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Adhesion Evaluation of Duplex Paint System for Sustainable Infrastructure

Sze C. Yang

University of Rhode Island, syang@uri.edu

Kang-Won Wayne Lee

University of Rhode Island, leekw@uri.edu

See next page for additional authors

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Authors

Sze C. Yang, Kang-Won Wayne Lee, Chen Lu, Maureen Mirville, and Anthony Parham

1 **Adhesion Evaluation of Duplex Paint System for Sustainable Infrastructure**

2 Sze Yang¹; K. Wayne Lee²; Chen Lu³; Maureen Mirville⁴; and Anthony Parham⁵

3

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

17

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

20

21 ¹Sze C. Yang, Ph.D., Professor of Chemistry, the University of Rhode Island, Kingston,
22 RI 02881, USA (401) 874-2377, syang@uri.edu

23 ²K. Wayne Lee, Ph.D., P.E., F. ASCE, Professor and Director of RI Transportation
24 Research Center (TRC), Department of Civil and Environment Engineering, the University of
25 Rhode Island, Kingston, RI 02881 (401)874-2695, leekw@uri.edu, Corresponding author

26 ³Chen Lu, Graduate Student, Department of Chemistry, the University of Rhode
27 Island, (401) 241-9773, binbinluchen@gmail.com

28 ⁴Maureen Mirville, Research Assistant, Department of Chemistry, the University of
29 Rhode Island, (781) 724-7098, Maureen.mirville@gmail.com

30 ⁵Anthony Parham, Graduate Student, Department of Chemistry, the University of Rhode
31 Island, (508) 963-3076, antparham@hotmail.com

32

33 **Introduction**

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

39 Paints are often applied to the zinc-coated steel surfaces for additional corrosion
40 protection and for an aesthetic color finish. The system of dual protection of steel structure with
41 zinc and paint is called the “duplex system”. Although the corrosion protection of steel is
42 regarded to be equal or better than that of the zinc-primer paints on bare steel, the frequent sights
43 of peeled off paints on duplex systems lead to a general impression that it is harder to achieve a
44 good paint adhesion on metallic zinc-coated steel surface than the traditional zinc primer coated
45 bare steel surface. In this project the authors compared the pull-off strengths of painted panels of

46 both types with the intent to show that the duplex system can perform as well as the zinc-rich
47 paints on steel if the zinc surface is roughened and the pairing between paint and substrate is
48 properly chosen.

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

56 Thermal spray of molten zinc droplets onto steel surface (a process known as zinc
57 metalizing) is increasingly used as an alternative to hot-dip galvanizing. The sprayed-on molten
58 zinc droplets result in naturally rough zinc surface so there is no need for the additional step of
59 roughening. The metalized test panels (labeled as M0 test panels) were tested along with the
60 galvanized/blast profiled test panels (labeled as Gb0 test panels) and the
61 galvanized/mechanically-roughened panels (labeled as M0 test panels) in this study for
62 comparisons. The NEPCOAT qualified zinc-rich primers (labeled as Z test panels) on
63 bare/blasted steel were tested as a benchmark to compare with the three types of roughened
64 metallic zinc surfaces. Because of the space limitation the results are not discussed here in
65 details. The main conclusion from the comparison with the three types of roughened zinc
66 surfaces with the zinc-rich primer benchmark is that the pull-off strengths are strong and
67 comparable as long as the liquid paint droplet contact angles are smaller than a certain threshold.
68 The focuses of this report are (1) the comparison of the pull-off strengths on three different

69 roughened zinc surfaces, and (2) the verification that low liquid paint contact angle correlates
70 with strong pull-off strength of the cured paints. The adhesion tests were performed on coatings
71 cured less than 1 month old. The long-term salt-spray and electrochemical impedance studies on
72 these test panels have not been done for this paper. In this paper only the adhesion tests before
73 weathering are reported.

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

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

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

88 A roughened zinc surface is potentially beneficial for stronger paint adhesion for the
89 following reasons: (1) Roughness increases metal surface areas for paint molecules to physically
90 adsorb or chemically bond to the metal atoms. (2) The surface roughening processes create
91 channels, the capillaries, and the pores. Paint penetration into the channels, capillaries and pores

92 creates mechanical interlocking that interrupts crack propagation at the interface. (Zisman 1964,
93 Petrie 2012).

94 These benefits afforded by zinc surface roughening are realized only if the liquid paint
95 wets the channels, the capillaries and the pores. Since a small liquid paint contact angle
96 indicates that the liquid-solid attractive force is stronger than the solid-air attractive by the paint
97 resin could create mechanical interlocking. Although the roughened Since molecular contact
98 (within 5 Å, or 5×10^{-8} cm) is required for adsorption and chemical bonding between the cured
99 paint It also provides anchor spots for the dried paint to mechanically lock onto the surface.
100 These advantages would not materialize if during the painting process the liquid paint sprayed on
101 the surface could not wet and penetrate the roughened surface. If the liquid paint does not wet
102 the nukes and crannies of the roughened zinc surface, it will trap air between the paint and zinc
103 interface. With the undesirable air-gap between the coating and the metal surface the physical
104 adsorption and chemical bonding would not take place, and thus the potential binding sites are
105 underutilized. Furthermore, the air gaps, even microscopic in size, become the seeds and links to
106 enhance the interfacial crack propagation that is a likely reason for the frequent sight of the
107 peeling off of paints on galvanized or metalized steel structures.

108

109 The attractive force between the liquid molecules and the molecules on the zinc surface
110 (a mixture of metallic zinc, zinc oxide, zinc hydroxide, and surface contaminants) is the driving
111 force for wetting and spreading of a liquid droplet on the surface. A strong attractive force at the
112 liquid-solid interface flattens the droplet to decrease the contact angle θ . The balance of the
113 forces can be derived with the thermodynamic principle that minimizes the Gibb's Free Energy
114 of the system. The relevant material properties are the surface tensions for three different

115 interfaces, γ_{LV} for the liquid/vapor interface, γ_{SV} for the solid/vapor interface, and γ_{SL} for the
 116 solid/liquid interface. The spreading coefficient, $S = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV})$, is an index for flattening
 117 and spreading of the liquid droplet (de Gennes 1985). If $S < 0$, the liquid droplet partially wets
 118 the solid surface with a finite contact angle θ to form a liquid cap. The contact angle decreases
 119 when the spreading coefficient approaches zero. A liquid droplet completely spreads to wet the
 120 solid surface when the contact angle is zero and $S = 0$.

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

$$127 \quad S_{LV} = \gamma_{SV} - \gamma_{LV} - \gamma_{SL} \xrightarrow[\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta]{\text{Young's equation}} \gamma_{LV} (\cos \theta - 1) \quad (1)$$

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

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

134 For the organic paints, 4 paint systems from the North East Protective Coating
 135 (NEPCOAT, <http://www.nepcoat.org/qualprod.htm>) qualified list B were used. In addition to the
 136 NEPCOAT paints, a commercial epoxy liquid sealer for zinc-metalized steel. All paints were
 137 formulated at the same commercial paint coating company, and test panels were spray painted

138 with the formulated liquid paints immediately after the formulation (including the “sweat” times
139 if applicable). The zinc coatings were done on the same day of the painting work.

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

154

155 **Experimental Works**

156 *Test Panel Preparation and the Work Plan*

157 **Steel Base Panels**: The steel test panels were purchased from KTA-Tator Corp (Pittsburgh, PA)
158 The dimension of the cold-rolled steel was 4” x 6” x ¼” in, and two types of base panels were
159 used for this study. Type A panel is a steel plate with a U-shaped “channel” welded
160 perpendicularly at one end of the panel to emulate a structure with welded joints. Each panel has

161 a ¼ in. mounting hole located near the top end of the panel. Panels were identified via three-
162 digit number inscribes (or stamped) in the panel, top front face. Type B base panel was a flat
163 rectangle plate. The diagrams showing the design for the steel base panels are shown in Fig. 1.

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

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

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

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

177

178 After the surface profiling is completed, the Type A and Type B panels were used for
179 different purposes. The Type A panels were painted with 4 different commercial paint systems
180 from the NAPCOAT qualified list B (North 2016) to produce panels for adhesion strength tests.
181 The Type B panels were used for the measurement of the wetting property of liquid paint on the
182 profiled zinc surface. All test panels reported here are freshly galvanized, roughened and spray
183 painted on the same day. The commercial paint formulations were prepared and spray-painted

184 by Boyed Coatings Research, Hudson, MA. The contact angle measurements were performed on
185 Type B panels using the same freshly formulated paint applied to Type A panels. The contact
186 angle measurements were measured at the same time when the spray paintings were performed.

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

190 *Zinc Coating on Steel Test Panels*

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

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

202 *Preparation of Surface Profiled Zinc Metal Substrates*

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

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

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

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

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

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

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

228 **Test Panel Group Z:**

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

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

237 ***Fabrication of the Galvanized and Metalized Test Panels***

238 Our research team delivered the steel panels to the zinc coating facilities on the day prior to the
239 zinc coating event. Plants D and V performed the galvanization in the morning following the
240 date of steel panel delivery. The measured thickness of zinc coating was in the range of 3.0 to
241 3.7 mil.

242 For test panel groups G0m, and G0b, the galvanizers performed the mechanical or blast
243 profiling on the same morning of galvanizing. Researchers from the University of Rhode Island
244 (URI) picked up the zinc-coated panels before noon on the day of the coating event. URI
245 researchers then transported the zinc coated and surface profiled metal plates to paint shop B at
246 noon of the same day. Workers at paint shop B started mixing two-part epoxy paints and begin
247 spray painting on the Type A zinc coated metal substrates in the early afternoon of the same day.
248 Portions of the freshly mixed liquid paints were brought to a room in paint shop B where the URI
249 researchers measured the wetting and spreading properties of small paint droplets (with volume
250 about 1 μ L) on zinc coated and profiled Type B test panels prepared from the same batch of
251 galvanizing or metalizing process. The shape parameters of the droplets were measured as a

252 function of time using a goniometer. The parameters recorded include the contact angle, the
253 height and the diameter of the liquid/solid contact area.

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

258 *Application of Paints on Metal Substrates*

259 **Paint Systems Coated on the Test Panels:** Five systems of commercial paints from the
260 NAPCOAT list B (North 2016) were applied to the Type A test panels. The components of these
261 5 paint systems are described in Table 1. The code names C, I, S1, S2 and S3 were adopted in
262 this paper as the abbreviations for the paint systems.

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

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

273 Figure 3 shows a photograph of the pulled-off dolly (at left) and a test spot (at right) from
274 Test 1 of Panel #641. The Pull-off Strength was 2,241 psi measured with the PosiTest Pull-off

275 tester. The dolly was placed on the test panel near the test spot. Because the dolly surface is
276 about ¾ in. closer to the lens of the camera, it appears to be larger than the test spot.

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

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

288 An example of the pull-off strength result for a given substrate (e.g. G0m) coated with
289 one of the paint systems (e.g., I) is shown in Figure 5. Typical standard deviation is 250 to
290 300 psi for the pull-off strength measurements on a specific substrate-paint pair. For example
291 the average strengths (\pm std dev) for G0m-I and M0-I are 2525 (\pm 260) psi and 1094 (\pm 300) psi.
292 The difference in strengths between different types of zinc surface is significantly larger than
293 the standard deviation of the strength measurement.

294

295 *Measurement of Contact Angle of Liquid Paint on Profiled Surfaces of Zinc Galvanized* 296 *and Metalized Steel*

297 A goniometer (Ramé-Hart Model 200) was used to measure the wetting properties. During the
298 test, a small droplet (about 1 μ L) of freshly formulated paint were placed on the surface of a
299 profiled Type B test panel. A camera in the instrument was used to record the image of the

300 droplet and the interface as a function of time. A software program “DROP” was used to
301 analyze the shape of the contacting interfaces and to compute the best-fit contact angle.

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

307

308 *Contact Angle Measurement Results*

309 A typical example of the contact angle measurement was first examined. This initial discussion
310 serves the purpose of familiarizing the reader with the measured data and their implications.

311 Figure 6 shows a time sequence of the image of a droplet on a profiled zinc surface. In this
312 example, a droplet of the fresh liquid paint C was placed on a G0b surface (Galvanized, same
313 day profiling/coating, blast profiled) at $t=0$ sec. The pictures show the image of the droplet at 2,
314 6, 12, 20 and 68 seconds, respectively. All contact angles were measured as a function of time t
315 after the initial liquid drop fell on the zinc surface. The θ vs. t curves are available from NETC
316 achieve. By examining all time evolutions of the droplet images the contact angles at $t=6$
317 second on the θ vs. t curves were used for comparison among different paint/substrate systems.
318 At this point of time the contact angles have better reproducibility and the change of angles after
319 $t=6$ sec were found to be small enough to be neglected.

320 The figure shows that the contact angle is less than 45° at $t=6$ sec which means significant
321 attractive force between the liquid paint and the surface. The contact angle at $t=6$ seconds was
322 used as a measure of the interfacial interaction. The reason for the 6-second delay is that for

323 some more viscous paints, the $t=0$ seconds droplet had not yet reached mechanical equilibrium
324 immediately after the initial impact at the surface.

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

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

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

339

340 **Discussions**

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

342 *Angle*

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

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

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

365 Figure 7 shows the scatter plot of Pull-off Strength as a function of the contact angles
366 for all the data pairs of Table 3. A sloped straight line was inserted in Figure 7 as a visual
367 guide indicating that the smaller the contact angle, the higher the pull-off strength,. The trend
368 line with negative slope is not intended to suggest a linear fit of the data. A linear fit would

369 give a relatively poor R-squared value of 0.49 (with the corresponding Pearson's correlation at
370 -0.7). It is not surprising that the data points are scattered because of the complexity of the
371 system and the measurements. The roughened surfaces are not microscopically uniform in
372 roughness. Although the painting and contact angle measurements were performed near the
373 time of galvanizing/metalizing (within 4 hours) the fresh zinc coatings on steel will have
374 started oxidation reactions in the air. Further more, different paint formulations have different
375 solvent contents and resin contents thus influencing the flow viscosity. What the authors
376 found was that despite all other influences the contact angle still comes through as an indicator
377 for the pull-off strength. A small contact angle of a liquid paint on a particular surface
378 correlates with high pull-off strength. The contact angle is the most accessible measurement
379 to test the paint/surface attraction but is not necessarily linearly correlated with the pull-off
380 strength. The work of adhesion between the paint and the surface is likely to be more linearly
381 proportional to the pull-off strength and it is dependent on the contact angle. But the work of
382 adhesion is not directly measurable and need other details of the surface and the paint before
383 one can calculate the values.

384 The preceding paragraph gives reasons for contemplating a non-linear dependence of
385 the strength vs. θ plot. A grossly simplified non-linear correlation is a step-function. The
386 same data used in Fig 7 were displayed in Fig. 8 except that a step function instead of a
387 sloping linear line. The step-function line is suggestive for a threshold of contact angle.
388 Below certain threshold contact angle (in this case ~ 50 degrees) the pull-off strength is high,
389 and above that threshold angle the pull-off strength is lower. The step function line is drawn
390 to suggest, but not to prove the existence of two clusters of data. However, anecdotal
391 evidences in the details of the pull-off experiment provide some support to this idea. During

392 the pull-off strength measurements not only recorded the strengths (psi) but also photographed
393 the test spots (along with the dollies for performing the pull test). Fig 3 shows that the pair of
394 surface-paint (G2b-I) as an example of low liquid contact-angle (35°) and high pull-off
395 strength (2258 psi). The break photographed after pull test for G2b-I (Fig. 3) indicates
396 cohesive break occurring mainly within the cured paint (at the top/primer paint interface, not at
397 the primer/zinc interface). In contrast, Fig 4 shows evidence of the presence of air gap due to
398 poor liquid paint wetting. The photograph of the break surfaces for the same paint (I) on a
399 different type of surface M0 shows adhesive break at the primer/zinc interface. The measured
400 liquid contact angle was high (75°), indicating the lack of wetting and the pull-off strength
401 was low (1,262 psi). The photograph in Fig 4 shows no paint left in the pores and the
402 channels of the metalized rough surface after pull-off. It is likely that the pores and channels
403 were not wetted by the liquid paint when the liquid formulation was sprayed on. This is
404 consistent with the high contact angle (75°) and the lack of wetting. The lack of liquid paint
405 wetting leads to the presence of air gap, and in turn the cause for poor pull-off strength (1260
406 psi). The photographs of the break surfaces were recorded in our NETC report. Upon
407 examination of the photographs it was found that almost all the substrate-paint pairs belonging
408 to the upper-left cluster (small θ , high strength) of Fig 8 when tested for pull-off strengths
409 show breaks of the type similar to Fig 3 (cohesive break). Most of the substrate-paints of Fig
410 8's lower-right cluster (larger θ , lower strength) of Fig 8 show break similar to Fig 4 (adhesive
411 break). These coincidences suggests plausible hypothesis for a threshold contact angle but
412 further tests are needed to verify this hypothesis.

413

414

415 **Summaries and Conclusions**

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

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

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

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

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

440 All paint systems show “strong” performance in most of the profiled zinc substrates including
441 the followings:

442 G0m substrate: Paints I and S2

443 G0b substrate: All paints show “strong” pull off strength. Paints I, C, S2, S1.

444 M0 substrate: Paint system S3.

445 G2b substrate: Paints C, S1 and I.

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

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

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

452 The test results displayed in Table 3 strongly support our recommendation. The data
453 show that the average pull-off strength for the S3 paint system (containing a sealer) is $2,023 \pm$
454 480 psi. The pull-off strengths for the other NEPCOAT epoxy intermediate paints C, I, S1
455 and S2 are clustered in the range between 1,079 to 1,178 psi, with estimated error bars at
456 about 200 psi.

457 The advantage of using a sealer for metalized steel has been recognized and has been
458 written into state Department of Transportation (DOT) paint specifications (e.g., Rhode Island
459 DOT metalizing specification). Thus the finding in this study is not surprising. But our data

460 showed that the improvement in performance due to the use of sealant is significant. This
461 study also showed the reason for the difference in performance.

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

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

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

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

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

487

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504 **References**

505

506 Bonn, D., J. Eggers, J. Indekeu, J. Meunier, E. Rolley, (2009). “Wetting and spreading”, Rev.
507 Modern Physics, 81, 739-805.

508

509 Cassie, A.B.D. and S. Baxter, (1944). “Wettability of porous surfaces,” Trans. Faraday Soc.
510 40, 546.

511

512 Chow, T.S. (1998). "Wetting of rough surfaces". *Journal of Physics: Condensed Matter* 10 (27):
513 L445. Bibcode:1998JPCM...10L.445C. doi:10.1088/0953-8984/10/27/001.

514

515 de Gennes, P. G. (1985). “Wetting: statics and dynamics”, Rev. Modern Physics, 57, 827.

516

517 North East Protective Coating Committee (NEPCOAT), (2016) “Qualified Products for
518 Protective Coatings for New and 100% Bare Existing Steel for Bridges” Web page updated
519 4/2016, on-line publication url: <http://www.nepcoat.org/qualprod.htm>

520

521 Petries, E, “Fundamentals of paint adhesion” on-line article published May 22, 2012, web
522 page, [http://www.materialstoday.com/metal-finishing/features/fundamentals-of-paint-](http://www.materialstoday.com/metal-finishing/features/fundamentals-of-paint-adhesion/)
523 [adhesion/](http://www.materialstoday.com/metal-finishing/features/fundamentals-of-paint-adhesion/)

524

525 Spori, Doris M., Tanja Drobek, Stefan Zürcher, Mirjam Ochsner, Christoph Sprecher,
526 Andreas Mühlebach, and Nicholas D. Spencer, (2008). “Beyond the Lotus Effect: Roughness
527 Influences on Wetting over a Wide Surface-Energy Range,” *Langmuir*, 24, pp. 5411-5417.

528
529 Wana, Yong, Zhongqian Wanga, Zhen Xua, Changsong Liua, and J Zhang, (2011).
530 “Fabrication and Wear Protection Performance of Superhydrophobic Surface on Zinc,”
531 *Applied Surface Science* 257, pp. 7486–7489.

532
533 Wenzel, R. N. (1936). “Resistance of solid surfaces to wetting by water,” *Ind. Eng. Chem.* 28,
534 988-944.

535
536 Yang, Sze C, K. Wayne Lee, Maureen Mirville, Chen Lu, Anthony Pahram, (2013),
537 “Measurement of adhesion properties between topcoat paint and metallized/galvanized steel
538 with surface energy measurement equipment” NETCR93 Report, achieve copy available at
539 Transportation Research Center, University of Vermont. Web address:
540 <http://www.uvm.edu/trc/?s=NETC>

541
542 Zisman, W.A. (1964). “Relation of the Equilibrium Contact Angle to Liquid and Solid
543 Constitution”, in Fowkes; “Contact Angle, Wettability, and Adhesion, American Chemical
544 Society, *Advances in Chemistry*, ACS Symposium Series, Vol 43, p. 1.

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Table 1. Paint Systems for Galvanized or Metalized Test Panels

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

549 Note: The paint system S3 was applied to substrate M0 only. It was not used for other metal
550 substrates.
551

552 **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

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

<i>Subgroup label</i>	<i>Average Pull-off Strength (psi)</i>	<i>Average Contact Angle (degree)</i>	<i>Average score ASTM-D-3359 (Ranking 1-5)</i>
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