Joint Technical Report

Final Report

Validation/Demonstration of a Zero-VOC/HAPS-free NC Wash Primer for Department of Defense Weapons Platforms

Weapons Systems and Platforms (WP) Projects
Project Number WP-201621

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14. ABSTRACT

This technology that was laboratory tested and field tested provided guidance to validate the performance of spray application pretreatment technology that will act as a replacement for the Cr(VI) containing DOD-P-15328 wash primer that is currently in use. The DOD-P-15328 wash primer that has been used in previous military coating requirement documents is now cancelled and ARL has qualified several alternatives to the DOD-P-15328 wash primer referenced to TT-C-490 types III and IV (June 2018).

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LIST OF ACRONYMS

Al	Aluminum
ARL	Army Research Laboratory
ASTM	American Standard Test Method
BIF	Blisters in field
CASS	Copper Accelerated Acetic Acid Salt Spray
CARC	Chemical Agent Resistant Coating
CCC	Chromate conversion coating
Cr(VI)	Hexavalent chromium
CRS	Cold rolled steel
CRADA	Cooperative Research and Development Agreement
CTIO	Coatings Technology Integration Office
^{o}F	Degrees Fahrenheit
DI water	Deionized water
DOD	Department of Defense
ESTCP	Environmental Security Technology Certification Program
FTMS	Federal Test Method Standard
GM9540	General Motors Accelerated Corrosion Test
HAPs	Hazardous Air Pollutants
HE	Hydrogen Embrittlement
HRS	Hot-rolled Steel
HSS	High Strength Steel
HATE	Hydraulic Adhesion Test Equipment
HCl	Hydrochloric acid
JTP	Joint Test Protocol
JTR	Joint Technical Report
MTVR	Medium Tactical Vehicle Replacement
MRAP	Mine-resistant Ambush Protected
mΩ	Milliohms
NACE	National Association of Corrosion Engineers
NAWCWD	Naval Air Warfare Center Weapons Division
NIOSH	National Institute for Occupational Safety and Health
NSS	Neutral salt spray
NSF	National Science Foundation
NSWCCD	Naval Surface Warfare Center Carderock Division
OSHA	Occupational Safety Health Administration
OEM	Original Equipment Manufacturer
PATTI	Pneumatic Adhesion Tensile Test Instrument
%	Percent
QPD	Qualified Products Database
SERDP	Strategic Environmental Research and Development Program
SBIR	Small Business Innovative Program
SLD	Scattering Length Density

USMC	United States Marine Corps
UTS	Ultimate Tensile Strength
VOC	Volatile Organic compounds
WTA	Wet Tape Adhesion
wt.%	Weight Percent
XRR	X-ray Reflectivity

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The work performed under this ESTCP project was completed by the Naval Air Warfare Center Weapons Division (NAWCWD), Naval Surface Warfare Center Carderock Division (NSWCCD), Army Research Laboratory (ARL), Ecosil Technologies LLC, and Aalberts Surface Treatments.

Dr. Peter Zarras (NAWCWD) directed the overall project, testing with Mr. Joseph R. Kromphardt (NAWCWD) sol-gel formulations as a pretreatment coating to meet military specifications as defined in TT-C-490. Sol-gel formulations and coated coupons were supplied by Dr. Danqing Zhu, CTO of Ecosil Technologies LLC and Mr. Art Helmstetter CFO of Ecosil. In-house testing of the Ecosil SILSBOND formulations for adhesion and accelerated corrosion tests were performed at Ecosil prior to shipment to co-performers. Formulations and coated coupons were supplied to ARL, Mr. John (Jack) V. Kelley, Mr. Thomas A. Considine, and Thomas E. Braswell for adhesion, accelerated corrosion testing, marine outdoor exposure testing, and field testing. Additional Ecosil formulations and coatings were supplied to NSWCCD, Andrew D. Sheetz, Jamaal D. Delbridge and Kunigahalli L. Vasanth for adhesion, accelerated corrosion and field testing. Dr. Wes Prince from Aalberts Surface Treatment coated coupons and non-critical military hardware for accelerated corrosion testing, marine outdoor exposure and field testing.

EXECUTIVE SUMMARY

This executive summary document provides the overall performance and assessment of the Ecosils SILSBOND coating pretreatment as a replacement for the hexavalent chromium (Cr(VI)) containing DOD-P-15328 wash primer that was formerly in use. The term "wash primer" is now cancelled and replaced with the term "pretreatment coating." There were nine non-Cr(VI) pretreatments approved in the Qualified Products Database (QPD) and used by the DOD at the time of this study. ARL has now qualified eighteen alternatives to the DOD-P-15328 coating specification and are referenced to TT-C-490 types III and IV (June 2018).

The Ecosil pretreatment coating that has been spray applied onto test substrates is referred to as "SILSBOND." This product is water-based, contains no Volatile Organic Compounds (VOCs), Hazardous Air Pollutants (HAPs) and is (Cr(VI))-free as well as phosphate-free. The previous DOD wash primer that is used on ground support equipment and vehicles was based on the DOD-P-15328 specification. The former document "DOD-P-15328" allowed for high amounts of isopropanol, zinc chromates (containing Cr(VI)) and phosphoric acid for etching and adhesion purposes. ARL has qualified eighteen alternatives to the DOD-P-15328 through TT-C-490.

SILSBOND is a patented, organic-inorganic hybrid pretreatment that synergistically combines advanced silicon compound oligomers and water-soluble inorganic compounds such as zirconium fluoric acid. SILSBOND forms a nano-structured film on a metal surface through immersion or spray application. The film provides a unique "self-sealing" effect that mitigates flash rusting typical of zirconium-based pretreatments on carbon steels. When applied by immersion or spraying, a SILSBOND hybrid film is formed which consists of two distinct regions: (1) an interfacial layer formed on the metal surface during immersion and (2) a surface layer formed on top of the interfacial layer primarily during drying-in-place.

Testing of the Ecosil pretreatment coating(s) was performed on various SILSBOND formulations on Al 2024-T3 and 1020 Steel substrates. After evaluation from laboratory results for adhesion, accelerated corrosion, and marine outdoor exposure testing, the best performing formulation was identified as SILSBOND 01 (at 2% concentration) pretreatment coating which was selected for field testing by both the NSWCCD and ARL on non-critical military components for a one- and two-year field test as determined by each service.

The one-year field testing was conducted by the NSWCCD at the Marine Corps Base Hawaii. Field testing was completed during a one-year program July 2021-July 2022 using SILSBOND 01 (2%) pretreatment coating on United States Marine Corps (USMC) vehicles with 4"x 6" panels on the Medium Tactical Vehicle Replacement (MTVR). The field test demonstration had coupons (aluminum and steel, 4" x 6" with a 4" diagonal line scribe) mounted onto racks, which were situated to the rear of the USMC MTVR. The coupons comprising a full coating stack-up passed the one-year field testing showing no extensive corrosion, delamination or blistering of the coating from the scribe.

Concurrently with the NSWCCD one-year field testing, the two-year field testing conducted by ARL examined the performance of Ecosil's SILSBOND 01 (2%) pretreatment coating which evaluated the SILSBOND pretreatment with full military coating systems on non-critical components for a military vehicle such as the Mine-resistant Ambush Protected (MRAP). The field test was located at the ARL Cape Canaveral Space Force Station, Florida marine outdoor exposure facility and started December 2020 and completed December 2022. Performance criteria that was evaluated by the field-testing included coating adhesion, intercoat compatibility, and corrosion protection. The limited scale demonstration was performed using vehicle components with participation from the Program Managers' Office (PMO). ARL has research agreements with the PMO for MRAP. Components of this vehicles (MRAP door) were obtained and abrasive blasted to bare metals and treated with Ecosil's SILSBOND 01 (2%) formulation with representatives from the manufacturer present during the coating process. Identical components were compared using the pretreatment Henkel Bonderite M-NT 7400 and the SILSBOND 01 (2%) pretreatment, resulting in both meeting the requirements called out in TT-C-490.

Both the NSWCCD and ARL field testing of the Ecosil SILSBOND 01 pretreatment coating passed each field test and SILSBOND 01 was approved to the TT-C-490 Qualified Products Database (QPD) on June 28, 2023.

1.0 INTRODUCTION

1.1 Background

This technology that was laboratory tested and field tested provided guidance to validate the performance of spray application pretreatment technology that will act as a replacement for the Cr(VI) containing DOD-P-15328 wash primer that is currently in use. **The DOD-P-15328 wash primer that has been used in previous military coating requirement documents is now cancelled and ARL has qualified several alternatives to the DOD-P-15328 wash primer referenced to TT-C-490 types III and IV (June 2018).**

The Ecosil pretreatment SILSBOND that was under investigation for this specific project is water-based, contains no VOCs, HAPs and is Cr(VI)-free as well as phosphate-free [1]. The DOD pretreatment currently used on aircraft components, ground support equipment and vehicles is based on the DOD-P-15328 specification [2,3] and this specification contained high amounts of isopropanol, zinc chromates (containing Cr(VI)) and phosphoric acid for etching and adhesion purposes.

Currently, over 18 qualified alternatives are considered replacements for the current TT-C-490 pretreatment coating. There is an urgent need for additional pretreatment replacements that meet current TT-C-490 coating specifications as pretreatments to populate the QPD, and thus continue to expand the sources of qualified alternatives. ARL is the custodian of the current specification, DOD-P-15328 which was canceled in 2022. TT-C-490 which governs pretreatments for metallic substrates, qualifies pretreatments to serve as the replacements for DOD-P-15328.

Previous pretreatment formulation based on the military specification DOD-P-15328 which was referred to as a "wash primer" contained 7.1% (w/w) of zinc chromate and has 6.5 lbs./gal of VOCs that are classified as HAPs. These pretreatments produced approximately 12,600 lbs. of zinc chromate, and 35,700 gallons of package/thinner solvents as pollutants each year. Approximately 6,000,000 lbs. of stripped chemical agent resistant coatings (CARC) waste is produced and must be disposed as a chromium-containing hazardous waste. The cost of disposing chromate-bearing paint waste is ~$0.61/lbs., or ~$3,600,000/year. Removing Cr(VI) from the paint waste would eliminate the need to dispose of it as a hazardous waste, thereby reducing the disposal costs by two-thirds, saving the DOD $2,400,000 annually [4-9]. The current state of pretreatments used by both the Army and Marines do not use chromated material but there is an urgent need for additional pretreatment coatings that can further populate the QPD.

Sol-gel materials have shown over the past several decades numerous applications ranging from optical, automotive, aircraft, medical, environment, electrical and corrosion protection [10-12]. Due to the unique processing and applications of sol-gel coatings formulations, coating specialists, and corrosion scientists/engineers have examined sol-gel coatings for their potential applications as corrosion-inhibiting coatings. Both solvent and water-based sol-gel coatings have been investigated for corrosion inhibiting properties on various metal substrates [13-18]. A recent comprehensive review regarding the synthesis, properties and corrosion applications of sol-gel coatings is referenced for the reader's interest [19].

Sol-gel coatings which were described in the preceding paragraphs have been investigated for a variety of applications including corrosion protection on various metal substrates. Enhanced corrosion protection has been achieved using organic functional groups to improve processability and the corrosion-inhibiting properties of the sol-gel material [20]. This report documents the efforts of our industrial partner Ecosil in cooperation with military laboratories to formulate, apply and test both at the laboratory level and field studies the corrosion-inhibiting properties of Ecosil's innovative sol-gel material. These studies documented in this Joint Technical Report (JTR) which is based on this industrial product, Ecosil's new formulation pretreatment, can be used as a DOD pretreatment coating that meets the current mil-spec TT-C-490 coating requirements.

SILSBOND is a patented, organic-inorganic hybrid pretreatment that synergistically combines advanced silicon compound oligomers and water-soluble inorganic compounds such as zirconium fluoric acid [5-8]. SILSBOND forms a nano-structured film on a metal surface by immersion or spraying. The film provides a unique "self-sealing" effect that mitigates flash rusting typical of zirconium-based pretreatments on carbon steels. The SILSBOND film structure is schematically shown in Figure 1. When applied by immersion or spraying, a SILSBOND hybrid film is formed which consists of two distinct regions: (1) an interfacial layer formed on the metal surface during immersion and (2) a surface layer formed on top of the interfacial layer primarily during drying-in-place. The interfacial layer is characteristic of a mixture of metal oxide on the substrate surface and ceramic particles such as zirconium oxide. The interfacial layer promotes paint adhesion on the substrate, but is susceptible to flash rusting on steel. The surface layer primarily consists of a cross-linked silsesquioxane network attached with organic functional groups (R'). The surface layer seals pores and other defects in the interfacial layer underneath, and thereby improves flash rust resistance of the steel substrate. Additionally, the organic functional groups in the surface layer also enhance paint adhesion. Figure 2 schematically compares the SILSBOND coating and DOD-P-15328 wash primer.

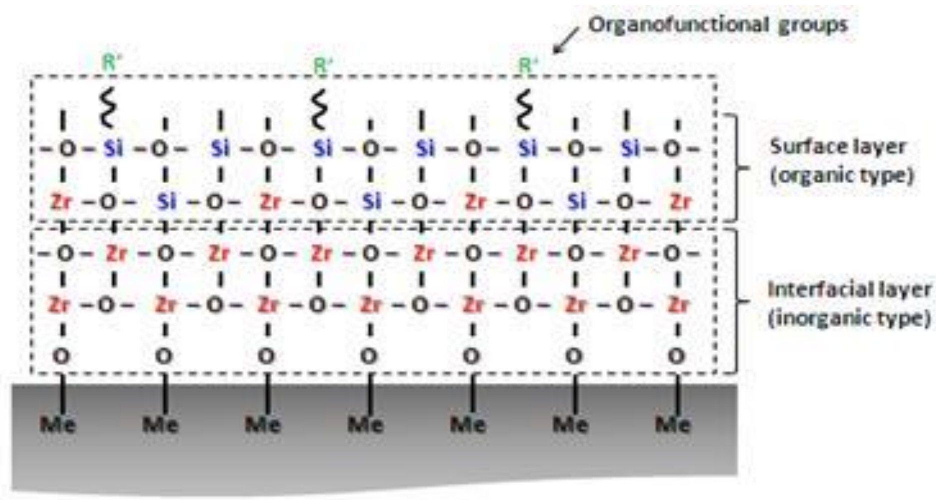

Figure 1. SILSBOND Film Structure

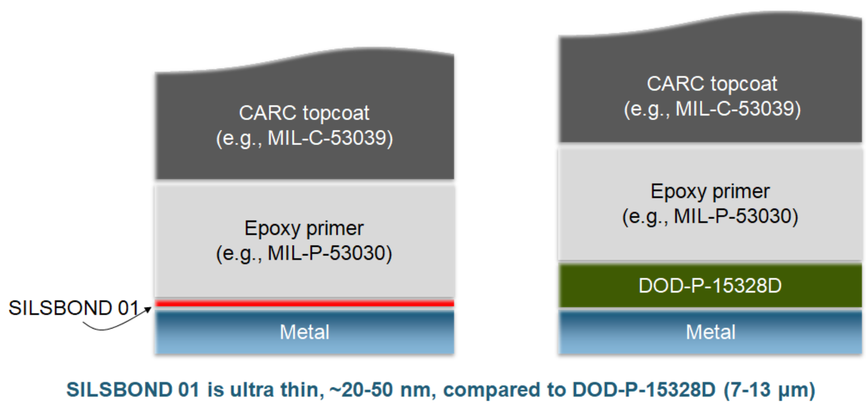

Figure 2. Comparison Between SILSBOND Coating and DOD-P-15328 Wash Primer

The SILSBOND 01 pretreatment formulation consists of an aqueous silesesquioxane oligomers and H_2ZrF_6. The SILSBOND 01 treated metal surfaces have been characterized and its coating structure has been revealed. Figure 3 shows an SEM image of a SILSBOND 01 treated cold-rolled steel (CRS) surface where uniform distribution of nano-particles, ranging from nano-meters to 25 nm, is evident. A SILSBOND 01 pretreatment coating on Al surface was also characterized using X-Ray Reflectivity (XRR) technique. The substrate was an Al-coated silicon (Si) wafer. The SILSBOND 01 coating on the Al surface was obtained by 30-sec immersion of the Al-coated Si wafer in a 2% SILSBOND 01 solution. The XRR data for the SILSOND 01 treated Al Si wafer was further interpreted by fitting the reflectivity vs. q profiles with a 4-layer model. The resulting Scattering Length Density (SLD) profiles is displayed in Figure 4. As shown in Figure 4, after 30 seconds of immersion in the 2% SILSBOND solution, the Al oxide layer is completely replaced by a 5 nm thick Zr-rich layer which is indicated as a spike (green) in the SLD profile. Also, a ~20 nm thick layer of lower SLD values is observed next to the Zr-rich layer. The lower SLD values indicate that this layer enriches with a polymeric structure.

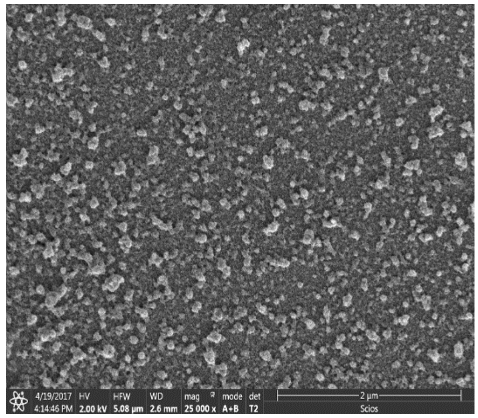

Figure 3. SEM Image of a SILSBOND 01 Treated CRS Surface

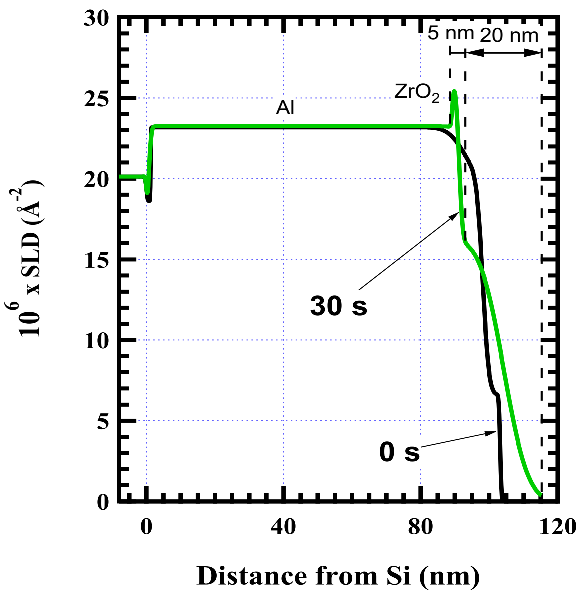

Figure 4. The Resulting SLD Profiles from the XRR data for a SILSBOND 01 Treated Al Surface. (Note: An Al Layer was Coated on a Si Wafer Surface Before SILSBOND 01 Immersion Treatment)

SILSBOND pretreatment significantly enhances the corrosion resistance of metals by offering excellent paint adhesion. The lab work performed by Ecosil Technologies LLC in a previous SERDP project (SERDP (WP-1675)), has demonstrated that SILSBOND can perform as well as the DOD-P-15328 pretreatment in ASTM B117 (NSS) and the since cancelled GM 9540 cyclic corrosion test on multiple metal substrates under military epoxy primers such as MIL-DTL-53022 and MIL-DTL-53030. The metal/alloy substrates tested with SILSBOND in the SERDP project included CRS, Al 7075-T6, and Al 2024-T3. Recent lab testing at ARL has also confirmed the performance of SILSBOND (test sample code: "Eco5-1") as a pretreatment coating on multiple metal substrates under MIL-DTL-53022 and MIL-DTL-53030 [9].

Ecosil initiated the development of low toxicity, dry-in-place SILSBOND pretreatment in 2009 with financial support from SERDP (WP-1675), National Science Foundation (NSF) Small Business Innovative Research (SBIR) Phase I, II and IIB (IIP-1152518), and MDA STTR Phase I (HQ0147-14-C-7919). Since 2011, SILSBOND pretreatment products have been sold to Original Equipment Manufacturers (OEMs) in general manufacturing industries as either a phosphate-free pretreatment or a sealer to produce improved performance for phosphate or zirconium based pretreatments. Ecosil has realized a sales volume of $1 million of SILSBOND in the United States by Ecosil's licensees and distributors of these products. Ecosil has also developed a distribution network to supply the Chinese market, and are in discussions with a potential licensee in Europe. Additional field testing of SILSBOND pretreatment is currently underway in the heavy equipment and machinery, automotive and sheet steel milling industries.

1.2 Objective(s) of the Demonstration

The primary objective of this completed research program was to validate the performance of Ecosils' SILSBOND pretreatment coating per TT-C-490 requirements and gain approval for the relevant QPD. Now validated, this technology was demonstrated at the user level via field-testing on non-critical military hardware for one to two years during Phases III and IV (FY19/20) depending on military service requirements:

1). The Ecosil pretreatment coating has been evaluated at the NSWCCD, South Florida Ocean Measurement Facility in Fort Lauderdale, Florida for one year in addition to the ARL testing at the Cape Canaveral Space Force Station marine outdoor exposure test site for 24 months exposure. This test was conducted to help assess the Ecosil pretreatment performance in outdoor weatherability testing. Laboratory accelerated corrosion tests have been completed at each facility (NAWCWD, ARL, NSWCCD and Ecosil). The outdoor exposure testing by ARL was completed (24 months) at their outdoor testing facility in Cape Canaveral Space Force Station, Florida.

2). Completion of the laboratory accelerated corrosion testing, a down selection of the best performing Ecosil pretreatment and topcoats from each facility has been determined (SILSBOND 01 (2% Ecosil SILSBOND Formulation)), and was applied to non-critical hardware for field testing (one to two–years duration) depending on service requirements.

The field demonstrations were successful and provided the DOD with another alternative to currently qualified pretreatments and populated the QPD.

Thus the expected benefit to the DOD is a robust, environmentally benign Cr(VI)-free pretreatment coating that now populates the QPD which gives end-users additional options. Having multiple products qualified under the QPD for TT-C-490 encourages open competition between manufacturers and products, and discourages any one company from monopolizing pretreatments within the DOD. This will result in lower cost, and higher quality products through innovation for the DOD end users.

1.3 Regulatory Drivers

Occupational Safety Health Administration (OSHA) has published a final standard for occupational exposure to Cr(VI) in the Feb. 28, 2006, Federal Register [21]. The standard covers occupational exposure to Cr(VI) due to the known carcinogenic nature of this compound and it is highly regulated by the Environmental Protection Agency (EPA) and OSHA. OSHA has determined based upon the best scientific evidence, that at the current permissible exposure limit (PEL) for Cr(VI), workers face a significant risk to their health. Therefore, a final rule establishes a PEL of 5 micrograms of Cr(VI) per cubic meter (5 $\mu g/m^3$) including all forms of Cr(VI), such as chromic acid, chromates, lead chromate, and zinc chromate. This ruling was based on extensive consideration of all comments and evidence submitted during this process.

1.4 Stakeholder/End-User Issues

Current alternative Cr(VI)-free pretreatments have been developed by industry for each service and several have been implemented for field use. The goal for this plan was to add a new sol-gel pretreatment coating to the TT-C-490 coating requirements. This demonstration was successful, and allowed for easy compliance with the new military Cr(VI)-free pretreatment coating requirements. The technology demonstration for each service, the co-performers (ARL, NSWCCD, Ecosil and NAWCWD) completed the in-house laboratory and marine outdoor exposure testing at the NSWCCD outdoor facility and ARL facility. A JTP for this program was submitted and approved for field demonstrations which were successfully carried out by each service and passed the TT-C-490 requirements.

2.0 DEMONSTRATION TECHNOLOGY

2.1 Technology Description

Coatings are normally defined as planar solid structures (either thick or thin films) that are chemically and/or mechanically attached to an underlying substrate (metal, glass, ceramic, silicon wafer, composite, etc.) [22]. Coatings can impart certain functionalities such as color, gloss, roughness, light reflectance, electrical and/or thermal conductivity, hydrophobicity/hydrophilicity, oleophobicity, omniphobicity, sensing, self-healing, anti-fouling, anti-corrosion, etc., to the coating in general and protection or surface enhancement of the underlying substrate [23]. There are many various coatings that have been investigated and applied to military and commercial substrates to inhibit corrosion. Corrosion costs accounts for ~3 % of the United States Gross Domestic Product and has a profound impact on the military's readiness and maintenance costs. Coatings such as solvent and waterborne liquid paints, powder, and e-coat paints have been investigated and utilized for corrosion protection of metal alloys [24]. Sol-gel coatings have been investigated for various applications such as corrosion-inhibition [25]. Sol-gel coatings have several attractive features such as a) low processing temperature, b) high chemical versatility, c) ease of application, d) strong bonding to a wide range of metallic substrates, and e) safe method of deposition.

Ecosil has developed an innovative, low toxicity sol-gel coating called SILSBOND. Sol-gel coatings are fabricated via two distinct methods (1) hydrolytic process in aqueous media, and (2) nonhydrolytic process in organic media [26, 27]. The sol-gel process is based on the hydrolysis and condensation reactions of metal alkoxides ($M(OR)_n$) where M = Si, Ti, Zr or Al and R = alkyl group (methyl, ethyl, butyl, etc.) [28, 29]. The sol-gel process involves two distinct and separate methods for the preparation of the "particles or films" which consists of either an inorganic or organic approach of which the latter is the preferred method. The sol-gel process involves the initial formation of a colloidal suspension or solution referred to as the ‘sol’ which is followed by the formation of the integrated network referred to as the ‘gel’ to give either discrete particles or network polymers (Figure 5).

Hydrolysis Reaction $\quad R\text{-}Si(OR)_3 \rightleftharpoons R\text{-}Si(OH)_3$

Condensation Reaction $\quad \text{-}Si\text{-}OH + HO\text{-}Si\text{-} \rightleftharpoons \text{-}Si\text{-}O\text{-}Si\text{-} + H_2O$

Figure 5. Hydrolysis and Condensation Reactions for Producing Sol-gel Films

The sol-gel process occurs in four stages: [30]
1). Hydrolysis,
2). Condensation and polymerization of monomers to form chains or particles,
3). Growth of the particles or chains, and
4). Agglomeration of the networks, thickening and formation of the gel.

The sol-gel process allows control over the surface properties on various substrates (e.g. metals, glass, silicon wafer, polymers, and textiles) through adjustments of the reactive species, organic functionalization, temperature, time, and pH [31]. This technique is a highly versatile, facile, and inexpensive method that allows one to control and manipulate composition and microstructure of a coating at the molecular level under ambient conditions and it provides a method to coat various surfaces with functionalized polymer hybrids. This system has been commercialized by several industrial paint companies and is currently used in the commercial aerospace industry as a pretreatment coating for improved adhesion between substrate and primer.

As examples of these inorganic-organic hybrids, Vasiljevic et al. developed a two-component inorganic-organic hybrid sol-gel coating that exhibited multifunctional properties including simultaneous super hydrophobicity/oleophobicity and passive antibacterial activity [32]. Hybrid nanostructured sol-gel coatings have also been investigated to inhibit bio-corrosion on stainless steels. These functional coatings consisted of an inner compact layer of titanium oxide and an outer dense layer of poly(vinyl-N-hexylpyridinium) brushes [33].

While organic sol-gel coatings have been investigated and studied extensively, aqueous sol-gel formulations have also been investigated. These aqueous sol-gel coatings are based on organofunctional silanes that offer low toxicity alternatives to Cr(VI) and organic sol-gel coatings [34, 35]. These coatings offer enhance resistance to corrosion/ oxidation, enhanced performance of coatings applied over them and very low-temperature cure when required.

Recently, Ecosil has developed a new and innovative water-based sol-gel pretreatment coating for corrosion-inhibition on military alloys. This formulation is known as SILSBOND which is a non-toxic, compliant chemical formulation. The pretreatment film has shown to significantly enhance the corrosion resistance of metals by improving paint adhesion. Its superior performance has been demonstrated on multiple metal substrates in government-funded research projects [1, 5-7].

2.2 Technology Development

This section documents the previous work of Ecosil in developing and testing the corrosion and adhesion properties of SILSBOND formulations which are described below in the following paragraphs.

SILSBOND has been investigated also in addition to the current ESTCP program (Cr(VI) pretreatment replacement) as an iron/zinc phosphate replacement on CRS. Figure 6 shows powder painted cold rolled steel panels after 1000 hours of NSS exposure in accordance with ASTM B117. The SILSBOND pretreatment shows equivalent performance to zinc phosphate with a non-chromium sealer.

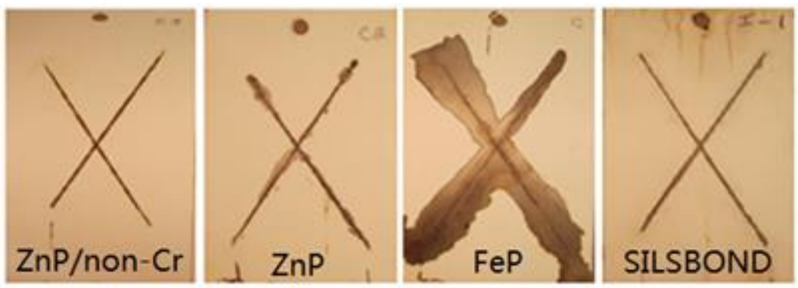

Figure 6. 1000-hour NSS, Powder Painted CRS

SILSBOND as a zinc phosphate replacement which was coated onto hot rolled steel (HRS) with a CARC coating is shown in Figure 7. This demonstrates that the HRS panels painted with a CARC coating system survived 800 hours NSS. The SILSBOND pretreatment provides the same performance as the test panel pretreated with ZnP/hexavalent chromium sealer.

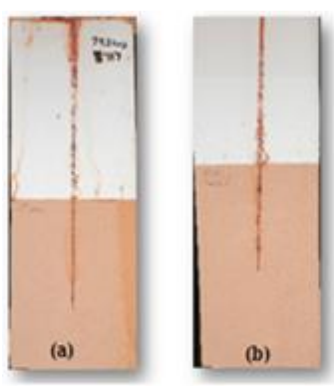

Figure 7. 800-hr NSS, CARC Painted HRS (a) SILBOND Pretreatment and (b) Zn/P Hexavalent Chromium Sealer

SILSBOND as compared to DOD-P-15328 on abrasive-blasted Al 6061 substrates is shown in Figure 8. This figure shows the results of 240 hours copper accelerated acetic acid salt spray (CASS, ASTM B638) of SILSBOND coated on abrasive blasted Al 6061 coated with epoxy primer MIL-PRF-23377N vs. control. The CASS is an aggressive accelerated corrosion test used to determine corrosion resistance of various aluminum alloys. Figure 8 (a) shows corrosion of control panel DOD-P-15328 and (b) shows the improved corrosion-inhibition with the SILSBOND formulation. These extensive studies have been performed using Ecosil's SILSBOND technology under various government funded programs which document the corrosion protection and low toxicity coating processes used for Ecosil's formulations as an attractive coating for military applications.

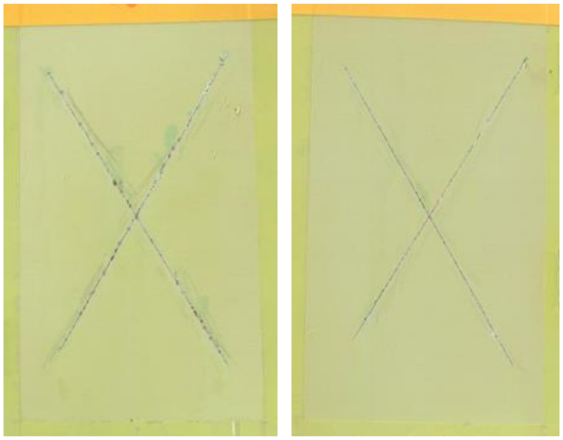

Figure 8. (a) DOD-P-15328 (b) SILSBOND 1.5%

2.3 Advantages and Limitations of the Technology

Ecosil initiated the development of low toxicity, dry-in-place SILSBOND pretreatment in 2009 and listed below are programs that documented the success of using the SILSBOND pretreatment coatings.

(1) SERDP (2009-2011, $455K): Ecosil has tested a variety of dry-in-place SILSBOND formulations on 1020 steel, Al 2024-T3 and Al 7075-T6 with MIL-DTL-53030 and MIL-DTL-53022 in both ASTM B117 and GM 9540 (now cancelled), and benchmarked against DOD-P-15328. The test results demonstrated that an optimized SILSBOND formula (Eco5-1) outperformed DOD-P-15328 on 1020 steel, Al 2024-T3 and Al 7075-T6. In this work, Eco5-1 was sprayed onto cleaned metal substrates and followed by drying-in-place under ambient conditions.

(2) NSF Small Business Innovative Research (SBIR) Phase II – Technology Enhancement for Commercial Partnerships (NSF SBIR Phase II-TECP) (2012 with Valspar Inc., $100K): SILSBOND was tested as dry-in-place pretreatment in a 3-stage washer process on metal substrates under a direct-to-metal (DTM) polyurethane coating used for heavy equipment manufacturing. This coating was benchmarked against a 5-stage iron-phosphate pretreatment both with and without sealer (Bonderite® 1000/P99X, Henkel iron phosphate product). SILSBOND performed equal to, and in some cases better than Bonderite® 1000/P99X. This research has also demonstrated the robustness of SILSBOND pretreatment when tested with a city water rinse rather than a DI water rinse typically used in the process, which is more easily available and cheaper to employ in applications.

In 2010, the optimized SILSBOND pretreatment (Eco5-1) was submitted to ARL for testing as an environmentally-compliant replacement of DOD-P-15328 Cr(VI)-wash primer. The test results were favorable, confirming that Eco5-1 can provide comparable, and in some cases superior, to the performance of the legacy DOD-P-15328 wash primer. One performance drawback that was observed with the Eco5-1 formulation occurred on Al

2024-T3 substrates with Cr(VI)-free epoxy primers (MIL-DTL-53022 and MIL-DTL-53030). Findings in the subsequent NSF Phase II project showed that lower SILBOND concentrations and heating of the SILSBOND solution (e.g., 105-110ºF) can significantly enhance the SILSBOND pretreatment performance on aluminum alloy substrates.

Therefore, optimization of SILSBOND performance on aluminum alloy substrates was completed during this ESTCP program. Specifically, Ecosil has optimized the process parameters for SILSBOND formulation including contact time, concentration of the SILSBOND working solution, heating of SILSBOND working solution, and hot air drying. In addition, the extensive laboratory testing, marine outdoor exposure and field testing have documented the robustness of the SILSBOND 01 pretreatment coating making it a viable product for military use by the DOD (Army/Marines) for military vehicles. As of June 28, 2023 this product (SILSBOND 01) has been approved to the TT-C-490 QPD. The following letter of approval (Figure 9) is included showcasing the acceptance by the CARC commodity manager the usefulness of the SILSBOND 01 pretreatment coating.

DEPARTMENT OF THE ARMY
U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND
ARMY RESEARCH LABORATORY
ARMY RESEARCH DIRECTORATE
ABERDEEN PROVING GROUND, MARYLAND 21005-5069

Army Research Directorate
FCDD-RLA-MC

28 June 2023

Ecosil Technologies LLC
ATTN: Ms. Danqing Zhu
160A Donald Drive
Fairfield, OH 45014

Dear Ms. Zhu:

Your product, Silsbond 01, has been evaluated by our laboratory and has been approved for use with the surface cleaning method(s) and on the substrate class(es) listed below. Additionally, Silsbond 01 has been assigned the following PT number on the Qualified Products Database (QPD): PT#00020.

Specification	Manufacturer Designation	Manufacturer Name/Address	Cage Code	Qualification Number	Surface Cleaning Method(s)	Type	Substrate Class(es)
TT-C-490	Silsbond 01	Same as above	343Y2	PT#00020	I, II	IV	B

Our test results indicate that your product complies with all qualification requirements for this specification. This letter serves as notification that the above product is approved for listing on the next revision of the QPD for TT-C-490. Your product will continue to appear on future QPDs associated with this specification for the method, type and class(es), as noted above, unless we receive notification that your product no longer complies with the specification requirements specified for this pretreatment method, coating and class(es).

There shall be no changes made to either the formulation (composition) or manufacturing procedures unless the material is re-examined by the qualifying agency responsible for maintaining the QPD and it is determined that your product complies with the requirements of the latest amendment or revision to this specification. The manufacturer is cautioned not to change any type or grade of compositional ingredient used in the product formulation at subsidiary plants or locations from the original formulation regardless of the extent of the change that qualified it for listing; such changes could affect product performance. Such a change is cause for removal from the QPD. If the product fails to meet all of the requirements of this specification or subsequent revisions, it would be cause for removal of the product from the QPD associated with the latest revision to TT-C-490.

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FCDD-RLA-MC
Ecosil Technologies LLC

28 June 2023

This letter of approval for qualification and listing on the QPD does not guarantee acceptance of products in a purchase, nor does it constitute a waiver of established specification requirements for acceptance, inspection, testing, scheduling or any other provision that may be specified in the contract for this product.

Any use of the listing for publicity, advertising, or sales will not state or imply that the product or the process is the only one of that type so qualified, or that the Government in any way recommends or endorses the manufacturer's product in preference to other qualified products. Violation is cause for removal from the electronic QPL/QPD in accordance with SD-6 Provisions Governing Qualification. NOTE: any reproduction must be done in full text.

It is the responsibility of your company to notify the various elements and subsidiaries of your company that your products have qualified. The points of contact for this action are the undersigned, who can be reached at 410-306- 0690 or Tom Considine at 410-306-2564.

Sincerely,

/s/ Daniel M. De Bonis

Daniel M. De Bonis
DEVCOM Army Research Laboratory
DoD CARC Commodity Item Manager

Figure 9. Letter of Approval by ARL CARC Manager

3.0 PERFORMANCE OBJECTIVES

The project's joint technical team identified engineering, performance, and operational impact (supportability) requirements for Cr(VI) and Cr(VI)-free coatings found in pretreatments used on aluminum alloys and steel which were based on a case by case study documented in TT-C-490. The technical team then reached consensus on tests with procedures, methodologies, and acceptance criteria for evaluating alternate pretreatment/primer/topcoat coating technologies which were based on the coating requirements found in TT-C-490. The data produced by tests is intended to be used as a guide for implementation for each user and users selected alternatives based on their respective business case and military requirements.

The major requirements for the tests for this ESTCP program were the following:

- Corrosion Resistance
- Pretreatment/Paint system adhesion
- Environmental, Safety and Occupational Health
- Field Testing and Evaluation/Replacement

Tests were conducted in a manner that eliminated duplication and optimized the testing of each coated coupon. For example, where possible, more than one test was performed on each coating formulation replicate sample coupon (recommendation 5 coupons per test). The number and type of tests that can be run on any one sample coupon was determined by the destructiveness of the test.

Testing was divided into two phases: alternative screening and field demonstration and validation. Alternatives were completed during the screening phase of the JTP before entering into the field portion of the testing phase. The screening processes, paint adhesion, and corrosion tests were completed first. It was not necessary to evaluate the corrosion performance of coating systems with unacceptable paint adhesion. For all testing, alternatives were applied and tested by DOD, contractor personnel, and at authorized vendor sites. Alternatives that were not available for “in-service” testing were considered immature for this project. Alternatives must reach maturity before depots and OEMs will consider them for implementation.

In the screening process, alternatives were also rated on process flexibility. Parameters such as number of solutions or steps in the process, heating requirements and curing requirements were detailed. Processes that require elevated temperatures for pretreatment or primer solutions or curing may be appropriate for immersion application, but were not applicable for spray or wipe application to already-assembled platforms. Processes were screened for appropriate application methods before testing. The Army and USMC CARC topcoat were used for all painted corrosion tests.

4.0 SITE/PLATFORM DESCRIPTION

The best performing (laboratory testing/marine outdoor exposure) SILSBOND pretreatment coated in a full military system (epoxy primer and Army/USMC CARC topcoats) was evaluated in field testing studies. The laboratory testing has shown that the SILSBOND 01 (2%) as the best performer and was accepted by each of the co-performers as the formulation for both Army and USMC for atmospheric exposure testing and field testing studies. After acceptance of the JTP and demonstration plan by the ESTCP Program Office, the Army and USMC evaluated the SILSBOND primer coating in a coating stack-up via field testing on non-critical military hardware for one-two-year duration depending on service requirements.

4.1 Test Platforms/Facilities

The demonstration platforms that were selected during Phase II were based on each service analyzing the laboratory and outdoor exposure testing and determining a suitable platform for testing Ecosil's SILSBOND formulations. Thus, after full completion of the laboratory adhesion, accelerated corrosion, and outdoor exposure testing a down-selection of the best performing SILSBOND formulation, SILSBOND 01 (2 wt.%) with primer and CARC topcoats was applied to non-critical military hardware for field testing.

4.1.1 Test Platforms/Facilities at ARL

ARL evaluated the SILSBOND pretreatment with full CARC stack-up on non-critical components for a military vehicle such as the MRAP vehicle. The field test was performed at the ARL Cape Canaveral Space Force Station, Florida marine outdoor exposure facility. Performance criteria that was evaluated by the field-testing included coating adhesion, intercoat compatibility, and corrosion protection. The limited scale demonstration was performed using vehicle components with participation from the PMO. ARL has research agreements with the PMO for both Stryker and MRAP. MRAP components were selected for this field demonstration. Components of the MRAP vehicle were obtained and abrasive blasted to bare metals and treated with Ecosil's SILSBOND 01 formulation with representatives from the manufacturer (Ecosil) present during the coating process. Identical components were prepared using Henkel Bonderite M-NT 7400 pretreatment coating for comparison and the new pretreatment coating did meet the coating requirements called out in TT-C-490.

The following test site for the ARL non-critical military hardware is documented below (Figure 10). The parts for the demo are MRAP rear doors, one door with control pretreatment coating, and the other with Ecosil. Both doors, test coupons and parts were primed with MIL-DTL-53022, type IV and topcoated with MIL-DTL-53039. The test site was at the Cape Canaveral Space Force Station, Florida. Test specimens were mounted on racks for a duration of 24 months and the demonstration performance objective was to meet the performance coating requirements of TT-C-490. Bonderite M-NT 7400 was selected as the pretreatment coating control and was used to measure the SILSBOND pretreatment coating performance vs. control.

A similar demonstration was conducted as part of the ESTCP WP-200906 for steel pretreatments. As seen below, a MRAP door was processed and placed for field testing (Figure 11). The inspections were conducted every three months during this field-testing for a two-year period.

Figure 10. Cape Canaveral Space Force Station
(Location of ARL Field Demonstration Exposure Site)

Figure 11. Freshly Abrasive Blasted MRAP Door Prior to the Application Pretreatment

4.1.2 Test Platform/Facilities at Marine Corps Base, Hawaii

The USMC under the direction of NSWCCD Code 613 conducted field testing using coated SILSBOND 01 (2%) on USMC vehicles with 4” x 6” panels on the MTVR. The NSWCCD required that the field test demonstration have plans that allow aluminum and steel coupons mounted onto racks, which were situated to the rear of the Marine Corps MTVR. The recommended panel size was 4” x 6” with a 4” diagonal line scribe or x-scribe on the panel. Either two or three panels in the configurations were mounted on each rack and this depended on the number of replicates and substrates. The panels were mounted with 1/4” nylon fasteners to the rack, which was then secured to the vehicle.

For the USMC field testing which was supervised by the NSWCCD Code 613, there were MTVR vehicles available at Marine Corps Base Hawaii which is shown in Figure 12.

Figure 12. USMC MTVR

There were 10 vehicles each with available racks in the Hawaii location (Figure 13). The units based at the USMC base in Hawaii operate in an environment that has a higher corrosion rate than those in a typical garrison location, but also have a lower operational tempo. Additionally, the vehicles were regularly transited by barge from Marine Corps Base Hawaii on Oahu to the Pakaloa Training Area on the island of Hawaii. The duration of the field test was one year.

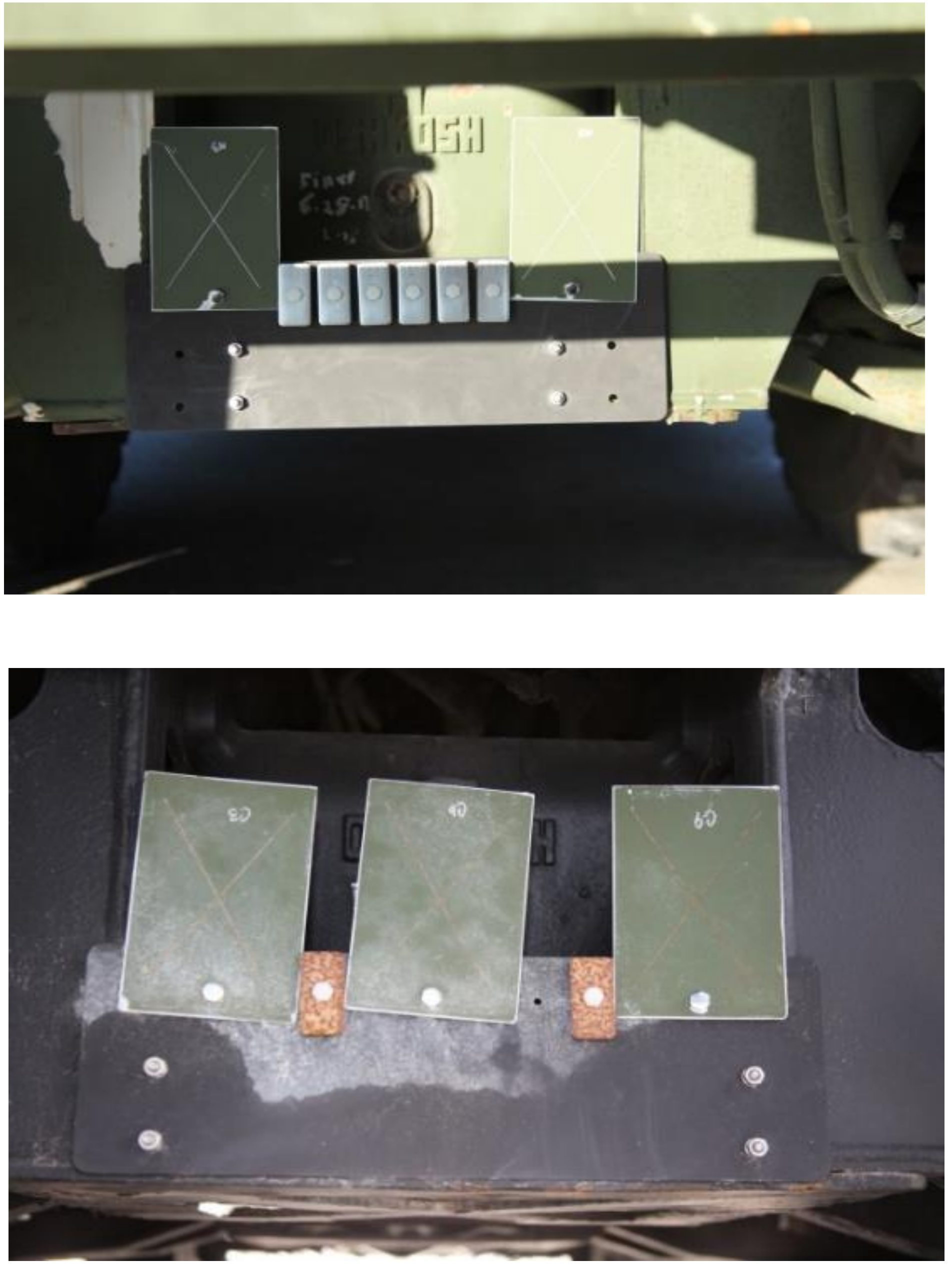


Figure 13. MTVR Vehicle with Racks for Holding Coated Coupons (top and bottom)

4.1.3 Test Platform/Facilities at Cape Canaveral Space Force Station

The Cape Canaveral Space Force Station, Florida was chosen for marine outdoor exposure testing for several reasons including the site's harsh marine conditions resulting in high corrosion rates, high solar loading, high humidity, salt spray, rain, and wind.

This test method evaluated a coating system's (pretreatment/primer/topcoat) ability to prevent corrosion and the effect that corrosion has on the adhesion of the coating system over a 24 month test period. Marine outdoor weathering was included in a battery of exposure tests to determine the effect natural weather patterns and environmental exposure has on a coating system because accelerated corrosion testing can only give an estimate as to the corrosion resistance, degradation, and adhesion characteristics of a coating system. This outdoor weathering data along with accelerated corrosion data provided more detail to the anticipated performance of the coating system prior to field testing. This test was performed on topcoated systems for Al 2024 and 1020 Steel substrates. ASTM D1014, Standard Practice for Conducting Exterior Exposure Tests of Paints and Coatings on Metal Substrates, or ASTM G50 Standard Practice for Conducting Atmospheric Corrosion Tests on Metals is used for guidance to run the test and to evaluate the samples. Samples were scribed with an X-scribe prior to exposure. To prevent loss of the coupon number during exposure, a weather-proof label was applied to the backs of each sample prior to exposure. There were a minimum of three replicates per coating system. Coated coupons were rated and photographed every 3 months until the end of the test.

Marine outdoor exposure testing was conducted at the appropriate beach site facility that has a corrosion rate of 1.8-4.7 mils per year (mpy) which was the ARL site located at Cape Canaveral Space Force Station, Florida. Test coupons were installed on appropriate test stands using non-conductive (insulating) durable plastic stand-offs. The rack angle of the coupons was 30 degrees from horizontal.

4.2 Site-Related Permits and Regulations

For each facility, no site-related permits or regulations allowing for field testing or marine outdoor exposure testing was required. The only basis for testing Ecosil's pretreatment coated panels on non-critical military components or marine outdoor exposure was the ability of the SILSBOND 01 pretreatment coating to meet minimum corrosion/adhesion requirements set down in the JTP.

5.0 TEST DESIGN

5.1. Product Testing-Laboratory Testing

For the ARL field testing of the Ecosil pretreatment coating: 2-coating systems was tested side-by-side on the MRAP rear doors. These 2-coated systems are listed below.

- The standard system of Bonderite M-NT 7400 pretreatment coating, MIL-DTL-53022 TIV non-Cr(VI) epoxy primer, and MIL-DTL-53039 polyurethane CARC topcoat
- The test system of Ecosil sol-gel pretreatment, MIL-DTL-53022 TIV non-Cr(VI) epoxy primer, and MIL-DTL-53039 polyurethane CARC topcoat

These coated systems provided comparative data from the same operational location of the test bed. The following ASTMs were referenced to record and analyze test data for this program.

- ASTM D1014 Conducting Exterior Exposure Tests of Paints and Coatings on Metal Substrates
- ASTM D610 Evaluating Degree of Rusting on Painted Steel Surfaces
- ASTM D714 Evaluating Degree of Blistering of Paints
- ASTM D660 Evaluating Degree of Checking of Exterior Paints

- ASTM D661 Evaluating Degree of Cracking of Exterior Paints
- ASTM D1654 Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments
- ASTM D4214 Evaluating Chalking

At the Marine Corps Base Hawaii test site, the demonstration took place on panels attached to the rear of the MTVR vehicle. After primer and topcoat application, coupons (control + Ecosil pretreatment) were put on the vehicle. Their performance was tracked using chalking and corrosion resistance as metrics.

5.1.1 Joint Test Protocol Guidelines

The JTP has been our reference guide for this ESTCP Program. This is a water-based formulation SILSBOND 01 (2%). This formulation refers to 2% SILSBOND composition (weight %) dissolved in 98% water, and this product posed no health risk to service personnel. The JTP which was developed and submitted for approval prior to the demonstration of the SILSBOND pretreatment coating was developed by the NAWCWD in cooperation with ARL, NSWCCD, and Ecosil. The JTP outlined testing that was required and metrics for determining the performance of the SILSBOND pretreatment coating during laboratory testing for this ESTCP program.

5.1.2 Demobilization

There was no demobilization of equipment for this field test. Each service applied the Ecosil SILSBOND 01 (2%) coating onto the non-critical equipment parts and monitored its performance.

5.1.3 Selection of Analytical/Testing Methods

Analytical methods for use by ARL and NSWCCD have been the following. This is a summation of the test design found in section 5.1 which was adhered to during the course of this program.

- ASTM D1014 Conducting Exterior Exposure Tests of Paints and Coatings on Metal Substrates
- ASTM D610 Evaluating Degree of Rusting on Painted Steel Surfaces
- ASTM D714 Evaluating Degree of Blistering of Paints
- ASTM D660 Evaluating Degree of Checking of Exterior Paints
- ASTM D661 Evaluating Degree of Cracking of Exterior Paints
- ASTM D1654 Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments
- ASTM D4214 Evaluating Chalking

5.1.4 Management and Staffing

Prior to the field testing of the Ecosil SILDSBOND formulation, laboratory testing by each of the co-performers was performed. These tests were documented and allowed for the down selection of the best performing system for field demonstrations. The PI (Dr. Peter Zarras) managed the overall program both for laboratory and field testing studies. Dr. Danqing Zhu, Ecosil Technologies LLC provided sufficient quantities of the Ecosil SILSBOND formulations for laboratory and field testing studies. The marine outdoor exposure testing were completed by both ARL and NSWCCD and these tests helped in evaluating the best performing SILSBOND formulation for field testing.

Mr. Thomas A. Considine monitored and managed the testing of the Ecosil coated coupons at the laboratory scale and field demonstration parts at Cape Canaveral Space Force Station, Florida. Dr. Kunigahalli L. Vasanth, Mr. Jamaal Delbridge, and Dr. Andrew Sheetz of NSWCCD, conducted the laboratory testing of the Ecosil formulations and Dr. Andrew Sheetz supervised the field testing of the SILSBOND 01 (2%) formulations, and he monitored and managed the testing of the Ecosil coated coupons at Marine Corps Base Hawaii. See Figure 14 for details outlining the relationship with the PI and co-performers.

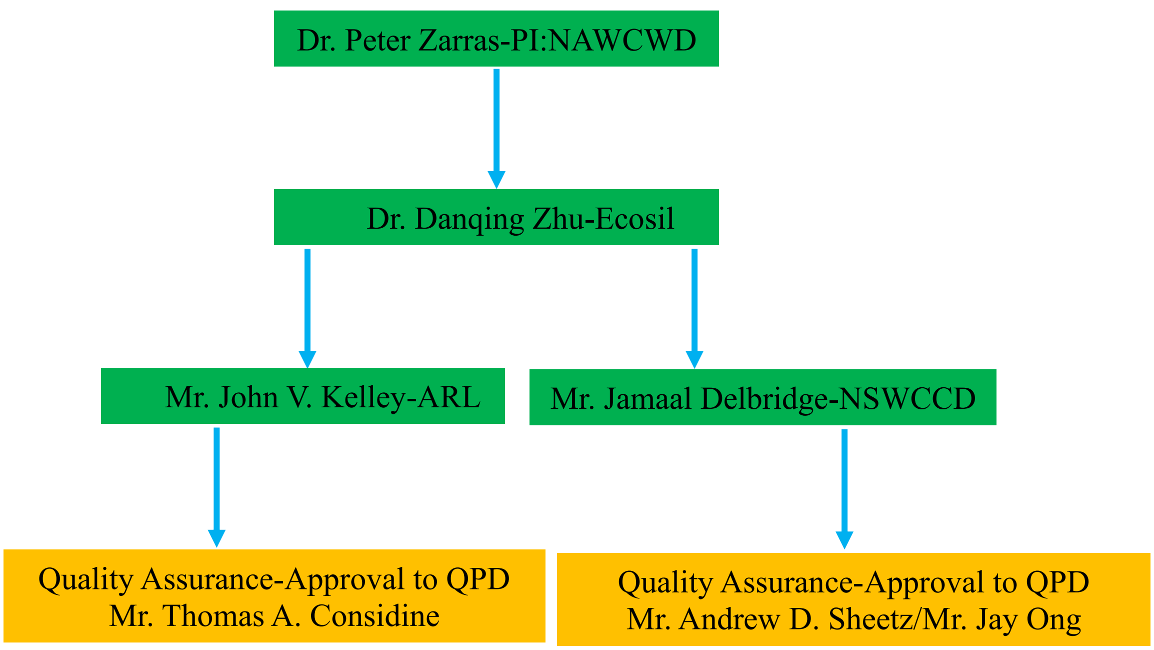


Figure 14. Flow Chart for SILSBOND Testing and Management/Staffing
Jamaal D. Delbridge and Kunigahalli L. Vasanth from the NSWCCD were responsible for laboratory testing of the Ecosil SILSBOND formulations.

5.1.5 Laboratory Testing

The tests outlined in Section 5.0 included test description, rationale, and methodology. Also included, as needed, were any major or unique equipment requirements, as well as data reporting and analysis procedures. The test methodology included the definition of test parameters, test specimens, number of trials per specimen, any experimental control specimens required, and acceptance criteria. The primary purpose of this JTP was to provide data to the joint user community, which it can use to select alternatives, if any, for field testing. Decision criteria varied by user, and that different users choose different alternatives based on their business cases.

Unless otherwise required by a specific test, test coupons were at least 4 inches wide by 6 inches long and of suitable thickness (0.020-0.060 inch). Additionally, metal coupon surfaces must be water break-free prior to coating application. Water break tests were performed in accordance with ASTM F2265 (*Standard Test Method for Hydrophobic Surface Films by the Water-Break Test*). Test coupons were painted within 24 hours of the application of the pretreatment. Where shipping was involved, this was taken into account for additional variables that could have been encountered during the shipping process.

5.1.6 Adhesion Testing Methods

The following sections document the specific adhesion tests that were used to determine the adhesive properties of Ecosil's SILSBOND formulations as pretreatment coatings with and without full military coatings.

5.1.7 Crosshatch Adhesion

Crosshatch adhesion testing was performed to determine the coating adhesion interface such as adhesion to substrate and intercoat adhesion. This test was performed on pretreated and primed systems for Al 2024-T3 aluminum and 1020 Steel substrates. ASTM D3359, *Standard Test Methods for Measuring Adhesion by Tape Test*, was used for guidance to run this test. Requirements for sample evaluation are provided in TT-C-490. Samples with pretreatment and primer only (no topcoat) were tested using the 2-millimeter spacing crosshatch blade. There were five replicates required for each coating system on aluminum or steel samples. The ratings provide only general information concerning the overall adhesion performance of the system. The description of the rating scale, as taken from ASTM D3359, is given in Table 1.

Table 1. ASTM D3359, Method B, Crosshatch Adhesion Rating Scale Description

Rating Scale	Visual Observation
5B	The edges of the cuts are completely smooth, none of the squares of the lattice is detached
4B	Small flakes of the coating are detached at intersections; less than 5% of the area is affected
3B	Small flakes of the coating are detached along edges and at intersections of cuts. The area affected is 5 to 15% of the lattice.
2B	The coating has flaked along the edges and on parts of the squares. The area affected is 15 to 35% of the lattice.
1B	The coating has flaked along the edges of cuts in large ribbons and whole squares have detached. The area affected is 35 to 65% of the lattice.
0B	Flaking and detachment worse than Grade 1.

A complementary method for evaluating adhesion of coated substrates was in accordance with ASTM D4541. The pneumatic adhesion tensile test instrument (PATTI) pull-off test is designed to give specific information concerning both the adhesion and the intra-coat cohesion of organic coating systems. This test is performed on pretreatment and primed systems for Al 2024-T3 and 1020 steel substrates. ASTM D4541, *Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers*, is used for guidance to run the test and to evaluate the samples. Light abrasion with 240-grit sandpaper was performed on primed samples. Samples were then cleaned with methanol prior to pull-stub application. There were 5 replicates for each coating system with 10 pulls per coupon. The data are the result of the calculated pull-off strength of either the coating layers that were removed or the maximum of the adhesive. For coating systems with multiple coatings a description of the nature of the coating failure was included with the reported numerical value of the pull-off and failure mode. A guideline to those descriptions are found in Table 2.

Table 2. PATTI Coating Failure Descriptions

Notation	Description	Failure Mode
T/T	Topcoat on pull stub and panel surface	Topcoat–Topcoat Cohesion
T/P	Topcoat on pull stub and primer on panel surface	Topcoat–Primer Adhesion
P/P	Primer on pull stub and on panel surface	Primer–Primer Cohesion
P/S	Primer on pull stub and no visible coating on panel surface (includes failures at the conversion coating, if visible)	Primer–Substrate Adhesion
T/E	Topcoat on panel and epoxy either on panel or on stub (Epoxy failure only – no coating failure noted)	Topcoat–Epoxy Adhesive
P/E	Primer on panel and epoxy either on panel or on stub (Epoxy failure only – no coating failure noted)	Primer–Epoxy Adhesive
Primer/Pretreatment	Primer on the stub and pretreatment on the panel	Primer–Pretreatment Adhesion
Pretreat/Pretreatment	Pretreatment on the stub and on the panel	Pretreatment–Pretreatment Cohesion

An Elcometer Model 108 Hydraulic Adhesion Test Equipment (HATE) (Figure 15) was used for this procedure as well as the Positest AT-A instrument and Table 3 provides performance criteria. This procedure was employed by the Army for measuring adhesion strength of new pretreatments/primer on substrates. In addition to being a more quantitative test method, pull-off adhesion was also less prone to human elements in testing such as variations in pressure applied during scribing as well as interpretation and perception of results. For the pull-off adhesion test, a loading fixture commonly referred to as a 20 mm "dolly" was secured normal to the coating surface using an adhesive. The adhesive used was typically cyanoacrylate or a two-part epoxy, so long as the bond strength of the adhesive was rated at more than 3000psi (pounds per square inch). After allowing the adhesive to cure for 24 hours at 25°C in ambient conditions, the attached dolly was inserted into the test apparatus. The outer perimeter of the dolly was isolated from the rest of the coating by etching with a blade not unlike a hole saw.

The load applied by the apparatus was gradually increased at a constant rate with a hydraulic testing device and monitored on the gauge until a plug of coating was detached. The failure value (in psi) was recorded and the failure mode was also characterized. For pull-off data to be valid, the specimen substrate must be of sufficient thickness to ensure that the coaxial load applied during the removal stage does not distort the substrate material and cause a bulging or "trampoline effect." When a thin specimen is used, the resultant bulge causes the coating to radially peel away outwards from the center instead of being uniformly pulled away in pure tension and this results in significantly lower readings than for identically prepared specimens with greater substrate thickness. Any test results in which the failure was entirely due to the adhesive were rejected (Table 3).

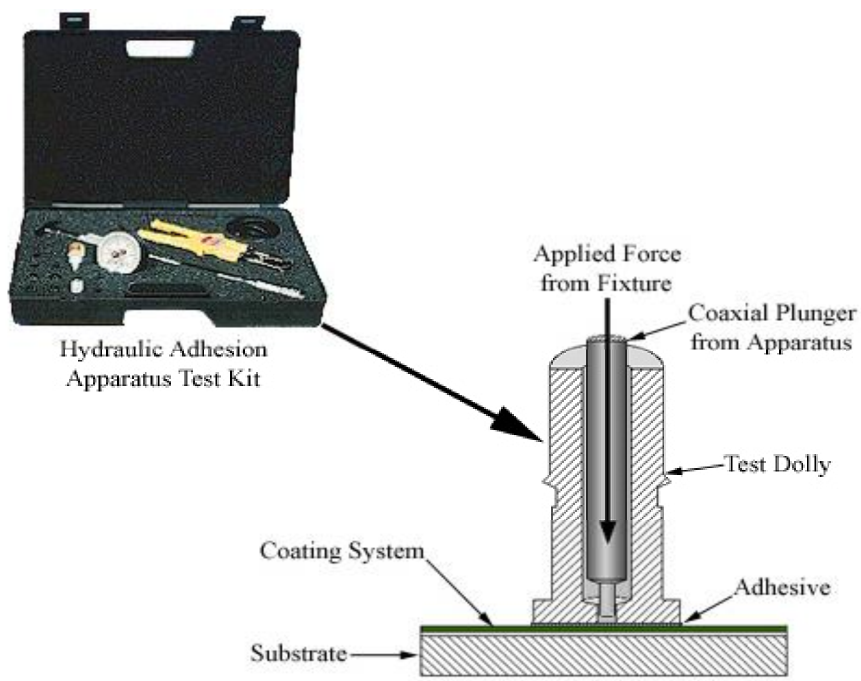


Figure 15. Hydraulic Adhesion Test Equipment and Dolly configuration

Table 3. Required Performance Parameters for PATTI Adhesion Test

Parameters	**Prep of substrate, application of coating, 5 replicates per coating system**
Number and Type of Specimens per Candidate Alternative	5 coupons per substrate per paint system for each test parameter
Trials per Specimen	10
Acceptance Criteria	See failure criteria (control samples should be used as guide here and related to their performance)

5.1.8 Wet-Tape Adhesion

The wet-tape adhesion test is designed to measure inter-coat adhesion of an organic coating immersed in water for a short time-period. This test was performed on pretreated and primed coated systems for Al 2024-T3 and 1020 Steel substrates. Federal Test Method Standard FED-STD-141 *Paint, Varnish, Lacquer and Related Materials: Methods of Inspection, Sampling, and Testing*, Method 6301, *Adhesion (Wet) Tape Test*, was used for guidance to run the test and to evaluate the samples (see Tables 4 and 5). There were five replicates per coating system. This test method covered a procedure for establishing adequacy of intercoat and surface adhesion of an organic coating immersed in water by applying pressure sensitive tape over a scribed area of the coating. The test also measured the coating's ability to resist penetration by water.

The test coupon was immersed in distilled water for 24 hours at 120 degrees Fahrenheit (^{o}F). The coupon was removed from the water and dried by wiping with a soft cloth. Two parallel lines were scribed approximately one inch apart; making sure that the coating had been scribed all the way through and into the substrate. Two incisions were scribed through the coating so that the smaller angle of the "X" was 30 to 45 degrees and the X-scribe incisions penetrated through the coating into the substrate. Each line of the "X" was approximately 1.5 inches long. Immediately after the incisions were made, a piece of tape was placed over the incisions parallel to the parallel scribe lines and smoothed out by rolling a 3-lb (pound) roller over it once. Then tape was removed rapidly at approximately a 180-degree angle. The incision area was inspected for peel away and the unscribed immersed area was inspected for blisters.

Table 4. ASTM D 3359 Adhesion, Method A, Rating Scale

5A	No peeling or removal of coating
4A	Trace peeling or removal along incisions or intersections
3A	Jagged removal along incisions up to 1/16 inch on either side
2A	Jagged removal along most of incisions up to 1/8 inch
1A	Removal from most of the inscribed area
0A	Removal beyond the inscribed area

Table 5. Required Performance Parameters for Wet Tape Adhesion Test

Parameters	**24-hour immersion at 120 degrees F, all in distilled water.**
Number and Type of Specimens per Candidate Alternative	5 coupons per substrate (Al 2024-T3,or Steel 1020) per paint system for each test parameter.
Trials Per Specimen	5
Acceptance Criteria	No peel away; at least 4A per ASTM D3359; no blistering of unscribed coating area.

5.1.9 Acccelerated Corrosion Tests

Accelerated corrosion testing often referred to as part of the "laboratory testing" was used to predict corrosion behavior of applied coatings onto various substrates prior to actual field testing. These types of tests are used as a screening mechanism to down-select the best performing coating system prior to field testing and service implementation. Accelerated corrosion tests include various kinds of cabinet-controlled and autoclave-controlled environments. These tests were appropriate for quality control, materials selection, material and environmental combinations and determining the mechanisms of corrosion inhibition.

5.1.10 NSS Exposure Testing ASTM B117 on Pretreated, and Primed Substrates

This test method evaluates a coating system's ability to prevent substrate corrosion and the effect that corrosion has on adhesion of the coating system. The operation of the salt spray chamber for this test was performed in accordance with ASTM B117, *Standard Practice for Operating Salt Spray Apparatus*. NSS exposure testing is performed to evaluate the ability of the coating systems to withstand a 5 weight percent sodium chloride solution, pH-adjusted to a range of 6.5-7.2. This test was performed on primed aluminum and steel substrates in accordance with ASTM B117. The TT-C-490 qualifications currently require only primed substrates for evaluation. All samples that are subject to NSS exposure are photographed before and after the test to document the coating performance. The recommendation is that the user have between three and five replicates per coating system, with preference for five replicates, but a minimum of three is required. The guidelines for sample evaluation are taken from TT-C-490, which calls for tests to run for 1008 hours with evaluations every 336 hours. Samples were X-scribed with a tungsten carbide scribe, exposed for 1008 hours and checked for blistering, loss of adhesion, undercutting, pitting, and corrosion build-up along the scribe. The scribe through the coating was prepared so that the smaller angle of the "X" is 30 to 45 degrees. Scribing must be done with enough force to ensure that the X-scribe has exposed the substrate. The scribe must have a 45-degree bevel, and each line of the "X" should be approximately 4 inches long. The back and edges of the coupon were coated with an appropriate material that helped to prevent edge corrosion products from developing and help maintain coupon identification when labelled on the backside. The scribed coupons were placed into a salt spray chamber at a 15-degree incline. The coupons were not allowed to contact other surfaces in the chamber, and condensate from any given was not permitted to contact any other coupons, as it could influence corrosion performance. The salt solution and the salt spray chamber were prepared and operated as specified in ASTM B117. The atomization manifold(s) in the salt spray chamber were oriented so that atomized salt solution did not directly impinge on the coupon surfaces. The salt spray chamber was continuously operated for 1008 hours or until failure of the new coating system.

Coupons were evaluated for surface corrosion and creepage from the scribe at 336 hour intervals. The coupons were carefully removed at the end of the test duration. Clean the coupons by gently flushing them with DI water or reagent grade IV water (water temperature less than 38 degrees C (100°F)). Then the coupons were dried with a stream of clean, compressed air, or allowed to dry ambient-air. The coupons were visually examined for corrosion. Slight surface corrosion in the scribe is generally acceptable as long as it does not undercut the paint film. Corrosive salts or oxides from the scribe running down the surface of the coupon were not considered evidence of severe corrosion. After completion of the corrosion resistance test evaluation, each test coupon was scraped with a 2-inch putty knife. The total loss of paint (maximum) was measured with an optical measuring magnifying device to determine long-term paint adhesion (see Table 6).

Table 6. Required Parameters for NSS Exposure Testing

Parameters	**Test coupons at a 15° angle.** **Temperature of exposed salt spray zone = 35 + 1.1 - 1.7°C (95 + 2 - 3°F).** **Every 80 cm^2 horizontal area, two collectors gather 1.0-2.0 ml salt spray/hour.** **5% salt solution (5 ± 1 parts by weight of NaCl in 95 parts of water).** **pH = 6.5-7.2 when atomized at 35°C (95°F).** **1008 hours.**
Number and Type of Specimens per Candidate Alternative	5 coupons per substrate (aluminum or steel substrates) per paint system
Trials Per Specimen	5
Experimental Control Specimens	5 coupons per substrate (aluminum or steel substrates) coated with pretreatment (control coupon) with same paint system as alternative
Acceptance Criteria	1008 hours with no evidence of corrosion. Minor surface corrosion in scribe acceptable with an ASTM D1654 rating of 6 or better for steel and 8 or better for Al and no blistering in excess of 5% with no blister greater than 1mm in diameter

5.1.11 Accelerated Cyclic Corrosion Test GMW14872 (Cyclic Corrosion on Scribed Pretreated and Primed Substrates)

This test method evaluated a coating system's ability to prevent corrosion and the effect that corrosion has on the adhesion between the pretreatment and coating primer. This test was operated in accordance with GMW14872 (*Accelerated Cyclic Corrosion Laboratory Test*), Exterior, Exposure C for 30 cycles. The GMW14872 test was developed by General Motors for the evaluation of assemblies and components. This test on scribed, pretreated and primed coated substrates is a key accelerated corrosion test to determine overall corrosion inhibition and paint adhesion. This test is used to evaluate the performance of various coating systems and was performed on pretreated and primed substrates of both aluminum and steel. Half of the samples were grit-blasted with 120-grit aluminum oxide prior to application of the pretreatment. The other half of the samples with a mill finish were solvent-cleaned with a combination of mineral spirits wipes, Brulin 815GD detergent cleaner immersion. Methyl ethyl ketone wipes are suggested to remove surface debris prior to application of the pretreatment. This provided two surface profiles denoted with "grit-blasted" and "mill-finished." One representative sample from each coating system was photographed at the initial conditions, prior to exposure to GMW14872. Pretreated and primed samples were X scribed and then exposed for 30 cycles and photographed every 10 cycles through the end of exposure and once more upon completion of the test.

For these systems, sample corrosion was rated based upon ASTM D1654 and coating requirements given in TT-C-490:

- ASTM D1654, S*tandard Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments*, for corrosion undercutting at the scribe, and
- TT-C-490, *Federal Specification Chemical Conversion Coatings and Pretreatments for Metallic Substrates (Base or Organic Coatings)*.

The rating scales for ASTM D1654 and coating requirements in TT-C-490 are given in Tables 7 and 8 respectively. The ratings assigned to corrosion creep width are shown in Table 7 and define the ratings requirements specified in TT-C-490 used for qualification approvals.

Table 7. ASTM D1654 Rating of Failure at Scribe Based on Mean Creepage

Millimeters	Inches (approximate)	Rating Number
Zero	0	10
Over 0. to 0.5	0 to $\frac{1}{64}$	9
Over 0.5 to 1.0	$\frac{1}{64}$ to $\frac{1}{32}$	8
Over 1.0 to 2.0	$\frac{1}{32}$ to $\frac{1}{16}$	7
Over 2.0 to 3.0	$\frac{1}{16}$ to $\frac{1}{8}$	6
Over 3.0 to 5.0	$\frac{1}{8}$ to $\frac{3}{16}$	5
Over 5.0 to 7.0	$\frac{3}{16}$ to $\frac{1}{4}$	4
Over 7.0 to 10.0	$\frac{1}{4}$ to $\frac{3}{8}$	3
Over 10.0 to 13.0	$\frac{3}{8}$ to $\frac{1}{2}$	2
Over 13.0 to 16.0	$\frac{1}{2}$ to $\frac{5}{8}$	1
Over 16.0 to more	$\frac{5}{8}$ to more	0

Table 8. Qualification Test Methods

Item	Method
Storage Stability	ASTM D1849
Adhesion	ASTM D3359
Flexibility	ASTM D522
NSS	ASTM B117
Cyclic Corrosion resistance	GMW14872
Atmospheric corrosion	ASTM D1014 or ASTM G50
HE	ASTM F519

5.2 Outdoor Exposure Testing

Because accelerated corrosion testing can only give an estimate as to the corrosion resistance, degradation and adhesion characteristics of a coating system, marine outdoor weathering was included in a battery of exposure tests to determine the effect natural weather patterns and environmental exposure had on a coating system. These data along with accelerated corrosion and adhesion data provided more detail to the anticipated performance of Ecosils pretreatment coating prior to field testing. This test was performed on a full CARC stack-up consisting of pretreated, primed, and topcoated systems for Al 2024-T3 and 1020 Steel substrates. ASTM D1014, *Standard Practice for Conducting Exterior Exposure Tests of Paints and Coatings on Metal Substrates*, was used for guidance to run the test and to evaluate the samples. Samples were scribed with an X-scribe prior to exposure. To prevent loss of the panel number during exposure, a label was applied to the backs of each sample prior to exposure. Samples were rated and photographed every quarter for the marine outdoor exposure testing performed by ARL until the end of the test.

5.2.1 Marine Outdoor Exposure Testing

This test method evaluated a coating system's (pretreatment/primer/topcoat) ability to prevent corrosion and the effect that corrosion has on the adhesion of the coating system. The 24-month outdoor exposure of scribed, pretreatment/primer/painted substrates was a key real world and real time test to determine overall corrosion inhibition and paint adhesion compared to controls. Outdoor weathering was therefore included in a battery of exposure tests to determine the effect natural weather patterns and environmental exposure will have on a coating system because accelerated testing can only give an estimate as to the corrosion resistance, degradation and adhesion characteristics of a coating system. This marine outdoor weathering data along with accelerated corrosion data provides more detail to the anticipated performance of the coating system prior to field testing. This test is performed on topcoated systems for aluminum and steel substrates. ASTM D1014, Standard Practice for Conducting Exterior Exposure Tests of Paints and Coatings on Metal Substrates, or ASTM G50 Standard Practice for Conducting Atmospheric Corrosion Tests on metals is used for guidance to run the test and to evaluate the samples. Samples are scribed with an X-scribe prior to exposure. To prevent loss of the coupon number during exposure, a label is applied to the backs of each sample prior to exposure. There were 5 replicates per coating system used for this study. Samples are rated and photographed every quarter until the end of the test.

Marine outdoor exposure testing was conducted at an appropriate beach side facility such as the ARL site located at Cape Canaveral Space Force Station, Florida that has a corrosion rate of 1.8-4.7 mils per year (mpy). Test coupons were installed on appropriate test stands using non-conductive (insulating) durable plastic stand-offs. The rack angle of the coupons is 30 degrees from horizontal. At the end of the test duration, test coupons were removed and visually examined. Slight surface corrosion in the scribe is generally acceptable as long as it does not undercut the paint film beyond the allowable distance (See Table 9).

Table 9. Required Parameters for Marine Outdoor (Beach Test) Exposure Testing

Parameters	• Test coupons at a 30° angle. • Temperature of exposed coupons varies with outdoor conditions. • 24 months (quarterly evaluations).
Number and Type of Specimens per Candidate Alternative	5 coupons per substrate (aluminum or steel alloys).
Acceptance Criteria	Performance equivalent to or better than controls following ASTM D1654 with an rating of 8 or better for aluminum and a rating of 6 or better for steel with no blistering in excess of 5% and no blisters greater than 1mm in diameter.

5.3 Mechanical Hydrogen Embrittlement (HE) Testing of Plating Processes ASTM F519

Direct tension specimens (Figure 16) were required for the HE testing using coating specifications found in TT-C-490. Ten specimens are overloaded mechanically to establish the average 100% notched ultimate tensile strength (UTS) loading strength of the base material. Once established, this average strength at 100% notched UTS is utilized to correlate a scale for percent of notched UTS. The specimen lot is then tested for hydrogen sensitivity at 75% of the notched UTS on an Instron model 1331 hydraulic test frame:

1) Three control specimens were stressed at 75% of the notched UTS
2) Three specimens were then treated with the pretreatment (e.g Ecosil coating) by coating with the pretreatment which was applied via spray and allowed to air dry.

Once dry, these specimens were stressed at 75% of the notched UTS. The times to failure were recorded and the accept/reject criterion for the test was to endure 200 hours at 75% of the notched UTS without fracture.

Figure 16. ASTM F-519 Hydrogen embrittlement specimen

6.0 Performance Assessment

6.1 Laboratory Testing

All laboratory testing was carried out independently by each organization. The following labs: Ecosil, ARL, NSWCCD, NAWCWD in accordance with the testing requirements that are documented in section 5.0. All testing done by each co-performer are listed independently to allow the reader a fuller understanding of what tests were conducted. The best-performing Ecosil SILSBOND pretreatment coating was down-selected for field testing and evaluation. Critical points are highlighted in bold type, tables or bullets to help the reader identify key elements of the test and the results.

6.1.1 Formulation/Initial Corrosion Studies of Ecosils SILSBOND Pretreatment Coating

The initial studies at Ecosil's facility in Fairfield, Ohio were conducted with the goal to down select several suitable SILSBOND pretreatments. This initial phase of testing was for eventual field coating repair applications based on corrosion resistance performance. Candidate pretreatments included SILSBOND 01, SILSBOND 02 and SILSBOND 03 which were evaluated at Ecosil and three DOD labs; (1) NAWCWD (China Lake, CA), (2) NSWCCD (MD) and (3) ARL (MD). Preliminary testing was done at Ecosil only, and then a round-robin test series was done at Ecosil with the three DOD laboratories.

This work was done between during the initial phase of this program (Phase I) to determine the best application process parameters for candidate pretreatments. As shown in Table 10, the SILSBOND pretreatments were compared at working concentrations of 1.5% and 3%. The coatings were evaluated on different metal substrates: alkaline-cleaned CRS; abrasive-blasted HRS; and alkaline-cleaned Al 2024-T3. The SILSBOND solutions were spray-applied onto the cleaned metal surfaces followed by ambient drying-in-place. No post rinse was done. DOD-P-15328 wash primer was used as a control for comparison purposes. The pretreated panels were coated with MIL-PRF-53022 Type IV epoxy primer for performance evaluation in NSS test in accordance with ASTM B117 for 500 hours and 1000 hours and the test results are shown in Figures 17-19.

Table 10. Candidate SILSBOND pretreatments and the application condition

<table>
<tr><th>Pretreatment</th><th>Concentration</th><th>Solution Temperature</th><th>Spray</th><th>Drying</th></tr>
<tr><td>SILSBOND 01-1</td><td>1.5%</td><td rowspan="5">1) ambient
2) 105-110°F
3) 115-120°F</td><td rowspan="5">Spray @10-15 psi for 90 sec.</td><td rowspan="5">Ambient drying for 30 minutes before coating</td></tr>
<tr><td>SILSBOND 01-2</td><td>3%</td></tr>
<tr><td>SILSBOND 02-1</td><td>1.5%</td></tr>
<tr><td>SILSBOND 02-2</td><td>3%</td></tr>
<tr><td>SILSBOND 03</td><td>3%</td></tr>
</table>

Figure 17 shows the coated CRS panels after NSS. All these pretreatments perform similarly based on the observation that there were no blisters on any of the intact painted areas and that there is a similar amount of creepage in all of the scribed areas.

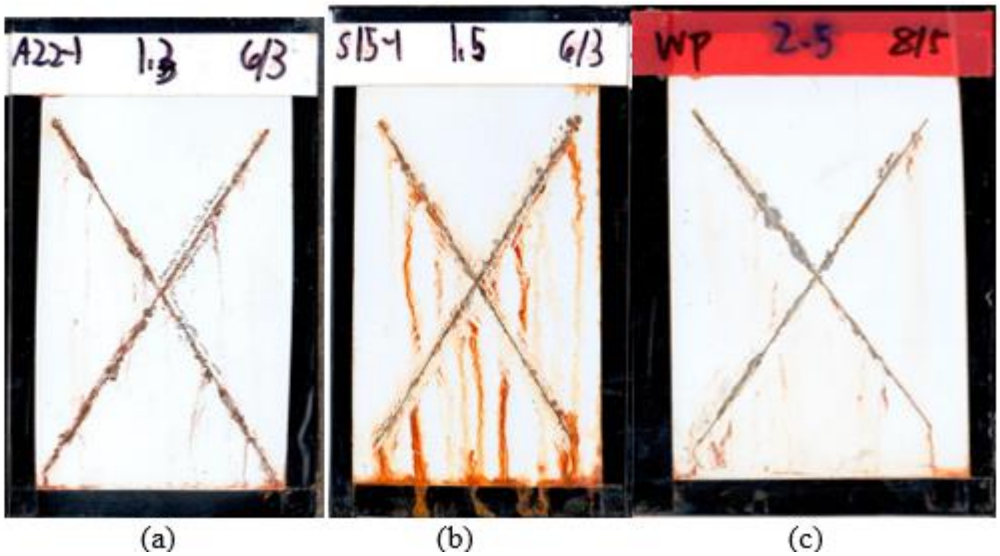


Figure 17. 500-hr NSS Results for MIL-DTL-53022 coated CRS; (a) DOD-P-15328, (b) SILSBOND 01 (1.5%) and (c) SILSBOND 02 (1.5%)

Figure 18 shows the coated abrasive blasted-HRS panels after 500 hour NSS. The panel pretreated with DOD-P-15328 primer (Figure 18(a) was rated as the best performer, followed by the panel pretreated with SILSBOND 01 (Figure 18(b)) and SILSBOND 02 (Figure 18 (c)).

(a) (b) (c)

Figure 18. 500-hr NSS Results for MIL-DTL-53022 coated blasted-HRS; (a) DOD-P-15328, (b) SILSBOND 01 (1.5%) and (c) SILSBOND 02 (1.5%)

Figure 19 shows the epoxy primed Al 2024-T3 panels after 500 hours NSS. SILSBOND 01 (Figure 19(b)) is the best performer, showing no creep in the scribes. The DOD-P-15328 (Figure 19(a)) shows a slight amount of paint loss in the scribes, while the panel pretreated with SILSBOND 02 (Figure 19(c)) shows several blisters along the scribes indicating poor paint adhesion.

(a) (b) (c)

Figure 19. 500-hr NSS Results for MIL-DTL-53022 coated Al 2024-T3; (a) DOD-P-15328, (b) SILSBOND 01(1.5%) and (c) SILSBOND 02 (1.5%)

Based on the Ecosils internal evaluation, three SILSBOND candidate pretreatments, i.e., SILSBOND 01 (1.5%), SILSBOND 01 (3%) and SILSBOND 05 (50%), were selected for a round robin test. The naming of the SILSBOND coatings were based on the formulation of the SILSBOND concentrate diluted in water. As an example SILSBOND 01 (1.5%) means that the SILSBOND concentrate at 1.5 wt.% was diluted in water to produce a solution that is a 98.5 wt.% water based formulation. The same process was duplicated for the remaining SILSBOND formulations described in this report.

The purpose of the round robin test was to further down select the best SILSBOND pretreatment for the QPD qualification tests. The round robin tests were conducted in parallel in 4 labs, including Ecosil lab (Fairfield OH) and the 3 DOD labs (ARL, NSWCCD, and NAWCWD). The reason that two concentration levels of SILSBOND 01 were included here was because Ecosil determined that these two concentration levels provide equally good paint adhesion. In addition, Ecosil decided to include a 50% concentration of SILSBOND 01 (SILBOND 05) because it has been shown to provide excellent flash rust resistance, which is of concern in the field repair applications we were targeting. Over 600 test panels were prepared at Aalberts at their facility in Baltimore, MD. As shown in Figure 20, the preparation work included alkaline cleaning of panels (Figure 20(a)), spray application of SILSBOND solution onto cleaned panels (Figure 20(b)). The panels were then topcoated with MIL-DTL-53022 Type IV and MIL-DTL-53039 (CARC-polyurethane topcoat)). After 2 weeks of ambient curing, the coated panels were sent to the 4 labs (Ecosil and 3 DOD labs) for testing. The adhesion and accelerated corrosion laboratory tests conducted in the round robin evaluation were; (1) ASTM B117 (1008 hrs); (2) GMW14872 (30 cycles), (3) ASTM D3359 (wet and dry adhesion) and (4) ASTM D4541 (Pull-off adhesion). The test matrix for the round robin test is shown in Table 11. The NAWCWD did not have a GMW14872 facility to conduct this test.

(a) (b)

Figure 20. Preparation of Test Panels; (a) Cleaning, (b) Pretreatment Spraying

Table 11. Test Matrix for the Round Robin Test (Ecosil only)

Ecosil	Substrate	ASTM B117	GMW14872	ASTM D 3359 Dry and Wet Adhesion	Pull-off adhesion ASTM D4541	
		53022 T4 / 53039	53022 T4 / 53039	53022 T4 / 53039	53022 T4 / 53039	
		4x6x0.0625	4x6x0.0625	4x6x0.0625	4x12x0.0625 (steel)	4x12x0.125 (alum)
Baseline DOD-P-15328	AL 2024	3	3	3		3
	1020 steel	3	3	3	3	
SILSBOND 01 (1.5)	AL 2024	3	3	3		3
	1020 steel	3	3	3	3	
SILSBOND 01 (3.0)	AL 2024	3	3	3		3
	1020 steel	3	3	3	3	
SILSBOND 05 (50)	AL 2024	3	3	3		3
	1020 steel	3	3	3	3	

6.1.2 Adhesion Testing

Tables 12 and 13 shows the adhesion test results from ASTM D3359 (wet and dry adhesion) and ASTM D4541 (Pull-off adhesion) for SILSBOND formulations. SILSBOND 01 (1.5%, no rinse) was the best performer on both steel and Al substrates. SILSBOND 01 (3%, no rinse) showed a noticeable amount of flash rust during ambient drying before CARC coating, while SILSBOND 05 (50%, no rinse) showed very good flash-rust resistance but its performance in other tests was inferior to the other SILSBOND formulations. Therefore, SILSBOND 01 (1.5%) was selected for the QPD qualification tests in the next step. Table 13 displays the dry and wet adhesion test results for primed Al 2024-T3 panels. All pretreatments except SILSBOND 05 (50 %) exhibit good adhesion in dry and wet conditions. The adhesion offered by SILSBOND 05 (50%) failed the adhesion testing.

Table 12. Dry and Wet Adhesion Test Results for CRS Coated with MIL-DTL-53022/ MIL-DTL-53039

pretreatment	Panel #	Dry Adheison		Wet adhesion
		Methed B	Method A	
Baseline DOD-P-15328	1	4B	4A	4A
	2	4B	4A	4A
	3	4B	4A	4A
SILSBOND 01 (1.5)	1	4B	5A	4A
	2	4B	5A	4A
	3	4B	5A	4A
SILSBOND 01 (3.0)	1	4B	5A	4A
	2	4B	5A	4A
	3	4B	5A	4A
SILSBOND 05 (50)	1	4B	4A	4A
	2	4B	4A	4A
	3	4B	4A	4A

Table 13. Dry and Wet adhesion Test Results for Al 2024-T3 Coated with MIL-DTL-53022/MIL-DTL-53039

pretreatment	Panel #	Dry Adheison		Wet adhesion
		Methed B	Method A	
Baseline DOD-P-15328	1	4B	5A	4A
	2	4B	5A	4A
	3	4B	4A	4A
SILSBOND 01 (1.5)	1	4B	4A	4A
	2	4B	4A	4A
	3	4B	4A	4A
SILSBOND 01 (3.0)	1	5B	5A	4A
	2	5B	5A	4A
	3	4B	5A	4A
SILSBOND 05 (50)	1	3B	3A	4A
	2	3B	3A	4A
	3	4B	4A	4A

Figure 21 compares the measured pull-off adhesion forces for CARC-coated CRS panels. The adhesion force (in psi) can be used as an indicator to show how strong the adhesion between the pretreatment layer and the CRC coating. The greater the value is, the stronger the adhesion is. SILSBOND 01 (3%) shows the highest value, followed by SILSBOND 01 (1.5%) and DOD-P-15328. The adhesion provided by SILSBOND 05 is the weakest. Figure 22 compares the pull-off adhesion test results for CARC-coated Al 2023-T3. SILSBOND 01 (1.5%) is the best performer, while the other pretreatments exhibit similar adhesion forces.

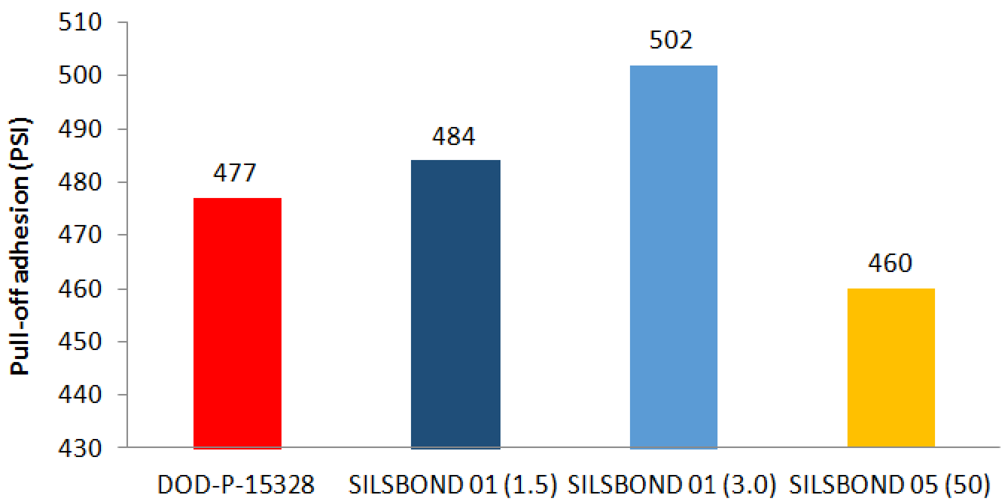


Figure 21. ASTM D4541 Pull-off Adhesion Test Results for CRS Coated with MIL-DTL-53022/MIL-DTL-53039

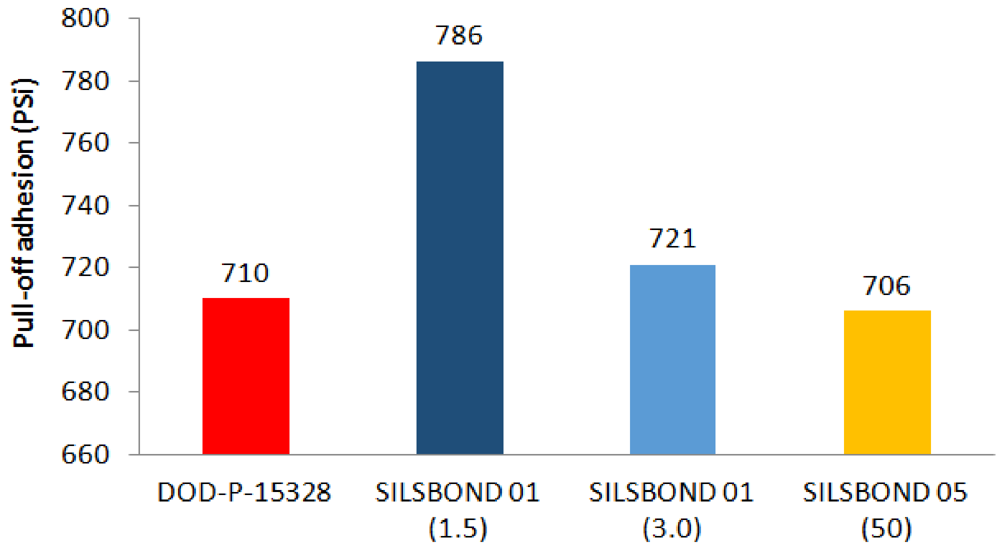
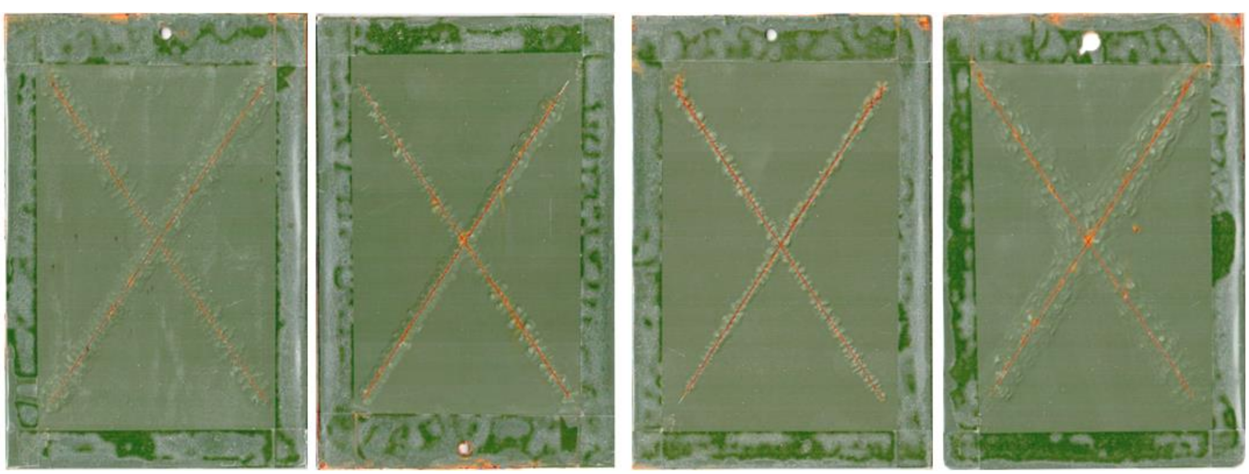


Figure 22. ASTM D4541 Pull-off Adhesion Test Results for Al 2024-T3 Coated with MIL-DTL-53022/MIL-DTL-53039

6.1.3 Accelerated Corrosion Testing

Figure 23 shows the CARC coated CRS panels after GMW14782 testing. Both SILSBOND 01 (1.5% and 3%) pretreated CRS panels (Figure 23(b) and (c)) displayed a smaller amount of paint loss in the scribes than the DOD-P-15328 treated CRS (Figure 23(a)) and the SILSBOND 05 treated CRS (Figure 23(d)). Figure 24 compares the measured creepage values for the panels shown in Figure 24 with the SILSBOND 01 (1.5%) showing the best performance.



(a) (b) (c) (d)

Figure 23. After 30 cycles of GMW14782 test, CRS panels coated with MIL-DTL-53022/MIL-DTL-53039; (a) DOD-P-15328 (b) SILSBOND 01 (1.5%) (c) SILSBOND 03 (3%) (d) SILSBOND 05 (50%)

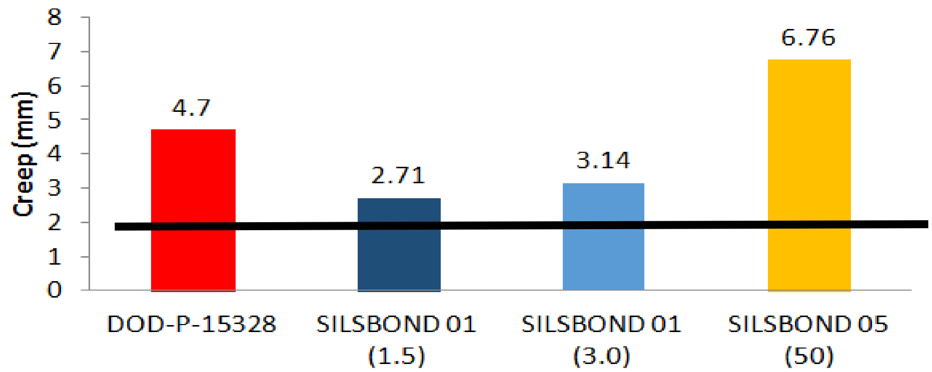
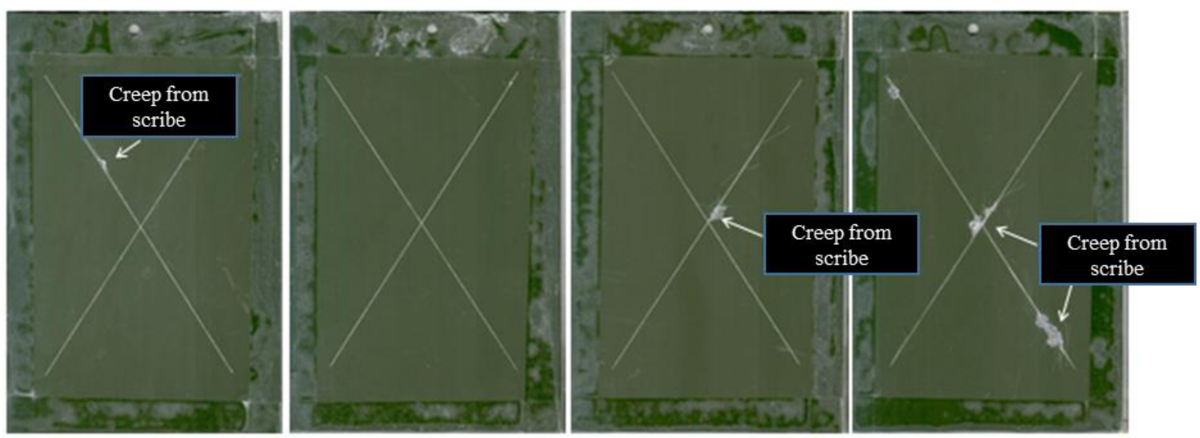


Figure 24. Measured Creepage (in mm) for the CARC-coated CRS Panels after 30 Cycles of GMW14782 Test

Figure 25 shows the CARC-coated Al 2024-T3 panels after 30 cycles of GMW 14782 testing. The panel pretreated with SILSBOND 01 (1.5%) (Figure 25 (b)) performs the best, followed by DOD-P15328 (Figure 25(a)), SILSBOND 01 (3%) (Figure 25(c)). The SILSBOND 05 pretreated panel in Figure 25(d) exhibits noticeable amount of paint loss in the scribes.



(a) (b) (c) (d)

Figure 25. 30 cycles of GMW14782 Test, Al 2024-T3 Panels, Coated with MIL-DTL-53022/MIL-DTL-53039; (a) DOD-P-15328 (b) SILSBOND 01 (1.5%) (c) SILSBOND 03 (3%) and (d) SILSBOND 05 (50%)

Figure 26 shows the CARC-coated CRS panels after 1008-hr NSS. Both SILSBOND 01(1.5%), and SILSBOND 01 (3%) in Figure 26 (b) and (c) perform the best, showing no or little paint delamination in the scribes, while the panel pretreated with SILSBOND 05(50%) (Figure 26(d) shows a large degree of paint loss in the scribes. The panel pretreated with DOD-P-15328 in Figure 26(a) exhibited complete paint delamination. This massive paint loss was likely due to inter-coat failure which was caused by poor adhesion between the DOD-P-15328 pretreatment (wash primer) and the epoxy primer.

(a) (b) (c) (d)

Figure 26. 1008 hrs of ASTM B117, CRS Panels Coated with MIL-DTL-53022 T4/MIL-DTL-53039; (a) DOD-P-15328 (b) SILSBOND 01 (1.5%) (c) SILBOND 03 (3%) and (d) SILSBOND 05 (50%)

Additional accelerated corrosion testing via NSS using CARC-coated Al 2024-T3 panels after 1008-hr NSS showed that the best performing system was the panels pretreated with DOD-P-15328. The SILSBOND 01 (1.5%) ranked second followed by SILSBOND 01 (3%). The panel pretreated with SILSBOND 05 exhibited noticeable paint loss and excessive scribe creep along the scribes showing very poor performance.

6.1.4 Optimization of Application Process for Abrasive-blasted Substrates (Blasted Steel 1020 and blasted Al 2024-T3)

This part of the work was based on the test results from the round robin tests, and SILSBOND 01 (1.5%) was down-selected for QPD qualification per TT-C-490 requirements. Prior to panel preparation for the QPD test, Ecosil requested an additional formulation consisting of SILSBOND 01 (2%) for further evaluation. These application process parameters for the SILSBOND 01 (2%) were further optimized by Ecosil for use on the applicable metal substrates. The optimized application process that was determined for SILSBOND 01 (2%) is as follows:

1) ***Application process for mill-finish substrates (1020 Steel and Al 2024-T3):***
   Step 1 – Alkaline cleaning (6.5% Cal Clean 657 AM, 150ºF / 2min immersion/spray)
   Step 2 – City water rinse (20 sec, ambient spray)
   Step 3 – DI water rinse (20 sec, ambient spray)
   Step 4 – 2% SILSBOND 01 spray (2 times for a total contact time of 60 seconds)
   Step 5 – DI water rinse (20 second ambient spray)
   Step 6 – Dry in place (ambient)
   Step 7 – epoxy primer spray within 24 hours.
2) ***Application process for abrasive-blasted substrates (blasted 1020 Steel and blasted Al 2024-T3):***
   Step 1 – Abrasive blasting
   Step 2 – City water rinse (20 sec, ambient spray)

Step 3 – DI water rinse (20 sec, ambient spray)
Step 4 – 2% SILSBOND 01 spray (2 times for a total contact time of 60 seconds)
Step 5 – DI water rinse (20 second ambient spray)
Step 6 – Dry in place (ambient)
Step 7 – epoxy primer spray within 24 hours.

In consideration of the fact that weather conditions, such as humidity levels, typically vary all the time during field applications, a mild DI water rinse (step 5) was added right after pretreatment spray (step 4). In doing so, the degree of flash rusting on carbon steel parts could be effectively mitigated during highly humid conditions. Accordingly, Ecosil adjusted the SILSBOND 01 concentration level from 1.5% to 2% to ensure enough film coverage after DI water rinse. Tables 14-15 show the test plans for panel preparation for the qualification tests. Four types of metal substrates were pretreated and epoxy-primed: (1) 1020 Steel mill-finish, (2) Al 2024-T3 mill-finish, (3) 1020 Steel abrasive blasted and (4) Al 2024-T3 abrasive blasted. DOD-P-15328 wash primer was also included in the test plan as a control and 120 pieces of panels in total were prepared at Aalberts Surface Treatment (formally Impreglon) for testing.

Table 14. Test Plan for Mill-finished Substrates

Mill-finished Substrates	ASTM B117	Cyclic Corrosion GMW14872	ASTM D3359 Dry Adhesion	Marine Outdoor Exposure	Mandrel Bend Test	Pull-off Adhesion Test
	MIL-DTL-53022 T4 (both sides)	MIL-DTL-53022 T4 (both sides)	MIL-DTL-53022 T4	MIL-DTL-53022 T4/ MIL-DTL-53039	MIL-DTL-53022 T4	MIL-DTL-53022 T4
	4”x 6”x 0.032”	4”x 6”x 0.032”	4” x 6”x 0.032”	4” x 6”x 0.032”	4” x 6”x 0.032”	4”x 6” x 0.032”
Al 2024-T3	7	5	2	5	2	2
1020 Steel	7	5	2	5	2	2

Table 15. Test Plan for Abrasive-blasted Substrates

Abrasive-blasted Substrates	ASTM B117	Cyclic Corrosion GMW14872	ASTM D3359 Dry Adhesion	Marine Outdoor Exposure	Mandrel Bend Test	Pull-off Adhesion Test
	MIL-DTL-53022 T4 (both sides)	MIL-DTL-53022 T4 (both sides)	MIL-DTL-53022 T4	MIL-DTL-53022 T4/ MIL-DTL-53039	MIL-DTL-53022 T4	MIL-DTL-53022 T4
	4”x 6”x 0.032”	4”x 6”x 0.032”	4” x 6”x 0.032”	4” x 6”x 0.032”	4” x 6”x 0.032”	4”x 6” x 0.032”
Al 2024-T3	7	5	2	5	2	2
1020 Steel	7	5	2	5	2	2

Figure 27 shows the set up used for panel preparation at Aalberts Surface Treatment. Figure 27(a) shows the metal panels after alklaine cleaning. Figure 27(b) shows how the cleaned metal panels were sprayed with a 2% SILSBOND solution. After spraying the panel surfaces were kept wet for 60 seconds. Figure 27(c) shows how the SILSBOND-treated panels were DI rinsed and then ambient dried for 1 hour. Figure 27 (d) showed the application of the epoxy primer onto the pretreated metal panel surfaces. Figure 28 showed the commercial epoxy primer used to coat the coupons. Figure 29 documented the SILSBOND 01 (2%) coated coupons followed by Figure 30 which shows the SILSBOND painted coupons.

(a) (b)

(c) (d)

Figure 27. Panel Preparation at Aalberts Surface Treatments (a) alkaline cleaned panels, (b) SILSBOND 01 spray on the panels, (c) the pretreated panels were dried in place after DI water rinse and (d) epoxy priming on both sides of the panels

Figure 28. Commercial Primer used in Coating Stack-up

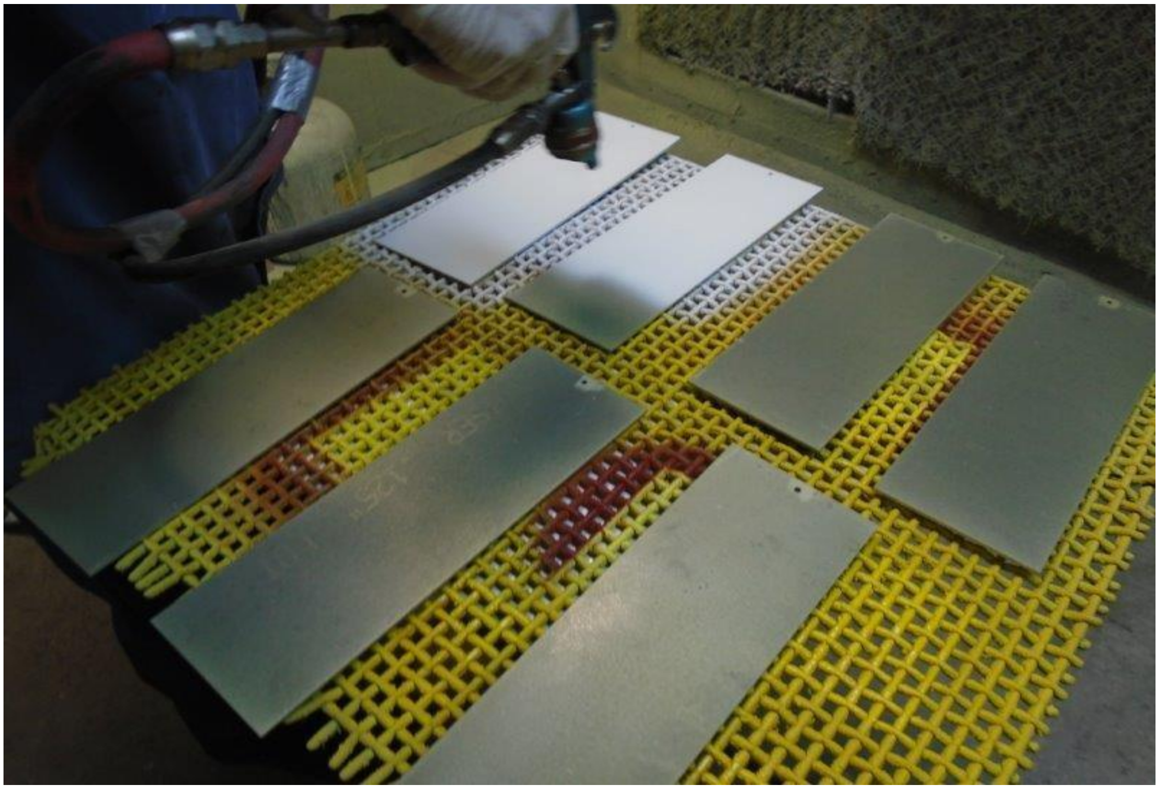


Figure 29. Coupons Coated with SILSBOND 01 (2%) Pretreatment coating

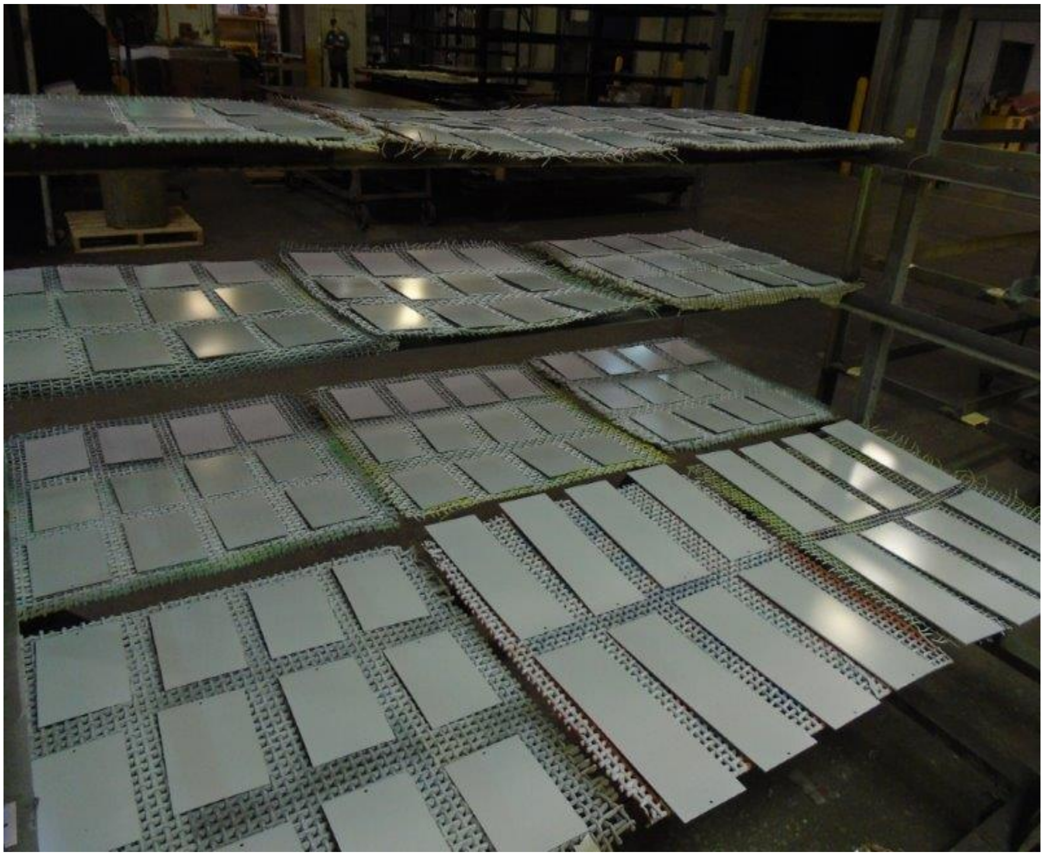


Figure 30. Painted SILSBOND Coated Coupons

The coated panels were ambient cured for two weeks. However, it was determined that the thickness of epoxy primer on those panels was too thick, > 2.5 mil which is out of the required range for the primer thickness of 1.0-1.5 mil. Therefore, these panels were not suitable for QPD testing. As a point of interest, Ecosil did 1008 hours of NSS for a few of these panels as a “quick check” of coating performance for internal information only. The NSS results are shown in Table 16.

Table 16. 1008-hours NSS Test Results for Epoxy Primed 1020 Steel Panels

ID	Substrate	Pretreatment	DFT (mil)	Rating
5-1	CRS/mill	SILS 01	2.1	7
5-2	CRS/mill	SILS 01	2.5	7
6-1	CRS/Abrasive	WP	3	8
6-2	CRS/Abrasive	WP	3	7
7-1	CRS/Abrasive	SILS 01	2.7	7
7-2	CRS/Abrasive	SILS 01	3	7
8-1	CRS/mill	WP	2.5	7
8-2	CRS/mill	WP	3.1	7

This section of the JTR documented the results obtained from the Ecosils results regarding formulations and laboratory testing in Ecosil’s testing facilities. This report documented all the tasks that Ecosil Technologies LLC conducted to achieve the program objectives during the time period between 2016 to 2020. The primary objective of this project was to demonstrate the effectiveness of SILSBOND pretreatment as a replacement for chromated wash primer (DOD-P-15328) in DOD repair applications. Specifically, the goal was to evaluate the performance of SILSBOND pretreatment per the TT-C-490 coating requirements to gain approval to be listed on the relevant QPD. Four types of metal substrates were tested under a CARC coating system, i.e., MIL-DTL-53022 Type 4/MIL-DTL-53039. They were: (1) mill-finish 1020 Steel; (2) abrasive blasted 1020 Steel; (3) mill finish Al 2024-T3; and (4) abrasive blasted Al 2024-T3 and the results are shown below:.

- 2% SILSBOND 01 was selected as a pretreatment product suited for field coating repair applications
- SILSBOND 01 consistently outperformed the Cr(VI)-based DOD-P-15328 wash primer in all lab tests
- SILSBOND 01 has been approved for QPD listing on abrasive-blasted Al 2024-T3

Although SILSBOND 01 was not qualified for CRS under TT-C-490 (only failed in GMW14782 test, in which DOD-P-15328 wash primer also failed), SILSBOND 01 was evaluated for corrosion resistance performance on non-critical military door panels and 1020 Steel and Al 2024-T3 panels by ARL in actual field conditions for 2 years. This allowed `further evaluation of the product for military field applications, and possible formula enhancements to achieve QPD listing for 1020 Steel subsequent to further testing according to TT-C-490.

6.1.5 Laboratory Testing at Participating DOD Labs

Each of the following DOD laboratories was tasked with evaluating the performance of Ecosils SILSBOND pretreatment coating. The following DOD labs were involved in this evaluation: ARL, NAWCWD, and NSWCCD. There were several candidate Ecosil formulas that were selected for the Round Robin testing: SILSBOND 01 (1.5%, 3%), and SILSBOND 05 (50%).

A down selection of the best was determined after all laboratory testing was completed by each of the participating DOD laboratories and marine outdoor exposure and field testing of the SILSBOND formulation. One formulation will be coated for these final two tests after final review by each of participating DOD laboratories (ARL, NAWCWD, NSWCCD) showed passing performance as described in Table 17.

6.1.6 DOD Laboratory Testing of SILSBOND Formulations

Ecosil's SILSBOND formulations were laboratory tested according to the following criteria using coating requirements for TT-C-490, MIL-DTL-53022 Type IV primer and MIL-DTL-53039 topcoat on SILSBOND pretreatment replacement (See Table 17). The following testing was done by the DOD co-performers with ARL testing for cyclic corrosion performance. The following substrates were examined: 1020 Steel (mill finished/abrasive blasted) and Al 2024-T3 (mill finished/abrasive blasted).

The pretreatments examined were the SILSBOND formulations and DOD wash primer (DOD-P-15328). Each pretreatment coating was primed with MIL-DTL-53022, Type IV. The tests that were performed (see Table 17) included for coating qualification per TT-C-490 were cross hatch adhesion, NSS, cyclic corrosion, and marine outdoor exposure (24 months).

Table 17. Quantitative Performance Objectives for TT-C-490

Performance Objective	Data Requirements	TT-C-490 Requirement	Success Criteria
Humidity Testing	Comparative test for flash rust inhibition	No	No flash rust after 24 hours of exposure to ambient temperature and 90% relative humidity
Adhesion Test	ASTM 4541 Pull-off Adhesion	No	Minimum average 30 events rating of 1200 psi on 1.5mil profile surface
Adhesion Test	ASTM D3359 Dry Adhesion	Yes	Adhesion rating > 4B
Adhesion Test	ASTM D3359 Wet Adhesion	No	Scribed area rating, ≥ 3A after 24 hours at ambient
Accelerated Corrosion Test	ASTM B117 (NSS)	Yes	After 1000 hours of exposure, steel substrate rating ≥ 6 scribed and ≥7 scribed aluminum
Cyclic Corrosion Test	GMW14872	Yes	After 30 cycles, scribed steel and aluminum substrate rating ≥ 7
Marine Outdoor Exposure Test	ASTM D1654	Yes	After 24 months steel substrate rating ≥ 7 and ≥ 8 for aluminum
HE	ASTM F519	Yes	No detrimental effect to K1c of the substrate. High Hard K1c @48-51Rc shall maintain K_{ieac} ≥19 (ksi/in)
Toxicity Clearance	Toxicity clearances and full disclosure from CHPPM	Yes	Approved by processing facility
Processing Time	TT-C-490	Yes	Equivalent or less than existing process

Described below are results from the round robin testing of the Ecosil pretreatment coatings. The objective of this round robin testing was to down-select a SILSBOND pretreatment coating for QPD testing at NAWCWD, ARL, and NSWCCD. Three SILSBOND formulations were tested: SILSBOND 01 (1.5%), SILSBOND 01 (3%) and SILSBOND 05 (50%).

Testing of the Ecosil formulations by the DOD co-performers are shown below and these results are representative of each of the co-performers. The best performing system was SILSBOND 01 (1.5%), which was identified from these early laboratory testing results.

6.1.6.1 NAWCWD Round Robin Results for Performance Evaluation of Ecosils Pretreatment Formulations

Table 18 documents the testing performed at the NAWCWD in accordance with TT-C-490 coating requirements. The following figures 31-37 and table 19 documents the results obtained from the NAWCWD round robin testing of the Ecosils SILSBOND formulations.

Table 18. NAWCWD Testing in Accordance with TT-C-490 Coating Requirements

NAWCWD qualifications	**Substrate**	**ASTM B117**	**ASTM D3359 Dry and Wet Adhesion**	**Pull-off adhesion ASTM D4541**
		MIL-DTL-53022 TIV /MIL-DTL-53039	**MIL-DTL-53022 TIV MIL-DTL-53039**	**MIL-DTL-53022 TIV/ MIL-DTL-53039**
		4x6x0.0625	**4x6x0.0625**	**4x12x0.0625 (steel) 4x12x0.125 (aluminum)**
Baseline DOD-P-15328	Al 2024	3	3	3
	1020 Steel	3	3	3
Candidate 1 (SILSBOND 01 (1.5%))	Al 2024	3	3	3
	1020 Steel	3	3	3
Candidate 2 (SILSBOND 01 (3%))	Al 2024	3	3	3
	1020 Steel	3	3	3
Candidate 3 (SILSBOND 05 (50%))	Al 2024	3	3	3
	1020 Steel	3	3	3

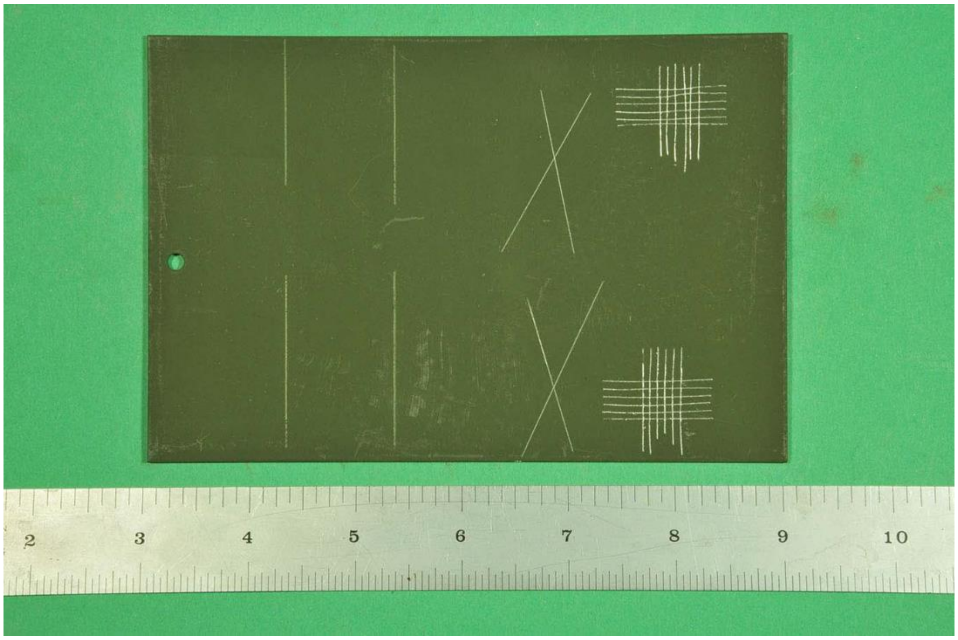


Figure 31. NAWCWD Representative Panel with SILSBOND 01 (1.5 %) Formulation Coating on Al 2024-T3 Dry and Wet Adhesion Testing.
(Parallel lines on the left are wet adhesion testing. X scribes and lattice scribes are dry adhesion testing which is Representative)

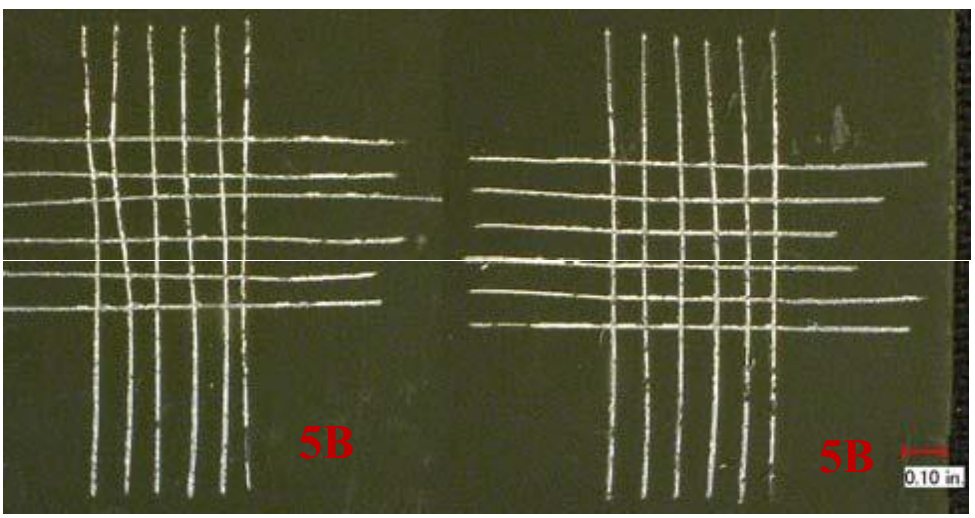


Figure 32. Dry Adhesion Testing Results with the Representative Figure Showing 5B Results (Passing)

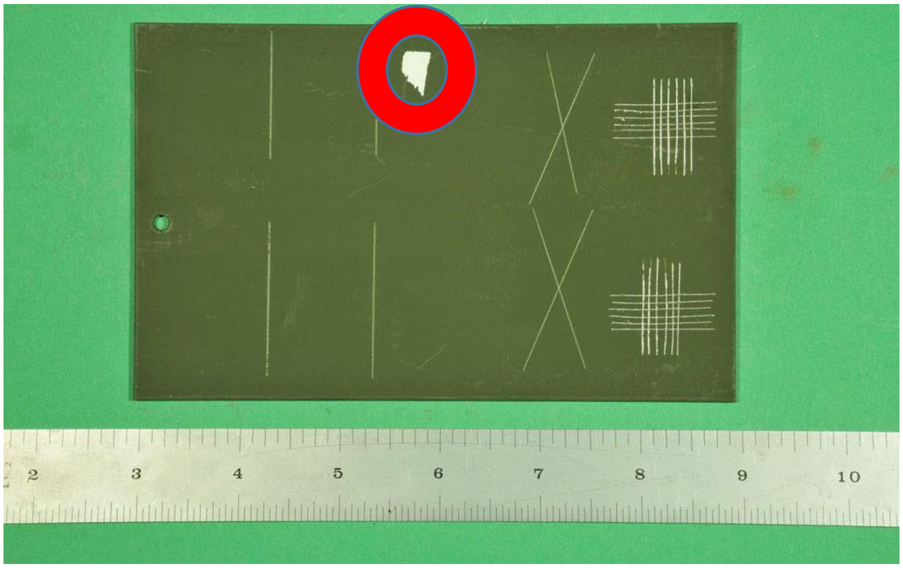


Figure 33. NAWCWD Wet Adhesion Test Result, Panel is SILSBOND 01(1.5%) Coating on Al 2024-T3 and the Defect is Circled in Red.

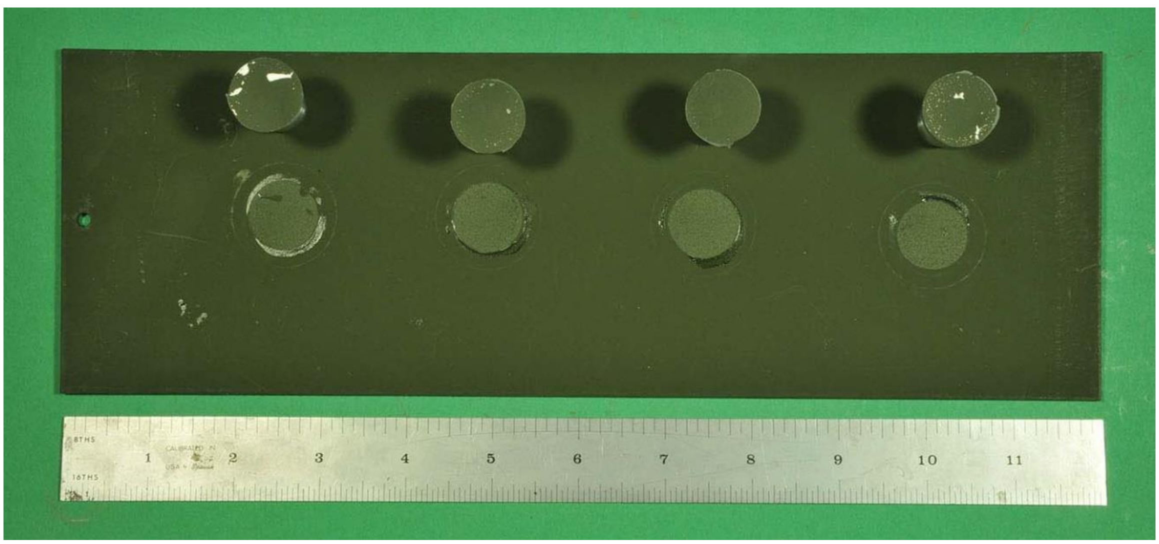


Figure 34. NAWCWD Round Robin Test Results Pull off Adhesion Tape ASTM D4541 Test Method with Candidate (SILSBOND 01 (1.5%)) which was Typical of the Remaining Candidates.

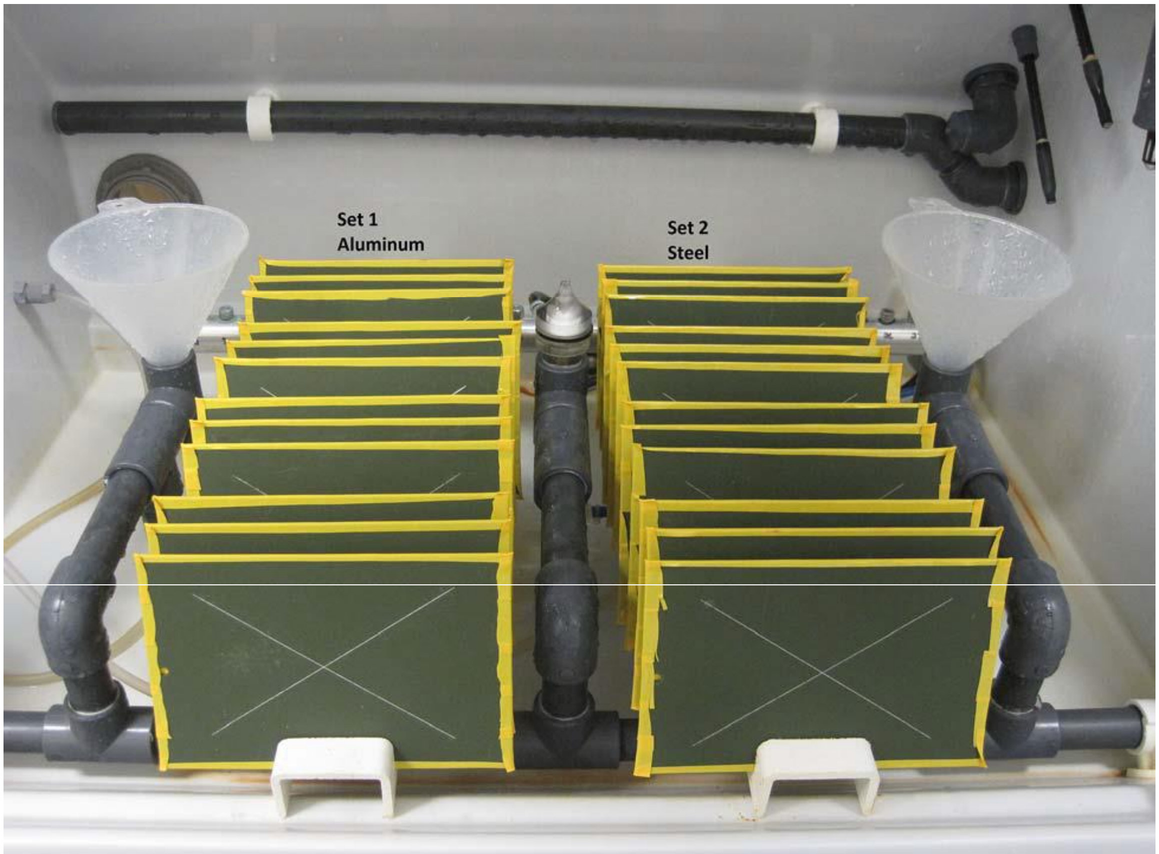
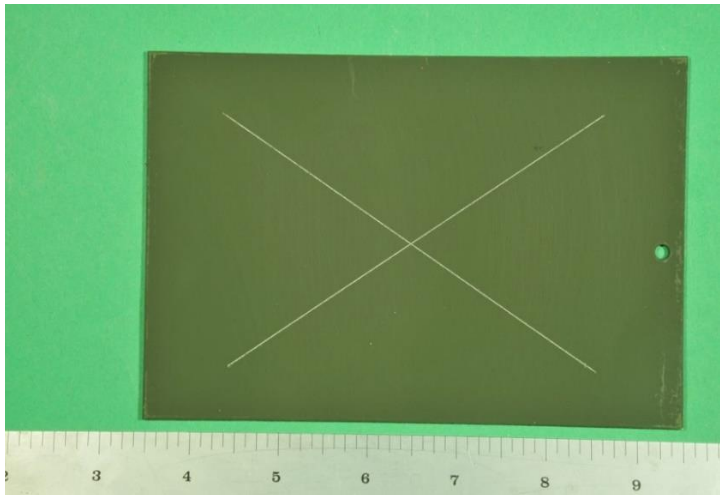
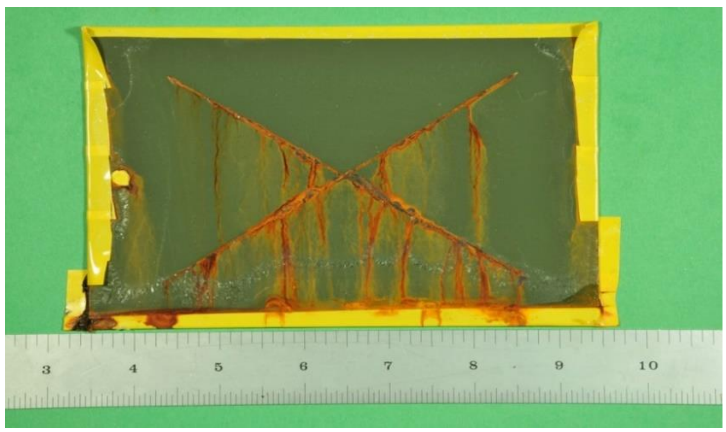


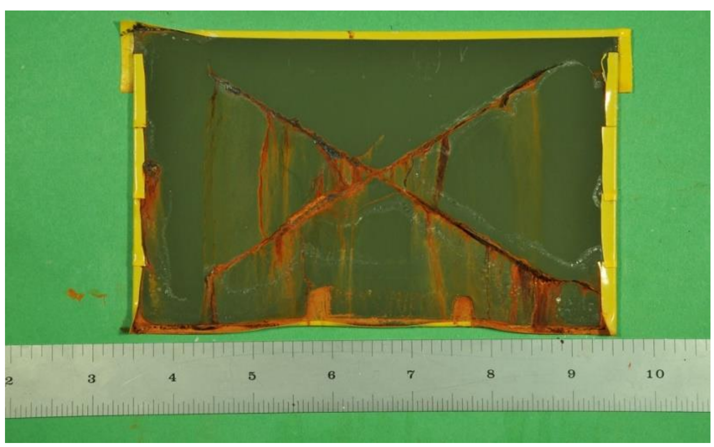
Figure 35. NAWCWD Round Robin Coupons for NSS Testing



Control Coupons DOD-P-15328 at 0 Hours

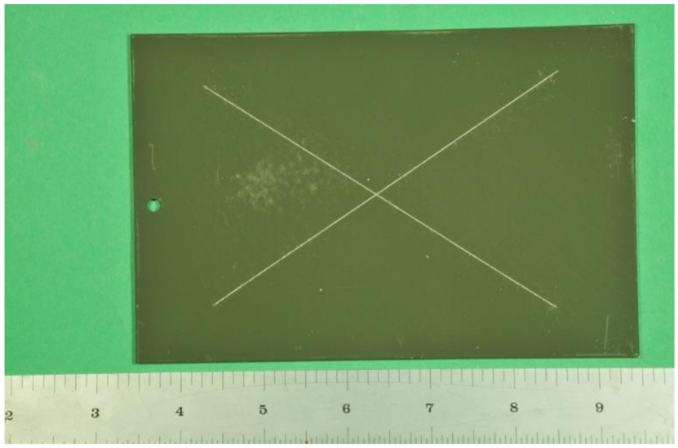


Middle: Control Coupons DOD-P-15328 at 500 Hours



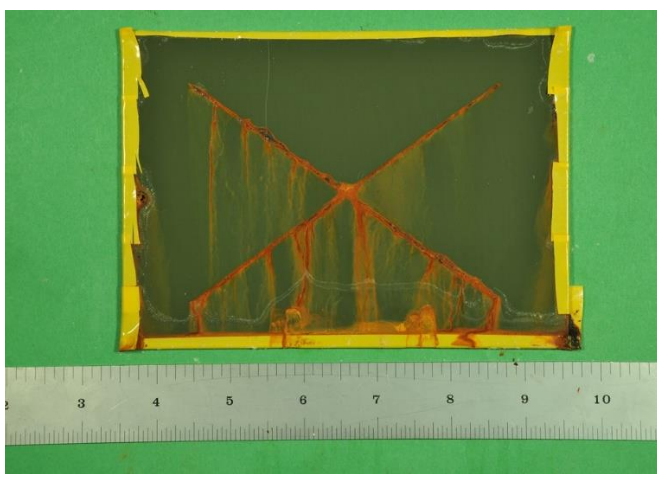
Bottom: Control Coupons DOD-P-15328 at 1022 Hours

Figure 36. NAWCWD Round Robin Test Results NSS Testing Results (Steel 1020, MIL-DTL-53022 TIV / MIL-DTL-53039) Top: Control Coupons DOD-P-15328 at 0 Hours; Middle: Control Coupons DOD-P-15328D at 500 Hours, Bottom: Control Coupons DOD-P-15328 at 1022 Hours



Top: SILSBOND 01 (1.5%) at 0 Hours

Middle: SILSBOND 01 (1.5%) at 500 Hours



Bottom: SILSBOND 01 (1.5%) at 1022 Hours

Figure 37. NAWCWD Round Robin Test Results NSS Testing Results (Steel 1020, MIL-DTL-53022 TIV / MIL-DTL-53039); Top: SILSBOND 01 (1.5%) at 0 Hours; Middle: SILSBOND 01 (1.5%) at 500 Hours; Bottom: SILSBOND 01 (1.5%) at 1022 Hours

Table 19. Round Robin Results of NAWCWD Testing

Pretreatment	Substrate	NSS ASTM B117	Dry Tape Adhesion Method A	Dry Tape Adhesion Method B	Wet Tape Adhesion	ASTM D 4541 (PSI)
Baseline DOD-P-15328	Al 2024-T3	Pass	Pass	Pass	Pass	792 ±53
	1020 Steel	Fail	Pass	Pass	Pass	555 ±50
Candidate 1 (SILSBOND 01 (1.5%))	Al 2024-T3	Fail	Pass	Pass	Fail	773 ±76
	1020 Steel	Pass	Pass	Pass	Pass	527 ±57
Candidate 2 (SILSBOND 01 (3 %))	Al 2024-T3	Fail	Pass	Pass	Pass	826 ±116
	1020 Steel	Fail	Pass	Pass	Pass	570 ±77
Candidate 3 (SILSBOND 05 (50 %))	Al 2024-T3	Fail	Pass	Fail	Pass	808 ±63
	1020 Steel	Pass	Pass	Fail	Pass	505 ±63

6.1.6.2 NSWCCD Round Robin Results for Performance Evaluation of Ecosils Pretreatment Formulations

Table 20 documents the testing performed at the NSWCCD in accordance with TT-C-490 coating requirements. The following figures 38-41 document the round robin results conducted by the NSWCCD NSS results for 1008 hours under ASTM B117 testing protocols using 1020 Steel coupons coated with Ecosil's SILSBOND pretreatment coating, epoxy primer (MIL-DTL-53022 TIV) and top coated with polyurethane topcoat (MIL-DTL--53039).

Table 20. NSWCCD Testing in Accordance with TT-C-490 Coating Requirements

NSWCCD Qualifications	Substrate	ASTM B117	Cyclic Corrosion GMW14872	ASTM D 3359 Dry and Wet Adhesion	Pull-off adhesion ASTM D4541	Outdoor exposure
		MIL-DTL-53022 TIV/ MIL-DTL-53039	MIL-DTL-53022 TIV/ MIL-DTL-53039	MIL-DTL-53022 TIV/ MIL-DTL-53039	MIL-DTL-53022 TIV/ MIL-DTL-53039	MIL-DTL-53022 TIV/MIL-DTL-53039
		4x6x0.0625	4x6x0.0625	4x6x0.0625	4x12x0.0625 (steel) 4x12x0.125 (aluminum)	4x6x0.0625
Baseline DOD-P-15328	Al 2024	3	3	3	3	3
	1020 Steel	3	3	3	3	3
Candidate 1 (SILSBOND 01 (1.5%))	Al 2024	3	3	3	3	3
	1020 Steel	3	3	3	3	3
Candidate 2 (SILSBOND 01 (3%))	Al 2024	3	3	3	3	3
	1020 Steel	3	3	3	3	3
Candidate 3 (SILSBOND 05 (50%))	Al 2024	3	3	3	3	3
	1020 Steel	3	3	3	3	3

Figure 38. NSWCCD Round Robin Test Results Baseline (No Treatment) 1020 Steel Panels

Figure 39. NSWCCD Round Robin Test Results SILSBOND 01 (1.5%) Coated 1020 Steel Panels

Figure 40. NSWCCD Round Robin Test Results SILSBOND 01 (3%) Coated 1020 Steel Panels

Figure 41. NSWCCD Round Robin Test Results SILSBOND 05 (50%) Coated 1020 Steel Panels

The following Figures 42-45 document the round robin results conducted by the NSWCCD NSS results for 1008 hours under ASTM B117 testing protocols using Al 2024-T3 coupons coated with Ecosil's SILSBOND pretreatment coating, epoxy primer (MIL-DTL-53022 TIV and top coated with polyurethane topcoat (MIL-DTL-53039).

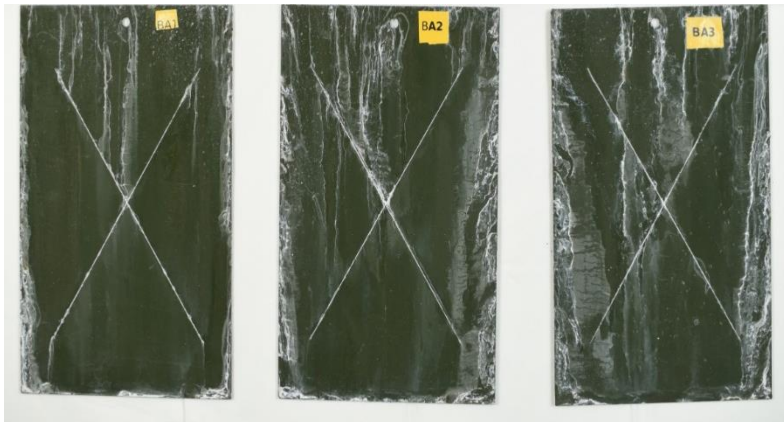


Figure 42. NSWCCD Round Robin Test Results Baseline – No treatment Al 2024-T3 Panels

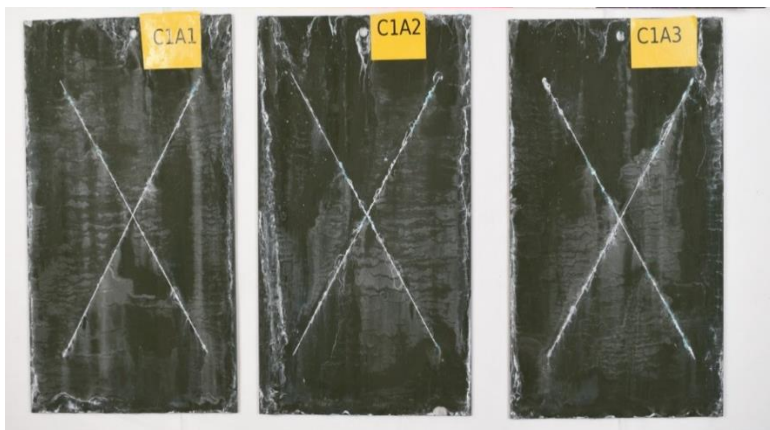


Figure 43. NSWCCD Round Robin Test Results SILSBOND 01 (1.5%) Coated Al 2024-T3 Panels

Figure 44. NSWCCCD Round Robin Test Results SILSBOND 01 (3%) Coated Al 2024-T3 Panels

Figure 45. NSWCCD Round Robin Test Results SILSBOND 05 (50%) Coated Al 2024-T3 Panels

A visual inspection of panels was made after 1008 hours ASTM B117 NSS testing. Steel panels showed severe corrosion showing running red rust in the scribes and on panel surfaces. It was difficult to make any distinction between the performances of steel panels treated with SILSBOND 01 (1.5%), and SILSBOND 01 (3%). SILSBOND 05 (50%) in which all showed severe corrosion approximately equivalent in performance to those with no treatment. (Baseline panels for example BS1, BS2, and BS3). Among coated aluminum panels, those with SILSBOND 01 (1.5%) performed better than those with SILSBOND 01 (3%) and SILSBOND 05 (50%). In the case of aluminum panels treated with SILSBOND 01 (1.5%) white aluminum corrosion products remained mostly in scribes where as in the case of those treated with 3% and 50% white aluminum product was spread out on surfaces outside of scribes. In other words, corrosion products were not only in scribes but on the adjoining surfaces of panels.

The following adhesion results from NSWCCD are listed below. Figure 46 provides the description of the Posi Test AT-A pull-off testing equipment. The actuator assembly is placed over the dolly head and the quick coupling is attached and tightened. The equipment is powered up by pressing the button marked “on” The right type of units are selected and the dolly size may be verified, if necessary. After readying the equipment, the button marked “on” is pressed again to perform testing. The test consists of 4 stages; Stage 1. Initiation- the LCD shows a blinking “0”. In Stage 2, the pump applies initial pressure to the dolly. In Stage 3, pressure builds and stops when the dolly is pulled from the surface when a pop noise is heard. In Stage 4, Retraction occurs when the maximum pull-off pressure value blinks and can be noted down or stored in its memory. After Stage 4, the dolly is removed from the actuator assembly. The testing can be repeated to pull other dollies that are glued onto test panels. Examination of dry and wet adhesion values for coated panels in Tables 21-22 indicated that that there was no difference between the dry and wet adhesion values.

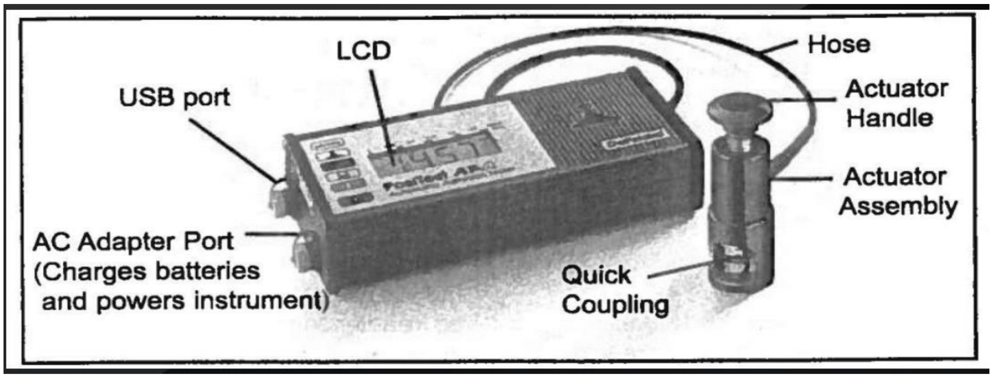


Figure 46. The Posi Test AT-A Pull-off Testing Equipment

Table 21. NSWCCD Dry and Wet Tape Adhesion Results for SILSBOND Pretreatment Coatings

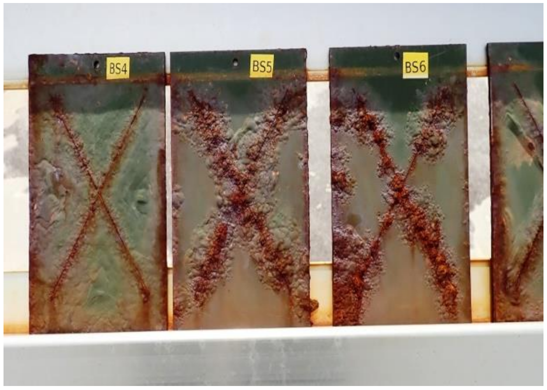
SILSBOND Formulation	Dry Adhesion	Wet Adhesion
SILSBOND 01 (1.5%) on 1020 Steel Substrate	5A	4A
SILSBOND 01 (1.5%) on 1020 Steel Substrate	4A	4A
SILSBOND 01 (1.5%) on 1020 Steel Substrate	4A	4A
SILSBOND 01 (3%) on 1020 Steel Substrate	4A	4A
SILSBOND 01 (3%) on 1020 Steel Substrate	5A	4A
SILSBOND 01 (3%) on 1020 Steel Substrate	4A	4A
SILSBOND 01 (1.5%) on Al 2024-T3	4A	4A
SILSBOND 01 (1.5%) on Al 2024-T3	4A	4A
SILSBOND 01 (1.5%) on Al 2024-T3	4A	4A

Table 22. NSWCCD Pull-off Adhesion Testing for Control and SILSBOND Pretreatment Coatings

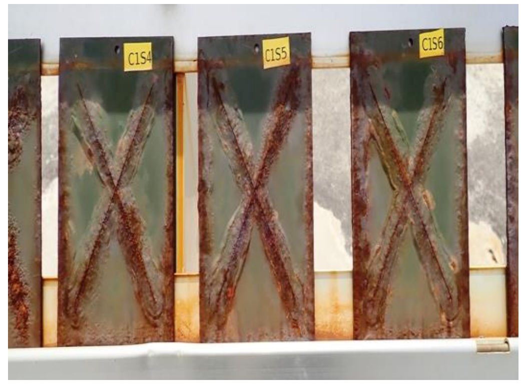
Panel ID	Results in psi (average values)
Control Coatings on 1020 Steel Substrate	720
SILSBOND 01 (1.5%) on 1020 Steel Substrate	722
SILSBOND 01 (3%) on 1020 Steel Substrate	739
SILSBOND 05 (50%) on 1020 Steel Substrate	751
Control Coatings on Al 2024-T3	1,128
SILSBOND 01 (1.5%) on Al 2024-T3	1,137
SILSBOND 01 (3%) on Al 2024-T3	1,338
SILSBOND 05 (50%) on Al 2024-T3	1,168

The following results are from the natural atmospheric exposure testing that was conducted at the NSWCCD satellite exposure facility in Fort Lauderdale, Florida with the

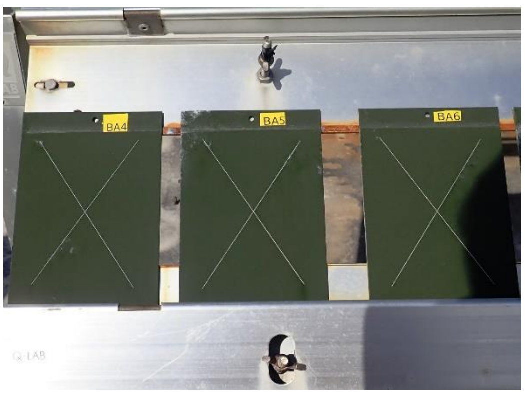
Al coated alloys showing outstanding performance at 18 months and the steel coated samples showing failure at 12 months (Figure 47).



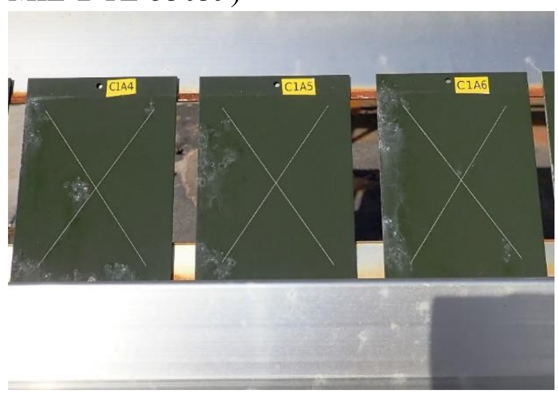
Steel control (Steel 1020, MIL-DTL-53022 TIV/MIL-DTL-53039)



Steel coated with SILSBOND 01 (1.5%) (Steel 1020, MIL-DTL-53022 TIV/ MIL-DTL-53039)



Al control (Al 2024, MIL-DTL-53022 TIV/ MIL-DTL-53039)



Al coated with SILSBOND 01 (1.5%) (A1 2024, MIL-DTL-53022 TIV/ MIL-DTL-53039)

Figure 47. Marine Outdoor Exposure at 12 Months for 1020 Steel (top) and 18 Months for Al 2024-T3 (bottom)

6.1.6.3 ARL Round Robin Results for Performance Evaluation of Ecosils Pretreatment Formulations

The following data represents ARL laboratory testing regarding the SILSBOND formulations, where qualification to coating performance found in TT-C-490 and using MIL-DTL-53022 Type IV required the following: a). ASTM B117 a minimum rating of 8.0 for scribed aluminum and 6.0 for scribed steel, and b). GMW-14872 - minimum blister rating of 7.0 for both aluminum and steel. The table listed below documents the round robin testing by ARL regarding testing to mil-spec TT-C-490 coating requirements (Table 23).

Table 23. ARL Round Robin Testing to mil-spec TT-C-490

ARL Mill Finish qualification	Mill finish Substrate	ASTM B117	Cyclic Corrosion GMW14872	ASTM D 3359 Dry Adhesion	Outdoor exposure	ASTM D522 Mandrel Bend test	Hydrogen Embrittlement ASTM F519
		53022 TIV	53022 TIV	53022 TIV	53022 T4/53039	53022 TIV	pretreatment only
		4x6x0.0625	4x6x0.0625	4x6x0.0625	4x6x0.0625	4x6x0.032	tensile bars
Baseline DoD-P-15328	Al 2024	5	5	3	5	2	0
	1020 Steel	5	5	3	5	2	0
Candidate 1 **SILSBOND 01 (1.5%)**	Al 2024	5	5	3	5	2	0
	1020 Steel	5	5	3	5	2	4340 Steel (3)
Candidate 2 **SILSBOND 01 (3%)**	Al 2024	5	5	3	5	2	0
	1020 Steel	5	5	3	5	2	4340 Steel (3)
Candidate 3 **SILSBOND 05 (50%)**	Al 2024	5	5	3	5	2	0
	1020 Steel	5	5	3	5	2	4340 Steel (3)

In addition, the majority of samples showed no HE during testing which were loaded @75% NSS for 200 + hours without failing, except (SILSBOND 01 @ 3%) failed after 32.2 hours. Listed below in Table 24 are the requirements for the number of coupons per testing according to TT-C-490 military coating performance specifications for abrasive blasted coupons.

Table 24. ARL Abrasive Blasted Qualifications

ARL abrasive blasted qualification	**Abrasive blasted Substrate**	**ASTM B117**	**Cyclic Corrosion GMW14872**	**ASTM D 3359 Dry Adhesion**	**Marine Outdoor exposure**
		53022 TIV	**53022 TIV**	**53022 TIV**	**53022 TIV / 53039**
		4x6x0.0625	**4x6x0.0625**	**4x6x0.0625**	**4x6x0.0625**
Baseline DOD-P-15328	Al 2024	5	5	3	5
	1020 Steel	5	5	3	5
Candidate 1 (SILSBOND 01 (1.5%))	Al 2024	5	5	3	5
	1020 Steel	5	5	3	5
Candidate 2 (SILSBOND 01 (3%))	Al 2024	5	5	3	5
	1020 Steel	5	5	3	5
Candidate 3 (SILSBOND 05 (50%))	Al 2024	5	5	3	5
	1020 Steel	5	5	3	5

The data below shows comparable performance to the control wash primer (pretreatment), and candidate #1 (SILSBOND 01 (1.5%)) and candidate #3 (SILSBOND 05 (50%)) (see Table 25).

Table 25. ARL ASTM B117 (NSS) Results for MIL-DTL-53022 Type IV Coated Substrates (original set of substrates) (1.5%, 3%, 50 % formulations)

Pretreatment	Substrate	ASTM B117 Avg Rating					
		Scribe			Blister in Field		
		336hrs	672hrs	1008hrs	336hrs	672hrs	1008hrs
Wash Primer	Al	3.6	3.4	2.8	10	10	10
	Fe	6.6	6.6	6.4	9.2	8	8
Candidate 1	Al	6.2	5	4.6	10	10	10
	Fe	7	6	5.4	10	8	8
Candidate 3	Al	5	5	4	10	10	10
	Fe	6.8	6.8	5.8	10	7.6	5.6

SILSBOND 01 was the best performer in the above round robin testing, with 1.5% being slightly better than 3% as confirmed by all co-performers. However, the application process parameters were further optimized at Ecosil for SILSBOND 01 to ensure it can be used in the field properly. Based on this process optimization work, SILSBOND 01 (2%) was selected for the subsequent QPD testing at ARL. Test panels for QPD testing were prepared at Aalberts Surface Treatment (Baltimore, MD). Figures 48-53 documents the results of ARL testing of the modified SILSBOND formulation (SILSBOND 01 (2%)).

Figure 48. ARL NSS Testing Passing Criteria for Al 2024-T3 >8, no blisters >1mm

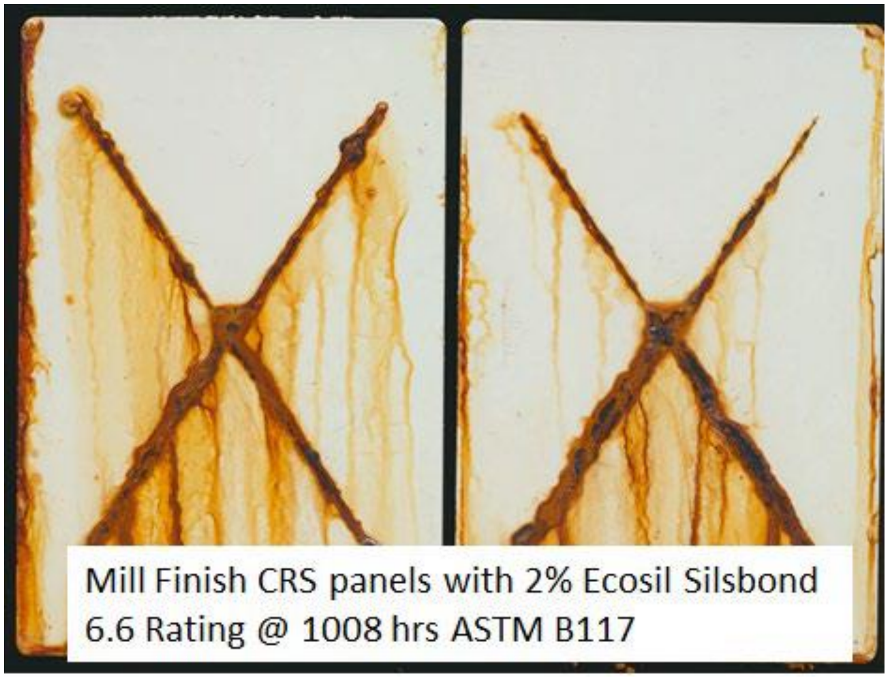


Figure 49. ARL NSS Testing Pass Criteria for 1020 Steel is >6

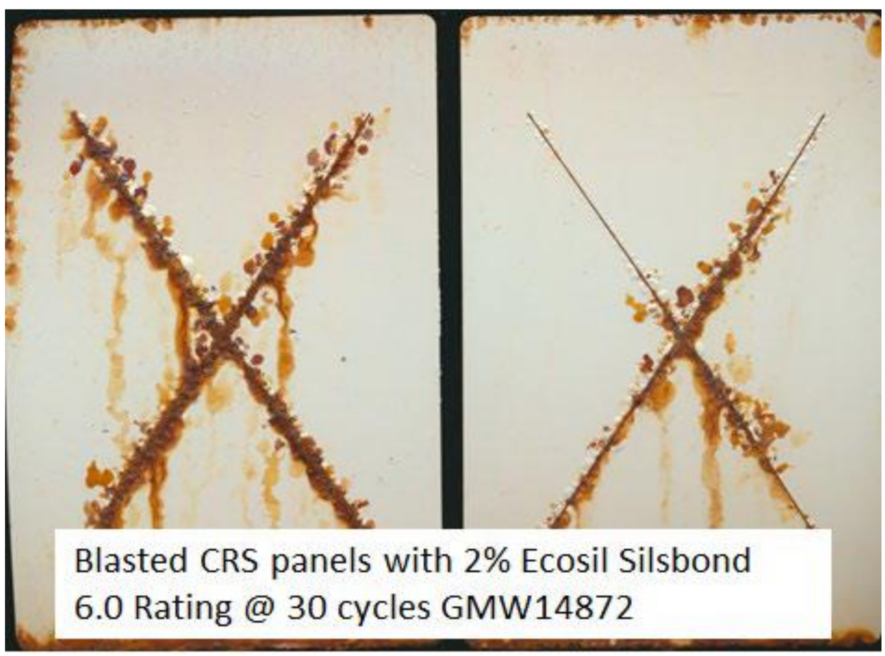


Figure 50. ARL Cyclic Corrosion Testing 1020 Steel with Rating of 6.0

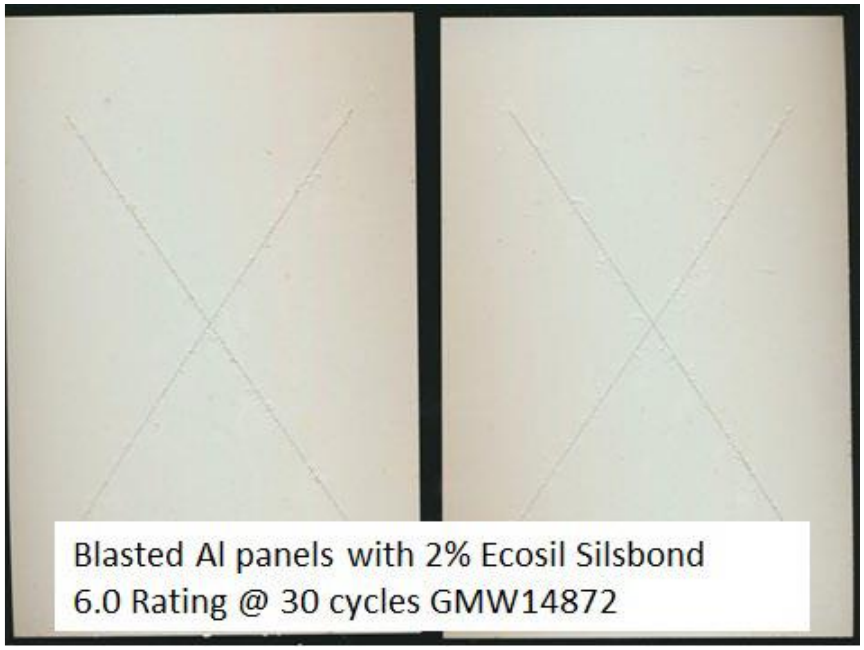


Figure 51. ARL Cyclic Corrosion Testing Al 2024-T3 with Rating of 6.0

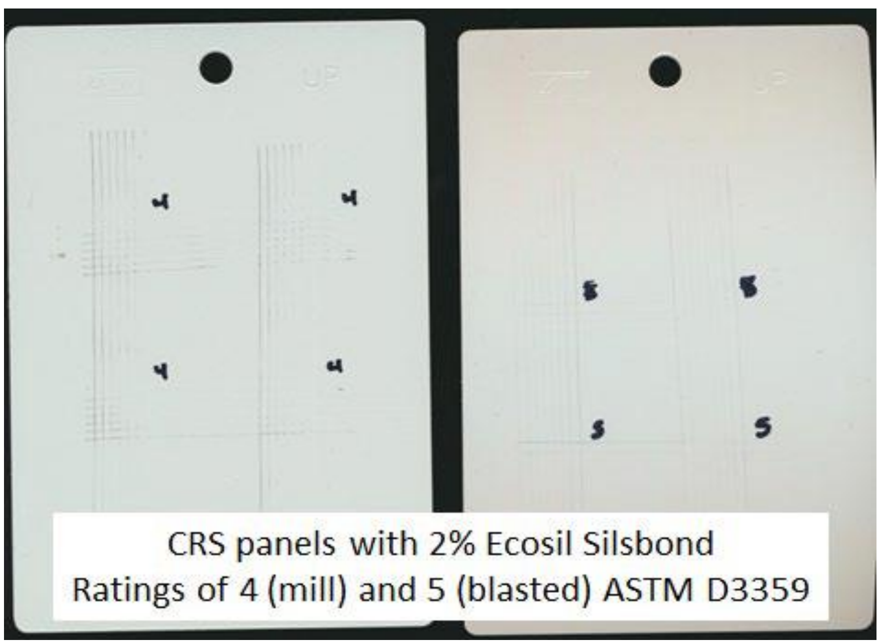


Figure 52. ARL Adhesion Testing of 1020 Steel Panels

Figure 53. ARL Adhesion Testing of Al 2024-T3 Panels

These panels were tested at ARL in accordance with TT-C-490 requirements. The following are the test results for these panels see Tables 26-29. There were four types of substrates included in this test: 1020 Steel (CRS), 1020 Blasted Steel (CRS-B), Al 2024-T3 mill finish and Al 2024-T3 blasted (Al-B). Pass criteria for steel is >6; for aluminum >8, and no blisters >1mm evident in the scribe.

Table 26. ARL GMW14872 Cyclic Corrosion Test Results for 1020 Steel and Al 2024 (Pretreatment: 2% SILSBOND 01, Primer: MIL-DTL-53022 TIV)

Pretreatment	Substrate	GMW14872 Avg Rating					
		Scribe			Blister in Field		
		10 cycles	20 cycles	30 cycles	10 cycles	20 cycles	30 cycles
2% Silsbond	CRS	5.8	5.2	5	10	10	10
	CRS-B	6.4	6	6	10	10	10
	Al	6.8	6	5.8	10	10	10
	Al-B	8	7.8	7.6	10	10	10

*blasted aluminum final ratings within standard deviation

Table 27. ARL ASTM B117 Neutral Salt Spray Test Results for 1020 Steel and Al 2024 (Pretreatments: 2% SILSBOND 01 and DOD-P-15328 Wash Primer, Primer: MIL-DTL-53022 TIV) (retested results)

Pretreatment	Substrate	ASTM B117 Avg Rating					
		Scribe			Blister in Field		
		336hrs	672hrs	1008hrs	336hrs	672hrs	1008hrs
Ecosil	Al	9.4	8.4	8.1	10	10	10
	Fe	8.8	7.6	6.6	10	10	10
Ecosil Blasted	Al	9	8.8	8	10	10	10
	Fe	8.8	8	6.8	10	9.6	9.6
Wash Primer	Al	9.4	9.4	9.2	10	10	10
	Fe	8.6	7.4	6	10	10	10
Wash Primer Blasted	Al	10	9.2	9	10	10	10
	Fe	9	8.8	7.2	10	10	10

Table 28. ARL ASTM D3359 Adhesion Test Results for 1020 Steel and Al 2024-T3 (Pretreatment: SILSBOND 01 (2%), Primer: MIL-DTL-53022 TIV)

ASTM D3359 Ratings		
Pretreatment	Substrate	Avg Rating
Silsbond 2%	Al	5
	Al-B	5
Silsbond 2%	CRS	4
	CRS-B	5

Table 29. Summation of ARL Results for SILSBOND 01 (2%) Formulation

	ASTM D3359 Adhesion	ASTM B117 Salt Fog	GMW14872 Cyclic	ASTM G50 Outdoor Exposure
Aluminum	PASS	PASS	FAIL	PASS
Aluminum (Blasted)	PASS	PASS	PASS	PASS
Cold Rolled Steel	PASS	PASS	FAIL	FAIL
Cold Rolled Steel (Blasted)	PASS	PASS	FAIL	PASS

6.2 Summation of Round Robin Results and Testing of SILSBOND 01 (2%) Formulation

The results based on the three candidates submitted by Ecosil for the Round Robin testing showed that SILSBOND 01 had the best performance rating with 1.5% being slightly better than 3%. After review of this data by all co-performers a decision was reached in which Ecosil provided a modified version of the SILSBOND formulation. These application process parameters were optimized at Ecosil for SILSBOND 01 to ensure it can be used in the field properly. Based on this process optimization work, a 2% SILSBOND 01 was selected for the subsequent QPD testing at ARL. Test panels for QPD testing were prepared at Aalberts Surface Treatment (Baltimore, MD). These panels were tested at ARL in accordance with TT-C-490 requirements. As shown in the previous Figures 48-53 that the SILSBOND 01 (2%) showed superior performance as compared to the previous testing and was chosen as the formulation for field testing by ARL and NSWCCCD during Phase II of this program.

6.3 Marine Outdoor Exposure Testing of SILSBOND Pretreatment Coatings

The Ecosil SILSBOND pretreatment coating formulations were exposed to costal marine atmospheric exposure testing at both the NSWCCD (Fort Lauderdale, Florida) and ARL (Cape Canaveral Space Force Station, Florida). At each facility the SILSBOND pretreatment coating was coated with epoxy primer and topcoated with polyurethane and was shipped to the outdoor corrosion test sites for coastal marine atmospheric exposure testing (24 months), prior to initiation of Phase II field testing. The physical evaluation tests are the following for marine outdoor exposure testing included: degree of scribed corrosion (ASTM D1654), degree of rusting (ASTM D610), degree of blistering (ASTM D714), color changes (ASTM D2244), and level of gloss (ASTM D523)

The following Figures 54-57 documents the marine outdoor exposure testing of the SILSBOND pretreatment coating at the NSWCCD marine outdoor corrosion site located in Fort Lauderdale, Florida.

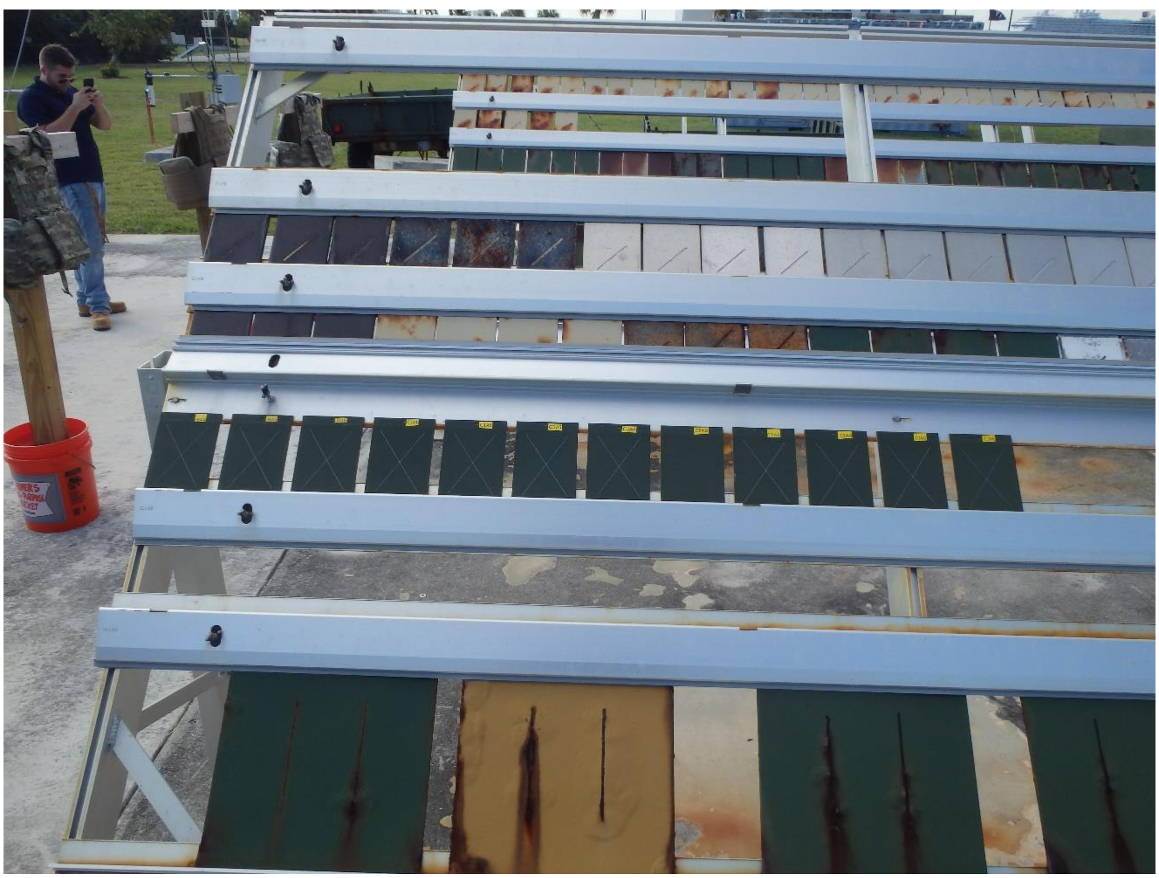


Figure 54. Racks Holding SILSBOND Pretreatment 01 (2%) + Primer + Topcoat at 0 months (location NSWCCD, Fort Lauderdale, Fl marine outdoor corrosion tesing site)

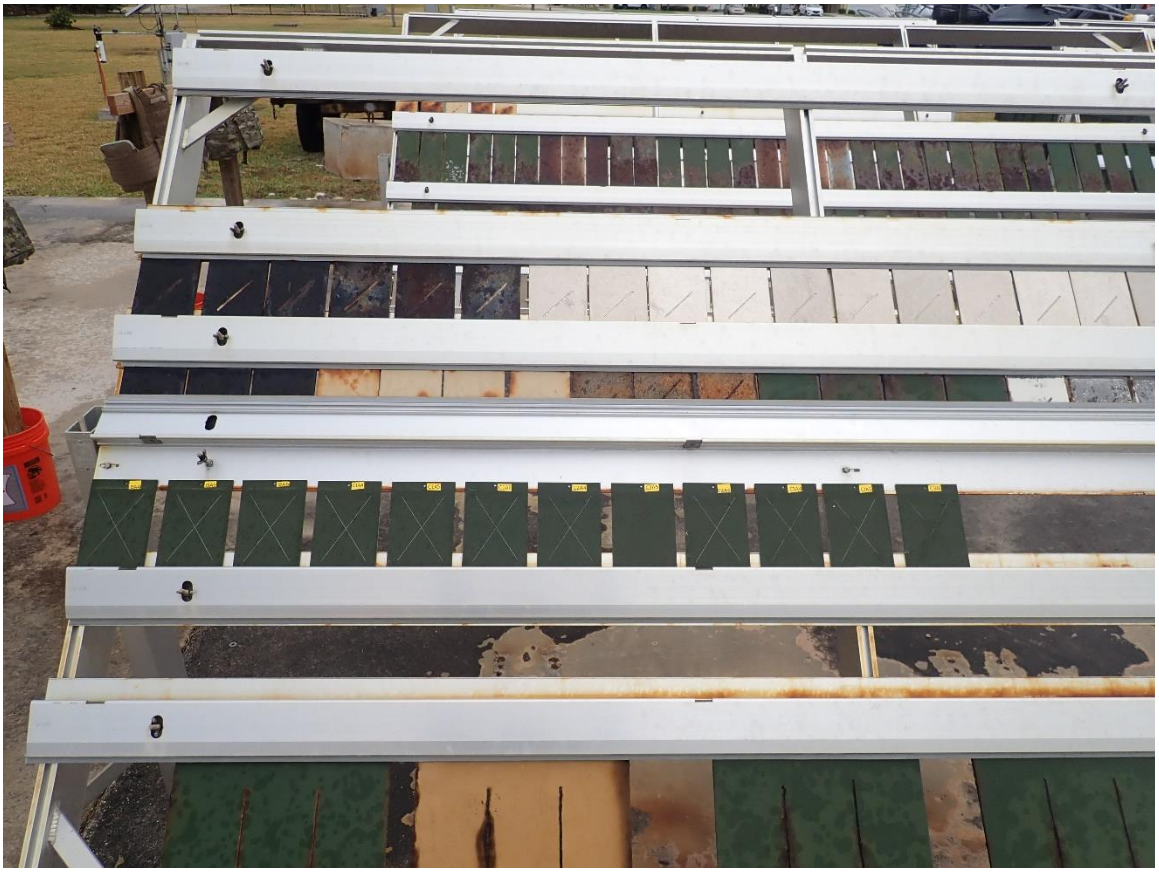


Figure 55. Racks holding SILSBOND Pretreatment 01 (2%) + Primer + Topcoat at 12 Months

Figure 56. Racks holding SILSBOND Pretreatment 01 (2%) + Primer + Topcoat at 18 Months

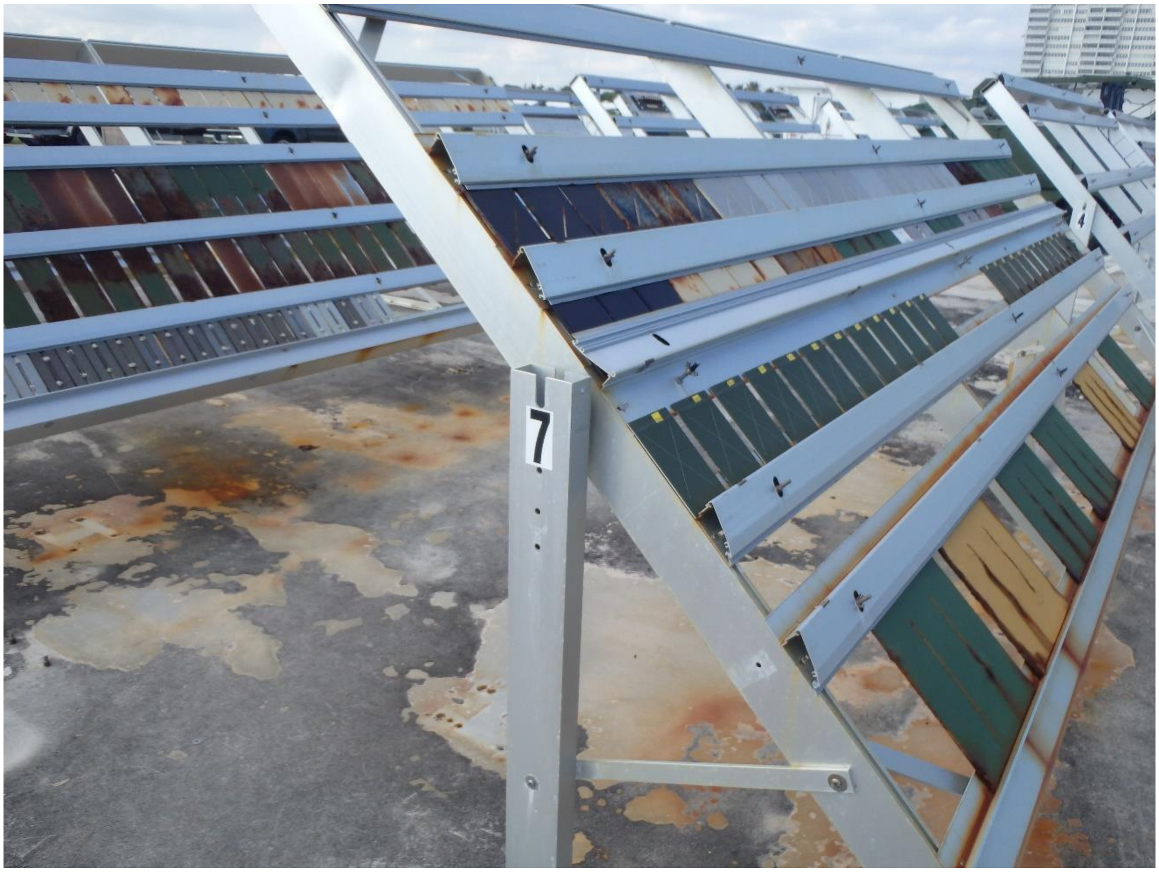


Figure 57. Racks Holding SILSBOND Pretreatment 01 (2%) + Primer + Topcoat at 24 Months

The following Figures 58-70 showcase specific coupons at various intervals during the 24 month marine outdoor exposure testing conducted by NSWCCD.

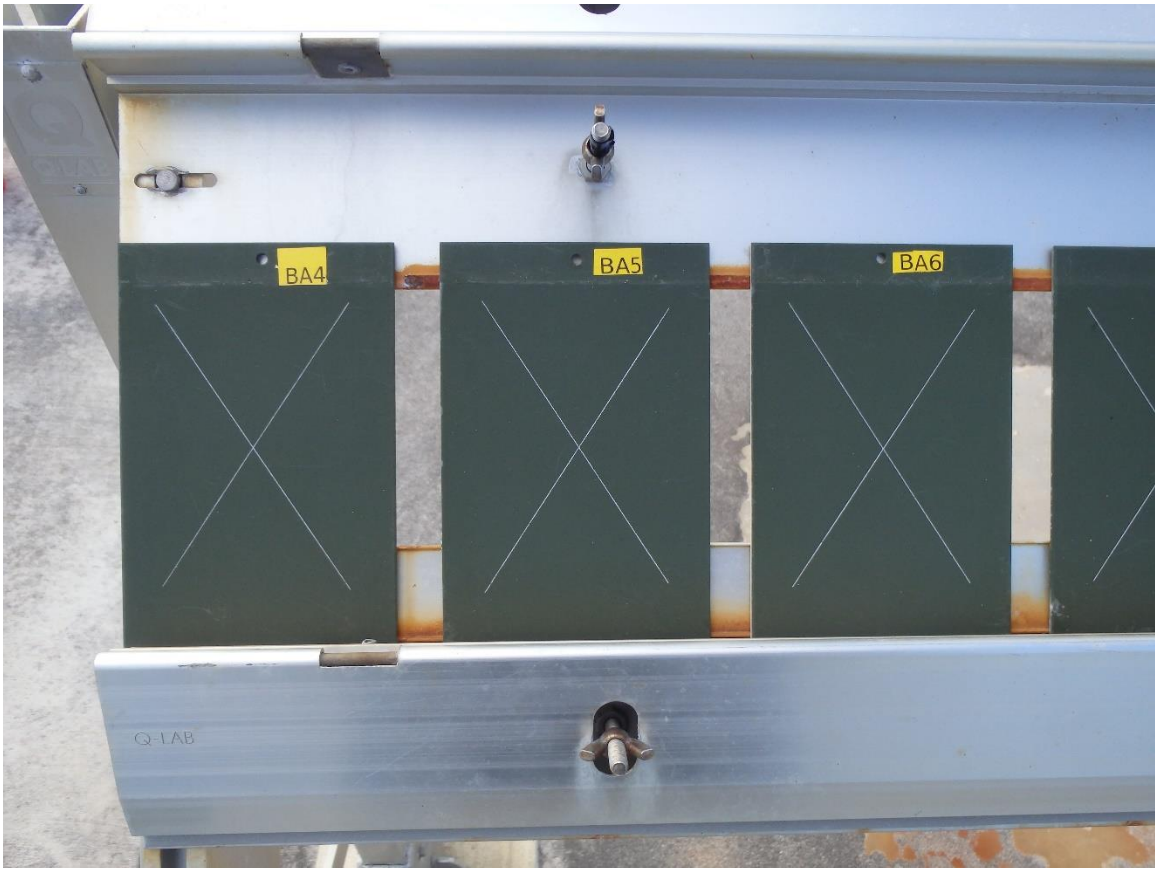


Figure 58. Baseline Control Coupon for Marine Outdoor Exposure Testing
(Al 2024-T3 at 0 Months)

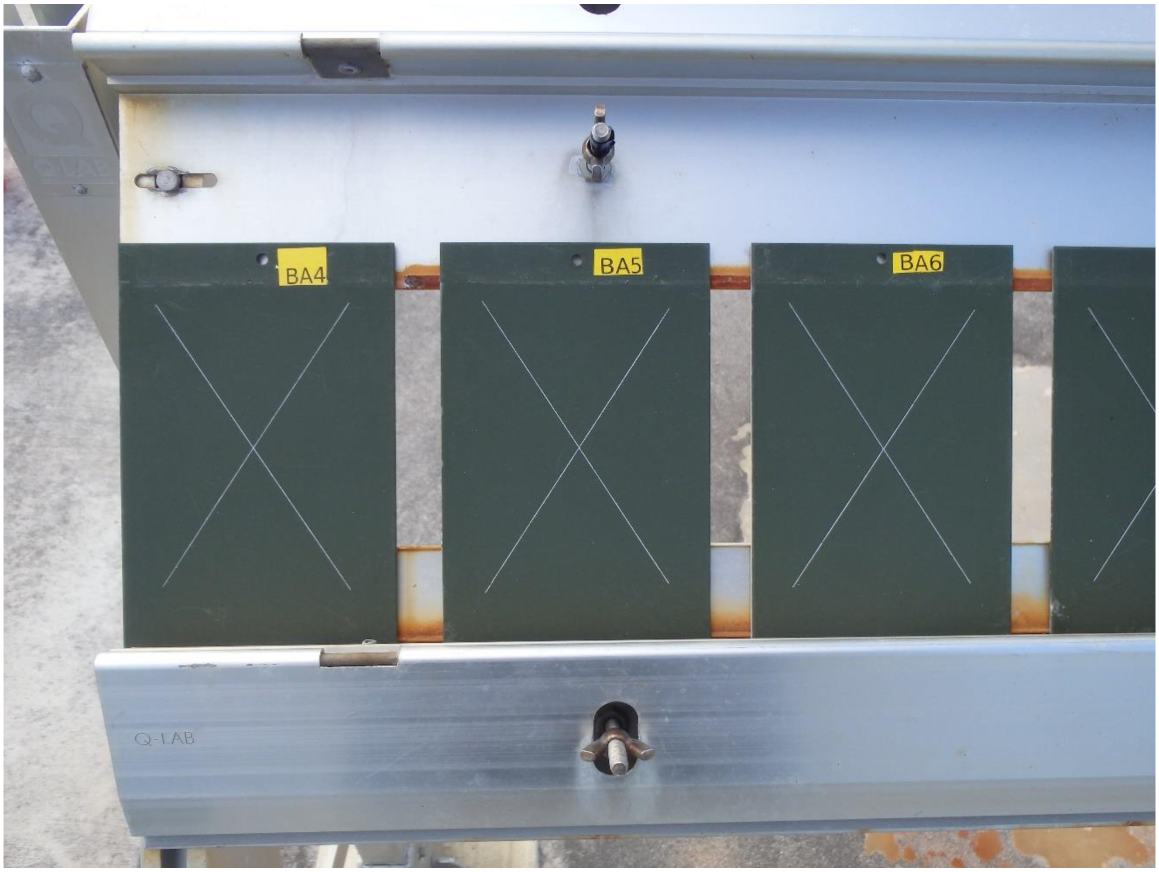


Figure 59. Baseline Control Coupon for Marine Outdoor Exposure Testing
(Al 2024-T3 at 12 months)

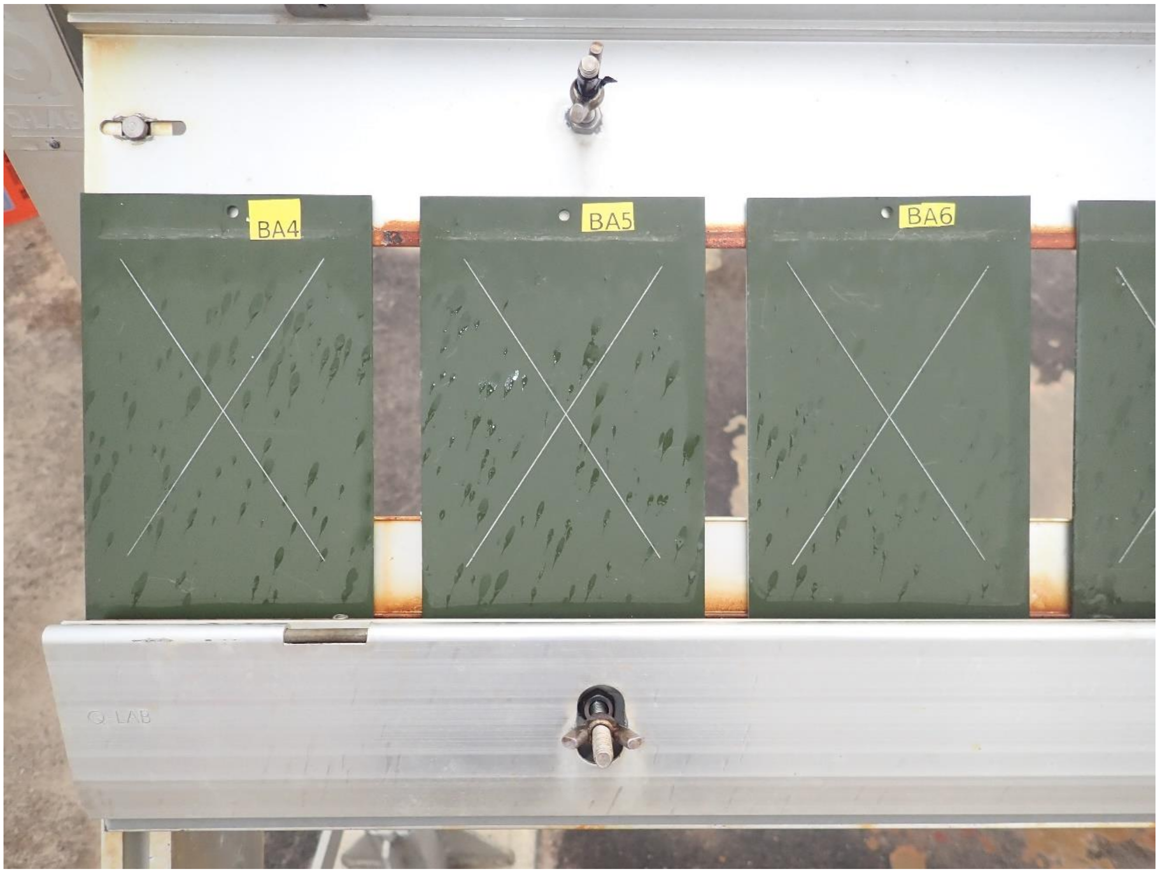


Figure 60. Baseline Control Coupon for Marine Outdoor Exposure Testing
(Al 2024-T3 at 24 Months)

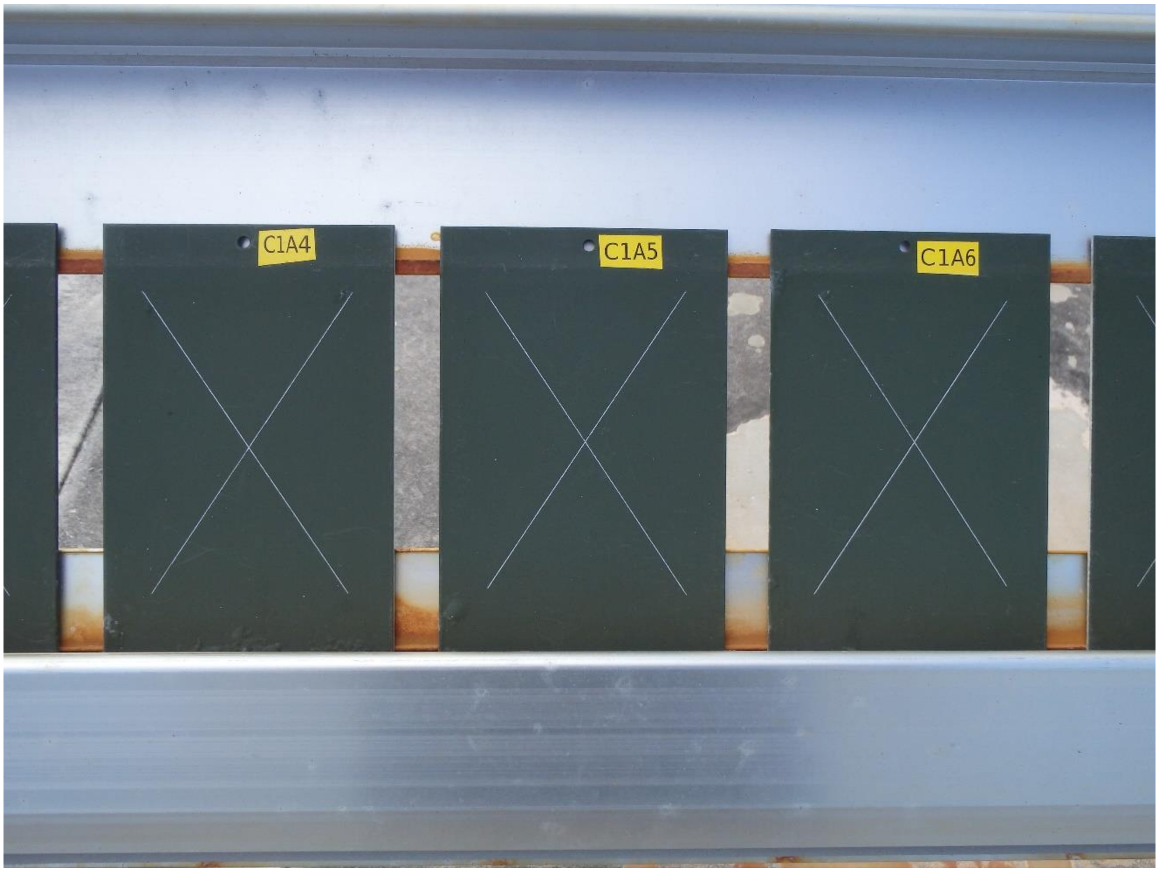


Figure 61. SILSBOND 01 (2%) on Al 2024-T3 at 0 Months

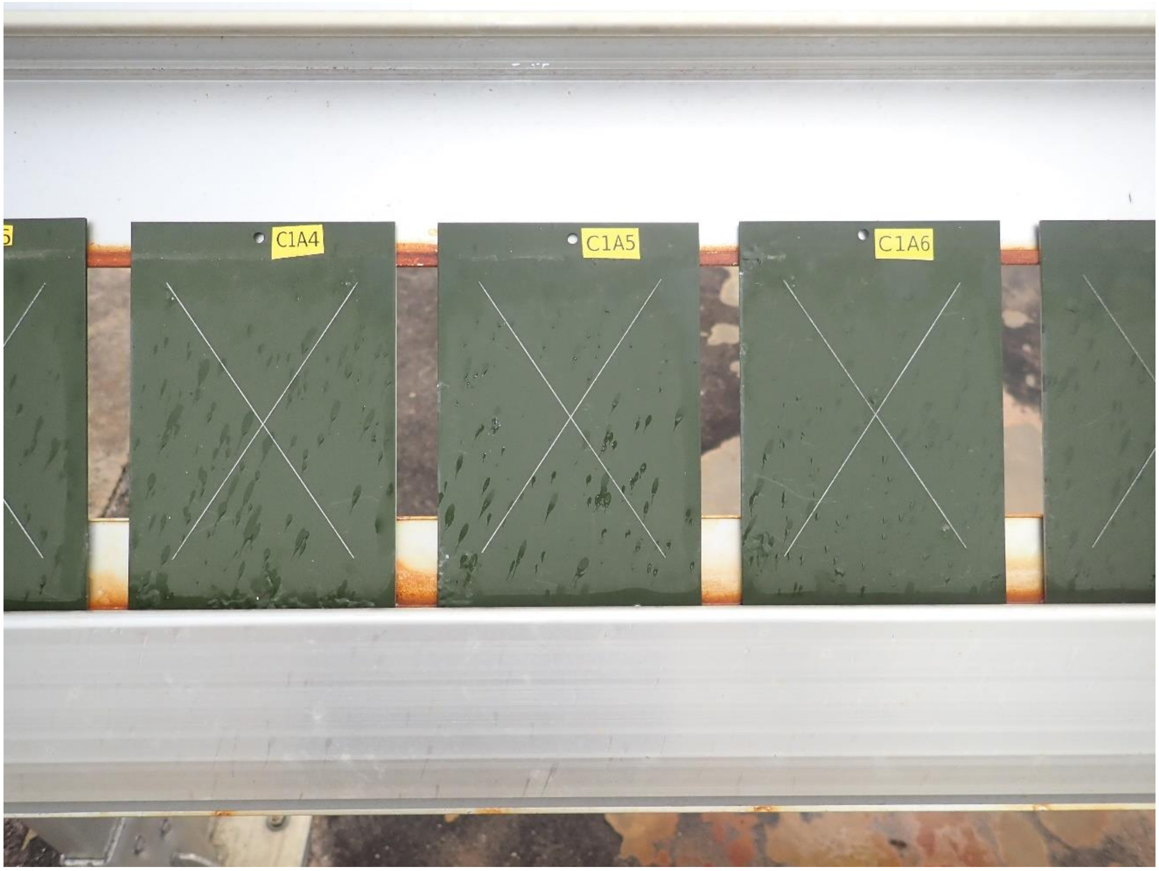


Figure 62. SILSBOND 01 (2%) on Al 2024-T3 at 24 Months

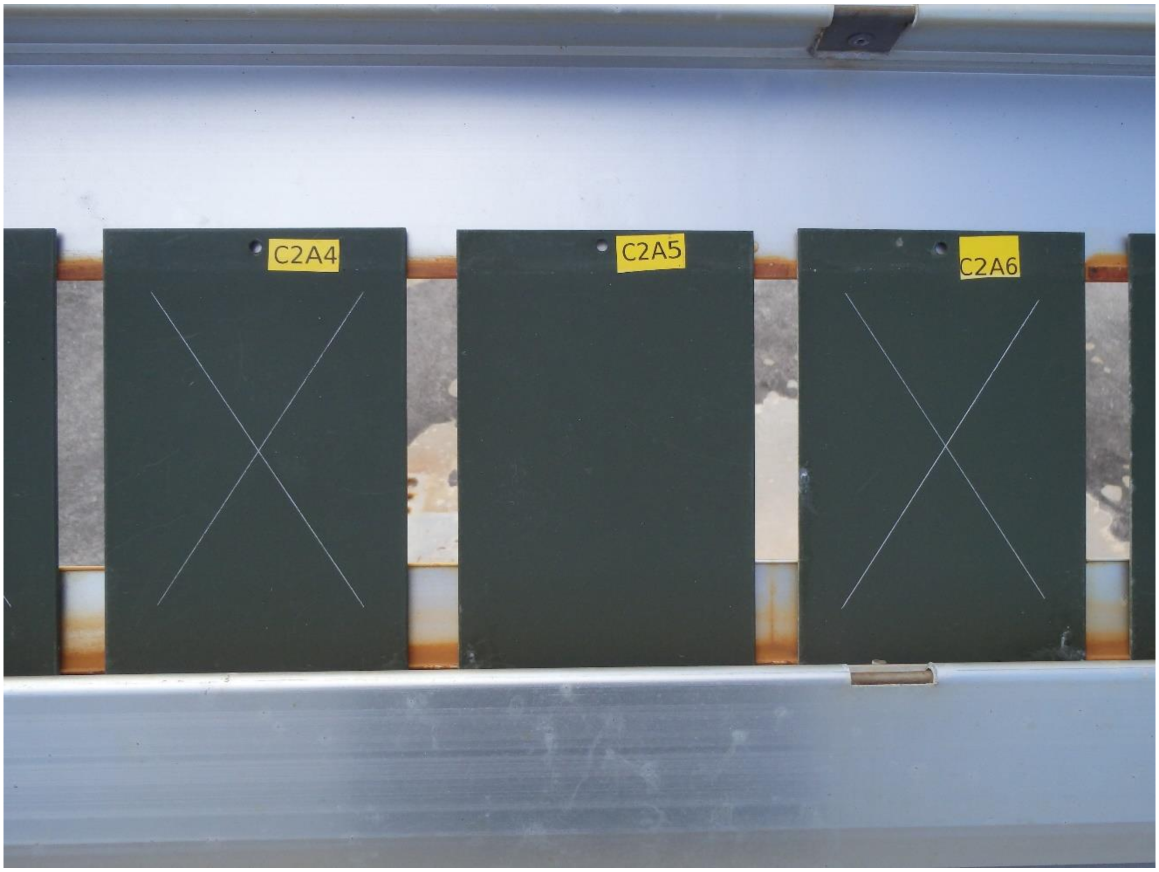


Figure 63. SILSBOND 01 (3%) on Al 2024-T3 at 0 Months

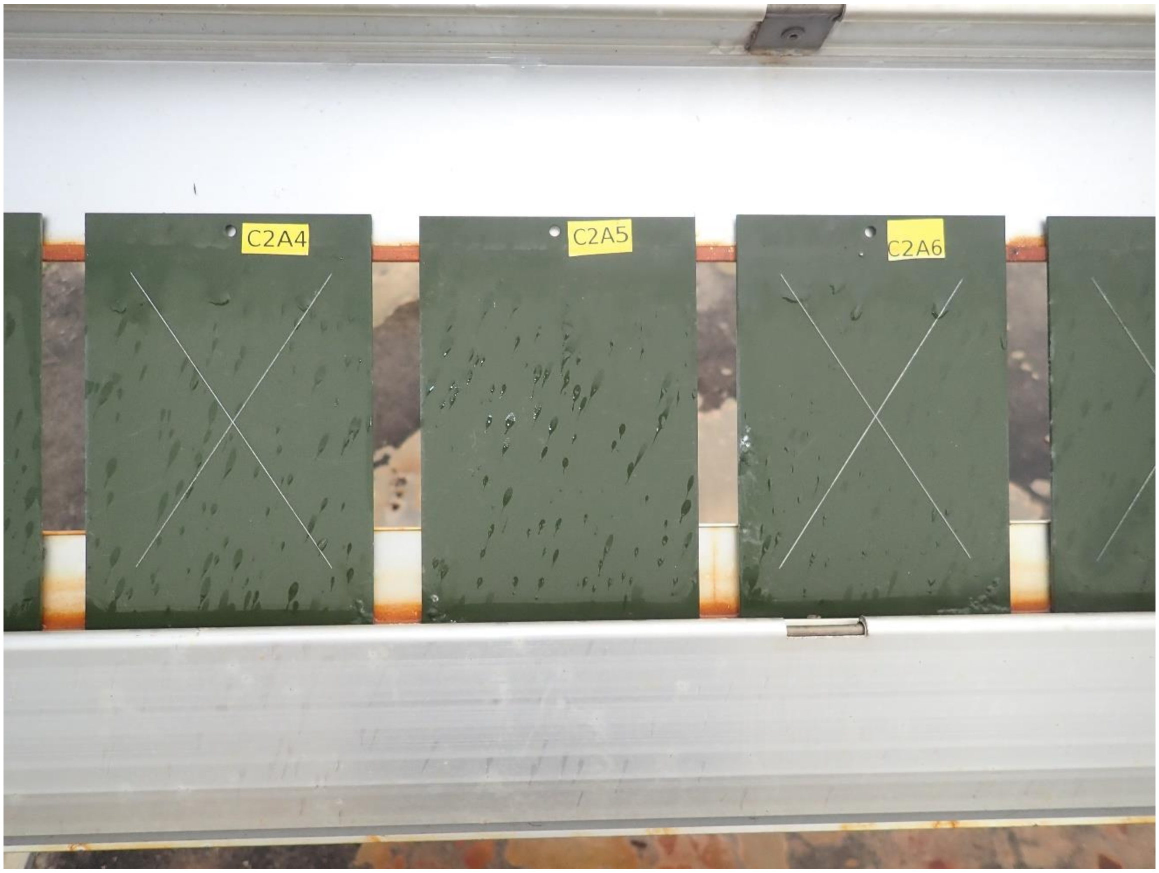


Figure 64. SILSBOND 01 (3%) on Al 2024-T3 at 24 Months

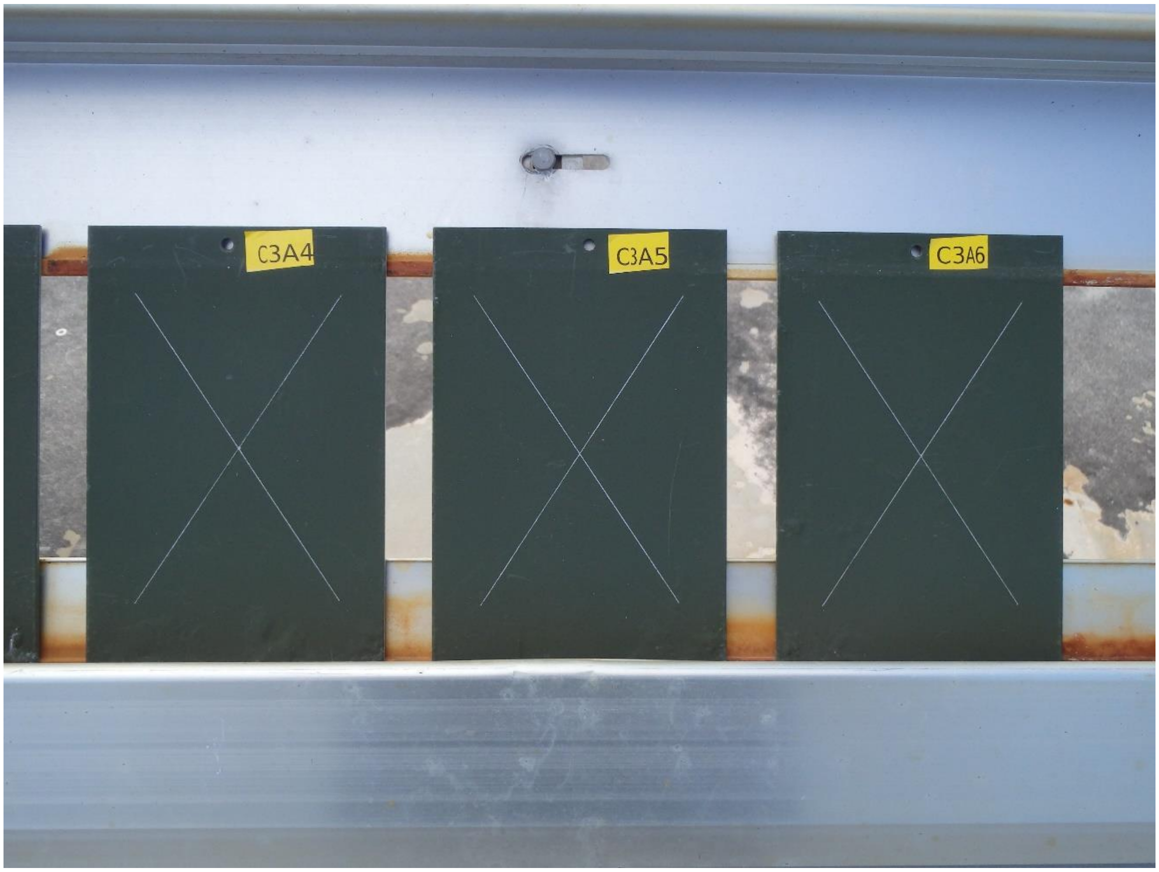


Figure 65. SILSBOND 05 (50%) on Al 2024-T3 at 0 Months

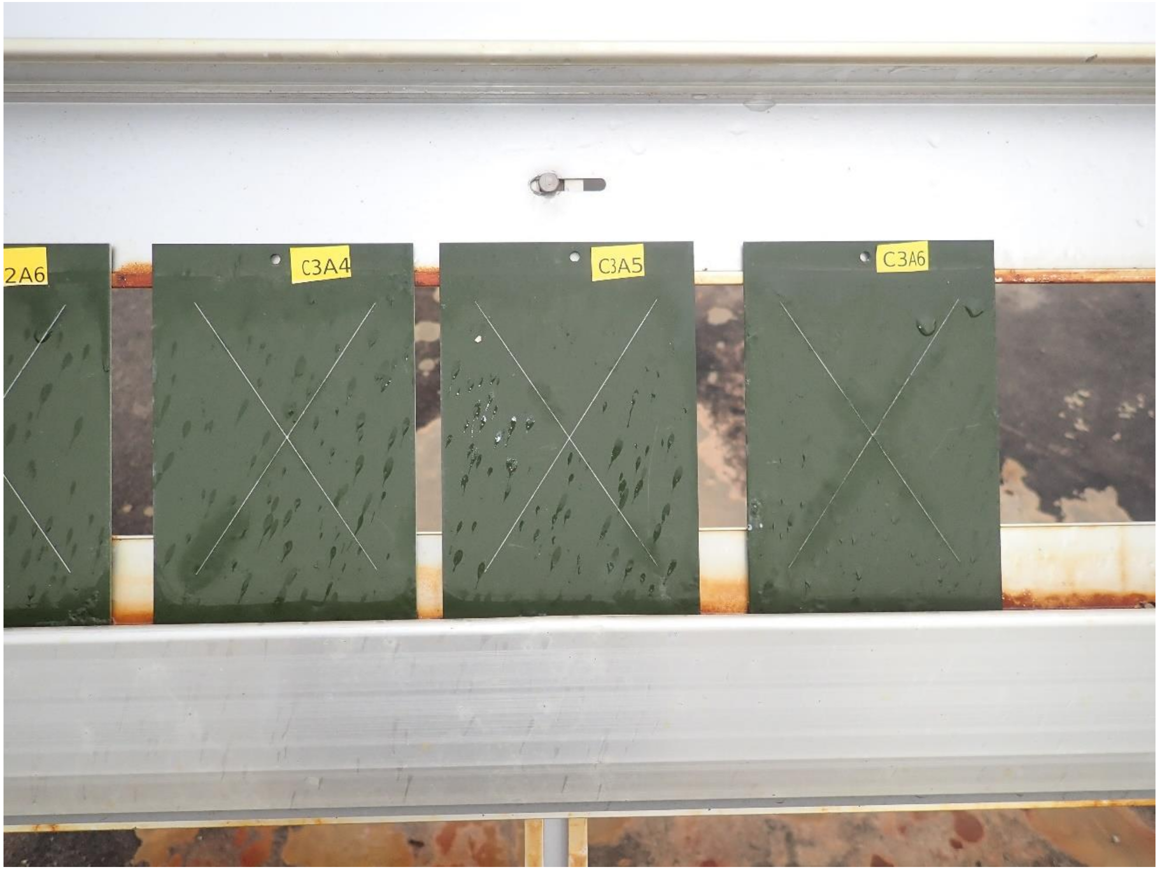


Figure 66. SILSBOND 05 (50%) on Al 2024-T3 at 24 Months

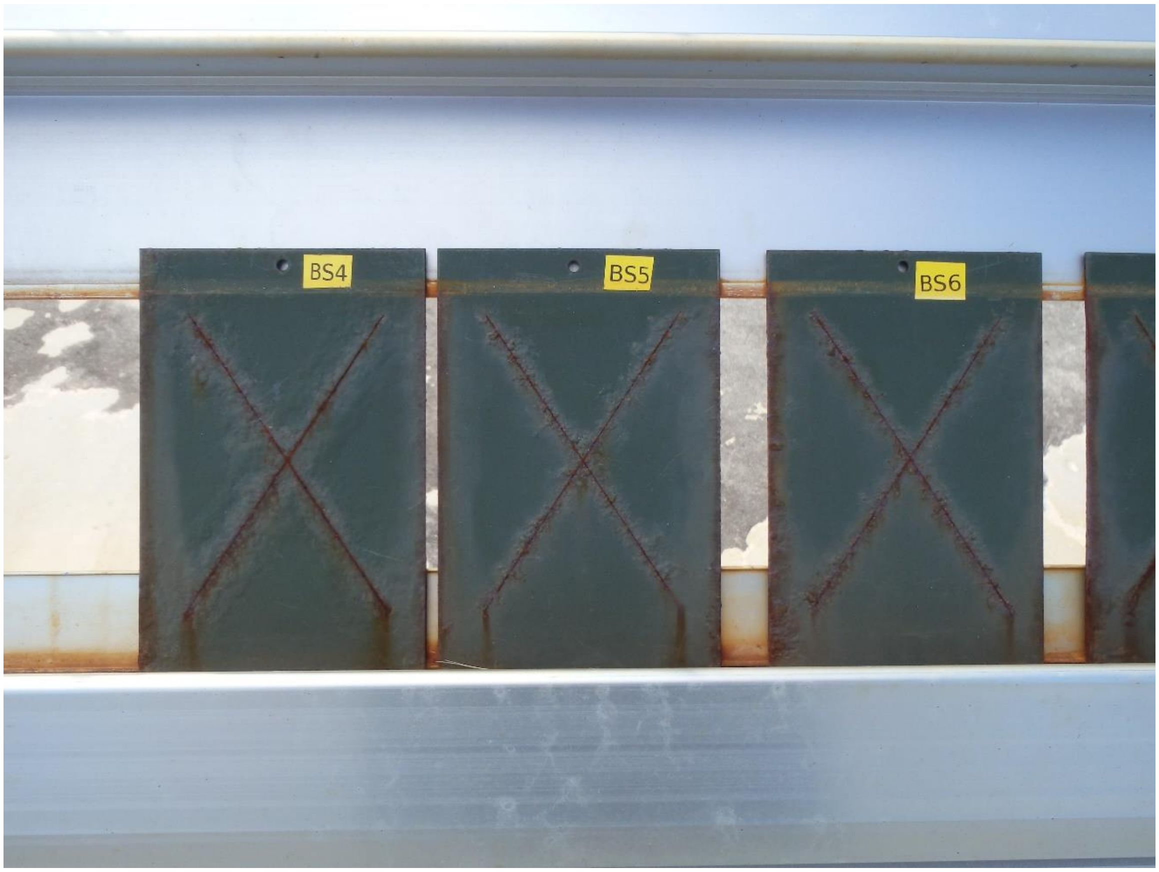


Figure 67. Baseline Coating on 1020 Steel at 12 Months

Figure 68. Baseline Coating on 1020 Steel at 24 Months

Figure 69. SILSBOND 01 (2%) coating on 1020 Steel at 12 Months

Figure 70. SILSBOND 01 (2%) on 1020 Steel at 24 Months

Listed below are Figures 71-103 documenting the marine outdoor exposure testing conducted by ARL at the Cape Canaveral Space Force Station, Florida site which is shown in Figure 71. Figures 72-103 are representative coupons documenting the marine outdoor exposure testing for 3, 6, 9, 12, 15, 18, 24, 27 months duration. The testing included a total of 5 replicates for the SILSBOND 01 (2%) pretreatment coating in a full military stack-up.

Figure 71. Racks Holding SILSBOND Pretreatment 01 (2%) + Primer + Topcoat
Cape Canaveral Space Force Station, Florida

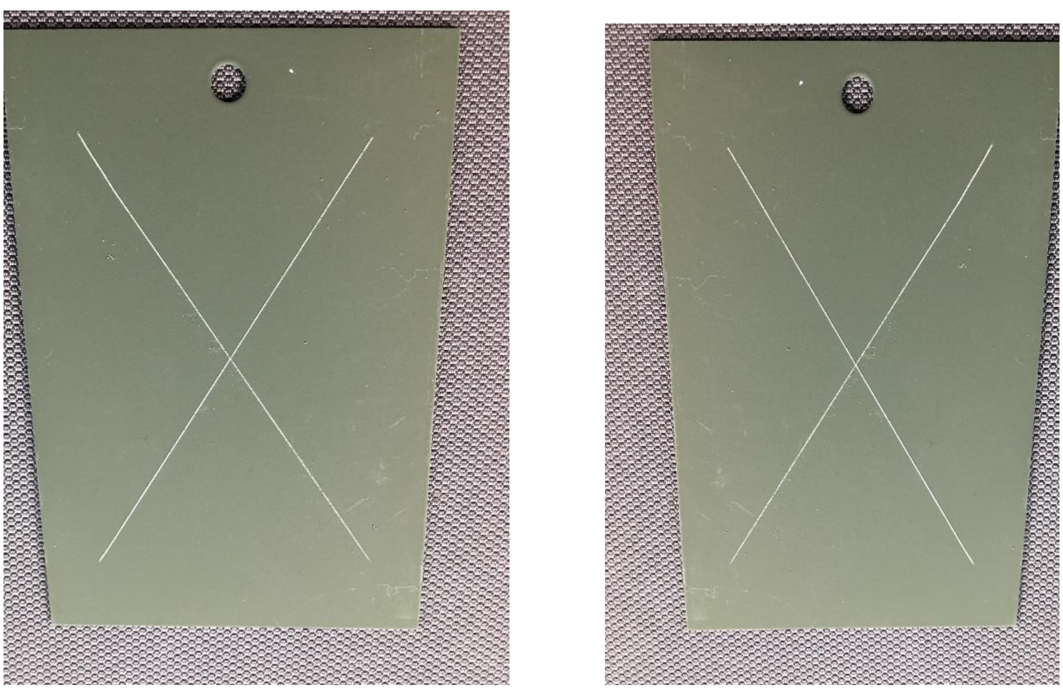


Figure 72. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on mil finished
Al 2024-T3 at 3 months

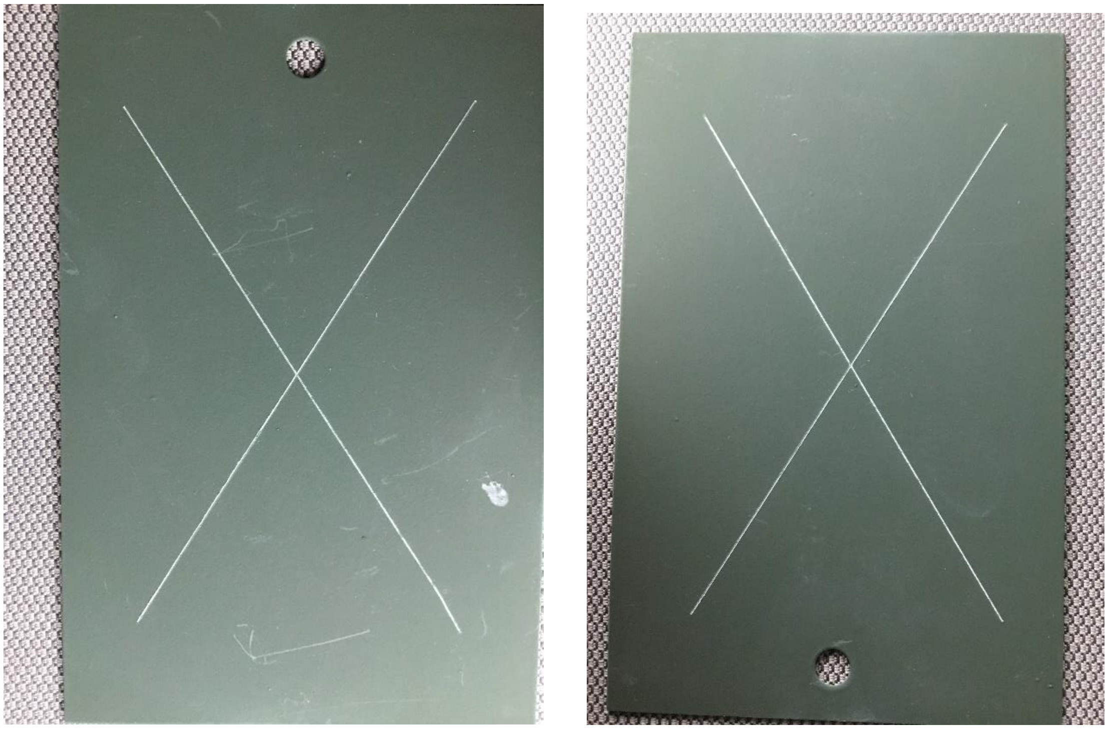


Figure 73. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on mil finished Al 2024-T3 at 6 months

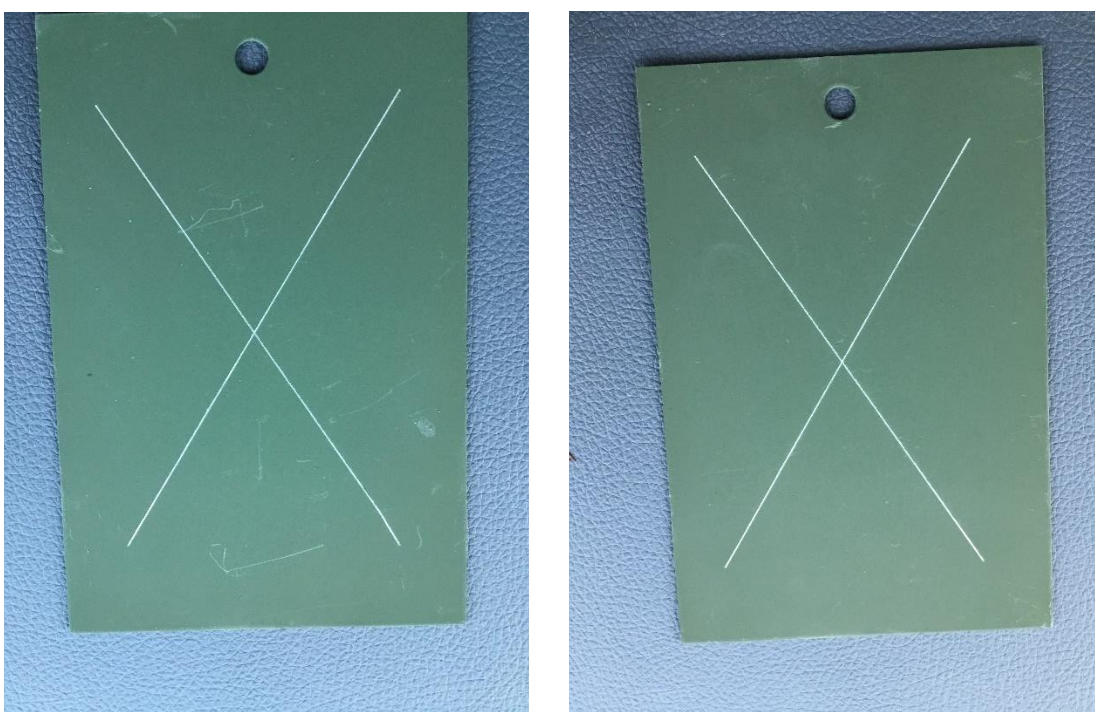


Figure 74. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on mil finished Al 2024-T3 at 9 months

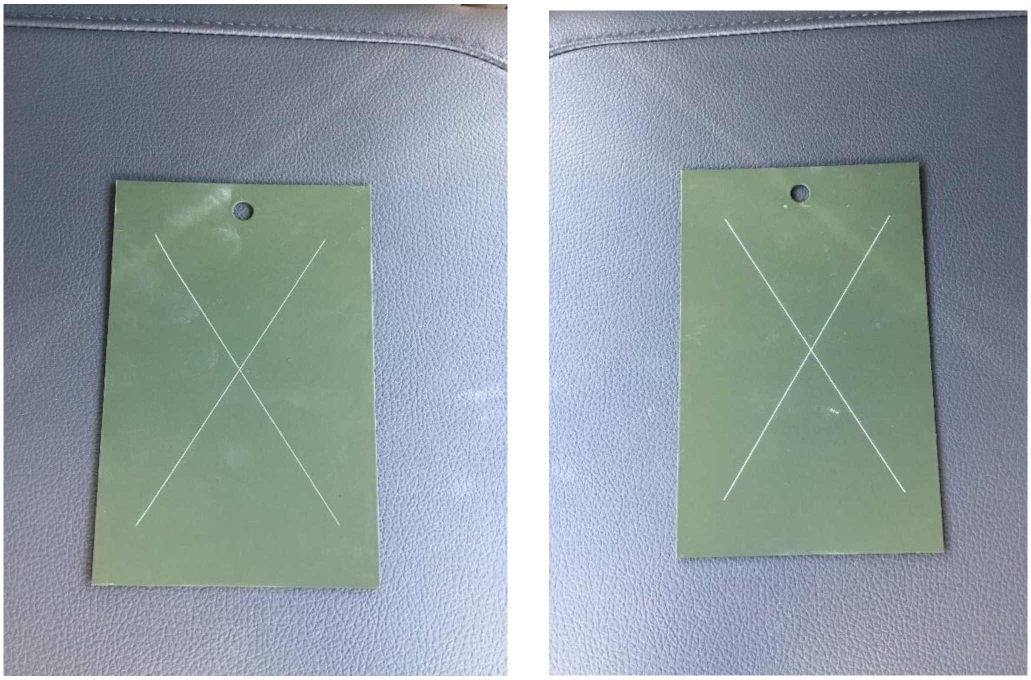


Figure 75. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on mil finished Al 2024-T3 at 12 months

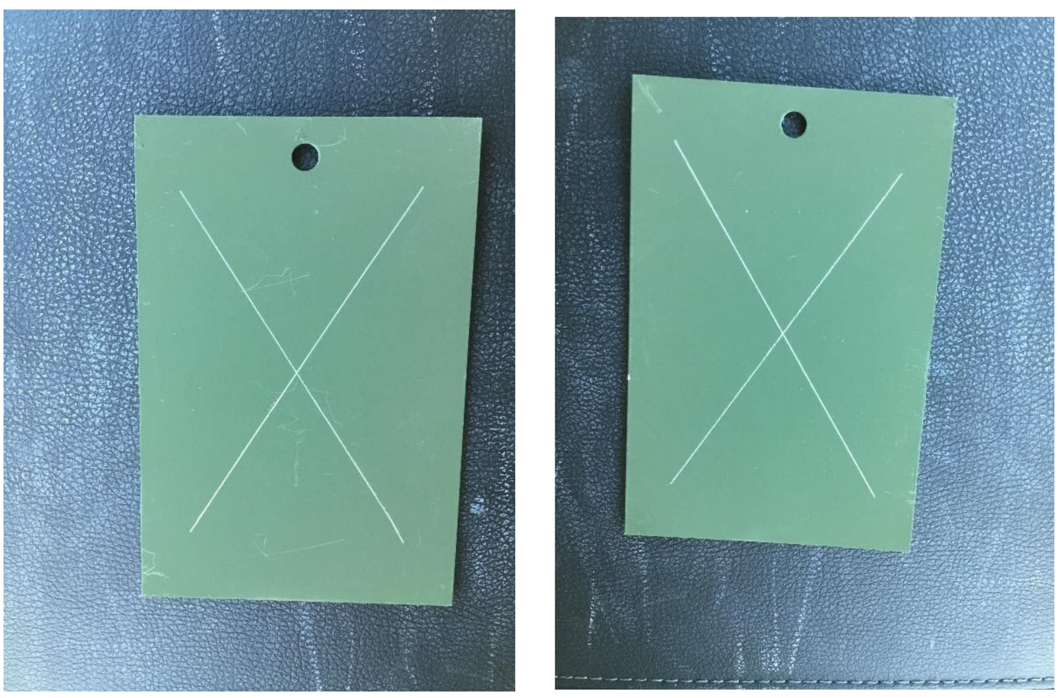


Figure 76. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on mil finished Al 2024-T3 at 15 months

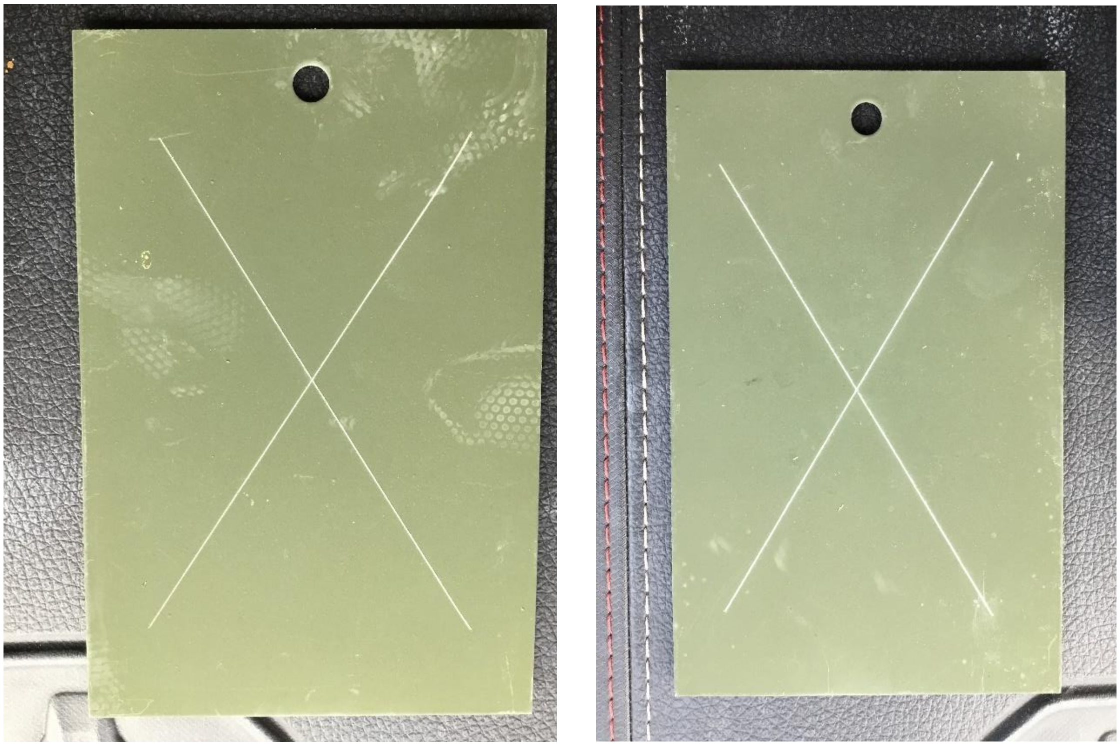


Figure 77. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on mil finished Al 2024-T3 at 18 months

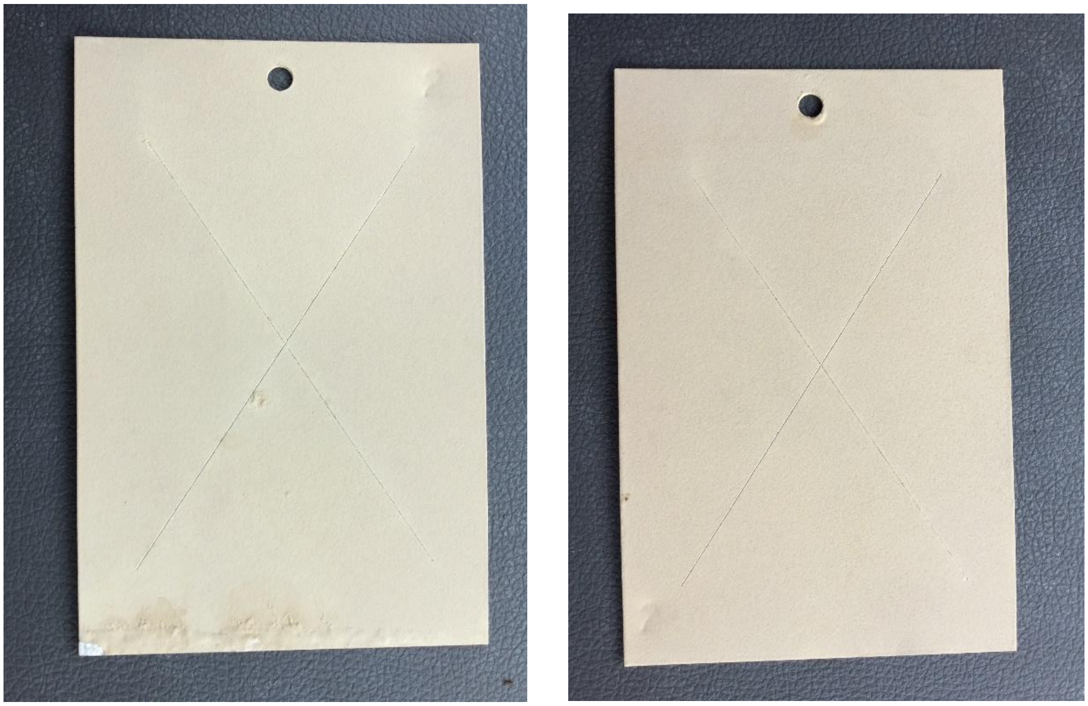


Figure 78. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on mil finished Al 2024-T3 at 24 months

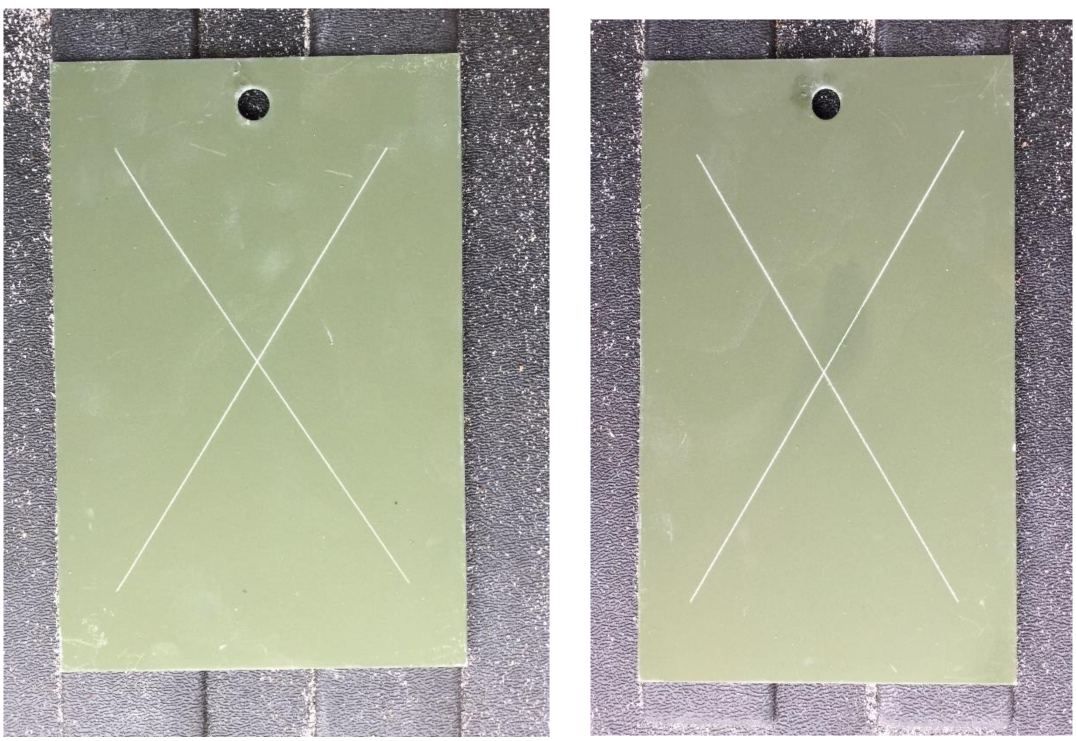


Figure 79. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on mil finished Al 2024-T3 at 27 months

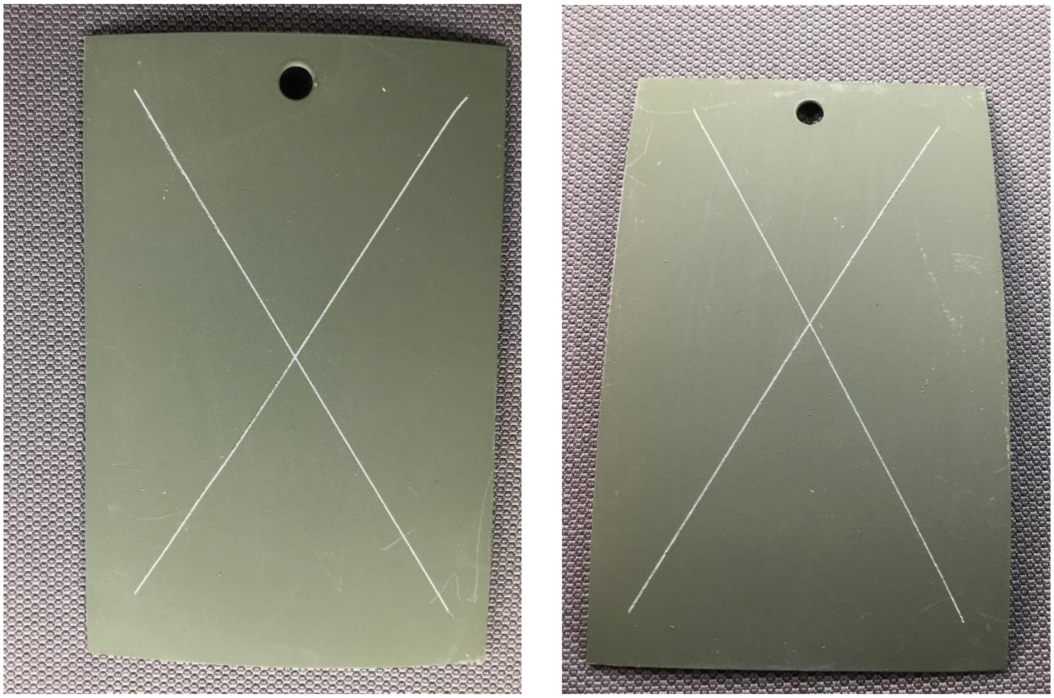


Figure 80. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on Blasted Al 2024-T3 at 3 months

Figure 81. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on Blasted Al 2024-T3 at 6 months

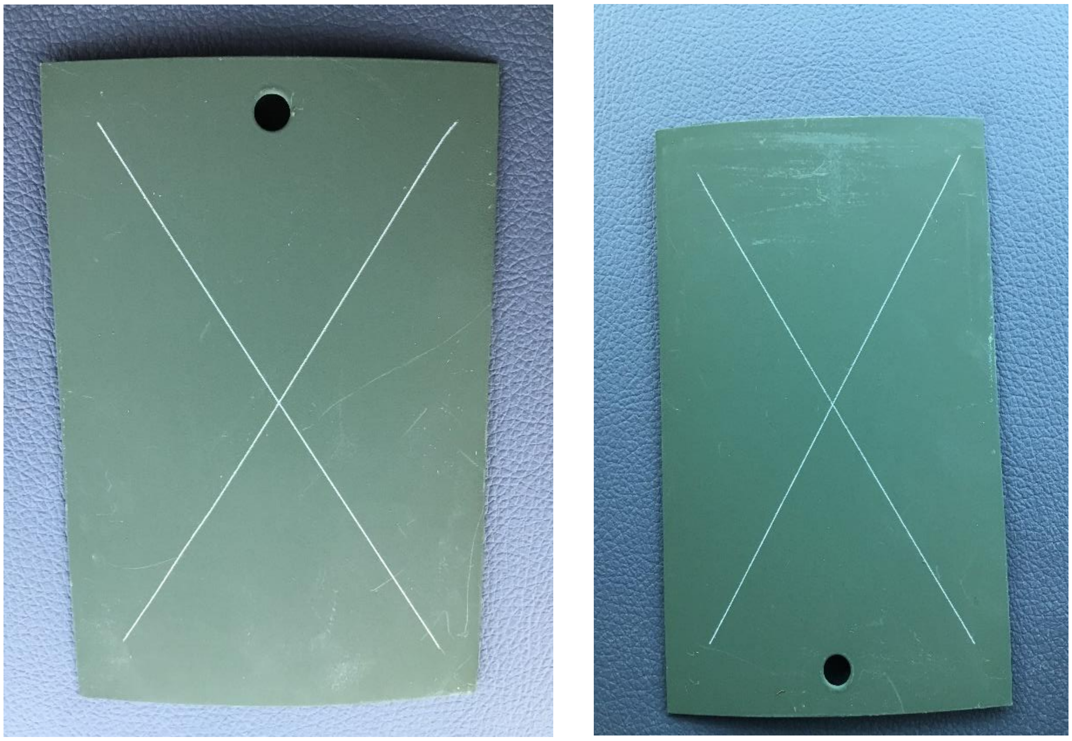


Figure 82. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on Blasted Al 2024-T3 at 9 months

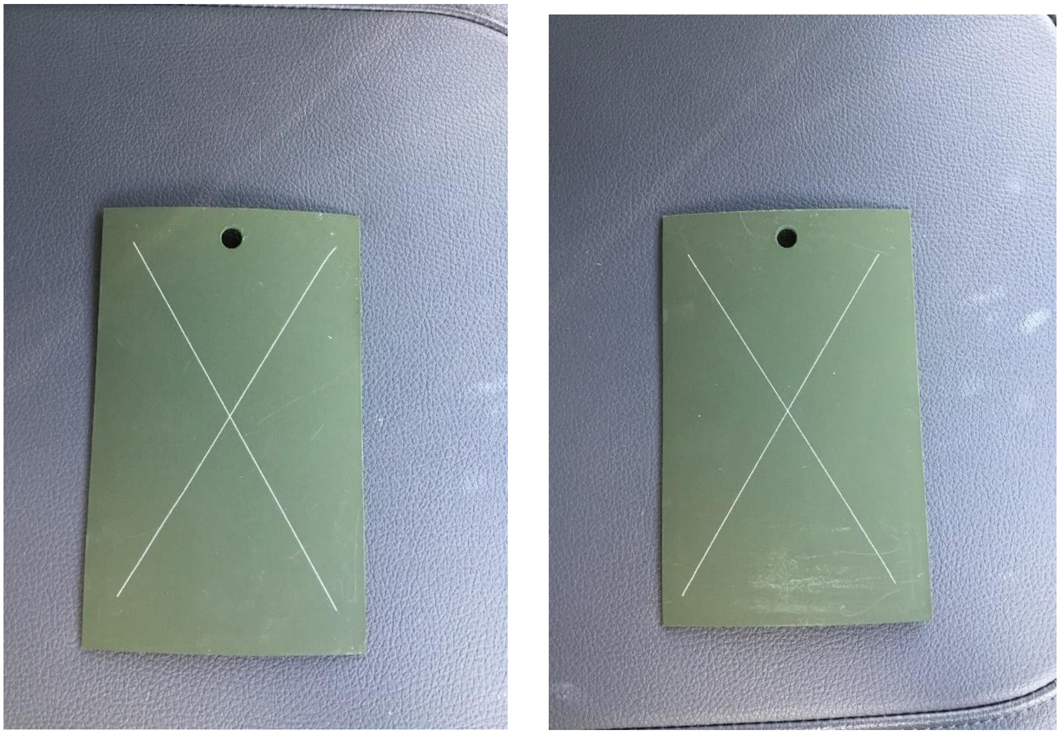


Figure 83. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on Blasted Al 2024-T3 at 12 months

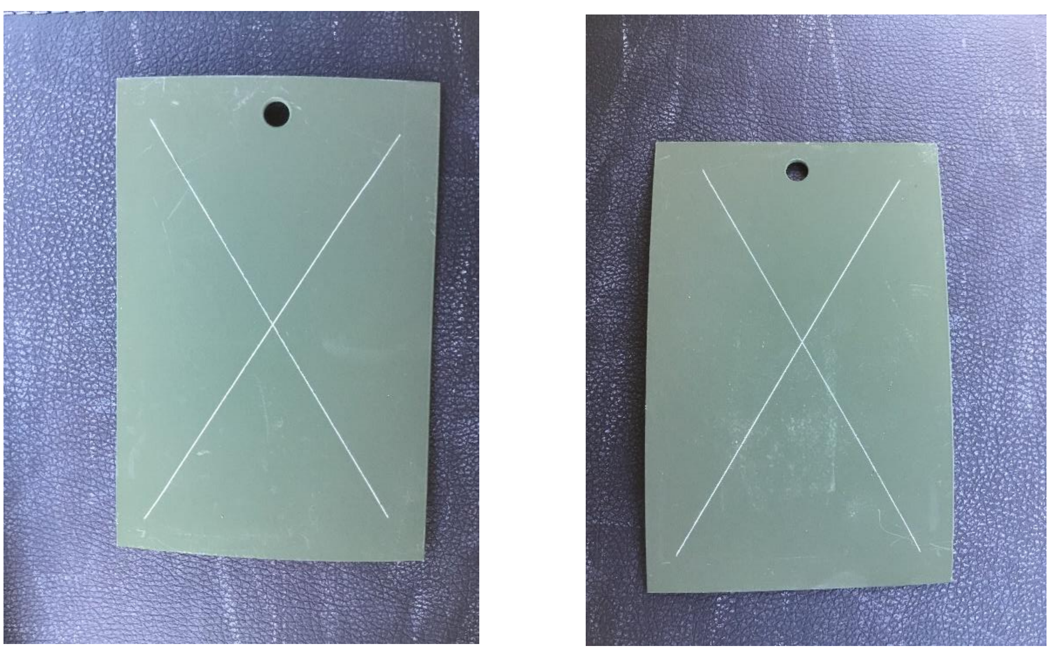


Figure 84. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on Blasted Al 2024-T3 at 15 months

Figure 85. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on Blasted Al 2024-T3 at 18 months

Figure 86. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on Blasted Al 2024-T3 at 24 months

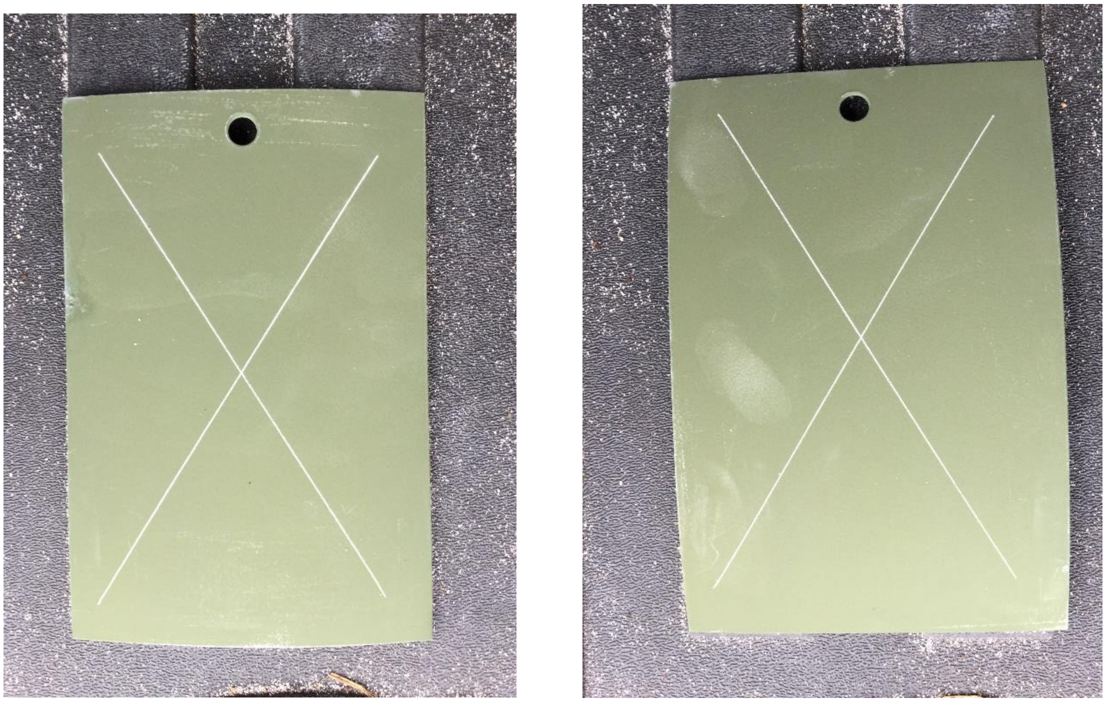


Figure 87. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on Blasted Al 2024-T3 at 27 months

Figure 88. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on mil finished CRS at 3 months

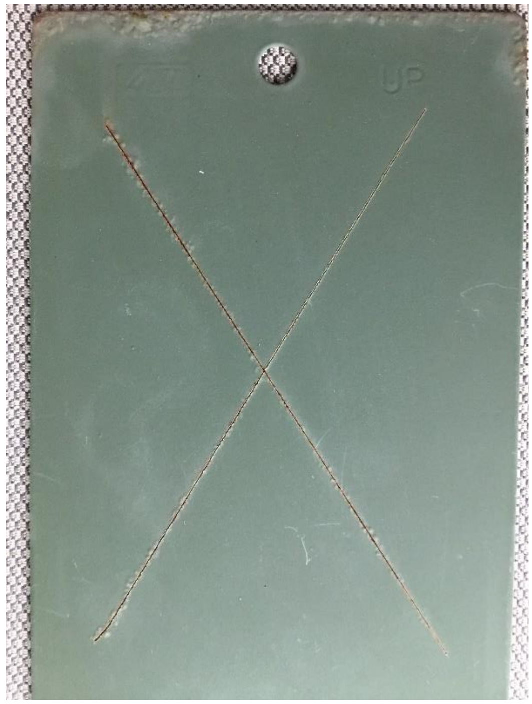


Figure 89. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on mil finished CRS at 6 months

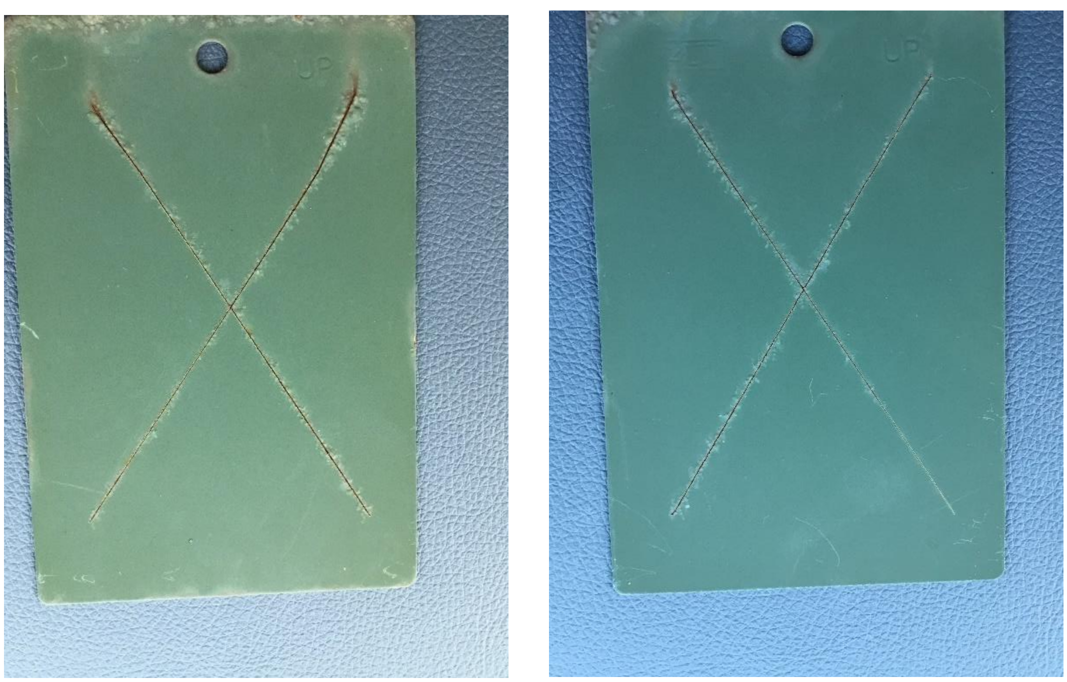


Figure 90. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on mil finished CRS at 9 months

Figure 91. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on mil finished CRS at 12 months

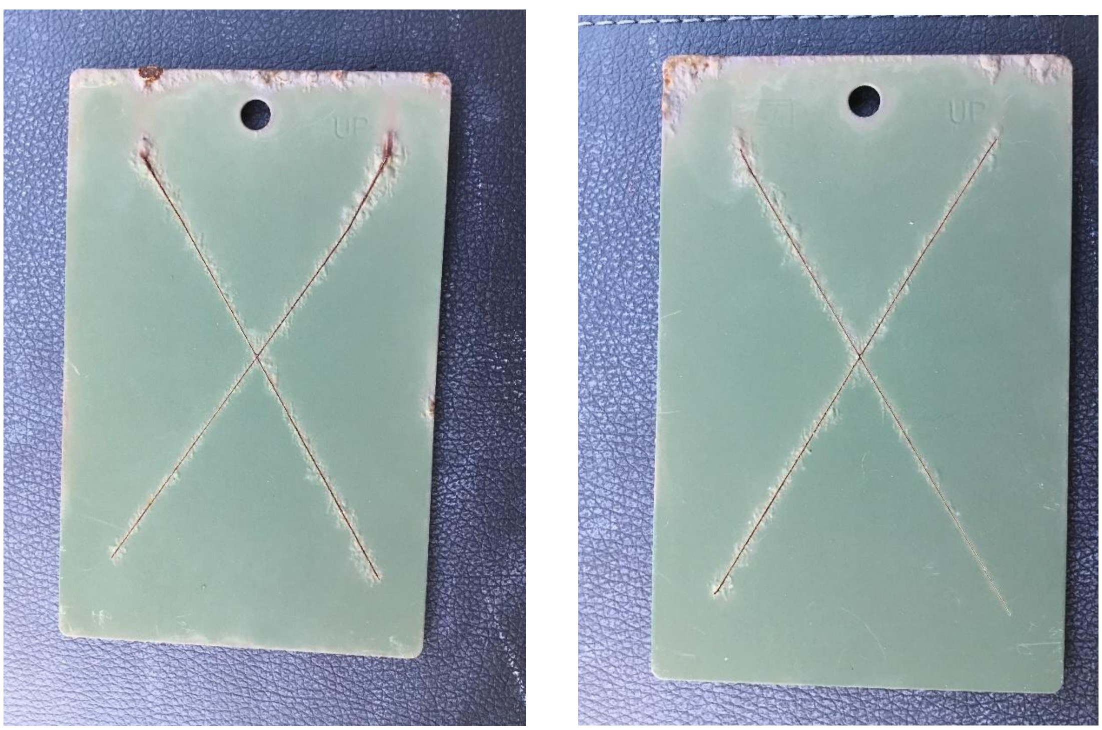


Figure 92. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on mil finished CRS at 15 months

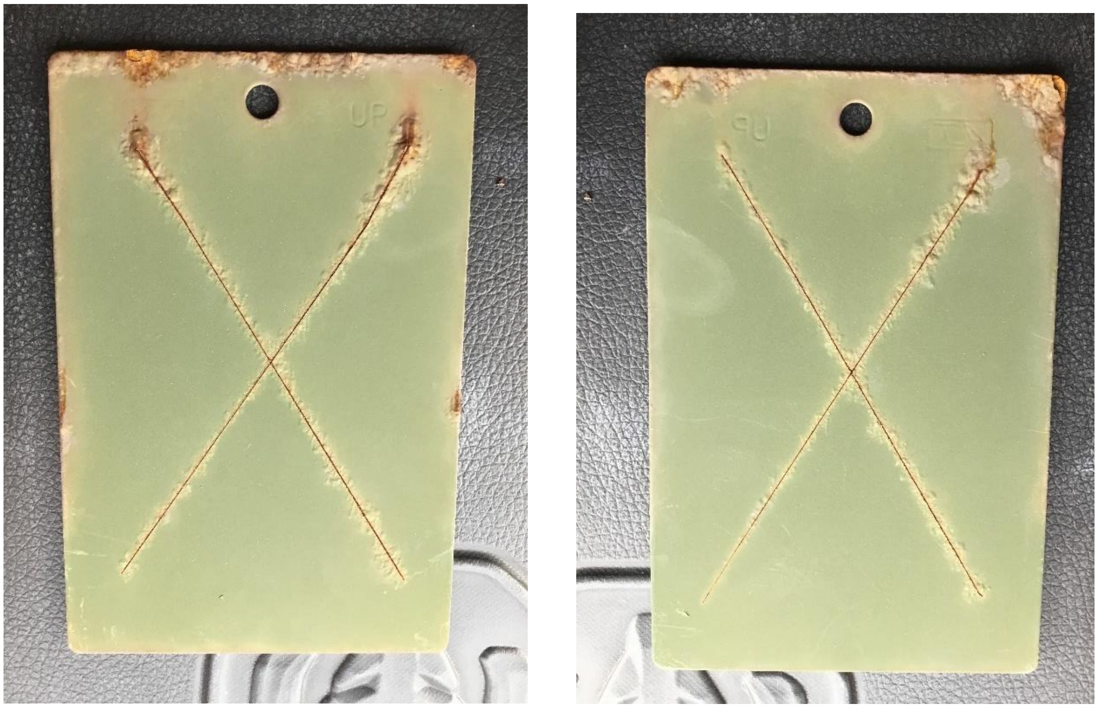


Figure 93. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on mil finished CRS at 18 months

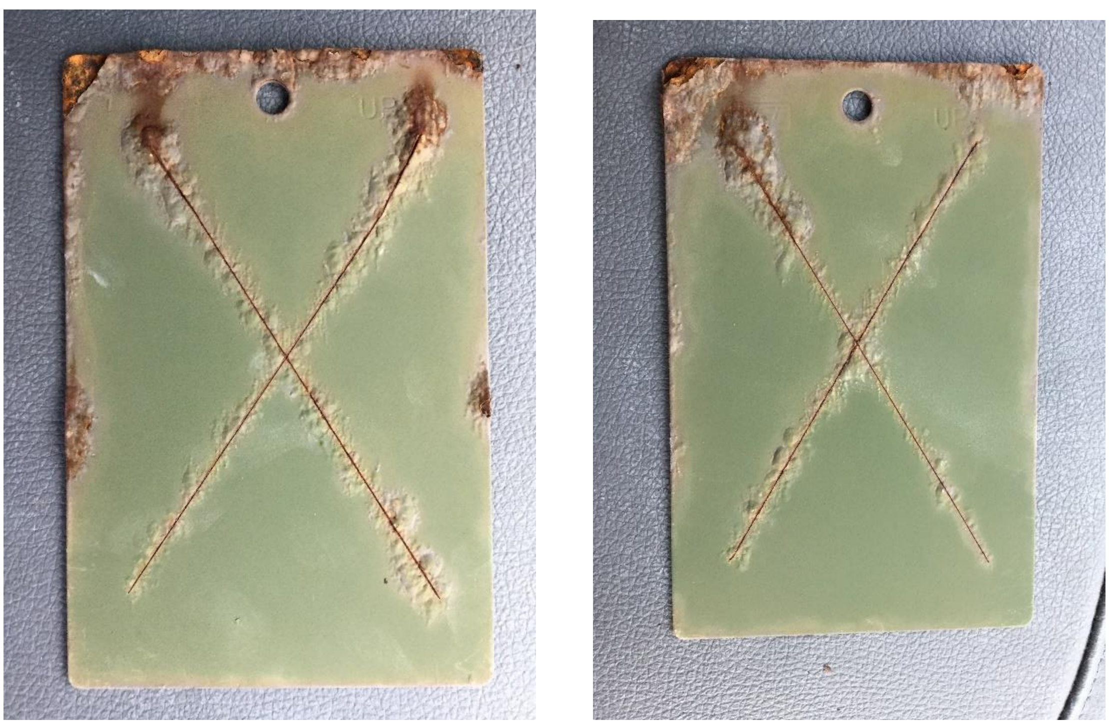


Figure 94. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on mil finished CRS at 24 months

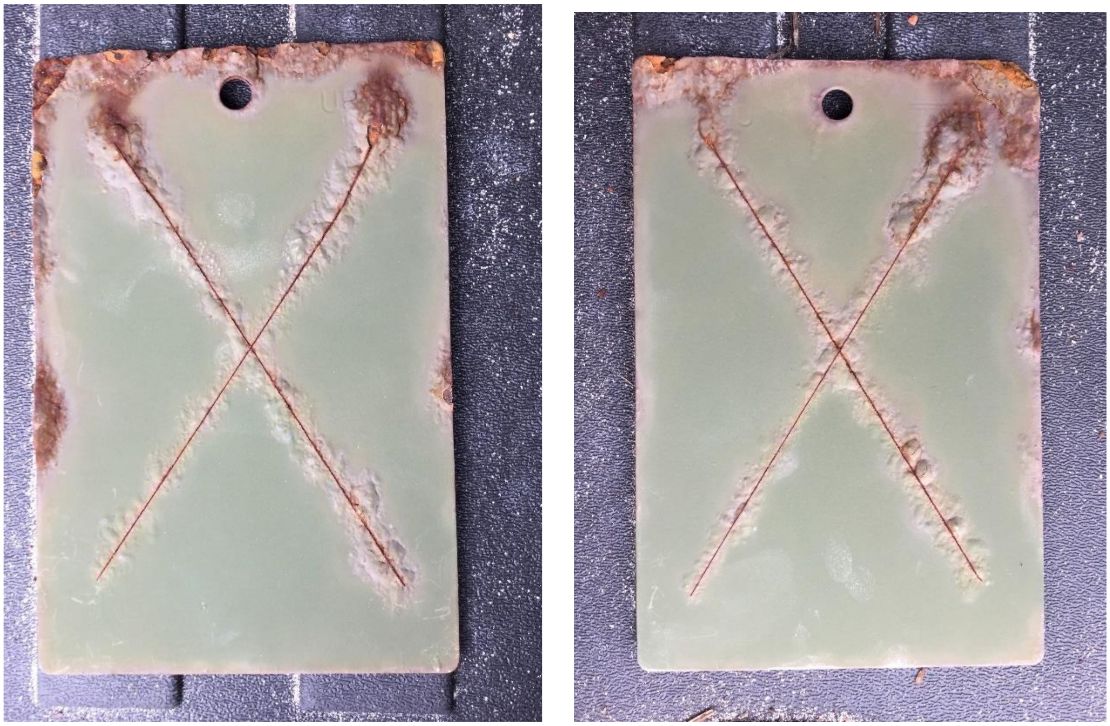


Figure 95. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on mil finished CRS at 27 months

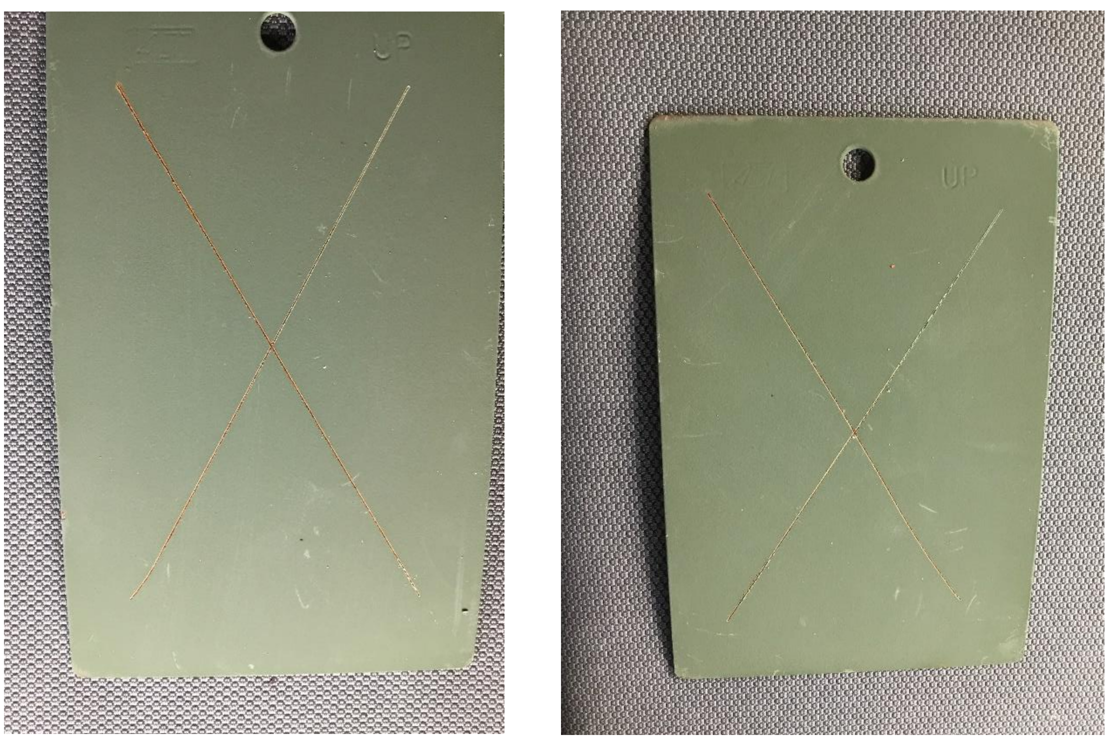


Figure 96. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on blasted CRS at 3 months

Figure 97. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on blasted CRS at 6 months

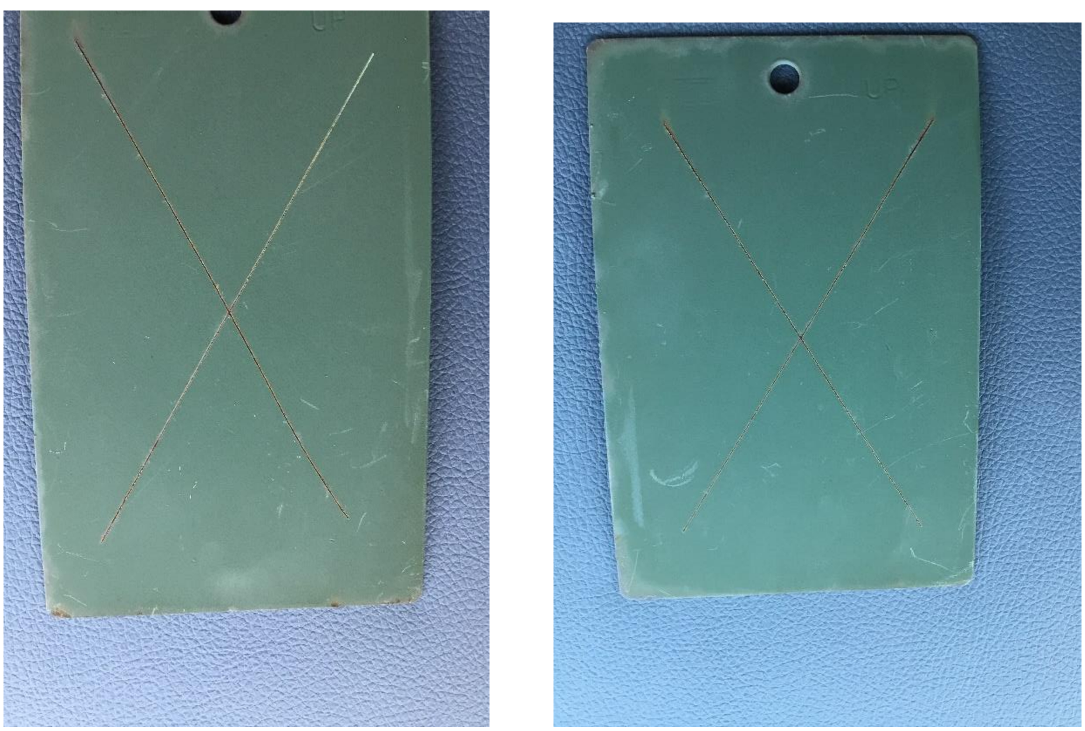


Figure 98. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on blasted CRS at 9 months

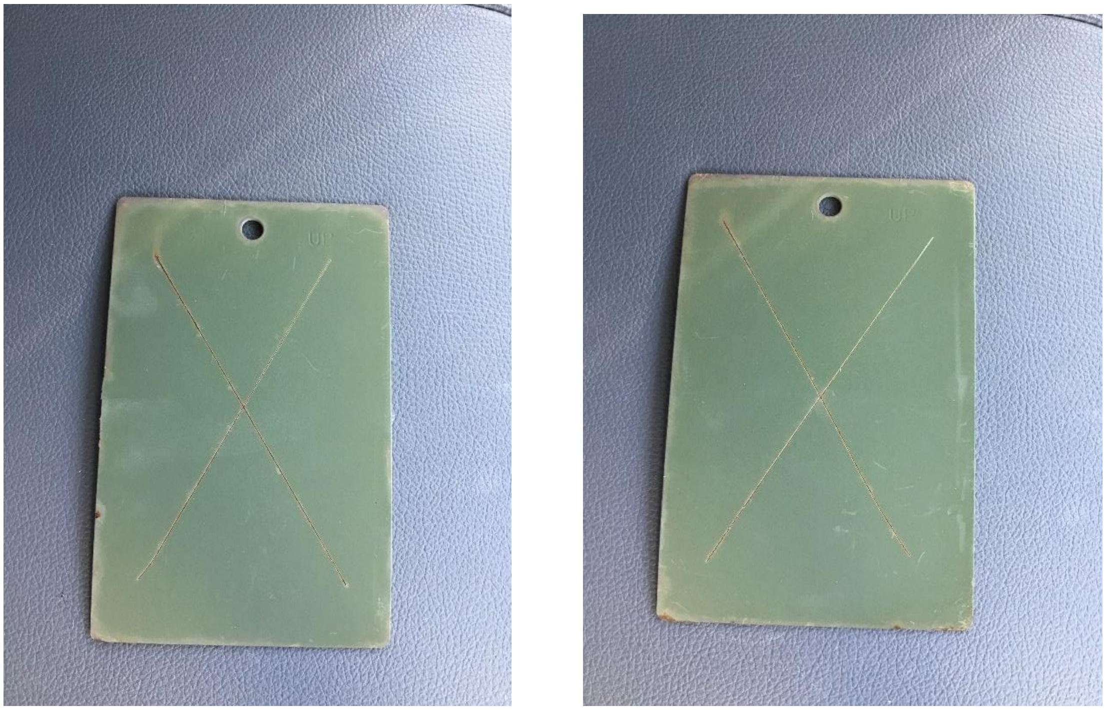


Figure 99. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on blasted CRS at 12 months

Figure 100. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on blasted CRS at 15 months

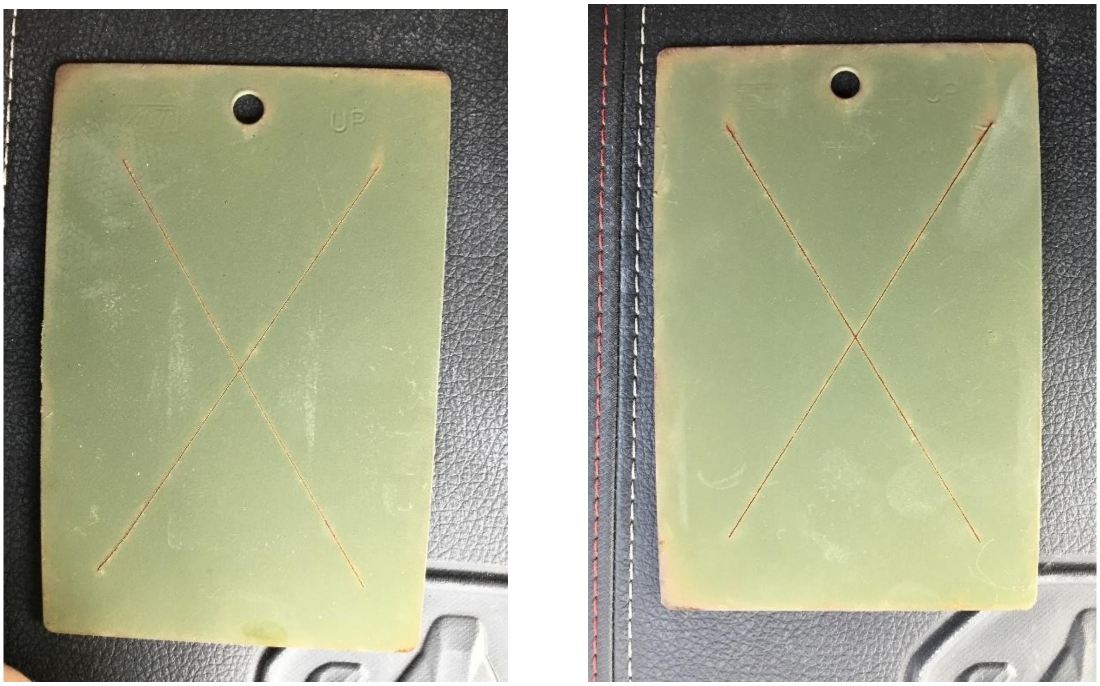


Figure 101. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on blasted CRS at 18 months

Figure 102. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on blasted CRS at 24 months

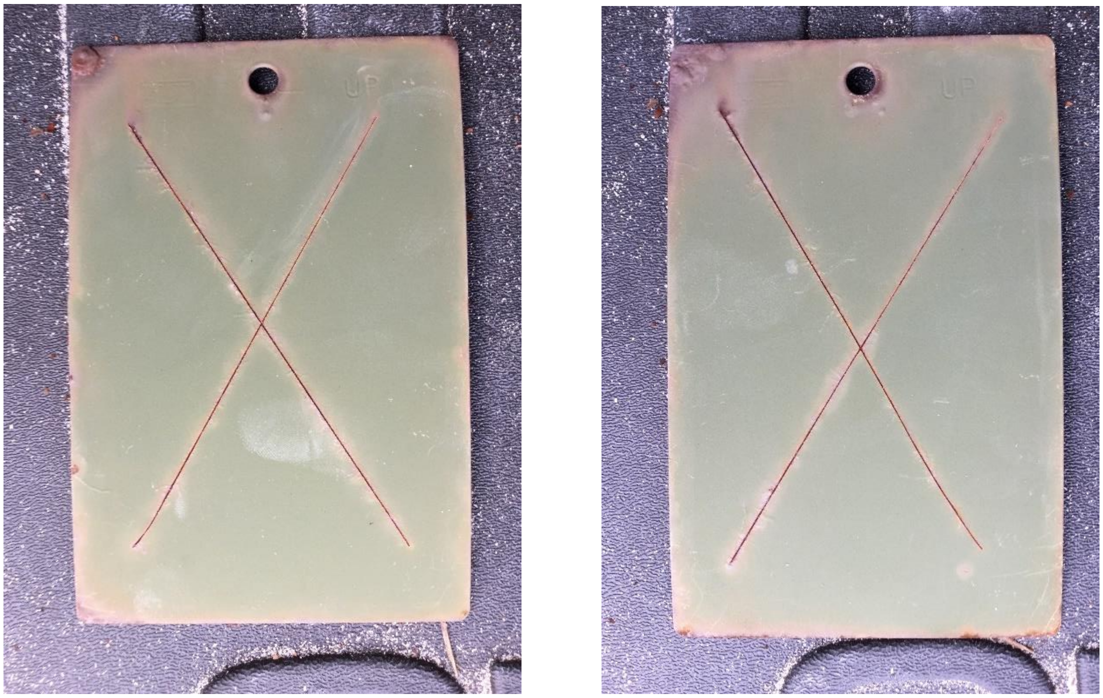


Figure 103. SILSBOND Pretreatment 01 (2%) + Primer + Topcoat on blasted CRS at 27 months

Table 30 documents the results of the SILSBOND 01 (2%) marine outdoor exposure testing for 1020 Steel and Al 2024-T3 conducted by ARL at the Cape Canaveral Space Force Station, Florida for a duration of 24 months. As shown in Table 30 the failure of the 1020 Steel unblasted coupons (mil finished) at 12 months with extensive corrosion in the scribe was observed. The 1020 Steel-blasted, aluminum-unblasted and aluminum-blasted passed 24 months of marine outdoor exposure with the scribe non-corroded and no blisters in the field after 24 months exposure time. The SILSBOND 01 (2%) pretreatment coating was therefore selected for field testing by both ARL and NSWCCD due to it meeting TT-C-490 coating requirements.

Table 30. ARL Marine Outdoor Exposure Testing (24 Months)

Pretreatment	Substrate	Outdoor Exposure Average Ratings															
		Scribe								Blister in Field							
		3 months	6 months	9 months	12 months	15 months	18 months	21 months	24 months	3 months	6 months	9 months	12 months	15 months	18 months	21 months	24 months
2% Silsbond	CRS	9.2	9.2	6.2	5.8	5.2	4.4	no ratings	4.4	10	10	10	10	10	10	no ratings	10
	CRS-B	10	10	10	9.6	9.25	8.2	no ratings	7.6	10	10	10	10	10	10	no ratings	9.8
	Al	10	10	10	10	10	10	no ratings	9.8	10	10	10	10	10	10	no ratings	10
	Al-B	10	10	10	10	10	10	no ratings	9.8	10	10	10	10	10	10	no ratings	10

*blasted aluminum final ratings within standard deviation

6.4 Factors Affecting Cost and Performance

A major risk is the compatibility of the ZVOC/HAPS-NC SILSBOND pretreatment with sealants and other materials that it may encounter, particularly composite materials. Another potential risk for implementing the Ecosil SILSBOND is possible hydrogen embrittlement particularly on high strength steels. There is a potential risk of the overspray having a negative effect on the adhesion of the new primer on an existing coating. However, all laboratory and marine outdoor exposure the testing has shown these factors to be negligible. For the abrasive blasted aluminum substrates using quantitative performance objectives based on MIL-DTL-53022 Type IV Primer and MIL-DTL-53039 Topcoat for the SILSBOND 01 (2%) pretreatment replacement all tests were met and this formulation was used for field testing by both the Marines and Army testing in field operations (Table 31). Table 30 are the results from the abrasive blasted aluminum alloy tested for SILSBOND 01 (2%) formulation in marine outdoor exposure testing which was also documented in Table 17. This table summarizes what parameters were met for qualification to TT-C-490. Table 31 shows that this substrate (abrasive blasted aluminum alloy) met all requirements for laboratory and marine outdoor exposure testing making it a suitable candidate for field testing.

Table 31. Abrasive Blasted Aluminum Substrate Only
Quantitative Performance Objectives using MIL-DTL-53022 Type IV Primer and MIL-DTL-53039 Topcoat on SILSBOND pretreatment replacement

Performance Objective	Data Requirements	TT-C-490 Requirement	Success Criteria	Met Not Met
Humidity Testing	Comparative test for flash rust inhibition	No	No flash rust after 24 hours of exposure to ambient temperature and 90% relative humidity	Met
Adhesion Test	ASTM 4541 Pull-off Adhesion	No	Minimum average 30 events rating of 1200 psi on 1.5mil profile surface	Met
Adhesion Test	ASTM-D3359 Dry Adhesion	Yes	Adhesion rating > 4B	Met
Adhesion Test	ASTM-D3359 Wet Adhesion	No	Scribed area rating, ≥ 3A after 24 hours at ambient	Met
Accelerated Weathering Test	ASTM B117 (NSS)	Yes	After 1000 hours of exposure, steel substrate rating ≥ 6 scribed and ≥7 scribed aluminum	Met
Accelerated Weathering Test	GMW 14872	Yes	After 30 cycles, scribed steel and aluminum substrate rating ≥ 7	Met
Outdoor Exposure Test	Tropical Climate Cape Canaveral	Yes	Two years exposure time	Met
Outdoor Exposure Test	ASTM D 1654	Yes	After 24 months steel substrate rating ≥ 7 and ≥ 8 for aluminum	Met
Hydrogen Embrittlement	ASTM F519	Yes	No detrimental effect to K1c of the substrate. High Hard K1c @48-51Rc shall maintain K_{ieac} ≥19 (ksi/in)	Met
Toxicity Clearance	Toxicity clearances and full disclosure from CHPPM	Yes	Approved by processing facility	Met
Processing Time	TT-C-490F	Yes	Equivalent or less than existing process	Met

The following summation lists all testing for the SILSBOND 01 (2%) Formulation that was used as a Pretreatment Coating for TT-C-490 Approval: During Phase I: laboratory testing ASTM B117 all substrates and surface profiles passed this test. For the GMW14872 blasted Al 2024-T3 substrates passed. Blasted and unblasted steel 1020 substrates failed as well as unblasted Al 2024-T3 substrates coated with SILSBOND formulations. All substrates and SILSBOND formulations passed adhesion testing (ASTM D3359-wet and dry). For the marine outdoor exposure testing blasted and unblasted Al 2024-T3 substrates and blasted 1020 Steel substrates passed while the unblasted 1020 Steel substrates failed.

6.5 Advantages and Limitations of the Technology

The expected benefit to the DOD is a robust, low toxicity, Cr(VI)-free pretreatment coating that will further populate the QPD which will give end-users options now that the DOD-P-15328 specification is cancelled. By having multiple products that meet the requirements in TT-C-490, this will encourage open competition between manufacturers and products, and discourage any one company from monopolizing pretreatments within the DOD. This will result in lower cost, and high quality products through innovation for the DOD users.

7.0 Demonstration Design

7.1 Selecting Test Platforms/Facilities

The best performing (laboratory testing/marine outdoor exposure) SILSBOND pretreatment coated in a full military system (epoxy primer and Army CARC) was evaluated in field testing studies. The laboratory testing has shown that the SILSBOND 01 (2%) as the best performer and has now been accepted as the formulation for both Army and USMC for field testing. After acceptance of the JTP and demonstration plan, the Army and USMC evaluated the SILSBOND primer coating in a full military coating.

7.1.1 Test Platform/Facility History/Characteristics for ARL

As was described in Section 4.0, the DOD co-performers NAWCWD, ARL and NSWCCD in cooperation with the industry co-performer Ecosil followed the demonstration plan guidelines and selections for the field test location and non-critical military hardware. The results of both laboratory and marine outdoor exposure testing confirmed an Ecosil formulation that met performance requirements found in TT-C-490. Therefore the test platforms described in Section 4.0 were maintained from the demonstration document and the field tests were conducted independently by both ARL and NSWCCD.

7.1.2 Test Platform/Facility History/Characteristics for NSWCCD

For the USMC field testing was supervised by the NSWCCD Code 613, and the selected platforms and location of the field testing was described in Section 4.0.

7.2 Pre-Demonstration Testing and Analysis

Laboratory testing has been completed by ARL, NSWCCCD, NAWCWD and Ecosil, including adhesion, NSS, cyclic corrosion, and HE. Marine outdoor exposure testing were completed for 24 months of exposure. Ecosil did request a redo of one Ecosil candidate (Candidate 1) at the ARL testing facility. The ARL team agreed to this redo and was successfully done and the results provided the data necessary to make the final decision regarding the SILSBOND formulation for field testing. The panels have been prepared and were re-tested with no additional costs to the ESTCP program.

7.2.1 Testing and Evaluation Plan

Table 32 provides the criteria for the field demonstration plan to be used by ARL and NSWCCD.

Table 32. Qualitative Performance Objectives using MIL-DTL-53022 Type IV Primer and MIL-DTL-53039 Topcoat on SILSBOND Pretreatment Coating

Performance Objective	Data Requirements	TT-C-490 Requirement	Success Criteria	Met or Not Met
Ease of Use	Feedback from field technician or usability of technology	YES	Minimal Operator training required	Met

7.2.2 Demonstration Set-Up and Start-Up

Selected parts were on a vehicle that was used locally. There was no special site preparation or utilities required. Performance schedules of the SILSBOND coatings were determined by each facility. Should failure occur, damage was noted and recorded.

7.2.3 Period of Operation

The start of the field-testing began once coated panels/non-critical military hardware were shipped to the appropriate field-testing site and tested for a period of two years for ARL and one-year for Navy/Marines requirements. Thus, the SILSBOND 01 (2%) coating system was evaluated according to each facilities maintenance schedule.

7.2.4 Amount /Treatment Rate of Material to be Treated

The amount of material that was used was between 1 pint to 1 gallon of the SILSBOND formulation in water. Material is in stock or can be prepared ahead of time prior to spray-out and delivered to the facility.

7.2.5 Operating Parameters for the Technology

The demonstration for both the ARL and NSWCCD field test sites included observations of coating performance of the Ecosil pretreatment versus the control system. Non-destructive testing at each field test site will include observations for chalking, corrosion, alligatoring, cracking, peeling, and corrosion.

7.2.6 Experimental Design

For the ARL field testing of the Ecosil pretreatment coating: 2-coating systems will be tested side-by-side on the MRAP rear doors. These 2-coated systems are listed below.

- The standard system of DOD-P-15328D Cr(VI) wash primer was not selected, rather Bonderite M-NT 7400 pretreatment was selected as the alternative pretreatment coating for this demonstration program. MIL-DTL-53022 TIV non-Cr(VI) epoxy primer, and MIL-DTL-53039 polyurethane CARC topcoat were used for the full military coating system.
- The test system of Ecosil sol-gel pretreatment, MIL-DTL-53022 TIV non-Cr(VI) epoxy primer, and MIL-DTL-53039 polyurethane CARC topcoat

These coated systems will provide comparative data from the same operational location of the test bed. The following ASTMs will be referenced to record and analyze test data for this program.

- ASTM D1014 Conducting Exterior Exposure Tests of Paints and Coatings on Metal Substrates
- ASTM D610 Evaluating Degree of Rusting on Painted Steel Surfaces
- ASTM D714 Evaluating Degree of Blistering of Paints
- ASTM D660 Evaluating Degree of Checking of Exterior Paints
- ASTM D661 Evaluating Degree of Cracking of Exterior Paints
- ASTM D1654 Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments
- ASTM D4214 Evaluating Chalking

At the Marine Corps Base Hawaii test site, the demonstration will take place on panels attached to the rear of the MTVR vehicle. After primer and topcoat application, coupons (control + Ecosil pretreatment + corrosion weight loss coupon) will be put on the vehicle. Their performance will be tracked using chalking and corrosion resistance as metrics

7.2.7 Product Testing/Health Risks

The JTP has been our reference guide for this ESTCP Program. This is a water-based formulation (98.0%) and this product will pose no health risk to service personnel. This product SILSBOND is a commercial product. It can be applied with standard personnel protective equipment (PPE) and has shown no toxic effects during application or normal usage in commercial applications.

7.2.8 Joint Test Protocol (JTP)/Demonstration Plan

A JTP has been developed by the NAWCWD in cooperation with ARL, NSWCCD, and Ecosil for coating and laboratory testing of their product during this ESTCP program. The field demonstrations were in accordance with the JTP and the demonstration plan that was submitted to the ESTCP Program office and was approved prior to the field demonstration by ARL and NSWCCD.

7.2.9 Demobilization

There is no demobilization of equipment for this field test. Each service will apply the Ecosil SILSBOND 01 (2%) coating onto the non-critical equipment parts and monitor its performance. Once the testing performance is completed and an assessment is made of its performance the coating system will be removed via chemical or mechanical means. The part(s) in question should remain unaffected by the sol-gel coating.

7.2.10 Selection of Analytical/Testing Methods

Analytical methods for use by ARL and NSWCCD will be the following:

- ASTM D1014 Conducting Exterior Exposure Tests of Paints and Coastings om Metal Substrates
- ASTM D610 Evaluating Degree of Rusting on Painted Steel Substrates
- ASTM D714 Evaluating Degree of Blistering of Paints
- ASTM D660 Evaluating Degree of Checking of Exterior Paints
- ASTM D661 Evaluating Degree of Cracking of Exterior Paints
- ASTM D1654 Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments
- ASTM D4214 Evaluating Chalking

7.2.11 Management and Staffing During Field Demonstrations

The PI (Dr. Peter Zarras) will manage the overall program. Dr. Danqing Zhu, Ecosil Technologies LLC will provide sufficient quantities of the Ecosil SILSBOND 01 (2%) formulation for each field test site.

Mr. Thomas A. Considine will monitor and manage the testing of the Ecosil coated parts at Cape Canaveral, Florida. Mr. Jamaal Delbridge of NSWCCD, Code 613 will monitor and manage the testing of the Ecosil coated coupons at Marine Corps Base Hawaii.

The relationships between the co-performers was described in Section 4.0 without any modifications to the organization flow chart.

7.2.12 Demonstration Schedule

Each service monitored the performance of the Ecosil pretreatment coated parts based on their normal service schedule. This included coating, corrosion performance, and servicing.

8.0 Performance Assessment during Field Demonstrations

8.1 Performance Criteria

The performance criteria are listed below in Table 33, which gives information on the Ecosil coated parts.

Table 33. Performance Criteria for Ecosil Pretreatment Coating

Performance Criteria	Description	Primary or Secondary
Coating Performance	Must pass individual product tests as described in TT-C-490 per ASTM testing (corrosion testing, adhesion, hydrogen embrittlement) found in JTP	Primary
Comparison to current Cr(VI) pretreatment (wash primer)	Removal of significant portion of Cr(VI) from coating process	Primary
Process Waste	No process waste from coating application and no hazardous waste generated from coating removal	Secondary
Reliability	The reliability of this coating in various environments: marine, humid, dry, and temperate must be demonstrated	Primary
Equipment Requirements	The need for special equipment to apply the Ecosil coating must be eliminated, only current spray equipment permitted for this coating allowed	Primary
Training Requirements/PPE	Specific handling and training requirements must be developed and documented for use of the Ecosil pretreatment coating	Primary
Coat whole or part of non-critical military hardware	Coating the Ecosil pretreatment coating on non-military hardware must be demonstrated and documented	Primary

8.1.2 Scope of Tests: Performance Confirmation Tests

The tests and criteria are listed in Table 34.

Table 34. Expected Performance and Confirmation Methods for Field Testing

Performance Criteria	Expected Performance Metric (Pre-demonstration)	Performance Confirmation Method	Actual Performance
Reduction in Cr(VI) volume	Elimination of Cr(VI) using Ecosil pretreatment coating	Mass Balance	Quantitative
Additional Pretreatment Coatings added to the QPD	Additional Options for end users	Performance Acceptance	Quantitative
Factors Affecting Technology Performance	Deposition Appearance Thickness Adhesion Corrosion-inhibition	Visual Visual Cross-section ASTM D1014 ASTM D610	Qualitative Qualitative Quantitative Quantitative Quantitative
Manpower/Skill	One skilled painter/technician required and initial training is mandatory	Operating Experience	Qualitative
Monitoring/OSHA Requirement	Coating of Ecosil pretreatment onto substrate must be monitored by key personnel and appropriate ventilation required during application	Record Keeping	Quantitative
Reliability	Only standard spray equipment allowed (robust/reliable)	Record Keeping	Qualitative
Versatility	Ecosil pretreatment coating must be applicable in various environments	Operating Experience Record Keeping	Qualitative

8.1.3 Material Applications and Restrictions

Components containing both aluminum and steel alloys were suitable candidates for this evaluation. There were no restrictions placed on the Ecosil formulation for testing military components at each service's facility.

8.1.4 Operational Testing Criteria

Identical components will be coated with the Ecosil pretreatment at each military facility as well as the current wash primer (Cr(VI)) pretreatment. The pretreated components will then be coated with the standard primer and topcoat, and then be placed in service for a period of one - two years determined by the sites and inspected/evaluated according to service/performance requirements at each facility.

8.1.5 Data Analysis, Interpretation and Evaluation

All data collected by each service field test were logged by the appropriately trained technician and the criteria for passing the field tests will be based upon the JTP procedures. A maintenance log was kept for the duration of the field testing of the Ecosil pretreatment coating. This log was completed when maintenance or repair is required on the high volume low pressure (HVLP) spray equipment or spray bottle. Consultation of manual for scheduled maintenance will be required during the field-testing of the Ecosil pretreatment coating. Operators should indicate on the log the unit repaired or maintained, a description of the repair or maintenance, any parts required, repair time in person-hours, and equipment downtime in days. In addition, include any comments on the application equipment (e.g., difficulty of use, coating application delayed or unable to be performed due to failure). An Evaluation Log was used to assess the condition of the coated component. Depending on service requirements the coated component should be visually inspected for durability and component protection. The first observation shall be made on the same day that the coating was applied or put into service. In addition to answering the questions on the log, add any comments or observations. The inspections should be continued for at least 12 months to 24 months depending on facility/service requirements.

8.2 Field Testing of SILSBOND 01 (2%) by ARL

Field testing of the SILSBOND 01 (2%) were carried out by the Army and Marines in accordance with their testing requirements.

The following data documents the field testing of Bonderite M-NT 7400 as the control and the SILSBOND 01 (2%) by the Army in field testing process that includes controls as a metric to measure the SILSBOND 01 (2%) performance against. Bonderite M-NT 7400 coating is currently used by the Army and was a suitable metric to measure the SILSBOND 01 (2%) performance.

Figures 104-107 document the coating of SILSBOND 01 (2%) by Alberts Surface Treatments facility coating SILSBOND and the epoxy and polyurethane topcoats on the Army vehicle door for field testing. The preparation of the surface follows Ecosils method prior to application of The SILSBOND 01 (2%) pretreatment coating which was agreed to by the DOD co-performers. The surface preparation was the following:

1. Abrasive blasting to remove old paints from the door panels
2. Blow clean the blasted door parts with compressed air
3. Spray on 2% SILSBOND 01 to wet the entire door panel surface
4. Rinse with DI water
5. Blow dry door panels
6. Ambient dry 30 min
7. Priming with MIL-DTL-53022TIV
8. Topcoated with MIL-DTL-53039

Figure 104. SILSBOND 01 (2%) Pretreatment Coating Application on MRAP Door Panel

Figure 105. Epoxy priming of SILSBOND 01 (2%) Pretreatment Coating with MIL-DTL-53022TIV Epoxy Primer on Pretreated Door Panel

Figure 106. Ambient Curing of the Epoxy Primed MRAP Door Panel

Figure 107. Full Military Coating w/SILSBOND 01 (2%) Pretreatment on Army MRAP Door Panel

Figures 108-114 documents the control panel (Bonderite M-NT 7400) coating on Army MRAP vehicle door for 24 months exposure time. Figures 115-121 documents the performance of the SILSBOND 01 (2%) pretreatment coating on Army MRAP vehicle door for 24 months exposure time.

Figure 108. 3 Months Exposure Time for Bonderite M-NT 7400 Coating on Army MRAP Vehicle Door

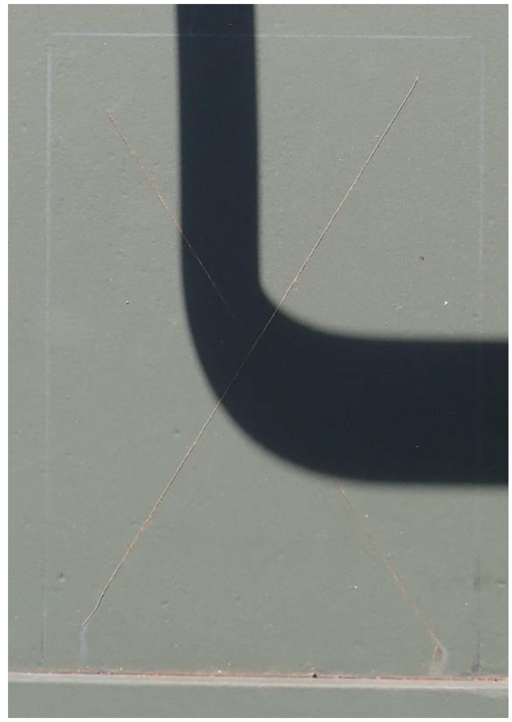
 

Figure 109. 6 Months Exposure Time for Bonderite M-NT 7400 Coating on Army MRAP Vehicle Door

Figure 110. 9 Months Exposure Time for Bonderite M-NT 7400 Coating on Army MRAP Vehicle Door

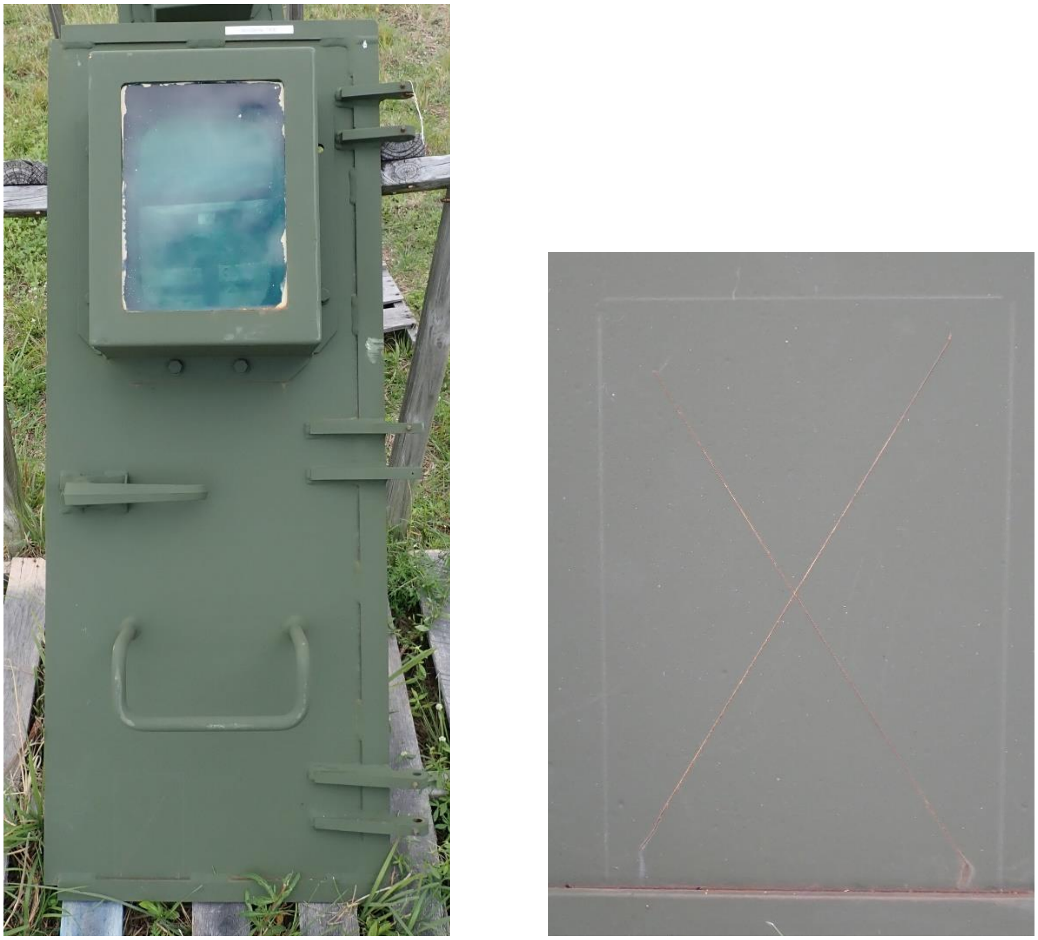


Figure 111. 12 Months Exposure Time for Bonderite M-NT 7400 Coating on Army MRAP Vehicle Door

Figure 112. 15 Months Exposure Time for Bonderite M-NT 7400 Coating on Army MRAP Vehicle Door

Figure 113. 18 Months Exposure Time for Bonderite M-NT 7400 Coating on Army MRAP Vehicle Door

Figure 114. 24 Months Exposure Time for Bonderite M-NT 7400 Coating on Army MRAP Vehicle Door

Figure 115. 3 Months Exposure Time for SILSBOND 01 (2%) Pretreatment Coating on Army MRAP Vehicle Door

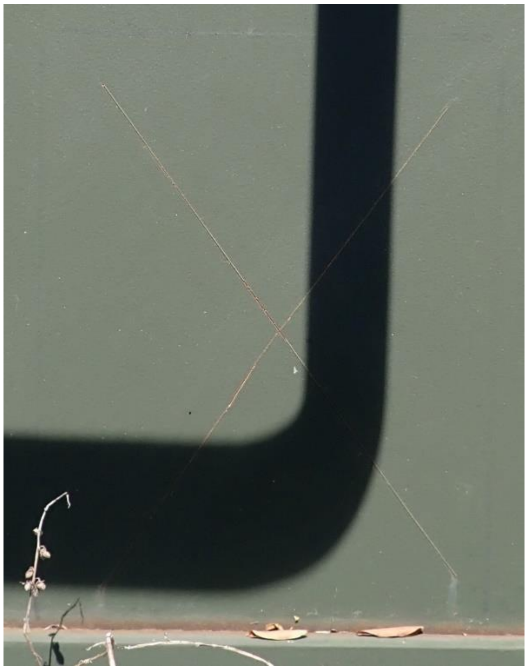
 

Figure 116. 6 Month Exposure Time for SILSBOND 01 (2%) Pretreatment Coating on Army MRAP Vehicle Door

Figure 117. 9 Month Exposure Time for SILSBOND 01 (2%) Pretreatment Coating on Army MRAP Vehicle Door

Figure 118. 12 Month Exposure Time for SILSBOND 01 (2%) Pretreatment Coating on Army MRAP Vehicle Door

Figure 119. 15 Month Exposure Time for SILSBOND 01 (2%) Pretreatment Coating on Army MRAP Vehicle Door

Figure 120. 18 Month Exposure Time for SILSBOND 01 (2%) Pretreatment Coating on Army MRAP Vehicle Door

Figure 121. 24 Month Exposure Time for SILSBOND 01 (2%) Pretreatment Coating on Army MRAP Vehicle Door

8.2.1 Summation of Field Testing Results by ARL

Table 35 documents the results of the field testing conducted by the Army at their field testing facility in Florida. The results show that the SILSBOND 01 (2%) pretreatment coating in a full military system performed as well as the control coating system. The doors (control and SILSBOND) showed minimum creep from the scribe-passing with a 9 rating and the doors (control and SILSBOND) showed no blisters in field-passing with a 10 rating. Doors were subjected to an impromptu immersion test during the final months due to the flooding of the site following a hurricane. This is notable because the sea water immersion did not accelerate corrosion on either door, further displaying efficacy of the coating systems.

Table 35. Field Testing Results of SILSBOND 01 (2%) Pretreatment in Full Military Coating Stack-up

Manufacturer			Ecosil		Test Method		Outdoor Exposure at CCSFS						
Product			Silsbond 01		Product Details		Pretreatment, Type IV						
Customer			NAWCWD		Coating System		MIL-DTL-53022 TIV, MIL-DTL-53039						
	Scale:		10	9	8	7	6	5	4	3	2	1	0
	Steel		<------------------------PASS------------------------>					<-------------------------------FAIL------------------------------->					
Creep from Scribe		#	3 mon	6 mon	9 mon	12 mon	15 mon	18 mon	21 mon	24 mon			
	Control	1	9	9	9	9	9	9	9	9			
	Silsbond	2	9	9	9	9	9	9	9	9			
Blisters in Field		#	3 mon	6 mon	9 mon	12 mon	15 mon	18 mon	21 mon	24 mon			
	Control	1	10	10	10	10	10	10	10	10			
	Silsbond	2	10	10	10	10	10	10	10	10			

8.2.2 Field Testing of SILSBOND 01 (2%) by NSWCCD

SILSBOND 01 (2%) pretreatment coating coupons were attached to the rear of a Marine vehicle in full military coating stack-up for a one-year field demonstration. Figures 122-129 document the field testing of the SILSBOND 01 (2%) pretreatment coating with epoxy primer and polyurethane topcoat for field testing from 3-12 months intervals in which photo-documentation was used to observe the SILSBOND performance in field testing environment.

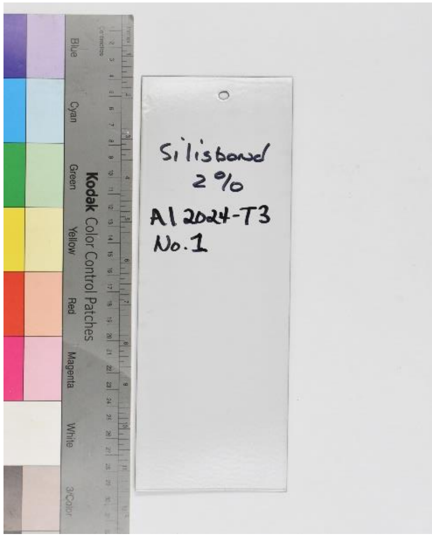


Figure 122. NSWCCD 3 Month Exposure Time of SILSBOND 01 (2%) Pretreatment in Military Coating Stack-up on Al 2024-T3 Coupons.

Figure 123. NSWCCD 3 Months Exposure Testing of SILSBOND 01 (2%) Pretreatment Coating in Military Coating Stack-up on 1020 Steel Coupons

Figure 124. NSWCCD 6 Month Exposure Testing of SILDSBOND 01 (2%) Pretreatment Coating in Military Coating Stack-up on Al 2024-T3

Figure 125. NSWCCD 6 Months Exposure Testing of SILDSBOND 01 (2%) Pretreatment Coating in Military Coating Stack-up on 1020 Steel Coupons

Figure 126. NSWCCD 9 Month Exposure Testing of SILDSBOND 01 (2%) Pretreatment Coating in Military Coating Stack-up on Al 2024-T3 Coupons

Figure 127. NSWCCD 9 Month Exposure Testing of SILDSBOND 01 (2%) Pretreatment Coating in Military Coating Stack-up on 1020 Steel Coupons

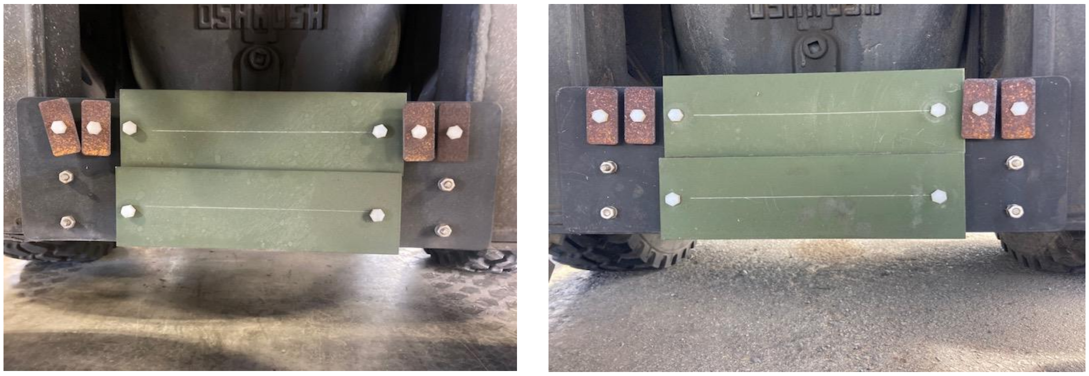


Figure 128. NSWCCD 12 Month Exposure Testing of SILSBOND 01 (2%) Pretreatment in Military Coating Stack-up on Al 2024-T3 Coupons

Figure 129. NSWCCD 12 Month Exposure Testing of SILSBOND 01 (2%) Pretreatment in Military Coating Stack-up on 1020 Steel Coupons

8.2.3 Summation of Field Testing Results by NSWCCD

The results from the 12 month field studies in Hawaii by the NSWCCD showed that Ecosils SILSBOND pretreatment coated panels passed field testing. The results showed no blistering, delamination or corrosion in the scribed areas for both AA2024-T3 and 1020 Steel coupons. With these results the Marines can now use the SILSBOND 01 (2%) pretreatment coating on military vehicles since the Army has now approved (June 2023) this product and is listed on the QPD.

9.0 COST ANALYSIS

Once the Ecosil pretreatment coating is approved for use by military organizations, the cost to implement between the Army, USMC should be minimal, because the Ecosil pretreatment coating can be applied via spray bottle or HVLP spray, the primary systems utilized by Army, USMC maintenance operations. The need for extensive PPE, hazardous waste removal, employee monitoring, and other expenses associated with Cr(VI) do not exist with the Ecosil pretreatment coating systems. Storage stability of Ecosil's pretreatment formulation will be the only issue that may deter the implementation of this system in place of wash primer (Cr(VI)) coating. Packaging and availability of the final product will need to be determined by the vendor who will receive this technology at the close of the program.

As there does not seem to be costs associated with equipment change for application of the Ecosil pretreatment, the change in cost would be due to preparation time, change in application time, savings from hazardous waste disposal costs, and savings in de-painting costs because Ecosils pretreatment is Cr(VI)-free.

9.1 Cost Reporting and Comparison

The costs associated with reducing Cr(VI) from current military hardware will be significant. By eliminating Cr(VI) from the pretreatment, a cost saving in reduction of hazardous waste and compliance with current and future regulatory directives will insure mission readiness and improve worker safety.

The currently-qualified alternative considered as a “drop-in” replacement for the DOD-P-15328D wash primer still contains phosphates but SILSBOND by contrast does not contain phosphates and therefore has low toxicity. As was previously stated, “the current cost of disposing chromate-bearing paint waste is ~$3,600,000/year for Cr(VI)-based military coatings.” By implementing this coating (SILSBOND) at DOD installations this would eliminate the need to dispose of Cr(VI) based paints as hazardous waste Furthermore, reducing the current disposal costs by two-thirds, saving $2,400,000 annually, which represents a 67% cost saving/year.

An assumption is made that since we are applying an sol-gel water-based solution onto non-critical equipment using a zero VOC solvent (water) we are eliminating all Cr(VI) coatings on these same non-critical equipment, thereby, significantly reducing costs associated with current hazardous coatings. This coating is a commercial product and has been used in non-military environments. With the success of the field testing and approval on the QPD this product is now available for military use. The following Table 36 documents associated costs with this product.

Table 36. Cost Assessment of SILSBOND 01 (2%) Pretreatment Coating

Characteristic	SILSBOND	DOD-P-15328
Product package	1 pack, water reducible	2-pack, mix before use
Pot life	Unlimited	8 hrs
Estimated price	\$15/gal concentrate, \$1.5/gal @1.5% working concentration	\$60/gal*
Waste treatment	Directly put into city sewage system (non hazardous materials)	High cost (contains chromate and phosphate)
Air pollution	None (water based)	High (VOCs/HAPs)
Film thickness	<1 micron	7-13 micron
Application	Spray on, dry in place	Spray on, dry in place
Paint compatibility	Military high solid epoxy primers, powder coatings	Military high solid epoxy primers
Metal compatibility	Al and Steel	Al and steel

Purchased from NCP Coatings catalog number B-875/T-99. Cost assessments based on DoD-P-15328 wash primer coating now replaced by TT-C-490 referred to as the pretreatment coating.

9.2 Technology Transfer

TT-C-490 is the overarching document referenced in dozens of military coating specifications and tens of thousands of military drawings for the cleaning and pretreatment prior to the application of organic finishes such as CARC. It has been the primary reference preferred by engineers to specify cleaning, pretreatment, and subsequent testing. It is widely used by all OEMS and services for finishing steel and aluminum. ARL can transition pretreatment materials that meet the established performance criteria through the QPD in a seamless structure that will eliminate the costly time consuming and expense of waivers and engineering change notices. This procedure will encourage innovation because of a well-defined path to approval for qualified products and provides new commercially available technologies, such as those used by the automotive industry, a pathway for implementation and use on military systems. The overall quality of new and existing processes is now controlled through Objective Quality Evidence (OQE). The revised document (TT-C-490) has been adopted by the entire DOD and industry for surface finishing of alloys and Ground Vehicle Systems Center (GVSC) has adopted the language and principles of OQE in the new TT-C-490 requirements. They have begun placing it in their Procurement Automated Data and Document System (PADDS clause) for pretreatments and CARC on all new contract requirements that requires all DOD and DOD contractors to follow the doctrine of the newly revised TT-C-490 requirements.

Calvary Industries is a chemical company that has been Ecosil's licensee for 10 years and, has toll manufactured Ecosil's products for 5 years. Calvary has chemical sales throughout the United States of over \$200 million of industrial process chemicals including pretreatment chemicals, metalworking fluid and process lubricants. Calvary as a major licensee of Ecosil pretreatment technology has been selling SILSBOND pretreatment products to the United States market since 2011 and providing technical service to the SILSBOND users in the field. Additionally, Calvary provided matching funds in 2014 for the NSF Phase IIB commercialization work of SILSBOND and related products. Calvary has the capacity to meet the needs for product production and technical support at all DOD facilities and industrial commercial customers, and is also working with ARL for QPD approval of one of their OEM pretreatments and has sold chemicals to DOD contractors in the past.

Calvary Industries, founded in 1983, is a chemical supplier and manufacturer with three locations with over 120,000 sq. ft. of manufacturing and warehouse space. Calvary's corporate office and Southern Ohio manufacturing plant are located near Cincinnati, Ohio. A central Ohio plant is located in Lima, Ohio. The southern plant is located in central Louisiana.

In this ESTCP program, Calvary will manufacture SILSBOND pretreatment solution (s) and deliver it to trial sites during this program. Both Ecosil and Calvary's technical personnel will provide support service to people at the trial sites responsible for correctly applying SILSBOND in the field. In addition, Calvary will also supply alkaline cleaners as needed to support these trials.

The Ecosil formulation will be qualified against the requirements set forth in TT-C-490. A QPD has been established for TT-C-490 that includes new types and classes. Type III and Type IV now govern organic and inorganic pretreatments.

10.0 Implementation Issues

10.1 Checklist

Removal of Cr(VI) from the pretreatment process would allow for improved compliance with 29 CFR 1910.1026 which calls for a permissible exposure limit (PEL) on Cr(VI) of 5 $\mu mg/m^3$, Time weighted Average (TWA) with an action level of 2.5 micrograms per cubic meter.

This should not be an issue since the substitution involves trading one toxic pretreatment containing a known human carcinogen that has prohibitive PELs and restrictive disposal options for a zero VOC/HAPs pretreatment without restrictive disposal requirements.

The appropriate personnel have applied the Ecosil pretreatment coatings for each facility and each laboratory has the required safety permits and EPA reporting in place to perform the field tests. Therefore, implementation issues are not a concern for utilizing this product in the field.

10.2 Other Regulatory Issues

It is not anticipated that there will be additional regulatory issues involved since the Ecosil is a water based pretreatment which is non-hazardous, and zero VOC/HAPs and the coatings de-paint and application activities will be performed in a permitted area where proper approvals from base Bioenvironmental already exist.

10.3 End-User/OEM Issues

The Ecosil pretreatment can be applied using pump spray, spray bottle, and potentially HVLP spray equipment, no special equipment would be necessary; therefore, this technology can be used at any facility without any burdensome investment in new equipment or training.

Potential end users for this material is anyone that applies the CARC system that is not an OEM. After successful outcome of this demonstration, the end user concerns were minimal. This product does not require special equipment for application and needs only a slight adjustment in application procedure. The concern that may negatively affect stakeholder buy-in is the surface preparation prior to application of the Ecosil pretreatment coating or storage stability issues which has now been shown to be minor adjustment to the coating process.

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12.0 POINTS OF CONTACT

The points of contact for this program are listed in Table 37.

Table 37. Points of Contact

POINT OF CONTACT Name	ORGANIZATION Name Address	Phone/Fax/email	Project Role
Peter Zarras	NAWCWD (Code 4L4200D) 19090 N. Knox Road (Stop 6303) China Lake, CA 93555-6106	(P) 760-939-1396 (F) 769-939-1617 Peter.zarras.civ@us.navy.mil	Management testing
John V. Kelley	US Army Research Laboratory Materials/Manufacturing Science Division B4600 Deer Creek Loop RDL-WM-MC Aberdeen Proving Ground, MD 21005	(P) 410-306-0837 (F) 410-306-0829 John.v.kelley8.civ@mail.mil	Coating processing testing
Danqing Zhu	Ecosil Technologies LLC 160-A Donald Drive Fairfield, OH 45014	(P) 513-858-2365 (F) 513-829-5387 zhud@ecosiltech.com	Coating formulation testing
Andrew D. Sheetz	NSWCCD (Code 614) 9500 MacArthur Blvd Building 60 West Bethesda, MD 20817	(P) 301-227-5037 (F) 301-227-5548 Andrew.d.sheetz2.civ@us.navy.mil	Testing
Wesley Prince	Aalberts Surface Treatment 2915 Wilmarco Avenue Baltimore, MD 21223	(P) 410-644-4500 (F) 410-644-1766 wprince@aalberts-st.us	Coating

13.0 LIST OF PAPERS/PRESENTATIONS

1. Validation/Demonstration of a Zero-VOC/HAPS-free Cr-Free Spray-in-Place Pretreatment for DoD Weapons Systems, Project Number: WP-201621, 2023 DoD Energy & Environment Innovation Symposium- November 28-December 1, 2023 Washington DC.
2. Dr. Danqing Zhu presentation "Water-based hybrid pretreatment coating as a replacement for chromated wash primer in military coating applications," at the 2023 ACS PMSE Roy W. Tess Award Symposium in honor of Dr. Peter Zarras, August 14, 2023; 2023 ACS Fall National Meeting, August 13-17, 2023, San Francisco, California.
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4. Validation/Demonstration of a Zero-VOC/HAPS-free NC Wash Primer for Department of Defense Weapons Platforms Project Number: WP-201621, 2022 SERDP-ESTCP Annual Symposium-November 29-December 2, 2022 Washington DC.
5. Validation/Demonstration of a Zero-VOC/HAPS-free NC Wash Primer for Department of Defense Weapons Platforms, Project Number:WP-201621, 2021 SERDP-ESTCP Annual Symposium -November 29-December 3, 2021 Washington DC.
6. Validation/Demonstration of a Zero-VOC/HAPS-free NC Wash Primer for Department of Defense Weapons Platforms, Project Number:WP-201621, 2020 SERDP-ESTCP Annual Symposium Washington DC.
7. Validation/Demonstration of a Zero-VOC/HAPS-free NC Wash Primer for Department of Defense Weapons Platforms, Project Number:WP-201621, 2019 SERDP-ESTCP Annual Symposium-December 3-5, 2019 Washington DC.
8. SERDP/ESTCP Funded Innovative, Environmentally Friendly Coating(s) Development at the Naval Air Warfare Center Weapons Division (NAWCWD), China Lake, California, 2016 ASETS Defense Poster Presentation.