ESTCP
Cost and Performance Report

(WP-200906)

Non-Chromate, ZVOC Coatings for Steel Substrates on Army and Navy Aircraft and Ground Vehicles

Non-Chromate Sealers for Zinc Phosphate

April 2017

This document has been cleared for public release; Distribution Statement A

ESTCP

ENVIRONMENTAL SECURITY
TECHNOLOGY CERTIFICATION PROGRAM

U.S. Department of Defense

Page Intentionally Left Blank

Page Intentionally Left Blank

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
04/30/2017

2. REPORT TYPE
Cost & Performance Report

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE
Non-Chromate, ZVOC Coatings for Steel Substrates on Army and Navy Aircraft and Ground Vehicles

Non-Chromate Sealers for Zinc Phosphate

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Mr. John Kelley, Army Research Laboratory

Amy Fowler, NAVAIR
William Nickerson, NAVAIR

5d. PROJECT NUMBER
WP-200906

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Army Research Lab
2800 Powder Mill Rd.
Adelphi, MD 20783

8. PERFORMING ORGANIZATION REPORT NUMBER
WP-200906

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Environmental Security Technology Certification Program
4800 Mark Center Drive, Suite 17D03
Alexandria, VA 22350-3605

10. SPONSOR/MONITOR'S ACRONYM(S)
ESTCP

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
WP-200906

12. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution unlimited; public

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The objective of this demonstration is to determine the viability of non-hexavalent chromium sealers for zinc phosphate as a base for organic coatings. By itself, zinc phosphate does not provide adequate corrosion protection. It is a porous coating that requires a sealer to enhance the corrosion protection and provide a good surface for paint adhesion. The current post treatment for zinc phosphate is a chromic acid rinse with hexavalent chromium, a known carcinogen. A successful demonstration of a non-hexavalent chromium sealer will reduce and eventually eliminate the use of hexavalent chromium in phosphating processes resulting in reducing health and environmental risks associated with hexavalent chromium.

15. SUBJECT TERMS
Chemical Agent Resistant Coating, Environmentally Assisted Cracking, Hydraulic Adhesion Test Equipment, High Hard Armor, Low Carbon Steel, Permissible Exposure Limit, Trivalent Chromium Process, Non-Chromate, Steel Substrates, Zinc Phosphate, Sealers

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON / 19b. TELEPHONE NUMBER *(Include area code)*
C&P Report				56	Mr. John Kelley / 410-306-0837

Page Intentionally Left Blank

COST & PERFORMANCE REPORT

Project: WP-200906

TABLE OF CONTENTS

Page

LIST OF FIGURES

Page

LIST OF FIGURES

Page

LIST OF TABLES

Page

ACRONYMS AND ABBREVIATIONS

ANAD	Anniston Army Depot
ARL	Army Research Laboratory
ASTM	American Society of Testing and Materials
CARC	Chemical Agent Resistant Coating
DoD	Department of Defense
EAC	Environmentally Assisted Cracking
ESTCP	Environmental Security Technology Certification Program
HATE	Hydraulic Adhesion Test Equipment
HHA	High Hard Armor
IAW	In Accordance With
in	inch(es)
JTP	Joint Test Protocol
LCS	Low Carbon Steel
NAVAIR	Naval Air Warfare Center
NSN	National Stock Number
OEM	Original Equipment Manufacturer
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
PPG	Pittsburgh Plate Glass Industries
psi	Pounds per Square Inch
QPD	Quality Products Database
SAE	Society of Automotive Engineers
SERDP	Strategic Environmental Research and Development Program
SSPC	Society for Protective Coatings
TCP	Trivalent Chromium Process

Page Intentionally Left Blank

ACKNOWLEDGEMENTS

The research team would like to acknowledge the following organizations and individuals for their important contributions. The Environmental Security Technology Certification Program (ESTCP) Review Board, and Mr. Bruce Sartwell for providing funding and valuable scientific input throughout the project. Others who have made significant contributions are: Alicia Farrell and Christopher Miller (U.S. Army Research Laboratory); Patricia Dodson, Christopher Coss, Austin Minter, and Stanley Wilson (Anniston Army Depot); Nabil Zaki and Ray Lindemann (SurTec International); and Jonathan Love and Larry Fitzgerald (Pittsburgh Plate Glass Industries).

Page Intentionally Left Blank

EXECUTIVE SUMMARY

OBJECTIVES OF THE DEMONSTRATION

The objective of this demonstration is to determine the viability of non-hexavalent chromium sealers for zinc phosphate as a base for organic coatings. By itself, zinc phosphate does not provide adequate corrosion protection. It is a porous coating that requires a sealer to enhance the corrosion protection and provide a good surface for paint adhesion. The current post treatment for zinc phosphate is a chromic acid rinse with hexavalent chromium, a known carcinogen. A successful demonstration of a non-hexavalent chromium sealer will reduce and eventually eliminate the use of hexavalent chromium in phosphating processes resulting in reducing health and environmental risks associated with hexavalent chromium.

TECHNOLOGY DESCRIPTION

The alternative sealers tested and demonstrated, SurTec 580 and Chemseal 100, are considered drop-in replacements for the chromic acid rinse used for sealing zinc phosphate. The product demonstrated at Anniston Army Depot (ANAD) was SurTec 580. It is a trivalent chromium product manufactured by SurTec International (Trivalent Chromium Process [TCP] licensee). When a freshly phosphated surface is immersed in the SurTec 580, there are two reactions that take place. First, a localized chemical reaction at the metal/solution interface which forms a hydroxide. As the pH increases locally, chromium (III) hydroxide (Cr[OH]3) is formed. The actual application of both alternatives is similar to using chromic acid rinse, but with some advantages. In addition to being non-chromate, both processes are carried out at ambient temperature. This reduces the utility burden on the facility. No capital improvements or modifications to the existing phosphate lines are needed to accommodate either of the technologies tested. These products are commercially available.

DEMONSTRATION RESULTS

Two non-chromate sealers for zinc phosphate; SurTec 580 and Chemseal 100, were laboratory evaluated. Based on the laboratory results, SurTec 580 was selected for demonstration on parts processed at ANAD. The M1 Abrams small fuel cap National Stock Number (NSN) 5340-01-460-5277 was the primary candidate part on the phosphate line used in the demonstration. Some miscellaneous parts and test panels were also included for the purpose of evaluating at the Army Research Laboratory (ARL) laboratory. One chromate sealed fuel cap was tested against one SurTec 580 fuel cap at ARL. The adhesion strength for the SurTec 580 sealed cap was nearly identical to the chromate cap. Both measured within 2 pounds per square inch (psi) of each other (1672 psi and 1674 psi). Both fuel caps also performed well after completing 60 cycles of cyclic corrosion tests. Although the statistical sample is small, when all data is considered, it is evident that the SurTec 580 compared well to the chromate seal.

IMPLEMENTATION

The synergy of this project and the revision of Federal Specification TT-C-490 has provided a pathway for the implementation of these and other new pretreatment technologies.

All three pretreatments evaluated in WP-200906 met the minimum performance requirements of TT-C-490 Revision F and were assigned a Quality Products Database (QPD) number making them available to any Original Equipment Manufacturer (OEM), or Depot for use on abrasive blasted steel. This is especially useful on contracts issued that must be free of hexavalent chromium.

1.0 INTRODUCTION

1.1 BACKGROUND

There are three basic types of phosphate coatings: Iron (TT-C-490 type II), Zinc (TT-C-490 type I)[1] and heavy Zinc or Manganese phosphate (DoD-P-16232).[2] Zinc Phosphate is a steel conversion coating that provides a crystal structure that is often used as a base for organic coatings such as paints and powder coatings. The zinc phosphate coating by itself does not provide adequate corrosion protection. It is a porous coating that is also commonly used to absorb lubricants like oils and waxes to reduce friction in some applications. To enhance the corrosion protection and provide a good surface for paint to adhere, a sealer or rinse is necessary. Zinc phosphate is currently sealed with a chromate sealer containing chromic acid prior to painting. The health and environmental risks associated with hexavalent chromium based compounds have necessitated reductions and even eliminations of usage of these compounds on U.S. Army weapon systems.

1.2 OBJECTIVE OF THE DEMONSTRATION

To validate the efficacy of non-hexavalent chromium sealing of zinc phosphated parts versus hexavalent chromium sealer. The intent is to identify one or more replacements for the chromic acid sealer for zinc phosphate. A successful demonstration of a non-hexavalent chromium sealer will reduce and eventually eliminate the use of hexavalent chromium in the phosphating process. Table 1-1 summarizes the hazards targeted and components that will be used for the demonstration of an alternative sealer for zinc phosphate.

Table 1-1. Target Hazardous Material Summary

Target Hazardous Material	Current Process	Applications	Current Specifications	Affected Programs	Candidate Parts and Substrates
Hexavalent Chromium	Zinc Phosphate with chromic acid seal	Steel and armor steel substrates	TT-C-490 SSPC-SP10 MIL-DTL-53072 [3]	All military systems using zinc phosphate	NSN 5340-01-460-5277, Cover Access (Fuel Cap), Stryker Cupola

1.3 REGULATORY DRIVERS

The Occupational Safety and Health Administration (OSHA) Final Rules effective May 30, 2006, Federal Register #71:10099-10385 states in part that OSHA has amended the standard limiting occupational exposure to hexavalent chromium. OSHA has determined that at the current permissible exposure limit (PEL) for hexavalent chromium and establishes an 8-hour time-weighted average exposure limit of 5 micrograms of hexavalent chromium per cubic meter of air (5 $\mu g/m^3$). This is a considerable reduction from the previous PEL of 1 milligram per 10 cubic meters of air (1 mg/10 m^3, or 100 micrograms [μg]/m^3) reported as chromium trioxide (CrO_3), which is equivalent to a limit of 52 $\mu g/m^3$ as hexavalent chromium.

In April of 2009, a memorandum from Office of the Secretary of Defense signed by Mr. Young was released outlining a new policy for reducing the use of hexavalent chromium for Department of Defense (DoD) applications. The memorandum specifically directs the military to restrict the use of hexavalent chromium unless no cost-effective alternative with satisfactory performance has been identified.

2.0 DEMONSTRATION TECHNOLOGY

The alternative sealers tested, SurTec 580 and Chemseal 100, can be used as drop-in replacements for chromate sealers for zinc phosphate. In addition to being non-chromate, both processes are carried out at ambient temperature. This reduces the utility burden on the facility. No capital improvements or modifications to existing lines are needed for the technologies described below.

2.1 TECHNOLOGY DESCRIPTION: SURTEC 580 (TCP)

The TCP was developed by the Naval Air Warfare Center (NAVAIR) in an effort to replace chromated sealers, post-treatments, and conversion coatings for aluminum alloys. The TCP forms predominately zirconium oxide/fluoride, chromium oxide conversion coating on the aluminum alloy surface. Electrochemical evidence suggests that the TCP forms a much more uniform film thickness across these inter-metallic sites with improved barrier coating properties from the denser zirconium oxide and localized corrosion inhibition through the ability of the trivalent chromium species to bind up attacking anions such as chlorides.[4] One of the key advantages to using TCP is that the processing and maintenance requirements are similar to currently used technologies, thus making them favorable alternatives for depots and OEMs. The technology demonstrated, SurTec 580, was formulated to seal phosphate coatings. It intensifies phosphate layers by filling the pores and enhances the adhesion of the primer to the substrate thereby improving the corrosion protection and preventing under film corrosion.

The SurTec 580 is manufactured by SurTec International (TCP licensee). It works by initiating a localized chemical reaction at the metal/solution interface and forms a hydroxide. As the pH increases locally, $Cr(OH)3$ is formed. SurTec 580 is a green, clear-turbid liquid with a density of 1.00–1.02 g/ml and an approximate pH of 3.8. The SurTec 580 is purchased as a concentrate. Using deionized water, it has a make-up value of 7 ml per liter of solution. Steps for make-up: (1) Dissolve SurTec 580 in deionized water portion by portion with strong agitation; and (2) Adjust the pH-value to pH 3.8 (if necessary) using sodium hydroxide solution (1% solution). The manufacturer’s recommended process steps are given in the process flow diagram in Figure 2-1. The SurTec operating temperature range is 20–40°C.

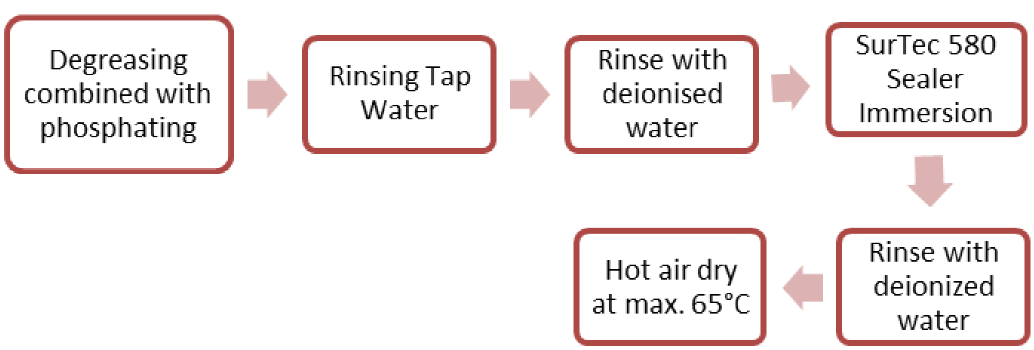


Figure 2-1. Flow Diagram for SurTec 580 Manufacturer Recommended Process Steps

2.2 TECHNOLOGY DESCRIPTION: PPG CHEMSEAL 100

Chemseal 100 is a post-phosphate, passivating sealer formulated to improve adhesion and corrosion protection of either zinc- or iron-phosphate. It was originally developed in the early 1990s to enhance the corrosion resistance of iron phosphated steel, specifically under high-solids, polyester, solvent-borne liquid paint systems. It was formulated to be a high-performing, environmentally sound alternative to established hexavalent chromium or trivalent chromium sealers. After evaluation of multiple epoxy and amine chemistry options, the final version of CS100 was commercialized and demonstrated equivalent performance to chromium-based products. The chemistry is patent-protected under US Patent Nos. 5,565,823 and 5,585,695. It incorporates organic and inorganic materials according to the following scheme. The animated epoxy resin is then reacted with a slight excess of fluorozirconic acid and a strong mineral acid to create water-soluble, protonated ammonium salts in mildly acidic solution. When phosphated parts are immersed into, or sprayed with a dilute solution of this product, mild etching of the phosphated steel results in both the deprotonation of the organic molecule onto the surface and the deposition of zirconium oxides.

Zirconium oxides serve to “seal” tiny voids in the phosphate surface, while the aromatic, organic molecule provides excellent opportunities for strong hydrogen bonding to both the underlying, “sealed” phosphate layer and the primer or single-coat finish applied after pretreatment.

2.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

In this section, the advantages and limitations of the demonstrated technology are listed as compared to the current zinc phosphate coating process that uses chromic acid rinse.

SurTec 580 (TCP)

Advantages:

- Proven to add corrosion protection while improving coating adhesion on aluminum
- Data showing performance comparable to hexavalent chromium sealer on steel
- Easy to apply drop-in replacement for existing sealer
- Safer: No hexavalent chromium, non-irritant to skin, or eyes

Limitations:

- Limited historical data for use on steel

PPG Chemseal 100

Advantages:

- Contains no chromium component
- Adds a layer of corrosion protection while improving coating adhesion
- Effectively used to seal phosphate coatings commercially for years

- Easy to apply drop-in replacement for existing sealer
- Non-irritant to skin, or eyes

Limitations:

- Not universally effective with all coatings technologies
- Only slight color change to substrate surface to indicate full coverage

Page Intentionally Left Blank

3.0 PERFORMANCE OBJECTIVES

The performance objectives with success criteria for the demonstrated technology were evaluated in accordance with (IAW) the tests delineated in the Joint Test Protocol (JTP) provided in final report. The functional performance objectives are summarized in Table 3-1. Since this technology area seeks to "replace" the existing chromate sealer, performance should meet or exceed the baseline chromate sealer.

Table 3-1. Performance Objectives for Alternative Sealers for Zinc Phosphate

Performance Objective	Data Requirements	Success Criteria		Results					
Quantitative Performance Objectives			Substrate	SurTec 580 CARC MIL-DTL- 53039	SurTec 580 CARC MIL-DTL- 64159	Chemseal 100 CARC MIL-DTL- 53039	Chemseal 100 CARC MIL-DTL- 64159	Chromic Acid CARC MIL-DTL- 53039	Chromic Acid CARC MIL-DTL- 64159
Adhesion Test	ASTM-4541 Pull-off Adhesion	Minimum average 30 events rating of 1200 PSI on 1.5 mil profile surface	LCS	Met	Met	Met	Met	Met	Met
			HHA	Met	Met	Met	Met	Met	Met
	ASTM- D3359 Dry Adhesion	Adhesion rating (steel) >4B; adhesion rating	LCS	Not Met	Not Met	Not Met	Met	Met	Met
			HHA	Met	Met	Met	Met	Met	Met
	ASTM- D3359 Wet Adhesion	Scribed area rating (steel) ≥ 3A after 24 hours at ambient;	LCS	Met	Met	Met	Met	Met	Met
			HHA	Met	Met	Met	Met	Met	Met
Chip Resistance	SAE-J400	After one cycle, chip rating NLT 5B for steel	LCS	Not Met	Not Met	Met	Met	Met	Not Met
			HHA	Met	Not Met	Not Met	Not Met	Met	Met
Accelerated corrosion	ASTM-B117 Salt Fog	After 500 hours of exposure: steel substrate rating ≥6 scribed	LCS	Met	N/A	Met	N/A	Met	N/A
			HHA	Met	N/A	Met	N/A	Met	N/A
	GM-9540P Cyclic Corrosion ASTM D 1654	After 60 cycles: steel substrate rating ≥ 4	LCS	Met	Not Met	Met	Met	Not Met	Met
			HHA	Met	Met	Met	Not Met	Met	Met
Outdoor Exposure*	Tropical climate exposure at Cape Canaveral Air Force Base FL ASTM D 1654 ASTM G50	Three years of exposure: meet or exceed baseline performance	LCS	Met	Met	Met	Not Met	N/A	N/A
			HHA	Not Met	Met	Not Met	Met	N/A	N/A
Hydrogen Embrittlement	ASTM E 399-97	No detrimental effect to K1c of substrate. High Hard K1c @ 48-51Rc shall maintain $K_{1EAC} \geq 19$ (ksi√in)	LCS	N/A	N/A	N/A	N/A	N/A	N/A
			HHA	Met	Met	Met	Met	Met	Met
Field Testing**	TT-C-490	Equivalent or less than existing process	—	N/A	N/A	N/A	N/A	N/A	N/A
Qualitative Performance Objectives									
Toxicity Clearance	Toxicity clearances and full disclosure from CHPPM	Approved by processing facility	—	Met		Met			
Processing time	TT-C-490	Equivalent or less than existing process	—	Met		N/A			
Ease of use	Feedback from field technician on usability of technology and time required during demonstration	Minimal operator training required	—	Met		N/A			
Monitor Solution collect data for OQE	TT-C-490 and manufacturers recommended operating parameters	No increase in downtime	—	Met		N/A			

* Modified outdoor exposure success criteria from 25% less creep from scribe to meet or exceed baseline performance
** Despite repeated efforts by ARL and ANAD, the parts that were fielded could not be located.

Page Intentionally Left Blank

4.0 SITES/PLATFORM DESCRIPTION

4.1 TEST PLATFORMS/FACILITIES

The demonstration of the zinc phosphate sealer was carried out at Anniston Army Depot (ANAD) in Building 114 in one of phosphate coating lines that support the Cleaning and Finishing Branch. The small fuel caps for the M1 Abrams described in section 1.2 are one of the demonstration parts. The ANAD site was selected for three reasons: (1) It was the site where WP-200906 for high hard armor (HHA) steel pretreatment demonstration was initiated; (2) ANAD conducts a significant amount of phosphating and has been exploring opportunities to evaluate alternatives to hexavalent chromium for many parts of their finishing operations; and finally, (3) Army Research Laboratory (ARL), has enjoyed a long standing productive working relationship with ANAD in other efforts.

4.2 PRESENT OPERATIONS

The current process utilized at ANAD begins with preparing the parts by abrasive blasting. Once the parts are properly cleaned and prepared, they are immersed in zinc phosphate and subsequently rinsed in cold water. To seal, the parts are dipped in a solution of 4 ounces chromic acid and 4 ounces of phosphoric acid per 100 gallons of water and maintained at a temperature of 150–200°F. Once sealed and dry, the parts are now ready to be primed and painted. If unpainted parts are stored long term, a corrosion preventive compound or preservative lubricating oil is applied. Figure 4-1 is a flow diagram of a typical zinc phosphating line currently employed at ANAD.

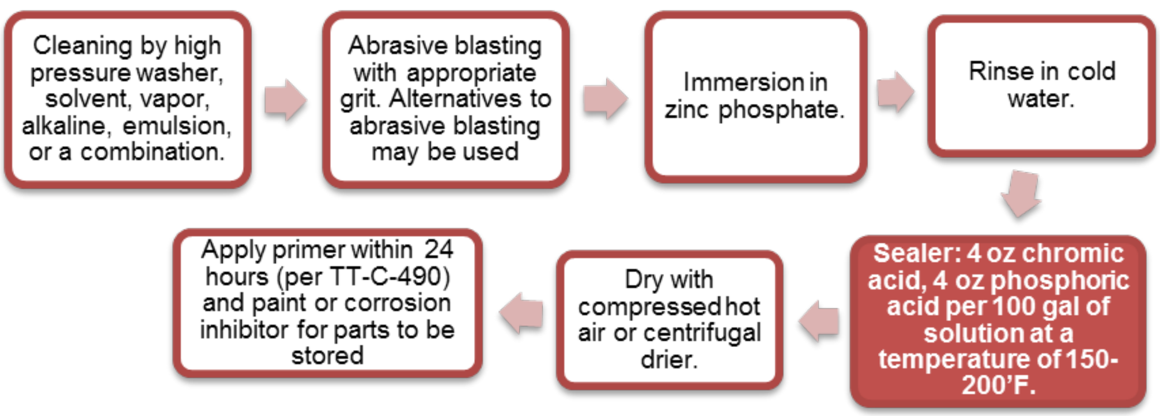


Figure 4-1. Flow Diagram of a Typical Phosphate Line Currently Employed at ANAD

The demonstrated technology is intended to replace the sealer in step 5 (highlighted in red) in the above flow diagram. Since the SurTec 580 is a drop-in replacement for the chromic acid solution, it does not add additional steps to the current process.

4.3 SITE-RELATED PERMITS AND REGULATIONS

Additional site related permits or regulations were not required for the demonstration to be conducted at ANAD. The facility has had the capability to process and apply pretreatments, including hexavalent chromium pretreatments, and holds the necessary documentation to perform the demonstrated chemical pretreatments and dispose of any waste if necessary.

5.0 TEST DESIGN

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

Although significant testing and evaluation of TCPs on steel substrates was performed as part of the Strategic Environmental Research and Development Program (SERDP) project WP-1521, trivalent chromium sealers for zinc phosphate were not adequately explored. For this reason the demonstrated technology, SurTec 580, was laboratory validated and selected for demonstration on zinc phosphate steel samples and components in accordance with the JTP.

5.2 LABORATORY EXPERIMENTAL PROCEDURE RIB

Sample Preparation:

The experiments were conducted using 4-in x 6-in x 3/16-in steel test panels fabricated from HHA steel MIL-A-46100 and low carbon steel (LCS). All of the HHA test panels were abrasive blasted to a 1.5 mil surface finish using 60 grit aluminum oxide blast media, while all LCS panels had a milled surface finish of approximately 100-63 micro-inches (μ in). All of the pretreatments were applied by the vendors in order to eliminate inconsistencies in the processes. All primer and topcoats were applied by ARL. The coatings used were MIL-DTL-53022 Type II primer,[5] solvent borne MIL-DTL-53039 Type III topcoat,[6] and water borne MIL-DTL-64159 Type II topcoat,[7] all manufactured by Hentzen. The test matrix is shown below in Table 5-1.

Table 5-1. Test matrix for both steel substrates

Coating System	Tests	Low Carbon Steel (4 x 6 panels)			High Hard Armor Steel (4 x 6 panels)		
		Dip Zn Phos w/ Chromate Seal Baseline	Spray Zinc Phosphate Sealers		Dip Zn Phos w/ Chromate Seal Baseline	Spray Zinc Phosphate Sealers	
			SurTec 580	PPG Chemseal 100		SurTec 580	PPG Chemseal 100
Low VOC MIL-DTL-53022 / MIL-DTL-53039	ASTM D 4541	3	3	3	3	3	3
	ASTM D 3359 Dry	1	1	1	1	1	1
	ASTM D 3359 Wet	2	2	2	2	2	2
	SAE J400	1	1	1	1	1	1
	ASTM B 117	5	5	5	5	5	5
	GM9540P	3	3	3	3	3	3
	Outdoor Exposure	5	5	5	5	5	5
Low VOC MIL-DTL-53022 / MIL-DTL-64159	ASTM D 4541	3	3	3	3	3	3
	ASTM D 3359 Dry	1	1	1	1	1	1
	ASTM D 3359 Wet	2	2	2	2	2	2
	SAE J400	1	1	1	1	1	1
	ASTM B 117	5	5	5	5	5	5
	GM9540P	3	3	3	3	3	3
	Outdoor Exposure	5	5	5	5	5	5

Pull-off Adhesion (ASTM D4541):

An Elcometer® Model 108 Hydraulic Adhesion Test Equipment (HATE) was used to obtain the pull-off adhesion strength in pounds per square inch (psi). The apparatus included a loading fixture commonly referred to as a "dolly" which was secured to the coating normal to the coating surface using Instabond™ S-100 cyanoacrylate adhesive. After allowing the adhesive to cure for 24 hours at 25 ºC at 50% relative humidity, the load applied to the dolly by the apparatus was gradually increased and monitored until a plug of coating was detached. The failure tension in psi, and the failure mode and location within the coating system was recorded.

Dry Tape Adhesion:

Tests were conducted at room temperature as defined in American Society of Testing and Materials (ASTM) D3924. An area of the panel free of blemishes was selected. Using a sharp cutting tool, 6 parallel cuts at 2 mm spacing through the paint film to the metal substrate were made. A second series of cuts at 90 degrees to the initial set were then made. Both cuts were made ensuring that they were long enough to make a complete set of 6x6 line grid. The grids were repeated in two other areas on test coupons in order to obtain three data points per coupon. The grid lines were then brushed lightly with a stiff brush to remove any detached flakes or ribbons of coating. A length of tape was removed at a steady rate and cut about 75 mm (3 in.) long. The center of the tape was placed over the grid and the area of the grid was rubbed firmly with the eraser on the end of a pencil to ensure good contact. The tape was removed by seizing the free end and rapidly pulling (without jerking) back upon itself at as close to an angle of 180° as possible. Each grid was rated IAW ASTM D3359.

Wet Tape Adhesion:

Wet tape adhesion test evaluates the coating's ability to resist penetration by water. This test was performed IAW Method 6301 of FED-STD-141 (Federal Test Method Standard: Paint, Varnish, Lacquer and Related Materials: Methods of Inspection, Sampling and Testing) and rated per ASTM D3359. An "X" scribe was required on all test panels. The HHA steel and LCS panels were evaluated in the 24- and 96-hour wet tape adhesion test. The samples were immersed in distilled water for 24 and 96 hours at room temperature and 120°F, respectively. The panels were then removed from the water and dried by wiping with a soft cloth. Two parallel lines were scribed approximately 1 inch (in) apart with an "X" scribed between the two parallel lines making sure that the coating had been scribed all the way through. A piece of tape was placed over the scribes and smoothed out by rolling with a 3-lb roller. The tape was then removed at an angle of approximately 180-degrees (parallel) to the surface. The areas around the scribes were inspected for peel-away/delamination and the unscribed immersed area was inspected for blisters. Each panel was rated IAW ASTM D3359 and photo-documented.

SAE-J400 Chip Resistance Test:

The tests were carried out at ambient temperature using a Q-Lab Gravelometer. The panels were held in a 45° angle specimen holder and air pressure (70 psi ± 0.30 psi) was used to propel gravel at the sample. The test sample was then removed and gently wiped off with a clean cloth.

Tape (3M #898 filament strapping tape as specified in Society of Automotive Engineers [SAE] J400) was then applied to the entire tested surface in order to remove any loose fragments of the coating. The tested panel was then compared to standard SAE transparencies to determine a chipping rating. The total number of chips inside a 4-in x 4-in grid (16 in^2 area) using a transparency overlay was counted and the rating recorded. The average size of the chips was measured and size rating obtained IAW SAE J400.

Accelerated Corrosion:

The test panels evaluated in neutral salt fog had a single diagonal scribe while the test panels exposed to GM9540P were "X" scribed. In each case, the panels were scribed completely through the coating making sure that the substrate was exposed. The samples were then placed in their respective chambers, tilted at an angle between no more than 15º from the vertical with the scribed surface facing upwards. The ASTM B117 neutral salt fog conditions are 95°F with saturated humidity and an atomized fog of 5% NaCl solution. The GM9540P test consists of 18 separate stages per cycle that include the following: saltwater spray, humidity, ambient, and heated drying. The standard 0.9% NaCl, 0.1% $CaCl_2$, 0.25% $NaHCO_3$ test solution was used. In addition, the cyclic chamber was calibrated with standard steel mass-loss calibration coupons as described in the GM9540P test specification.

Outdoor Exposure Testing:

Test panels were prepared as described above and scribed with a carbide scribe all the way through the coating to the substrate as described in ASTM D1654 before being. The 4-in x 6-in coupons of both HHA and LCS were transported to Cape Canaveral Air Force Station in Florida and mounted to racks using Teflon fixtures, scribed side up on a 30º angle to the vertical. The racks are set facing the Atlantic Ocean and are approximately 100 yards inland from the water. The coupons inspected and evaluated biannually until failure IAW ASTM D1654. Weather data is collected utilizing a data-logging weather station and downloaded annually. Mass loss coupons placed with the test coupons are analyzed biannually.

Stress Corrosion Cracking Evaluation:

The resistance to environmentally assisted cracking (EAC) was assessed using the rising step load method for determination of K1EAC. For this procedure, CV2 Charpy specimens of MIL-A-46100D were machined in the longitudinal-transverse (L-T) orientation IAW ASTM E399-97. The Charpy specimens were spray zinc phosphated and subsequently sealed prior to testing. The phosphate systems which included the alternative sealers were evaluated to determine if they would have any detrimental effect on the K1EAC of the HHA steel. The specific procedure and specimen fatigue pre-cracking of each of the samples is described in the JTP and elsewhere.[8]

5.3 PHOSPHATE LINE COMPONENT DEMONSTRATION

All of the chemicals for the demonstration were provided by the manufacturers along with specific instructions on the application process. These can be seen in the process flow diagrams in section 2.0. A vat near the zinc phosphate line was cleaned and made available for the SurTec 580 sealer. All wastes generated from the clean out were disposed of by ANAD's waste contractor IAW all state and federal regulations. The SurTec 580 sealer is essentially a drop-in replacement for the chromic acid solution. No additional modifications to the vats were necessary.

Representatives from SurTec International worked closely with ARL and ANAD to properly mix the SurTec 580 solution, and carry out the sealing of the demonstration parts. In order to minimize disrupting the throughput on the phosphate lines, a 450-gallon vat located one row over from an active phosphate line was used.

The M1 Abrams small fuel cap NSN 5340-01-460-5277 was the primary candidate part in the demonstration. Some miscellaneous parts and test panels were also treated for the purpose of evaluating at the ARL. Below in Figure 5-1 are the fuel caps and test panels treated in the same zinc phosphate line during the demonstration. The caps were first steam cleaned, and the paint chemically removed. They were then abrasive blasted and repaired if necessary before phosphate and painting completed. The test panels were used to obtain the weight of the zinc phosphate coatings for the lines as well as corrosion tests at ANAD. ARL was also given the opportunity to treat a cupola from Stryker. The cupola shown in Figure 5-1 was the largest part that would fit in the 450 gallon SurTec vat.

Figure 5-1. M1 Abrams Fuel Caps and Test Panels Zinc Phosphate and Sealed (left), Stryker Cupola Rising Out of the SurTec 580 Vat after Seal (right)

According to section 3.5.4 of TT-C-490, the organic coating shall be applied to thoroughly dried surfaces within 24 hours after pretreatment. The research team was careful to follow this specification in order to minimize any variables during the demonstration. The information on the routing tickets for each part was recorded in order to track their location for inspection at a later date.

5.4 FIELD TESTING

A variety of parts and components were identified for the demonstration. The parts that are processed in the phosphate line are typically small miscellaneous parts and components. These parts, by themselves are usually not easily identified for tracking. The M1 small fuel cap was selected because it was thought it could be tracked as part of a major platform by matching it with the serial number of the vehicle. Table 5-2 below lists all of the parts that were processed in the phosphate line used in the demonstration in building 114.

Table 5-2. List parts and test panels processed during demonstration at ANAD

QTY	Substrate	Sealer	Testing Facility
4	Steel (ANAD)	SurTec 580	ANAD
4	Steel (ANAD)	Chromate	ANAD
4	Steel (ANAD)	SurTec 580	ARL
4	Steel (ANAD)	Chromate	ARL
3	HHA	SurTec 580	ARL
2	HHA	Chromate	ARL
3	LCS	SurTec 580	ARL
2	LCS	Chromate	ARL
1	Fuel Cap	SurTec 580	ARL
1	Fuel Cap	Chromate	ARL
5	Fuel Cap	SurTec 580	Field
5	Fuel Cap	Chromate	Field
1	Copula	SurTec 580	Field

ARL was also given a variety of miscellaneous parts not listed in Table 5-2. These parts received zinc phosphate and were sealed with baseline hexavalent chromium and the SurTec 580, then tested and analyzed at the ARL.

As previously mentioned, identifying information of the demonstrated parts was recorded in an effort to track the parts (and respective platform) in the field. The tracking information was taken from the parts routing tags. Below is a list of the "fielded" parts along with the identifying information recorded during the demonstration.

5 - ZnPhos/SurTec 580 M1 Fuel Caps: Basket# 3096587, 3100357, 3100369

5 - ZnPhos/Cr6+ M1 Fuel Caps: Basket# 3095674, 3089137, 3096764

1 - ZnPhos/SurTec 580 Cupola: Basket# 3092341, WBS Code 10MFE001-K0

Once the parts were completed, the path taken for reassembly is monitored by Mr. Jeb Nabors. Therefore, all tracking of processed parts was attempted through Jeb Nabors, email: jeb.nabors@us.army.mil, Systems Branch, DPM, Anniston Army Depot, PH: 256-240-3620

Parts that are immersion phosphated are typically "miscellaneous parts" and many cannot be tracked once they have left the depot. In discussions with ANAD, we were hopeful that the M1 fuel caps were substantial enough parts that they could be matched with a vehicle serial number and located for inspection. Unfortunately, that was not the case. Despite repeated efforts by ARL and ANAD, the parts that were fielded could not be located. Several parts were however, retained and brought back to ARL laboratories to evaluate the performance of the SurTec 580 against the baseline chromate sealer. These parts were assessed using the same success criteria: performance greater than or equal to the baseline system using Society for Protective Coatings' (SSPC) SSPC-VIS 2. Table 5-3 quantifies the degree of rusting on painted steel surfaces with a zero to ten scale based on percentage of visible rust present on the surface. Visible rust includes rust blisters and undercutting of the coating.

Table 5-3. SSPC-VIS 2 ratings for percent corrosion of painted surfaces

Rust Grade	Percent of Surface Rusted	Photographic Standard		
		Spot	General	Pinpoint
10	Less than or equal to 0.01 percent	NONE		
9	Greater than 0.01 percent to 0.03 percent	9-S	9-G	9-P
8	Greater than 0.03 percent to 0.1 percent	8-S	8-G	8-P
7	Greater than 0.1 percent to 0.3 percent	7-S	7-G	7-P
6	Greater than 0.3 percent to 1 percent	6-S	6-G	6-P
5	Greater than 1 percent to 3 percent	5-S	5-G	5-P
4	Greater than 3 percent to 10 percent	4-S	4-G	4-P
3	Greater than 10 percent to 16 percent	3-S	3-G	3-P
2	Greater than 16 percent to 33 percent	2-S	2-G	2-P
1	Greater than 33 percent to 50 percent	1-S	1-G	1-P
0	Greater than 50 percent	NONE		

6.0 PERFORMANCE ASSESSMENT

6.1 LABORATORY RESULTS

Candidate zinc phosphate sealers have undergone a comprehensive evaluation as determined by the JTP. The target substrate material for this demonstration is steel and therefore all tests were validated on two steel alloys: HHA and LCS.

Adhesion Performance:

The purpose of zinc phosphate as a base for paint is to enhance the adhesion of the primer and topcoat to the substrate. Figure 6-1, Figure 6-2, and Table 6-1 are indicators of adhesion provided by the zinc phosphated and sealed surface. Figure 6-1 contains pull-off strength and dry tape adhesion ratings on milled finish (63–125µ in) LCS surface. The success criteria for pull-off adhesion was set at 1200 psi. A 1200 psi threshold was selected because it represents the average pull-off strength achieved for DOD-P-15328 wash primer on LCS with a milled finish (63–125µ in) and was considered to be an ample pull off strength for an organic coating. All of the tested surface conditions shown in Figure 6-1 met the pull off strength criteria; therefore we must consider the dry adhesion tape test results overlaying the pull off results. This test was done IAW ASTM D3330 and ASTM D3359. Only the chromate seal met the tape test requirement of a 4B with both Chemical Agent Resistant Coating (CARC) systems. The Pittsburgh Plate Glass industries (PPG) Chemseal 100 met the requirement with the MIL-DTL-53022/ MIL-DTL-64159 paint system only, and was the only instance of a tape with greater than a 4B rating. A rating of 4B is required by TT-C-490F. As such, only the zinc phosphates with Chemseal 100 or the chromium seal would meet the success criteria for the QPD.

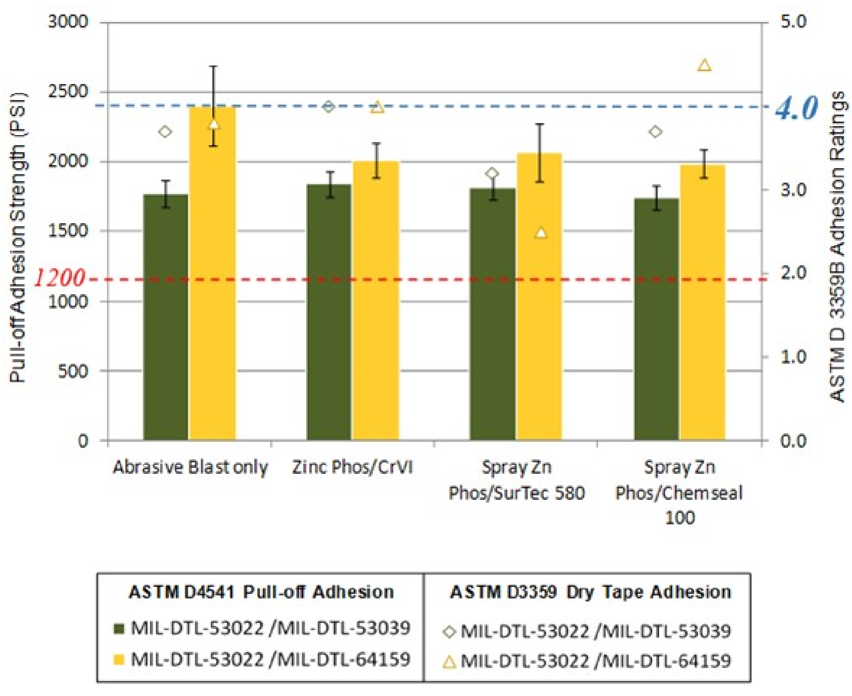


Figure 6-1. Pull-off and Dry Tape Adhesion Strength on Milled Finish LCS

All of the HHA test panels were abrasive blasted to remove mill scale. A surface finish of approximately 1.5 mils is expected to improve adhesion of all systems. This is typically how HHA surfaces are prepared in both production and during rework, so it is considered an accurate representation of HHA surfaces with zinc phosphate. Figure 6-2 is interesting in that the only samples to fail any of the adhesion tests were the panels that were only abrasive blasted without zinc phosphate and sealer. All passed the pull-off requirement, but it is clear that the phosphate surface improves adhesion regardless of the sealer used on abrasive blasted surfaces. All sealers met the performance objectives for adhesion on HHA.

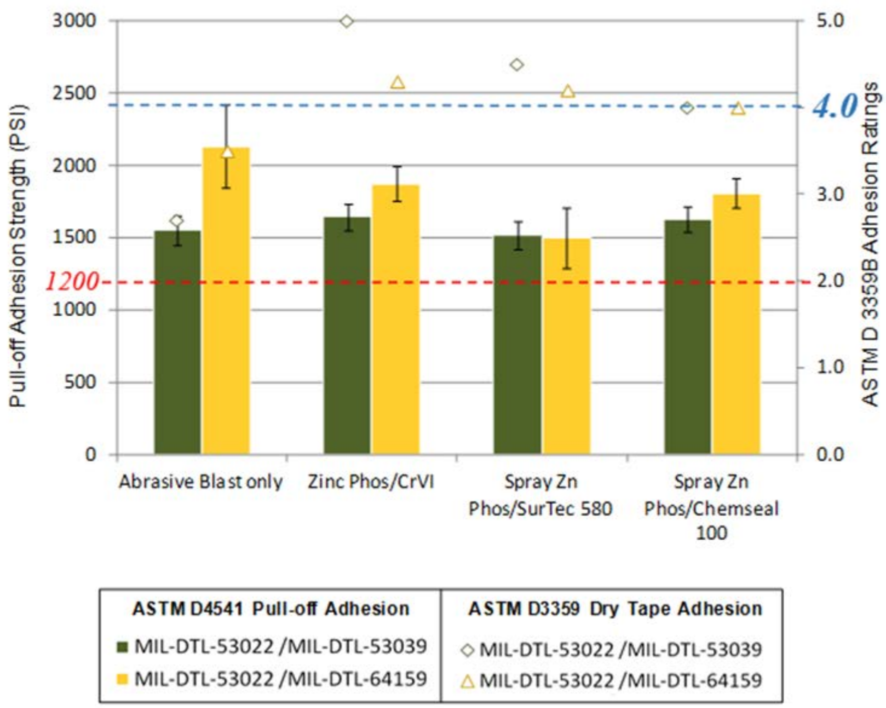


Figure 6-2. Pull-off and Dry Tape Adhesion Strength on Abrasive Blasted HHA

Wet adhesion tests were carried out IAW ASTM D3359 Method A's scribing technique, with the caveat that the specification did not prescribe water, temperature, or duration. The success criteria was derived using NAVAIR requirements. The wet tape adhesion test results are shown in Table 6-1. The success criterion here is a rating of 3A after 24 hours immersed in ambient DI water. All of the samples tested easily met the minimum 3A rating. The abrasive blasted surfaces with or without zinc phosphate provided the most consistent results. There is no specific requirement for wet tape adhesion testing for inclusion on the TT-C-490F QPD.

Table 6-1. ASTM D3359A Ratings for Wet Tape Adhesion for LCS and Abrasive Blasted HHA at 24 Hours Immersion

Surface Treatment	Low Carbon Steel		High Hard Armor	
	MIL-DTL-53022/ MIL-DTL-53039	MIL-DTL-53022/ MIL-DTL-64159	MIL-DTL-53022/ MIL-DTL-53039	MIL-DTL-53022/ MIL-DTL-64159
Abrasive Blasted only	5	5	5	5
Zinc Phos/Cr(VI)	4	5	5	5
Spray Zn Phos/SurTec 580	4	4	5	5
Spray Zn Phos/Chemseal 100	5	5	5	4

Another indication of proper adhesion is the ability of the coating system to resist chipping. This is particularly important for military ground vehicles that are navigated through rough terrain. Table 6-2 shows the results of the SAE J400 Gravelometer test for chip resistance. The pass criterion for chip resistance is a rating of 5B. The baseline chromate sealed zinc phosphate met the 5B requirement in three of the four systems. The LCS with MIL-DTL-53022/MIL-DTL-64159 was the only chromate sealed system rated below a 5B. Of the two alternative sealers, the Chemseal 100 provided the best chip resistance with 5B/A ratings on LCS. When compared with the baseline, both alternatives performed relatively well and provided adequate adhesion and chip resistance. However, in terms of meeting the performance objectives for chip resistance, the sealers vary by application. SurTec 580 met the objective on HHA with the MIL-DTL-53022/MIL-DTL-53039 CARC system, while Chemseal 100 did better on LCS. None of the sealers, including the baseline, exceeded the performance objectives. Therefore, it could be argued that a 4B may be a sufficient threshold for chip resistance on a non-abrasive blasted surface. There is no specific requirement for chip resistance testing in TT-C-490F.

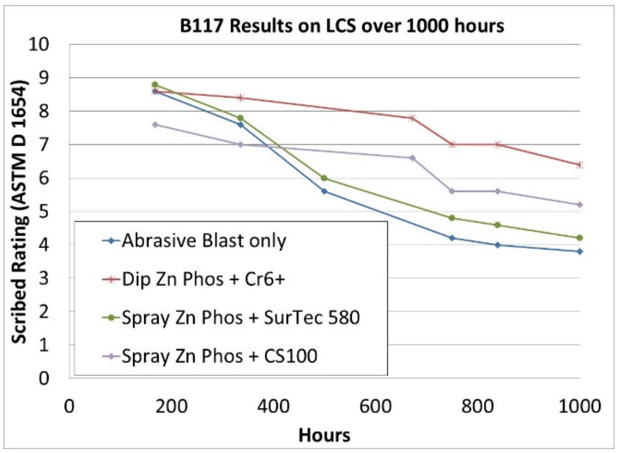
Table 6-2. Chip Resistance of Pretreatments on Abrasive Blasted HHA Steel

Surface Treatment	Milled Finish Low Carbon Steel				Abrasive Blasted High Hard Armor			
	MIL-DTL-53022/ MIL-DTL-53039		MIL-DTL-53022/ MIL-DTL-64159		MIL-DTL-53022/ MIL-DTL-53039		MIL-DTL-53022/ MIL-DTL-64159	
Abrasive Blasted Only	4	B	4	B	6	A/B	5	B/A
Dip Zinc Phosphate/Cr6+	5	B	4	B	5	B	5	B/A
Spray Zinc Phos/Surtec 580	4	B	4	B	5	B	4	B/A
Spray Zinc Phos/Chemseal 100	5	B/A	5	B/A	4	B/A	4	B

Accelerated Corrosion:

Only test panels coated with CARC system MIL-DTL-53022/MIL-DTL-53039 were tested in ASTM B117. The primary mode of failure for all of the test panels was creepage from the scribe. The ratings of five replicates of each pretreatment were averaged and presented in Figure 6-3. The success criterion for salt fog test is a scribed rating of ≥ 6 IAW ASTM D1654 Method A after 500 hours of exposure. The requirement for ASTM B117 testing required by TT-C-490F for steel is a rating of ≥ 6 at 336 hours. Each system tested met the success criteria for TT-C-490.

At 500 hours of exposure, all of the alternatives met this performance objective. The SurTec 580 just achieved a rating 6.0 on LCS at 500 hours. Beyond that, the SurTec 580 provided slightly more protection for the LCS panels that were abrasive blasted. The SurTec 580 performed far better on the abrasive blasted HHA panels. In Figure 6-3, the SurTec 580 performed as well as the chromate sealer throughout 1000 hours of exposure. On the abrasive blasted HHA, the SurTec 580 and Chemseal 100 easily met the success criterion. After all samples completed 1000 hours, they were scraped with a 2-in putty knife before the final measurements were made.



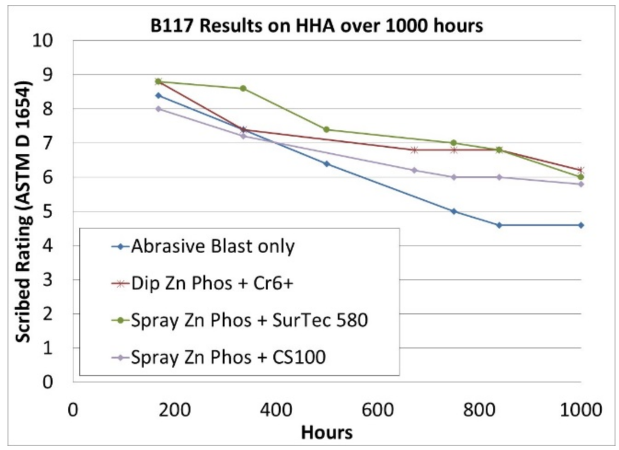


Figure 6-3. ASTM D1654 Ratings for LCS (left) and HHA (right) Panels through 1000 Hours of ASTM B117 Salt Fog Exposure

Sets of panels with two CARC coating systems, MIL-DTL-53022 / MIL-DTL-53039 and MIL-DTL-53022 / MIL-DTL-64159 were tested in GM 9540P cyclic corrosion on LCS and HHA. Replicates of three were used for the GM 9540P tests for each pretreatment and baseline.

A summary of the GM9540P tests ratings are presented in Table 6-3. The success criterion is an average ASTM D1654 Method A rating of ≥ 4 for "X" scribed panels after 60 hours of exposure.

The abrasive blasted only samples, also known as direct-to-metal, are clearly inferior to those prepared with zinc phosphate when coated with paint. None of the direct-to-metal panels could meet the success criterion of ≥ 4 rating at 60 cycles. All of the zinc phosphate panels outperformed the direct-to-metal with both paint systems on both substrates. The baseline chromate sealed zinc phosphate panels met the success criterion on only three of the four substrate/coating combinations, failing on the LCS with MIL-DTL-53022 / MIL-DTL-53039. Success is determined after 60 cycles, because 80 cycles of GM9540P is a challenging metric for even a chromated zinc phosphate to endure without the benefit of an abrasive blasted surface.

The test was carried out to 80 cycles before scraping the panels for a final rating. Representative test panels are shown in Figure 6-4 and Figure 6-5 to illustrate the performances of the alternatives vs. the baseline chromate sealer. Although the ASTM D1654 rating numbers are the success criteria, the creepage measurements are taken at several selected areas, but the majority of the coating around the scribe may still be well adhered. For example, in Figure 6-4 the Chemseal 100 sample failed primarily in the lower half of the panel, while the SurTec 580 showed more uniform corrosion along the scribe.

In Figure 6-4 on LCS, both outperformed the chromate phosphate in this case. In Figure 6-5, the low rating for SurTec 580 on LCS was due to the blister in the lower left corner of the panel. By comparison, this SurTec panel is obviously in better condition than the 0-rated chromate sealed panel in Figure 6-4. All of these photographs show that the alternatives performances were very comparable to the chromate, and in some cases, performed better. Note that there is no specific requirement for cyclic testing for inclusion on the TT-C-490F QPD for MIL-DTL-53022 Type II.

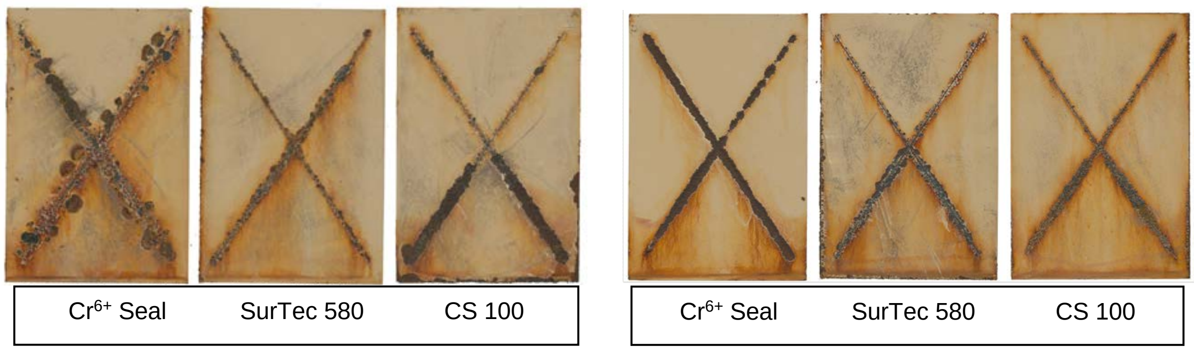


Figure 6-4. LCS (left) and HHA (right) with MIL-DTL-53022/MIL-DTL-53039, Scraped after 80 Cycles of GM 9540P Exposure

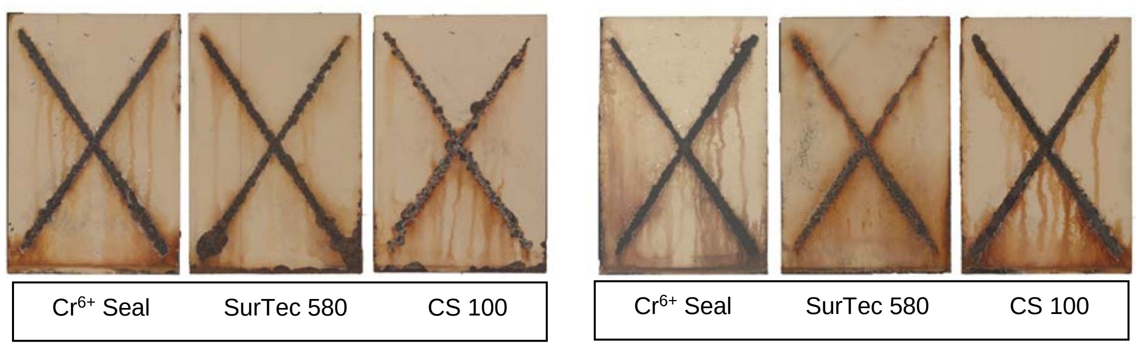


Figure 6-5. LCS (left) and HHA (right) with MIL-DTL-53022/MIL-DTL-64159, Scraped after 80 Cycles of GM 9540P Exposure

Table 6-3 is a summary of the average ratings for GM 9540P testing. This table illustrates how effective zinc phosphate is as a base for organic coatings. The abrasive blasted only (direct-to-metal) was not able to rate better than a 2.0 average. All of the alternatives and chromate outperformed the direct-to-metal on abrasive blasted and non-abrasive blasted surfaces. However, with the exception of the Chemseal 100, all benefited from the 1.5 mil profile provided by abrasive blasting prior to zinc phosphating. This shows that abrasive blasting coupled with zinc phosphate has superior performance in GM 9540P testing than each process individually.

Table 6-3. Summary of Average Ratings at 60 Cycles of GM 9540P Indicating Success Criteria

Pretreatment	MIL-DTL-53022/MIL-DTL-53039		MIL-DTL-53022/MIL-DTL-64159	
	LCS	HHA	LCS	HHA
Abrasive Blast Only	1.7	1.3	1.0	2.0
Dip Zn Phos/Cr6+	3.0	6.0	4.3	5.0
Spray Zn Phos + SurTec 580	4.3	4.7	2.7	6.0
Spray Zn Phos + Chemseal 100	4.7	5.7	4.3	3.0

Outdoor Exposure:

As previously discussed in section 3.0, the success criteria of 25% less creepage from the scribe was modified because this technology area seeks to “replace” the existing technology rather than provide an additional level of protection. For this reason, the success criteria is to meet or exceed the performance of the baseline hexavalent chromium sealer after three years of outdoor exposure at the Cape Canaveral corrosion test site. Inspections and ratings were conducted at three years and those results are presented in Figures 6-6 and 6-7. The photographs of the representative test panels in Figures 6-6 and 6-8 help illustrate the overall performance of the candidates versus the baseline. In almost all cases, the alternatives SurTec 580 and Chemseal 100 met or exceeded the performance of the chromate seal. Figure 6-7 is a side-by-side bar chart rating comparison on LCS. SurTec 580 and Chemseal 100 provided better corrosion protection over the three years and were more consistent from panel to panel which is indicated by a significantly lower standard deviation.

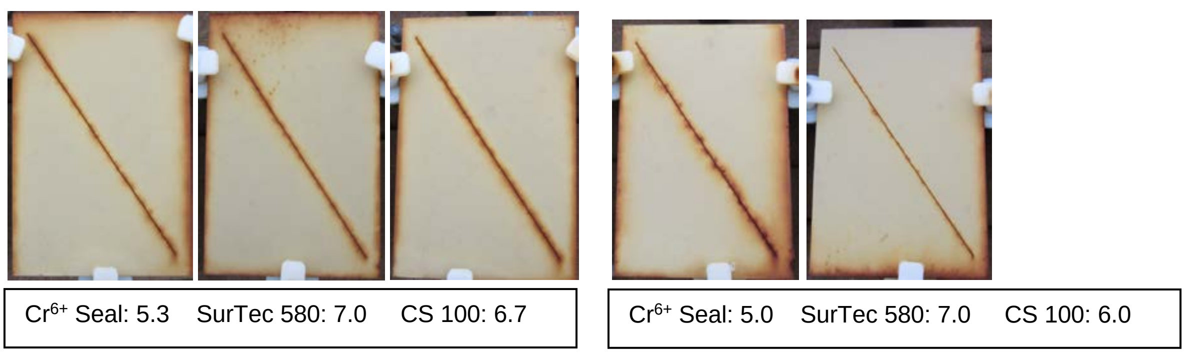


Figure 6-6. LCS Panels with MIL-DTL-53022 Primer and MIL-DTL-53039 (left) and MIL-DTL-64159 (right), with Ratings Indicated after Three Years in Outdoor Exposure at Cape Canaveral FL

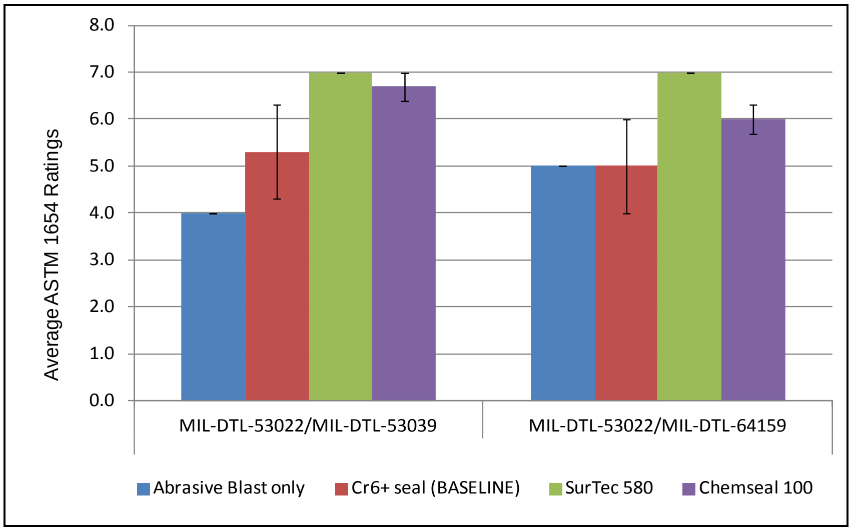


Figure 6-7. ASTM D1654 Ratings with Standard Deviation for LCS after Three Years in Outdoor Exposure at Cape Canaveral FL

The abrasive blasted HHA panels in Figure 6-8 (left) show the only case where the alternative sealers did not exceed the performance objective set by the chromate baseline. However, one can clearly see that the performances were actually comparable with all rating a 7.0 or higher. The standard deviation of a 0.6 for the chromate set indicates that the alternatives performed as well as, and perhaps more consistently, than the chromate. For this reason, the performance objectives are considered met for both alternative sealers used on abrasive blasted HHA with the MIL-DTL-53022/MIL-DTL-53039 coating system. It is more evident in Figure 6-8 (right) that both alternatives met the performance objectives by exceeding the performance of the chromate sealed panels. More importantly, over the three years of outdoor exposure at Cape Canaveral, both alternatives, SurTec 580 and Chemseal 100 exceeded the performance objective of the chromate in three of the four cases reported here. Only abrasive blasted HHA panels with MIL-DTL-53022/MIL-DTL-53039 (Figure 6-9) failed to exceed, but still met, the objectives. The requirement for outdoor exposure testing for inclusion on the TT-C-490F QPD for steel is a rating of ≥ 6 at 2 years. As such, each system tested met the success criteria for the QPD.

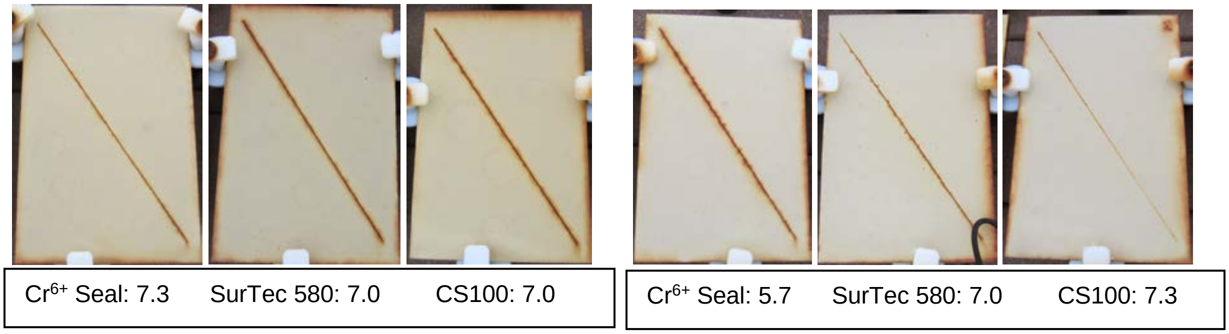


Figure 6-8. Abrasive Blasted HHA Panels with MIL-DTL-53022 Primer and MIL-DTL-53039 (left) and MIL-DTL-64159 (right), with Ratings Indicated after Three Years in Outdoor Eposure at Cape Canaveral FL

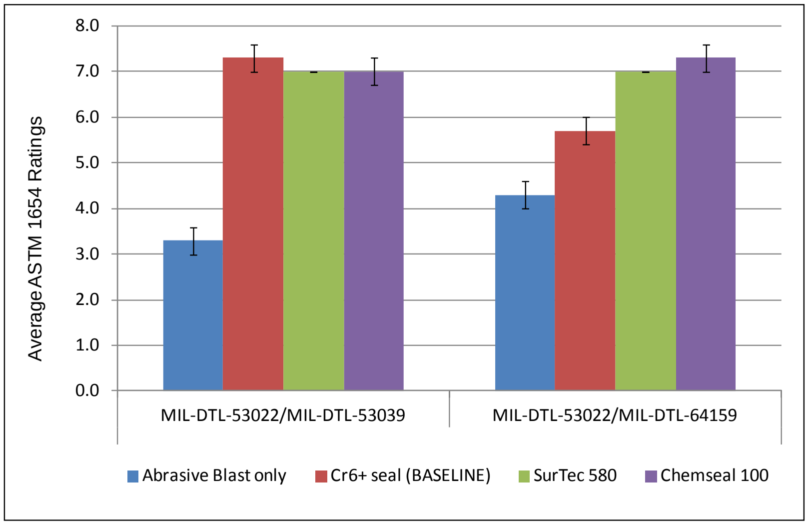


Figure 6-9. ASTM D1654 Ratings with Standard Deviation for HHA after Three Years in Outdoor Exposure at Cape Canaveral FL

Hydrogen Embrittlement:

It is important to determine if either of the proposed sealers would have a detrimental effect on the HHA resistance to EAC. The K_IEAC results were measured using the rising step load method. When the empirical data for K_IEAC was analyzed and compared with that found in the literature for MIL-A-46100, it is clear that the alternatives had no influence on the MIL-A-46100 resistance to EAC.[9,10] All values fell well within the historic K_IEAC range of 17-23 K_IEAC.[11]

6.2 COMPONENT DEMONSTRATION RESULTS

This section discusses the results of the demonstration in a full scale production environment. The demonstration required no major capital investment. The manufacturers of the SurTec 580 were consulted and provided recommended parameters for the application of their product. Step-by-step instructions for mixing the concentrate and the operating parameters were provided to ARL, and SurTec technical representatives were on site at ANAD to guide the process. As previously mentioned, the SurTec 580 is essentially a drop-in replacement for the chromic acid solution used at ANAD. Therefore, no changes to the existing zinc phosphate line were necessary. A separate sealing tank was set up adjacent to the phosphate line and parts. Panels proceeded through the traditional zinc phosphating process and then were redirected to the SurTec 580 tank for sealing. The zinc phosphating process that was performed at ANAD including the modifications suggested by SurTec International is as follows:

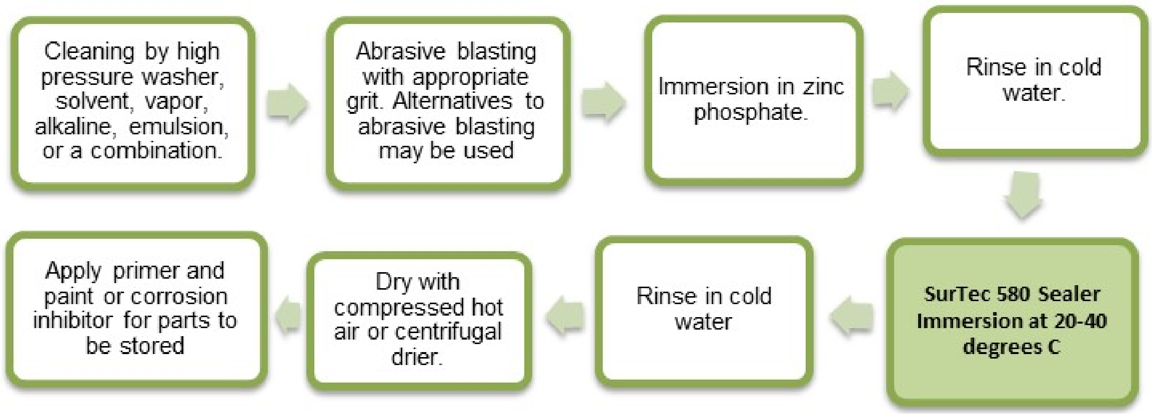


Figure 6-10. ANAD phosphate Process with SurTec 580 Modification

Representative parts and test panels were retained and brought back to ARL for validation tests. The primary example of the parts tested is in Figure 6-11. These are two of the M1 fuel caps shortly after being zinc phosphated, sealed, and following the application of the CARC system MIL-DTL-53022 / MIL-DTL-53039. For consistency, the fuel caps remained together throughout the process with the exception of the sealing step.

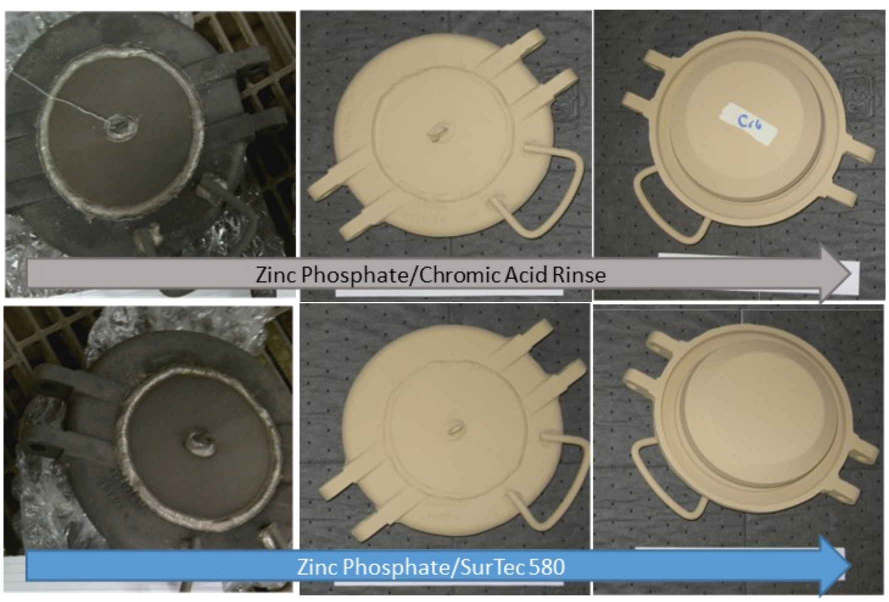


Figure 6-11. Phosphated, Sealed, Primed and Top-coated with CARC System at Anniston Army Depot

The largest parts treated in the demonstration were the cupola rings for Stryker. Figure 6-12 shows two cupola rings treated with SurTec 580 each having a slight variation in the rinse process. The cold water rinse resulted in flash rusting, while the hot water flashed off quicker which reduced the likelihood of corrosion. Although the cold water rinse was adequate for processing smaller parts such as the fuel caps, larger parts with complex geometries should be rinsed using hot water.

Figure 6-12. Close Up View of the Cupola.

On the left shows flash rust when cold rinsed and no flash rusting when hot rinsed

Figure 6-13 and Figure 6-14 show the accelerated corrosion test results for test panels processed at ANAD along with the demonstration parts (Figure. 6-15). In each case, the SurTec 580 met or exceeded the baseline chromate seal. All three panel sets are essentially different substrates. The steel panels in Figure 6-13 were provided by ANAD and represent the test panels they use for periodic measurements of phosphate weights, while the other two sets were provided by ARL and are identical to the substrates used in the laboratory evaluations. The results here are also consistent with accelerated corrosion testing of the laboratory prepared samples reported earlier in Section 6.0. One example is the poor performance of the chromate panel shown in Figure 6-14 (2.0 rating) mimics the performance observed for same substrate/coating stack-up seen on previous panels.

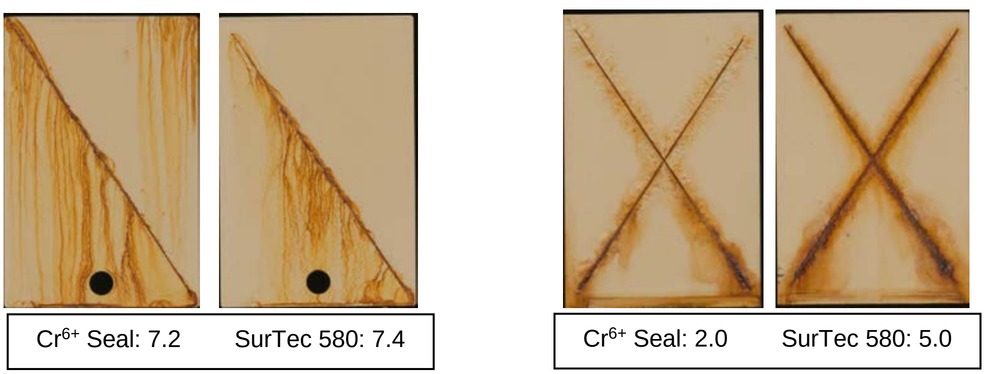
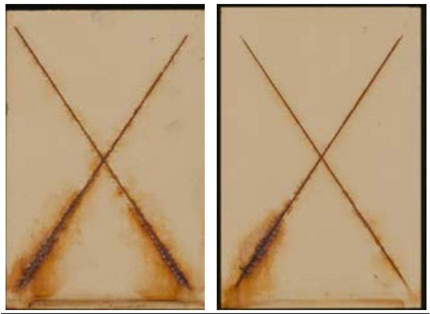


Figure 6-13. Representative Steel Test Panels from ANAD. Single Diagonal Scribe Panels Tested through 1008 Hours of ASTM B117 Salt Spray.

"X" scribed panels tested 60 cycles of GM 9540P Captions contain the ASTM D1654 rating

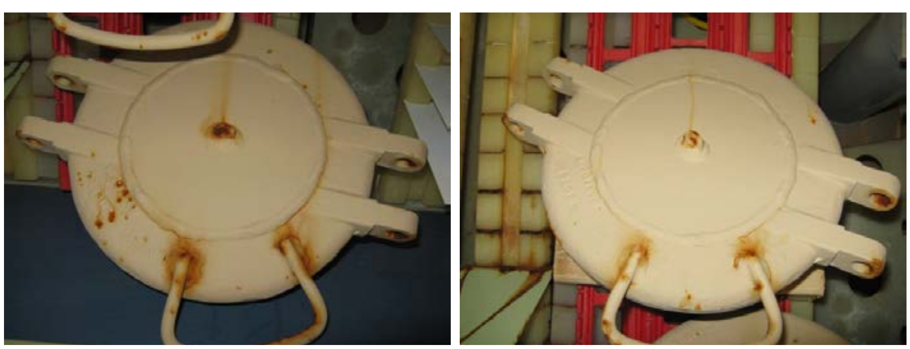


Cr^{6+} Seal: 6.0 SurTec 580: 6.0

Figure 6-14. Representative HHA Steel Panels after 60 Cycles of GM 9540P Cyclic Corrosion Test.

Captions contain ASTM D1654 rating

Two of the fuel caps processed at ANAD were brought back the ARL Rodman Laboratory for further testing. The intent was to validate the laboratory results using actual components on platforms in the field as well as using laboratory tests. Figure 6-15 shows the components tested at ARL. One chromate sealed fuel cap was compared with one that was sealed with SurTec 580. Prior to exposing the caps to the GM 9540P test chamber, pull off adhesion was performed. The adhesion strength for the SurTec 580 sealed cap was nearly identical to the chromate cap. Both measured in excess of 1670 psi and within 2 psi of each other (1672 psi and 1674 psi). Both fuel caps then completed 60 cycles of cyclic corrosion tests. Examining the caps in Figure 6-15, one may conclude that the SurTec 580 provided better corrosion protection than the chromate. We understand that this is one component and the statistical sample is very small. However, when considering all of the data presented in this report, it is evident that the performance of the SurTec 580 overall is "comparable" to the chromate seal. Figure 6-15 and the results presented in Table 6-4 serve as validation for the laboratory and outdoor exposure results compiled thus far. In each case, the SurTec 580 met or exceeded the performance of the baseline and met the performance objectives stated in Table 3-1.



Cr^{6+} seal: 4-S rating SurTec 580: 6-S rating

Figure 6-15. Representative M1 Armor Steel Fuel Caps after 60 Cycles of GM 9540P Cyclic Corrosion Test with SSPC-VIS 2 Ratings

Table 6-4. Summary of Average ASTM 1654 Ratings after 60 Cycles of GM 9540P Exposure

QTY	Substrate	Sealer	Average Rating
4	Steel (ANAD)	Chromate	7.2
4	Steel (ANAD)	SurTec 580	7.4
3	LCS	Chromate	2.0
2	LCS	SurTec 580	5.0
3	HHA	Chromate	6.0
2	HHA	SurTec 580	6.0
1	Fuel Cap	Chromate	4-S*
1	Fuel Cap	SurTec 580	6-S*

*Corrosion of the irregular surface of the fuel cap was estimated using SSPC-VIS 2 (Table 5-3)

In order to mimic a rework scenario, follow-on tests were conducted using the same fuel caps. Each of the fuel caps was reworked by abrasive blasting the corroded areas to bare metal while the well adhered coated areas were left intact. Both fuel caps were pretreated differently and subsequently primered and painted using the CARC system MIL-DTL-53022 / MIL-DTL-53039. The fuel cap that was previously zinc phosphated and sealed with chromate was pretreated with DOD-P-15328 chromated wash primer (Figure 6-16, left). The fuel cap that was previously zinc phosphated and sealed with SurTec 580 was pretreated with Oxsilan 9810/2 (Figure 6-16, right). The Oxsilan 9810/2 was one of the products demonstrated as part of WP-200906 [12] and added to the TT-C-490 QPD. Once the coatings were fully cured, both caps were subjected to GM 9540P testing. After only 40 cycles, the chromated wash primer cap was noticeably more corroded than the one pretreated with Oxsilan 9810/2. Although this was rather anecdotal, it was interesting to see that the combination of the two alternatives (SurTec 580 sealed zinc phosphate / Oxsilan 9810/2) held up better that a double treatment of chromate (chromate sealed zinc phosphate / DOD-P-15328).

Figure 6-16. Reworked M1 Armor Steel Fuel Caps after 40 Cycles of GM 9540P Cyclic Corrosion Test.

The primary and secondary performance criteria evaluated in a production setting during the demonstration are listed in Table 6-5, while the metrics for evaluating the SurTec 580 sealer are described in the JTP. The metric for evaluating the fuel caps during the field inspections is a visual comparison with the base vehicle using the SSPC-VIS-2 "Standard Method for Evaluating the Degree of Rusting on Painted Steel Surfaces." The success criteria for the fielded fuel caps is performance greater than or equal to that of the baseline phosphate system, as well as the results of a separate test of the parts that are treated and subjected to accelerated corrosion testing at ARL-Aberdeen Proving Grounds. Any fielded demonstration parts located for inspection and assessed as "failed" will be field repaired using a CARC field repair kit developed by ARL and placed back in service.

Table 6-5. Validation methods and expected performance metrics

Performance Criteria	Expected Performance Metric (Pre-Demonstration)	Performance Evaluation Method	Actual Performance (Post-Demonstration)
Primary Performance Criteria			**SurTec 580**
Product Testing	Alternative technology will meet or exceed the current technology at ANAD defined in the JTP	Laboratory results of demonstration components from ANAD	Met
		Field Testing*	N/A
Hazardous Materials	Maintains a hexavalent chromium free platform	Assessment of product constituents and previous studies	Met
Hazardous Waste	Meets or exceeds current process used at ANAD	Operating experience and assessments	Met
Factors Affecting Technology Performance	Comparison of alternatives in identical operating conditions	Operating Experience	Met
Secondary Performance Criteria			
Ease of Use	Man hours and training shall be equivalent to current process.	Operating experience	Met
Maintenance	Requirements for record keeping for storage, and clean up shall be equivalent to current process	Compare records	Met
Scale up capability	Identify additional equipment, if any, necessary to scale up process for full vehicle treatment.	Operating experience and investigation	Met

* Data not available. Despite repeated efforts by ARL and ANAD, the parts that were fielded could not be located.

Page Intentionally Left Blank

7.0 COST ASSESSMENT

This project is unique in that it has three technology areas being demonstrated: Pretreatments for Armor Steel; Zero-Volatile Organic Compound Topcoats for Ground Support Equipment; and Non-Hexavalent Chromium Sealers for Zinc Phosphate. It would be cost prohibitive and time consuming to conduct a comprehensive cost assessment on all of the technology areas. An attempt was made earlier in the project to conduct the cost analysis during the Mine Resistant Ambush Protected Armored Vehicles demonstration at Camp Lejeune, but events occurring during the demonstration prevented us from making a reasonable cost and performance assessment. Therefore, an economic and environmental impact study was performed for this demonstration by Dr. Keith Legg of Rowan Technology Group and presented here.

Technology

Zinc phosphate coatings are sealed with a dilute chromic acid passivate. The alternative tested in this program is a non-chromate product, SurTec 580, a derivative of the trivalent chromium Zr passivated NAVAIR TCP chemistry. The primary processing differences are:

1. Chromic acid is applied at 175 -200°F, while the alternative is applied at ambient temperature.
2. The alternative requires a post-process rinse not used for chromate. In some cases, a hot water spray rinse may be used for a better visual appearance of the product, but this is not a standard process requirement.
3. The chromate tank requires ventilation, but no additional personal protection equipment beyond rubber gloves and aprons.

The chromic acid process in Figure 4-1 is compared with the alternative SurTec 580 process in Figure 2-1.

Cost Benefit

The costs for the two processes are compared in Table 7-1. This table shows the primary costs. Costs that are unaffected or largely unchanged are not included in the analysis. It is immediately clear that the primary difference in cost comes from the difference in bath temperatures.

Table 7-1. Cost Factors – Chromic Acid Seal versus SurTec 580

Direct Manufacturing	Annual or Per-item cost Chromate	Annual or Per-item cost SurTec 580	Notes
Chemicals			
Tank volume	2,400	2,400	
percentage sealer required (wt%)	0.03%	1.5%	
Total volume of chemical requirement to fill tank	6.00	36	
Chemical cost per gal	$ 1.10	$ 25.00	
Bath replenishment chemical volume	$ 6.61	$ 900.00	
Dragout rate	1	1	
Dragout losses, annual	2,000	2,000	
Bath replenishment chemical frequency			
Annual chemical usage	$ 6.61	$ 900.00	
Annual water usage for plating			
Utilities			
Bath temperature, mid-range (deg F)	175	85	
Evaporation rate (l/hr)	81.7	4.56	
Evaporation rate (l/year)	715,692	39,946	
Makeup water cost	$ 379	$ 21	
Evaporation energy (kWh/year)	515,298	0	SurTec is ambient
Bath heating cost (steam)	$ 30,918	$0	SurTec is ambient
Bath heating cost (electrical)	$ 36,071	$0	SurTec is ambient
Labor			Same
Indirect Manufacturing			Same
Environmental and Health Costs			
Regulatory compliance			Minimal change
Pollution prevention equipment			Minimal change
Worker health			Minimal change
Waste management			Minimal change
Adoption Costs for New Technology			
Additional equipment			
Drain and dispose of chromate		$ 1,000	
Tank cleaning and liner replacement		$ 1,000	
Recharge with SurTec 580		$ 900	
Control equipment, filter			Probably not needed
Paperwork changes			Unknown
Year 1 cost	**$ 31,303.82**	**$ 3,821.17**	
Annual cost (steam heat)	**$ 31,303.82**	**$ 921.17**	

The high temperature chromic acid bath must be maintained at temperature 24 hours a day/7 days a week. During this time water is evaporated and makeup water must be added. The evaporation rate depends on temperature, bath surface area and air flow rate over the water surface. The evaporation rate for the two baths was calculated using the National Metal Finishing Resource Center Plating Tank Evaporation Calculator.[13] This makeup water must be raised to bath temperature. The evaporating water carries off latent heat of vaporization, which must also be replaced to maintain bath temperature. Since the SurTec 580 bath operates at ambient, it only requires water replenishment (to compensate for evaporation and dragout), not water heating. This calculation is shown in Table 7-2.

The annual saving is strongly dependent on the chromate bath temperature used and the efficiency of the heating system. Baths are usually steam heated by steam piped throughout the plant. If the energy conversion and transmission efficiency were both 100%, the cost would be very low. If the efficiency is in the region of 50% for converting gas thermal energy to water thermal energy, and about 50% for transmission and bath heating (overall thermal efficiency 25%), this makes gas 10–15% lower in cost than electrical immersion heating, which is close to 100% efficient (Figure 7-1).

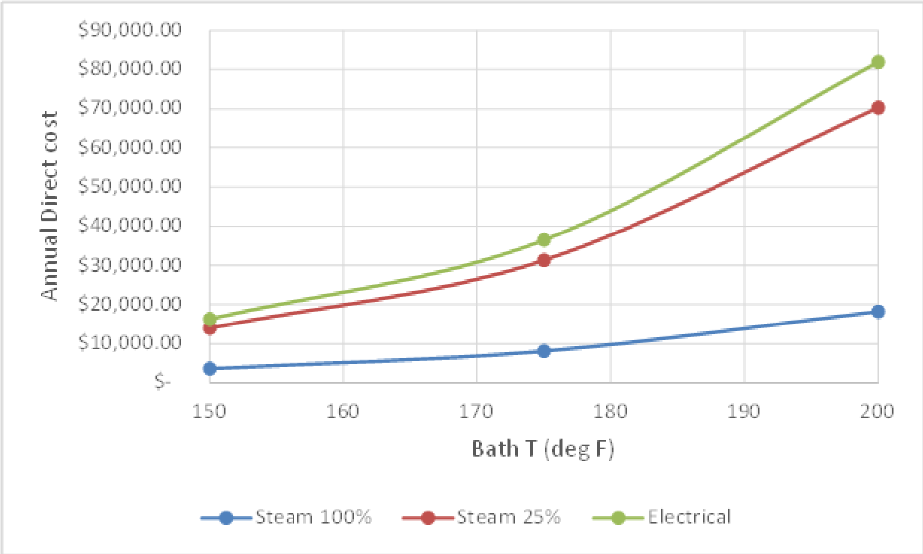


Figure 7-1. Direct Cost of Chromate Processing as Function of Bath Temperature and Heating Efficiency

Assuming gas heating with overall efficiency of 25% (very similar to electrical heating), the annual saving achieved by replacing chromic acid passivation with SurTec 580 is about $30,000/year. This produces a 15-year net present value of $270,600, with an immediate payback since the changeover will cost only $3,000 plus any costs for changes to paperwork, local specs, and the cost of disposing of the chromic acid in the bath to the base publically owned treatment work. Since there is no capital cost and the adoption is so low, the annualized return on investment is about 1,000%, making measures such as return on investment and internal rate of return essentially meaningless. The annual cost saving and the net present value roughly double if the chromate bath typically operates at the upper end of its range (200°F), and are roughly halved if it typically operates at the lower end (150°F).

Table 7-2. Calculation of Evaporation and Water Usage

Item	Amount	Units	Chromic acid	SurTec 580	Units	Notes
Bath dimensions						
width	60	inch	152	152	cm	approx
height	40	inch	102	102	cm	approx
length	240	inch	610	610	cm	approx
Bath liquid volume	2,400	gal	9,120	9,120	liters	
Surface area	14,400	in2	92,903	92,903	cm2	
Temperature			175	85	deg F	Cr 150-200, SurTec 70-104
Air flow velocity						Not known
Water balance	Amount	Units	Chromic acid	SurTec 580	Units	
Evaporation rate (avg T)			81.7	4.56	l/hr	http://nmfrc.org/subs/evapcalc.cfm
			715,692	39,946	l/yr	
Water makeup cost	0.0005263	$/l	$377	$21	per yr	
85F				4.56	l/hr	
150F			36.48		l/hr	
175F			81.7		l/hr	
200F			183.54		l/hr	
Dragin and dragout rate						Not known
Energy balance						
Heat	0.09	kWh/l				Heat makeup water 60 to 175F
Evaporation	0.63	kWh/l				Evaporate at 175F
Heat + Evaporation	0.72	kWh/l	58.64		kW	power to replace evaporation
Evaporation power/year			5.1E+05		kWh	power to replace evaporation/year
Natural gas heating cost			$ 7,706		per year	Natural gas heating plant
Cost inc energy efficiency	Steam 25%		$ 30,822		per year	50% generation and 50% transmissions losses
Electrical heating cost			$ 35,960		per year	100% efficiency for immersion heater
Heat loss from surface						Small
Heat loss from walls						Small
Heat loss from parts						Small
Chemical balance						
Initial charge Surtec 580	1.5%			136.8	kg	
	$ 6.60	/liter		$903		Total cost for tank charge
Initial charge CrO3	0.03%		2.7		kg	
	$ 2.22	per kg	$ 6.08			Total cost for tank charge
Annual chemicals			$ 6.08	$903		One bath turnover/year

8.0 IMPLEMENTATION

The implementation of non-hexavalent chromium sealers for zinc phosphate will be expedited by the recent publication of the reconstructed Federal specification TT-C-490F. This specification has been the overarching document referenced in dozens of military coating specifications and tens of thousands of military drawings for the cleaning and pretreatment of (only) ferrous substrates 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. However, major technical gaps existed in this specification that motivated significant changes. First, previous versions of TT-C-490 continued to specify the use of hexavalent chromium in surface finishing although hexavalent chromium has been targeted for elimination for years. With many other specifications that continue to require hexavalent chromium usage, there was no official mechanism to validate, approve and implement alternative surface finishing operations except through contract waivers, drawing changes and engineering change notices, which can be an expensive and a cumbersome process. Also, no comprehensive specification existed governing the cleaning and pretreatment of DoD relevant metallic and multi-metal substrates.

ARL recognized the synergy that existed between the TT-C-490 reconstruction and this effort on alternative steel pretreatments and sealers for zinc phosphate. Several of the candidates evaluated were found to at least achieve the performance requirements, and in some cases, exceed the performance of existing hexavalent chromium pretreatments. With this improved testing regimen, ARL can transition pretreatments and sealers that meet ARL's established performance criteria into use 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.

The revised TT-C-490 includes new Types and Classes and ties them to specific cleaning methods to accommodate steel, aluminum and multi-metal substrates as well as corrosion resistant metal-rich coatings. It has been adopted by entire DoD and beyond (i.e., industry) for surface finishing of alloys. The U.S. Army Tank-automotive & Armaments Command (TACOM) has adopted the language and principles of Objective Quality Evidence in the new TT-C-490F specification, and has begun placing it in their Procurement Automated Data and Document System (PADDS clause) for pretreatments and CARC on all new contract requirements that require all DoD and DoD contractors to follow the doctrine of the newly revised TT-C-490F specification.

The QPD has been populated by two of the products evaluated in WP-200906: SurTec 650 and Oxsilan 9810/2. These two spray applied pretreatments have been approved for abrasive blasted steel substrates. Additionally, SurTec 580, the product demonstrated in this report, has met or exceeded the success criteria and a letter of compliance was issued in 2015 to SurTec for the 580 product.

Page Intentionally Left Blank

9.0 REFERENCES

1. TT-C-490 Cleaning Methods for Ferrous Surfaces and Pretreatments for Organic Coatings.

2. MIL-DTL-16232, Detail Specification: Phosphate Coating, Heavy Manganese or Zinc Base.

3. MIL-DTL-53072: U.S. Department of Defense, "Chemical Agent Resistant Coating (CARC) System Application Procedures and Quality Control Inspection", Washington, DC, June 2003.

4. Non-Chromate/No VOC Coating System for DoD Applications, Strategic Environmental Research and Development Program (SERDP) final report March 31, 2009, Dr. John LaScala, US Army Research Laboratory.

5. MIL-DTL-0053022: "Primer, Epoxy Coating, Corrosion Inhibiting, Lead and Chromate Free," U.S. Department of Defense, Washington DC, January 2007.

6. MIL-DTL-53039: "Coating, Aliphatic Polyurethane, Single Component, Chemical Agent Resistant," U.S. Department of Defense, Washington DC, June 2005.

7. MIL-DTL-64159 Chemical Agent Resistant Coating (CARC), polyurethane, water dispersible.

8. Examination of Alternative Pretreatments to Hexavalent Chromium-Based DOD-P-15328D Wash Primer for MIL-A-46100D High Hard Steel Armor, Brian E. Placzankis, Chris E. Miller, and John V. Kelley.

9. Herman, W. A.; Campbell, G. M. Environmental Assisted Cracking in High Hardness Armor Steel. TR-85-28; U.S. Army Materials and Mechanics Research Center: Watertown, MA, 1985.

10. Herman, W. A.; Campbell, G. M. Environmental Assisted Cracking in High Hardness Armor Steel. TR-85-28; U.S. Army Materials and Mechanics Research Center: Watertown, MA, 1985.

11. Herman, W. A.; Campbell, G. M. Environmental Assisted Cracking in High Hardness Armor Steel. TR-85-28; U.S. Army Materials and Mechanics Research Center: Watertown, MA, 1985.

12. Jack Kelley, Tom Braswell, "Non-Chromate, ZVOC Coatings for Steel Substrates on Army and Navy Aircraft and Ground Vehicles: Technology Area 1-"Demonstration of Steel Pretreatments on High Hard Armor Steel" Army Research Laboratory, ESTCP Project 200906 Final Report, 2014.

13. Available at http://nmfrc.org/subs/evapcalc.cfm

Page Intentionally Left Blank

APPENDIX A POINTS OF CONTACT

Point of Contact Name	Organization Name Address	Phone Fax Email	Role in Project
Jack Kelley	US Army Research Laboratory B4600 Deer Creek Loop Aberdeen Proving Ground MD	PH: 410-306-0837 FX: 410-306-0829 BB: 240-429-8485 jkelley@arl.army.mil	Project Lead
Tom Braswell	US Army Research Laboratory B4600 Deer Creek Loop Aberdeen Proving Ground MD	PH: 410-306-0935 FX: 410-306-0829 Thomas.e.braswell@arl.army.mil	Testing, and Specifications
Amy Fowler	NAVAIR, Code 4.3.4.2 48066 Shaw Road, Bldg. 2188 Patuxent River, MD 20670	PH: 301-342-0986 FX: 301-342-7566 amy.fowler1@navy.mil	Navy Co-Performer
Luwam Hagos	NAVAIR, Code 4.3.4.2 48066 Shaw Road, Bldg. 2188 Patuxent River, MD 20670	PH: 301-342-8159 FX: 301-342-8062 luwam.hagos@navy.mil	Navy Co-Performer
Patricia Dodson	Patty Dodson Anniston Army Depot 7 Frankford Avenue Bld. 106 Anniston, AL 36201	Patricia.dodson@us.army.mil COMM: 256-235-6700	Coordinate demonstration at Anniston
Dr. Keith Legg	Rowan Technology Group 1590 South Milwaukee Ave., Suite 205 Libertyville, IL 60048	Telephone: 847-680-9420 FAX: 847-680-9682 klegg@rowantechnology.com	Cost Assessment

ESTCP Office
4800 Mark Center Drive
Suite 17D08
Alexandria, VA 22350-3605
(571) 372-6565 (Phone)
E-mail: estcp@estcp.org
www.serdp-estcp.org