Metal adhesion and corrosion resistance in waterborne, styrenated acrylic direct to metal (DTM) resins

Allen S. Bulick[1], Chris R. LeFever, Glenn R. Frazee, Kailong Jin, Matt L. Mellott
Engineered Polymer Solutions
[1]allen.bulick@eps-materials.com, 815-568-4156

Abstract

Design of waterborne styrenated acrylic resins for metal protection requires balancing a multitude of often competing properties. An extensive benchmarking study of polymers and commercial paints revealed a significant gap in delivering both good corrosion resistance and a robust wet and dry adhesion profile across multiple metal substrates. Early attempts at in-house prototype development yielded similar results. The adhesion/corrosion balance drove an investigation into the fundamental mechanisms by which acrylic polymers both adhere to substrates and inhibit corrosion. Film properties such as adhesion, hardness, barrier properties, and electrochemical impedance were measured and correlated with corrosion resistance on bare cold rolled steel in ASTM B117 salt fog. Leveraging the structure/property relationships derived from this work, a next generation styrenated acrylic DTM was developed targeting the industry gap of corrosion resistance and adhesion. Additionally, formulation effects on corrosion performance from pigment volume concentration (PVC) and additive selection were evaluated.

1. Introduction

Historically, 1K waterborne styrenated acrylic resins have been utilized in the light duty industrial maintenance sector, often sold direct to metal (DTM) coatings. DTM in this context refers to the direct application of a single coat (or optionally multi-coat) paint to a metal substrate without a primer coat to provide adhesion and corrosion resistance. Thus, the DTM coating must provide the full balance of properties expected of a metal protective system including corrosion resistance, adhesion, chemical resistance, UV resistance, and hardness. This presents significant challenges in polymer design, forcing the chemist to balance what often appear to be competing properties. When considering ASTM B117 as the accelerated corrosion testing method, performance ranges for commercially available 1K DTMs based on styrenated acrylics are typically between 24-300 hrs exposure in a single coat at ~ 2 mil dry film thickness (DFT). More specialized styrenated acrylic DTMs can achieve > 500 hrs.

One of the major driving forces for new development in this space is volatile organic content (VOC) reduction. Legacy DTM products tend to be formulated to < 250 g/L, but a combination of regulation, consumer pull-through, and voluntary adoption by suppliers has driven a demand for high performance under 100 g/L and, subsequently, under 50 g/L and under 25 g/L. In a recent development project for a < 100 g/L VOC capable styrenated acrylic DTM, significant difficulties arose in maintaining corrosion resistance while trying to improve adhesion to aluminum substrates. Working of the platform of an in-house incumbent polymer, the initial project focus was to improve its corrosion resistance as measured by ASTM B117 salt fog on flat, untreated cold rolled steel (CRS). Early prototypes accomplished this, but yielded reduced adhesion to aluminum (Figure 1). A significant improvement in corrosion resistance was achieved at the expense of aluminum adhesion as measured by 3 mm crosshatch.
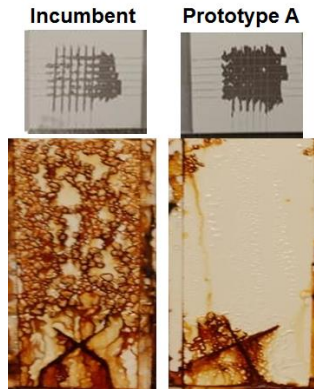
Figure 1: Aluminum crosshatch adhesion vs. corrosion resistance on CRS (2mil DFT, 400hrs B117) of incumbent resin vs. Prototype A.

In developing prototype A, the compositional changes necessary to deliver the improved corrosion resistance reduced its ability to adhere to aluminum. Another round of prototype synthesis was conducted to improve the aluminum adhesion. Results were mixed with a general trend emerging of improved adhesion at the expense of corrosion resistance. A representative subset of the evaluated prototypes is summarized in Figure 2.
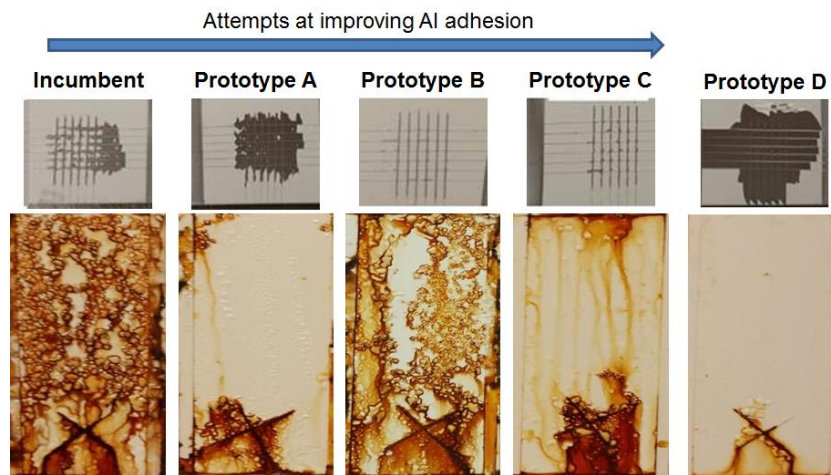

Figure 2: Prototype resins with aluminum adhesion vs. corrosion resistance on CRS (2mil DFT, 400hrs B117).

In light of these findings, an additional prototype (Prototype D) was synthesized specifically deemphasizing aluminum adhesion as a property (Figure 2). Prototype D produced a 0b crosshatch adhesion result, but yielded the best corrosion resistance seen to that point. The results prompted an in depth review of corrosion and adhesion mechanisms in an attempt to explain the apparent inverse relationship between the two properties.

2. Steel Corrosion and Mechanisms of Protection

A simplified schematic of steel corrosion is presented in Figure 3. For corrosion to initiate and propagate, certain conditions are required – 1) an anode, 2) a cathode, 3) oxygen (or other reducible species, e.g. CO_2), 4) water (for ion flow), and 5) electrolytes (e.g. NaCl, accelerate corrosion processes). For steel, there is an additional requirement of a pH < ~ 9.5. A thin passivation layer of oxide forms above this pH, shutting down further corrosion. Elimination of any one of these components can inhibit the corrosion process. For corrosion prevention with organic coatings, without considering anticorrosive pigments or small molecule corrosion inhibitors, there are several potential inhibition mechanisms:
1. Prevention of water and/or oxygen from penetrating the coating film – these mechanisms will be collectively referred to as barrier properties.

2. a) Exclusion of water from the surface or prevention of anode/cathode formation via strong coating wet adhesion properties.
    b) Passivation of either the anode or cathode as it forms via the adhesion properties of the coating
3. Inhibition of electrolyte flow via film resistance – generally measured via electrochemical impedance spectroscopy (EIS).
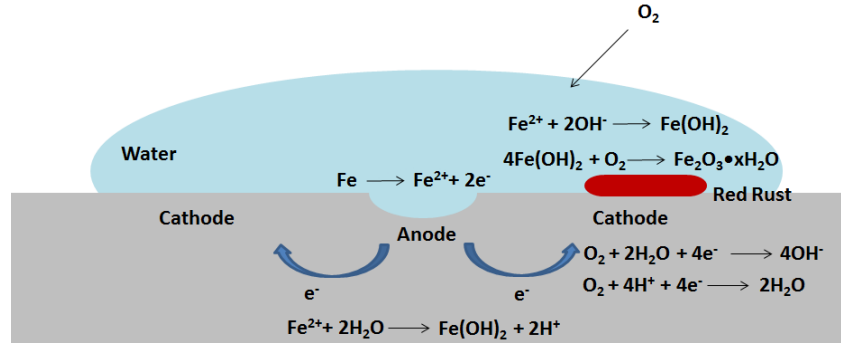

Figure 3: Simplified schematic of corrosion on steel.

2.1 Literature Review

Attempts at elucidating the role organic coatings play in preventing corrosion stretch back decades. There has been significant disagreement over the primary mechanism by which coatings inhibit corrosion with examples of studies concluding that any one of the three components – barrier properties, adhesion properties, or impedance – is the limiting factor. Historically, barrier properties were thought to be of primary importance. One of the earliest challengers to this was Mayne and coworkers[1-3]. Mayne performed extensive work beginning in the late 1940's on the mechanisms of corrosion protection in coatings. The common theme that arose from this work was that the rate of permeation of the elements necessary for corrosion to occur (i.e. water and oxygen) was anywhere from one to several orders of magnitude too high, depending on the chemistry, for barrier properties to be a limiting factor in corrosion control. Instead, Mayne argued that the coating provided a high resistive barrier to electrolyte flow, inhibiting the formation of a complete galvanic cell[3]. This was confirmed via EIS measurements which appeared to correlate well with accelerated corrosion testing on steel immersed in salt water.

Similar results were observed independently in 1948 by Bacon and coworkers who completed an extensive EIS study of 300 coatings systems of different chemistries and arrived at the general rule of thumb that maintaining an impedance of >$10^6 \Omega$ was required for good corrosion resistance[4]. Other researchers disagreed with the barrier property findings of Mayne and others, producing research that suggested oxygen transport through the coating was the rate limiting factor in corrosion resistance[5-7]. A more sophisticated model was proposed by Funke that posited that a combination of oxygen transport inhibition and loss of adhesion via water incursion drove corrosion[8].

Additional researchers concluded that adhesion under saturated conditions, or wet adhesion (as opposed to dry adhesion), either alone or in concert with barrier properties, was of primary importance in inhibiting corrosion[5,9]. The combined efforts of these works and countless others proved that both corrosion and its control by organic coatings were extremely complex and difficult to understand processes. More recent works have tended to favor EIS as the standard predictive tool[10-13]. An in-depth review and theoretical treatment of EIS as a technique applied to coatings is provided by van Westing[14]. Despite this, adhesion and barrier properties continue to be a significant component of the corrosion conversation.

Several potential issues arise when attempting to compare the various models of corrosion resistance generated by different researchers. The cited studies and other works in this area are not necessarily consistent with one another in their resin chemistry, formulation, metal type, surface prep, accelerated corrosion method, analytical techniques, etc. This can make attempting to develop a unifying theory of corrosion protection via organic coatings difficult. As a resin supplier, we are primarily concerned with the

development and study of waterborne, styrenated acrylic resins. As relatively polar, 1K systems, styrenated acrylics are likely to exhibit significantly different behavior in, say, barrier properties vs. highly crosslinked epoxies, chlorinated rubbers or semi-crystalline polyolefins. To develop styrenated acrylics with optimal corrosion resistance, while retaining the necessary balance of other properties, a more focused study is required to isolate the structure/property relationships for a single chemistry.

To better make comparisons between experiments and draw conclusions specific to a single chemistry, the work presented here will focus on corrosion resistance of waterborne, styrenated acrylics as measured by ASTM B117 salt fog on flat, untreated CRS. Specifically, the CRS panels tested were R-series Q-panels which were received clean and received no further surface prep prior to coating.

3. Experimental Observations

The results from Figure 2 indicate that seeking to optimize adhesion properties can be detrimental to corrosion resistance. Figure 4 illustrates an example in which a prototype with good dry adhesion, but poor wet adhesion to CRS was adjusted compositionally to impart wet adhesion via an increase in acid monomer content. Wet adhesion is tested by applying a 10 mil wet drawdown, curing at ambient conditions for seven days, forming a 3 mm crosshatch, and exposing to a wet paper towel for 30 min. After 30 min, the paper towel is removed, the film patted dry, and the crosshatch immediately tested with adhesion tape.
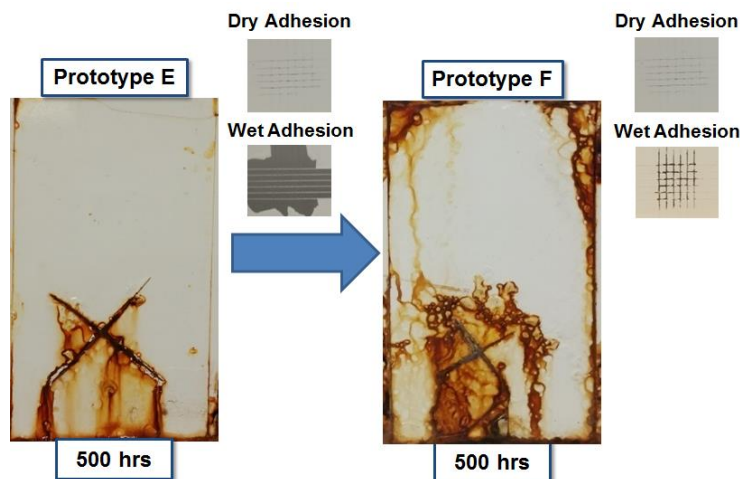

Figure 4: Effect of wet adhesion on corrosion resistance (2-2.2mil DFT, B117).

An additional prototype was then made reducing the adhesion properties of Prototype E via acid monomer reduction such that the resin failed dry crosshatch adhesion on CRS. The observed corrosion resistance (Figure 5), presented both in a pigmented high gloss formulation (2 mil DFT) and a clear formulation (1 mil DFT), exhibited an incremental improvement in corrosion resistance over Prototype E. Even with poor dry and wet adhesion, scribe propagation was unexpectedly minimal (< 3mm) and field corrosion was isolated to a few pin points.

Insight as to the underlying mechanism and interplay between these properties may lie in work performed by Ulfvarson and Khullar, where they demonstrated an inverse correlation between the ion exchange capacity of the resin and its corrosion resistance[15]. Framed another way, increasing the acid monomer content of a resin is expected to be detrimental to corrosion resistance. For waterborne styrenated acrylics, this presents an interesting challenge as these polymers rely on acid groups both for metal adhesion and colloidal stability. To test this, a series of resins was synthesized changing nothing but the acid monomer level. Each resin was tested for corrosion resistance in a clear formulation (Figure 6). A significant correlation between acid level and corrosion resistance emerged, with lower acid levels yielding superior corrosion resistance.
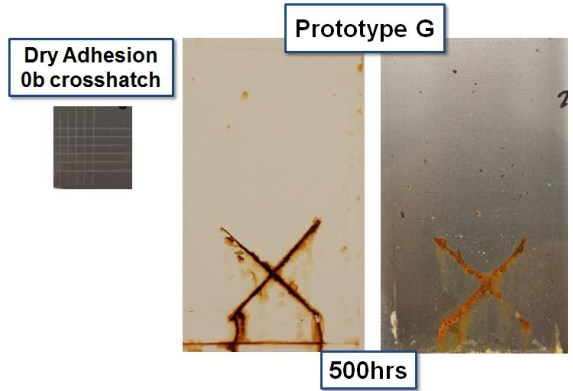
Figure 5: Corrosion resistance (2mil DFT for white, 1mil for clear, 500hrs B117) of prototype with poor dry adhesion on CRS.
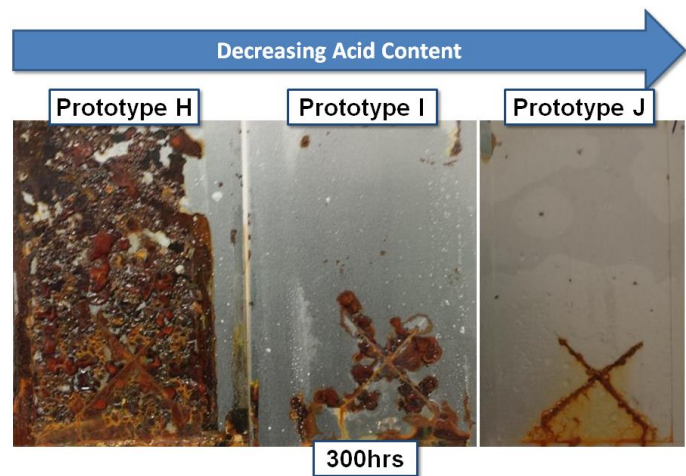

Figure 6: Corrosion resistance (1.5mil DFT, 300hrs B117) of three prototypes with decreasing acid monomer levels.

Clear films provide easily observable visual cues, particularly in the cases of field corrosion and water incursion. In the case of Prototype J (Figure 6), water has visibly penetrated the film and is present at the film/substrate interface on > 70% of the surface area. Yet, in the vast majority of the field area, no visible corrosion is present and corrosion protection continues even after water has penetrated to the substrate surface. This indicates that water incursion, in and of itself, is not the rate limiting step in the initiation and propagation of corrosion at the steel surface. Additionally, polymers that pass the standard wet adhesion test quickly lose adhesion strength in the salt fog cabinet. This is consistent with the work of Walker[16]. Resins that pass wet adhesion as measured by one hour immersion in water fail crosshatch adhesion upon removal from the salt fog cabinet. Adhesion strength is typically low enough after 300 hrs exposure to salt fog that the entire film could be lifted from the substrate with minimal effort (Figure 7).

Figure 7: Loss of adhesion after 300hrs exposure to the B117 salt fog cabinet.

Also, despite the loss of substrate adhesion, it is apparent from Figure 7 that no significant scribe propagation or field rust had occurred.

4. Systematic Study of Styrenated Acrylics

4.1 Experimental

In an effort to understand both the findings from literature and experimental observations and begin to pursue a more unified theory of corrosion protection specifically for styrenated acrylics, a study evaluating 21 commercially available styrenated acrylics (henceforth referred to as Resin A through Resin U) was conducted. The resins were formulated into identical clear formulations only adjusting coalescing solvent level based on the minimum film formation temperature (MFFT) of each resin (Table 1). Based on the mechanistic understanding of corrosion processes, a number of film properties were selected and measured (Table 2). These properties were then evaluated for correlation with accelerated corrosion in a B117 salt fog cabinet (Q-FOG, Q-lab) at a target of 3-3.5 mil DFT in a single coat on flat, untreated CRS (4"x6" R-series Q panels) via drawdown. Results discussed here will focus on adhesion, impedance, film hardness, and water vapor transmission (at the time of this writing, O_2 transmission data is still underway). Future papers will extend the structure/property model to other performance tests such as Cleveland humidity and cyclic prohesion.

Table 1: Start Point Clear Formulation for Film Property Testing

Pounds	Gallons	NAME	NVMW
640.00	74.85	**Resin**	**288.00**
2.00	0.27	Ammonium Hydroxide	0.00
4.00	0.46	Silicone Wetting Agent	4.00
3.00	0.34	Silicone Defoamer	2.94
4.00	0.44	Biocide	0.60
xx.xx	xx.xx	Water (adj. for resin)	0.00
xx.xx	xx.xx	DPnB (adj. for resin)	0.00
15.00	1.80	Sodium Nitrite 4%	0.60
12.00	1.31	High Shear HEUR Thickener	2.40
3.00	0.33	Low Shear HEUR Thickener	0.65
	100.00	TOTALS	299.19

Table 2: Test Matrix for Development of a Mechanistic Model of Corrosion Resistance of Waterborne Styrenated Acrylics (Items in Bold Discussed in this Paper)

Test	Technique
Dry Adhesion	Pull off
Wet Adhesion	Water immersion/cross hatch
Film Hardness	Konig
Water Vapor Transmission	
Impedance	EIS
O2 Transmission	
Liquid Water Uptake	

Each of the resins was exposed in B117 salt fog and monitored for progression of corrosion at 66 hrs, 240 hrs and 560 hrs (560 hr panels in Figure 8). To analyze the data, the panels were force ranked on a discrete 10 unit scale, with 10 being the best ranked panel and 1 being the worst.

For dry pull off adhesion, coatings were applied over 4"x6" R-series Q panels at 10 mil wet DFT and cured at ambient conditions for seven days. Metal dollies were fixed to the film via an epoxy adhesive for

24 hr. The test area was separated from the rest of the film by cutting around the dolly and the peak force (psi) necessary to remove the film from the substrate was measured (results in

Table **3**).

In an effort to quantify the wet adhesion properties of the films, a series of immersion tests were run with a ladder of exposure times. Coatings were applied over 4"x6" R-series Q panels at 10 mil wet DFT and cured at ambient conditions for seven days. The initial test was the 30 min wet paper towel test described before. The crosshatches were rated on a scale of 0b-5b, with 0b meaning > 65% film removal and 5b meaning 0% film removal. Resins that retained ≥ 2b adhesion in this test were then immersed in water for one hour and retested for adhesion. Additional immersion times were 24 hr, 48 hr, 4 day, and 1 week. At each time point, resins that exhibited ≥ 2b adhesion were carried through to the next immersion time point. An average of the six runs was taken with results summarized in

Table **3**. As evidenced by the 95% confidence intervals for pull off adhesion, variability is high for the test.

Barrier properties are known to be directly related to polymer T_g, which is in turn directly related to measured film hardness. Coatings were applied over 4" x 6" glass panels at 10 mil wet DFT and cured at ambient conditions for seven days. Konig hardness was measured via oscillations at 3^0 on a Pendulum Hardness Tester from Byk (results in

Table **3**).

For water vapor transmission, each coating was drawn down on a silicone release liner at 15mil WFT and cured at RT for seven days. Three 4 cm diameter disks were cut from each film. Samples were measured for water vapor transmission on an Illinois Instruments 7002 WVT for 24 hrs at 90% humidity, 100 ^{0}F.

For EIS, samples were prepared in an equivalent manner to those prepared for B117 salt fog. EIS was conducted on the films upon initial immersion in a 5% NaCl solution and after 24 hrs of immersion. Impedance values at low frequency (0.01Hz, via potentiostat) at 24hrs immersion were used for correlation assessment.

Figure 8: Corrosion results (560hrs B117) and ratings of Resin A through U (3-3.5mil DFT, CRS).

Table 3: Pull Off Adhesion on CRS (R-series Q panel), Average Wet Adhesion Rating, and Konig Hardness for Resin A Through U

System	Dry Adhesion Peak Force (psi)	Avg Wet Adhesion Rating	Konig Hardness (#3° Oscillations)	System	Dry Adhesion Peak Force (psi)	Avg Wet Adhesion Rating	Konig Hardness (#3° Oscillations)
Resin A	277	4.7	5	Resin L	180	1.8	11
Resin B	132	0.3	10	Resin M	111	0.2	13
Resin C	172	3.2	6	Resin N	95	0.3	11
Resin D	214	2.8	6	Resin O	222	2.0	6
Resin E	294	2.7	5	Resin P	233	1.5	7
Resin F	94	0.5	9	Resin Q	219	3.0	7
Resin G	216	1.7	8	Resin R	165	2.8	9
Resin H	163	1.7	13	Resin S	172	1.8	8
Resin I	289	1.7	16	Resin T	208	2.3	10
Resin J	215	4.0	8	Resin U	320	2.0	9
Resin K	212	1.5	8				

4.2 Results & Discussion

A series of plots (Figure 9) were generated to investigate any correlations that might arise amongst the following pairs: dry adhesion/wet adhesion, dry adhesion/corrosion resistance, wet adhesion/corrosion resistance, water vapor transmission/corrosion resistance, Konig hardness/corrosion resistance, and 24 hr low frequency impedance/corrosion resistance.
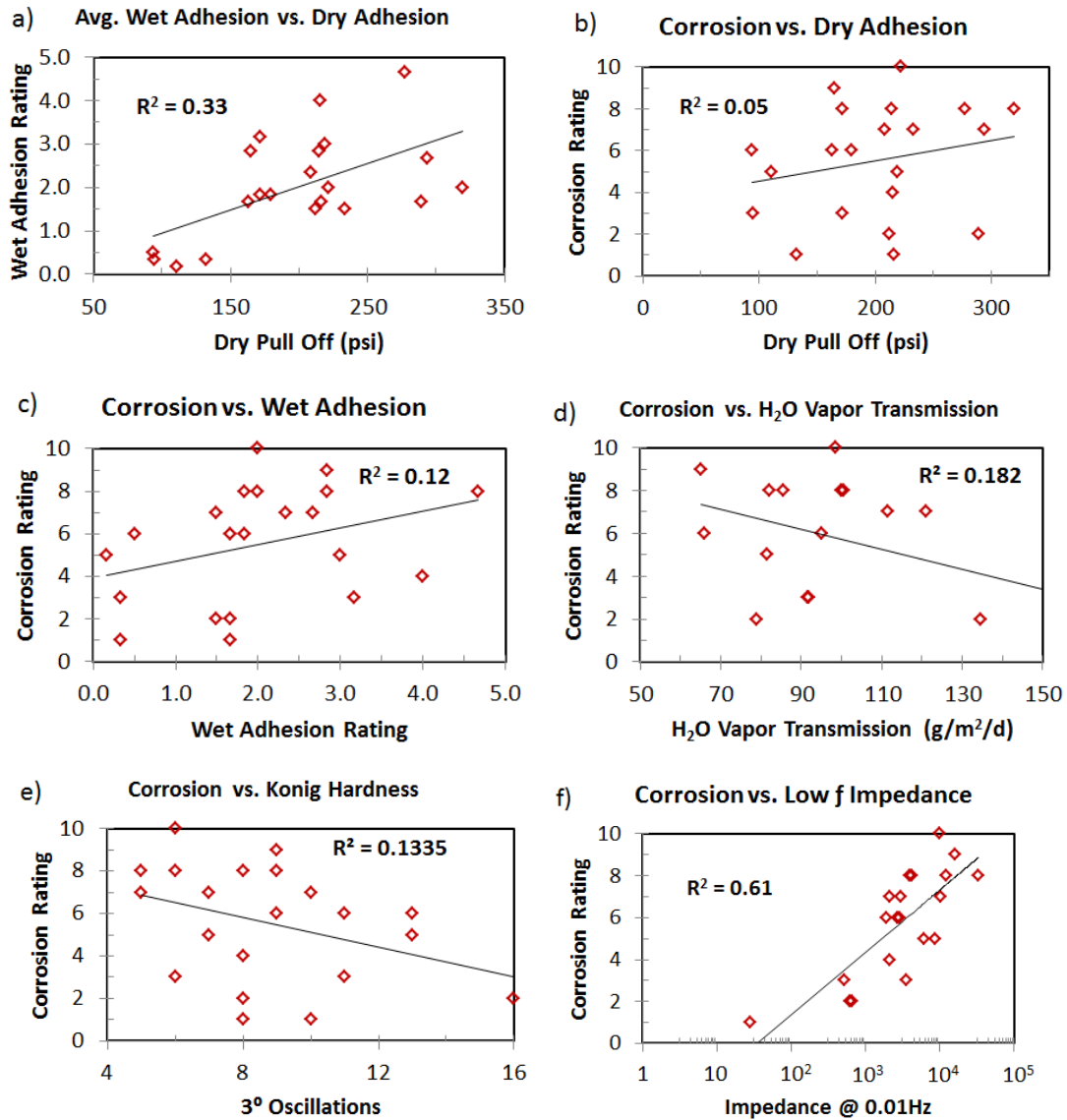
Figure 9: Correlation of physical properties - a) dry pull off adhesion vs. avg. wet adhesion, b) corrosion resistance vs. dry pull off adhesion, c) corrosion resistance vs. avg. wet adhesion, d) corrosion vs. H2O vapor transmission, e) corrosion vs. Konig hardness, f) corrosion resistance vs. low frequency impedance (0.01Hz, 24hr immersion).

Dry and wet adhesions were moderately correlated, with initial strength of dry adhesion explaining a small portion of the wet adhesion data. Neither dry nor wet adhesion showed a significant correlation with corrosion resistance. Prior to this study, based on experimental observations, the hypothesis was that a *negative* correlation between adhesion characteristics and corrosion resistance would emerge, but this was not the case. Similarly, neither water vapor transmission, nor Konig hardness exhibited strong correlation with corrosion resistance. Future work will compare water vapor transmission with liquid water uptake data and any respective correlation with corrosion resistance. The two physical forms of water represent two different aspects of barrier properties as water vapor transmission is dominated by bulk diffusion while liquid water transport proceeds primarily via capillary action.

Low frequency impedance correlated strongly with the observed corrosion resistance, with impedance explaining a majority of the experimental data (R^2 = 0.61). The remaining variability may arise in film properties still to be measured and may also be inherent to the test due to panel to panel inconsistencies in film quality. Data correlation may also change/be improved by extending the EIS exposure time to one

week. However, one week, or 168 hrs, is approaching a meaningful timescale to be able to observe differences in B117 corrosion performance of styrenated acrylic resins, thus reducing its effectiveness as a quick screening tool.

Based on these findings, film impedance is an important part of the model of coating corrosion resistance. However, a significant portion of the data remains unexplained. Work is now ongoing to determine how O_2 permeability, liquid water uptake, and resin acid number fit into the corrosion model. Upon completion of all film property measurements, a more rigorous statistical treatment of the collected data will be conducted to generate a structure/property model of the experimental observations.

An important takeaway from the adhesion results is that, contrary to previous experimental observations, achieving good wet adhesion properties is not necessarily detrimental to corrosion resistance. Good adhesion is also not strictly *necessary* to achieve good corrosion resistance. In real world applications, however, good adhesion properties serve another important purpose in reducing the likelihood of coating film damage and substrate exposure. Polymers with good wet adhesion are more likely to resist delamination/removal from the substrate from mechanical damage when hydrated due to rain or high humidity. Any damaged area without coating coverage is readily susceptible to corrosion processes.

5. Next Generation Development

The adhesion/corrosion balance of the previous study yielded significant new insights into resin design. Polymers with good wet adhesion and good corrosion resistance could be isolated and those properties correlated back to their monomer compositions and particle morphologies. The knowledge gained drove development of a next generation, low VOC (< 50 g/L) styrenated acrylic DTM resin with high performing adhesion and corrosion properties. A new prototype was synthesized that provided a robust adhesion profile across many substrates, capable of passing dry and wet adhesion within 72 hrs of application (Figure 10). Additionally, the corrosion resistance (Figure 11) surpassed that of most previously evaluated prototypes while delivering a comprehensive wet and dry adhesion profile. The novel synthetic approaches demonstrated here achieved improved adhesion without negatively impacting the film's impedance or relying on high levels of acidic functional groups.
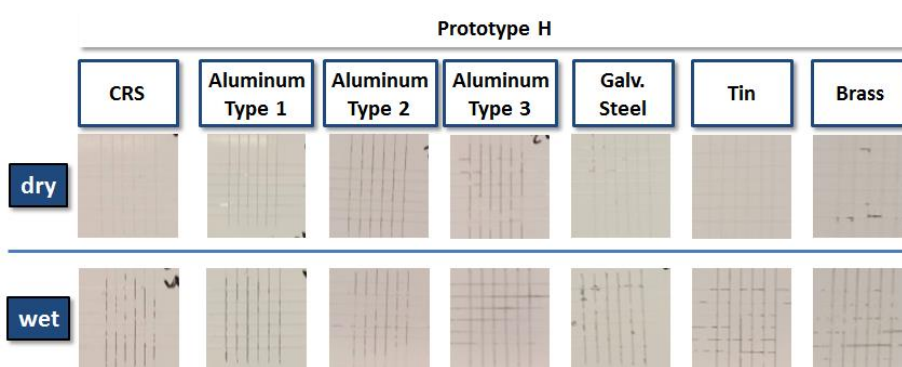

Figure 10: 24hr wet and dry crosshatch adhesion of Prototype H across a variety of metal substrates.

Figure 11: Corrosion resistance (600hrs B117, 2mil DFT, CRS) of Prototype H.

Current efforts are focused on further optimizing the performance of Prototype H and continuing to drive down the VOC demand of waterborne styrenated acrylic DTMs. Additional unmet needs in this space such as adhesion to poorly prepared substrates (e.g. oily/greasy, dirty, rusted, etc.) are also being explored leveraging learnings from the study presented in this report.

6. Impact of Formulation

Finally, formulation choices in DTM coatings are as important as the resin design for performance. One example of this is the effect of increasing pigment to binder (P:B) ratio or pigment volume concentration (PVC) on corrosion resistance (Figure 12).

Figure 12: Impact increasing PVC on corrosion resistance (48hrs B117, 2mil DFT, CRS).

Insight as to the mechanism for accelerated failure with increasing PVC may be derived from the work of Donkers, et al which showed that increasing PVC led to increased water uptake which they were able to demonstrate both via a wet cup method and an NMR method known as GARField (Figure 13)[17]. Using NMR, the researchers determined that the pigment/dispersant interface was the weakest point of the film and, as surface area of this interface increased with increasing PVC (or decreasing extender particle size), liquid water uptake also increased. This phenomenon has implications for corrosion resistance as liquid water, unlike water vapor, can transport with it O_2 and corrosion accelerating electrolytes such as chlorides in B117. To maximize corrosion performance, care should be taken to minimize PVC and dispersant loading where possible, while ensuring formulation stability.
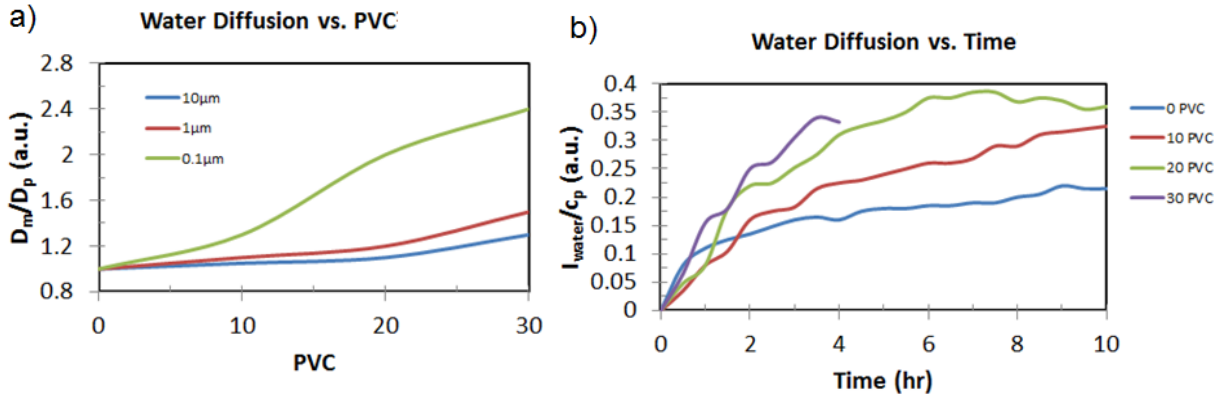
Figure 13: a) Effects of increasing PVC and decreasing particle size on water uptake (wet cup method), b) effect of increasing PVC on water uptake (GARField NMR)[17].

Additive package choices can also influence the corrosion performance of a coating. Figure 14 illustrates the effect of moving from a lower HLB wetting agent to a higher one while Figure 15 shows the impact of moving from a water immiscible coalescing solvent to a water miscible one. Thus, a general guideline of favoring hydrophobic additive packages to maximize corrosion resistance is recommended.
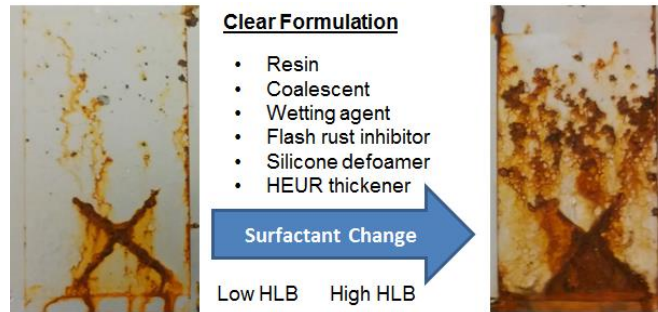

Figure 14: Impact of wetting agent/surfactant selection on corrosion resistancee (500hrs B117, 2mil DFT, CRS) moving from more hydrophobic to more hydrophilic.
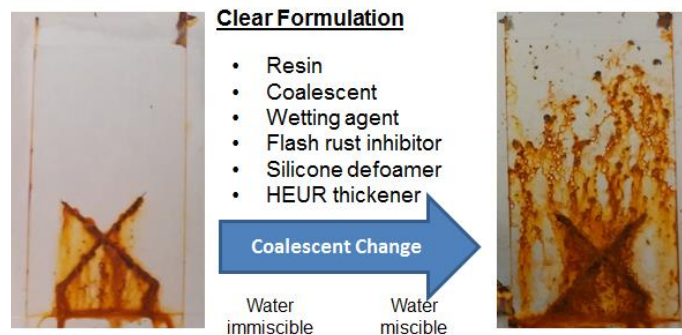

Figure 15: Hydrophobic vs. hydrophilic coalescing solvent in corrosion resistance (500hrs B117, 2mil DFT, CRS).

Works Cited

[1]   J. Mayne, *JOCCA,* vol. 32, no. 352, pp. 481-487, 1949.

[2]   J. Mayne, *JOCCA,* vol. 40, p. 183, 1957.

[3]   J. Mayne, "The Mechanism of the Protective Action of Paints," in *Corrosion*, Newnes-Butterworths, 1976, pp. 15:24-15:37.

[4]   C. Bacon, J. Smith and a. R. FM, *Ind Eng Chem,* vol. 40, no. 1, pp. 161-168, 1948.

[5]   W. Funke and H. Haagen, *Ind Eng Chem Prod Res Dev,* vol. 17, p. 50, 1978.

[6]   S. Guruviah, *JOCCA,* vol. 53, p. 660, 1970.

[7]   P. Kresse, *Pigment Resin Tech,* vol. 2, no. 11, p. 21, 1973.

[8]   W. Funke, *JOCCA,* vol. 62, p. 63, 1979.

[9]   E. Parker and H. Gerhart, *Ind Eng Chem,* vol. 59, no. 8, p. 53, 1967.

[10] G. Bierwagen, D. Tallman and e. al, *Prog in Org Ctgs,* vol. 46, no. 2, pp. 149-158, 2003.

[11] F. Floyd and e. al, *Prog in Org Ctgs,* vol. 66, no. 1, pp. 8-34, 2009.

[12] M. O'Donoghue and e. al, *Coatings & Linings,* pp. 36-41, September 2003.

[13] S. Shreeptahi, A. Guin and e. al, *J Coat Tech & Res,* vol. 8, no. 2, pp. 191-200, 2011.

[14] E. van Westing, "Determination of coating performance with impedance measurements," Delft, 1992.

[15] U. Ulfvarson and M. Khullar, *JOCCA,* vol. 54, p. 604, 1971.

[16] P. Walker, *Off Dig Fed Soc Paint Technol,* vol. 37, p. 1561, 1965.

[17] Donkers, PAJ, Huinink, HP, Erich, SJF, van Meef, PA, Baukh, V, Adan, OCG, *Proc. of Euro. Coat. Conf. Waterborne Coat.*, 2013.