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Chrome-Free Modifications for MIL-DTL-16232, “Phosphate Coating, Heavy, Manganese or Zinc Base”

by Thomas Considine, Thomas Braswell, John Kelley, Christopher P Mulligan, and Theresa Dillon

NOTICES

Disclaimers

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14. ABSTRACT
Heavy phosphate coatings provide both corrosion and wear resistance for steel assemblies. A chromic acid sealer is required for enhancing corrosion resistance of the coating per MIL-DTL-16232. It has been known for quite some time that hexavalent chromium (Cr^{6+}) 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 specifically directing 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-Cr^{6+} sealers to replace and meet the performance of the previously required chromic acid. Eleven candidate sealers, along with the baseline sealer, were tested. Several alternative sealers demonstrated performance similar to or better than the baseline Cr^{6+}. The results of this work allowed for the MIL-DTL-16232 specification to be updated to allow alternative sealers to Cr^{6+} where allowed.

15. SUBJECT TERMS
hexavalent chromium, Cr^{6+}, zinc phosphate, manganese phosphate, sealers, corrosion

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1. Introduction

Phosphate conversion coating is one of the most important surface treatment methods for steel. These treatments are often used together with oils and waxes for corrosion protection and wear and galling resistance. Phosphating is especially useful for parts and equipment that might be exposed to severe environmental conditions. Heavy phosphating, described in MIL-DTL-16232,[1] is chosen for its ability to retain rust-preventive oils and waxes since it acts as an absorbent coating on the substrate due to its porosity, unlike fine-grain or light phosphating, which has a finer crystalline structure.

Military specification MIL-DTL-16232, *Phosphate Coating, Heavy, Manganese or Zinc Base,* is one of the established methods for finishing both unpainted and painted ferrous components for weapons, tooling, and other mechanical components for the military. Heavy phosphate is a conversion coating with a strong affinity for oils and waxes, which increase corrosion resistance. It is also used to enhance appearance, promote coating adhesion, provide wear resistance, and facilitate cold-forming manufacturing techniques. Phosphate conversion coatings are formed in an immersion bath at 175–185 °F. Phosphating transforms the surface of the base metal into a nonmetallic crystalline coating. The reaction occurs in an acidic solution containing phosphate ions. Loss of hydrogen at the metal/solution interface results in a localized rise in pH and subsequent precipitation of the coating at 5–15 µm thickness and 11–16 g/m^2.

Following the phosphate coating, a hexavalent chromium (Cr^{6+}) rinse/sealer is applied as the final stage, per specification MIL-DTL-16232. This requirement for a Cr^{6+}-containing compound is currently driven by dated documents, including parts drawings and contracts. Cr^{6+} 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,[3] states in part that OSHA has amended the standard limiting occupational exposure to Cr^{6+}. OSHA has determined the current permissible exposure limit (PEL) for Cr^{6+} and establishes an 8-h time-weighted average exposure limit of 5 µg of Cr^{6+} per cubic meter of air (5 µg/m^3). This is a considerable reduction from the previous PEL of 1 mg per 10 cubic meters of air (1 mg/10 m^3, or 100 µg/m^3) reported as chromium trioxide, which is equivalent to a limit of 52 µg/m^3 as Cr^{6+}.

The types of phosphate coatings in MIL-DTL-16232 are manganese (Type M) and zinc (Type Z). Because of the minimum conversion coating weights in MIL-DTL-16232 of 11 g/m^2 for Type Z and 16 g/m^2 for Type M, the term "heavy" is used to differentiate these coatings from the similar phosphate coatings referenced in TT-C-490F,[4] *Chemical Conversion Coatings and Pretreatments for Metallic Substrates (Base for Organic Coatings)*. Heavy manganese and zinc phosphates are used for corrosion resistance and lubricity, and unlike iron phosphate (TT-C-490F Type II) and "light" zinc phosphate (TT-C-490F Type I), are applied only by immersion. Light zinc phosphates are typically used as a base for further coatings or painting and may be applied by immersion or spraying. Type M and Type Z phosphates are conversion coatings applied on ferrous parts and equipment. Heavy phosphate conversion coatings are formed when manganese or zinc phosphate salts are dissolved in phosphoric acid and applied to ferrous substrates. With the exceptions of Class 4 for Types M and Z, all classes are currently sealed with a chromic acid rinse. The end product is an adherent crystalline finish that works as an excellent base and pretreatment for complementary corrosion prevention methods such as oils and other supplementary treatments. The chemical conversion coating creates a protective surface layer that displays strong corrosion-inhibiting properties, lubricant absorption, and wear resistance.

This effort evaluates and substantiates the effectiveness and performance of non-Cr^{6+} alternative sealers for specification MIL-DTL-16232. It provides the evidence to eliminate the need for Cr^{6+} as a post treatment for Type M and Type Z finishes by validating effective alternatives for the eventual revision of MIL-DTL-16232G to provide users non-Cr^{6+} options. The driver here is to continue the campaign set forth by the Young memo.[5] In April 2009, a memorandum from Office of the Secretary of Defense signed by Mr Young outlined a new policy for reducing the use of Cr^{6+} for DOD applications. The memorandum specifically directs the military to restrict the use of Cr^{6+} unless no cost-effective alternative with satisfactory performance has been identified. Eliminating Cr^{6+} in the phosphate conversion coating process essentially relieves the OSHA requirements for managing exposure determination, action levels, regulated areas, methods of compliance, respiratory protection, protective work clothing and equipment, housekeeping, hygiene, medical surveillance, hazard training and communication, and record keeping. The costs associated with having to manage the aforementioned requirements, as well as the costs associated with Cr^{6+} disposal in contaminated wastes, clothing, and personal protective equipment, would be significantly reduced with the implementation of a Cr^{6+}-free sealer.

2. Sample Preparation

Sets of 4- × 6- × 0.032-inch cold rolled steel test coupons were coated in accordance with MIL-DTL-16232 representing Types Z and M, Class 2 (supplementary treatment with lubricating oil conforming to MIL-PRF-16173) and Class 3 (no supplementary treatment). A post-treatment sealer was applied to each set of test panels in accordance with the manufacturer's instructions on their corresponding technical data sheets. Supplemental instructions from technical representatives of each chemical supplier were used to tailor the products for specific applications. The baseline chromic acid rinse was applied in accordance with MIL-DTL-16232. A set of the coupons was then given a supplemental treatment (oil) of MIL-PRF-16173 and allowed to drain vertically in polymer trays overnight. A list of the MIL-DTL-16232 types and subsequent treatments is given in Table 1.

Table 1 List of post-treatment sealers applied to MIL-DTL-16232 Types Z and M

MIL-DTL-16232				
Zinc phosphate (Type Z)	**Manganese phosphate (Type M)**	**Post-treatment sealer**	**Sealer manufacturer**	**Supplementary treatment (oil)**
Class 2 Class 3	Class 2 Class 3	Baseline Chromic Acid	N/A	MIL-PRF-16173 None
Class 2 Class 3	Class 2 Class 3	Bonderite M-CR T5900	Henkel	MIL-PRF-16173 None
Class 2 Class 3	Class 2 Class 3	Bonderite M-NT 7400	Henkel	MIL-PRF-16173 None
Class 2 Class 3	Class 2 Class 3	Cal-Prep	Calvary	MIL-PRF-16173 None
Class 2 Class 3	Class 2 Class 3	Chemeon TCP	Chemeon	MIL-PRF-16173 None
Class 2 Class 3	Class 2 Class 3	Chemseal 100	PPG	MIL-PRF-16173 None
Class 2 Class 3	Class 2 Class 3	Emerald Seal 308	Hubbard Hall	MIL-PRF-16173 None
Class 2 Class 3	Class 2 Class 3	Pantheon ST-1	Pantheon	MIL-PRF-16173 None
Class 2 Class 3	Class 2 Class 3	S Bond	PPG	MIL-PRF-16173 None
Class 2 Class 3	Class 2 Class 3	SurTec 555	SurTec International	MIL-PRF-16173 None
Class 2 Class 3	Class 2 Class 3	SurTec 580	SurTec International	MIL-PRF-16173 None
Class 2 Class 3	Class 2 Class 3	SurTec 590	SurTec International	MIL-PRF-16173 None
Class 2 Class 3	Class 2 Class 3	Zircoseal 200	PPG	MIL-PRF-16173 None

3. Testing

3.1 ASTM B117 Neutral Salt Fog Testing

A set of sealed Type M and Type Z steel coupons were tested in neutral salt fog using an Autotechnology standard salt fog chamber (Fig. 1).[6] The coupons were placed in polypropylene trays tilted at an angle of no more than 15° from the vertical with the primary surface facing upward. 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. Test panels were evaluated in accordance with MIL-DTL-16232. Sealed Type M and Type Z coupons, Class 3, were exposed for a period of 24 h. The appearance of any corrosion products, emerging from either the base metal or phosphate, was considered failure. Upon completion of testing, the panels were rinsed in deionized water, air dried, and scanned on a flatbed scanner. A second set of test coupons with a supplemental treatment (Class 2) conforming to MIL-PRF-16173[7] were exposed in the same manner as before, but for an extended duration of 72 h. These panels were also visually assessed for corrosion products, the appearance of which constituted failure, and were cleaned and scanned following exposure.

Fig. 1 Salt fog chambers

3.2 ASTM D1748 Humidity Testing

Similar to the salt fog exposure, sealed steel test coupons of Types Z and M, Classes 2 and 3, were tested in accordance with ASTM D1748.[8] Testing was performed in a programmable humidity cabinet (Fig. 2) set to run at a constant 100 °F and 90% relative humidity (RH). Sample coupons were placed in polypropylene racks and set at 15° from vertical. Samples were inspected at 1, 2, 4, 8, and 24 h, and every 24 h thereafter until failure. The appearance of any corrosion products was considered cause for failure. Following testing, panels were cleaned and scanned on a flatbed scanner.

Fig. 2 Humidity test chamber

3.3 Outdoor Exposure Testing

Panels of both Types M and Z, bearing each sealer in sets of three, Classes 2 and 3, were mounted to aluminum racks for outdoor exposure testing at Aberdeen Proving Ground, Maryland (Fig. 3). Panels were mounted at roughly a 30° incline facing south and approximately 5000 ft from the Chesapeake Bay. Typical mass loss rates on standard steel mass loss coupons is 0.06 MPY for the area. Panels were inspected weekly until failure. Any appearance of corrosion products on the panels was considered cause for failure. Following testing, panels were cleaned and scanned on a flatbed scanner.

Fig. 3 Outdoor exposure racks at Aberdeen Proving Ground

3.4 ASTM D522 Mandrel Bend Testing

Mandrel bend testing was performed in accordance with ASTM D522, Method B.[9] The test panels were placed and folded around a 0.25-inch cylindrical mandrel using uniform pressure and velocity. The panels were then examined for cracking or delamination of the phosphate. Any instance of damage to the coating visible to the unaided eye was considered a failure.

3.5 ASTM D3359 Paint Adhesion

Dry tape adhesion testing was performed in accordance with ASTM D3359, Method B.[10] MIL-DTL-53022 Type IV[11] chemical agent resistant coating (CARC) primer was applied in accordance with MIL-DTL-53072[12] using standard high-volume, low-pressure paint spray equipment to test panels bearing each sealer on Types Z and M, Class 3 only. Using a cross-hatch adhesion test tool, a lattice of six parallel cuts spaced at 2 mm was scribed through the coating to the substrate. A second set of cuts was made to intersect normal to the plane of the initial cuts to create a 6 × 6 grid. This was replicated at least four times per panel, or as space permitted. Grid lines were lightly brushed before tape application. A lap of 3M 250 flatback masking tape was applied to the surface of the panel over each grid, where it was firmly adhered to the substrate using a pencil eraser and allowed to stand for 30 s. Tape was removed by pulling at 180° in a quick, steady motion and then inspected for damage. Damage to the coating was rated in accordance with the classifications given in ASTM D3359. Following testing, panels were scanned on a flatbed scanner.

3.6 ASTM G99 Pin on Disc Abrasion

Coupons of Type M and Type Z, Class 2 were evaluated at US Army Futures Command, US Army Combat Capabilities Development Command Armaments Center, Benét Laboratories. Prior to testing, each specimen was fully submerged in a lubricant in accordance with MIL-PRF-3150[13] for roughly 1 h. Each sealer was evaluated daily over the course of 4 days. Excess oil was removed with a rubber scraper and then wiped with a lint-free cloth before each evaluation. The testing was carried out under a fixed set of conditions, which are listed in Table 2. Tribological properties were measured by sliding 440C stainless steel balls, the counter face, against the phosphated samples using a Nanovea Series tribometer, as shown in Fig. 4, using ball-on-disk geometry as per ASTM G99.[14] Frictional force was measured continuously during testing. Testing was carried out at room temperature in laboratory air (RH < 48%) for 1000.0 m, 13,045 total rotational cycles at 0.2 m/s with a 9.6-N load. The wear track diameter was fixed at 25 mm.

A minimum of three replicate runs were conducted for each sample to determine level of uncertainty. For each run, and in accordance with ASTM G99, the coefficient of friction (μ) was recorded in terms of initial coefficient of friction (μ_i) and steady-state kinetic coefficient of friction (μ_s). The μ_i was taken as the average μ over the first 1000 cycles to account for initial run-in behavior and the μ_s was taken as the average over the remaining cycles of the test. The initial run-in behavior is recorded separately as this can be dominated by wear of surface asperities for dry sliding or enhanced initial hydrodynamic lubrication conditions in the case of lubricated sliding.

Table 2 Test conditions for tribological testing

ASTM standard	G99
Stroke/circumference (m)	0.125
Normal load (N)	9.6
Counterface material	440C
Cycles/minute	156.6
Contact velocity (m/s)	12
Sliding distance (m)	1000
Lubricant	MIL-PRF-3150
Ball diameter (m)	0.006

Fig. 4 Tribological test cabinet

4. Results and Discussion

4.1 ASTM B117

No single sealer met the requirements for salt fog testing across both Type M and Type Z, Classes 2 and 3, including the baseline chromic acid sealed coupons (Fig. 5). Across the range of sealers tested on Type M, Class 3 coupons, after 24 h only three sealers met the visual assessment criteria for no corrosion products: Bonderite M-CR T5900 (a trivalent chrome [Cr^{3+}] sealer), SurTec 555, and SurTec 590 (Fig. 6). Class 2 coupons, when exposed for a longer duration, yielded results that were more disparate. The baseline Cr^{6+} sealer and the two Cr^{3+} sealers each had one panel pass and one panel fail, as did a number of other sealers. The only sets of panels that both passed were sealed with SurTec 580 and again SurTec 590 (Fig. 7). For Type Z, Class 3 phosphate, all but three of the sealers passed the 24-h exposure, including the Cr^{6+} and Cr^{3+} sealers. The extended exposure for the Type Z, Class 2 coupons also had a majority of sealers pass, though this time there were issues with both types of chromate sealer (Cr^{6+} and Cr^{3+}). The Bonderite M-CR T5900 could be considered borderline, as the corrosion seen was limited to a single pit per panel. The SurTec 580 and 590 sealers had similar issues with a single pit on the Type Z, Class 2 phosphate panels (Fig. 8). These results can be seen in Table 3.

Fig. 5 Type M, Class 3 coupon sealed with chromic acid

Fig. 6 (L to R) Type M, Class 3 coupon sealed with Bonderite M-CR T5900, SurTec 555, and SurTec 590

Fig. 7 Type M, Class 2 coupon sealed with SurTec 580 (L) and SurTec 590 (R)

Fig. 8 Type Z, Class 2 coupon sealed with SurTec 580 (L) and SurTec 590 (R)

Table 3 ASTM B117 results

Product	No.	Type Z, Class 2	Type Z, Class 3	Type M, Class 2	Type M, Class 3
Baseline Cr6+	1	Pass	Pass	Pass	Fail
	2	Fail	Pass	Fail	Fail
Bonderite M-CR T5900	1	Fail*	Pass	Pass	Pass
	2	Fail*	Pass	Fail	Pass
Bonderite M-NT 7400	1	Fail	Fail	Fail	Fail*
	2	Fail	Fail	Fail	Fail*
Cal-Prep	1	Pass	Pass	Pass	Fail
	2	Pass	Pass	Fail	Fail
Chemeon TCP	1	Pass	Pass	Pass	Fail
	2	Fail	Pass	Fail	Fail
Chemseal 100	1	Pass	Pass	Fail	Fail
	2	Fail	Pass	Fail	Fail
Emerald Seal 308	1	Pass	Pass	Pass	Fail
	2	Pass	Pass	Fail	Fail
Pantheon ST-1	1	Pass	Fail	Pass	Fail
	2	Pass	Fail	Fail	Fail
S Bond S-10	1	Fail*	Pass	Fail*	Fail
	2	Fail*	Pass	Fail*	Fail
SurTec 555	1	Pass	Pass	Fail	Pass
	2	Pass	Pass	Fail	Pass
SurTec 580	1	Fail*	Pass	Pass	Fail
	2	Fail*	Pass	Pass	Fail
SurTec 590	1	Fail*	Pass	Pass	Pass
	2	Fail*	Pass	Pass	Pass
Zircoseal 200	1	Pass	Fail	Fail	Fail
	2	Pass	Fail	Fail	Fail

*marginal

4.2 ASTM D1748 Humidity Testing

The results from humidity testing on the Type M and Type Z panels are shown in Fig. 9. The vast majority of the sealers tested on Type M coupons failed by 8 h, including both of the Cr^{3+} seals. The baseline Cr^{6+} seal (Fig. 10) failed much earlier, with panels failing at 2 and 4 h. The best two performers were again SurTec products, the 555 and the 590 (Figs. 11 and 12). The 555 had panels fail after 1 and 2 days, but the 590 far exceeded the longevity of the other products tested with failures occurring at 1, 2, and 3 weeks. Testing on Type Z panels yielded similar results. This time, the Cr^{6+} sealer (Fig. 13) performed better than several of the alternative sealers, failing at 24 h. The Cr^{3+} sealers performed similarly, also failing at 24 h. The majority of the remaining alternative sealers failed between 4 and 24 h, with the exception of the SurTec products, which again outperformed the chrome products. While the SurTec 580 failed at 24 h, the 555 (Fig. 14) and 590 (Fig. 15) sealers lasted as long as 240 and 336 h. The results seen on these two products were very similar to those seen on the Type M panels.

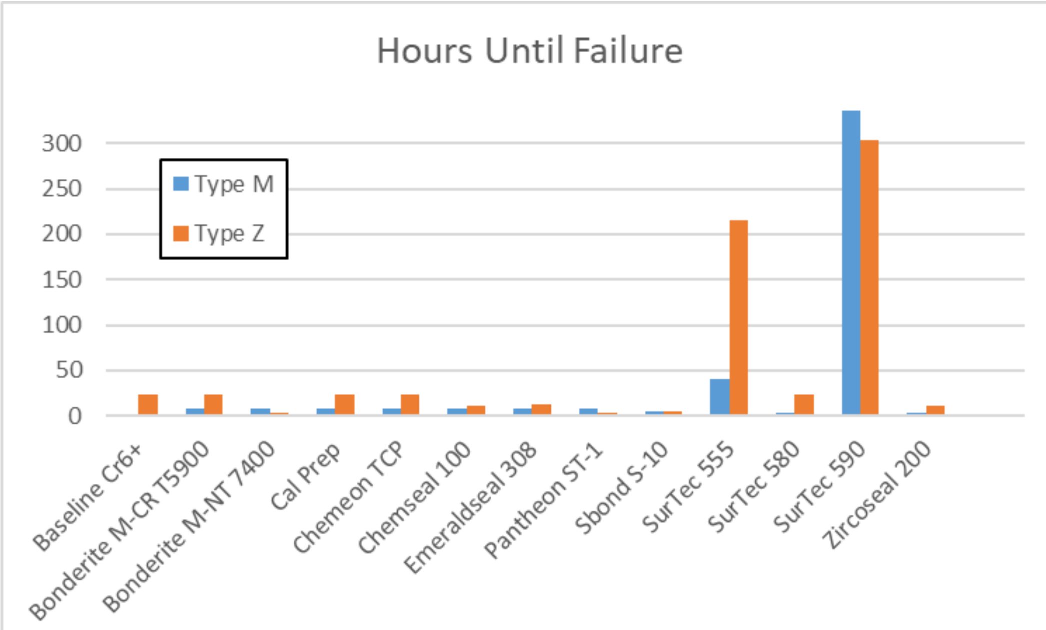

Fig. 9 Humidity test results for Type M and Type Z panels

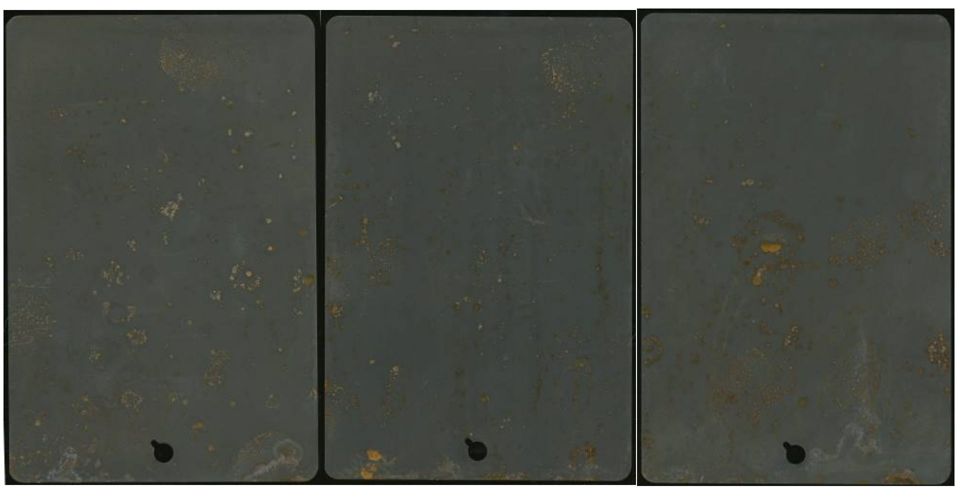

Fig. 10 Humidity test results on Type M panels sealed with Cr^{6+}

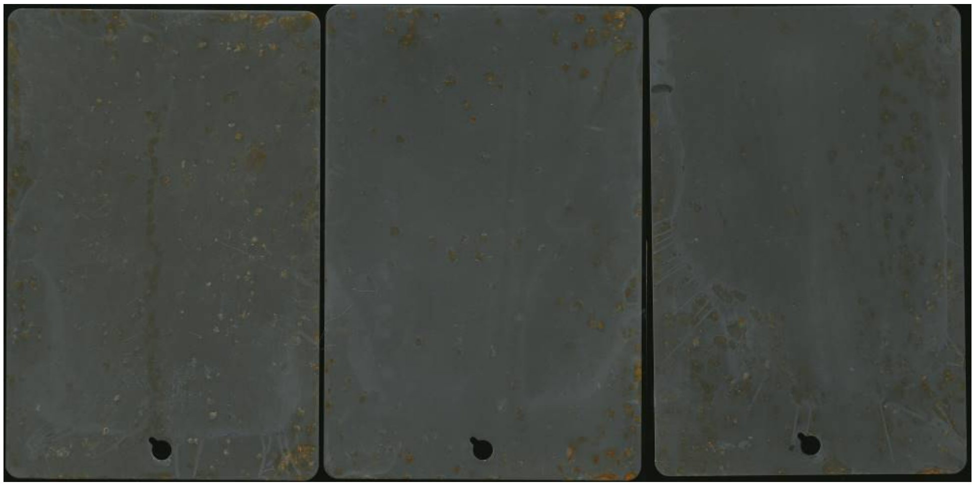

Fig. 11 Humidity test results on Type M panels sealed with SurTec 555

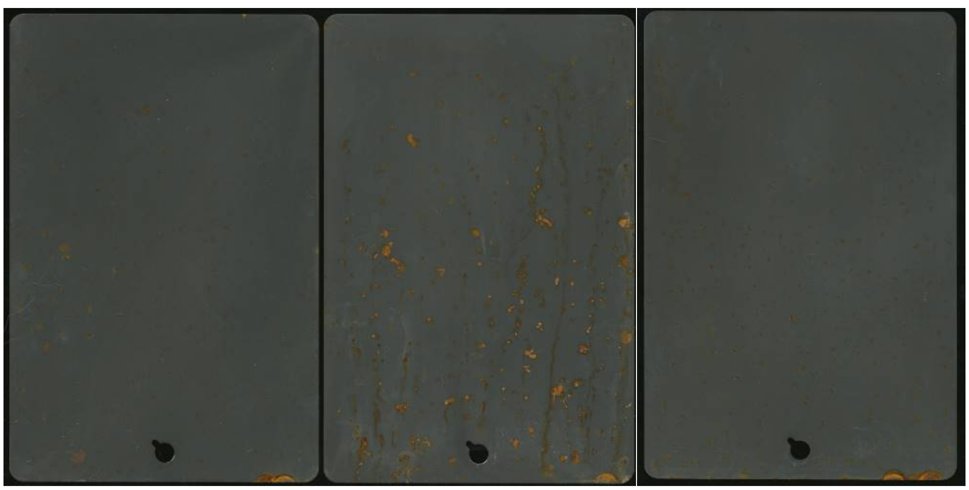

Fig. 12 Humidity test results on Type M panels sealed with SurTec 590

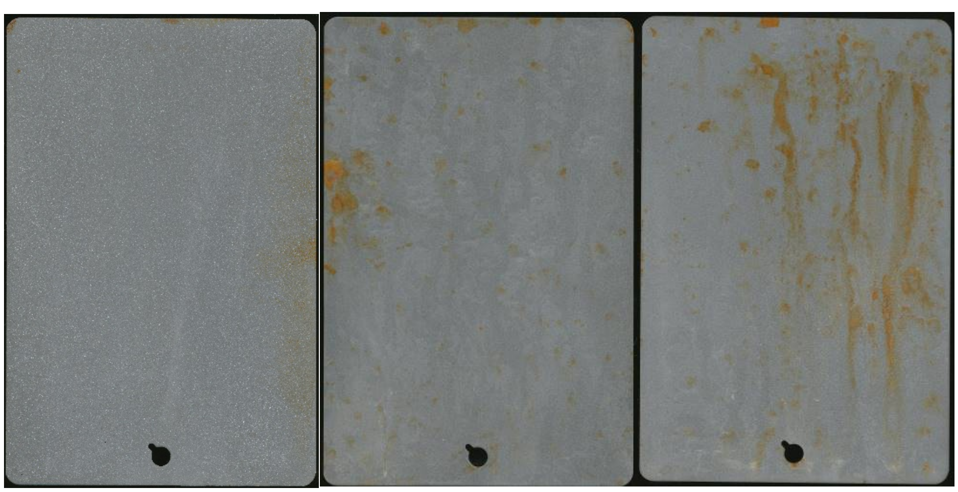

Fig. 13 Humidity test results on Type Z panels sealed with Cr^{6+}

Fig. 14 Humidity test results on Type Z panels sealed with SurTec 555

Fig. 15 Humidity test results on Type Z panels sealed with SurTec 590

4.3 ASTM D522 Mandrel Bend Results

Mandrel bend testing was performed in accordance with ASTM D522. No panel of any sealer on either Type M or Type Z demonstrated any deformation, delamination, or cracking of the coating. As such, all sealers tested were considered to have passed mandrel bend testing.

4.4 ASTM D3359 Adhesion Test Results

Adhesion results are given in Table 4. All sealers tested met or exceeded the pass/fail criteria given for CARC over Type M (a rating of 4 or higher). The results of the same systems over Type Z had more varied results. Only four of the sealers tested met the criteria for passing, including one of the Cr^{3+} sealers (Fig. 16) and one of the SurTec products. The SurTec 590 (Fig. 17) came in just under the average needed, with an average rating of 3.75.

Table 4 Adhesion test results

	Product	ASTM D3359 rating				
		#1	#2	#3	#4	Avg
Type M	M-NT 7400	4	4	4	4	4
	SurTec 555	5	5	5	5	5
	SurTec 580	5	5	5	5	5
	SurTec 590	5	5	5	5	5
	M-CR T5900	5	5	5	5	5
	Cal Prep	5	5	5	5	5
	Chemseal 100	5	5	5	5	5
	Chemeon TCP	5	5	5	5	5
	Emerald Seal 308	5	5	5	5	5
	S Bond S-10	5	5	5	5	5
	ST-1	5	5	4	5	4.75
	Zircoseal 200	5	5	5	5	5
Type Z	M-NT 7400	3	4	3	4	3.5
	SurTec 555	3	3	3	4	3.25
	SurTec 580	4	4	4	4	4
	SurTec 590	3	3	4	5	3.75
	M-CR T5900	4	4	5	4	4.25
	Cal Prep	3	3	3	3	3
	Chemseal 100	4	4	3	4	3.75
	Chemeon TCP	3	3	3	3	3
	Emerald Seal 308	3	4	3	4	3.5
	S Bond S-10	4	4	5	4	4.25
	ST-1	3	4	3	3	3.25
	Zircoseal 200	4	4	4	4	4

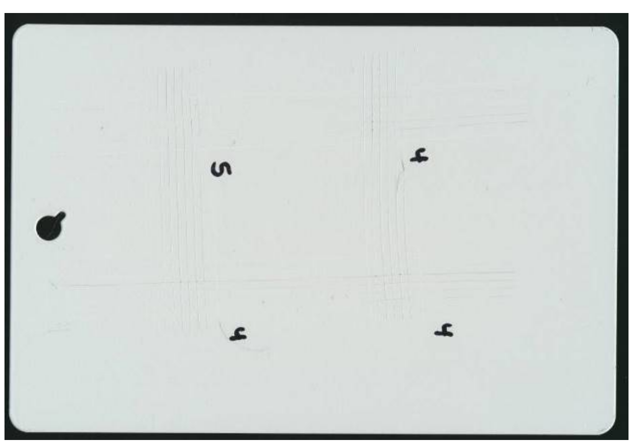

Fig. 16 Adhesion test results of Bonderite M-CR T5900 over Type Z phosphate

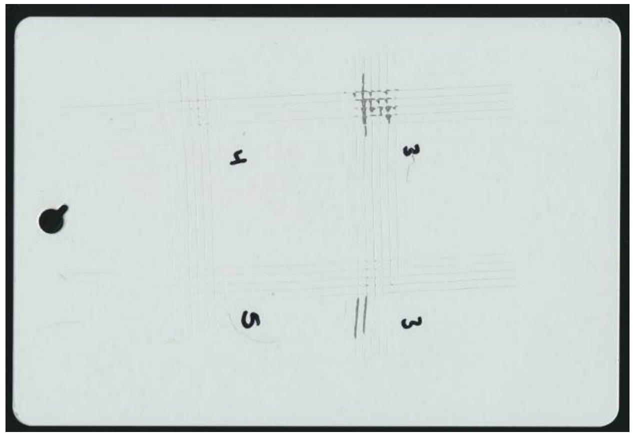

Fig. 17 Adhesion test results of SurTec 590 over Type Z phosphate

4.5 ASTM G99 Results

Figure 18 illustrates the initial and steady-state coefficients of friction, μ_i and μ_s, for a representative sample of sealed zinc phosphate tested at daily intervals for 4 days. For this particular specimen, μ_i and μ_s exhibited ranges of 0.154 to 0.165 and 0.201 to 0.224, respectively. This indicates there is no dependence of tribological behavior as a function of post soak interval up to 4 days. This behavior was consistent across all specimens tested. Therefore, the rest of the data presented in this work is in terms of the average μ_i and μ_s for each sealer with the stated uncertainty equal to ±1 standard deviation.

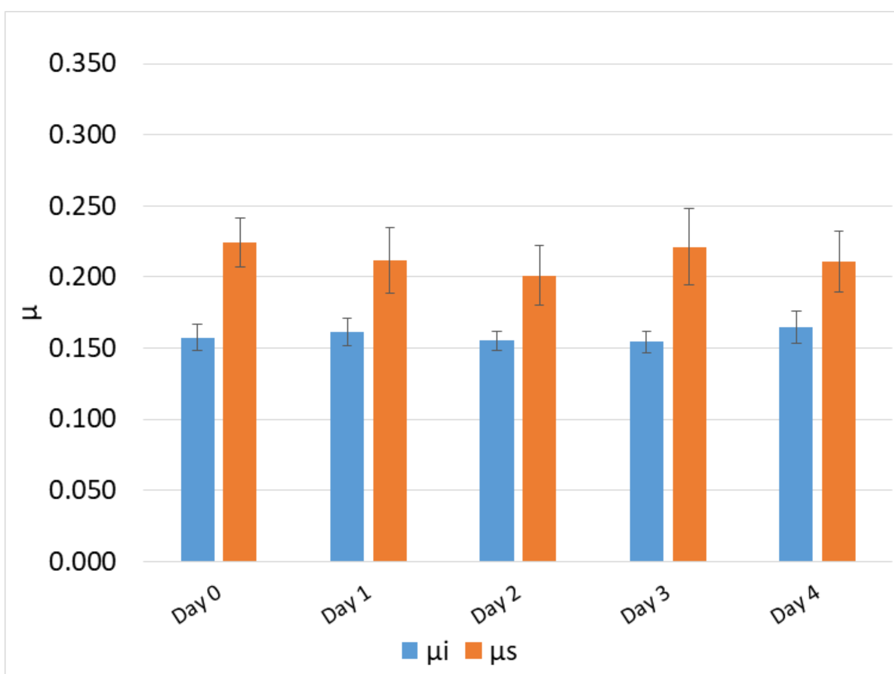

Fig. 18 Representative sample of coefficients of friction of sealed zinc phosphate

Figures 19 and 20 illustrate initial and steady-state coefficient of friction, μ_i and μ_s, for each Type Z and Type M sealer specimen tested, respectively. Initial observations for both the initial coefficient of friction, μ_i, and steady-state coefficient of friction, μ_s, indicate more variability in behavior of the Type Z sealers. The data can be split into two groups: specimens exhibiting a μ_s above 0.2 and those below 0.15. For instance, M-CR T5900, SurTec 580, and SurTec 590, exhibited μ_i of 0.075 ± 0.0002, 0.074 ± 0.010, and 0.070 ± 0.005, respectively, along with μ_s of 0.106 ± 0.004, 0.121 ± 0.014, and 0.100 ± 0.003, respectively. These sealers perform comparably to the baseline Cr^{6+} sealer. This is compared to an average of μ_i and μ_s of 0.165 ± 0.013 and 0.227 ± 0.015, respectively, for all specimens in the group with μs above 0.2. Intermediate behavior is observed for SurTec 555 with a μ_i and μ_s of 0.104 ± 0.005 and 0.142 ± 0.002, respectively. A potential reason for this behavior may be related to the characteristics of each sealer. For instance, different sealers may affect the wettability of the oil on the phosphate surface, or alternatively, may clog the inherent porosity in the phosphate surface and prevent oil penetration. Overall, the SurTec 580 and SurTec 590 sealers are the only two that performed comparably to the baseline Cr^{6+} sealer in both Type Z and Type M phosphate coatings.

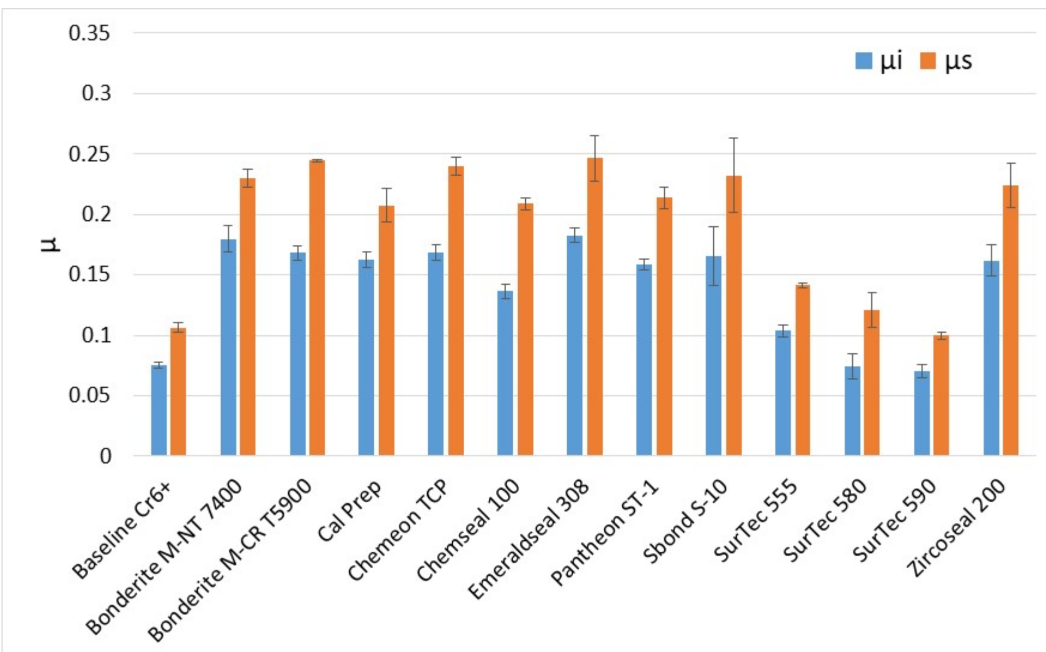

Fig. 19 Tribological test results on Type Z sealers

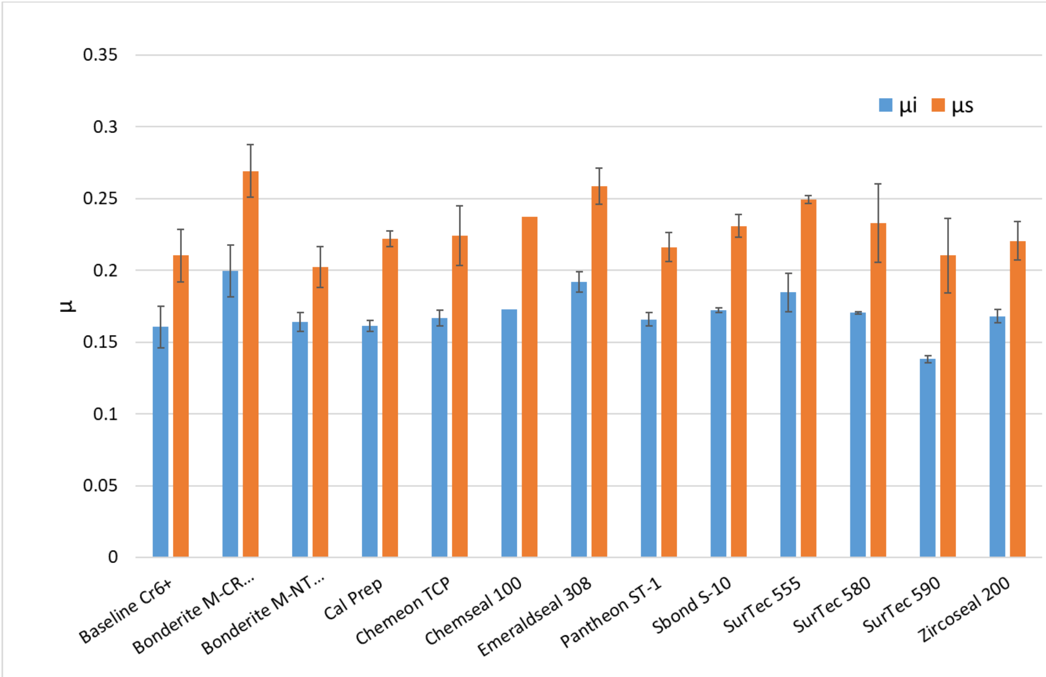

Fig. 20 Tribological test results on Type M sealers

4.6 Summary of Results

A comprehensive, color-coded summary of the results of all testing is given in Table 5. Items that meet the success criteria are given in green and those that did not are given in red. In general, the Type M phosphate sealers fared better than the Type Z counterparts. No failures were observed across three of the tests performed on the Type M sealers (outdoor exposure, mandrel bend, and paint adhesion), and only a few failures were observed in the humidity and abrasion resistance tests. The largest volume of failures observed in the Type M sealers was during neutral salt fog testing, where even the baseline Cr^{6+} did not meet the success criteria. Four of the alternative sealers performed better in corrosion testing than the baseline, with two of these meeting the success criteria for every test. Testing for the Type Z sealers encountered a higher rate of failure. No single alternative sealer tested over zinc phosphate successfully passed each test, though several sealers performed equivalently to the baseline Cr^{6+} sealer. Overall, the SurTec 590 performed the best across both types of phosphate.

Table 5 Summary of results

Magenese Phosphate														
Performance Objective	Success Criteria	Chromic Acid Rinse	Surtec 555	Surtec 590	Surtec 580	Bonderite NT 7400	Bonderite M-CR T5900	Chemeon TCP	Chemseal 100	Emerals Seal 308	Sbond S10	Zircoseal 200	ST-1	Cal Prep 4064
Accelerated Corrosion Resistance, ASTM B117	Shall show no evidence of corrosion after 1.5 hours of exposure when tested with no supplimentary treatment	Not Met	Met	Met	Not Met	Met	Met	Not Met	Not Met	Not Met	Not Met	Not Met	Not Met	Not Met
Humidity Tests, ASTM D 2241	Better than or equal to the performance of the chromic acid baseline (24hrs)	N/A	Met	Met	Not Met	Met	Met	Met	Met	Met	Not Met	Not Met	Met	Met
Outdoor exposure, ASTM D714	Better than or equal to the performance of the chromic acid baseline	N/A	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met
Mandrel Bend, ASTM D522	Coating shall show no signs of chipping or cracking	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met
Paint adhesion, ASTM 3359	Minimum ASTM D3359 rating of 4B as per MIL-DTL-53072	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met
Abrasion resistance, ASTM G99	Friction coefficient maintained relative to baseline Cr6+ seal	N/A	Not Met	Met	Met	Met	Not Met	Met	Met	Not Met	Met	Met	Met	Met

Zinc Phosphate														
Performance Objective	Success Criteria	Chromic Acid Rinse	Surtec 555	Surtec 590	Surtec 580	Bonderite NT 7400	Bonderite M-CR T5900	Chemeon TCP	Chemseal 100	Emerals Seal 308	Sbond S10	Zircoseal 200	ST-1	Cal Prep 4064
Accelerated Corrosion Resistance, ASTM B117	Shall show no evidence of corrosion after 2 hours of exposure when tested with no supplimentary treatment	Met	Met	Met	Met	Not Met	Met	Met	Not Met	Met	Met	Not Met	Not Met	Met
Humidity Tests, ASTM D 2241	Better than or equal to the performance of the chromic acid baseline (24hrs)	N/A	Met	Met	Not Met	Not Met	Not Met	Not Met	Met	Met	Met	Not Met	Met	Not Met
Outdoor exposure, ASTM D714	Better than or equal to the performance of the chromic acid baseline	N/A	Met	Met	Met	Not Met	Met	Met	Not Met	Met	Met	Met	Not Met	Not Met
Mandrel Bend, ASTM D522	Coating shall show no signs of chipping or cracking	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met	Met
Paint adhesion, ASTM 3359	Minimum ASTM D3359 rating of 4B as per MIL-DTL-53072	Not Met	Not Met	Not Met	Met	Not Met	Met	Not Met	Not Met	Not Met	Met	Met	Not Met	Not Met
Abrasion resistance, ASTM G99	Friction coefficient maintained relative to baseline Cr6+ seal	N/A	Not Met	Met	Met	Not Met	Not Met	Not Met	Not Met	Not Met	Not Met	Not Met	Not Met	Not Met

In the spirit of the memorandum "Minimizing Use of Hexavalent Chromium" by the Chairman of the Joint Chiefs of Staff, John Young Jr, this research effort investigated Cr^{6+}-free sealer candidates for substitution of existing chromic acid sealers for MIL-DTL-16232. Testing protocol dictated by MIL-DTL-16232 guided the focus of the chemistries for material selection to produce the most favorable performance results to equal or surpass the current chromic acid–based sealers. Respectively, the outcome of the research allowed us to recast MIL-DTL-16232, dictating the use of chrome-free sealers over those that contain Cr^{6+}, effectively limiting its use for heavy zinc phosphate and manganese conversion coatings. This revision was published in September 2020 and was subsequently revised again in March 2021.

5. Conclusions

The following are our conclusions:

- No sealer, including the baseline Cr^{6+}, met the salt spray requirements across all classes and types of phosphating. SurTec 555 and SurTec 590 were the best performers overall. Cal Prep, Emerald Seal 308, and SurTec 555 outperformed Cr^{6+} on Type Z coatings, and Bonderite M-CR T5900 and SurTec 590 outperformed Cr^{6+} on Type M coatings.

- Almost every sealer outperformed Cr^{6+} in humidity testing, with SurTec 590 lasting up to 252 times longer than the baseline Cr^{6+}.
- All sealers met the requirements for adhesion on Type M coatings, only four sealers met the requirements for adhesion on Type Z coatings: Bonderite M-CR T5900, SurTec 580, S Bond S-10, and Zircoseal 200.
- Most sealers met the criteria for abrasion on Type M coatings, and only SurTec 580 and 590 met this requirement on Type Z coatings.
- Tribological behavior was comparable to the baseline for most of the sealers on Type M coatings. SurTec 580 and 590 were the only sealers to perform comparable to the baseline for Type Z coatings.
- Given that the Cr^{6+} sealer was not able to meet all the requirements of MIL-DTL-16232 on either Type M or Z coatings, this study was able to identify several viable alternative products that will enhance the performance of phosphate coatings on Army hardware. The SurTec 580 and 590 were determined to have shown the greatest potential as replacements to Cr^{6+} as a phosphate sealer.

6. References

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List of Symbols, Abbreviations, and Acronyms

CARC	chemical agent resistant coating
Cr^{3+}	trivalent chromium
Cr^{6+}	hexavalent chromium
DOD	Department of Defense
NaCl	sodium chloride
OSHA	Occupational Safety and Health Administration
PEL	permissible exposure limit
RH	relative humidity
TT-C-490F Type I	zinc phosphate
TT-C-490F Type II	iron phosphate
Type M	manganese
Type Z	zinc

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