- EPS Overview
- Innovation Drivers in Coatings
- National Volatile Organic Content (VOC) Restrictions
- Challenges of Lowering VOC
- Hardness/Block/Corrosion Performance Survey
- Adhesion/Corrosion Mechanisms & Tradeoffs
- Other Properties
- Summary



Engineered Polymer Solutions (EPS)

A leading supplier of compliant acrylic emulsion technologies as well as conventional resins to supply the Architectural, Industrial, Construction, Adhesives and Sealants markets.

Products

Water Based/Acrylic Emulsions Solvent Based

Polyester

Alkyd

Polyurethanes

Other resins

Low VOC coalescent

Colorants

Capabilities

Fully equipped labs in USA and Netherlands

Synthesis

Formulation

Application Support



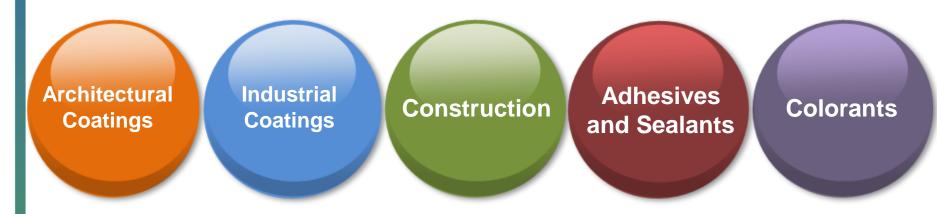


Global Operational Excellence





Technology Offering









Innovation Drivers

- All about EHS many examples driving technology changes some by regulation, some by market demand
 - VOC reduction
 - Reduction/elimination of coalescing solvents
 - Low maximum incremental reactivity (MIR)
 - Low hazardous air pollutants (HAPs)
 - APEO-free
 - Chromate-free
 - Isocyanate-free
 - BPA-free
 - Other green and sustainability initiatives (eg LEED)



NA VOC Restrictions

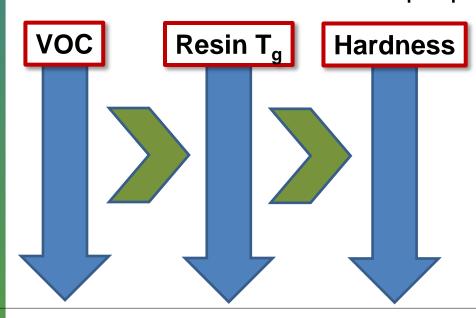
Regulatory Body	Industrial Maintenance VOC Limit (g/L)	Rust Preventive Limit (g/L)
EPA	450	400
CARB	250	150
South Coast (SCAQMD)	100	100
OTC	250	250
Canada	340	400
LADCO	340	400

Elimination of quart exemption may result in the reduction of VOCs of legacy products and SKU reduction for national suppliers.



Balance of Properties

- Direct to metal (DTM) coatings must balance a larger number of performance properties
 - Corrosion resistance, adhesion, block resistance, gloss, hardness, chemical resistance, early water resistance, weatherability, etc
- Lower VOC demands result in higher technical complexity in an effort to maintain these properties

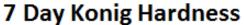


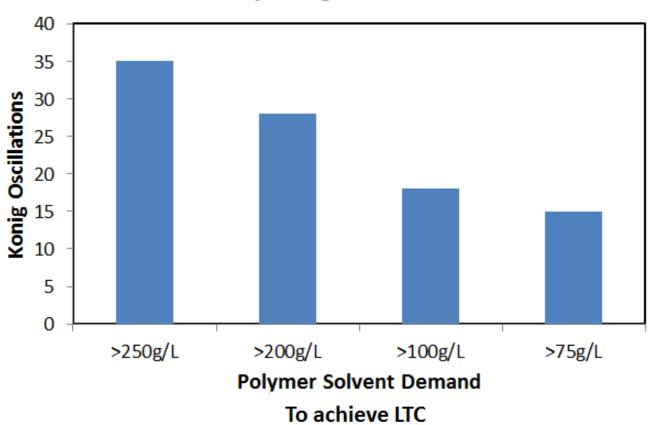
Performance Tradeoffs

- Lower T_g (or low VOC plasticizer) to lower VOC reduces hardness and block resistance
- Some formulation mitigations available, but not ideal
 - Fluorosurfactants



VOC Performance Tradeoffs

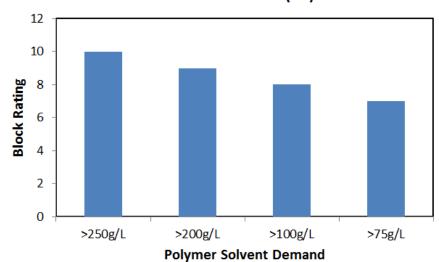




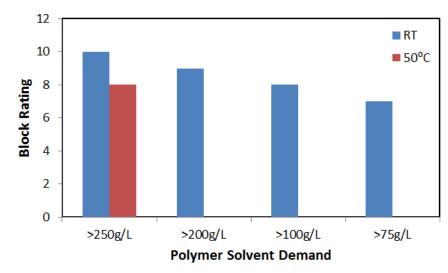


VOC Performance Tradeoffs

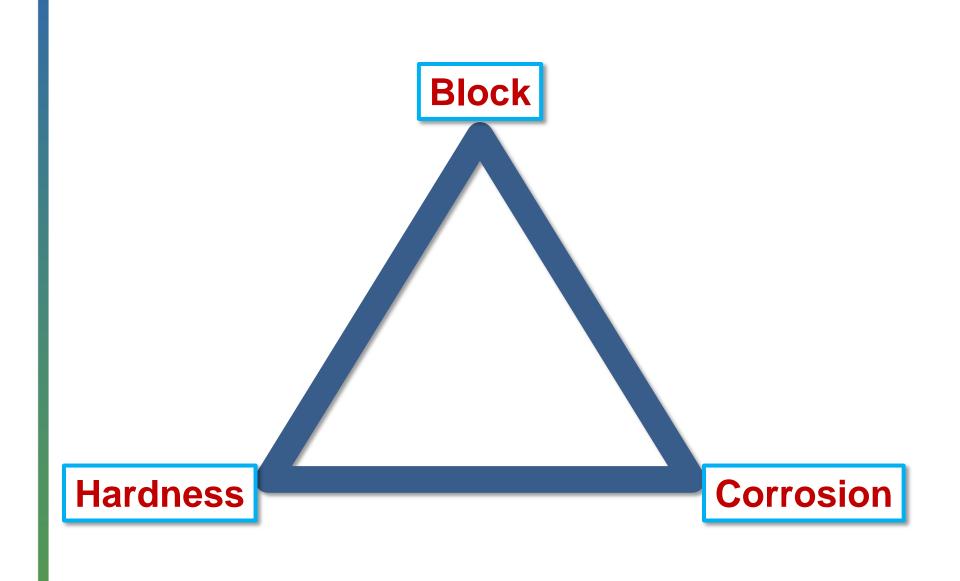




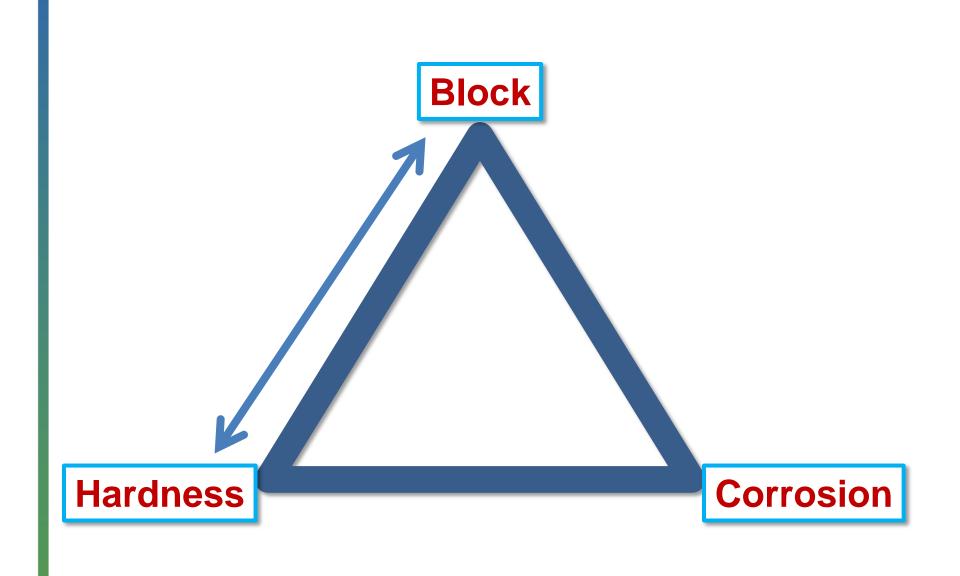
24hr Block Resistance



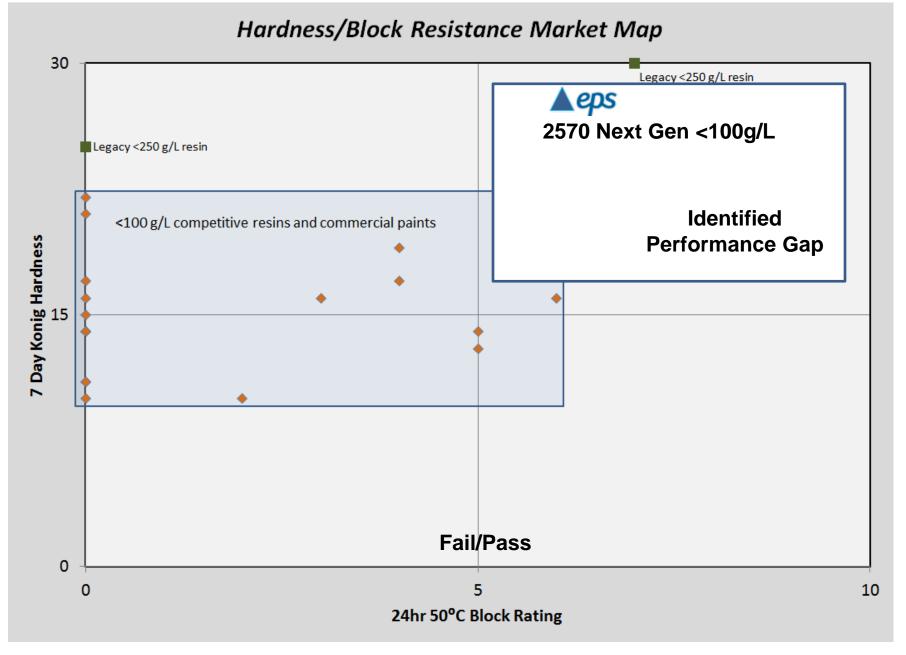




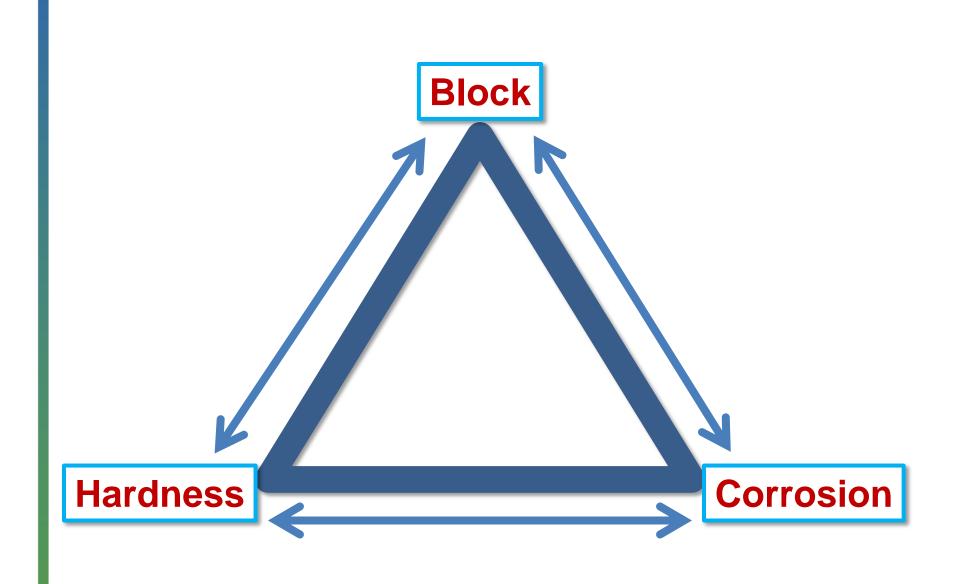






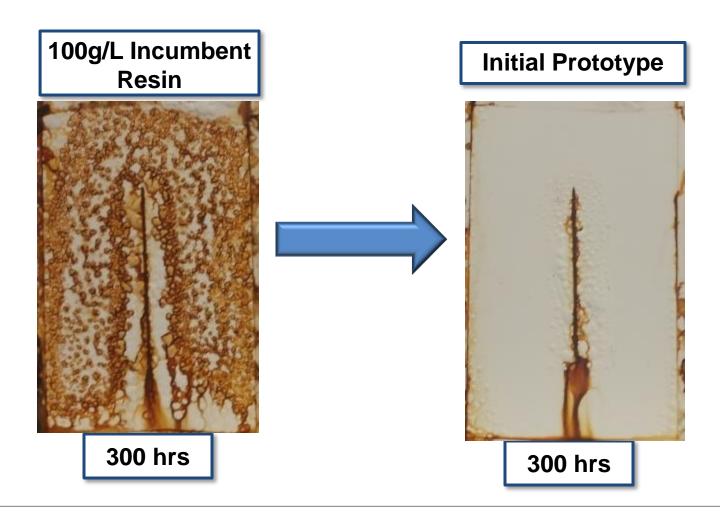


• Market survey (17 resin and paint systems) showed difficulty in achieving >20 Konig and hot block resistance, even in high VOC resins



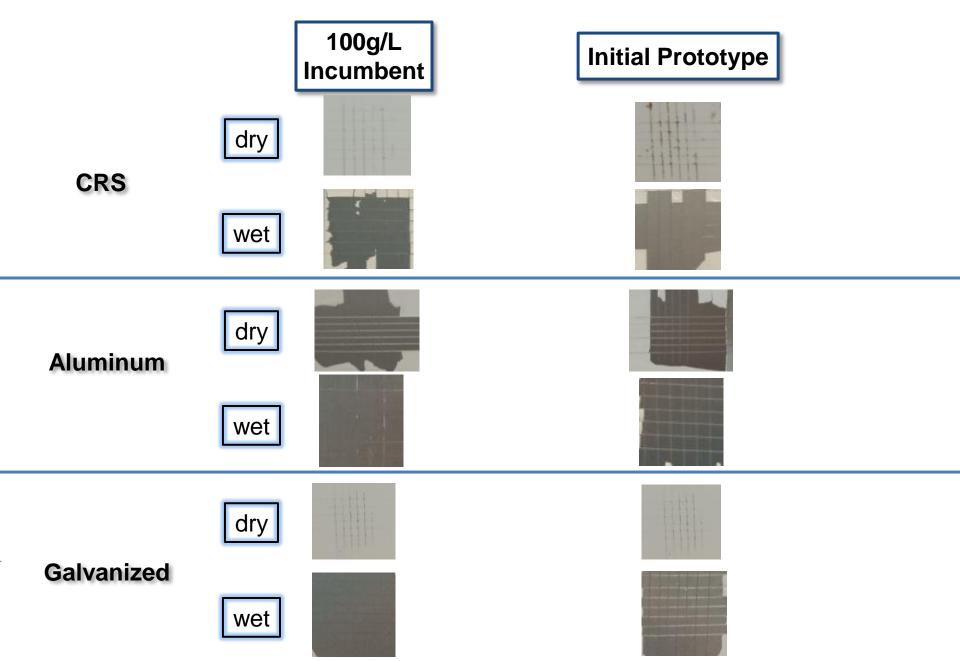


B117 Salt Fog, 2-2.3mil DFT, Flat CRS





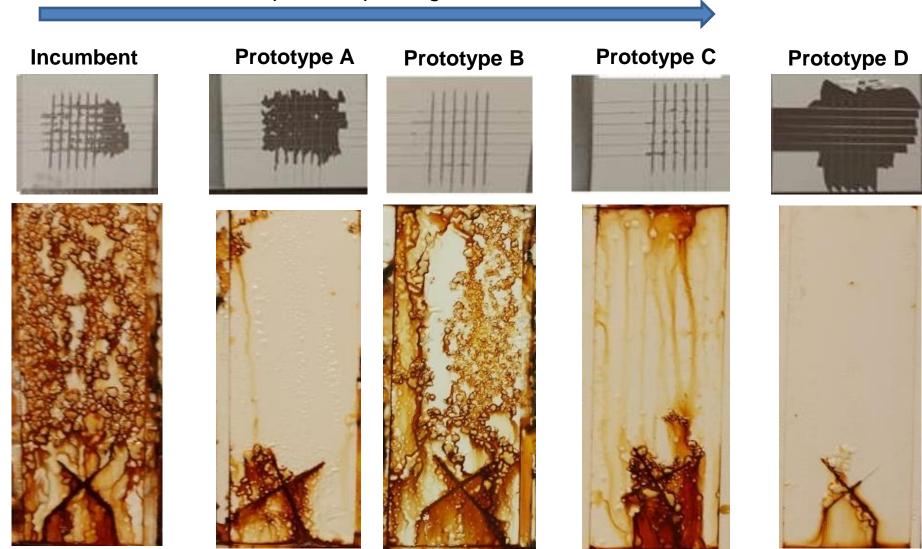
Adhesion Properties



Adhesion vs. Corrosion Resistance

2-2.5mil DFT, 12PVC High Gloss, 400hr B117

Attempts at improving Al adhesion

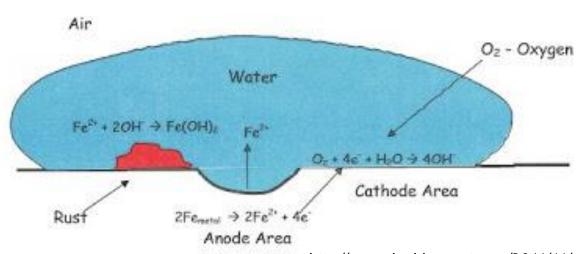


Accelerated Testing Methods

- ASTM B117 Salt Fog
 - 5% NaCl, constant fog
 - Rapid screening tool
 - Excessively harsh vs. exterior exposure
- Cyclic Prohesion
 - Cycles humid/dry cycles in salt fog cabinet with QUV (condensation/UV exposure)
 - Introduces more representative conditions
 - Tests more failure modes
 - Long cycle times vs. B117



Corrosion on Steel Substrates



Requires

- Water
- O₂ (CO₂, or other reducible species)
- Electrolytic pathway

http://acnosite.blogspot.com/2011/11/water-corrosion.html

Possible mechanisms of corrosion prevention

- Block water penetration
- O₂ transport inhibition



Barrier Properties

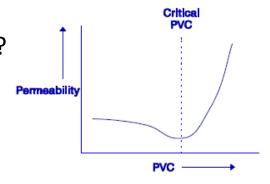
- Adhesion surface passivation, exclusion of water, etc.
- Interference with electrolytic pathway coating resistance

Barrier Properties

Coating Type	Water Vapor Permeability ^{1,2} (g/m²/25μm/day)	O ₂ Permeability ^{1,2} (cm³/m²/25μm/day)
Chlorinated rubber	30	50
Coal tar epoxy	75	213
Al epoxy mastic	105	110
Read-lead oil	535	734
Pigmented Alkyd	645	595
Acrylic primer	1800	500

¹Thomas, NL, *Prog Org Ctgs*, 19, 101, 1991

• What about pigment considerations – ie tortuosity?



²Thomas, NL Proc Symp Advances in Corr Prot by Org Ctgs, Echem Soc, 1989, 451

Adhesion in B117 Cabinet



Styrenated Acrylic Emulsion

Clear Formulation

Easy film delamination out of salt fog cabinet

2k Epoxy Primer Solventborne Epoxy Ester Salt Fog Wet Adhesion (300hrs) Salt Fog Wet Adhesion (300hrs)



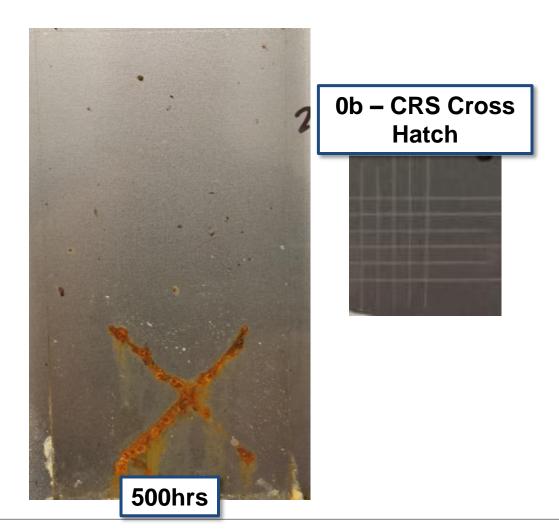


Solventborne Sytems

Cross hatch failure

Corrosion without Adhesion

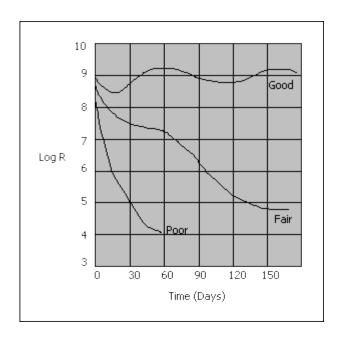
B117, Clear formulation, ~1mil DFT





Electrolytic Resistance

Likely most important film property in corrosion resistance



Ind Eng Chem, 40(1), 1948, 161-167

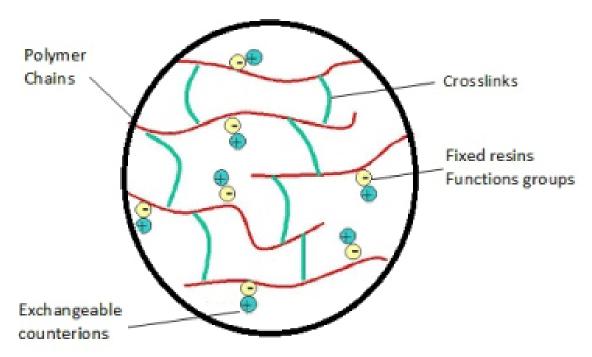
- Study of 300 coatings showed resistance thresholds of ~108Ohm for the best coatings and at least ~106 Ohm for fair performance1
- Coating resistance falls with increasing electrolyte concentration

Maitland CC, Mayne JEO, Official Digest, Sept 1962

 Inverse study between ion exchange capacity and corrosion resistance of film

Ulfvarson, U and Khullar, M, JOCCA, 54, 604, 1971

Styrenated Acrylic Emulsions as Ion Exchange Systems



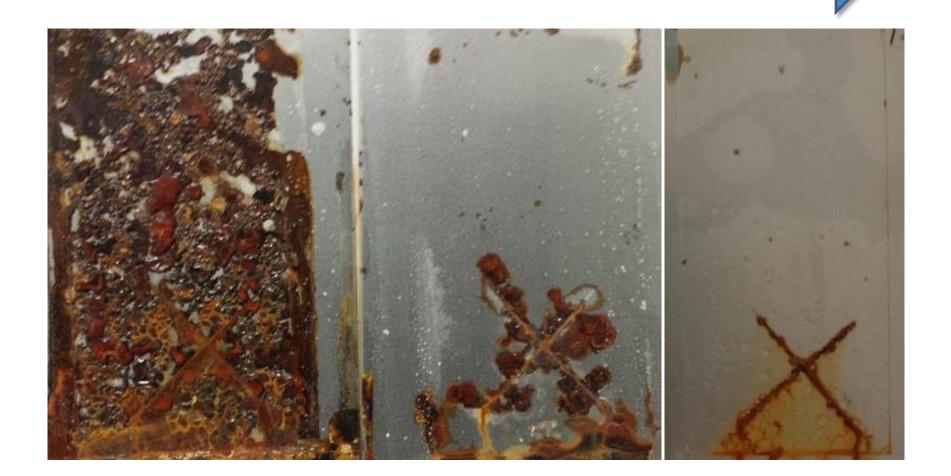
http://esciencecentral.org/ebooks/advances-in-protein-chemistry/new-protein-approaches.php



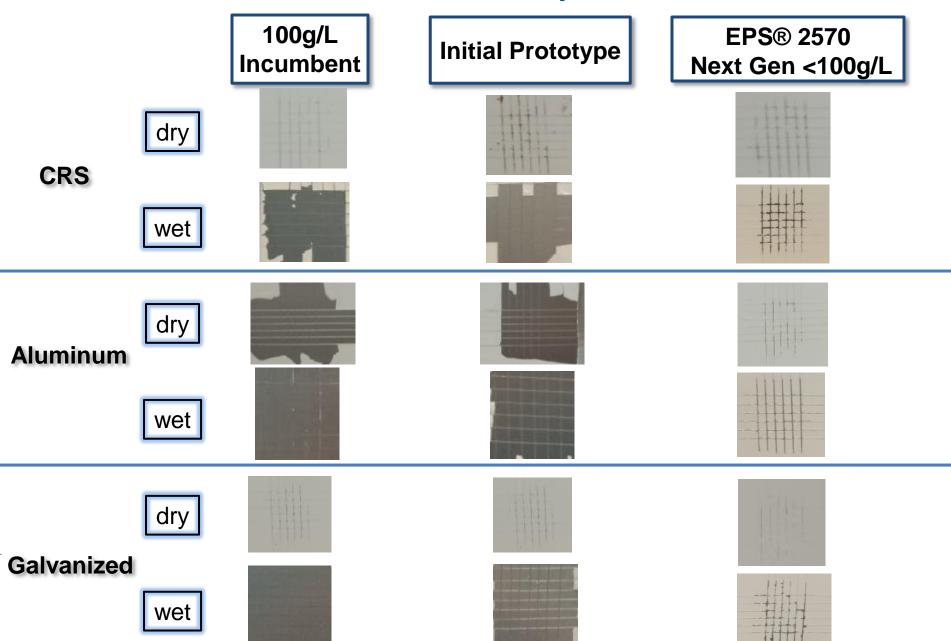
Corrosion vs. Acid Content

Clear films, 1.2mil DFT, 300hrs B117

Decreasing Acid Content



Adhesion Properties



Panel Label:

Resin System 7day Konig/24hr 50°C Block







Panel Label:

Resin System 7day Konig/24hr 50°C Block







Panel Label:

Resin System 7day Konig/24hr 50°C Block







Panel Label:

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Commercial Paints – Corrosion Resistance









Commercial Paints – Corrosion Resistance

2-2.5mil DFT, CRS



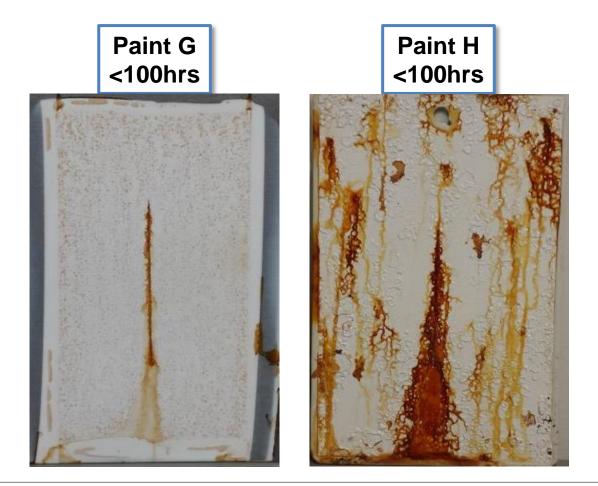






Commercial Paints – Corrosion Resistance

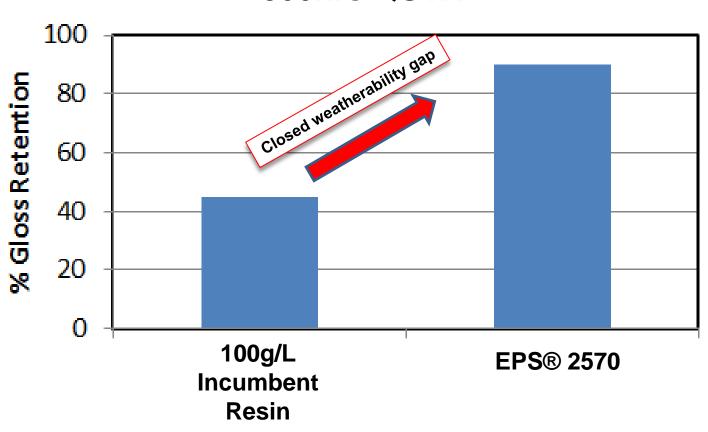
2-2.5mil DFT, CRS





Weatherability

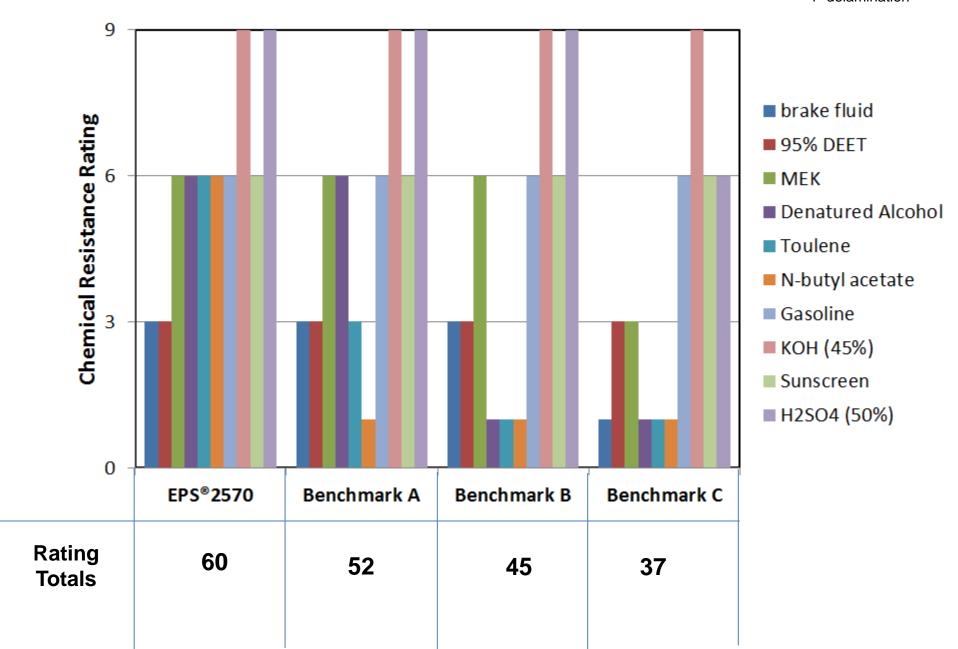
800hrs QUVA



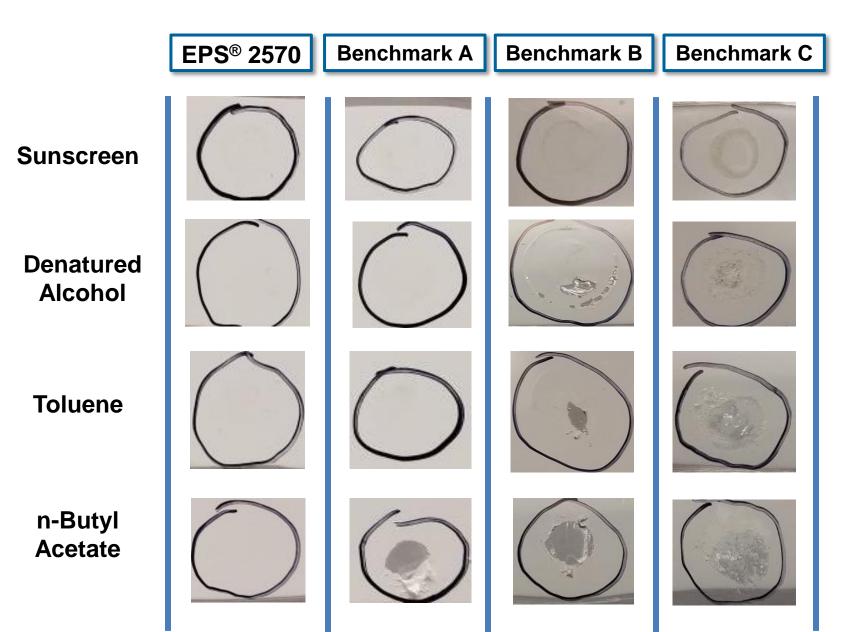


Chemical Resistance

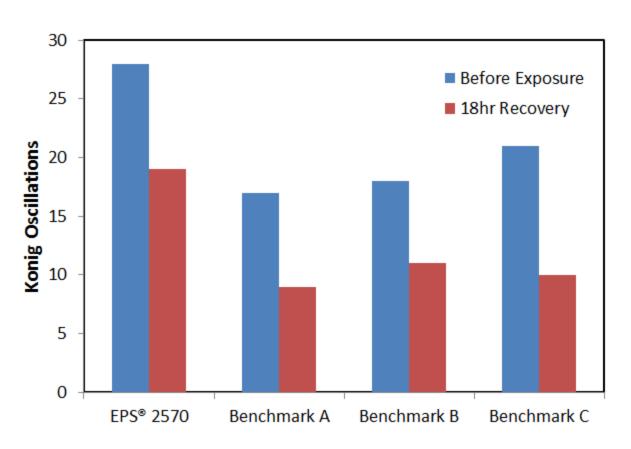
9=no change to gloss 6=reduction in gloss 3=film softening 1=delamination



Chemical Resistance Pictures



Lotion Exposure



- Films exposed 4hrs
- All polymers softened by lotion
- EPS® 2570 maintains hardness advantage on recovery



Summary

- Market survey of incumbent <100g/L technologies showed a significant performance gap in a balance of hardness/block/corrosion resistance
- Low VOC trends place significant difficulties on resin selection and design
- EPS sought to develop the best overall balanced polymer in the <100g/L DTM category
- A next generation development based on current state of the art polymer understanding fills that performance gap
- Balancing adhesion and corrosion requires special consideration in waterborne styrenated acrylic systems
- Ongoing work to fully understand formulation space/performance of the new polymer



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- Chris LeFever Associate Chemist
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Questions?



