The challenge of balancing adhesion and corrosion resistance in waterborne styrenated acrylic direct to metal (DTM) resins

Allen Bulick, Chris LeFever, Glenn Frazee, Kailong Jin, Matt Mellott*
Engineered Polymer Solutions
*allen.bulick@eps-materials.com, 815-568-4156

Abstract

Design of waterborne acrylic and styrenated acrylic resins for metal protection requires balancing a multitude of often competing properties. One classic example is attempting to maintain hardness and block resistance while simultaneously reducing the volatile organic content (VOC) demand of waterborne paints. During a recent new product development project, another recurring tradeoff emerged – attempting to deliver a robust adhesion profile while maximizing corrosion resistance. The adhesion/corrosion balance drove an investigation into the fundamental mechanisms by which acrylic polymers both adhere to substrates and inhibit corrosion. Topics such as the role of barrier properties, passivation via adhesion and electrochemical impedance are covered with respect to polymer composition and the role of acid monomers. Applying these learnings, several newly designed polymers are discussed to illustrate the level of corrosion resistance that high performing styrenated acrylics can achieve.

1. Introduction

Waterborne styrenated acrylic resins can be broadly categorized into the light duty industrial maintenance sector. They are often sold as direct to metal (DTM) coatings. DTM in this context refers to the direct application of a single coat (or optionally multi-coat) paint 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.

In a recent development project for a next generation, <100g/L volatile organic content (VOC) capable styrenated acrylic DTM, significant difficulties arose in maintaining corrosion resistance while trying to improve adhesion to aluminum substrates. The initial focus of the new development was to improve the corrosion resistance as measured by ASTM B117 salt fog of the incumbent polymer on flat, untreated cold rolled steel (CRS). Early prototypes accomplished this, but exhibited reduced adhesion to aluminum. Figure 1 shows cross hatch adhesion to aluminum overlaid with B117 salt fog panels for the initial prototype vs. the incumbent resin.

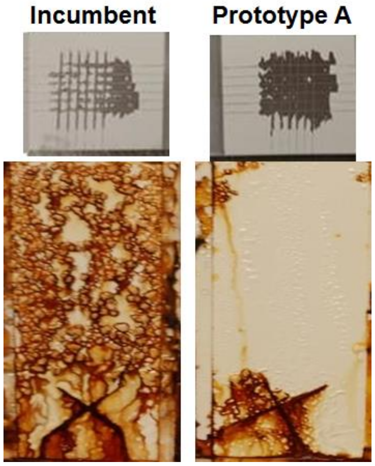

Figure 1: Aluminum crosshatch adhesion vs. corrosion resistance on CRS (2mil DFT, 400hrs B117) of incumbent resin vs. Prototype A

A significant improvement in corrosion resistance was achieved at the expense of aluminum adhesion as measured by 3mm crosshatch. Though the incumbent polymer’s adhesion performance was not optimal, the compositional changes necessary to deliver the improved corrosion resistance further limited its adhesion.

Another round of prototype synthesis was undertaken 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.

In light of these findings, an additional prototype (Prototype D) was synthesized specifically deemphasizing aluminum adhesion as a property (Figure 3). 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 relationship between the two properties.

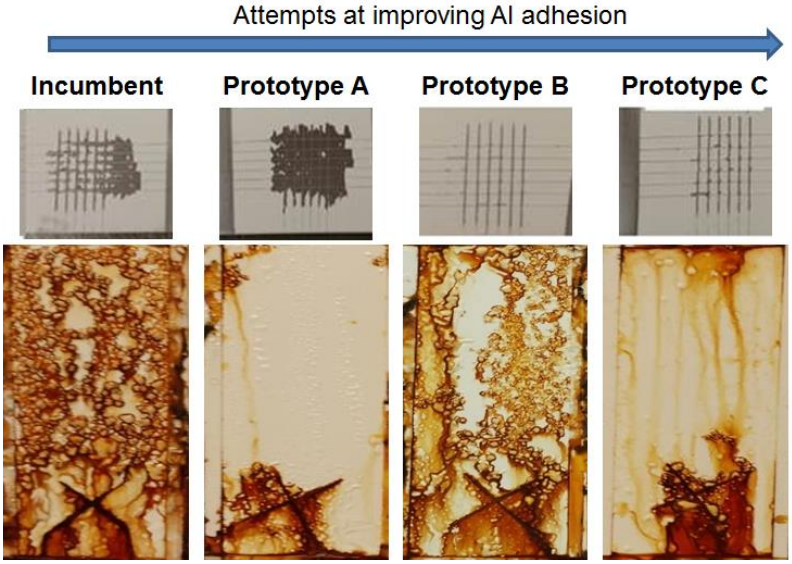

Figure 2: Prototype resins with aluminum adhesion vs. corrosion resistance on CRS (2mil DFT, 400hrs B117)

Figure 3: Aluminum adhesion vs. corrosion resistance on CRS (2mil DFT, 400hrs B117) of Prototype D

2. Mechanisms of Corrosion Protection

A simplified schematic of steel corrosion is presented in Figure 4. 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, not necessarily required, but can accelerate corrosion process). 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 – collectively known as barrier properties
2. Exclusion of water from the surface or prevention of anode/cathode formation via strong coating wet adhesion properties
3. Passivation of either the anode or cathode as it forms via the adhesion properties of the coating
4. Inhibition of electrolyte flow via film resistance – generally measured via electrochemical impedance spectroscopy (EIS)

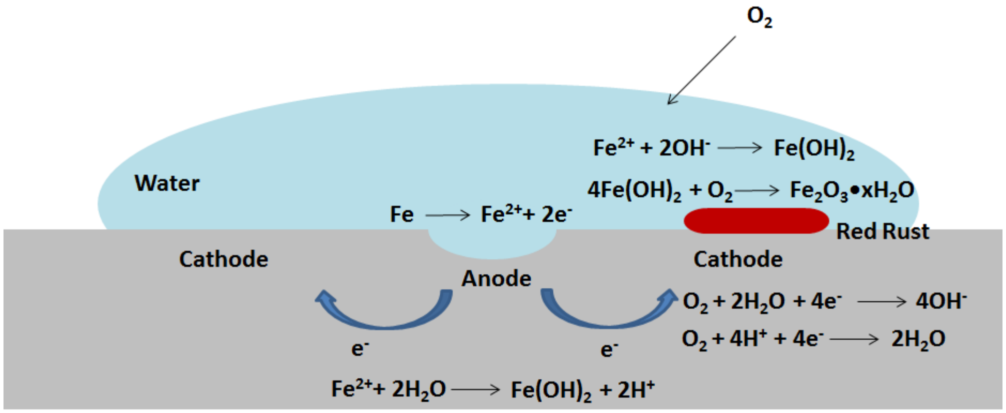

Figure 4: Simplified schematic of corrosion on steel

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 coworker [1, 2, 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 oxygen transport through the coating was the limiting factor of corrosion resistance [5, 6, 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 reached the conclusion 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, 11, 12, 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 best make comparisons between experiments and draw conclusions, 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. In the interest of space, this paper will primarily investigate impedance and adhesion properties and how they relate to the observed corrosion resistance of the evaluated resins. Unless otherwise noted, the formulations presented are white high gloss systems at a PVC of 12 without anticorrosive pigments.

Future papers will extend the study to include barrier properties as measured by water vapor and O_2 transmission as well as liquid water uptake. There is a large body of work presented in various journal articles and technical conferences discussing the validity and correlation of different accelerated corrosion testing methods. In light of this, an additional study extension will include cyclic prohesion as an accelerated testing method, the effects of the aforementioned film properties, and how it compares to B117.

3. Experimental Observations

The results from Figure 2 indicate that seeking to optimize adhesion properties can be detrimental to corrosion resistance. Figure 5 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 10mil wet film, curing at ambient conditions 7 day, forming a 3mm crosshatch and exposing to a wet paper towel for 30min. After 30min, the paper towel is removed, the film patted dry, and the crosshatch immediately tested with adhesion tape.

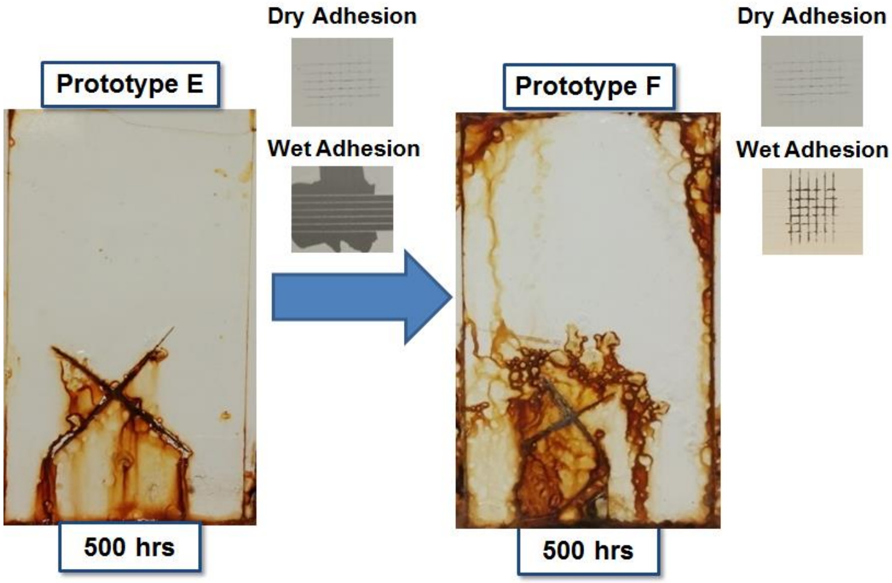

Figure 5: Effect of wet adhesion on corrosion resistance (2-2.2mil DFT, B117)

An additional prototype was then made reducing the adhesion properties further via acid monomer reduction such that the resin failed dry crosshatch adhesion on CRS. The observed corrosion resistance (Figure 6), presented both in a pigmented high gloss formulation (2mil DFT) and a clear formulation (1mil DFT), exhibited an incremental improvement in corrosion resistance over Prototype E. Even without the presence of significantly measurable dry or wet adhesion, scribe propagation was unexpectedly minimal and field corrosion was isolated to a few pin points.

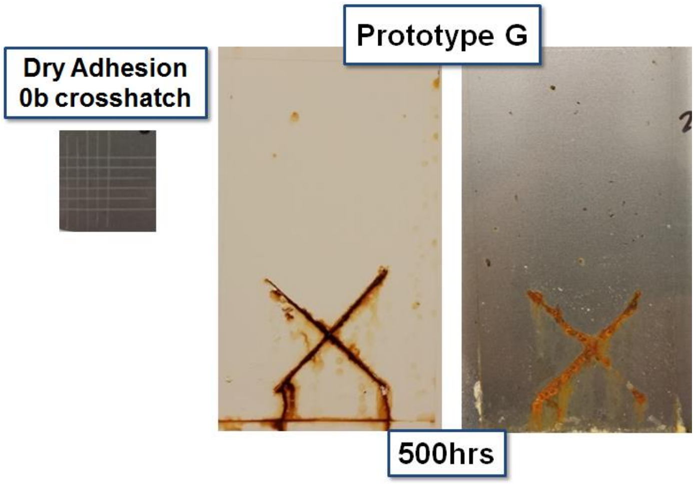

Figure 6: Corrosion resistance (2mil DFT for white, 1mil for clear, 500hrs B117) of prototype with poor dry adhesion on CRS

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 7). A significant correlation between acid level and corrosion resistance emerged, with lower acid levels yielding superior corrosion resistance.

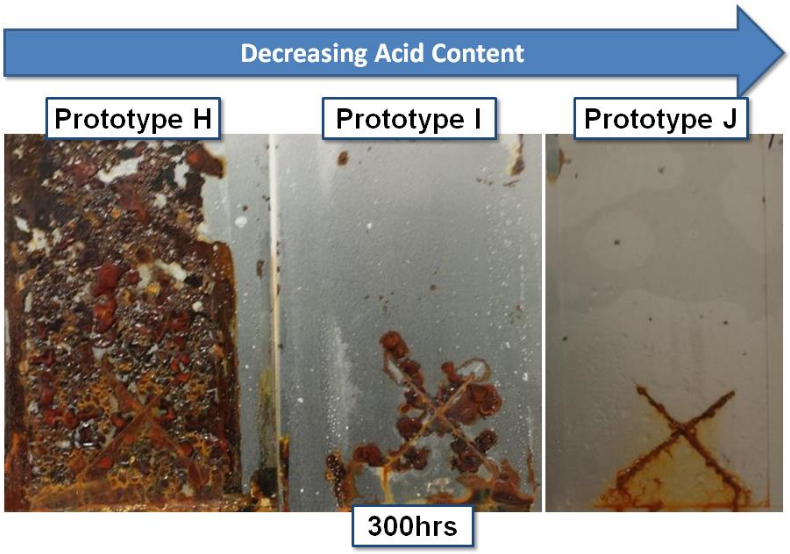

Figure 7: Corrosion resistance (1.5mil DFT, 300hrs B117) of three prototypes with decreasing acid monomer levels

Clear films provide easily observable visual cues, particularly in the cases of field corrosion and water incursion. In the case of Prototype J (Figure 7), 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 occurring 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, it was observed that even 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 1hr immersion in water fail crosshatch adhesion upon removal from the salt fog cabinet. Adhesion strength was low enough that the entire film could be lifted from the substrate with minimal effort (Figure 8).

Figure 8: Loss of adhesion after 300hrs exposure to the B117 salt fog cabinet

Despite the loss of substrate adhesion, it is apparent from Figure 8 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. A number of film properties were then measured (Table 1) and accelerated corrosion in a B117 salt fog cabinet (Q-FOG, Q-lab) was run at a target of 3-3.5mil DFT in a single coat on flat, untreated CRS (4”x6” R-series Q panels) via drawdown. As previously mentioned, the results discussed here will focus on the adhesion and impedance components of the study. Future papers will consider the other film properties to develop a more rigorous statistical model for corrosion resistance. The structure/property model will then be extended to other performance tests such as Cleveland humidity and cyclic prohesion. Additionally, each of the tested resins will be re-evaluated in a high gloss pigmented system to include pigment and dispersant effects.

Table 1: Test matrix for development of a mechanistic model of corrosion resistance of waterborne styrenated acrylics

Test	Technique
Dry Adhesion	Pull off (quantitative)
Wet adhesion	Water immersion
Impedance	EIS
Resin T_g	DSC
Film Hardness	Konig
Water vapor transmission	
Oxygen transmission	
Liquid water uptake	

Each of the resins was exposed in B117 salt fog and monitored for progression of corrosion at 66hrs, 240hrs and 560hrs (560hr panels in Figure 9). 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. Dry adhesion was quantified by a pull off method in which metal dollies are fixed to the film via an epoxy adhesive for 24hr. The test area is separated from the rest of the film by cutting around the dolly and the peak force necessary to remove the film from the substrate is measured (results in

Table **2**). 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. The initial test was the 30min wet paper towel test described before. The crosshatches were rated on a scale of 0b-5b, with 0b meaning no film remains and 5b meaning no film was removed. Resins that retained ≥2b adhesion in this test were then immersed in water for 1hr and retested for adhesion. Additional immersion times were 24hr, 48hr, 4day, and 1week. At each time point, resins that exhibited ≥2b adhesion were carried through to the next immersion time point. An average of the 6 runs was taken with results summarized in

Table **2**. As evidenced by the 95% confidence intervals for pull off adhesion, variability is high for the test.

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 24hrs of immersion. Impedance values at low frequency (0.01Hz) at 24hrs immersion were used for correlation assessment.

4.2 Results & Discussion

A series of plots (Figure 10) 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, and 24hr low frequency impedance/corrosion resistance.

Figure 9: Corrosion results (560hrs B117) and ratings of Resin A through U (3-3.5mil DFT, CRS)

Table 2: Pull off adhesion on CRS (R-series Q panel) for resin A through U with 95% confidence intervals and wet adhesion ratings

System	Average Peak Force (psi)	95% CI	Avg Wet Adhesion Rating	System	Average Peak Force (psi)	95% CI	Avg Wet Adhesion Rating
Resin A	277	11.9	4.7	**Resin L**	180	20.3	1.8
Resin B	132	72.4	0.3	**Resin M**	111	30.0	0.2
Resin C	172	53.0	3.2	**Resin N**	95	42.6	0.3
Resin D	214	45.4	2.8	**Resin O**	222	48.1	2.0
Resin E	294	65.5	2.7	**Resin P**	233	49.3	1.5
Resin F	94	24.8	0.5	**Resin Q**	219	55.2	3.0
Resin G	216	67.6	1.7	**Resin R**	165	20.3	2.8
Resin H	163	41.8	1.7	**Resin S**	172	24.3	1.8
Resin I	289	26.7	1.7	**Resin T**	208	35.2	2.3
Resin J	215	79.1	4.0	**Resin U**	320	99.6	2.0
Resin K	212	87.1	1.5				

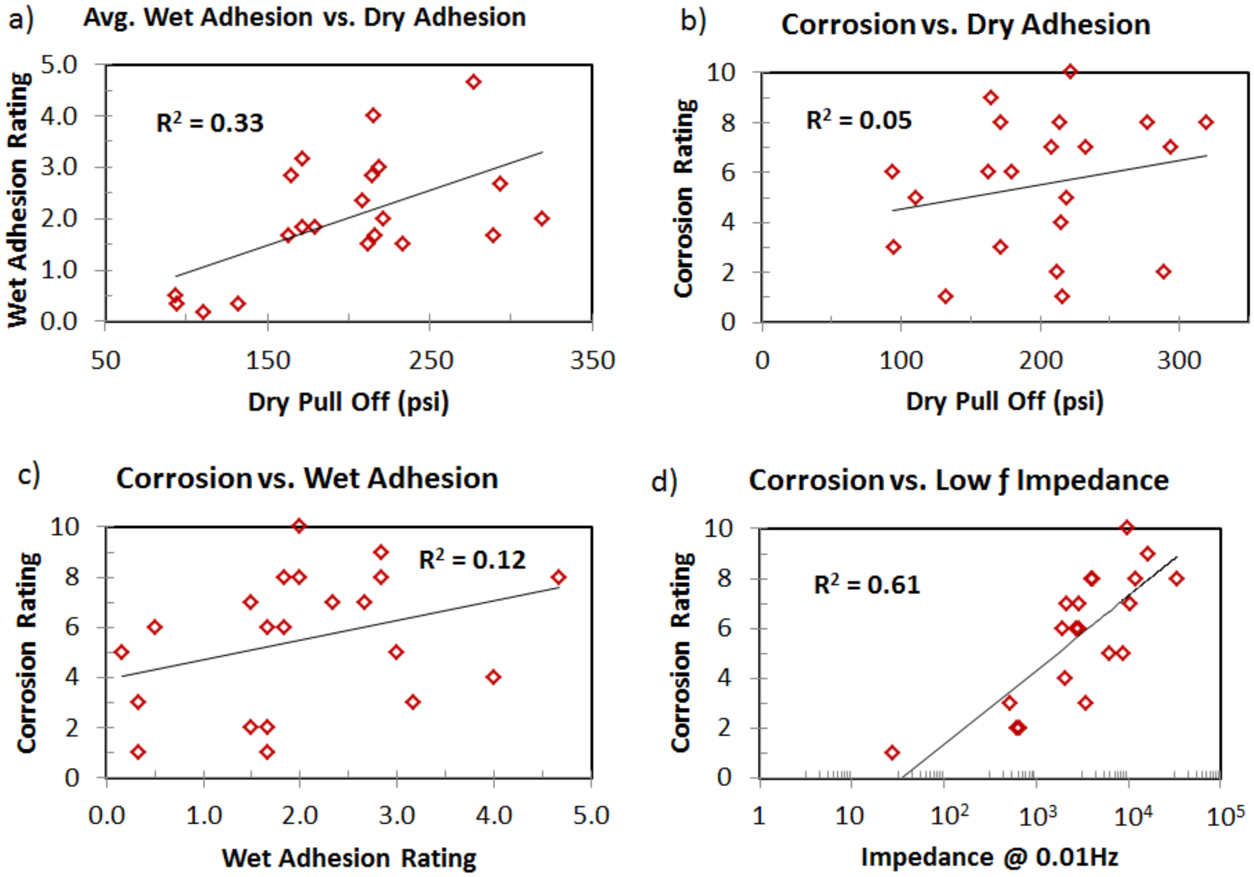

Figure 10: Correlation of physical properties - a) dry pull off adhesion vs. avg. wet adhesion, b) corrosion resistance vs. dry pull off adhesion, c) corrosion resistance vs. avg. wet adhesion, d) corrosion resistance vs. low frequency impedance (0.01Hz, 24hr immersion)

Dry and wet adhesions were moderately correlated, with initial strength of dry adhesion explaining a small portion of the wet adhesion data. However, when the variability in the dry adhesion test is considered, the correlation is not statistically significant. 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.

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 1 week. However, 1 week, or 168hrs, 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 water vapor permeability, O_2 permeability, liquid water uptake, and resin acid number fit into the corrosion model. 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 & Conclusion

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 (<50g/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 24hrs of application (Figure 11). Additionally, the corrosion resistance (Figure 12) surpassed that of most previously evaluated prototypes and delivered 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.

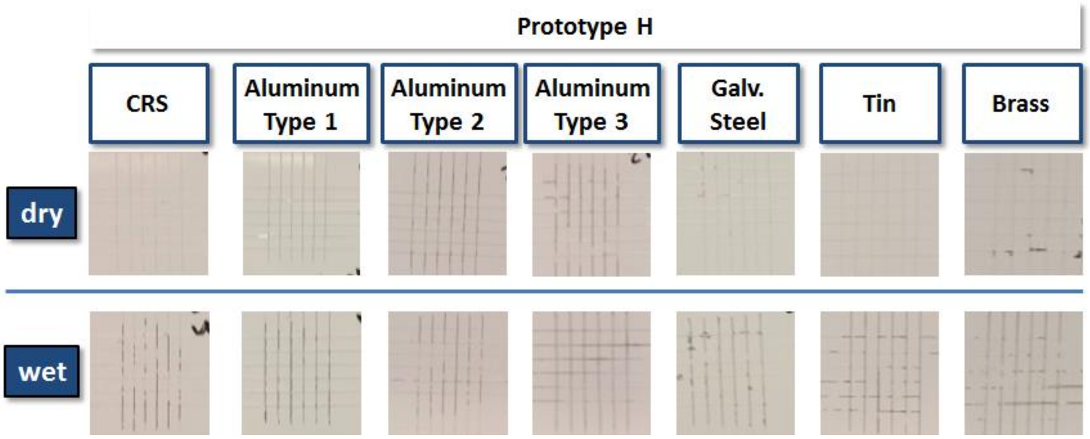

Figure 11: 24hr wet and dry crosshatch adhesion of Prototype H across a variety of metal substrates

Figure 12: 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.

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