

# Water-based hybrid pretreatment coating as a replacement for chromated wash primer in military coating applications

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# Outline

## Background

## SILSBOND – a water-based hybrid pretreatment coating

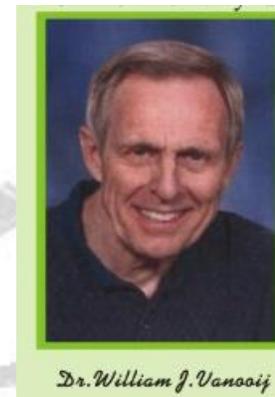
- Commercial applications
- Coating structure characterization

## Investigation of SILSBOND 01 coating in military CARC system

- Phase I: Accelerated corrosion test results (per TT-C-490 specification)
- Phase II: Field testing results
- Conclusions

## Acknowledgement

# About our company



*Dr. William J. Vanooij*



Ecosil Technologies LLC is a R&D company, located in the great Cincinnati area. Since its founding in 2003, Ecosil conducts research and development, formulates environmentally safe coatings, provides strong technical support to industries and collaborates with government agencies to combat metallic corrosion



Ecosil Founder- Dr. Wim J. Vanooij In early 1990s, Dr. Vanooij pioneered research on the utilization of eco-friendly silane chemistry for metallic corrosion prevention, with the aim of eliminating the use of toxic chromates and environmentally-unfriendly phosphates in industry. His research work has led to silane surface technology in industrial applications: 1) pretreatment of metals for improved paint adhesion and corrosion resistance and 2) silane-based adhesive for tire cord in “green tires”

# Background

- DOD-P-15328D<sup>1</sup> is a metal pretreatment, two package, acid catalyzed vinyl wash primer. It has been used for DoD ground support equipment and vehicles for improved paint adhesion. However, this wash primer has severe environmental and human health issues (listed below), and hence needs to be replaced
  - **HEAVY METALS** – the wash primer contains 7.1% zinc chromate (CrVI)
  - **SOLVENTS** - the wash primer contains 6.5 lb/gal of VOCs that are also classified as HAPs
  - **DOD ANNUAL environmental discharges:** (based on estimated usage): 12,600 lbs of zinc chromate and 35,700 gals of VOC/HAPs



Field coating repair<sup>2</sup>

- DOD-P-15328D specification has been cancelled as of May 2018. TT-C-490<sup>3</sup> specification serves as a replacement for DoD-P-15328D. The Army Research Laboratory (ARL) is the custodian of the TT-C-490 specification and has approved several alternatives to the DOD-P-15328D under TT-C-490. But there is still an urgent need to add more alternatives to the QPD (Qualified Product Database) for DoD use.
- During the ESTCP program (WP-201621), a water-based hybrid pretreatment coating “SILSBOND” has been investigated as an alternative to the DOD-P-15328D primer under TT-C-490.

1. [DOD-P-15328 D PRIMER PRETREATMENT \(everyspec.com\)](http://everyspec.com)
2. <https://www.army-technology.com/contractors/vehicles/milspray/>
3. [TT-C-490 CHEMICAL CONVERSION COATINGS PRETREATMENTS \(everyspec.com\)](http://everyspec.com)

# SILSBOND commercial applications

- **SILSBOND** hybrid pretreatment coating is water-based, contains no VOCs/HAPs and is Cr(VI)-free as well as phosphate-free.
- **SILSBOND** products has found multi-industrial applications where both improved paint adhesion and excellent corrosion resistance are needed. SILSBOND are often applied onto metal surfaces by ambient spraying or immersion process
  - Ex. 1: pretreatment of steel panels before powder coating for making office metal cabinets
  - Ex. 2: pretreatment of Tin-plated steel sheets for packaging market
- **SILSBOND 01**, has been investigated as a candidate to replace DOD-P-15328D wash primer for DoD use



Spray process  
(substrate: Steel)



Immersion process  
(Substrate: Tin-plated steel sheet)



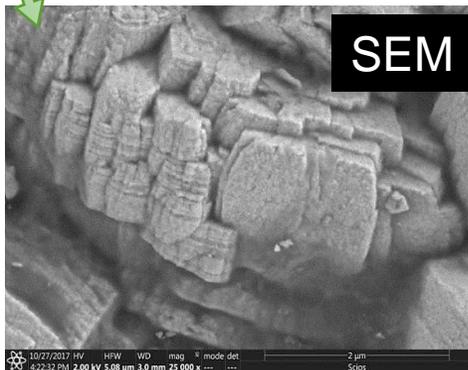
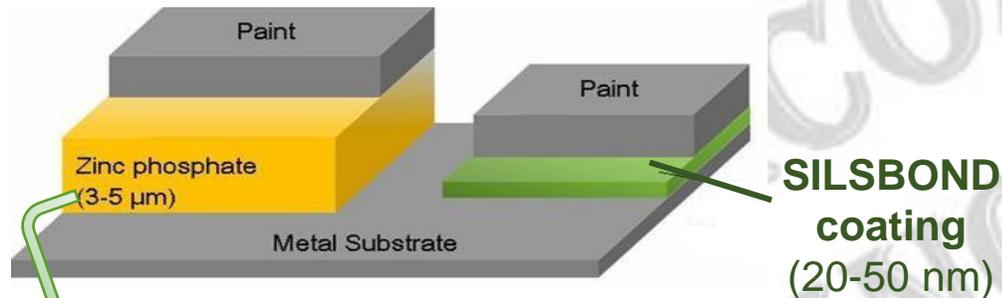
Powder-coated metal cabinets  
(Market: Office Appliance)



Tin can  
(Market: packaging)

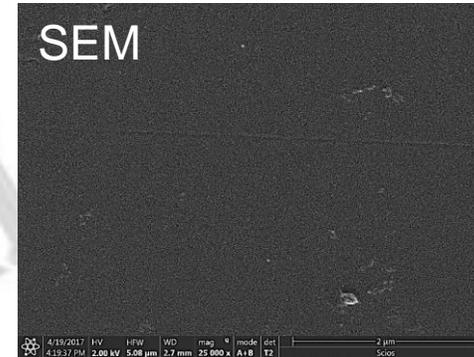
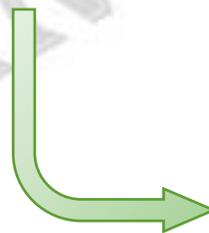
# What is SILSBOND coating: characterization

**Background-** SILSBOND pretreatment technology has been developed and commercialized with the support by NSF SBIR program (SBIR Phase I, II, IIB). The aim was to replace chromate- and phosphate-based pretreatments in industry

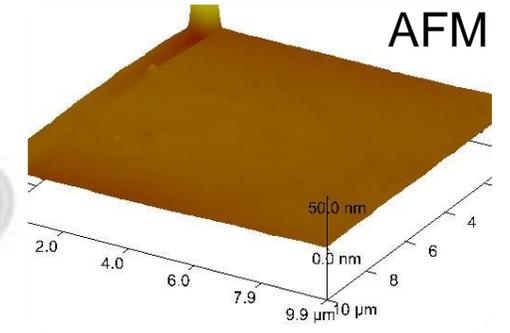


zinc phosphate coating on CRS surface

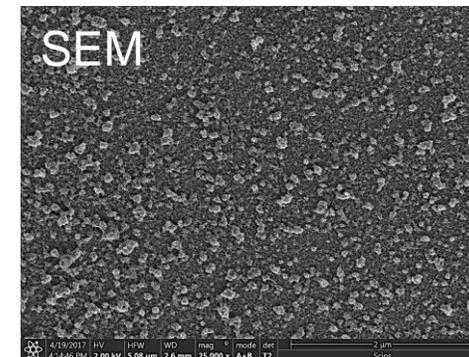
SILSBOND coating (20-50 nm)



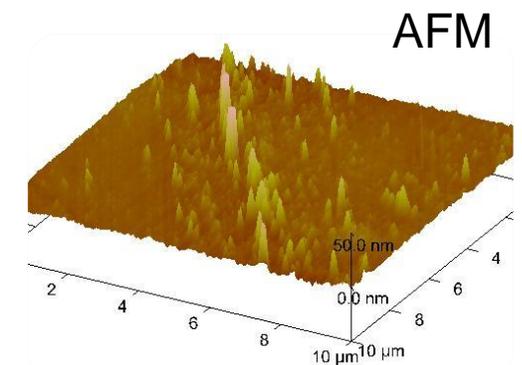
Polished CRS surface before SILSBOND pretreatment



spray/immersion



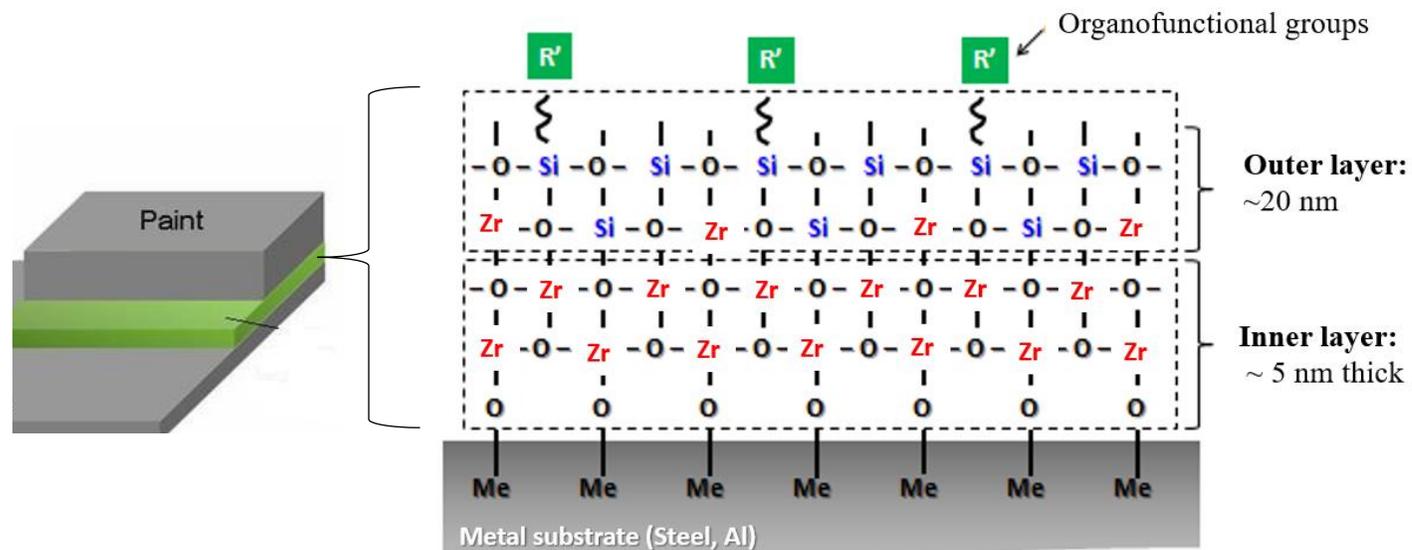
SILSBOND coating formed on the polished CRS surface



CRS: Cold-rolled steel  
SEM: Scanning Electron Microscope  
AFM: atomic force microscope

# SILSBOND pretreatment coating structure

SILSBOND 01 coating on metal was further characterized using XRR(X-ray Reflectivity) technology<sup>1</sup>. Based on the results, the SILSBOND coating structure has been revealed and is shown below:



**Outer layer:** ~20-nm thick, which is a mixed region consisting of a highly crosslinked siloxane network embedded with amorphous Zr oxide nano-particles

**Inner layer:** ~ 5-nm thick, which is a region consisting of amorphous Zr oxide nano-particles tightly anchoring to the metal surface

A schematic of SILSBOND coating structure

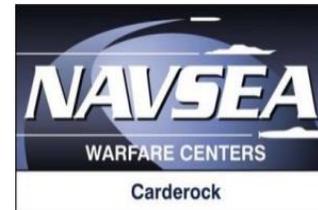
1. D. Zhu, N. Hu and D. W. Schaefer, "Water-based Sol-Gel Coatings for Military Coating Applications" in: " Handbook of Waterborne Coatings", edited by, P. Zarras et al. , Elsevier 2021

# ESTCP Project (WP-201621)

**Objective:** to investigate SILSBOND hybrid pretreatment coating as an alternative to DOD-P-15328D wash primer in military Chemical Agent Resistant Coating (CARC) system

## Team:

- ❑ **NAWCWD:** Peter Zarras (PI), Joseph R. Kromphardt
- ❑ **NSWCCD:** Jamaal D. Delbridge, Kunigahalli L. Vasanth, Andrew D. Sheetz
- ❑ **Ecosil Technologies LLC:** Danqing Zhu, Art Helmstetter
- ❑ **ARL:** Thomas A. Considine, John V. Kelley, Thomas E. Braswell
- ❑ **Aalberts Surface Treatment Inc:** Wes Prince



**NAWCWD:** Naval Air Warfare Center Weapons Division

**NSWCCD:** Naval Surface Warfare Center Carderock Division

**ARL:** U.S. Army Research Laboratory

# ESTCP Project (test plan)

- **Performance Tests**

- ***Phase I:*** Evaluate SILSBOND 01 pretreatment coating on steel and 2024-T3 aluminum alloy under CARC per TT-C-490<sup>1</sup> specification

- ✓ ASTM B117 (Neutral salt fog test) – 1008 hrs
- ✓ GMW 14872 (Cyclic corrosion test) – 30 cycles
- ✓ ASTM D 3359 (Cross hatch test) – rating  $\geq$  4A, 4B
- ✓ ASTM D522 (Mandrel bend test) – no cracking or flaking
- ✓ ASTM F519 (Hydrogen embrittlement test)
- ✓ 2-year marine outdoor exposure test

- ***Phase II:*** Field testing of SILSBOND 01 pretreatment coating on non-critical military hardware

- **Benchmarking against**

- ✓ Chromated acid wash primer (DOD-P-15328D)
- ✓ Bonderite M-NT-7400<sup>®</sup> (approved phosphate pretreatment coating per TT-C-490 specification)



2-yr marine outdoor exposure site: Cape Canaveral Space Force Station, FL

# CARC System

**CARC** is a coating system that provides surfaces that are easily and effectively decontaminated after exposure to liquid chemical agents.

Aliphatic polyurethane topcoat  
MIL-DTL-53039 (1.8 – 2.4 mil)

Epoxy polyamide primer  
MIL-DTL-53022 (1.5-2.5 mil)

Pretreatment coating /Wash primer  
TT-C-490

Substrate (Steel or 2024-T3 Al alloy)



USMC Medium Tactical Vehicle Replacement (MTVR)

# ESTCP Phase I: Preparation of test metal panels



## SILSBOND 01 pretreatment

- 1) Alkaline clean
- 2) Rinse
- 3) 2% SILSBOND spray
- 4) Rinse
- 5) Ambient dry

## Priming and topcoating

- 1) Epoxy priming (MIL-DTL-53022 Type IV ), ambient curing
- 2) PU topcoating (MIL-DTL-53039), ambient curing for 2 weeks

## Metal substrates:

- Blasted 2024-T3 Al alloy
- Mill Finish 2024-T3 Al alloy
- Blasted Steel
- Mill Finish Steel

## Tests:

- ASTM B117 – 1008 hrs
- GMW 14872 – 30 cycles
- ASTM D 3359 – rating  $\geq$  4A, 4B
- ASTM D522 – no cracking
- ASTM F519
- 2-year marine outdoor exposure test

# ESTCP Phase I : TT-C-490F Qualification

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
DOD-P-15328	CRS	6.8	5.2	3.6	9.8	9.4	9.4
	CRS-B	7.6	5.8	4.4	10	10	10
	Al	10	10	10	9.6	9.6	8
	Al-B	10	10	10	10	10	10

\*blasted aluminum final ratings within standard deviation

Pretreatment	Substrate	ASTM B117 Avg Rating					
		Scribe			Blister in Field		
		336hrs	672hrs	1008hrs	336hrs	672hrs	1008hrs
Ecosil	Al	9.4	8.4	8.13333333	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

Fail

Pass

- In 30-cycle GMW 14872: SILSBOND 01 passed on blasted Al alloy
- In 1008-hr ASTM B117: SILSBOND 01 passed on all substrates

# Phase I: TT-C-490F Qualification (outdoor exposure)



Unblasted CRS panels with 2% Ecosil Silsbond



Blasted CRS panels with 2% Ecosil Silsbond



Unblasted Al panels with 2% Ecosil Silsbond



Blasted Al panels with 2% Ecosil Silsbond

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		7.6	10	10	10	10	10	10		9.8
	Al	10	10	10	10	10	10		9.8	10	10	10	10	10	10		10
	Al-B	10	10	10	10	10	10		9.8	10	10	10	10	10	10		10

\*blasted aluminum final ratings within standard deviation

Fail

Pass

- In 2-year outdoor exposure: SILSBOND 01 passed on blasted CRS, mill-finished Al alloy and blasted Al alloy

# Phase I: TT-C-490F Qualification (summary)

	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

Fail
Pass

SILSBOND 01 conforms to TT-C-490 Type IV on blasted Al alloys

# ESTCP-Phase II: Test parts preparation



**SILSBOND 01 pretreatment**

- 1) Abrasive blasting of steel door panel
- 2) Air blow to remove the residual dusts on the surface
- 3) Spray 2% SILSBOND on the blasted steel surface (60 sec)
- 4) Water rinse
- 5) Blow air dry



**Epoxy priming**

(MIL-DTL-53022 Type IV )

**Metal substrates:**

- 1) Blasted Army MRAP door panel (picture above)
- 2) Blasted CRS panels
- 3) Blasted Al 2024-T3 panels



**PU topcoating**

(MIL-DTL-53039)

# Phase II: ARL Field testing (24 months)



## Field Testing of SILSBOND 01 Pretreatment Coating on Army MRAP door located at the Cape Canaveral Space Force Station, FL

### Ecosil Coating Stack-up

Pretreatment: Ecosil SILSBOND 01 (2%)

Primer: MIL-DTL-53022 TIV Topcoat:  
MIL-DTL-53039

### Control Coating Stack-up

Pretreatment: Henkel Bonderite M-NT-7400®

Primer: MIL-DTL-53022 TIV  
Topcoat: MIL-DTL-53039

○ "X" scribed area

# Phase II: ARL Field testing (24 months)



3 month



12 month



24 month\*

SILSBOND 01



3 month



12 month

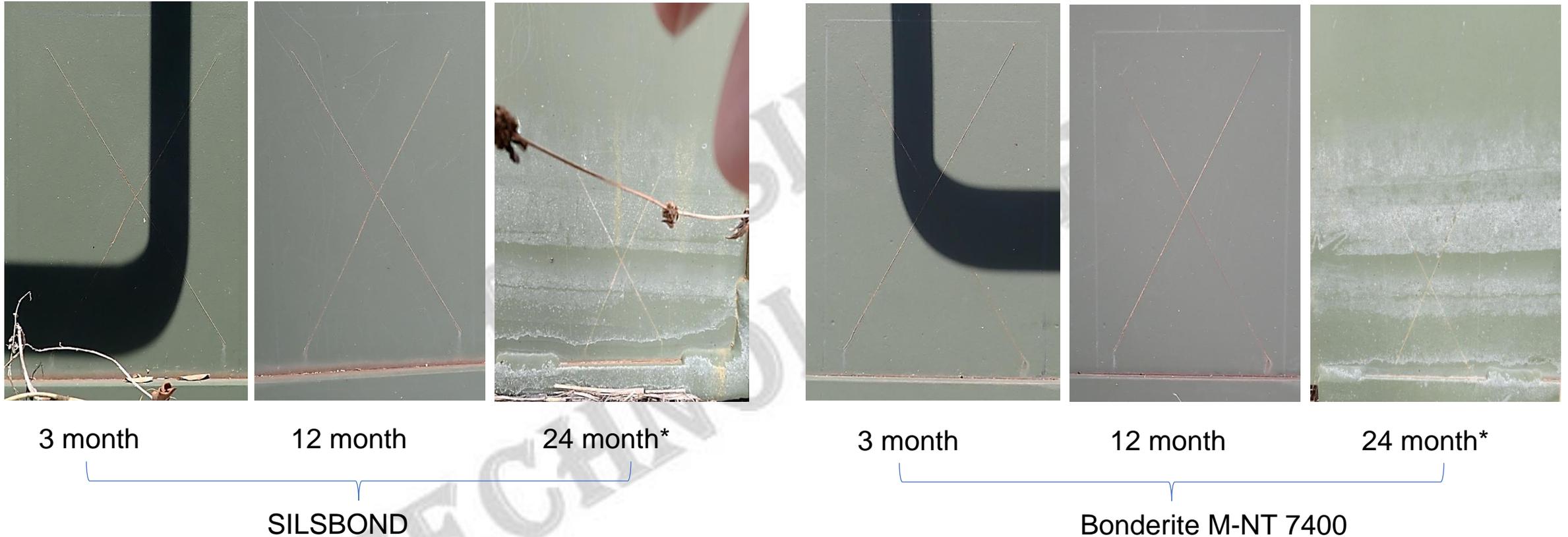


24 month\*

Bonderite M-NT 7400

SILSBOND 01 performed equally well as Bonderite M-NT 7400 (Benchmark)

# Phase II: ARL Field testing (24 months)



3 month

12 month

24 month\*

SILSBOND

3 month

12 month

24 month\*

Bonderite M-NT 7400

\* Comment: "All scribed areas survived an impromptu salt water immersion due to the Ian hurricane for "probably a couple weeks". There is still no scribe corrosion and the doors would be considered passes."

# Phase II: ARL Field testing (24 months)

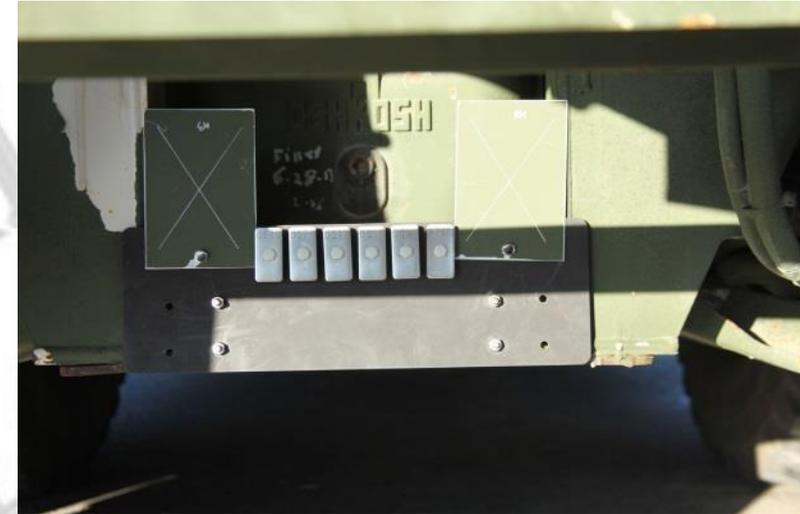
<b>Manufacturer</b>	Ecosil		<b>Test Method</b>	Outdoor Exposure at CCSFS								
<b>Product</b>	Silsbond 01		<b>Product Details</b>	Pretreatment, Type IV								
<b>Customer</b>	NAWCMD		<b>Coating System</b>	MIL-DTL-53022 TIV, MIL-DTL-53039								
<b>Scale:</b>		10	9	8	7	6	5	4	3	2	1	0
<b>Steel</b>		← PASS →					← FAIL →					
<b>Creep from Scribe</b>	#	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			
	Silsbond	2	9	9	9	9	9	9	9			
<b>Blisters in Field</b>	#	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			
	Silsbond	2	10	10	10	10	10	10	10			

- ✓ Doors (control-Bonderite M-NT 7400 and SILSBOND 01) show min. creep from the scribe-passing w/9 rating
- ✓ Doors (control -Bonderite M-NT 7400 and SILSBOND 01) show no blisters in field-passing w/10 rating

## Phase II: NSWCCD Field testing (12 months)



USMC Medium Tactical Vehicle Replacement (MTVR)



MTVR vehicle with racks for holding coated coupons

**Field Testing of SILSBOND 01 (2 %) Pretreatment Coating on 2024-T3 and steel test panels (scribed surface), located at Marine Corps Base, Hawaii**

### **Ecosil Coating Stack-up**

Pretreatment: Ecosil SILSBOND 01 (2%)

Primer: MIL-DTL-53022 TIV Topcoat: MIL-DTL-53039



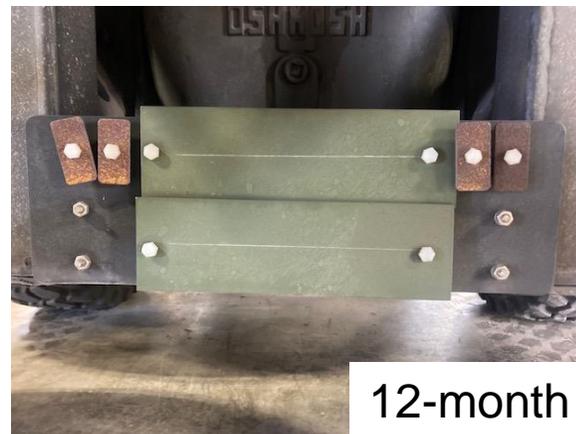
# Phase II: NSWCCD Field testing (12 months)

Blasted 2024-T3 Al alloy panels



3-month exposure

Blasted CRS panels



12-month exposure



SILSBOND 01 passed on both blasted Al alloy and CRS substrates

# Conclusions

- ❑ A water-based, hybrid pretreatment coating, “SILSBOND 01”, has been investigated as a replacement for chromated wash primer, DOD-P-15328D, in military coating systems (CARC). This work consisted of two phases:
  - Phase I: Evaluate SILSBOND 01 pretreatment coating on steel and 2024-T3 aluminum alloy under CARC per TT-C-490 specification
  - Phase II: Field testing of SILSBOND 01 pretreatment coating on non-critical military hardware
  
- ❑ The major outcomes of the ESTCP project are as follows:
  - From Phase I: SILSBOND 01 conforms to TT-C-490 Type IV on blasted Al alloys
  - From Phase II: SILSBOND 01 has been successfully demonstrated at the user level via field-testing on non-critical military hardware. Specifically,
    - 1) on Army MRAP door located at the Cape Canaveral Space Force Station, FL
    - 2) on 2024-T3 and steel test panels, located at Marine Corps Base, Hawaii

# Acknowledgment

**Ecosil acknowledges the support provided by,**

**The Naval Air Warfare Center Weapons Division (NAWCWD); Army Research Laboratory (ARL); Naval Surface Warfare Center Carderock Division (NSWCCD) and Aalbert Surface Treatment Inc., in testing and qualifying SILBOND 01 for DoD use.**

