Durable Hydrophobic Coatings for Corrosion Protection

Bryan E. Koene, Rebecca Martin, Adam Goff, Jennifer Hay

Luna Innovations, 3155 State Street, Blacksburg, VA 24060; koeneb@lunainc.com

ABSTRACT

Luna has developed an exceptionally durable, transparent, fluid resistant coating for corrosion mitigation on selected metals and alloys. There have been many recent research and commercial efforts in the area of superhydrophobic or water repellent coatings that have demonstrated the ability to shed fluids quickly off of surfaces. Whereas many surface treatments and coatings have achieved the primary goal of good fluid shedding properties, they have all lacked mechanical / environmental durability, or are difficult and expensive to apply. This new polymer-inorganic hybrid coating has a unique combination of fluid repellency and exceptional toughness for improved abrasion resistance and environmental stability. The coating formulation can be easily applied in a single step by dip, flow, brush, or spray with excellent adhesion to multiple surfaces including glass, plastic, paint, and a variety of metallic materials. The coating possesses low surface energy leading to easy cleaning, rain repellency, and excellent corrosion resistance. In addition to good fluid shedding properties, the coating has significantly higher density than traditional organic polymer coatings and is electrically insulating, resulting in improved barrier properties to water and corrosive ion permeation. The protective coating has numerous uses for automotive, aerospace, marine, and industrial applications.

Keywords: hydrophobic, coating, corrosion protection

1. INTRODUCTION

Current academic and commercial research has focused on development of superhydrophobic coatings to shed water for various applications. Current coatings rely on development of a controlled morphology that results in a low surface energy. An example of a textured, superhydrophobic surface and the resultant water droplet beading behavior is shown in Figure 1.

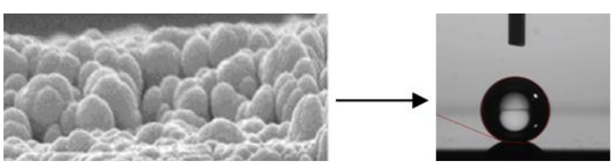

Figure 1: (Left) SEM of a material exhibiting hierarchical surface morphology and (right) water beading on a superhydrophobic surface.

While current superhydrophobic coatings are marketed to have extremely high contact angles (> 150°) and low watershed angles, they are fragile and exhibit poor durability, as the surface patterning is readily damaged by even the mildest abrasion, impact or contact with water and other fluids. In addition, existing superhydrophobic coatings do not exhibit good adhesion to many types of surfaces, as the nanoparticles used to produce the surface texture do not form a covalent bond with the substrate. Therefore, the use of commercially available superhydrophobic coatings for applications where abrasion resistance and durability are critical is severely limited.

As a viable alternative to superhydrophobic coatings, our team has developed a hydrophobic coating that provides excellent watershedding capabilities, but is based on a highly durable, mechanically stable, fluoro-functionalized hybrid organic–inorganic matrix. An example of the interaction of water with the surface of our hydrophobic polymer/inorganic hybrid coating is shown in Figure 2. The hydrophobic coating is comprised of a transparent, hybrid organic–inorganic matrix based on silane-modified polymer chemistry. The coating combines the flexibility, impact resistance, durability, abrasion resistance, corrosion protection and UV resistance of commercially available organic polymer coatings combined with a low surface energy for enhanced watershedding performance. The ultra-thin (<5 µm), rapid-cure, single coat system has been applied to previously-painted, bare metallic and polymeric surfaces using common application techniques such as flow coat, brush or spray. The high optical transparency of the hydrophobic coating does not alter the appearance of target substrates, but enhances water shed capability, improves corrosion resistance, resists mechanical abrasion and impact damage, reduces salt accumulation, and resists weathering degradation of the object.

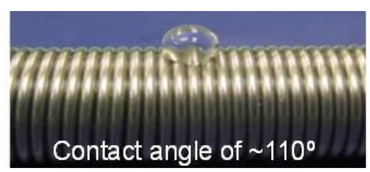

Figure 2: Appearance of a water drop on the surface of the transparent polymer/inorganic hybrid hydrophobic coating applied to a stainless steel coil.

2. EXPERIMENTAL PROCEDURE

The hydrophobic polymer/inorganic hybrid coating is a simple, transparent, one coat system that self-assembles to orient fluoro groups on the surface. The fluoro-functionalities are covalently bonded into the coating, imparting long-term hydrophobicity and watershed properties. Due to the low concentration of fluoro moieties necessary to impart hydrophobicity, they do not interfere with the coating adhesion to the substrate. The silane-functionalities of this hybrid coating provide a mechanism for covalent bond formation between the coating and the metal substrate, resulting in superior adhesion to metallic, plated and painted surfaces. In addition to the silanes used during synthesis, ceramic nanoparticle additives are used to maintain toughness, strength and abrasion resistance.

The organic portion of the coating imparts flexibility and durability to the coating system. These features combine to produce a highly durable coating with excellent watershedding capability and abrasion resistance. Key attributes of the hydrophobic polymer/inorganic hybrid coating are shown in Table 1.

Table 1. Key Attributes of the hydrophobic polymer/inorganic hybrid coating

Hydrophobicity and Watershed	Coating exhibits > 110° contact angle and <5° watershed angle.
Corrosion protection	Excellent water shedding attributes reduces corrosion and extends the service lifetime of metal components.
Flexibility, abrasion resistance	The hybrid inorganic–organic coating exhibits excellent flexibility via a tough crosslinked polymer matrix and abrasion/wear resistance associated with the inclusion of hard nanoparticles.
Thickness and Weight	The coating is extremely thin (1-5 µm) and lightweight
Adhesion	The coating has robust adhesion to metallic (aluminum, steel, etc.) substrates, glass, polymer (acrylic, polycarbonate), and paint (polyurethane, latex, acrylic).
Environmental Durability	Coating shows excellent resistance to degradation resulting from salt spray and UV exposure.
Facile synthesis and ease of application	The coating is readily prepared from commercial precursors. It is applied in a single coat using spray, flow or brush methods with minimal surface preparation.

The isopropanol solutions of the coating formulations were cast by flow, spray, or dip coating onto selected substrates – glass, polycarbonate, acrylic, Nitronic 50 stainless steel (UNS S20910), 2024-T0 (UNS A92024) aluminum alloy, and 316 stainless steel (UNS S31600) screws and washers. Coated substrates were air cured at ambient temperature or 80°C for 30 minutes. Coating thickness was measured at 2-5 µm depending on substrate and application method. Three specimens were used for each test and the data was averaged. Testing procedures are discussed below in the results section.

3. RESULTS

3.1 Hydrophobicity and Transparency

The hydrophobicity and light transmission properties of the hydrophobic polymer/inorganic hybrid coating as applied to glass substrates are shown in Table 2. The coating exhibits contact angles of >110° and an average watershed angle of ~3–11°, depending on water drop size and the coating formulation. The hydrophobic coating does not affect the transparency of the substrate, exhibiting negligible haze and retention of 100% clarity.

Table 2. Hydrophobicity and light transparency of coatings; WS denotes "watershedding"

	Contact Angle	WS Angle (50 µL)	WS Angle (120 µL)	Transp. (%)	Haze (%)
Glass	50	40	30	93.9	0.8
Coating	112	6	3	94.1	0.3

3.2 Corrosion Resistance

Electrochemical Impedance Spectroscopy (EIS) was used to evaluate the barrier properties of the hydrophobic coating. Aluminum alloy UNSA92024 coupons were coated with MIL PRF 85285 polyurethane (1.0 mil thick) and tested with and without the addition of the hydrophobic coating (~1 µm thick). Initial testing (i.e. "dry") of the samples showed similar impedance across the full frequency range (Figure 3). After exposure to ASTM B117[1] salt fog conditions for 336 hours, the samples were retested. The polyurethane only sample showed a signicantly larger reduction in impedance (~two decades) compared to the sample treated with the hydrophobic coating, indicating significantly better barrier properties for the coupon containing the addition of the hydrophobic coating.

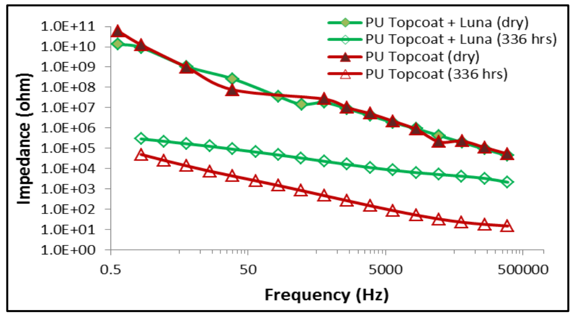

Figure 3. Electrochemical Impedance Spectroscopy (EIS) testing: MIL PRF 85285 Polyurethane coated UNSA92024 aluminum alloy with and without the hydrophobic polymer/inorganic hybrid coating.

Galvanic corrosion around cathodic fasteners mated to anodic aluminum alloy structures is a common problem in the aircraft community. It is known that galvanic corrosion of aluminum is controlled by the available cathodic current, and that a reduction in available current should result in less corrosion damage.[1–3] As an assessment of the possible galvanic protection attributes of the hydrophobic coating, polarization testing was conducted on a bare 316 stainless steel flat coupon and compared to a similar coupon with the hydrophobic coating applied. Results from the tests are observed in Figure 4. The addition of the hydrophobic coating resulted in an approximate two-order of magnitude reduction in cathodic current density compared to the bare 316 stainless steel coupon. As a further assessment, several 316 stainless steel screws and washer assemblies were prepared bare, and separately coated with the subject hydrophobic coating. The fasteners were attached to primed and topcoated aluminum alloy 7076-T6 (UNS A97075) coupons and exposed to accelerated corrosion conditions for galvanic corrosion assessment. Specifically, the fastener assemblies consisted of ¼-20 x 1" full-thread screws and corresponding mated flat washers (Figure 5), with and without hydrophobic coating applied. Select screws and washers were also cadmium plated per ASTM F1941 FE/CD 5A. The 7075-T6 aluminum coupons were approximately 1"x1.375"x0.032" and a ¼-20 drill and tapped hole was created in the middle region of each one for mated fastener attachment. All aluminum panels were initially deoxidized with Alumiprep 33 and treated with SurTec 650 chromitAL. The coupons were then primed with Deft 44GN072 and top coated with Deft 03-W-127 white polyurethane. The coated coupons were hand-scribed to expose fresh, bare metal prior to fastener attachment. During galvanic assembly, nylon spacers and 18-8 stainless steel nuts were used on the backside of the aluminum coupons and torqued to 25 in-lbs. Each distinct assembly type was tested in triplicate via placement in ASTM B117 cyclic salt fog conditions.

Representative fastener assembly images and corresponding stripped aluminum coupons post cyclic salt fog exposure are shown in Figure 6. It is readily apparent that both the bare 316 and Cd plated 316 stainless steel fastener assemblies that also contained the hydrophobic coating exhibited reduce corrosion. This is apparent in the reduction of aluminum coupon material loss in the images. The average aluminum coupon mass loss and overall maximum damage depth was measured for each fastener assembly type (Figure 7). The graph clearly shows a significant reduction in mass loss and damage depth for all coupons in which the hydrophobic coating was applied to the 316 stainless steel fasteners. It is also interesting to note that the coating appears to improve the longevity of the Cd plating in Figure 6 which could be extremely valuable in extending the lifetime of sacrificial coatings commonly used on fasteners (e.g. Cd, Zn, ZnNi, etc.).

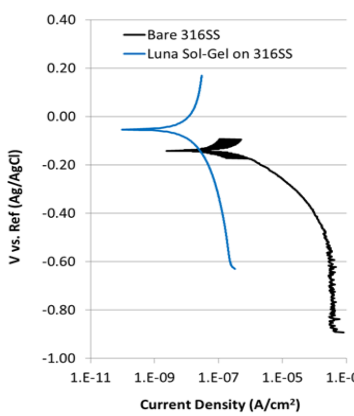

Figure 4. Polarization test results for a bare 316 stainless steel substrate compared to a similar substrate with the hydrophobic coating applied.

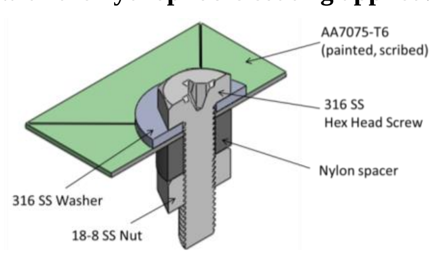

Figure 5. Galvanic fastener assembly components used for corrosion assessment of the hydrophobic coating as applied to 316 stainless steel fasteners.

ASTM G48[2] was performed to assess the crevice corrosion resistance of Nitronic 50 stainless steel coupons with and without the hydrophobic polymer/inorganic hybrid coating. The test method consisted of assembling two polytetrafluoroethylene (PTFE) crevice washers against each face of a 1"x2"x0.050" Nitronic 50 stainless steel coupon. The procedure was modified by cutting scribes into the coated surfaces corresponding to each crevice location on the washers. It was decided to test the coupons in the scribed condition to represent heavy damage on the steel component. Each assembly was torqued to 42 in-ounces in order to create a consistent crevice condition on both sides of the coupons. The samples were then immersed in an acidified ferric chloride solution and allowed to sit for 5 days at room temperature.

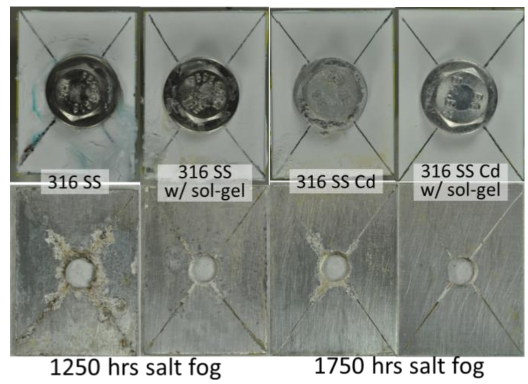

Figure 6. Galvanic fastener assemblies post salt fog exposure (top row) and corresponding stripped aluminum panels showing corrosion damage around the fastener holes and scribes (bottom row).

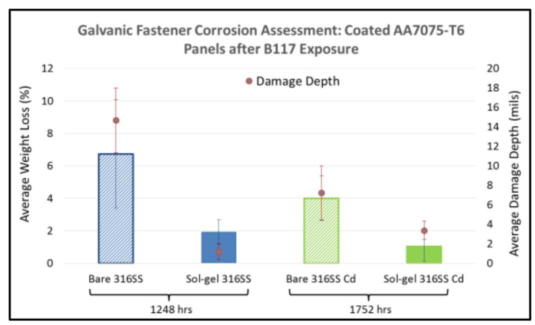

Figure 7. The average aluminum coupon mass loss and overall maximum damage depth for each fastener assembly type.

Figure 8 shows a typical scribed and assembled test coupon, and coupons immersed in the test solution. The percent mass loss of the coupons as a result of corrosion was then compared (Figure 9). The bare coupons exhibited an average of 8.5 wt% loss while the hydrophobic coating drastically reduced material removal to below 2 wt%.

Figure 8. A representative coated and scribed fully assembled crevice coupon (left) and three assemblies immersed in the test solution (right).

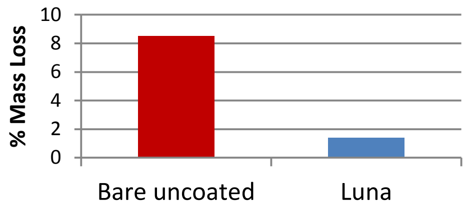

Figure 9. Average percent mass loss for coated and uncoated stainless steel tested per ASTM G48[3]

3.3 Salt Spray Resistance

To assess the stability and hydrophobic durability of the hydrophobic coating to a moist environment, the coating was applied to polycarbonate substrates and exposed to 5% salt spray for a period of up to 571 hours (3.4 weeks) in accordance with ASTM B117.[1] No visual signs of degradation, discoloration, delamination, etc. were observed. The effect of salt spray exposure on the hydrophobicity and light transparency of the hydrophobic coating are shown in Table 3. From these results, it is evident that salt spray exposure results in < 5% change in contact angle and does not affect the transparency of the coating.

Table 3. Effect of 3.4 weeks of salt spray exposure on hydrophobicity and light transmission properties of the hydrophobic polymer/inorganic hybrid coating.

	0 hours	571 hours
Contact Angle (°)	112.4	107.7
Transparency (%)	92.5	92.6
Haze (%)	0.78	0.58
Clarity (%)	99.8	99.7

3.4 Abrasion Resistance

Bare acrylic and hydrophobic coated coupons were evaluated for optical quality post 500 cycles of Taber abrasion testing using CS10 wheels and a 500 g load. Note a haze of 30% was measured for the uncoated control sample. This haze is visibly apparent after the abrasion test compared with the coated sample, which is still pristine with no loss of transparency and minimal loss in haze (Table 4).

Table 4. Effect of Taber Abrasion on light transmission properties of the hydrophobic polymer/inorganic hybrid coating.

	Before abrasion		After abrasion (500cycles)	
Sample	Tran.(%)	Haze(%)	Tran.(%)	Haze(%)
Acrylic	94.0	0.69	93.3	29.4
Coating	93.8	0.8	93.8	4.2

Likewise, panels of stainless steel were coated with the durable hydrophobic coating and compared with a commercial superhydrophobic coating for abrasion resistance. Initially, the as-prepared hydrophobic coating had a water contact angle of 110° compared to >150° for the commercial superhydrophobic coating. After reciprocal abrasion (Figure 10) with ScotchBrite™ abrasive pads, the superhydrophobic sample was degraded significantly and the durable hydrophobic coating was unchanged under the same conditions. More importantly, the watershed angle of the commercial coating increased drastically after a small amount of abrasion, but the hydrophobic coating watershed angle did not change significantly even after extensive harsh abrasion. This same result was observed when the test was performed pre and post an immersion soak in seawater.

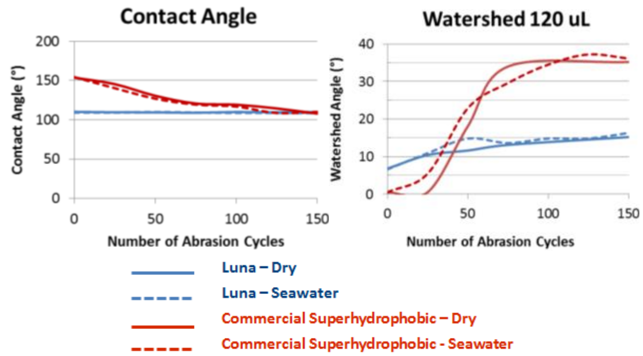

Figure 10. Water repellency (water contact angle and watershed angle) after reciprocal abrasion testing: hydrophobic polymer/inorganic hybrid vs commercial superhydrophobic

4. CONCLUSIONS

Hydrophobic and superhydrophobic coatings are a new, growing market in the coatings industry, as evidenced by the introduction of several commercial superhydrophobic coatings. While these products boast high contact angles and watershedding capabilities, consumer response to their claims is mixed and highlights the lack of durability in these coatings. Unlike these products, the hydrophobic polymer/inorganic hybrid coating described herein exhibits excellent abrasion resistance and durability. These coatings have shown significant improvements in corrosion resistance as well, making them directly relevant to protection of metal assets. For these reasons, the polymer/inorganic hybrid technology described here represents a significant advance in the hydrophobic coatings market and will find use in numerous commercial applications including automotive, aerospace, solar panels, anti-ice coatings, marine coatings, coatings to mitigate industrial and residential pipe-corrosion and fouling, bridge corrosion protection, etc. This hydrophobic coating will be especially useful in applications where long lifetime, wear resistance, abrasion resistance, corrosion resistance, chemical resistance, and hydrophobicity are important.

5. ACKNOWLEDGEMENTS

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[1] ASTM B117; Standard Practice for Operating Salt Spray (Fog) Apparatus.
[2] ASTM G48-11; Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels.
[3] ASTM G85 Standard Practice for Modified Salt Spray (Fog) Testing.