Film Properties and Formulation Considerations for Corrosion Resistance in Styrenated Acrylic Metal Coatings

Eastern Coatings Show - 2017

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Agenda

- Project Background
- Adhesion & Corrosion Protection Mechanisms
- Literature Review
- Commercial Resin Film Property Study
- Next Generation Development
- Formulation Considerations
- Conclusions

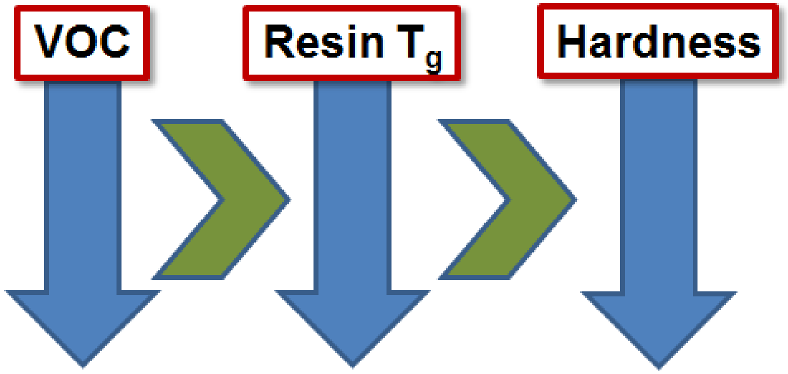
Project Background

Project Mandate

Deliver best in class balanced, low VOC DTM resins

Lower VOC demands result in higher technical complexity in an effort to maintain full balance of properties

Interplay between adhesion and corrosion prompted in depth structure/property investigation



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

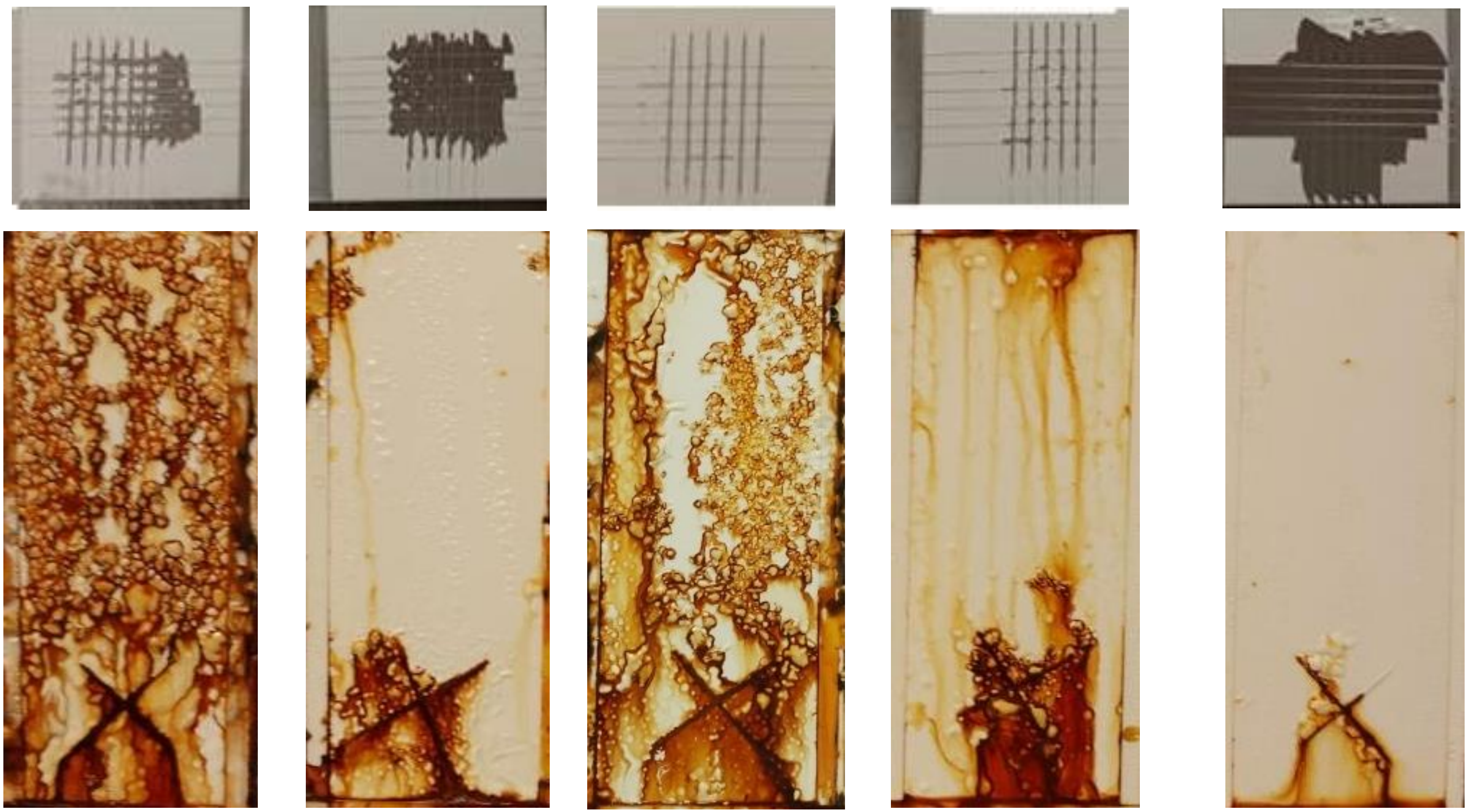
Adhesion vs. Corrosion Resistance

~50µm DFT, 12PVC High Gloss, 400hr B117

Attempts at improving Al adhesion

Reduction of adhesion monomers

Incumbent	Prototype A	Prototype B	Prototype C	Prototype D



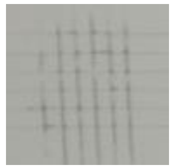
Adhesion/Corrosion Balance

B117, ~50µm DFT, CRS

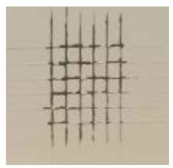
Prototype E

500 hrs

CRS Dry



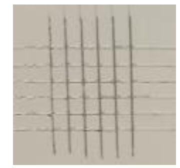
CRS Wet



Prototype F

500 hrs

CRS Dry

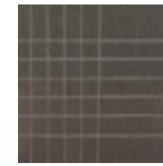


CRS Wet

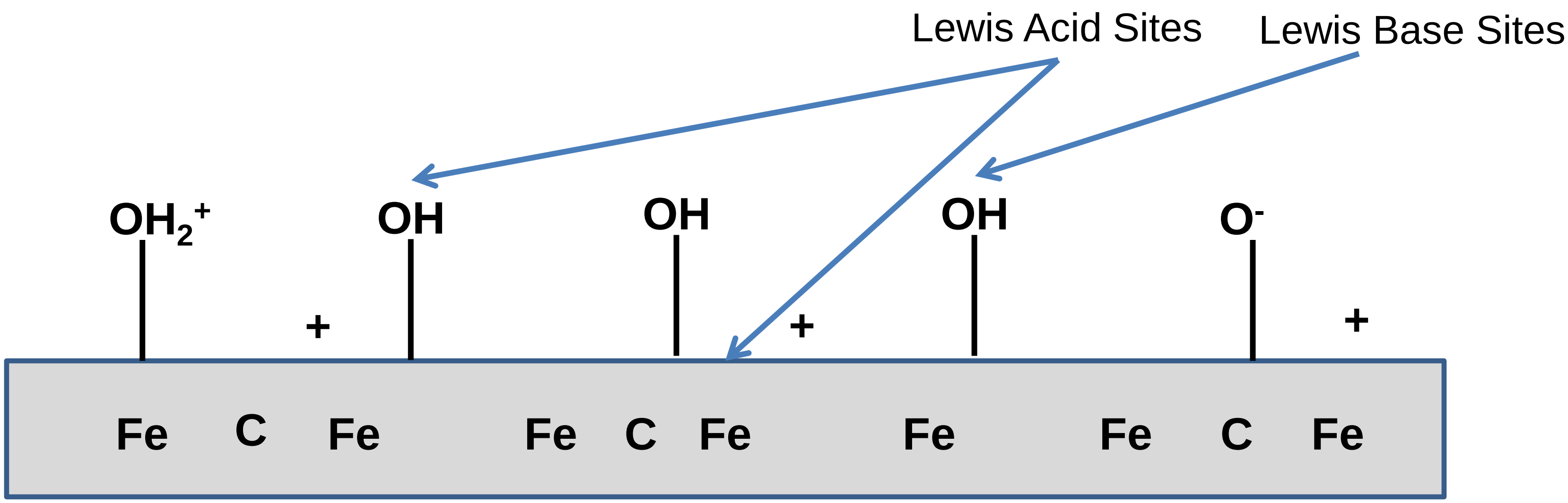
Prototype G

500 hrs

CRS Dry



Adhesion to Steel



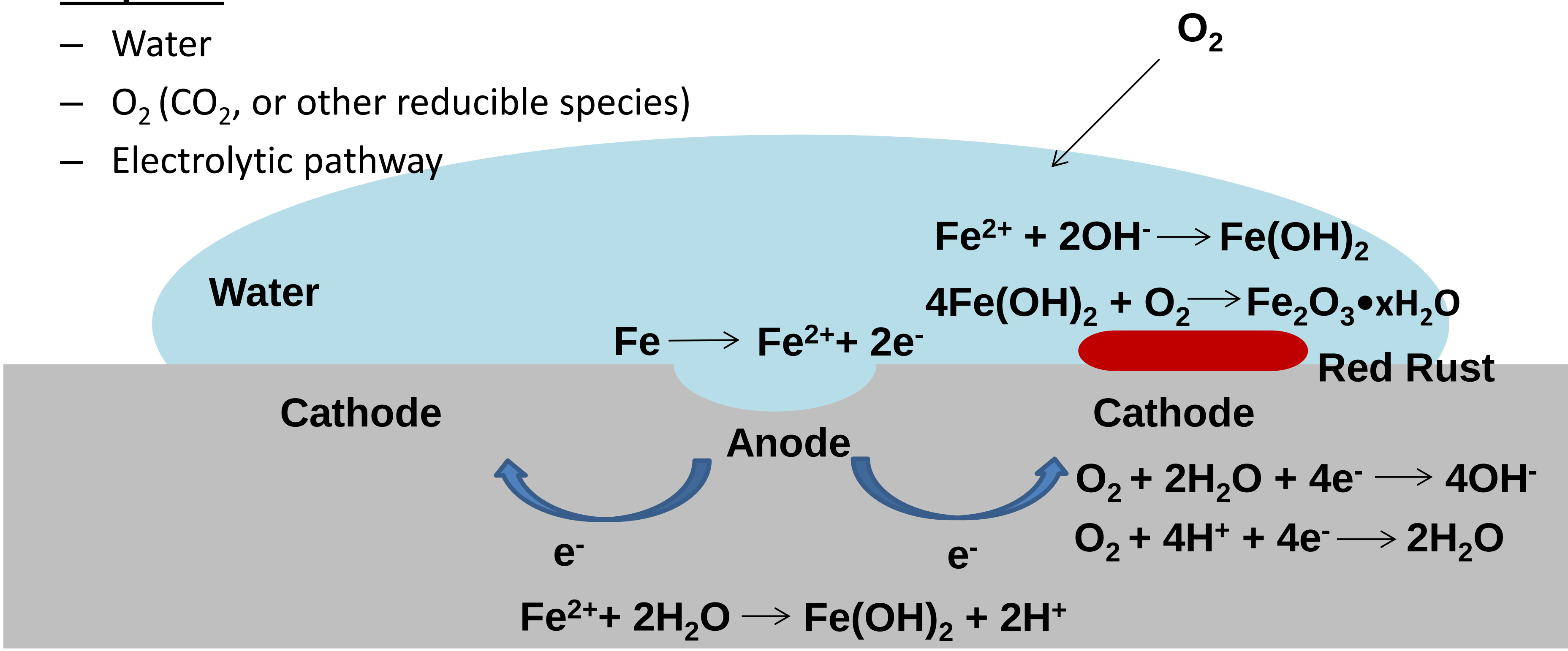
- Provided sufficient wetting is present, acid/base interactions, ionic interactions and van der Waals forces considered of primary importance[1]
- Isoelectric point of steel difficult to pinpoint, but likely around pH ~8-9
- As ammonia evaporates and pH drops, cationic sites arise allowing for electrostatic interactions
- Mechanical interlocking also significant in blasted substrates

[1]Fowkes, F.M., *J Polym Sci J Polym Chem Ed,* **1984**, 22, 547

Corrosion Process - Steel

Requires

– Water
– O_2 (CO_2, or other reducible species)
– Electrolytic pathway



Possible mechanisms of corrosion prevention

- Block water penetration
- O_2 transport inhibition

Barrier Properties

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

Literature Review

Barrier Properties

S. Guruviah, *JOCCA*, 53, 1970, 660; P. Kresse, *Pigment Resin Tech,* 2(11), 1973, 21

- O_2 transport limiting factor in corrosion protection

Impedance

J. Mayne, *Corrosion*, 1976, pp15:24-15:37; Bacon, et al, *Ind Eng Chem*, 40(1), 1948, 161

- Films generally too permeable for barrier properties to be important
- Inhibition of galvanic cell via a high film resistance which impedes electrolyte transport most important factor

Adhesion

W. Funke, H. Haagen, *Ind Eng Chem Prod Res Dev*, 17, 1978, 50; E. Parker, H. Gerhart, *Ind Eng Chem*, 59(8), 1967, 53

- Loss of adhesion leads to onset of corrosion

See appendix for further reading suggestions

Electrolytic Resistance

- Study of 300 coatings showed resistance thresholds of ~10^8Ohm for the best coatings and at least ~10^6 Ohm for fair performance

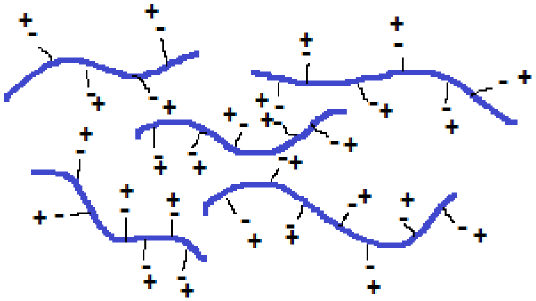
  Ind Eng Chem, 40(1), 1948, 161-167

- 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



Acrylic film as ion exchange system

Study Description

- 21 internal and external styrenated acrylic systems
- Wide variety of performance capabilities, Tg's, MFFTs, etc
- Formulated into single clear formulation – adjusted coalescent level for MFFT
- Evaluated in a number of performance tests to develop a film property/corrosion model

Study Design

Test*

B117 Corrosion**
Cyclic Prohesion
QUV
Humidity Resistance

Performance Properties

Dry Adhesion
Wet Adhesion
Electrochemical Impedance
Film Hardness
Water Vapor Transmission
Oxygen Transmission
Liquid Water Uptake

Film Properties

*Tests in bold will be discussed here, other pieces will be tied into future presentations
** Panels were force ranked on a 1-10 scale for corrosion resistance, 10 being best

Corrosion Resistance

B117, CRS (4"6" R-series Q-panel), ~75µm DFT, 66hrs

Corrosion Resistance

B117, CRS (4”6” R-series Q-panel), ~75µm DFT, 230hrs

Resin 1

Resin 2

Resin 3

Resin 4

Resin 5

Resin 6

Resin 7

Resin 8

Resin 9

Resin 10

Resin 11

Resin 12

Resin 13

Resin 14

Resin 15

Resin 16

Resin 17

Resin 18

Resin 19

Resin 20

Resin 21

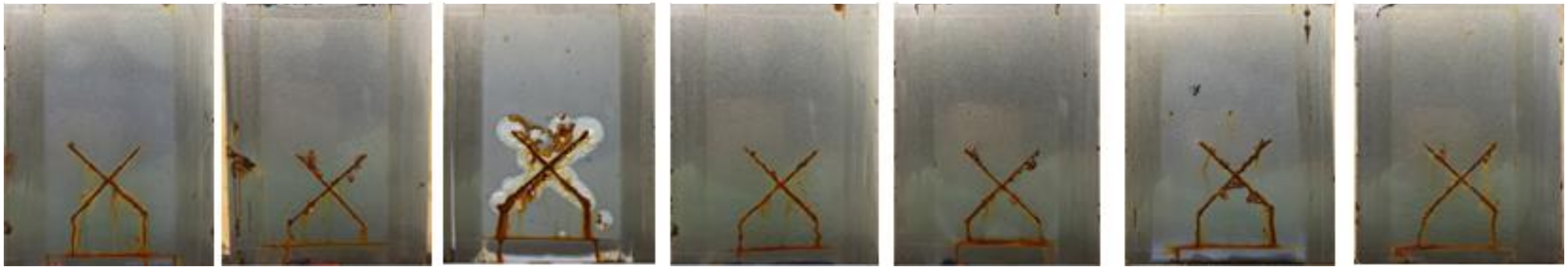
Corrosion Resistance

B117, CRS (4”6” R-series Q-panel), ~75µm DFT, 560hrs

8	1	3	8	7	6	1
Resin 1	**Resin 2**	**Resin 3**	**Resin 4**	**Resin 5**	**Resin 6**	**Resin 7**

6	2	4	2	6	5	3
Resin 8	**Resin 9**	**Resin 10**	**Resin 11**	**Resin 12**	**Resin 13**	**Resin 14**

10	7	5	9	8	7	8
Resin 15	**Resin 16**	**Resin 17**	**Resin 18**	**Resin 19**	**Resin 20**	**Resin 21**



Dry Adhesion

10mil wet drawdown, CRS (4”6” R-series Q-panel)

Resin	Pull-off Adhesion		Corrosion rating
	Standard	Dolly	
Resin 1	5	**272.0**	8
Resin 2	0	**68.0**	1
Resin 3	5	**241.3**	3
Resin 4	5	**231.3**	8
Resin 5	5	**271.0**	7
Resin 6	0	**91.5**	6
Resin 7	5	**188.0**	1
Resin 8	3	**168.0**	6
Resin 9	5	**290.5**	2
Resin 10	4	**224.0**	4
Resin 11	4	**212.3**	2
Resin 12	4	**179.7**	6
Resin 13	0	**106.5**	5
Resin 14	1	**116.0**	3
Resin 15	4	**200.0**	10
Resin 16	4	**211.0**	7
Resin 17	4	**205.0**	5
Resin 18	4	**177.0**	9
Resin 19	4	**172.0**	8
Resin 20	4	**208.3**	7
Resin 21	4	**213.3**	8

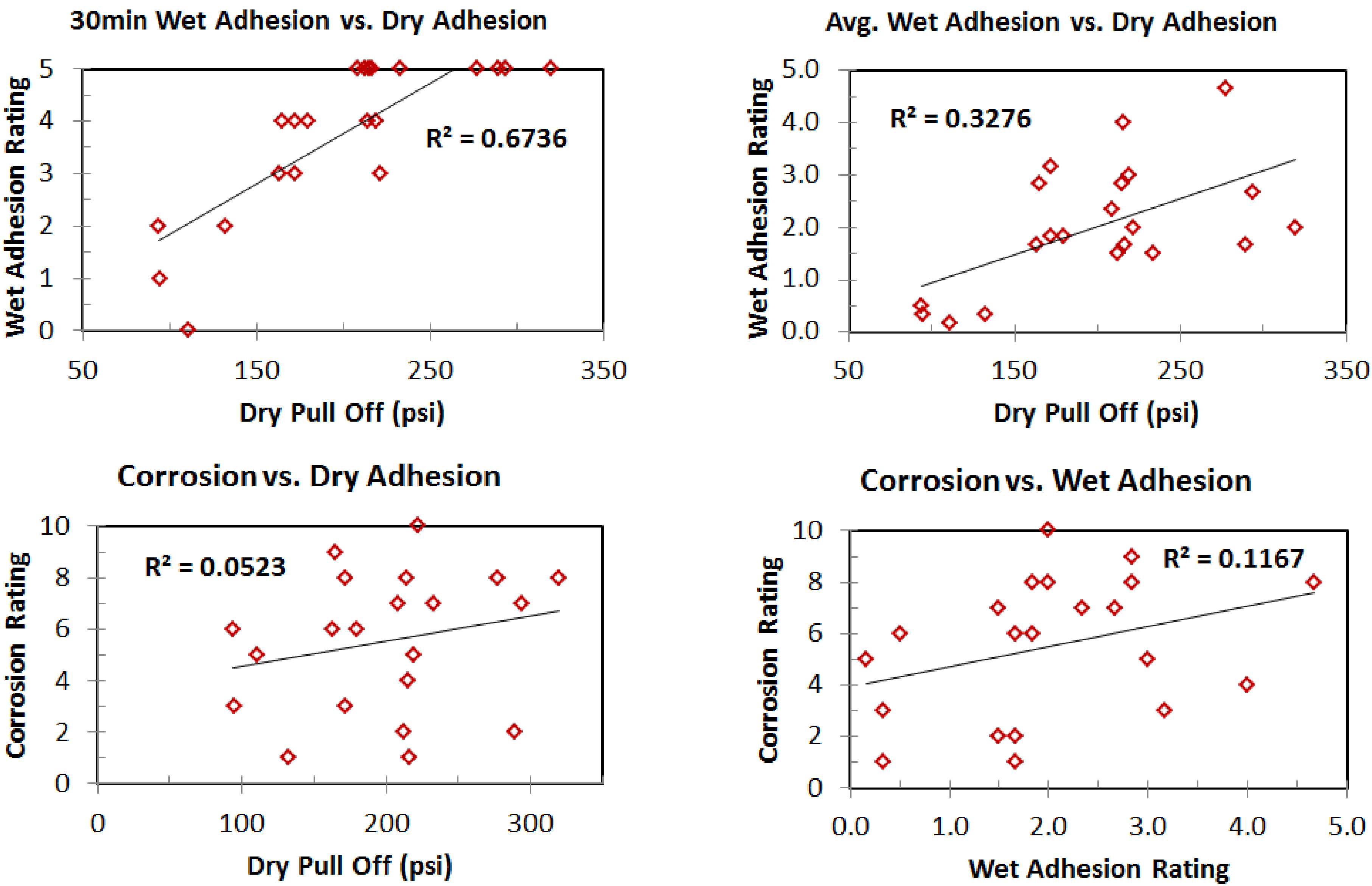
Wet Adhesion

10mil wet drawdown, CRS (3”6” R-series Q-panel)

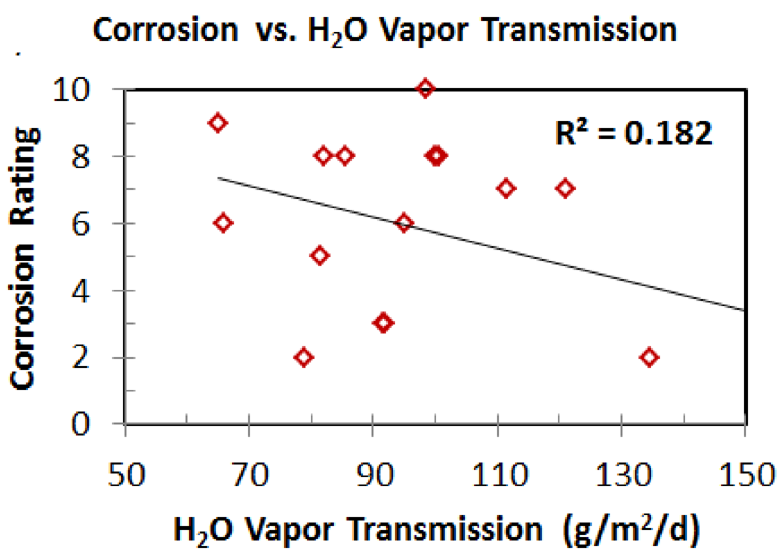
Resins	30 min*	1 hr**	24 hr**	48 hr**	4 day**	1 wk**	2 wk**	Average***
Resin 1	5	5	5	5	5	3	0	4.7
Resin 2	2	0	0	0	0	0	0	0.3
Resin 3	3	4	4	3	3	2	0	3.2
Resin 4	4	5	5	3	0	0	0	2.8
Resin 5	5	5	5	0	1	0	0	2.7
Resin 6	2	0	1	0	0	0	0	0.5
Resin 7	5	5	0	0	0	0	0	1.7
Resin 8	3	3	4	0	0	0	0	1.7
Resin 9	5	5	0	0	0	0	0	1.7
Resin 10	5	4	5	5	5	0	0	4.0
Resin 11	5	4	0	0	0	0	0	1.5
Resin 12	4	4	3	0	0	0	0	1.8
Resin 13	0	0	1	0	0	0	0	0.2
Resin 14	1	1	0	0	0	0	0	0.3
Resin 15	3	4	5	0	0	0	0	2.0
Resin 16	5	4	0	0	0	0	0	1.5
Resin 17	4	4	5	3	2	0	0	3.0
Resin 18	4	4	4	3	2	0	0	2.8
Resin 19	4	4	3	0	0	0	0	1.8
Resin 20	5	4	5	0	0	0	0	2.3
Resin 21	5	4	3	0	0	0	0	2.0

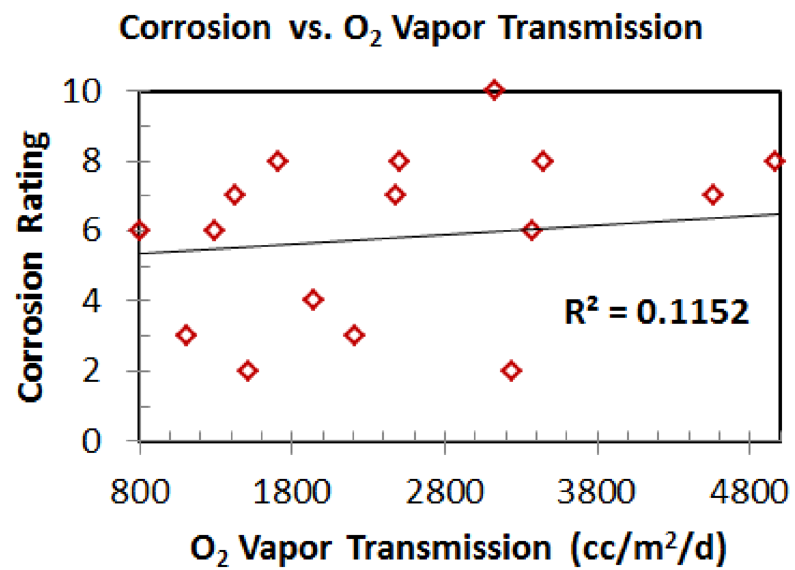
*****adhesion after covering with wet paper towel; ******adhesion after immersion in water;
***average through 1 week

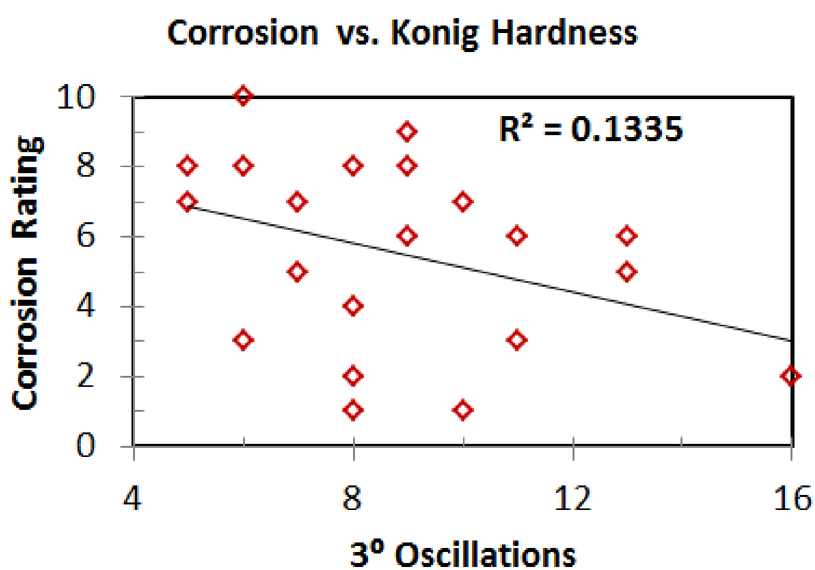
Adhesion/Corrosion Correlation



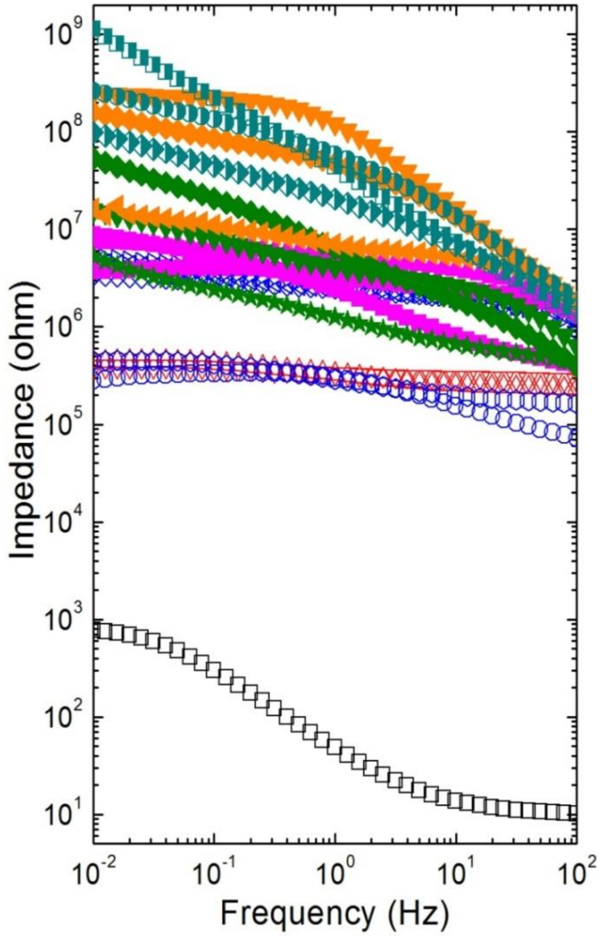
Corrosion Correlations

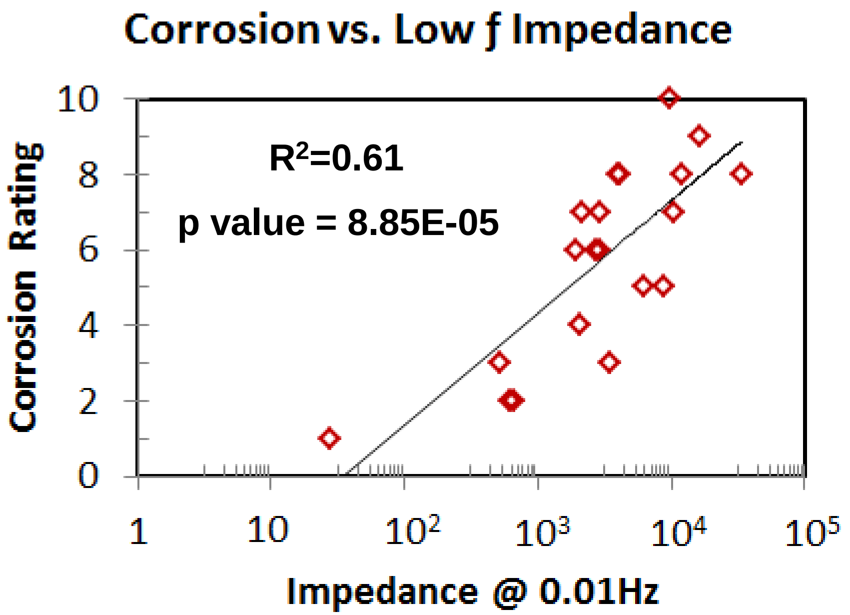






Impedance Studies





Next Generation Development

B117, ~50µm DFT, CRS

New Prototype

700hrs

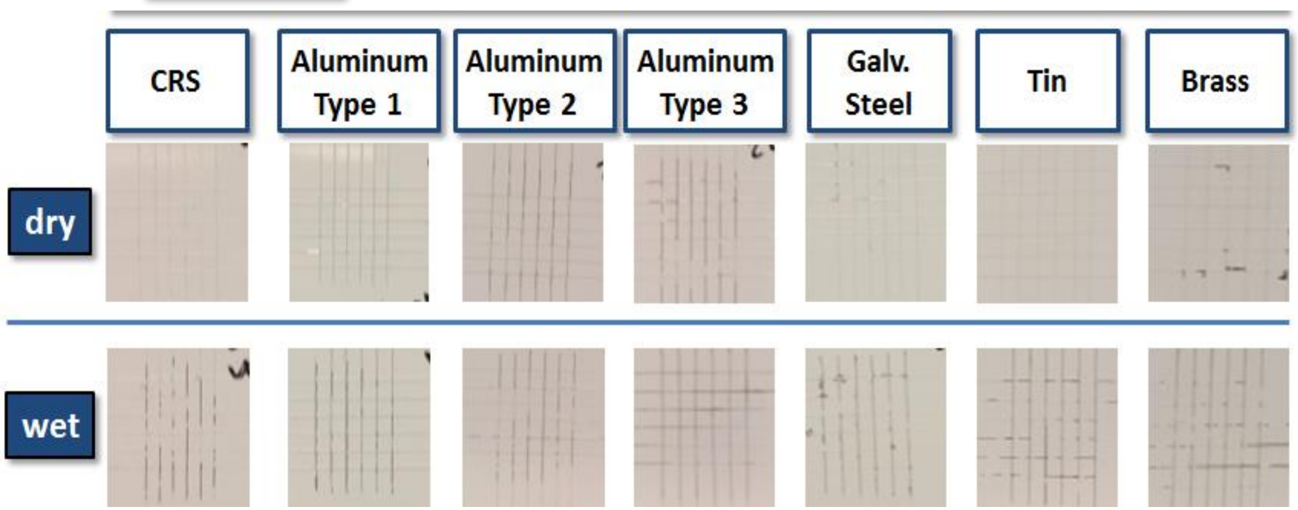
Market Leading 50g/L DTM

350hrs

< 50g/L DTM Prototype

- Self-crosslinking styrenated acrylic
- Market leading corrosion resistance
- Excellent humidity resistance
- Good block resistance

Broad spectrum adhesion properties



Thin Film Corrosion Resistance

B117, CRS, 300hrs

50g/L Prototype

1mil DFT

Prototype shows competitive corrosion resistance to solvent based alkyd

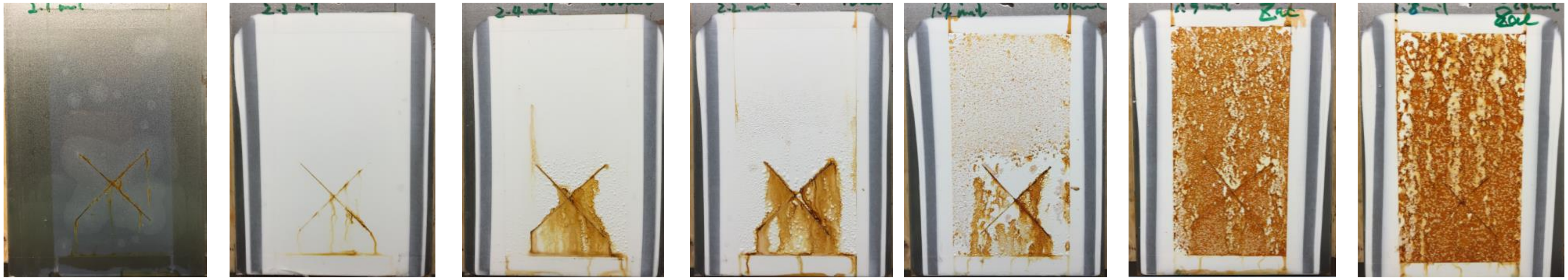
Solventborne Alkyd Short Oil Chain Stopped

1mil DFT

Impact of P:B or PVC

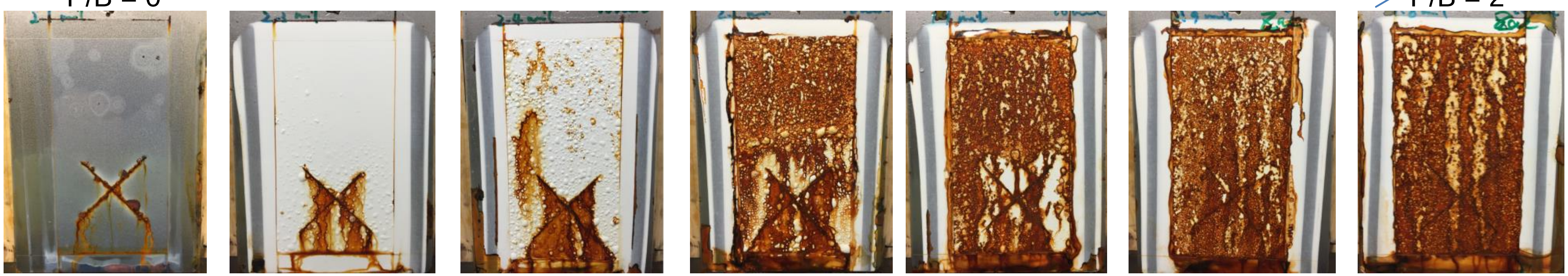
48hr

P/B = 0 → P/B = 2



285 hr

P/B = 0 → P/B = 2

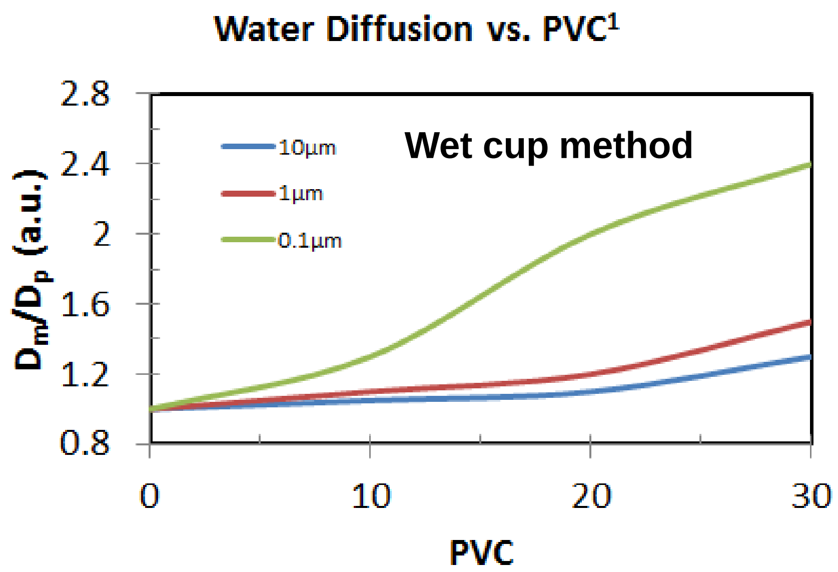


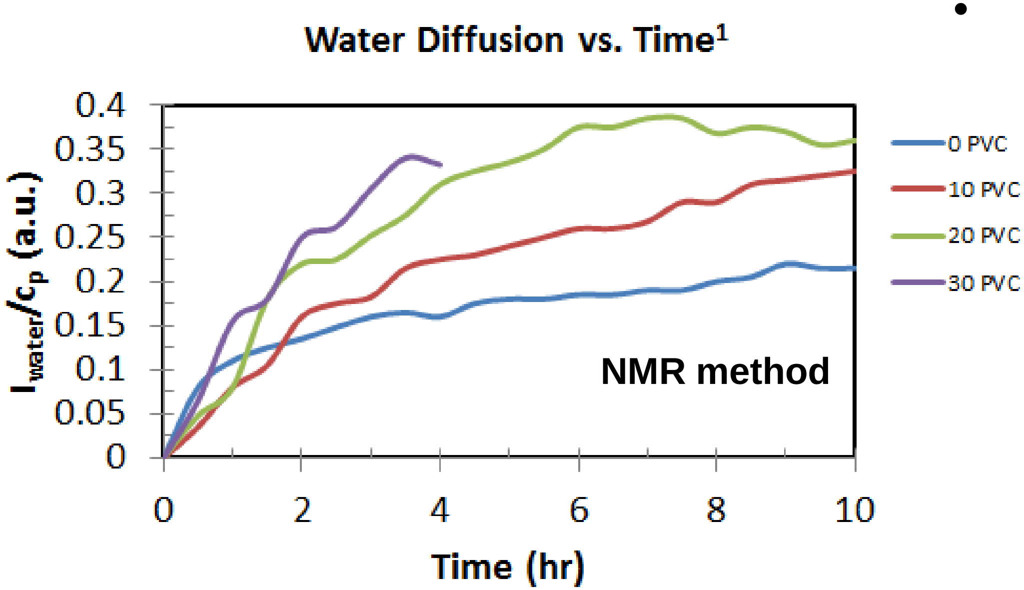
Corrosion resistance decreases with increasing P/B ratio (reproduced with other resins)

Possible explanations:

1. Increased porosity with increasing P/B ratio; liquid water uptake increases
2. Interfacial layer around the pigment particles facilitates water migration and increases diffusion

PVC On Liquid Water Uptake





- Increasing PVC increases water uptake[1]
- Decreasing particle size increases water uptake[1]
  - Related to surface area
- Dispersant/pigment interface identified as coating weak point[1]
- Liquid water uptake can also be measured by EIS – related to corrosion resistance
- Acrylic coatings can take months to achieve final barrier properties[1]

[1]Donkers, PA et al, Proc. of Europ. Coat. Conf. Waterborne Coat., 2013

Resin in Grind

B117, ~50µm DFT, 300hrs, CRS

Importance of Formulation

B117, 1mil DFT, CRS, 500hrs

<u>Clear Formulation</u>

- Resin
- Coalescent
- Wetting agent
- Flash rust inhibitor
- Silicone defoamer
- HEUR thickener

Surfactant Change

Importance of Formulation

B117, 1mil DFT, CRS, 500hrs

Clear Formulation

- Resin
- Coalescent
- Wetting agent
- Flash rust inhibitor
- Silicone defoamer
- HEUR thickener

Coalescent Change

Conclusions

- Protective action of coatings on steel is a complex process with disagreement in literature over relative importance of barrier properties, adhesion, and electrochemical impedance
- Experimental observations and more recent studies point towards impedance as primary indicator of corrosion protection in B117 salt fog
- Other film properties may play a role in under different corrosion testing conditions – e.g. cyclic prohesion, exterior exposure
- Study of 21 styrenated acrylics showed no correlation between adhesion properties and corrosion resistance
- Adhesion still an important property in real world substrate protection
  - Easily chipped/damaged coatings will leave parts of substrate unprotected
- Future work expands study to include barrier properties and impedance as well as other accelerated testing methods – prohesion, QUV, humidity
- Learnings led to development of 50g/L DTM with previously unachieved balance of adhesion and corrosion resistance

Acknowledgements

- Howard Killilea
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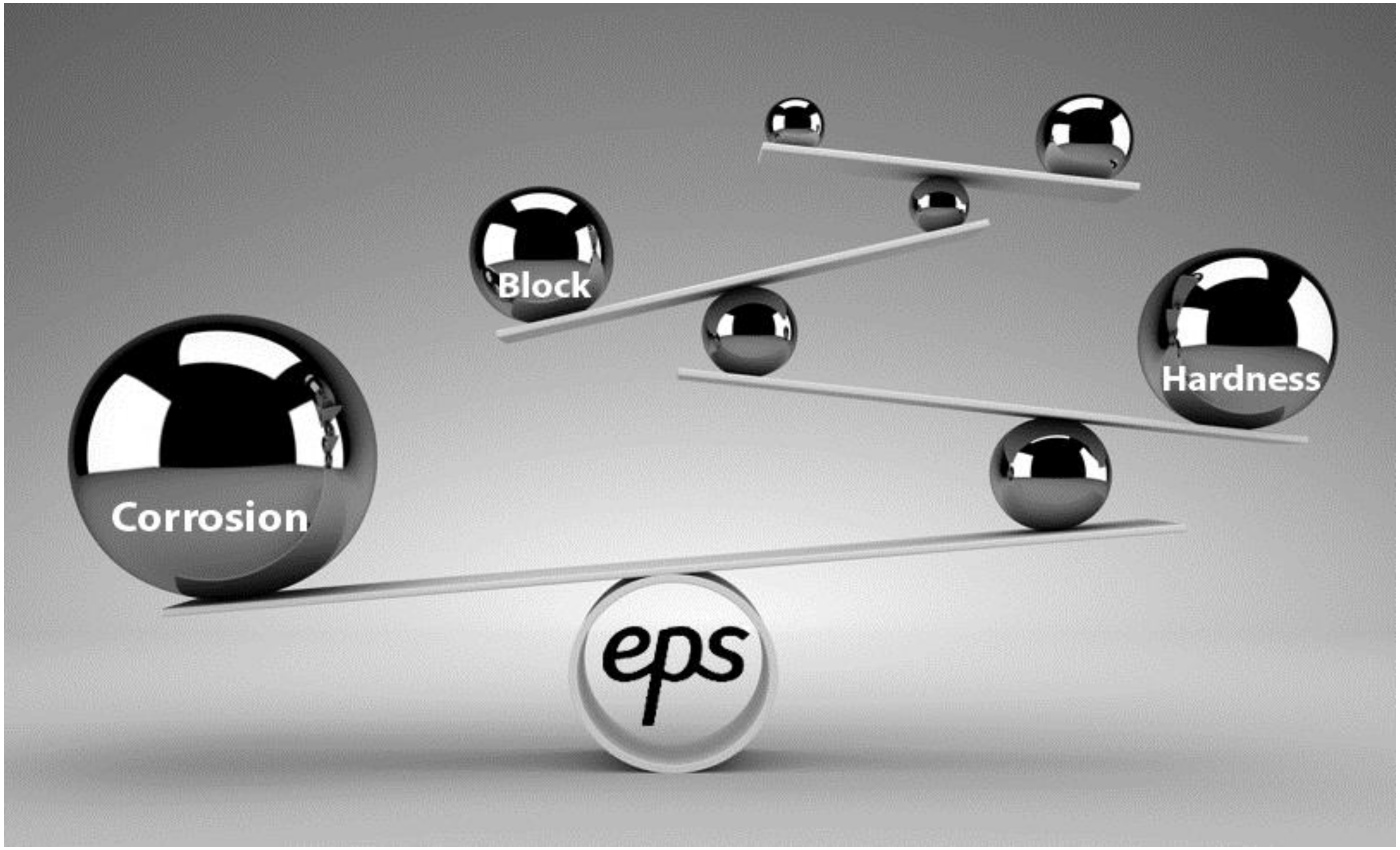
- Matt Andersson
- Zac Cowser
- Niteen Jadhav
- Dave Nevison

Questions?



Further Reading

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