



ARL-TR-8809 • SEP 2019



Examination of Non-Hexavalent Chromium, Low-Volatile Organic Compound (VOC) Alternative Sealers for MIL-DTL-13924D Black Oxide Coatings on Ferrous Substrates

by Thomas Considine, Jack Kelley, and Thomas Braswell

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Examination of Non-Hexavalent Chromium, Low-Volatile Organic Compound (VOC) Alternative Sealers for MIL-DTL-13924D Black Oxide Coatings on Ferrous Substrates

by Thomas Considine, Jack Kelley, and Thomas Braswell
Weapons and Materials Research Directorate, CCDC Army Research Laboratory

REPORT DOCUMENTATION PAGE

Form Approved
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1. REPORT DATE (DD-MM-YYYY) September 2019		2. REPORT TYPE Technical Report		3. DATES COVERED (From - To) 1 October 2015–27 August 2019	
4. TITLE AND SUBTITLE Examination of Non-Hexavalent Chromium, Low-Volatile Organic Compound (VOC) Alternative Sealers for MIL-DTL-13924D Black Oxide Coatings on Ferrous Substrates				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Thomas Considine, Jack Kelley, and Thomas Braswell				5d. PROJECT NUMBER WP-200906	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) CCDC Army Research Laboratory ATTN: FCDD-RLW-MC Aberdeen Proving Ground, MD 21005-5069				8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-8809	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) Office 4800 Mark Center Drive, Suite 16F16 Alexandria, VA 22350-3605				10. SPONSOR/MONITOR'S ACRONYM(S) SERDP-ESTCP	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Military specification MIL-DTL-13924, <i>Detailed Specification: Coating, Oxide, Black, for Ferrous Metals</i> , is the mainstay for finishing unpainted ferrous and stainless steel components for firearms, fasteners, tooling, and other mechanical components for the military. Black oxide coatings provide mild corrosion resistance and minimize light reflection. A chromic acid (Cr(VI)) post rinse is required for enhancing corrosion resistance of the coating. It has been known for quite some time that hexavalent chromium is a risk to both human health and the environment. In April 2009, a memo was released from the Office of the Secretary of Defense that specifically directed the military to approve the use of alternatives to Cr(VI) where they can perform adequately for the intended application and operating environment. This effort examines the efficacy of non-hexavalent chrome sealers and passivating rinses to replace the required chromic acid. A total of 11 candidates along with the baseline were tested. Four candidates demonstrated excellent overall performance and exceeded that of the baseline Cr(VI) rinse.					
15. SUBJECT TERMS black oxide, sealers, chrome, chromium, ferrous, steel					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 31	19a. NAME OF RESPONSIBLE PERSON Thomas Considine
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) 410-306-2564

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1. Introduction

Military specification MIL-DTL-13924, *Detailed Specification Coating, Oxide, Black, for Ferrous Metals*, is the established method for finishing unpainted ferrous and stainless steel components for firearms, tooling, and other mechanical components for the military. Likened to the commercial use of black oxide or blackening, which is a conversion coating for ferrous materials, stainless steel, copper and copper-based alloys, zinc, powdered metals, and silver solder, it is used to add mild corrosion resistance, for cosmetic appearance, and to minimize light reflection.

Black oxide is a conversion coating formed by a chemical reaction produced when steel alloy parts are immersed in an alkaline aqueous salt solution typically operated at 285 °F. The reaction between the iron within the ferrous alloy and the hot oxide bath produces magnetite (Fe_3O_4) on the surface of the part. Specification MIL-DTL-13924D¹ describes four classes of black oxide: Class 1) alkaline oxidizing process for wrought iron, cast and malleable irons, plain carbon, and low-alloy steels; Class 2) alkaline chromate oxidizing process for use on certain corrosion resistant steel alloys that are tempered at less than 900 °F (482 °C); Class 3) fused salt oxidizing process for corrosion-resistant steel alloys that are tempered at 900 °F (482 °C) or higher; and Class 4) alkaline oxidizing process for other corrosion-resistant steel alloys. Only Class 4 black oxide requirements are based on performance while Classes 1–3 have more subjective requirements. Additionally, black oxide Classes 1–3 specifically require a hexavalent chrome post treatment (sealer) to enhance corrosion resistance. This requirement for a hexavalent chrome-containing compound is currently driven by dated documents including parts drawings and contracts. Hexavalent chromium compounds (including chromium trioxide, chromic acids, and chromates) are toxic and carcinogenic.²

The Occupational Safety and Health Administration (OSHA) Final Rules effective May 30, 2006, Federal Register #71:10099-10385³ 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-h time-weighted average exposure limit of 5 μg of hexavalent chromium per cubic meter of air (5 $\mu\text{g}/\text{m}^3$). This is a considerable reduction from the previous PEL of 1 mg per 10 m^3 of air (1 $\text{mg}/10 \text{m}^3$, or 100 $\mu\text{g}/\text{m}^3$) reported as chromium trioxide (CrO_3), which is equivalent to a limit of 52 $\mu\text{g}/\text{m}^3$ as hexavalent chromium.

In April 2009, a memorandum from Office of the Secretary of Defense signed by Mr Young⁴ was released outlining a new policy for reducing the use of hexavalent

chromium for Department of Defense applications. The memorandum specifically directed the military to restrict the use of hexavalent chromium unless no cost-effective alternative with satisfactory performance has been identified.

This report summarizes a two-part effort: the first being to identify and validate effective alternative, non-hexavalent chrome sealers for black oxide and the second being to revise the existing MIL-DTL-13924 specification to enable pathways for implementation of non-hexavalent chrome sealers. Testing was performed on MIL-DTL-13924 Class 1, alkaline oxidizing for low-alloy steels, and Class 4, alkaline oxidizing for corrosion-resistant steels. MIL-DTL-13924 does not mandate a specific post-rinse/sealer for Class 4; therefore, experimental evaluations were performed to determine if an optimum sealer for Class 4 could be identified. These two classes were selected as they are the most prevalently represented classes in use by the US Army. As the testing for these classes is somewhat limited and subjective as presented in the specification, additional evaluations were performed beyond those required in order to fully prove out effective alternative sealers.

2. Experimental Procedure

2.1 Sample Preparation

The test panels were made from two substrates, AISI 1010 cold-rolled steel (CRS), and 304 stainless steel to represent MIL-DTL-13924 Class 1 and Class 4, respectively. In accordance with MIL-DTL-13924, all panels were racked to allow sufficient spacing for solution exposure and immersed into a hot alkaline detergent bath at approximately 150 °F for 10 min to remove all dirt and grease. The samples were then immersed into an ambient-temperature water bath to remove any detergent residue for 5 min. Without allowing the samples to flash off, they were immersed into the hot black oxide tank for approximately 30 min. Using the manufacturers' technical data sheets and guidance, sets of samples were rinsed and prepped with the 11 candidate alternative sealers and the baseline chromic acid rinse listed in Table 1. The exact chemical compositions are difficult to obtain because of proprietary issues, therefore Table 1 lists what is reported in the product safety data sheets.

Table 1 List of sealers and operating parameters used for preparing test specimens

MFG/Vendor	Sealer Name	Chemistry	Working Concentration	Dwell Time (seconds)	Recommended Operating Temperature	Test Sample Preparation Temperature	Working pH
Baseline	Chromic Acid Rinse	Chromic acid	0.06%	30	150°F - 190°F	180°F	2-3
SurTec Int	Surtec 555	Polymer based, aqueous, Cr free	10-15%	30	Ambient	Ambient	8.0
SurTec Int	Surtec 590	Mineral oil, emulsifiers, surfactants, aqueous based, Cr free	15%	30	Ambient - 190°F	Ambient	8.9
SurTec Int	Surtec 580	dihydrogen hexafluorozirconate(2-), chromium hydroxide sulphate, sodium sulphate, potassium tetrafluoroborate	1.5-2.0%	40	68°F- 104°F	Ambient	3.7-4
Henkel	Bonderite M-CR T5900	Dipotassium hexafluorozirconate, Trivalent Chromium	3.8-4.0%	60	70°F - 100°F	Ambient	3.8-4.0
Chemeon Surface Technology	Chemeon TCP-HF	Trivalent Chromium Salt, sulfuric acid	25%	300 (5 min)	65°F - 120°F	Ambient	3.6-4.0
PPG Industries	Chemseal 100	Dihydrogen hexafluorozirconate (2-), (2-methoxymethylethoxy) propanol, nitric acid	4.0-4.8%	120	Ambient - 140°F	Ambient	4-4.8
Hubbard Hall	Emerald Seal 308	Hexafluorozirconic acid	4.8-5.0%	30	Ambient - 120°F	Ambient	3-4
PPG Industries	Sbond S10	Dihydrogen hexafluorozirconate(2-)	4.0-5.0%	60	Ambient	Ambient	4-5
PPG Industries	Zircoseal 200	Dihydrogen hexafluorozirconate(2-), copper dinitrate	4.0-5.0%	60	60°F - 100°F	Ambient	4-5
Pantheon	ST-1	DGBE (Diethylene glycol monobutyl ether)	as received	60	Ambient - 110°F	Ambient	9.5-11.5
Calvary	Cal Prep 4064	Chromium Sulfate, Basic Solution, Fluorozirconic acid	as received	30	Ambient - 120°F	Ambient	2.0-3.0

Following the sealer step, some test panels were given an application of a supplementary preservative conforming to MIL-PRF-16173. Samples were tested as required by MIL-DTL-13924 as well as additional procedures in an effort to obtain a more comprehensive assessment of each sealer candidate. Table 2 lists the tests along with relevant test specifications and performance objectives.

Table 2 Test methods and performance objectives

Test methods	Data requirements	Performance objective
Coverage and color and smut	MIL-DTL-13924D	No reddish brown or green smut. Only a slight amount of smut that is inherent to the process is acceptable.
Oxalic acid test	MIL-DTL-13924D	Color retention following 60-s exposure to 5% oxalic acid solution.
Humidity testing	ASTM D2247 ⁵ ASTM D714 ⁶	Corrosion equivalent or less than existing process after 1008 h of exposure at 100 °F and 90% relative humidity. A few size 8 blisters are acceptable.
Accelerated corrosion	ASTM B117 ⁷ ASTM D610 ⁸	After 24 h of exposure: steel substrate shall show no visual corrosion.
Outdoor exposure	ASTM G50 ⁹	6 weeks (1008 h) of exposure: Performance equivalent to or better than existing process.
Toxicity assessment	Toxicity assessments and full disclosure from Public Health Command	Approved by processing facility.
Processing time	MIL-DTL-13924D	Equivalent or less than existing process.

2.1.1 Smut Test

In accordance with MIL-DTL-13924, panels were wiped with a lint-free, dry, white cloth to ensure that no significant residue from the black oxide process was left on the panels after application. Any substantial indication of a dark-colored powder on the cloth was noted as a failure of test. In addition to the smut test, a visual test was made to ensure the panels were a uniform black color. Any deviations in color or spottiness were also considered failures.

2.1.2 Oxalic Acid Test

An oxalic acid test was performed as described in MIL-DTL-13924. Three drops of a 5% oxalic acid solution were deposited onto the surface of each panel and allowed to dwell for 8 min. After exposure, the panels were rinsed in deionized (DI) water and observed for discoloration. Only panels that retained their original black color, or were slightly faded with a light border, were considered passing. Any other discoloration with the effect of lightening was considered a failure of the test. Examples of each are given in Fig. 1.



Fig. 1 Passing oxalic acid test (left) and failed oxalic test (right)

2.1.3 Mandrel Bend Testing (ASTM D522)

Mandrel bend testing was performed in accordance with Method B in ASTM D522.¹⁰ The test panels were placed and folded 180° around a 1/4-inch cylindrical mandrel at uniform pressure and velocity and examined for cracking or deformation of the black oxide coating. Any instance of either cracking or deformation visible to the unaided eye was considered a failure of testing. Elongation was not a factor in meeting the performance objective and therefore was not measured.

2.1.4 Humidity Testing (ASTM D1748)

Humidity testing was performed using guidelines provided in ASTM D1748¹¹ with an adjustable humidity cabinet set at 100 °F and 90% humidity (Fig. 2). The test coupons with sealer and supplementary preservative were nested in polypropylene racks and positioned at approximately 15° from vertical. The duration of exposure was extended to 1008 h after the first week when no failures were observed, with visual inspections at 24-h intervals for the first week, and weekly inspections were made thereafter. Inspection was performed in accordance with Sections 10.2.1 and 10.2.2 of ASTM D1748 using the visual pass/fail criteria.



Fig. 2 Photo of panels in humidity cabinet

2.1.5 Accelerated Corrosion: Neutral Salt Fog (ASTM B117)

The test panels evaluated in neutral salt fog were placed in an Auto-technology Standard Salt Fog Chamber (Model 22), in polypropylene trays tilted at an angle approximately 15° from the vertical with the primary surface facing upward (Fig. 3). Neutral salt fog conditions are 95°F with saturated humidity and an atomized fog of a certified 5% sodium chloride (NaCl) solution. Daily fog deposit volumes, pH, and other records are available upon request. The supplementary preservative was applied prior to exposure.

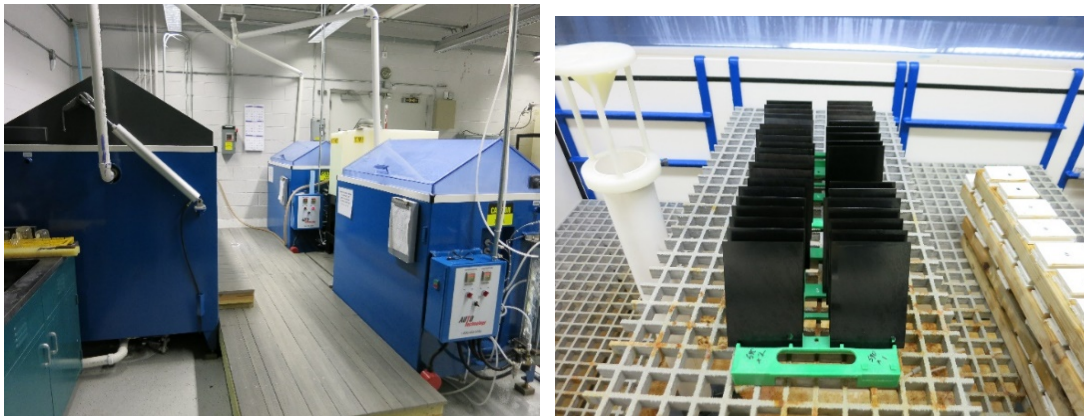


Fig. 3 Photos of salt fog chambers (left), panels in chamber (right)

2.1.6 Outdoor Exposure Testing (ASTM G50)

Panels with supplementary preservative were placed in outdoor exposure testing on Aberdeen Proving Ground, Maryland, and mounted to aluminum racks using Teflon fixtures, with the primary surface facing vertical (Fig. 4). The aluminum racks are oriented facing south and are located within 1 mile of the Chesapeake

Bay. Panels were exposed to winter conditions, including snow and salt from snow removal, over the course of 1008 h. Mass loss rates on standard coupons is typically 0.06 mils per year (MPY) in the area. Panels were evaluated for signs of corrosion following collection and rinsing in DI water. Any sign of corrosion visible to the unaided eye indicated failure. A summary of the weather data is given in the Appendix.



Fig. 4 Outdoor exposure racks at Aberdeen Proving Ground facing south

3. Results and Discussion

3.1 Coverage, Color, and Smut Performance

These test requirements are in accordance with MIL-DTL-13924. Table 3 displays the results from the smut test. The performance objective for visual and smut testing was a uniform black surface free of spottiness and, when wiped, the wipe media was free from a significant amount of dark-colored powder residue. All of the CRS panels tested met the requirement; however, all of the stainless steel panels had a significant amount of smut and were unable to meet this requirement. One cause of the smut present on stainless steel panels (Fig. 5) is the over activation of the test panels during cleaning and prior to blackening.¹² Another potential cause of the smut would be an improper etchant concentration in the bath.¹³ In either case, the panels should have been desmuted before immersion in the blackening bath. The smut that remained on the panels during the blacking process likely prevented a stable black oxide from being formed.

Table 3 Coverage, color, and smut test results on cold-rolled and stainless steels

Sealer	Class 1	Class 4
Chromic Acid	Met	Not Met
Bonderite M-NT 5900	Met	Not Met
Cal Prep 4064	Met	Not Met
Chemeon TCP	Met	Not Met
Chemseal 100	Met	Not Met
Emerald Seal 308	Met	Not Met
Pantheon ST-1	Met	Not Met
Sbond S10	Met	Not Met
Surtec 555	Met	Not Met
Surtec 580	Met	Not Met
Surtec 590	Met	Not Met
Zircoseal 200	Met	Not Met



Fig. 5 Photo showing heavy smutting present on stainless steel panels

3.2 Oxalic Acid Performance

Table 4 displays the results of the oxalic acid test. This is a specification requirement of Classes 1, 2, and 3 only. Therefore, the Class 4 samples, which already failed the smut test, were not subjected to oxalic acid test. The performance objective for oxalic acid testing is that there shall be no significant lightening of the coating in the exposed area. Some lightening along the edge of the exposure zone is allowed; however, lightening of the center area is unacceptable. All of the Class 1 panel tested and sealer candidates met the performance objective in this case, including the stainless steel panels. These results can be seen in Figs. 6–8.

Table 4 Oxalic test results on cold rolled steel

Sealer	Oxalic Acid Test
	Class 1
Chromic Acid	Met
Bonderite M-NT 5900	Met
Cal Prep 4064	Met
Chemeon TCP	Met
Chemseal 100	Met
Emerald Seal 308	Met
Pantheon ST-1	Met
Sbond S10	Met*
Surtec 555	Met
Surtec 580	Met
Surtec 590	Met*
Zircoseal 200	Met*

* no significant staining detected

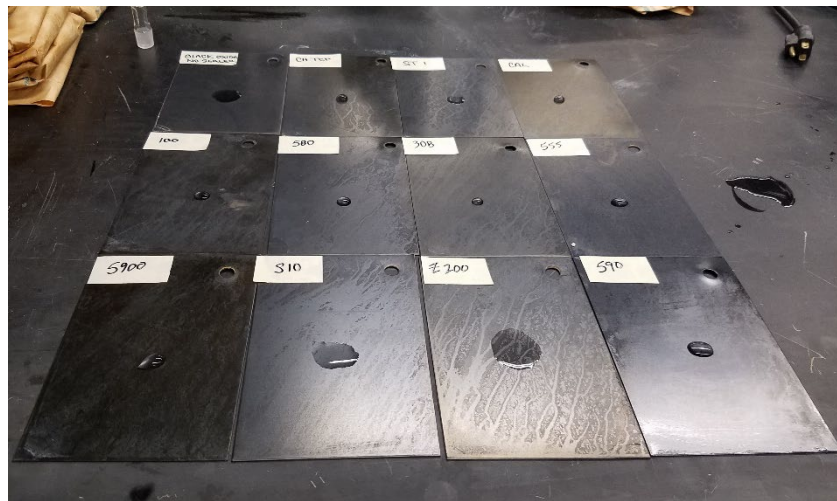


Fig. 6 Showing oxalic test in progress on CRS



Fig. 7 Oxalic acid test results on Class 1 black oxide. From left to right: chromic acid seal, Bonderite M-CR 5900, and SurTec 555.

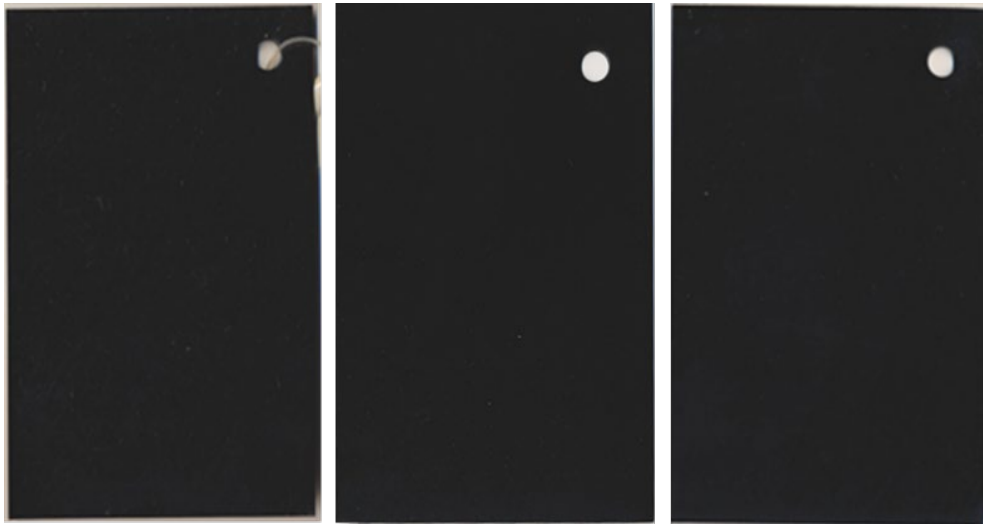


Fig. 8 Humidity test results for Class 1 black oxide, sealed, and with supplementary preservative. From left to right: chromic acid seal, Bonderite M-CR 5900, and SurTec 555.

3.3 Mandrel Bend Testing

Sealed test coupons without the supplementary preservative were subjected to mandrel bend testing. No evidence of cracking or deformation of the coatings was observed on either substrate regardless of sealer, indicating that the sealers had no adverse effect on the black oxide layer. The results for each sealer and substrate can be seen in Table 5.

Table 5 Mandrel bend test results on cold-rolled and stainless steels

Sealer	Class 1	Class 4
Chromic Acid	Met	Met
Bonderite M-NT 5900	Met	Met
Cal Prep 4064	Met	Met
Chemeon TCP	Met	Met
Chemseal 100	Met	Met
Emerald Seal 308	Met	Met
Pantheon ST-1	Met	Met
Sbond S10	Met	Met
Surtec 555	Met	Met
Surtec 580	Met	Met
Surtec 590	Met	Met
Zircoseal 200	Met	Met

3.4 Humidity Testing

Humidity test results are displayed in Table 6 and Figs. 8 and 9. All samples were tested with the supplementary preservative. Ratings were made in accordance with ASTM D714⁶ and are based on general reference to photographic standards. Following the humidity exposure, each test panel was given a rating of 1–10 with a 10 indicating no evidence of corrosion, while lower ratings indicate progressively worse corrosion. The second half of the rating, if necessary, indicates the frequency of blistering. This four-step scale goes from few, to medium, to medium dense, to dense.

Observations of the CRS panels were similar, with all panels having a few scattered number of small blisters after 1008 h of exposure, including chromic acid-sealed panels. A few scattered (size 8) blisters are acceptable. All but the chromic acid-sealed stainless steel panels were able to meet the performance objective. A few samples, such as the Zircoseal 200 and the Bonderite M-CR 5900 displayed some small blistering, but were still able to meet the performance objective given in Table 2.

Table 6 Humidity test results of sealed 13924D Class 1 with supplementary preservative

Sealer	Humidity Testing - 1008hrs - D714 Rating			
	Class 1		Class 4	
Black Oxide + Cr6+	Met	Met	Not Met	Not Met
Bonderite M-NT 5900	Met	Met	Met	Met
Cal Prep	Met	Met	Met	Met
Chemeon TCP	Met	Met	Met	Met
Chemseal 100	Met	Met	Met	Met
Emerald Seal 308	Met	Met	Met	Met
Pantheon ST-1	Met	Met	Met	Met
Sbond S10	Met	Met	Met	Met
Surtec 555	Met	Met	Met	Met
Surtec 580	Met	Met	Met	Met
Surtec 590	Met	Met	Met	Met
Zircoseal 200	Met	Met	Met	Met



Fig. 9 Humidity test results for Class 4 black oxide, with supplementary preservative. From left to right: chromic acid seal, Bonderite M-CR 5900, and SurTec 555.

3.5 Neutral Salt Fog

The requirement for neutral salt fog testing in accordance with MIL-DTL-13924 only refers to stainless steel and permits no visible corrosion after 96 h. Since there was no official salt fog requirement in the specification for Class 1 (low-carbon steels), a 24-h period of exposure was estimated using the requirement for a Class 4 uncoated phosphate in MIL-DTL-16232. The ratings of three replicates of each sealer are presented in Table 7 while representative panels are given in Figs. 10–12. The Bonderite M-CR 5900 was the only candidate that met the performance objective on all three replicates of CRS at 24 h. Additionally, Cal Prep 4064, Chemseal 100, Emerald Seal 308, and Sbond S10 provided good corrosion protection demonstrated by two of the three replicate panels meeting the performance objective. Moreover, none of the chromic acid sealed panels could meet the performance objective at 24 h of salt fog. The poor quality of the blackened Class 4 panels was evident after testing in neutral salt fog. Figure 12 shows two of the more effective sealers versus the chromic acid panel on Class 4. No sealer was capable of protecting the smutted stainless steel panels and all failed to meet the 96-h requirement.

Table 7 ASTM B117 neutral salt fog test results for Class 1 and Class 4

Sealer	Class 1 - 24hrs - B117			Class 4 - 96hrs - B117		
	Panel 1	Panel 2	Panel 3	Panel 1	Panel 2	Panel 3
Chromic Acid	Not Met	Not Met	Not Met	Not Met	Not Met	Not Met
Bonderite M-NT 5900	Met	Met	Met	Not Met	Not Met	Not Met
Cal Prep 4064	Not Met	Met	Met	Not Met	Not Met	Not Met
Chemeon TCP	Not Met	Not Met	Met	Not Met	Not Met	Not Met
Chemseal 100	Met	Not Met	Met	Not Met	Not Met	Not Met
Emerald Seal 308	Met	Not Met	Met	Not Met	Not Met	Not Met
Pantheon ST-1	Not Met	Not Met	Not Met	Not Met	Not Met	Not Met
Sbond S10	Met	Not Met	Met	Not Met	Not Met	Not Met
Surtec 555	Met	Not Met	Not Met	Not Met	Not Met	Not Met
Surtec 580	Not Met	Met	Not Met	Not Met	Not Met	Not Met
Surtec 590	Not Met	Met	Not Met	Not Met	Not Met	Not Met
Zircoseal 200	Not Met	Not Met	Not Met	Not Met	Not Met	Not Met

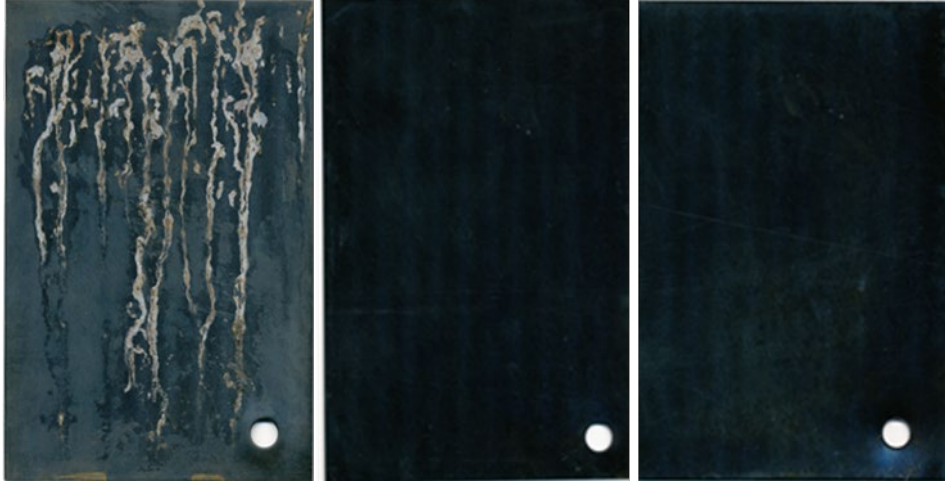


Fig. 10 Salt fog test results: (L to R) baseline chromic acid seal, Bonderite M-CR 5900, and Cal Prep 4064 on CRS

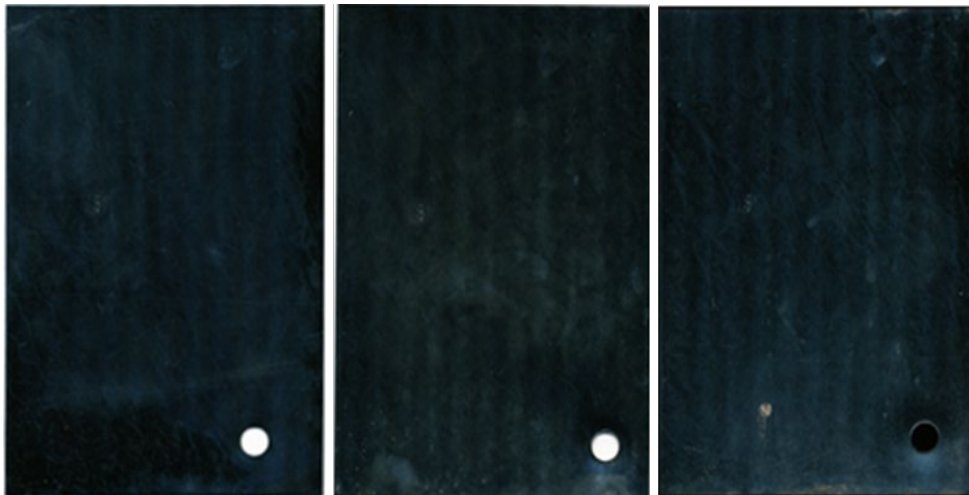


Fig. 11 Salt fog test results: (L to R) Chemseal 100, Emerald Seal 308, and Sbond S10 on CRS

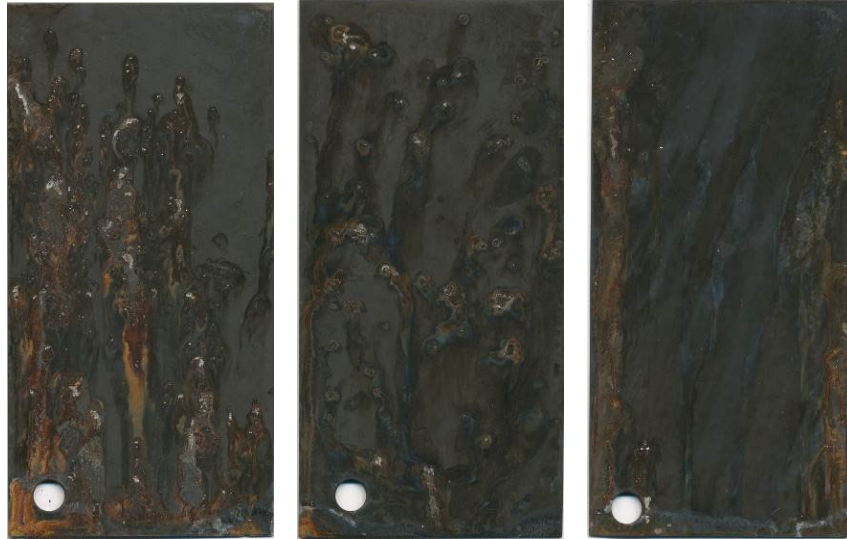


Fig. 12 Salt fog test results: (L to R) chromic acid, Bonderite M-CR 5900, and SurTec 555 on stainless steel

3.6 Outdoor Exposure Testing

Panels mounted in outdoor exposure were evaluated at 14 days (336 h), 28 days (672 h), and 42 days (1008 h). The results of the outdoor exposure are presented in Table 8. The performance objective for outdoor exposure is that there shall be no visible evidence of corrosion after 672 h of exposure. The Class 4 panels were not included in outdoor exposure testing because the panels showed evidence of flash rust before the supplemental preservative could be applied. An example of this is given in Fig. 13. Most of the sealers performed similarly to the baseline chromate-sealed black oxide samples, with only ST-1, Sbond S10, and SurTec 590 failing at 672 h. The samples were left outside through 1008 h to observe any additional separation in performance. As expected, the supplementary preservative provided enhanced corrosion protection in outdoor exposure over a sealer-only configuration (Fig. 14).

Table 8 Outdoor exposure of 13924D Class 1, sealed and with supplementary preservative

Sealer	Class 1 - Outdoor Exposure		
	336 hrs	672 hrs	1008 hrs
Chromic Acid	Met	Met	Not Met
Bonderite M-NT 5900	Met	Met	Not Met
Cal Prep 4064	Met	Met	Not Met
Chemeon TCP	Met	Met	Not Met
Chemseal 100	Met	Met	Not Met
Emerald Seal 308	Met	Met	Not Met
Pantheon ST-1	Not Met	Not Met	Not Met
Sbond S10	Not Met	Not Met	Not Met
Surtec 555	Met	Met	Met
Surtec 580	Met	Met	Not Met
Surtec 590	Not Met	Not Met	Not Met
Zircoseal 200	Met	Met	Not Met



Fig. 13 Class 4 panel without supplementary preservative with flash rust that occurred in ambient laboratory environment



Fig. 14 Chrome seal after 1008 h of outdoor exposure (left, with supplementary preservative; right, without supplementary preservative)

The SurTec 555 panels were observed to have no corrosion at the end of the 1008-h period of exposure. Unfortunately, it did not meet the 24-h ASTM B117⁷ salt fog performance objective. This is not uncommon, as the corrosion mechanisms are not identical to real-world outdoor exposure. Salt fog testing in accordance with ASTM B117 consists of a full time 100% RH and 35 °C environment in which the time of wetness is maximized leading to limited avenues for corrosion development. Although there are more variables (wet, dry, and temperature cycling), the conditions encountered in outdoor exposure at the Aberdeen Proving Ground are not as aggressive. The chloride levels are low and corrosion develops at a much more varied and realistic rate.

3.7 Comparison of Performance Objectives

Table 9 provides a comprehensive summary of the performance of the sealers on blackened CRS test coupons. The oxalic acid, smut, and humidity test results showed that all sealers had similar performance. The two tests that saw the greatest performance differential were the neutral salt fog chamber testing and the outdoor exposure testing. Though salt fog testing is not currently a requirement for Class 1 sealers, it is an industry standard for assessing the relative corrosion resistance of a system. Only five candidates (Bonderite M-CR 5900, Cal Prep 4064, Chemseal 100, Emerald Seal 308, and Sbond S10) were able to meet the ASTM B117⁷ performance objective of 24-h salt fog exposure. Interestingly, the baseline chromic acid seal was unable to meet this performance objective.

Table 9 Results of performance objectives for all sealer candidates

Quantitative Performance Objectives													
Performance Objective	Success Criteria	Chromic Acid	Cal Prep 4064	Chemeon TCP	Bonderite M-CR T5900	Emerals Seal 308	ST-1	Chemseal 100	Sbond S10	Zircoseal 200	Surtec 555	Surtec 590	Surtec 580
Coverage and Color and smut: per MIL-DTL-13924D	No reddish brown or green smut. Only a slight amount of smut that is inherent to the process is acceptable	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met
Oxalic Acid Test: per MIL-DTL-13924D	Color retention following 60 second exposure to 5% oxalic acid solution	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met
Humidity Testing, ASTM D 2247	Equivalent or less than existing process after 1008 hours of exposure at 100F and 90% relative humidity	---	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met
Accelerated corrosion, ASTM B117	After 24 hours of exposure: steel substrate no visual corrosion	Not Met	Met	Not Met	Met	Met	Not Met	Met	Met	Not Met	Not Met	Not Met	Not Met
Outdoor Exposure, ASTM D714	Equivalent or less than existing process after 4 weeks (672 hours) of exposure.	Met	Met	Met	Met	Met	Not Met	Met	Not Met	Met	Met	Not Met	Met
Toxicity Assessment, Public Health Command	Approved by processing facility	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met
Processing time, TT-C-490	Equivalent or less than existing process	---	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met

Of the five candidates that satisfied the implemented salt fog requirement, the Sbond S10 success did not carry over to outdoor exposure. However, the Chemeon TCP, SurTec 555, SurTec 580, and Zirco seal 200 successfully met the performance objectives in outdoor exposure. Overall, only the Cal Prep 4064, Bonderite M-CR 5900, Emerald Seal 308, and Chemseal 100 met all performance objectives.

4. Summary and Conclusion

The four candidates that demonstrated the best performance overall, including exceeding the performance of the baseline chromic acid seal, were Bonderite M-CR 5900, Cal Prep 4064, Emerald Seal 308, and Chemseal 100. Of those, all contain a zirconate component, while two (Cal Prep 4064, and Bonderite M-CR T5900) also contain trivalent chromium. This is significant if the use of any chromium compound is prohibited.

One alternative sealer, the SurTec 555, lasted 6 weeks (1008 h) in outdoor exposure, but was unable to meet the 24-h ASTM B117⁷ salt fog performance objective. Although 24 h of salt fog is not currently a specification requirement, it proved valuable for screening the sealers' corrosion performance.

The alternatives offer additional advantages with regard to operating parameters. While the chromic acid baseline requires operating at elevated temperature, all of the alternatives tested had operating ranges beginning at ambient temperature. Moreover, the characteristics of many of the alternatives make them environmentally compliant and conducive to a safer working environment.

Finally, the successful results of this project afforded ARL the opportunity to revise MIL-DTL-13924 to provide a pathway for implementation and use of hexavalent chromium-free sealers, and allow the user options other than hexavalent chrome. Furthermore, strengthening the performance requirements in the specification revision by adding a 24-h salt fog test may help produce a more robust coating system.

5. References

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10. ASTM D522. Standard Test Methods for Mandrel Bend Test of Attached Organic Coatings. ASTM International, West Conshohocken, PA, 2017
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Appendix. Weather Data for Outdoor Exposure Testing

U.S. Department of Commerce
 National Oceanic & Atmospheric Administration
 National Environmental Satellite, Data, and Information Service
 Current Location: Elev: 57 ft. Lat: 39.4716° N Lon: -76.1697° W
 Station: ABERDEEN PHILLIPS FIELD, MD US USW00013701

Global Summary of the Month for 2018
 Generated on 02/08/2019

National Centers for Environmental Information
 151 Patton Avenue
 Asheville, North Carolina 28801

Date	Temperature (F)										Precipitation (Inches)												
Elem ->	TAVG	TMAX	TMIN	HTDD	CLDD	EMXT		EMNT			DX90	DX32	DT32	DT00	PRCP	EMXP		SNOW	EMSD		DP01	DP10	DP1X
Month	Mean	Mean Max.	Mean Min	Heating Degree Days	Cooling Degree Days	Highest	High Date	Lowest	Low Date	Number of Days				Total	Greatest Observed		Snow, Sleet			Number of Days			
										Max >= 90	Max <= 32	Min <= 32	Min <= 0		Amount	Date	Total Fall	Max Depth	Max Date	>=.01	>=.10	>=1.0	
Jan	29.6	38.8	20.4	1097	0	64	13	3	08	0	12	25	0	1.19	0.65	13	1.0	0	31	9	4	0	
Feb	39.3	47.3	31.4	719	0	78	22	14	04	0	1	17	0	5.17			1.5	1	18				

List of Symbols, Abbreviations, and Acronyms

ARL	Army Research Laboratory
CCDC	US Army Combat Capabilities Development Command
Cr(VI)	chromic acid
CRS	cold-rolled steel
MPY	mils per year
OSD	Office of the Secretary of Defense
OSHA	Occupational Safety and Health Administration
PEL	permissible exposure limit
VOC	volatile organic compound

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(PDF) FCDD RLD CL
TECH LIB

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1 CCDC ARL
(PDF) FCDD RLW MC
T CONSIDINE