SERDP/ESTCP Funded Innovative, Environmentally Friendly Coating(s) Development
at the Naval Air Warfare Center Weapons Division (NAWCWD), China Lake, California

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Abstract: The NAWCWD in cooperation with its industrial and government partners are exploring several innovative coating technologies to reduce the environmental liabilities associated with current military coatings that contain either hexavalent chromium (Cr(VI)), isocyanates or phosphates. These compounds are carcinogenic and/or toxic to the environment. Their replacement with currently available technologies can negatively impact mission readiness but their use is often at odds with compliance to federal and state environmental regulations. At NAWCWD novel, environmentally benign coatings are being prepared on various substrates, and tested in the laboratory and field tested where appropriate.

Environmentally-benign Conductive Polymer Passivating Coatings

SERDP SEED Project Number: WP-2525

Abstract: A SERDP SEED program titled "Environmentally-benign Conductive Polymer Passivating Coatings" in which synthesis and characterization of innovative conductive polymers (CPs) based on pyrroles and thiophenes that can replace Cr(VI) on ZnNi coated high strength steels are being investigated. These newly synthesized CPs are being processed and tested for their ability to provide passivation/self-healing properties on high strength steel coupons meeting the requirements listed in MIL-DTL-38999L,Class Z.

Co-Performers: Paul A. Goodman, John D. Stenger-Smith, Andrew P. Chafin, Matthew Davis, Alfred J. Baca, Roxanne L. Quintana, Tom Groshens, Kalle Harrison (ESDP student), Hannah L. Moody (ESDP student), Lee Cambrea, Joseph E. Estevez (ESDP student), Lawrence Baldwin, Jeffery Bottaro, Todd M. Dames (ESDP student), Shelly Vang (ESDP Student), Mark Moran, Linda Johnson, John A. Baronowski, Gregory S. Ostrom, Leon Miguel (NAWCWD), Diane E. Buhrmaster, Alexander N. Khramov (WPAFB) and Douglas C. Hansen (UDRI)

Acknowledgements: Financial support for this program, SERDP: Dr. Robin Nissan, WP Program Manager, ONR: Dr. Airan Perez, Code 333, NAWCWD 219 Program Dr. Phil Peters, DE Thrust Manager

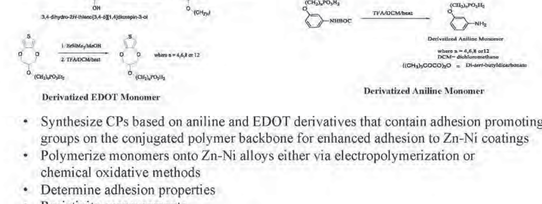
Objective(s)

- Demonstrate environmentally-benign coating processes using conductive polymers (CP) as an alternative to hexavalent chromium (Cr(VI)) containing passivates
- Provide passivation
- Acceptable shell-to-shell contact resistance
- Meet the requirements detailed in MIL-DTL-38999L, Class Z
- Show compatibility with, strong adhesion to, and corrosion-inhibition of the existing low hydrogen embrittlement (LHE) alkaline Zn-Ni coatings

Background/Introduction

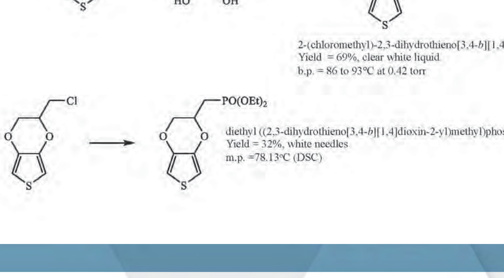
- Zinc provides anodic protection of ferrous substrates via a sacrificial mechanism
- Commercialized by both private industry and the military
- Electroless deposition of zinc (Zn) have focused on creating alloys that contain Zn with other elements such as Zn-Ni alloys
  - ✓ Sacrificial anodic protection/lower corrosion rates/thin coatings
- Disadvantages
  - ✓ Bath used are acidic
  - ✓ Introduction of H_2 gas to the steel surface-hydrogen embrittlement (HE).
  - ✓ Toxic, carcinogenic, and highly regulated Cr(VI) passivate coating required
  - ✓ Non-Cr(VI) passivates do not meet corrosion protection requirements
  - ✓ Non-Cr(VI) passivates do not meet contact resistance requirements

Approach



- Synthesize CPs based on aniline and EDOT derivatives that contain adhesion promoting groups on the conjugated polymer backbone for enhanced adhesion to Zn-Ni coatings
- Polymerize monomers onto Zn-Ni alloys either via electropolymerization or chemical oxidative methods
- Determine adhesion properties
- Resistivity measurements
- Measure corrosion-inhibiting properties

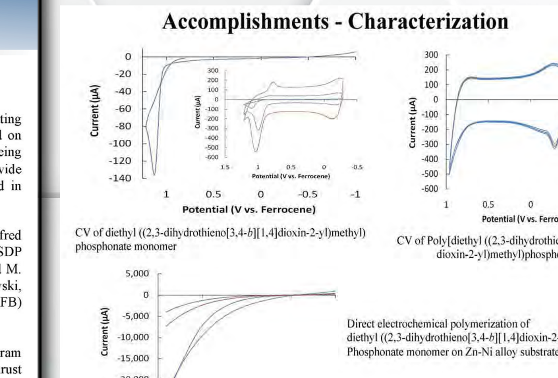
Accomplishments
Synthesis of Diethyl ((2,3 dihydrothieno[3,4-*b*][1,4]dioxin-2 yl)methyl)phosphonate



2-(chloromethyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine
Yield = 69%, clear white liquid
b.p. = 86 to 93°C at 0.42 torr

diethyl ((2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methyl)phosphonate
Yield = 32%, white needles
m.p. =78.13°C (DSC)

Accomplishments - Characterization



CV of diethyl ((2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methyl) phosphonate monomer

CV of Poly[diethyl ((2,3-dihydrothieno[3,4-*b*][1,4] dioxin-2-yl)methyl)phosphonate]

Direct electrochemical polymerization of diethyl ((2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methyl) Phosphonate monomer on Zn-Ni alloy substrate

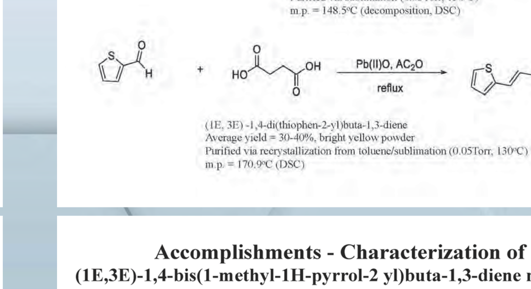
Accomplishments - Characterization

Adhesion Test – ASTM D3359, Method B | CP Coated Zn-Ni Alloy substrates

Coating Thickness Measurements/Adhesion Test Ratings

Sample #	Mils	Mils	Mils	Adhesion Rating	Pass (Y or N)
1	0.80	0.74	0.70	5B	Y
2	0.68	0.88	0.76	4B	Y
3	0.80	0.92	0.76	4B	Y

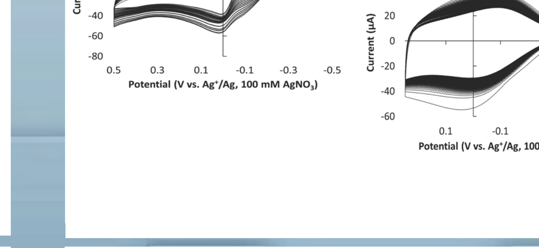
Accomplishments-Synthesis of (1E,3E)-1,4-bis(1-methyl-1H-pyrrol-2-yl)buta-1,3-diene and (1E, 3E)-1,4-di(thiophen-2-yl)buta-1,3-diene monomer(s)



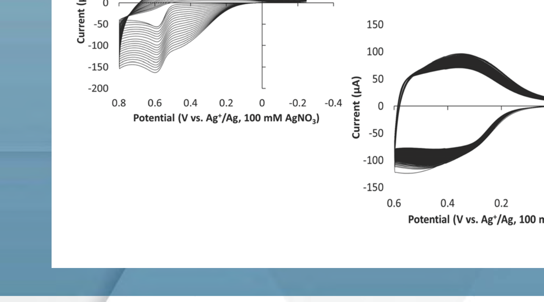
(1E,3E)-1,4-bis(1-methyl-1H-pyrrol-2-yl)buta-1,3-diene
Average yield = 40-45%, bright yellow powder
Purified via sublimation (0.05Torr, 150°C)
m.p. = 148.5°C (decomposition, DSC)

(1E, 3E) -1,4-di(thiophen-2-yl)buta-1,3-diene
Average yield = 30-40%, bright yellow powder
Purified via recrystallization from toluene/sublimation (0.05Torr, 130°C)
m.p. = 170.9°C (DSC)

Accomplishments - Characterization of (1E,3E)-1,4-bis(1-methyl-1H-pyrrol-2 yl)buta-1,3-diene monomer



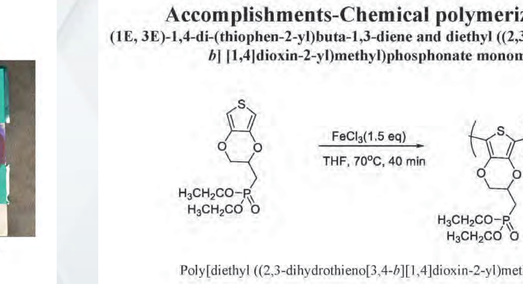
Accomplishments - Characterization of (1E, 3E)-1,4-di(thiophen-2-yl) buta-1,3-diene monomer



Accomplishments - Characterization of poly[(1E, 3E)-1,4-di-(thiophen-2-yl)buta-1,3-diene], poly[(1E,3E)-1,4-bis(1 methyl-1H-pyrrol-2-yl)buta-1,3-diene] and poly[diethyl ((2,3-dihydrothieno [3,4-*b*][1,4]dioxin-2-yl)methyl)phosphonate]

Polymer	Bandgap	Conductivity (S/cm)
Poly[(1E,3E)-1,4-bis-(1-methyl-1H-pyrrol-2-yl)buta-1,3-diene	2.23 eV	7.44 x 10^{-4} S/cm
Poly[(1E, 3E) -1,4-di(thiophen-2-yl) buta-1,3-diene	2.00 eV	1.64 x 10^{-3} S/cm
Poly[diethyl ((2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methyl)phosphonate]	1.75eV	5 x 10^{-6} S/cm

Accomplishments-Chemical polymerization of (1E, 3E)-1,4-di-(thiophen-2-yl)buta-1,3-diene and diethyl ((2,3 dihydrothieno[3,4-*b*] [1,4]dioxin-2-yl)methyl)phosphonate monomer(s)



Poly[diethyl ((2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methyl)phosphonate]

Poly[(1E, 3E)-1,4-di(thiophen-2-yl)buta-1,3-diene]

Results/Conclusions to Date

- Synthesized and characterized novel monomers compounds for potential passivating CP polymers
- Fully characterized polymers based on these new monomers
- Can polymerize these monomers using both electrochemical and chemical oxidative methods
- Fully characterized these polymers for bandgap and conductivity

Future Work

- Coat Zn-Ni panels using polymers obtained from chemical polymerization method
- Determine corrosion-inhibiting properties
- Determine HE introduction on coated CP Zn-Ni alloy panels
- Determine passivation and meet the requirements detailed in MIL-DTL-38999L, Class Z

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Sustainable, Environmentally Green Polyurethanes for Erosion-resistant Coatings

SERDP Project Number: WP-2601

Abstract: A new start SERDP program titled "Sustainable, Environmentally Green Polyurethanes for Erosion-resistant Coatings." Here we are developing innovative, sustainable, non-toxic, water-dispersible, non-isocyanate polyurethanes (NIPU) based on non-isocyanate chemistries that can be applied via conventional high volume low pressure spray (HVLP) equipment eliminating volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) while maintaining or exceeding critical performance requirements specified in SAE AMS-C-83231. The NIPU that are being investigated focuses on reactions that eliminate isocyanates by using polycondensation reactions between dicarbonates and diamines or dicarbamates and diols. In addition we are exploring a second route that utilizes a polyaddition reaction by ring-opening polymerization of polyfunctional cyclic carbonates with diamines.

Co-Performers: Benjamin G. Harvey, Paul A. Goodman, John D. Stenger-Smith, Andrew P. Chafin, Matthew Davis, Alfred J. Baca, Roxanne L. Quintana, Kalle Harrison (ESDP student), Hannah L. Moody (ESDP student), Lee Cambrea, Lawrence Baldwin, Todd M. Dames (ESDP student), Shelly Vang (ESDP Student), Markku A. Savolainen (Post-doctoral fellow) (NAWCWD), Edward W. Lipnickas (NAWCAD), Diane E. Buhrmaster and Alexander N. Khramov (WPAFB), Douglas C. Hansen (UDRI), Mark R. Kolody (NASA-KSC) and William S. Eck (APHC)

Acknowledgements: Financial support for this program, SERDP: Dr. Robin Nissan, WP Program Manager

Objective(s)

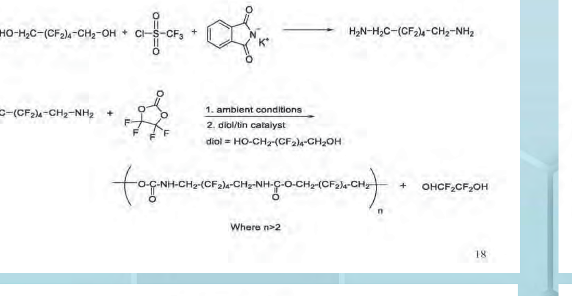
- Develop novel polyurethanes that are based on innovative non-isocyanate chemistries
- The resulting non-isocyanate polyurethanes (NIPU) will be sustainable, non-toxic, water-dispersible and/or dissolved in appropriate VOC-exempt solvents
- Applied to substrates via conventional HVLP equipment
- These NIPU will eliminate VOCs and HAPs during the application process
- Meet, or exceed, the critical performance requirements specified in SAE AMS-C-83231

Background/Introduction

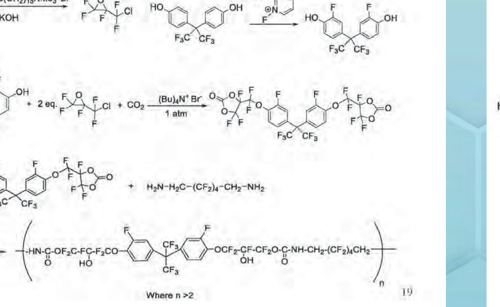
- Current polyurethanes (PU) are produced through the reaction of isocyanate compounds with alcohols to form carbamate (urethane) linkages
- Isocyanates are highly reactive and excellent precursors to form PU
- Isocyanates are highly toxic compounds

Additional issues exist with the currently employed polyurethane erosion coatings
- ✓ The solutions used during the coating deposition process contain up to 800 g/L of VOCs and high levels of HAPs, such as xylene, toluene, and MIBK.
- ✓ During the polyurethane deposition process-individual components are mixed with curing agents, sprayed onto the substrate and cured
- ✓ Excess solvent-based isocyanates are disposed of as hazardous waste
- ✓ Significant production time-costs, both during application and curing
- ✓ Coatings are very thick (9-12 mils) and require multiple passes during application
- ✓ Tedious application process includes (1) long flash-off times for each coat; (2) 5-7 days of curing under ideal conditions
- ✓ Production/repair backlog, which produces significant down time, impacts mission readiness and reduces the availability of weapon systems to the warfighter

Approach
Two routes to NIPU – Polycondensation reaction



Approach
Two routes to NIPU – Polyaddition reaction

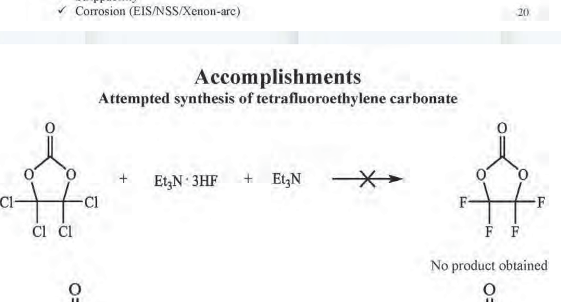


Approach

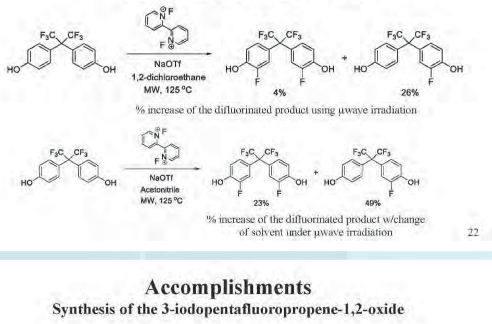
The production of the proposed NIPU will follow two distinct synthetic strategies.

(1) A two-step polycondensation approach that involves the reaction between cyclic carbonates and fluorinated diamines to produce an intermediate that is then reacted with a fluorinated diol to produce the NIPU
(2) The polyaddition, by ring-opening polymerization, of fluorinated bifunctional cyclic carbonates with fluorinated diamines.
- Fully characterize all monomers, prepolymers and polymers via NMR, FTIR, EA, DSC, TGA, GPC
- Determine curing rates via DSC and ATR-FTIR for polycondensation/polyaddition reaction
- Determine VOC or HAPs release via headspace GC-MS and TGA-FTIR
- Determine toxicity properties of monomers/polymers via QSAR and *in-vitro* testing
- Determine properties of erosion NIPU coating system as per the specifications in SAE AMS-C-83231
  - ✓ Peel strength/flexibility
  - ✓ Water/aromatic fuel resistance
  - ✓ Rain erosion resistance
  - ✓ Electrical transmission
  - ✓ Surface resistivity
  - ✓ Outdoor weather resistance
  - ✓ Strippability
  - ✓ Corrosion (EIS/NSS/Xenon-arc)

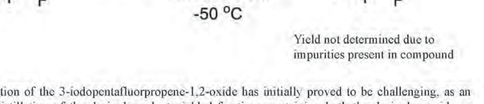
Accomplishments
Attempted synthesis of tetrafluoroethylene carbonate



Accomplishments
Attempted synthesis of the difluorinated species



Accomplishments
Synthesis of the 3-iodopentafluoropropene-1,2-oxide

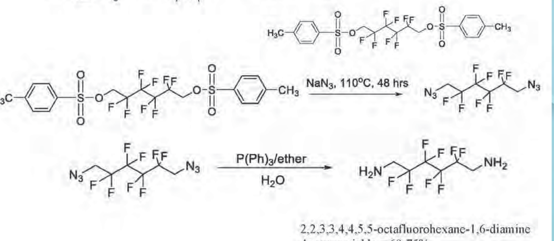


Yield not determined due to impurities present in compound

Purification of the 3-iodopentafluorpropene-1,2-oxide has initially proved to be challenging, as an initial distillation of the desired product yielded fractions containing both the desired epoxide as well as dichloromethane.

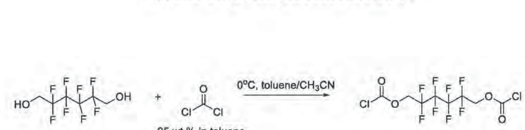
In upcoming work, we plan to elucidate methodology by which to isolate 3-iodopentafluoropropene-1,2-oxide which includes the exploration of different solvent systems in which to perform the reaction. Next, we plan to scale-up this reaction appropriately for use in the next step to prepare the cyclic-carbonate containing monomer.

Accomplishments
Synthesis of the 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diamine



2,2,3,3,4,4,5,5-octafluorohexane-1,6-diamine
Average yields = 60-75%
white needles

Accomplishments
Attempted Synthesis of 2,2,3,3,4,4,5,5-octafluoro-hexane-1,6 diylbis(carbonochloridate)

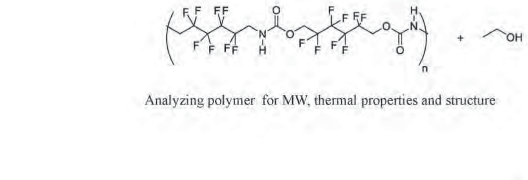


2,2,3,3,4,4,5,5-octafluorohexane-1,6-diylbis(carbonochloridate)
Product obtained as a mixture
Impurities present as determined by GC-MS and NMR

Accomplishments
Synthesis of diethyl(2,2,3,3,4,4,5,5-octaflouoro-hexane-1,6-diyl)bis(carbonate)

diethyl(2,2,3,3,4,4,5,5-octaflouorohexane-1,6-diyl)bis(carbonate)
Average yield = 50-55%
Light yellow oil, 98% purity as determined by GC-MS

Accomplishments
Preparation of the NIPU



Analyzing polymer for MW, thermal properties and structure

Results/Conclusions to Date

- Repeated attempts at the synthesis to obtain the tetrafluorethylenecarbonate was unsuccessful
- Successful synthesis/characterization of new precursors and monomers for incorporation into NIPU
- Attempts at obtaining the electrophilic substitution of bisphenol A gave mixed results
- Successful synthesis of the 3-iodopentafluoropropene-1,2-oxide
- Successful synthesis/characterization and scale-up of the diethyl(2,2,3,3,4,4,5,5-octaflouorohexane-1,6-diyl)bis(carbonate) complete

Future Work

- ✓ Continue to optimize the reaction to obtain the difluoro substituted compound for the bisphenol A
- ✓ Optimize reaction conditions to isolate and fully characterize the 3-iodopentafluoropropene-1,2-oxide
- ✓ Continue to optimize reaction conditions leading to NIPU and fully characterize prepared polymers
- ✓ Determine coating parameters for drying time, coating thickness and VOC and HAPs release during coating deposition

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

ESTCP Project Number: WP-201621

Abstract: A new start ESTCP program titled" Validation/Demonstration of a Zero-VOC/HAPS-NC Wash Primer for Department of Defense Weapons Platforms." Here we examine the viability of innovative, environmentally benign organic-inorganic hybrid pretreatment coatings as a replacement for the current military Cr(VI) wash primer. Ecosil's SILSBOND wash primer replacement per TT-C-490F specifications will be laboratory tested and upon successful completion of these studies will be field tested at the user level on non-critical military hardware for one year duration.

Co-Performers: Kunigahalli L. Vasanth (NSWCCD), Danqing Zhu (Ecosil), Art Helmstetter (Ecosil), John V. Kelley (ARL), Thomas E. Braswell (ARL), Thomas A. Considine (ARL), and Wes Prince (Impreglon Inc.)

Acknowledgements: Financial support for this program, ESTCP: Dr. Robin Nissan, WP Program Manager

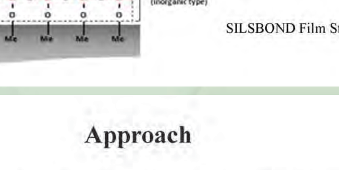
Objective (s)

- Validate the performance of Ecosils's SILSBOND wash primer replacement per TT-C-490F specifications and gain approval for the relevant QPD
- Once validated, demonstrate at the user level via field testing on non-critical military hardware for one year

Background/Introduction

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 by immersion or spraying
- ✓ The formed film provides a unique "self-sealing"
- ✓ Interfacial layer promotes paint adhesion
- ✓ Enhances the corrosion resistance of metals



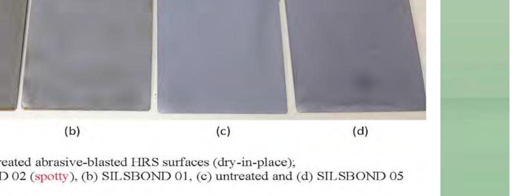
SILSBOND Film Structure

Approach

Phase I:
- Validate the processing and testing conditions of the new ZVOC/HAPS-NC wash primer system developed by Ecosil
- Testing for corrosion (ASTM B117 1000 hours, NSS exposure time GMW 14872 (40 cycles for Al and steel substrates))
- Adhesion
- Flexibility performance with the dry-in-place process will be required for qualification to TT-C-490F
- Hydrogen embrittlement studies
- Outdoor exposure testing
- Toxicity clearance studies

Phase II:
- Field testing studies (one-year duration) on non-critical military hardware (Marine Corps System Command, Quantico, Virginia and Aberdeen Test Center, Aberdeen Proving Grounds (APG), Maryland)

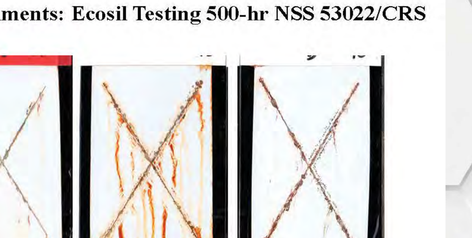
Accomplishments: SILSBOND testing at Ecosil



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

SILSBOND treated abrasive-blasted HRS surfaces (dry-in-place);
(a) SILSBOND 02 (spotty), (b) SILSBOND 01, (c) untreated and (d) SILSBOND 05

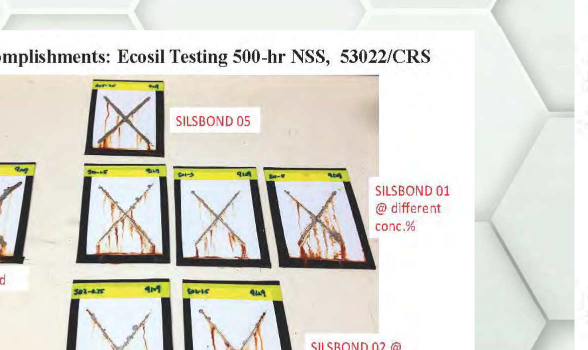
Accomplishments: Ecosil Testing 500-hr NSS 53022/CRS



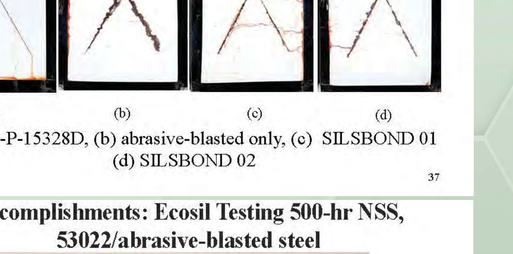
(a) (b) (c)

(a) DOD-P-15328D, (b) SILSBOND 01 and (c) SILSBOND 02

Accomplishments: Ecosil Testing 500-hr NSS, 53022/CRS



Accomplishments: Ecosil Testing 500-hr NSS, 53022/ abrasive-blasted steel

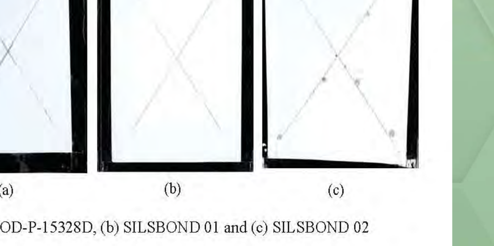


(a) (b) (c) (d)

(a) DOD-P-15328D, (b) abrasive-blasted only, (c) SILSBOND 01 (d) SILSBOND 02

Accomplishments: Ecosil Testing 500-hr NSS, 53022/abrasive-blasted steel

Accomplishments: Ecosil Testing 1000-hr NSS, 53022/AA 2024-T3



(a) (b) (c)

(a) DOD-P-15328D, (b) SILSBOND 01 and (c) SILSBOND 02

Accomplishments: Ecosil Testing 1000-hr NSS, 53022/AA 2024-T3

Results/Conclusions to Date

- SILSBOND candidate solutions were sprayed onto steel and Al 2024-T3 alloy substrates, followed by drying-in-place.
- Their corrosion performance was evaluated under MIL-DTL-53022 in NSS for 500 hrs and 1000 hrs
  - ✓ SILSBOND 05 shows the best flash rust resistance, followed by SILSBOND 01 and SILSBOND 02
  - ✓ SILSBOND 01 performed the best on cleaned CRS in 500-hr NSS
  - ✓ Both SILSBOND 01 and SILSBOND 05 performed the best on abrasive-blasted steel in 500-hr NSS
  - ✓ Both SILSBOND 01 and SILSBOND 05 performed the best on AA 2024-T3 in 1000-hr NSS

Future Work:

- ➢ Round Robin Test planned for FY17
- ➢ The total number of test panels is 601, including CRS, abrasive-blasted CRS and AA 2024-T3
- ➢ Test panels were ordered and will be prepared at Impreglon (MD)
- ➢ The tests to be performed include: ASTM B117, D 3359, D 4541, D522, F519, GMW 14872 and outdoor exposure

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