

Environmentally Friendly Pretreatment for Department of Defense Applications

SERDP Project WP-1676

Thor Lingenfelter
PPG Industries, Inc.

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SERDP-1676 Technical Objectives

- Develop an environmentally friendly pretreatment system for multi-material Department of Defense applications
 - Free of hexavalent chromium (Cr^{6+})
 - No volatile hazardous air pollutants (HAPs)
 - Ease of application using existing infrastructure
 - Cost effective
 - **Broad substrate/topcoat compatibility**

Current Zirconium Pretreatment Commercial Activity

- Over 60 general industrial lines converted to zirconium pretreatments (spray and immersion lines).
- Several major North American and European automotive OEM pretreatment lines converted to zirconium pretreatments



Zirconium Pretreatment Benefits

Performance

- Excellent corrosion resistance
- Promotes coating adhesion to substrate

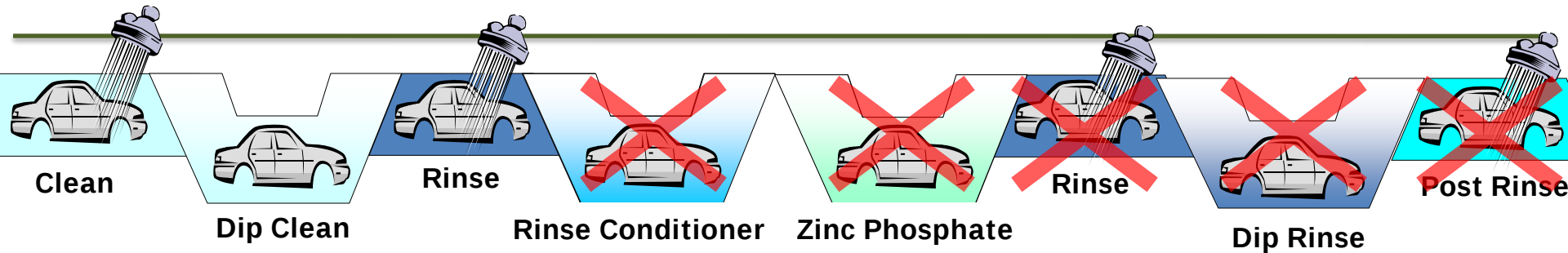
Environmental

- No volatile hazardous air pollutants (HAPs)
- Reduced waste concerns
 - 80% less waste than zinc phosphate
 - No regulated heavy metal species

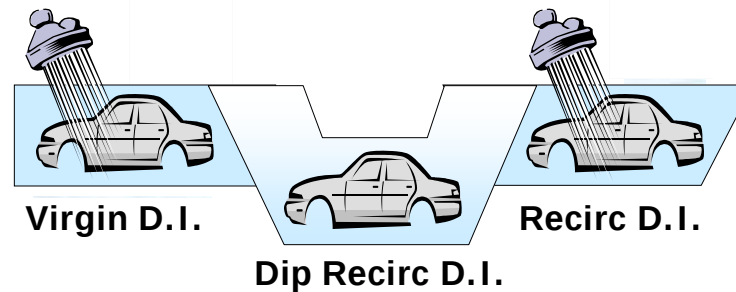
Processing

- Application at ambient temperature
- Milder pH than zinc phosphate and chromate pretreatments (pH = 4.5 vs. 1.5 – 3.0)

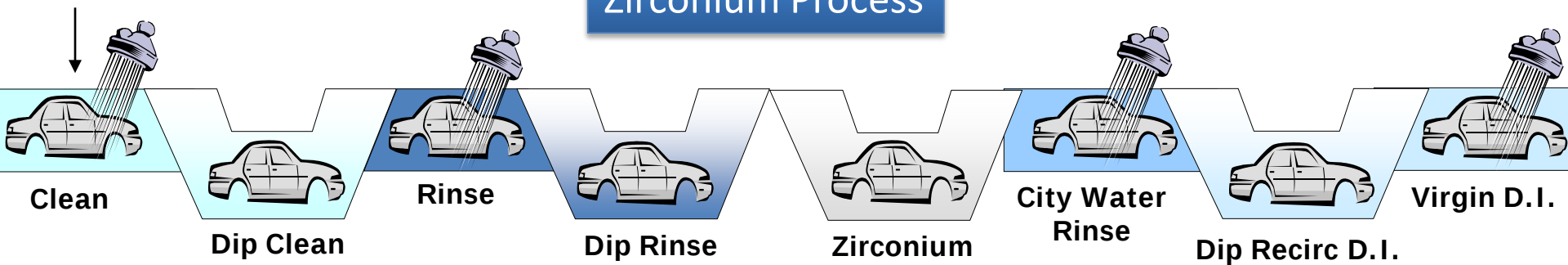
Pretreatment Process



Zn Phosphate Process



Deluge,
Pre-wipe



Appearance of Zirconium Pretreatment



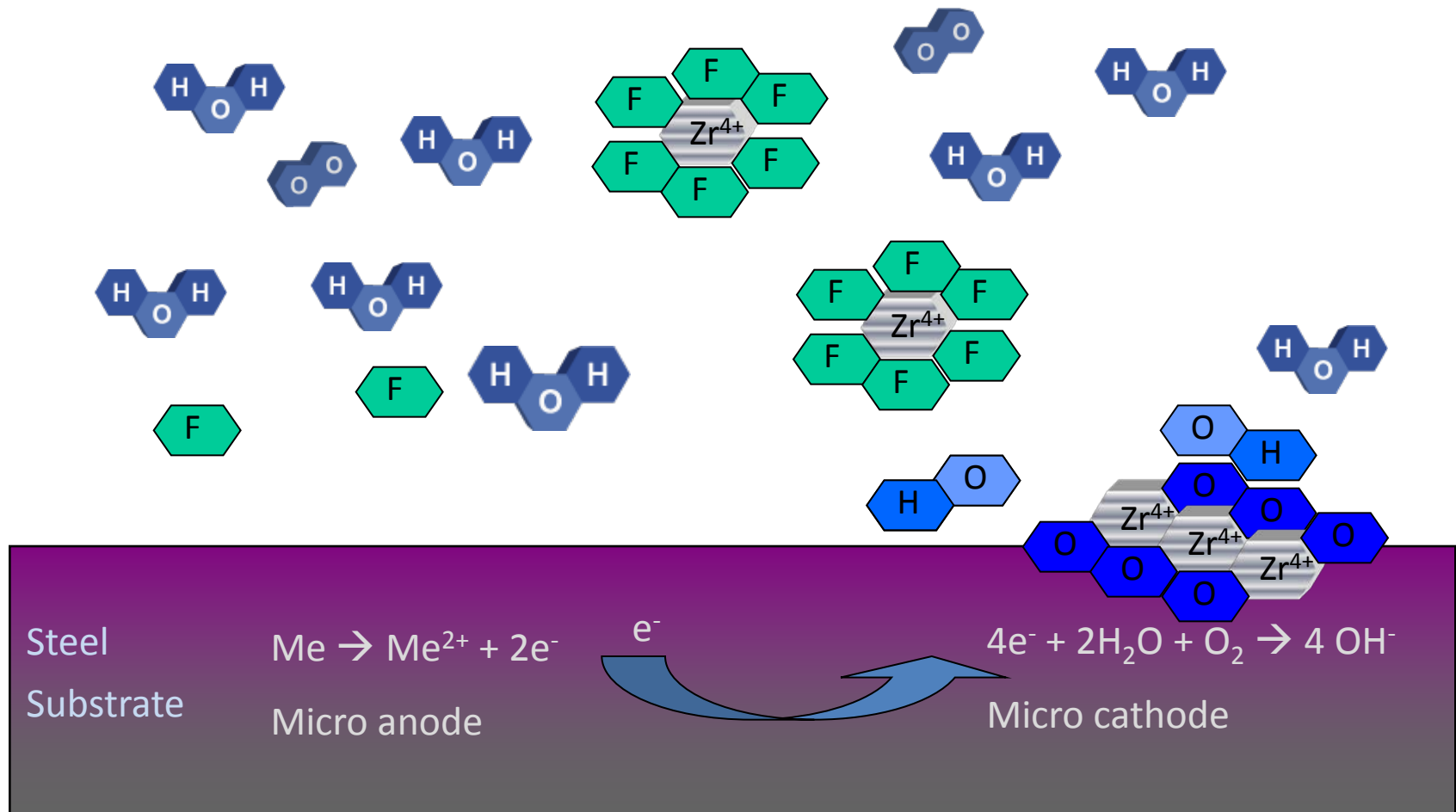
Before Zirconium Pretreatment



After Zirconium Pretreatment

Zirconium pretreatment coatings are visible.

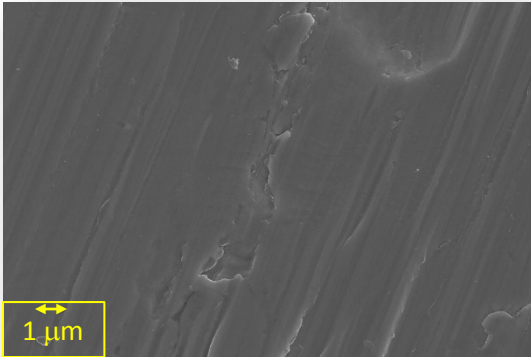
Zirconium-Based Pretreatment



Coating thickness: 20-200 nm.

Coatings on Cold-Rolled Steel

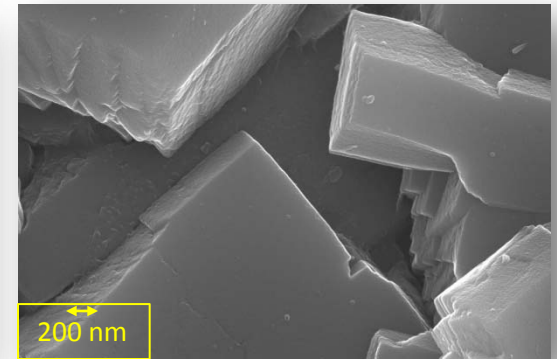
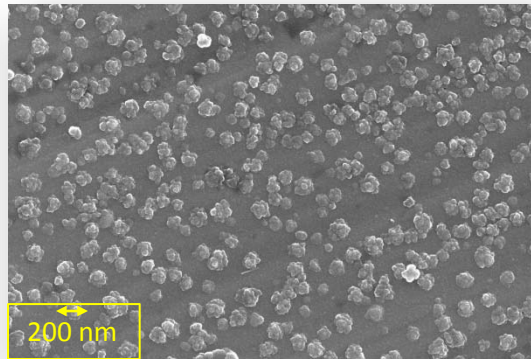
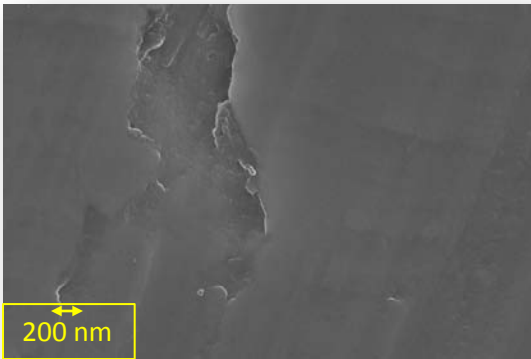
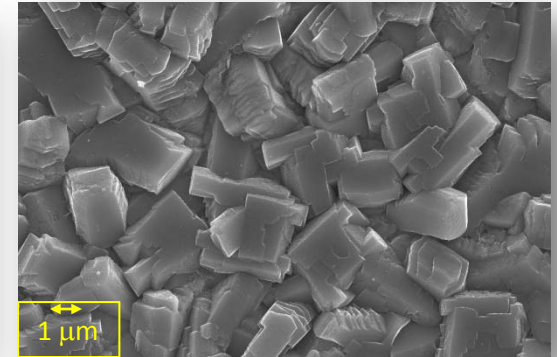
clean only



Zirconium Pretreatment



Zn Phosphate



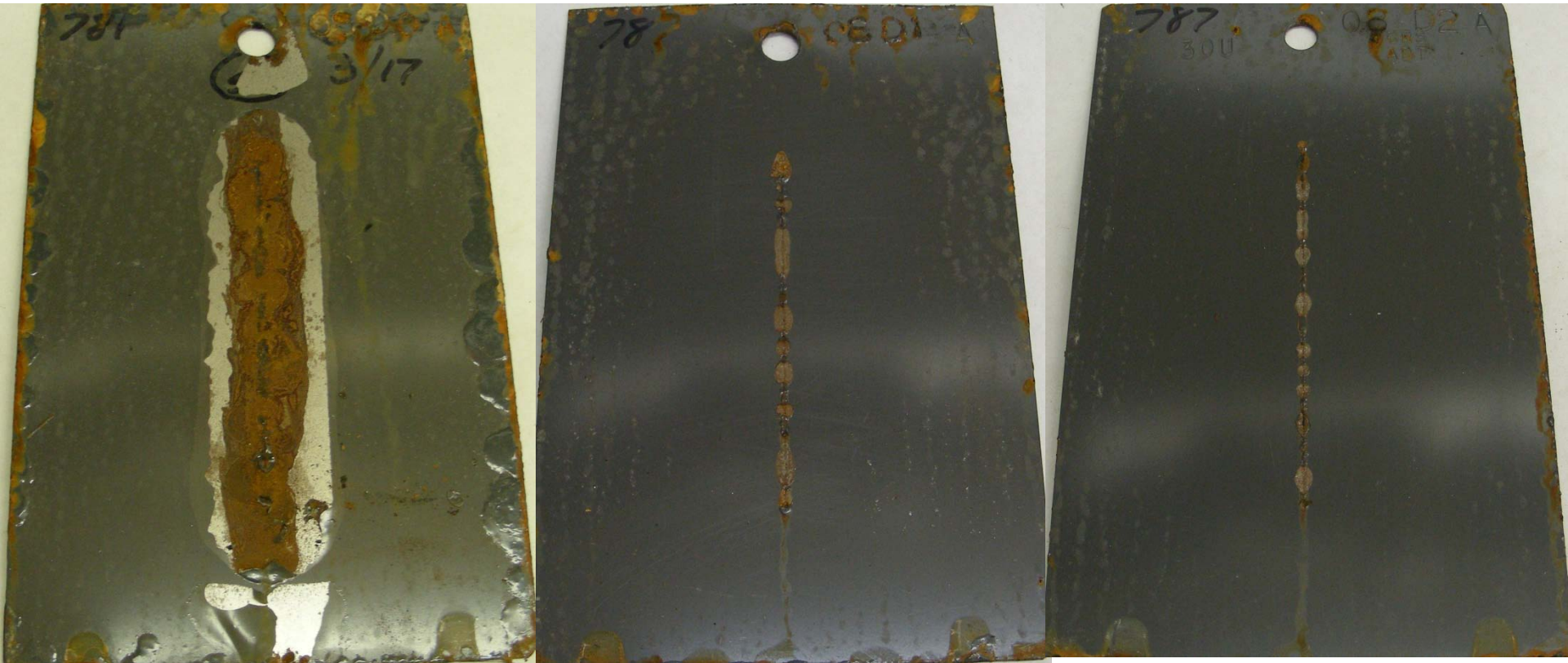
- Morphology and coating thickness of the zirconium pretreatments are unique when compared to zinc phosphate

Commercial Pretreatment performance

cleaned only

Zirconium Pretreatment

Zinc phosphate



Modified GMW14872 with Electrocoat over CRS

Environmentally Friendly Zirconium Oxide Pretreatment

Task 1: OEM Pretreatment Development



immersion-applied ZrOx

Task 3: Repair Pretreatment Development



Task 2: Depot Pretreatment Development



Environmentally Friendly Zirconium Oxide Pretreatment

Task 1: OEM Pretreatment Development



immersion-applied ZrOx

- Evaluate commercial immersion formulae with DoD substrates and coatings - reformulate as needed (Mil-Spec testing at ARL).

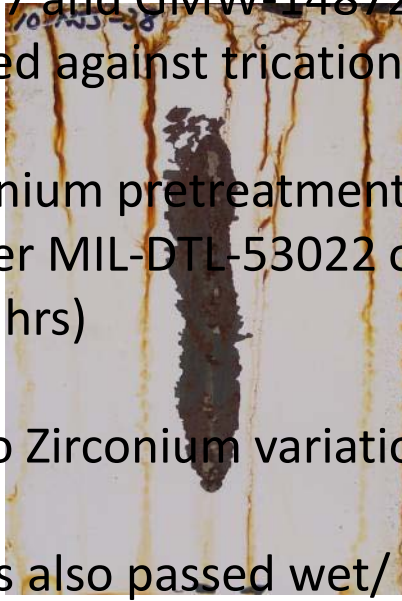
Limited Mil-Spec testing at ARL: Immersion Pretreatment

- Samples submitted for accelerated corrosion testing (CRS, 2024-T3, and 7075-T6).
 - Commercial and experimental formula modifications submitted
 - B-117 and GMW-14872
 - Tested against tricationic Zn phosphate and chrome wash primer

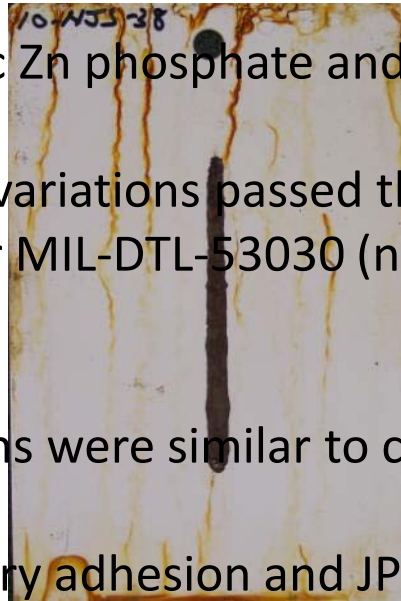
- Two Zirconium pretreatment variations passed the 336 hr and 1000 hr B-117 outlined per MIL-DTL-53022 or MIL-DTL-53030 (not as strong as zinc phosphate after 1000 hrs)

- Same two Zirconium variations were similar to controls in 40 cycles GMW-14872

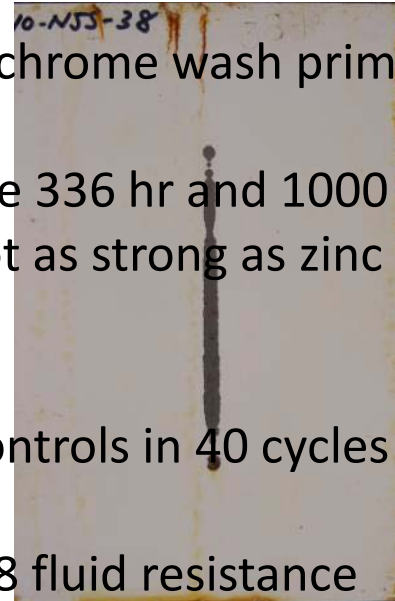
- Variations also passed wet/ dry adhesion and JP-8 fluid resistance



Commercial
formula



Modified
formula



Zn Phosphate

- Panels with passing results were sent to NASA's Cape Canaveral beachside corrosion site
500 hours B117 MIL-PRF-53022 Type II

Environmentally Friendly Zirconium Oxide Pretreatment

- Visit DoD depot facilities to benchmark application process/conditions
- Determine compatibility of immersion formula with depot equipment.
- Formula optimization, if needed
- Comprehensive Mil-Spec testing

Task 2: Depot Pretreatment Development



Benchmark of Depot Sites

Benchmark Depot Application Systems

Marine Corps Logistics Base at Albany, GA

- Uses immersion pretreatment
- Two tanks currently not in use suitable for zirconium pretreatment

Letterkenny Army Depot

- Uses immersion pretreatment
- Wash primer replacement high priority
- Would need to supply immersion tank for zirconium application

Environmentally Friendly Zirconium Oxide Pretreatment

- Suitable for small areas
- Spray-Gun applied
- Wand applied
- Wipe-on

Task 3: Repair Pretreatment Development



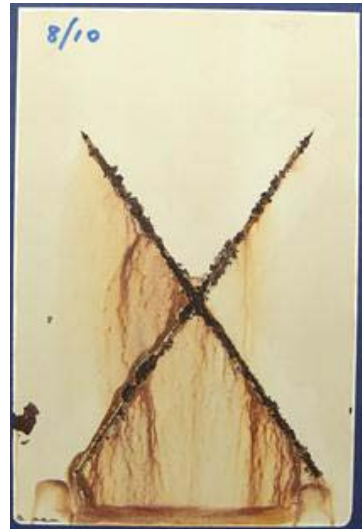
Field repair zirconium pretreatments

- Two potential formulations are in development:
 - ◆ Spray-on/ Rinse-off application
 - ◆ Dry-in-Place application
- Both materials utilize zirconium technology and are based on prototype formulations from Task 1
- Spray-on/ Rinse-off formula uses an inorganic shear-thinning rheology modifier
 - ◆ Material can be sprayed on using a hand or garden sprayer, but then “gels” after application; adheres to vertical surfaces until rinsed off
 - ◆ Need to collect rinse water
- Dry-in-place formula is designed to be spray applied, then ambient air dried

Field repair zirconium pretreatments

- Limited Mil- spec testing by ARL:
 - Spray-on/ Rinse-off passed wet/dry adhesion and JP-8 testing
 - Dry-in-Place formulation had inconsistent wet adhesion
- Further development with application conditions of Dry-in-Place formula has resulted in a more consistent pretreatment coating

1000 hours B117 (MIL-DTL-53030 Type II)



Dry-in-Place



Zinc phosphate

Path Forward

- Qualification to Mil specification
- Continue to develop a field application zirconium system appropriate for depot needs
- Proposal submitted to ESTCP for a demonstration/ validation of immersion technology at DoD depots

Project Team SERDP WP-1676

PPG Industries Inc.

Dr. Nathan Silvernail
Mr. Thor Lingenfelter
Dr. Michael Pawlik
Mr. Scott Benton



US Army Research Laboratory

Mr. John Escarsega
Mr. Fred Lafferman
Mr. Daniel Pope

