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Adhesion Evaluation of Duplex Paint System for Sustainable Infrastructure

Sze Yang[1]; K. Wayne Lee[2]; Chen Lu[3]; Maureen Mirville[4]; and Anthony Parham[5]

Abstract. Organic paints are applied to galvanized or metalized steel surfaces in a duplex system, which is potentially more sustainable than the zinc-rich primer/steel system. A series of experimental tests were performed to measure and investigate adhesion strengths on three different types of roughened zinc surfaces. The contact angles were also measured for freshly formulated liquid paints on the roughened zinc surfaces to test if there is a correlation between the paint wetting property and the adhesive strengths. By comparing duplex system and zinc-rich primer/steel qualified North East Protective Coating (NEPCOAT) panels, it was found the paint adhesion of duplex system is as strong as the zinc primer/steel panels based test results. It was also found that adhesive strengths depend on the match between the paint and type of roughened zinc surfaces. The measurement of liquid paint wetting properties indicates small contact angles correlate with stronger pull-off adhesive strength. The authors of this study suggest that contact angle/strength correlation could be useful as a tool for optimizing the match between paints and the profiled zinc surface.

KEY WORDS: Paint adhesion, Galvanized steel, Metalized steel, Duplex system, Paint adhesion, Paint wetting, Bridge painting.

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Introduction

For many highway transportation steel structures, a metallic zinc coating is applied to the structural steel to act as a sacrificial layer for corrosion protection. Zinc is applied to steel in three ways – by zinc-rich primer paint, by metalizing (where hot zinc is sprayed onto the steel surface), or by galvanizing (where the steel part is immersed in a molten zinc bath and a zinc layer on the steel).

Paints are often applied to the zinc-coated steel surfaces for additional corrosion protection and for an aesthetic color finish. The system of dual protection of steel structure with zinc and paint is called the "duplex system". Although the corrosion protection of steel is regarded to be equal or better than that of the zinc-primer paints on bare steel, the frequent sights of peeled off paints on duplex systems lead to a general impression that it is harder to achieve a good paint adhesion on metallic zinc-coated steel surface than the traditional zinc primer coated bare steel surface. In this project the authors compared the pull-off strengths of painted panels of both types with the intent to show that the duplex system can perform as well as the zinc-rich paints on steel if the zinc surface is roughened and the pairing between paint and substrate is properly chosen.

The coating industry had long recognized that paint adheres poorly on a smooth metallic zinc surface formed by hot-dip galvanizing. A freshly galvanized zinc surface is shinny and smooth. Paint adhesion on the shinny surface is poor. The zinc surface needs to be profiled (or roughened) to provide a “bite” between the paint and the zinc/steel surface. Roughening by blast profiling and mechanical grinding are two methods used in commercial galvanizers and painters. Since the metallic zinc layer is relatively thin, the roughening process for galvanized steel is somewhat delicate.

Thermal spray of molten zinc droplets onto steel surface (a process known as zinc metalizing) is increasingly used as an alternative to hot-dip galvanizing. The sprayed-on molten zinc droplets result in naturally rough zinc surface so there is no need for the additional step of roughening. The metalized test panels (labeled as M0 test panels) were tested along with the galvanized/blast profiled test panels (labeled as Gb0 test panels) and the galvanized/mechanically-roughened panels (labeled as M0 test panels) in this study for comparisons. The NEPCOAT qualified zinc-rich primers (labeled as Z test panels) on bare/blasted steel were tested as a benchmark to compare with the three types of roughened metallic zinc surfaces. Because of the space limitation the results are not discussed here in details. The main conclusion from the comparison with the three types of roughened zinc surfaces with the zinc-rich primer benchmark is that the pull-off strengths are strong and comparable as long as the liquid paint droplet contact angles are smaller than a certain threshold. The focuses of this report are (1) the comparison of the pull-off strengths on three different roughened zinc surfaces, and (2) the verification that low liquid paint contact angle correlates with strong pull-off strength of the cured paints. The adhesion tests were performed on coatings cured less than 1 month old. The long-term salt-spray and electrochemical impedance studies on these test panels have not been done for this paper. In this paper only the adhesion tests before weathering are reported.

In the present study three different types of zinc-on-steel substrates were prepared for painting:

1. Galvanized and blast roughened test panels (abbreviated as G0b substrates),
2. Galvanized and mechanically roughened test panels (abbreviated as G0m substrates), and
3. Metalized (thermal sprayed zinc on steel) panels (abbreviated as M0).

The wetting properties of different profiled zinc surfaces have not been studied previously, even though the conventional wisdom shared among painters is that if the paint beads up (large droplet contact angles) the paint will not adhere well. One of the objectives of this study is to experimentally measure the wetting properties of a variety of paints on three differently roughened zinc-on-steel surfaces and to correlate with the adhesive strength of the coating after curing. In the field of surface science the liquid droplet contact angle on a solid surface is often used as an indicator for the extent of wetting. In 1964 Zisman (Zisman 1964) discussed the reasons why a small contact angle indicates efficient wetting of the liquid adhesive on solid surfaces, and why wetting of paint is a prerequisite for strong adhesive bonding.

A roughened zinc surface is potentially beneficial for stronger paint adhesion for the following reasons: (1) Roughness increases metal surface areas for paint molecules to physically adsorb or chemically bond to the metal atoms. (2) The surface roughening processes create channels, the capillaries, and the pores. Paint penetration into the channels, capillaries and pores creates mechanical interlocking that interrupts crack propagation at the interface. (Zisman 1964, Petrie 2012).

These benefits afforded by zinc surface roughening are realized only if the liquid paint wets the channels, the capillaries and the pores. Since a small liquid paint contact angle indicates that the liquid-solid attractive force is stronger than the solid-air attractive by the paint resin could create mechanical interlocking. Although the roughened Since molecular contact (within 5 Å, or $5x10^{-8}$ cm) is required for adsorption and chemical bonding between the cured paint It also provides anchor spots for the dried paint to mechanically lock onto the surface. These advantages would not materialize if during the painting process the liquid paint sprayed on the surface could not wet and penetrate the roughened surface. If the liquid paint does not wet the nukes and crannies of the roughened zinc surface, it will trap air between the paint and zinc interface. With the undesirable air-gap between the coating and the metal surface the physical adsorption and chemical bonding would not take place, and thus the potential binding sites are underutilized. Furthermore, the air gaps, even microscopic in size, become the seeds and links to enhance the interfacial crack propagation that is a likely reason for the frequent sight of the peeling off of paints on galvanized or metalized steel structures.

The attractive force between the liquid molecules and the molecules on the zinc surface (a mixture of metallic zinc, zinc oxide, zinc hydroxide, and surface contaminants) is the driving force for wetting and spreading of a liquid droplet on the surface. A strong attractive force at the liquid-solid interface flattens the droplet to decrease the contact angle θ. The balance of the forces can be derived with the thermodynamic principle that minimizes the Gibb’s Free Energy of the system. The relevant material properties are the surface tensions for three different interfaces, γ_{LV} for the liquid/vapor interface, γ_{SV} for the solid/vapor interface, and γ_{SL} for the solid/liquid interface. The spreading coefficient, $S \equiv \gamma_{SV} - \left(\gamma_{SL} + \gamma_{LV}\right)$, is an index for flattening and spreading of the liquid droplet (de Gennes 1985). If S < 0, the liquid droplet partially wets the solid surface with a finite contact angle θ to form a liquid cap. The contact angle decreases when the spreading coefficient approaches zero. A liquid droplet completely spreads to wet the solid surface when the contact angle is zero and S = 0.

A droplet (e.g., Mercury) on a flat surface (e.g., glass) beads up if S is greater than zero. In our test panels the surface are rough, not flat. In some special cases of this study the paint droplets were found to bead up with high contact angles. The reason for the beading of the paint droplet is different from that of the Mercury-on-glass system. It is due to the super-hydrophobic effect on certain roughened surface (Chow 1998). For $S \leq 0$, the contact angle θ are related to S according to the Young-Dupre equation (Bonn 2009).

$$S_{LV} = \gamma_{SV} - \gamma_{LV} - \gamma_{SL} \xrightarrow[\gamma_{SV} - \gamma_{SL} = \gamma_{LV} Cos\theta]{Young's\ equation} \gamma_{LV}\left(\cos\theta - 1\right) \qquad (1)$$

Equation (1) shows that wetting of the surface is favored when the value of the surface tension γ_{LV} for the liquid-vapor interface is small, and the contact angle θ is small.

In the present study the authors address following questions: Would one method of profiling (surface roughening) more advantageous than the other method? How would the adhesive strength of the paints on profiled galvanized steel compare with the metalized zinc surface?

For the organic paints, 4 paint systems from the North East Protective Coating (NEPCOAT, http://www.nepcoat.org/qualprod.htm) qualified list B were used. In addition to the NEPCOAT paints, a commercial epoxy liquid sealer for zinc-metalized steel. All paints were formulated at the same commercial paint coating company, and test panels were spray painted with the formulated liquid paints immediately after the formulation (including the “sweat” times if applicable). The zinc coatings were done on the same day of the painting work.

It is generally believed that good liquid paint wetting on a substrate surface is important for strong adhesive strength of the cured organic epoxy coating. There is no doubt this conventional wisdom holds true for the same formulation of paint on the same type of substrate surface. For a single pair of paint/surface poor wetting is a result of improperly cleaned surface. In this study 5 different paint formulations and 3 different profiled zinc surfaces were used. This allows the authors to investigate the question of whether there is a correlation between wetting and the adhesive strength across the different choices of paint/surface pairs. If such correlation exists, could one use the data to optimize the adhesive strength by matching a specific paint with one of the profiled surfaces (metalized, galvanized and mechanically roughened, or galvanized and blast profiled)? Fortunately, the experimental results suggest this type of paint/surface matching might be possible and beneficial. In this study the contact angle of freshly formulated liquid paint droplet on the profiled zinc surface were used as an index for paint/surface wetting property (Ziesman 1964). The pull-off strength of the cured paint were tested according to the ASTM D4541 standard procedure.

Experimental Works

Test Panel Preparation and the Work Plan

Steel Base Panels: The steel test panels were purchased from KTA-Tator Corp (Pittsburgh, PA) The dimension of the cold-rolled steel was 4” x 6” x ¼” in, and two types of base panels were used for this study. Type A panel is a steel plate with a U-shaped “channel” welded perpendicularly at one end of the panel to emulate a structure with welded joints. Each panel has a ¼ in. mounting hole located near the top end of the panel. Panels were identified via three-digit number inscribes (or stamped) in the panel, top front face. Type B base panel was a flat rectangle plate. The diagrams showing the design for the steel base panels are shown in Fig. 1.

Both types of steel panels underwent the following processes for coating with zinc metal and for profiling the surface: (1) they were coated with metallic zinc by either galvanizing or metalizing, and (2) the galvanized plates were roughened by either blasting or by mechanical grinding to produce a profiled zinc surface.

Galvanizing were performed by Duncan Galvanizing, Everett, MA and V&S Galvanizing, Taunton, MA. Galvanizing was performed according to ASTM A123 dry kettle process, no water quenching, no chromate conversion. Duncan supplied galvanized test panels roughened by mechanical profiling. V&S supplied galvanized test panels roughened by sweep blasting according to the respective ASTM standards.

The thickness of zinc coating by galvanizing ranges from 3.0 to 4.0 mil with RMS thickness at 0.4 mil. The roughness profile for galvanized zinc surface is between 1 to 2 mils.

The thickness of zinc coating by thermal spray is 6 to 10 mils. The surface of thermal sprayed zinc is porous with internal channels of complex structures.

After the surface profiling is completed, the Type A and Type B panels were used for different purposes. The Type A panels were painted with 4 different commercial paint systems from the NAPCOAT qualified list B (North 2016) to produce panels for adhesion strength tests. The Type B panels were used for the measurement of the wetting property of liquid paint on the profiled zinc surface. All test panels reported here are freshly galvanized, roughened and spray painted on the same day. The commercial paint formulations were prepared and spray-painted by Boyed Coatings Research, Hudson, MA. The contact angle measurements were performed on Type B panels using the same freshly formulated paint applied to Type A panels. The contact angle measurements were measured at the same time when the spray paintings were performed.

The pull-off strength tests of the cured paints were performed according to the procedure of ASTM D4541 using a PosiTest AT-M tester. The X-cut adhesive tape tests were performed according to the procedure of ASTM D3359.

Zinc Coating on Steel Test Panels

Galvanized test panels were prepared per ASTM A123 by Duncan Group, Everett, MA, and by V&S Galvanizing, Taunton, MA. Metalizing was performed per SSPC-CS23.00/AWS C2.23M/NACE No. 12 Specification for the "Application of Thermal Spray Coatings (Metalizing) of Aluminum, Zinc and Their Alloys and Composites for the Corrosion Protection of Steel". The metalizing was performed by Falmer Thermal Spray, Salem, MA.

In addition to test panels a control group of test panels named Group Z were tested for comparison. The Group Z panels were not galvanized or metalized but were painted with zinc rich organic primers as the zinc containing layer. The organic zinc primers were selected from the list of NEPCOAT approved list of primers for bare steel. The organic zinc primers were applied on the control steel panels according to the technical specification from the zinc primer paint manufacturers.

Preparation of Surface Profiled Zinc Metal Substrates

The photographic images and test data of the Type A test panels after the pull-off and x-cut adhesion tests were documented in a supplemental report NETCR93 available from New England Transportation Consortium (NETC) (Yang et al. 2013).

Test Panel Group G0m: The G0m zinc coated metal substrates were galvanized steel profiled by mechanical grinding of the zinc surface to produce surface roughness.

The galvanizing and mechanical profiling of zinc surface was performed at a plant D. The galvanizing and mechanical profiling of the surface were performed on the same day. This group of test panels were labeled as group G0m, where "G" signifies "Galvanizing", "0" signifies zero delay, and "m" signifies "mechanical profiling".

Test Panel Group G0b: G0b is a group of galvanized steel profiled by sweep blasting to produce rough surfaces. The galvanizing and blast profiling process were performed by another plant V, using aluminum oxide grit to produce a profile of 1-2 mils.

Galvanizing and blasting were performed on the same day (less than 3 hours of delay). This group of test panel is designated as group "G0b". In this group name, "G" signifies galvanizing as the process of coating zinc, "0" signifies zero delay (within the same day, less than 3 hours) between galvanizing and profiling of the surface, and "b" signifies the use of blasting as a means for surface roughening.

Test Panel Group M0: For the group of M0, zinc coated steel substrates were produced by thermal spray of molten zinc particles on steel. Since the surface of the zinc-metalized steel is rough and porous no further surface profiling was required. The zinc metalized steel test panels were processed by a metallizer F, using 99.99% zinc wire thermal sprayed over steel panels blasted with aluminum oxide grit to produce a 2 mil profile.

The code name "M0" was designated for this group of test panels, where "M" signifies the "metalizing", and "0" signifies zero delay in surface profiling. There is zero delay for profiling because the rough surface is an inherent property of the metalized surface.

Test Panel Group Z:

The authors were aware the importance of the inorganic zinc primers as specified in NEPCOAT qualified list A. In this specific research project the authors used organic zinc primer in accordance with the suggestion of the technical committee of the sponsoring agency, NETC.

A set of panels containing organic zinc rich primer was prepared as a reference for comparing with the galvanized and the metalized steel test panels. The steel panels were white blasted before application of the zinc-rich primer. The code name “Z” signifying “Zinc rich organic primer” were given for this group of test panels.

Fabrication of the Galvanized and Metalized Test Panels

Our research team delivered the steel panels to the zinc coating facilities on the day prior to the zinc coating event. Plants D and V performed the galvanization in the morning following the date of steel panel delivery. The measured thickness of zinc coating was in the range of 3.0 to 3.7 mil.

For test panel groups G0m, and G0b, the galvanizers performed the mechanical or blast profiling on the same morning of galvanizing. Researchers from the University of Rhode Island (URI) picked up the zinc-coated panels before noon on the day of the coating event. URI researchers then transported the zinc coated and surface profiled metal plates to paint shop B at noon of the same day. Workers at paint shop B started mixing two-part epoxy paints and begin spray painting on the Type A zinc coated metal substrates in the early afternoon of the same day. Portions of the freshly mixed liquid paints were brought to a room in paint shop B where the URI researchers measured the wetting and spreading properties of small paint droplets (with volume about 1 μL) on zinc coated and profiled Type B test panels prepared from the same batch of galvanizing or metalizing process. The shape parameters of the droplets were measured as a function of time using a goniometer. The parameters recorded include the contact angle, the height and the diameter of the liquid/solid contact area.

For test panel group M0, a metalizer F coated zinc metal on Type A steel substrates by thermal spray during the morning. The zinc coating thickness was 6 – 10 mils according to SSPC-PA2 specification. The URI researchers picked up the metalized panels at noon and brought them to paint shop B at noon of the same day.

Application of Paints on Metal Substrates

Paint Systems Coated on the Test Panels: Five systems of commercial paints from the NAPCOAT list B (North 2016) were applied to the Type A test panels. The components of these 5 paint systems are described in Table 1. The code names C, I, S1, S2 and S3 were adopted in this paper as the abbreviations for the paint systems.

Paint Systems Coated on the Control Panels: The control panels have the same systems of the Intermediate and the Finish (Top) paints as those used for the test panels but used an organic Zinc-Rich Primer from the NEPCOAT approved list of primers for bare steel. The zinc rich primers used for control Panels are listed in Table 2. The coated control panels were labeled with a code starting with Z signifying the zinc-rich primer on steel surface. The control panels as Z-C, Z-I, Z-S1, and Z-S2 were used to signify the paint system used for fabricating the zinc-rich primer test panels

The pull-off test result: illustrative examples: Pull-off strength tests were performed according to the procedure of ASTM D4541 using PosiTest AT-M. Figure 2 shows the pull-off tester and the test panels.

Figure 3 shows a photograph of the pulled-off dolly (at left) and a test spot (at right) from Test 1 of Panel #641. The Pull-off Strength was 2,241 psi measured with the PosiTest Pull-off tester. The dolly was placed on the test panel near the test spot. Because the dolly surface is about ¾ in. closer to the lens of the camera, it appears to be larger than the test spot.

Figure 3 shows the coexistence of two kinds of break interfaces. The green colored area, with about 80% of the dolly surface coverage, shows coherent break within the Top paint. The grey area on the left of the dolly surface and at the peripheral area of the island at the right of the dolly surface is judged as the cohesive break within the intermediate paint. The middle region on the island at the right shows spots of shiny reflection. This shiny and flat region is the contacting interface between the intermediate paint and the galvanized zinc surface. This shinny region (estimated to be about 10% of the surface of the dolly) is recorded as the adhesive break between the intermediate paint and the Galvanized Zinc surface.

Figure 4 shows another example of the image of a Pull-off Test dolly and test spot for a zinc metalized steel substrate. This picture shows that the break occurred at the epoxy/zinc interface. The pull off strength was much lower.

An example of the pull-off strength result for a given substrate (e.g. G0m) coated with one of the paint systems (e.g., I) is shown in Figure 5. Typical standard deviation is 250 to 300 psi for the pull-off strength measurements on a specific substrate-paint pair. For example the average strengths (±std dev) for G0m-I and M0-I are 2525 (±260) psi and 1094 (±300) psi. The difference in strengths between different types of zinc surface is significantly larger than the standard deviation of the strength measurement.

Measurement of Contact Angle of Liquid Paint on Profiled Surfaces of Zinc Galvanized and Metalized Steel

A goniometer (Ramé-Hart Model 200) was used to measure the wetting properties. During the test, a small droplet (about 1 μL) of freshly formulated paint were placed on the surface of a profiled Type B test panel. A camera in the instrument was used to record the image of the droplet and the interface as a function of time. A software program "DROP" was used to analyze the shape of the contacting interfaces and to compute the best-fit contact angle.

The information about the wetting property of a liquid paint on a zinc-coated surface was obtained by measuring the interfacial contact parameters (θ = contact angle, h = height of liquid cap, d = diameter of the liquid cap) of the droplets as a function of time. For some liquid/surface pairs a 10 seconds measurement was sufficient. For some other liquid/surface pairs, the useful data is contained in the parameters as a function of time for 20 minutes duration.

Contact Angle Measurement Results

A typical example of the contact angle measurement was first examined. This initial discussion serves the purpose of familiarizing the reader with the measured data and their implications. Figure 6 shows a time sequence of the image of a droplet on a profiled zinc surface. In this example, a droplet of the fresh liquid paint C was placed on a G0b surface (Galvanized, same day profiling/coating, blast profiled) at t=0 sec. The pictures show the image of the droplet at 2, 6, 12, 20 and 68 seconds, respectively. All contact angles were measured as a function of time t after the initial liquid drop fell on the zinc surface. The θ vs. t curves are available from NETC achieve. By examining all time evolutions of the droplet images the contact angles at t=6 second on the θ vs. t curves were used for comparison among different paint/substrate systems. At this point of time the contact angles have better reproducibility and the change of angles after t=6 sec were found to be small enough to be neglected.

The figure shows that the contact angle is less than 45^{o} at t=6 sec which means significant attractive force between the liquid paint and the surface. The contact angle at t=6 seconds was used as a measure of the interfacial interaction. The reason for the 6-sceond delay is that for some more viscous paints, the t=0 seconds droplet had not yet reached mechanical equilibrium immediately after the initial impact at the surface.

The contact angle and the droplet height h continued to decrease over time. The diameter of the cap expanded. This time sequence revealed another aspect of the wetting property, i.e., the spreading of the paint liquid on the surface.

By measuring the height (h), the width (d) and the contact angle simultaneously the total volume of the liquid droplet were calculated as a function of t for the spreading of the liquid paint. For the droplet shown in Figure 6 the volume of the droplet is nearly the same at t=68 sec as that at t=0 sec. This means that although the liquid paint was spreading, the paint was not absorbed into the surface voids. This implies that the profiled surface does not have microscopic channels that siphon away the paint by capillary action. Or, if there were microscopic cavities under the surface, the paint was not penetrating into the cavities as time t lapsed

For droplets with slower rate of change, the photographed images as a function of time were analyzed using an image analysis program. For fast changing droplets on the surface the "auto run" mode of the goniometer were employed to capture the changes in the droplet width and height parameters without saving the photographed images.

Discussions

Experimentally Measured Correlation between Pull-off Strength and the Liquid Paint Contact Angle

Table 3 shows the average pull-off strength and the liquid paint contact angle (at t = 6 sec) for different subgroups of coatings. The subgroups are arranged according to the order of the average pull-off strength. It can be seen that for most of the test panels, the coating systems of

"Strong" pull-off strength defined in Table 3 show contact angles in the range of 30 to 45 degrees (with an exception for G0b-S2 that has angle of 54 degree). The coating systems with "Medium" strength show contact angles scattered (35, 106 and 82 degree). The coating systems with "Weak" strength show contact angles in the 60 to 100 degrees. Table 3 shows the average contact angles for the NEPCOAT epoxy paints (C, I, S1 and S2) on the metalized zinc surface (M0) are large (60 – 100 degree). The liquid droplets on the surface beaded up with images similar to that of water droplets on lotus leaves. Such phenomenon is not observed for organic liquids on smooth surfaces. It is only possible when the surface was microscopically porous for specific liquid/surface interactions (Wenzel 1936; Cassie and Baxter 1944). When the contact angles exhibit "lotus effect" (Spori et al. 2008) the paint wetting is poor and the corresponding pull-off strength is not high (in the 1000 psi range). Table 3 also shows a contrasting example in the surface-paint pair of M0-S3. In this case the same porous surface M0 absorbs a liquid droplet of paint S3 (a sealer) within 2 seconds and the contact angle is 0 at our preset measuring time at 5 seconds. In this case the surface-paint match leads to low contact angle (0 degree) and strong pull-off strength (2,023 psi) due to the same interaction but at a different regime (Wana 2011).

The general trend is that the lower contact angles correlate with stronger pull-off strength. This means that despite the high possibility of interfering factors that reduce the correlation, our experimental data do show a certain degree of correlation.

Figure 7 shows the scatter plot of Pull-off Strength as a function of the contact angles for all the data pairs of Table 3. A sloped straight line was inserted in Figure 7 as a visual guide indicating that the smaller the contact angle, the higher the pull-off strength,. The trend line with negative slope is not intended to suggest a linear fit of the data. A linear fit would give a relatively poor R-squared value of 0.49 (with the corresponding Parson's correlation at -0.7). It is not surprising that the data points are scattered because of the complexity of the system and the measurements. The roughened surfaces are not microscopically uniform in roughness. Although the painting and contact angle measurements were performed near the time of galvanizing/metalizing (within 4 hours) the fresh zinc coatings on steel will have started oxidation reactions in the air. Further more, different paint formulations have different solvent contents and resin contents thus influencing the flow viscosity. What the authors found was that despite all other influences the contact angle still comes through as an indicator for the pull-off strength. A small contact angle of a liquid paint on a particular surface correlates with high pull-off strength. The contact angle is the most accessible measurement to test the paint/surface attraction but is not necessarily linearly correlated with the pull-off strength. The work of adhesion between the paint and the surface is likely to be more linearly proportional to the pull-off strength and it is dependent on the contact angle. But the work of adhesion is not directly measurable and need other details of the surface and the paint before one can calculate the values.

The preceding paragraph gives reasons for contemplating a non-linear dependence of the strength vs. θ plot. A grossly simplified non-linear correlation is a step-function. The same data used in Fig 7 were displayed in Fig. 8 except that a step function instead of a sloping linear line. The step-function line is suggestive for a threshold of contact angle. Below certain threshold contact angle (in this case ~50 degrees) the pull-off strength is high, and above that threshold angle the pull-off strength is lower. The step function line is drawn to suggest, but not to prove the existence of two clusters of data. However, anecdotal evidences in the details of the pull-off experiment provide some support to this idea. During the pull-off strength measurements not only recorded the strengths (psi) but also photographed the test spots (along with the dollies for performing the pull test). Fig 3 shows that the pair of surface-paint (G2b-I) as an example of low liquid contact-angle (35^o) and high pull-off strength (2258 psi). The break photographed after pull test for G2b-I (Fig. 3) indicates cohesive break occuring mainly within the cured paint (at the top/primer paint interface, not at the primer/zinc interface). In contrast, Fig 4 shows evidence of the presence of air gap due to poor liquid paint wetting. The photograph of the break surfaces for the same paint (I) on a different type of surface M0 shows adhesive break at the primer/zinc interface. The measured liquid contact angle was high (75^o), indicating the lack of wetting and the pull-off strength was low (1,262 psi). The photograph in Fig 4 shows no paint left in the pores and the channels of the metalized rough surface after pull-off. It is likely that the pores and channels were not wetted by the liquid paint when the liquid formulation was sprayed on. This is consistent with the high contact angle (75^o) and the lack of wetting. The lack of liquid paint wetting leads to the presence of air gap, and in turn the cause for poor pull-off strength (1260 psi). The photographs of the break surfaces were recorded in our NETC report. Upon examination of the photographs it was found that almost all the substrate-paint pairs belonging to the upper-left cluster (small θ, high strength) of Fig 8 when tested for pull-off strengths show breaks of the type similar to Fig 3 (cohesive break). Most of the substrate-paints of Fig 8's lower-right cluster (larger θ, lower strength) of Fig 8 show break similar to Fig 4 (adhesive break). These coincidences suggests plausible hypothesis for a threshold contact angle but further tests are needed to verify this hypothesis.

Summaries and Conclusions

1. Adhesive strength of duplex paint system is competitive with the zinc-primer/bare steel system.

The NEPCOAT qualified list of paint systems were originally tested for application of zinc-rich primers on bare steel substrate. In a duplex paint system the zinc-rich primer is replaced by a metallic zinc coating on the steel substrate. One question of interest was whether the intermediate and top paints in a duplex paint system would have adhesive strength comparable with that of the original NEPCOAT paints on bare steel.

Based on the comparison between the control panels (the Z panels with the organic zinc-rich primers from NEPCOAT List B) and the test panels (the G0m, G0b, M0 and G2b panels), the test results show that the initial pull-off strengths of the duplex system are comparable with the performance of NEPCOAT system on bare steel surfaces. The experimental test results also suggest that, in most cases, the intermediate epoxy paints listed in qualified list B of NEPCOAT are suitable as a primer on the galvanized surface with initial pull-off strengths in the 1,500 to 2,500 psi range. However, the same epoxy paints when paired with the metalized zinc surface the pull-off strength is not as strong (in the 900 to 1,100 psi range) although higher the NEPCOAT passing score of 600 psi.

In the literature there is a perception of poor adhesion of paint on the galvanized steel. The experimental results (from an admittedly small number of tests) suggest that there is no reason to expect poor adhesion in all duplex paints. It was found that the pull-off strengths reach the 1,500 to 2,500 psi range when the zinc surface is profiled with ordinary commercial procedure. The unsightly peeling of paints from duplex painted structures is likely the result of inadequate surface profiling of zinc coating of galvanized steel.

2. Adhesive strengths of a specific paint depends on the choice of a specific type of roughened zinc surfaces

All paint systems show "strong" performance in most of the profiled zinc substrates including the followings:

G0m substrate:	Paints I and S2
G0b substrate:	All paints show "strong" pull off strength. Paints I, C, S2, S1.
M0 substrate:	Paint system S3.
G2b substrate:	Paints C, S1 and I.

One paint system (S3) on the metalized substrate (M0) show clear advantage over the paint systems C, I, S1 and S2 (see Table 3).

3. A Sealer (S3) for M0 substrate provides significantly better adhesion.

Based on the data for the thermally sprayed zinc test panels (M0, metalized, painted on the same day as metalizing) the authors suggest that sealer should be always used for the Duplex Paint System on zinc-metalized surfaces.

The test results displayed in Table 3 strongly support our recommendation. The data show that the average pull-off strength for the S3 paint system (containing a sealer) is 2,023 ± 480 psi. The pull-off strengths for the other NEPCOAT epoxy intermediate paints C, I, S1 and S2 are clustered in the range between 1,079 to 1,178 psi, with estimated error bars at about 200 psi.

The advantage of using a sealer for metalized steel has been recognized and has been written into state Department of Transportation (DOT) paint specifications (e.g., Rhode Island DOT metalizing specification). Thus the finding in this study is not surprising. But our data showed that the improvement in performance due to the use of sealant is significant. This study also showed the reason for the difference in performance.

Based on the empirical data (admittedly a small set of data) and the understanding gained from the contact angle measurement, the authors of this study recommend that sealers be always used for the zinc metalized surface. The NEPCOAT intermediate paint could be replaced by a sealer (which is how our M0-S3 panels were fabricated) or be applied on top of the sealed metalized surface.

4. The correlation between the pull-off strengths and the contact angles.

We found there is a negative correlation between the contact angle of a liquid paint droplet and the pull-off strength of the cured paint. As shown in Figure 7, a higher pull-off strength of a test panel is associated with a smaller contact angle measured for the corresponding intermediate paint droplet on the profiled zinc surface. This observation suggests the wetting/adhesion correlation is not limited to a single pair of paint/surface but the correlation exists for a variety of paint/surface pairs formed from 5 different epoxy paints and 3 different types of roughened zinc surfaces. The data points on a pull-off strength vs. contact angle plot are somewhat scattered but the connection between the low contact angle and strong adhesion is supported by the data. There is a correlation but not a strong correlation. The imperfect correlation is not unexpected in considering both the materials (paints, roughened surfaces) and the tests (contact angle and pull-off strength) are influenced by a number of other factors. The data show that liquid paint wetting plays important role in the adhesive strength of the paint.

The correlation between the contact angle and pull-off strength is probably not a linear function judging from the clustering of high-strength and low-angle points. More tests are needed to test this hypothesis.

The number of tests performed in this project is not large enough for us to be confident about the applicability of the contact angle/strength correlation in optimizing the paint/surface pairing. Our data suggest this type of experimentally determined correlation could be a useful method for selecting an optimized paint/surface match.

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Table 1. Paint Systems for Galvanized or Metalized Test Panels

Paint Systems	Primer	Intermediate	Finish
Paint System C	galvanizing, or metalizing, or Carbozinc 859	Carboline 888 Epoxy	Carboline 133 LH Aliphatic Polyurethane
Paint System I	galvanizing or metalizing, or Interzinc® 52	Intergard 345 Epoxy	Interthane 870 UHS
Paint System S1	galvanizing or metalizing, or Zinc Clad III	Macropoxy 646 Fast Cure Epoxy	Acrolon 218 HS Acrylic Polyurethane
Paint System S2	galvanizing or metalizing, or Zinc Clad III	Recoatable Epoxy Primer Series B67	High Solids Polyurethane Series B58
Paint System S3	Metalizing	Macropoxy 920 Sealer	Acrolon 218 HS Acrylic Polyurethane

Note: The paint system S3 was applied to substrate M0 only. It was not used for other metal substrates.

Table 2. Paint Systems for Control Panels

Paint systems on test panels	Primer	Intermediate	Finish
Test panels subgroup Z-C	Carbozinc 859 Organic Zinc Rich Epoxy Primer	Carboline 888 Epoxy	Carboline 133 LH Aliphatic Polyurethane
Test panels subgroup Z-I	Interzinc® 52 Epoxy Zinc Rich (Green)	Intergard 345 Epoxy	Interthane 870 UHS
Test panels subgroup Z-S1	Zinc Clad III HS Organic Zinc Rich Epoxy Primer	Macropoxy 646 Fast Cure Epoxy	Acrolon 218 HS Acrylic Polyurethane
Test panels subgroup Z-S2	Zinc Clad III HS Organic Zinc Rich Epoxy Primer	Recoatable Epoxy Primer Series B67	High Solids Polyurethane Series B58

Table 3. Correlation between the Average Pull-off Strengths and the Average Contact Angles

Subgroup label	*Average Pull-off Strength (psi)*	*Average Contact Angle (degree)*	*Average score ASTMD-3359 (Ranking 1-5)*
G0m-I	2525	36	5.00
G2b-C	2502	36	5.00
G2b-S1	2389	46	5.00
G2b-I	2257	35	5.00
G0b-I	2052	37	5.00
G0b-C	2038	37	5.00
M0-S3	2023	0	5.00
G0m-S2	1988	42	5.00
G0b-S1	1815	46	4.75
G2b-S2	1742	35	5.00
G0m-S1	1650	106	5.00
G0m-C	1372	82	4.75
M0-C	1178	87	4.88
M0-S2	1103	58	4.75
M0-I	1087	75	4.88
G0b-S2	1083	54	4.75
M0-S1	1079	103	4.88