

Superhydrophobic Post Treatment and Coating Extenders for Improved Asset Sustainability

Steve Trigwell, Eliza L. Montgomery, and Luz M. Calle
Corrosion Technology Laboratory
NASA's John F. Kennedy Space Center, FL 32889
steven.trigwell-1@nasa.gov

ABSTRACT

Launch structures, hardware, and ground support equipment, at NASA's John F. Kennedy Space Center in Florida, are exposed to a highly corrosive natural coastal marine environment. In addition, during launches, rocket exhaust deposition is also highly corrosive. Superhydrophobic coatings are being considered for additional corrosion protection on existing structures to enhance corrosion resistance and add an additional layer of protection against harsh environmental elements. These coatings have come into their own recently, and are now being investigated as corrosion protective coatings due to their water repelling capability. These coatings can be used on existing coatings, newly coated materials, or used on bare substrates. The coatings are not suitable for permanent corrosion protection, but can be used where additional corrosion control is desired or only when temporary corrosion control is needed, such as in hardware sitting on a launch pad for 30-45 days prior to a launch. In this study, superhydrophobic coatings were applied on various coated and uncoated substrates and exposed to the spaceport environment for various times up to 60 days. This paper highlights the current results of the superhydrophobic coatings performance evaluated by X-ray photoelectron spectroscopy, and contact angle measurements.

Key Words: superhydrophobic coatings, corrosion protection, x-ray photoelectron spectroscopy, contact angle

INTRODUCTION

The work presented on this paper was performed as part of a project to identify, test, and develop qualification criteria for the use of environmentally friendly corrosion protective coatings and corrosion preventive compounds (CPCs) for flight hardware and ground support equipment at NASA's John F. Kennedy Space Center (KSC) in Florida. Typically, when a bare metal surface could or should not be coated with a permanent coating (barrier or sacrificial coating), a temporary coating, CPC, is used to protect the exposed surface from corrosion. CPCs commonly contain corrosion inhibitors dispersed in a mixture of solvents and a base oil or grease. The base oil acts as a carrier fluid for the inhibitors and also as a protective barrier to environmental elements. The solvent acts as a base oil and inhibitor dispersant and is intended to evaporate after application. CPCs can be soft or hard films, and can be primarily composed of a petroleum, hydrocarbon, or fluoropolymer material depending on their end use requirements.

Significant research has previously been performed in identifying and testing numerous CPC coatings over several years at KSC. Recent advances in the development of superhydrophobic (SHP) coatings have made them suitable to be considered as corrosion protection coatings⁽¹⁻⁵⁾. SHP coatings are based on the naturally observed "lotus leaf" effect, called such by the observation that water droplets ball up and are easily displaced from the surface of lotus leaves. Examination of the leaf surfaces revealed that they are coated in nanometer sized fine hairs that prevent the water droplets from spreading and wetting the surface. Recent developments in nanotechnology, have prompted

attempts to mimic this effect by creating surfaces with similar topographies utilizing nanoparticles in surface films. This has led to a plethora of research activities with new commercial SHP coating products starting to hit the market.

The first step of this study was to coat various common substrates with commercially available SHP coatings to test their performance by standard beachside atmospheric exposure testing. A literature search revealed that there are several commercially available SHP coatings. Three were chosen for the initial phase of the study (Table 1). During this first part of the study, the effects of beachside atmospheric exposure on the superhydrophobicity, and therefore water repelling capability of the coatings, were analyzed by contact angle measurements. The changes in surface chemistry were analyzed by X-ray Photoelectron Spectroscopy (XPS).

SHP coatings are characterized by a contact angle of greater than 151° on a water droplet on a substrate. Monitoring the contact angle as a function of atmospheric exposure time gives valuable information regarding the robustness and long-term corrosion protection effectiveness of the coatings. For ideal corrosion protection, an SHP surface will repel water and not let the surface get wet. However, if the contact angle falls below 90° , the water will wet the surface. It is also important that the surface of the coating stays intact. Changes in the substrate composition with exposure will indicate breakdown of the SHP.

Table 1. Physical Property Testing

Engineering, Performance, and Testing Requirements			
Test	Test Specimen	Acceptance Criteria	Test Methodology References
Surface chemistry, XPS	Uncoated and coated specimens after 3, 7, 14, 30, 60, and 90 days beachside atmospheric exposure	Monitor surface chemistry evaluation after exposure to determine the SHP coating effectiveness	ASTM E2108 ⁽⁶⁾
Contact Angle, Wettability of SHP coating	Uncoated and coated specimens after 3, 7, 14, 30, 60, and 90 days beachside atmospheric exposure	Determine robustness of superhydrophobicity as a function of exposure time	ASTM D7334 ⁽⁷⁾

Selected Alloys and Coatings

For this study, five different metal substrates were chosen. The first three specimens were standard metals used in the aerospace industry: carbon steel (CS), stainless steel (SS), and aluminum (Al). The next two are stainless steel coupons physical vapor deposition (PVD) coated with 1000\AA pure silver and copper, respectively. These specimens were used to determine the effects of highly thermal conductive and reflective metal layers on the SHP coatings. Table 2 contains a listing of the types of substrates that were used for testing.

Table 2. Test specimen codes and substrate descriptions

<i>Test Coupon</i>	<i>Substrate Description</i>
1010 CS (CS)	Carbon Steel: Low-carbon, cold-rolled steel complying with SAE* 1008/1010 specifications (ASTM A109) ⁽⁸⁾
304 L SS (SS)	Stainless Steel: Austenitic Cr-Ni stainless steel complying with ASTM A240/A240M specifications ⁽⁹⁾
2219-T87 (Al)	Aluminum: an age-hardenable copper containing alloy of aluminum complying with ASTM B209 ⁽¹⁰⁾
Silver (Ag)	304 L SS stainless steel coupon PVD coated with 1000Å pure silver
Copper (Cu)	304 L SS stainless steel coupon PVD coated with 1000Å pure copper

*Society of Automotive Engineers

Table 3 shows the SHP coatings used in this study. These coatings were chosen primarily for the ease of availability. Coating 1 is a single part liquid that claims to dry transparent. Coating 2 is a 2-part spray, but is only available for industrial use. Coating 2 is a readily commercially available 2-part spray product. Coatings 2 and 3 cure to form a “milky” opaque coating.

Table 3. SHP coatings included in this study

<i>Product Name</i>	<i>Primary Composition</i>
Coating 1	Silica gel based liquid
Coating 2	Fluoro-silica-based 2-part liquid
Coating 3	Silica gel based 2-part liquid spray

EXPERIMENTAL PROCEDURE

Prior to coating, each coupon was cleaned in acetone, followed by iso-propanol and allowed to air dry. The optimal method of applying coating 1 was using a mist sprayer as it was determined that dip coating or spin coating produced an observable uneven layer. The coating application was performed in a lab hood, due to the fumes from the solvent base, and allowed to cure for 1 hour. Coating 2 came as a base coat and a top coat. In this case, the liquids were more viscous and it was determined that spin coating produced the most even coatings. After the application of the base coat, the specimens were allowed to cure in a lab hood for 1 hour prior to applying the top coat. Coating 3 came in 2 spray cans: a base coat and a top coat. The coatings were spray applied also in a lab hood and allowed to fully cure for 2 hours.

Specimen coupons of control (uncoated, as-prepared coupons), and the coated coupons were placed out at the Beachside Atmospheric Exposure Test Site. The coupons were mounted in racks as shown in Figure 1. Specimens of each were retrieved after 3, 7, 14, 30, and 60 days of exposure for analysis.

Optical micrographs were taken of each coupon before coating, as-coated, and after each exposure period.



Figure 1: Coupons mounted on a rack at the Beachside Atmospheric Exposure Test Site

XPS Analysis

The XPS analysis was performed on a Thermo Scientific K-Alpha system. The system uses a Al K α x-ray source utilizing a 1436.6 eV x-ray beam in a 400 μm spot size. The base pressure for each analysis was better than 5×10^{-9} mbar. The system was calibrated as per ASTM E2108, Practice for Calibration of the Electron Binding-Energy Scale of an X-Ray Photoelectron Spectrometer ⁽⁶⁾. Spectra were taken on three points on each sample and the mean elemental composition taken. Quantification was performed by measuring the area under each elemental peak identified and normalized by using sensitivity factors. The sensitivity factors are based on the ionization potential for each element and are unique to the instrument. The data is presented as relative atomic percent. XPS is a very sensitive surface analysis technique, as the escape depth of the escaping photoelectrons is in the order of 50-100Å.

Contact Angle Measurements

ASTM D7334, Standard Practice for Surface Wettability of Coatings, Substrates and Pigments by Advancing Contact Angle Measurement ⁽⁷⁾, was used to measure the wettability of the SHP coatings on the specimen surface in ambient conditions. A droplet of deionized (DI) water was placed, via a 100 μl syringe and needle, onto the specimen surface and the corresponding angle of the droplet was measured immediately. The contact angle instrument used was an AST Products Optima XE, utilizing a precision motor controlled attachment for the syringes allowing precise accurate deposition of known amounts of fluid. For this study, 3 μl in volume of DI water was deposited onto the specimen surface. Due to the spreading of the hydrophilic fluids, any larger droplet size would have spread out of the visual angle of the camera. The method of deposition was to allow the droplet to form on the end of the syringe, and raise the platform containing the coupon to meet the droplet. The platform was lowered

	As received	Control Day 60	Coating 1 Day 60	Coating 2 Day 60	Coating 3 Day 60
Al					
SS					
CS					
Cu					
Ag					

Figure 2: Optical micrographs of the metal coupons exposed at the Beachside Atmospheric Exposure Test Site for 60 days.

with the deposited droplet. The image of the droplet was captured within 3 seconds of the droplet deposition.

Prior to the actual analysis on the coupons, the system was calibrated using DI water on cleaned polytetrafluoroethylene (PTFE). Ten drops were deposited and the mean contact angle was measured at 94°. This is consistent with values obtained from the literature for PTFE in the laboratory ambient conditions. Ten droplets of DI water in total were deposited for SHP coated coupons and the mean was taken.

RESULTS

Optical micrographs of the control and coated coupons, as-received and after exposure for 60 days at the Beachside Atmospheric Exposure Test Site, are shown in Figure 2. Only the final exposure pictures are shown for brevity.

All the Control samples showed considerable corrosion after 60 days with no evidence of the Cu and Ag coatings. The CS sample showed the most severe corrosion as expected. Coating 1 did not fare much better. The optical images (not included) showed corrosion after only the 3rd and 6th day exposure. Coating 2 fared a lot better, with only the CS sample showing signs of severe corrosion after 60 days. Coating 3 performed the best of the three coatings. Corrosion was only observed around the edges of the Al and CS samples. This was probably due to edge effects because the coupons were not coated on the backside. The Ag coupon showed some minor corrosion spots, but on the Cu and SS coupons, the coating still appeared intact.

Contact Angle Measurements Results

Example images for the contact angle measurements are shown in Figure 3.

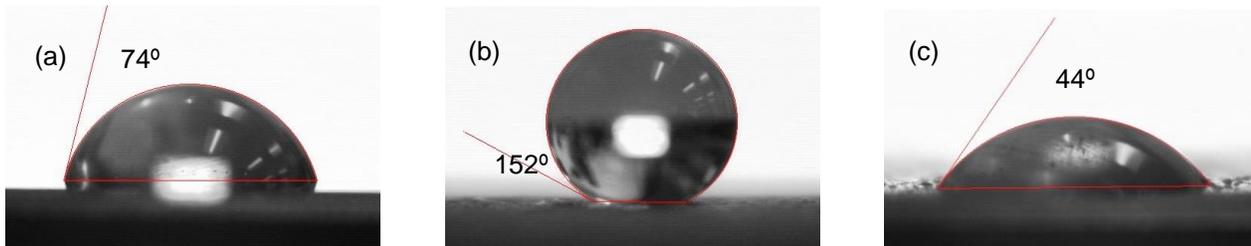


Figure 3: Contact angle for (a) bare metal surface, (b) SHP coated surface, and (c) surface coated with coating 1 after 60 days exposure.

The contact angle results for the metal control and coated specimens as a function of exposure time are shown in Figures 4 to 7.

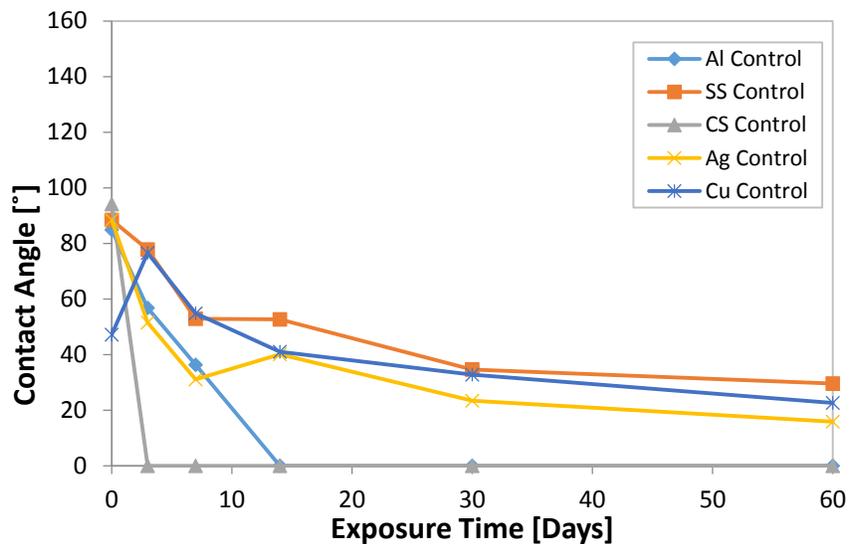


Figure 4: Contact angle as a function of atmospheric exposure time for the control (uncoated) coupons.

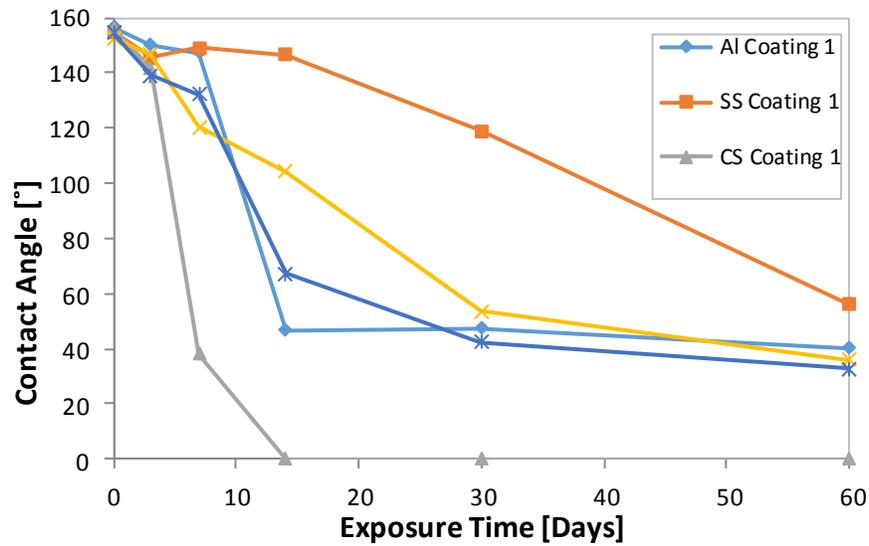


Figure 5: Contact angle as a function of atmospheric exposure time for the coated (Coating 1) coupons.

The Control coupons showed contact angles on the as-received surfaces in the order of 90° (Figure 4) which is considered neither hydrophilic or hydrophobic. This is typical of metal surfaces exposed to ambient conditions where they are coated with a natural oxide layer. The CS sample was the first to show a significant drop, with complete wetting of the surface after only 3 days exposure.

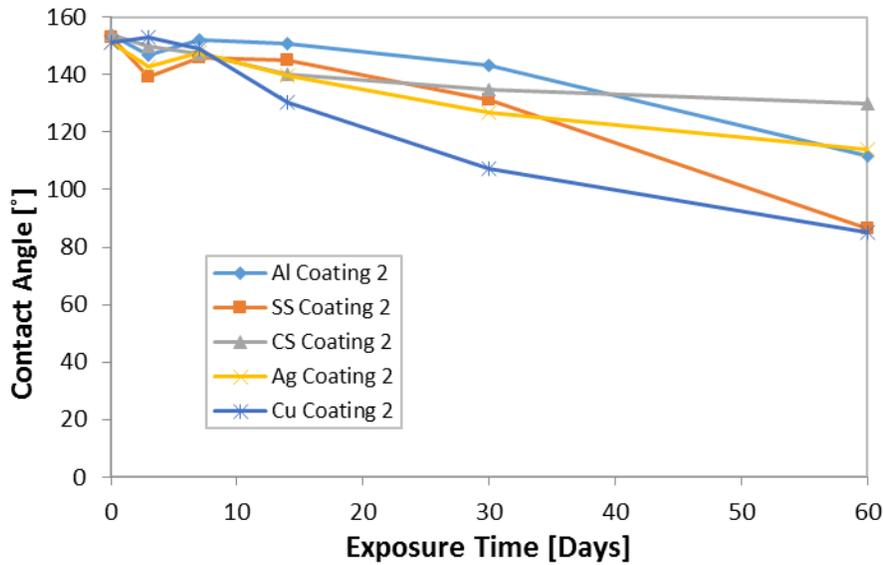


Figure 6: Contact angle as a function of exposure time for the coated (Coating 2) coupons.

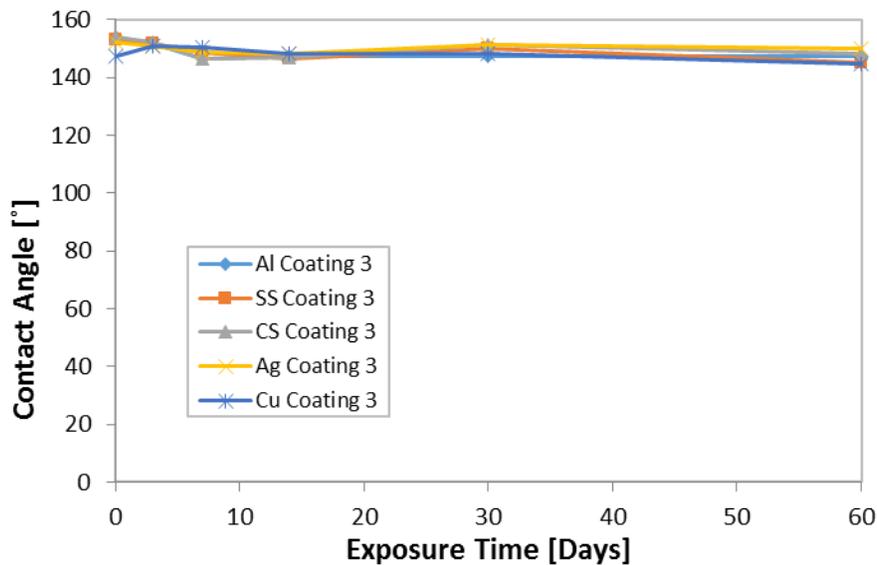


Figure 7: Contact angle as a function of exposure time for the coated (coating 3) coupons.

This was followed by the Al samples after 14 days exposure. The SS, Ag and Cu coated samples showed a steady drop in the contact angle to approximately 20° - 40° after the 60 days. This is indicative of a hydrophilic surface.

Coating 1 (Figure 5) performed marginally better. Although all samples showed a superhydrophobic contact angle of approximately 150° -155° after coating, the CS sample showed complete wetting after 14 days. There was also an initial significant drop of the contact angle for the Al and Cu coated samples at 14 days, but they stabilized after that showing a slight improvement over the control samples to 40° – 45° after the 60 days. Coating 1 showed the best results on the SS coupon. However, after 60 days, the contact angle was measured at 60° which makes it hydrophilic.

Coating 2 (Figure 6), showed significant improvement with the contact angles dropping from an initial value of approximately 150° - 155° to a lowest of 90° for the SS and Cu coatings. Interestingly, the CS sample showed the highest contact angle of 130° after 60 days, even though, visually it showed signs of corrosion.

Coating 3 proved to be the best performer, with only a slight drop in the contact angle for all samples after 60 days to about 145° - 150°. Although this is no longer considered superhydrophobic, for the application of a temporary coating for that time period, it showed significant potential.

XPS Analysis Results

Typical XPS spectra of an SHP as-coated surface and the SHP coated carbon steel after 30 days exposure are shown in Figure 8. The iron (Fe) from the carbon steel substrate is now clearly detected through the SHP coating showing its integrity has been compromised.

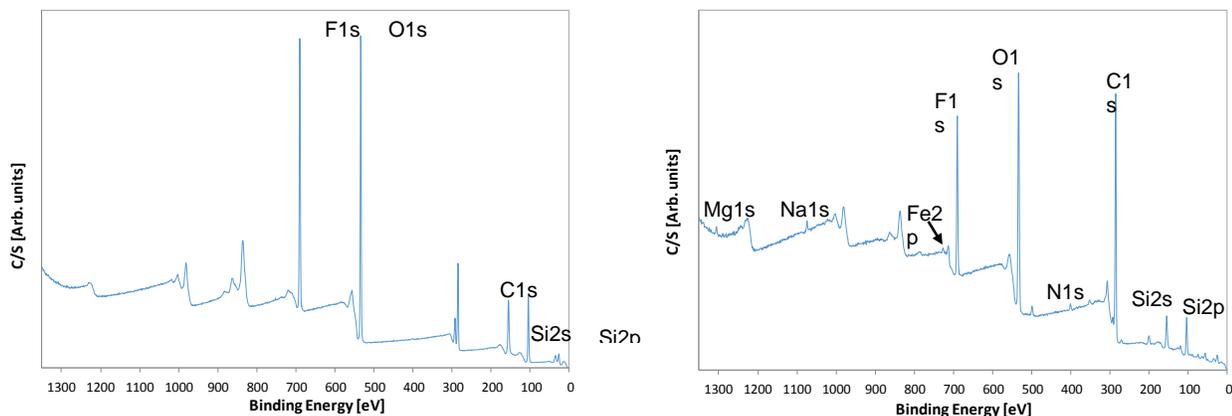


Figure 8. XPS spectra of anSHP coated specimen and SHP coated carbon steel after 30 days beachside atmospheric exposure where the Fe from the substrate is now clearly detected.

XPS analysis was performed on the as-coated samples to get a control composition of the coated surfaces. In each case, the metal surface composition underneath the coating was not detected. XPS analysis was performed on each coupon as it came back from the Beachside Atmospheric Exposure Test Site. In all tests, three points were analyzed on each sample. The survey scans of the surface in all cases after the various periods of exposure showed minor amounts of sodium (Na), chlorine (Cl), magnesium (Mg), calcium (Ca), nitrogen (N), and sulfur (S). This is expected of surfaces exposed in the beachside environment. The combination of ionic contaminants and coastal marine environment is the leading cause of such high corrosion rates. For this study, the time period in which the metal substrate underneath the superhydrophobic coating was detected in the surface scan was recorded and taken as the point at which the surface coating was considered to have arbitrarily broken down. For the SS and CS samples, the predominant element scanned to detect the substrate was Fe. A summary of the XPS data for each specimen is shown in Figure 9.

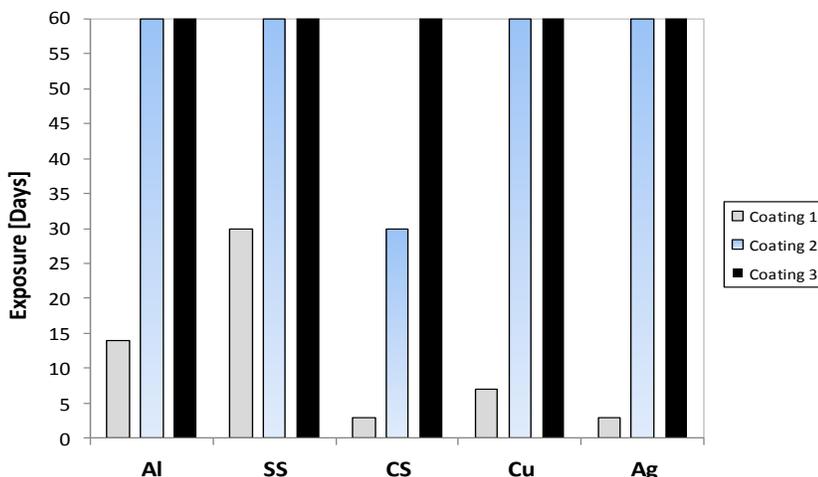


Figure 9. Detection of the substrate metal as a function of atmospheric exposure time for all three superhydrophobic coatings.

From Figure 9, it can be seen that for coating 1, the CS sample showed the worst performance with Fe from the substrate detected after only 3 days exposure. The contact angle at this point was approximately 140°, but after 14 days the surface was completely wetted, and the XPS showed that the coating had completely disappeared. The Ag and Cu samples did not fare much better, with the Ag and Cu substrates detected after 3 and 7 days, respectively. The Al sample lasted 14 days, and the SS performed the best at 30 days.

Coating 2 performed a lot better, with only the CS sample showing Fe after 30 days. The other samples did not show evidence of the substrate through the coating after 60 days.

No substrate elements were detected on all samples for coating 3. Although corrosion was observed around the edges of the Al and CS samples after 60 days, it was not detected in the areas analyzed at the center of the coupon. The Ag coupon showed some small discoloration spots after 60 days, but no Ag was detected.

CONCLUSIONS

As expected, the data collected on the control specimens showed severe corrosion on unprotected metals, with the carbon steel showing the worst effect. The stainless steel specimen fared better, but it is interesting to note that by the contact angle measurements, the Ag and Cu coated stainless steel specimens actually fared slightly worse as shown by a drop in the contact angle indicating that they became more hydrophilic. This may have to do with the different oxidation kinetics of the Ag and Cu coating compared to the 304 stainless steel that typically forms a chromium (Cr) enriched passive layer.

The coating 1 specimens fared better than the control, but the coating failed as a corrosion protection coating. Significant corrosion was detected after a few days, with most specimens severely corroded after 60 days. This cannot be considered a candidate as a long term corrosion protection coating. This was the only coating that was transparent and was applied with a single application. Coating 2 performed well, but was only good up to 30 days of exposure on carbon steel, compared to coating 3 that lasted all 60 days with minimal degradation and therefore shows excellent potential for additional corrosion protection on spaceport structures.

Future Work

Metal panels have been coated with several selected good performing CPCs, and additionally coated with the two better performing superhydrophobic coatings, 1 and 2. These panels are currently undergoing exposure testing at the Beachside Atmospheric Exposure Test Site. Future work will include uncoated and superhydrophobic coated scribed panels to compare corrosion protection performance.

ACKNOWLEDGEMENTS

This project was funded by NASA's Ground Systems Development and Operations (GSDO) Program. This is one of three NASA programs based at the agency's Kennedy Space Center in Florida. The program was established to develop and use the complex equipment required to safely handle rockets and spacecraft during assembly, transport and launch.

REFERENCES

1. P.M. Barkhudarov *et al.*, "Corrosion inhibition using superhydrophobic films", *Corrosion Science* 50 (2008): pp. 897-902.
2. J-D Brassard, D.K. Sarkar, and J. Perrou, "Fluorine based superhydrophobic coatings", *Applied Sciences* 2 (2012): pp. 453-464.
3. N. Valipour, *et al.*, "Durable, superhydrophobic, superoleophobic, and corrosion resistant coating on stainless steel surface using a scalable method", *Applied Surface Science*, 293 (2013): pp. 636-647.
4. A. Venkateswara Rao, *et al.*, "Mechanically stable and corrosion resistant superhydrophobic sol-gel coatings on copper substrate", *Applied Surface Science* 257 (2011): pp. 5772-5776.
5. F. Zhang *et al.*, "Corrosion resistance of superhydrophobic layered double hydroxide films on aluminum", *Angew. Chem. Int. Ed.* 47 (2008): pp.2466-2469.
6. ASTM E2108 -10, "Practice for Calibration of the Electron Binding-Energy Scale of an X-Ray Photoelectron Spectrometer" (West Conshohocken, PA, ASTM International)
7. ASTM D7334-08, "Standard Practice for Surface Wettability of Coatings, Substrates and Pigments by Advancing Contact Angle Measurement" (West Conshohocken, PA, ASTM International)
8. ASTM A109/A109M-03, "Standard Specification for steel, strip, carbon (0.25 max. %), cold-rolled", (West Conshohocken, PA, ASTM International).
9. ASTM A240/A240M-15a, "Standard Specification for Cr and Cr-Ni stainless steel plate, sheet, and strip for pressure vessels and general Applications", (West Conshohocken, PA, ASTM International).
10. ASTM B209-14, "Standard Specification for Al and Al-alloy Sheet and Plate", (West Conshohocken, PA, ASTM International).