QUALIFICATION OF TRIVALENT CHROMATE AS A HEXAVALENT CHROMATE ALTERNATIVE FOR PROPELLANT AND CARTRIDGE ACTUATED DEVICES

Harry L. Archer

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A low toxicity trivalent chromate conversion coating (TCP) over a zinc-phosphate conversion coat was qualified to replace toxic hexavalent chromate conversion coating (CCC) on zinc-nickel plated steel. Unpainted test panels exhibited at least 42 days of resistance to cyclic salt fog. These panels lasted at least 4 days when subjected to cyclic sulfur dioxide and cyclic salt fog testing with full red rust evident on the seventh day. Painted and scored TCP panels previously subjected to 10 days of humidity and 120 days of salt cyclic fog were subject to 78 days of cyclic sulfur dioxide and salt fog. This paint was still largely intact with only moderate score corrosion and paint blistering near the score. Breakaway torque required to unscrew adhesively bonded TCP over zinc-phosphate conversion coated zinc-nickel plated exceeded their initial assembly torque on representative propellant actuated device and cartridge actuated device parts.
FOREWORD

The work reported herein was performed at the Indian Head Division, Naval Surface Warfare Center, Indian Head, MD.

John L. Goodwin
Manager, Propellant Actuated
Devices Development Branch

Approved and released by:

Phillip R. Sturgill
Director, CAD/PAD Engineering Division
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ACKNOWLEDGMENTS

I give special thanks to:

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- Fred Zimmerman, (patent support), IHDIV/NSWC.
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INTRODUCTION

On February 28th, 2006, the Occupational Safety and Health Administration changed the permissible exposure limit for hexavalent chromate from 52 to 5μgrams per cubic meter. This change came after IHDIV/NSWC qualified a hexavalent chromate conversion coating (CCC) for use on unpainted PADs. This new requirement will make hexavalent chromated products difficult to procure in the near future.

Testing described herein qualifies a non-proprietary trivalent chromate (also known as TCP) over zinc-phosphate coating system to replace hexavalent chromate on zinc-nickel plated carbon steel PADs and CADs. We previously tested and qualified a zinc-nickel plating system (see IHTR 26943). These include:

- hexavalent chromate on zinc–nickel
- primed/painted hexavalent chromate on zinc–nickel,
- primed/painted TCP over zinc-phosphate on zinc–nickel.

However, IHDIV/NSWC did not previously test unpainted TCP over zinc-phosphate on zinc–nickel. The photo in the bottom of Table VIII in IHTR 26943 shows no corrosion, even in the score on the bottom of the painted TCP test panel. Therefore, only limited testing is required to qualify this TCP plating system. Moreover, unpainted TCP weren’t previously tested for gravel resistance.

Often CADs have more exposure to marine and shipboard smoke stack sulfur dioxide emissions than PADs, therefore testing for this type environment would be useful.

Plating typically changes the torque retaining power of threads. Adhesives used to lock thread in place often lubricate threads to facilitate assembly. Therefore, it is useful to determine if this new plating adversely affect the holding power of the torqued thread.

OBJECTIVE

IHDIV/NSWC’s objective is to qualify plating (Figure 1) 513-174-0215, Zinc-Nickel Plating, Low Nickel, Low Embrittlement, Hexavalent Chromate Free and a higher nickel version (12 percent versus 5 percent) (Figure 2) SK07005-E213K-2 for steel unpainted shipboard/marine propellant actuated devices (PADs), cartridge actuated devices (CADs) environments. We also desire to establish the durability of steel plated in accordance with drawing 513-174-0215 and a higher nickel (12 percent versus 5 percent) version of SK07005-E213K-1 (Figure 2) to withstand shipboard smokestack sulfur/sulfuric acid and salt fog emissions.
**Figure 1. Zinc-Nickel Plating, Low-Nickel, Low Embrittlement, Hexavalent-Chromate Free (ID 12)**

6, 2, 3, 1

NOTE:
1. INTERPRET DRAWING IN ACCORDANCE WITH
   ANSI Y14.30-1984 WITH APPENDICES
   B, C, D, AND E

2. BEFORE ANY HEAT TREATING OR ANODIZING
   CLEAN ALL SURFACES IN ACCORDANCE WITH ASTM D 322-83.
   ALL CLEANING SHALL BE FREE FROM CHROMATE.

3. AFTET FINAL ROLLING
   INSPECT SURFACE IN ACCORDANCE WITH ASTM D 3614-80
   OR AFTER STRESS RELIEF AND BEFORE ANY PLATING.
   ALL SURFACES SHALL REMAIN FREE FROM CHROMATE.

4. PROGRESSIVE WASHING BEFORE DISCHARGING.
   DISCHARGE FIVE TIMES THE WEIGHT OF PLATING.
   IMMEDIATELY CLEAN AFTER DISCHARGING.
   DISCHARGING AND CLEANING SHALL BE FREE FROM CHROMATE.

NON-MANDATORY ADVISORY INFORMATION:
A LOW TOXIC POST-FORM WAS FOUND AS AN EFFECTIVE
PREVENTIVE MEASURE TO DETECT ANY DISCHARGE.

POST CLEANING EP 1020
SUNOCO STEEL PROCESSING PRODUCTS
1550 DEERHOLE ROAD
W. CLEMORENVILLE, 11350
301-874-3111

5. IMMEDIATELY AFTER WASHING, ACTIVATE AND
   COLLECT MUD PELLETS.
   ACTIVATE COAT AS PER ASTM C 371-79.
   APPLY TO CLASS II SERVICE CONDITION DCC 10
   OR APPROPRIATE ENGINEERED.

6. ZINC-NICKEL PLATE IN ACCORDANCE WITH ASTM B811-88
   CLASS 1, WITH 50% TO 50% HARDNESS.
   COAT AS PER ASTM C 371-79
   WITH 50% TO 50% WITHIN THREE HOURS AFTER PLATING.
   MAXIMUM TIME IT SHALL BE IN MUD.

7. ZINC PRECIPITATE CONVERSION COAT PER ASTM D2592-85
   METHOD K

8. TRANSPARENT CHROMATE CONVERSION COAT PER MIL-D-23716A/1000.
   TYPE II, CLASS IIB, FORM 1, METHOD E
   OWM-795354 (L)
   Using drawings 513-74-1708 Qualified Source(S).

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**DISTRIBUTION STATEMENT C:**
Distribution authorized to U.S. Government Agencies and Department of Defense Contractors.
All requests for this document shall be referred to Commander, Indian Head Division, Indian Head, MD 20743-5350.
Figure 2. Zinc-Nickel Plating, High-Nickel, Low Embrittlement, Hexavalent-Chromate Free (ID 12x)5,6,7,8,9,14,12,13
Figure 3. Trivalent Chromate Conversion Coating
**APPROACH**

**Test Panel Environmental Testing: Salt Fog and Chip Resistance Testing**

Salt fog and chip resistance testing were both performed at Naval Surface Warfare Center, Carderock Division using the same equipment used to test panels qualified in IHTR 2694. Sulfur dioxide testing was performed at NAVAIR Patuxent River.

**Test Article**

Panels were fabricated in accordance with 5130K-CAD-REPL-0100 (see Figure 4). These panels used the same steel roll stock as the ones used in IHTR 2694 and the low volatile organic content paint system qualification. Moreover, all these test panels were the same configuration except the unpainted controls, which were larger, flat, and not from this steel stock.

**Preparation**

Panels were plated in accordance with Table I.

**Testing**

Panels were exposed to Table II cyclic salt fog testing. This is the same cyclic salt fog testing used to qualify the PAD paint system.

**Torque Testing**

We also compared the torque required to unscrew typical plated PAD and CAD items bonded with Eccobond® 45, Catalyst 15 (Figure 5) to assure that the coating does not significantly contribute to the loss of bonded screwed joint holding torque.

**PADs**

**Test Article**

There are many types of PAD parts. The Mk 74 underseat rocket motor (USRM) with its many threaded surfaces should be a good representation of threaded PADs.

**Preparation**

The Mk 74 is no longer a production item, so the igniter threads were trimmed, shown in Figure 6, to prevent them from reentering production.
The USRM and associated motor tubes (Figure 7), were plated according to Table III and assembled in accordance with Figure 8 with the same plating. All torque test items were from reworked parts. Therefore, they were stripped and plated according to 513-174-0213 (Figure 10) and SK07005-E213K-1 (Figure 11).

**Testing**

All assemblies were allowed to cure for at least 1 week. Afterwards, the tubes were unscrewed from the bodies with a torque wrench and the torque at first movement was recorded.

**CADs**

**Test Article**

MC 50 initiator steel body with aluminum M720 initiator heads represents typical CADs. This CAD was chosen because the parts were readily available and they have established torque test procedures.

**Preparation**

The bodies were plated according to Table III, and assembled according to Figure 9.

All torque test items were from reworked parts. Therefore, they were stripped and plated according to 513-174-0213 (Figure 10) and SK07005-E213K-1 (Figure 11).

**Testing**

All assemblies were allowed to cure for at least 1 week. Afterwards, the tubes were unscrewed from the bodies with a torque wrench and the torque at first movement was recorded.

**Compatibility**

As with any new coating, its compatibility must be considered if it is in contact with or outgases to propellant. Samples Mechanite 19 propellant were tested with samples of TCP to assess whether or not the TCP makes the propellant more reactive.
Figure 4. Test Panel Configuration
Table I. Test Panel Plating Preparation

<table>
<thead>
<tr>
<th>Item No.</th>
<th>Qty</th>
<th>Preparation Description for Drawing SK5130K-CAD-REPL-0100 (Figure 4)</th>
</tr>
</thead>
</table>
| 12       | 9   | 1. Mark the number “12” (no quotes) on a corner near the ¼ in hole.  
2. Plate panel in accordance with drawing 513-174-0215 (Figure 1). |
| 12x      | 8   | 1. Mark the number “12x” (no quotes) on a corner near the ¼ in hole so that the item number can be seen after finishing.  
2. Plate panel in accordance with drawing SK07005-E213K-1 (Figure 2). |
| Control  | 6   | 4 ½ in x 6 in 4130 Steel panels without weldment or plating |

6p2\[^2\] Reference only

|       | 6   | 1. Mark the number “6p2” (no quotes) on a corner near the ¼ in hole so that the item number can be seen after finishing.  
2. Plate panel in accordance with drawing 513-174-0215.  
3. Prime and paint as per MIL-DTL-85097[15]. Primer coating shall be per MIL-P-53030[16]. Paint shall be as per MIL-PRF-85285[17], Color, Gloss White No. 17935 in accordance with FED-STD-595[18]. |

Note: The 6p2 panels were previous subjected to 10 day humidity per ASTM D2247-99[19], and MIL-P-83126A[20], Section 4.4.2.14.2 and 120 day salt fog per ASTM G85 ANNEX 5[21]. Each panel has been scored diagonally in an “X” pattern on the side opposite the channel. Also, the paint adhesion was tested.

Table II. Hexavalent Chromate Replacement Panel Test Matrix

<table>
<thead>
<tr>
<th>Tests</th>
<th>Zinc – Nickel with Trivalent Chromate Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unpainted</td>
</tr>
<tr>
<td></td>
<td>Drawing SK5130K-CAD-REPL-0100 Panel Plated Per 513-174-0215 or 513-174-0213 if Reworked</td>
</tr>
<tr>
<td>Rain test[^6]</td>
<td>ID# 12, Qty 3</td>
</tr>
<tr>
<td>Humidity[^7] test</td>
<td>Use the same panels used in “h” above</td>
</tr>
<tr>
<td>Salt fog[^8]</td>
<td>Use the same panels used in “i” above</td>
</tr>
<tr>
<td>Chip resistance[^9]</td>
<td>ID# 12, Qty 3</td>
</tr>
<tr>
<td>Salt fog[^5] SO(_2)</td>
<td>ID# 12, Qty 3</td>
</tr>
</tbody>
</table>

\[^5\] MIL-P-83126A[20], Section 4.4.2.14.1  
\[^6\] ASTM D2247-99[19], and MIL-P-83126A[20], Section 4.4.2.14.2  
\[^7\] ASTM G85[21] ANNEX 5, 168hours and 1000hours (2000 & 3000 hours optional)  
\[^8\] ASTM D3170-03[22]  
Figure 5. Typical Adhesive Used to Seal USRM Motor Tubes
Figure 6. PAD MK 74 Manifold Torque Test Item
5. PLATE IN ACCORDANCE WITH TABLE III
### Table III. Plating Preparation for PADs and CADs

<table>
<thead>
<tr>
<th>Item designation</th>
<th>Quantity</th>
<th>Preparation description</th>
</tr>
</thead>
</table>
| Control          | 1 Mk 74 per Figure 4.  
3 Motor tubes per Figure 5.  
3 MC 50 (see Figure 6) | 1. Strip and cadmium plated as per MIL-STD-870[24], Type II, Class 1, with plating .0005 in (0.013 mm) to .0007 (0.018 mm) thick on all surfaces.  
2. Heat treat, to embrittlement relieve, as soon as possible after plating, but no later than 4 hours after plating at 374°F to 446°F (190°C to 230°C) for at least 24 hours. |
| (12) Trivalent coating Low-nickel | 1 Mk 74 per Figure 4.  
3 Motor Tubes per Figure 5  
3 MC 50 (see Figure 6) | Strip and plate panel in accordance with drawing 513-174-0213 (Figure 6). |
| (12x) Trivalent coating High-nickel | 1 Mk 74 per Figure 4.  
3 Motor tubes per Figure 5. | Strip and plate panel in accordance with drawing SK07005-E213K-1 (Figure 7). |
Apply Figure 4 adhesive (Eccobond 45) to both external and internal threads. Torque tube to 45 ft-lbs (3 places).

Figure 8. Modified MK 74 to Motor Tube Test Assembly
Apply Figure 5 adhesive (Eccobond 45) to both external and internal threads. Torque tube to 400 to 424 in-lbs.

Plate in accordance with Table III
Figure 10. Zinc-Nickel Plating, Low-Nickel, Low Embrittlement, Hexavalent-Chromate Free Rework (ID 12)5,11,8,9,10,12,13
Figure 11. Zinc-Nickel Plating, High-Nickel, Low Embrittlement, Hexavalent-Chromate Free Rework (ID 12x)
TEST RESULTS AND DISCUSSION

Environmental Testing

Test Panel Rain, Humidity, Cyclic Salt Fog

Figures 12 and 13 show results from the six TCP panels designated 12-1, 12-2, 12-3, 12x-1, 12x-2, and 12x-3 subject to rain, humidity and 1000 hours of cyclic salt-fog testing per Table II, displayed no apparent damage from chalking or rusting. Figure 14 shows 2000 and 3000 hours cyclic salt fog testing. Although these panels were not evaluated for blistering, checking, cracking, flaking, or filiform corrosion, these panels displayed no apparent damage of any type. By comparison, the untreated control panels exhibited increasing levels of rust. It became totally covered by thick corrosion by the 1000-hour salt-fog evaluation. After 3000 hours, the control lost 36% of its original weight to rust. White residue observed on the panels during salt-fog testing are artifacts of salt deposits related to the test environment and not damage to sample’s surface. Whiter residue appears on the low-nickel panels more than the high-nickel panels.

These results are superior to cadmium with CCC or zinc high-nickel with CCC shown in IHTR 2694, Table XI3.

Test Panel Sulfur Dioxide and Cyclic Salt Fog Unpainted

Figure 15 shows the progress of corrosion during sulfur dioxide/salt fog testing. Figure 16 shows that the higher nickel content fairs somewhat better at 4 days than the low nickel content. Figure 15 and 17 show that all panels exhibited substantial red rust in one week.

Test Panel Sulfur Dioxide and Cyclic Salt Fog Painted

Figure 18 illustrates a comparison between painted cadmium plated panels and painted TCP on low zinc nickel. These painted CCC on cadmium plated panel resist blistering and score corrosion the best. Painted TCP on low zinc nickel that was previously rain/humidity/salt fog tested exhibited only moderate blistering and score corrosion throughout the 78 day testing.

Figure 19 illustrates how effective TCP is in reducing corrosion in sulfur dioxide testing. The second panel from the left has substantially more corrosion than the two TCP panels on the right. Also note that the cadmium panel has no blistering whereas the three panels on the right have blisters.

Test Panel Chip Resistance

Table IV shows evaluations on the five TCP panels (three as the control with TCP over zinc-nickel (5 percent), and two with TCP over zinc-nickel (12 percent) subjected to chip resistance testing, indicated
minimal and acceptable damage to panels with both TCP treatments.) Both groups of panels displayed similar chipping resistance ratings for both treatments. Therefore, the 12 percent nickel TCP receives a “pass” for this test.

### Torque Retention

Table V shows results from the tube breakaway torque tests. All the assemblies required more torque to unscrew than the torque used to assemble them.

### Compatibility

Appendix A contains a series of differential scanning calorimetry (DSC), and Thermogravimetric Analysis compatibility test. They revealed that TCP is compatible with Mechanite 19. Mechanite 19 is a double-base (nitrocellulose/nitroglycerine) propellant used in some CAD/PAD items.
<table>
<thead>
<tr>
<th></th>
<th>As Received</th>
<th>Rain Test</th>
<th>10 Day Humidity</th>
<th>168 Hr</th>
<th>1000 Hr</th>
<th>1000 Hr Rear View</th>
</tr>
</thead>
</table>

Note: All ASTM G85 salt fog tests were performed in Auto-Technology Model CCT-NC-20.

*Figure 12. Photos of TCP/Zinc-Nickel/Steel Panels After Various Stages of Salt Fog Testing*
Note: All ASTM G85 salt fog tests were performed in Auto-Technology Model CCT-NC-20.

*Figure 13. 1000 Hr Cyclic Salt Fog Test of TCP/Zinc-Nickel/Steel Panels*
Note: All sulfur dioxide salt fog tests were performed in a Harshaw Environmental Test Chamber of Engehard Corporation, Cleveland, OH.

**Figure 14. 2000 and 3000 Hr Cyclic Salt Fog Test of TCP/Zinc-Nickel/Steel Panels**
<table>
<thead>
<tr>
<th></th>
<th>As Received</th>
<th>24 Hr</th>
<th>48 Hr</th>
<th>72 Hr</th>
<th>96 Hr</th>
<th>168 Hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Panel (12)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(TCP/zinc-low-nickel)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Panel (12x)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(TCP/zinc-high-nickel)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(uncoated)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: All sulfur dioxide salt fog tests were performed in a Harshaw Environmental Test Chamber of Engehard Corporation, Cleveland, OH.

*Figure 15. Sulfur Dioxide/Salt Fog Testing on TCP/Zinc-Nickel/Steel Panels After Various Stages*
Note: All sulfur dioxide salt fog tests were performed in a Harshaw Environmental Test Chamber of Engehard Corporation, Cleveland, OH.

*Figure 16.* 92 Hr (4 days) Sulfur Dioxide/Salt Fog Testing on TCP/Zinc Nickel
Note: All sulfur dioxide salt fog tests were performed in a Harshaw Environmental Test Chamber of Engehard Corporation, Cleveland, OH.

*Figure 17. 168 Hr (1 Week) Sulfur Dioxide/Salt Fog Testing on TCP/Zinc Nickel*
Note: All sulfur dioxide salt fog tests were performed in a Harshaw Environmental Test Chamber of Engehard Corporation, Cleveland, OH.

Figure 18. Painted After Various Stages Of Sulfur Dioxide/Salt Fog Testing Per Table II
Prime and painted per MIL-DTL-85097[15]. Primer coating per MIL-P-53030[16]. Paint per MIL-PRF-85285[17], Color, Gloss White No. 17935 per FED-STD-595[18].

Note: All sulfur dioxide salt fog tests were performed in a Harshaw Environmental Test Chamber of Engehard Corporation, Cleveland, OH.

Figure 19. Photos of Painted after 1872 Hrs (78 days) Sulfur Dioxide/Salt Fog Testing
Table IV. Chip Resistance Test TCP/Zinc-Nickel Results

<table>
<thead>
<tr>
<th>Designation</th>
<th>Panel ID Chip No. Rating(^1)</th>
<th>Chip Size Rating(^1)</th>
<th>Pass/Fail</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-4</td>
<td>7</td>
<td>A</td>
<td>Pass</td>
</tr>
<tr>
<td>12-5</td>
<td>6</td>
<td>A</td>
<td>Pass</td>
</tr>
<tr>
<td>12-6</td>
<td>6</td>
<td>A</td>
<td>Pass</td>
</tr>
<tr>
<td>12x-4</td>
<td>6</td>
<td>A</td>
<td>Pass</td>
</tr>
<tr>
<td>12x-5</td>
<td>6</td>
<td>A</td>
<td>Pass</td>
</tr>
</tbody>
</table>

(Plated per drawing 513-174-0215 (Figure 1))

(Plated per drawing SK07005-E213K-1 (Figure 2))

\(^1\) Chip number and size ratings evaluated per ASTM D3170-03[22] and SAE J400[25] (Nov. 2002 Rev), using the "physical count method" (number of chips of each size).
Table V. Unscrew Torque Typical PADs and CADs Test Results

<table>
<thead>
<tr>
<th>Designation</th>
<th>PADs: Underseat rocket motor manifold/tubes (See Figure 8)</th>
<th>Unscrew torque ft-lb</th>
<th>As a percent of 45 ft-lb applied torque&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>(12) Zinc-low nickel plated per 513-174-0213 (Figure 10)</td>
<td></td>
<td>90</td>
<td>200%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>270%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>270%</td>
</tr>
<tr>
<td>Avg: 110 ± 17</td>
<td></td>
<td></td>
<td>240%</td>
</tr>
<tr>
<td>(12x) Zinc-high nickel plated per SK07005-E213K-1 (Figure 11)</td>
<td></td>
<td>95</td>
<td>210%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>85</td>
<td>190%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>220%</td>
</tr>
<tr>
<td>Avg: 93 ± 8</td>
<td></td>
<td></td>
<td>210%</td>
</tr>
<tr>
<td>Figure 8; Cadmium plate per table III (control)</td>
<td></td>
<td>80</td>
<td>180%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>110</td>
<td>240%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>125</td>
<td>280%</td>
</tr>
<tr>
<td>Avg: 105 ± 23</td>
<td></td>
<td></td>
<td>230%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Designation</th>
<th>CADs: MC 50 Steel Body (See Figure 9)</th>
<th>Unscrew torque in-lb</th>
<th>As a percent of Avg. 400-425 in-lb Applied Torque&lt;sup&gt;3&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>(12) Zinc-low nickel plated per 513-174-0213 (Figure 10)</td>
<td></td>
<td>960</td>
<td>230%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>480</td>
<td>120%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>220%</td>
</tr>
<tr>
<td>Avg: 780 ± 260</td>
<td></td>
<td></td>
<td>190%</td>
</tr>
<tr>
<td>(Control) cadmium plate per table III</td>
<td></td>
<td>1500</td>
<td>360%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>840</td>
<td>200%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1560</td>
<td>380%</td>
</tr>
<tr>
<td>Avg: 1300 ± 400</td>
<td></td>
<td></td>
<td>320%</td>
</tr>
</tbody>
</table>

<sup>1</sup> All assemblies cured one week at room temperature after assembly.

<sup>2</sup> Torque wrench serial number is 11389. Calibration due 06-16-2007.
CONCLUSION

- Zinc-Nickel plate on 4130 steel prepared in accordance with 513-174-0215 or 513-174-0213 is qualified for CAD/PAD service provided it is compatible with the materials it may be in contact in the CAD/PAD.

- TCP/zinc-phosphate conversion coating offers a low toxicity alternative to hexavalent chromate on zinc-nickel plated 4130 steel. The TCP without zinc-phosphate on zinc-nickel plated steel is unlikely to provide corrosion protection due to the porous nature of zinc-nickel and the aqueous nature of TCP corroding from within these pores. This is based on testing by the TCP’s co-inventor and previous testing using aqueous Teflon® to replace hexavalent chromate (See IHTR 2694, Table XII)[3].

- TCP is compatible with Mechanite 19 propellant.

- TCP/zinc-phosphate/zinc-low-nickel is qualified for all PADs and CADs assuming it is compatible with the various materials (i.e., propellants) used in the same.

- TCP/zinc-phosphate/zinc-high nickel has somewhat better corrosion resistance in sulfur dioxide/salt fog environments than TCP/zinc-phosphate/zinc-low-nickel.

- TCP/zinc-phosphate/zinc-low-nickel offers much better corrosion protection than CCC/cadmium or CCC/zinc-low-nickel.

- TCP/zinc-phosphate/zinc-nickel is non-proprietary.

- TCP/zinc-phosphate/zinc-low/high nickel plating on thread wetted with Eccobond 45 adhesive is unlikely to lose preload torque after cure.

- TCP/zinc-phosphate/zinc-low or high-nickel plated CAD can endure shipboard marine application provided exposure to sulfur dioxide is not too extreme.

- TCP/zinc-phosphate/zinc-low or high-nickel plated CAD can endure long term exterior marine applications even unpainted (painted TCP/zinc-phosphate/zinc-high nickel was never tested).

- TCP/Zn-P/Zn-Ni used as prescribed in Figures 1, 2, 10, and 11 exceeds all of our objectives.

- TCP/Zn-P/Zn-Ni used as prescribed in Figures 1, 2, 10, and 11 is qualified to replace CCC/Cd on steel CADs and PADs, provided it is compatible with materials it would be exposed to in the CAD or PAD (e.g., propellant, energetics, dissimilar material etc.).
RECOMMENDATIONS

• If the trivalent chromate described in this report is compatible with materials it would be exposed to in a CAD or PAD, replace the hexavalent chromate/cadmium plating on steel PAD or CAD surfaces with trivalent chromate/zinc phosphate/zinc nickel/nickel strike in accordance with drawing number:
  ➢ 513-174-0215 (Figure 1) on new parts
  ➢ 513-174-0213 (Figure 10) on reworked parts
  ➢ SK07005-E213K-2 (Figure 2) on new parts subject to severe SO₂ fog on unpainted surfaces
  ➢ SK07005-E213K-1 (Figure 11) on reworked parts subject to severe SO₂ fog on unpainted surfaces.

• This plating is thicker than cadmium plating. Therefore, if final part dimensions apply after plating, assure that this coating system does not violate any minimum wall or size requirements before any final production.

• Replace cadmium plating on steel in all CAD/PAD rework specifications as recommended in the first and second bullets.

• Replace cadmium plating on steel in all production CAD/PAD technical data packages as recommended in the first and second bullets.
REFERENCES

1. US Department of Labor Occupational Safety and Health Administration, Hexavalent Chromium Standards, Section 5(a)(1) and 5(a)(2) of the OSHA Act, February 28, 2006.


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Appendix A

MECHANITE 19 AND TCP COMPATIBILITY
MEMORANDUM

From: R312DS (D. Sorensen)
To: E213K (H. Archer)
Via: R312

Subj: DSC/TGA THERMAL COMPATIBILITY TESTING OF MECHANITE 19 WITH CONVERSION COATINGS

Ref:
(a) Lab Reference 200039569, Mechanite 19
(b) Lab Reference 200039570, Cr (III) based conversion coating
(c) Lab Reference 200039571, Cr (VI) based conversion coating
(d) NATO STANAG 44147

Enc: Nineteen thermal curves

1. Summary

Per your request, Differential scanning calorimetry (DSC), and Thermogravimetric Analysis (TGA) thermal compatibility testing was performed on the admixtures of Mechanite 19, ref (a), with two conversion coatings, ref (b) and (c). By the methods used, both conversion coatings are considered compatible via the methods used.

2. General Information on Compatibility

Under guidelines developed in ref (d) and (e), the definition of compatibility here is in terms of the relative predictive shelf life of the energetic component in intimate contact with another material. Thermal compatibility as determined by DSC or TGA involves running components individually and as admixtures. In DSC curves, the major decomposition peak is measured for the individual sample components and is compared with the major decomposition peak of the admixture. The greater the shift to lower temperatures for the admixture is the greater the degree of incompatibility between the ingredients. Reference (e) further develops the temperature shift guidelines per Table 1 to assess the degree of incompatibility in an admixture. It does not address changes to the Thermomechanical properties of the inert material, such as adhesive properties.

<table>
<thead>
<tr>
<th>Degree of Incompatibility</th>
<th>DSC Peak Temperature Shift (°C)</th>
<th>TGA Change in Weight % (%mixtures- %ingred)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0-4</td>
<td>0-4</td>
</tr>
<tr>
<td>Slight</td>
<td>5-9</td>
<td>5-9</td>
</tr>
<tr>
<td>Small</td>
<td>10-19</td>
<td>10-19</td>
</tr>
<tr>
<td>Moderate</td>
<td>20-29</td>
<td>20-29</td>
</tr>
<tr>
<td>Large</td>
<td>≥ 30</td>
<td>≥ 30</td>
</tr>
</tbody>
</table>

3. DSC Analyses

All DSC analyses were performed on the TA Instruments Model 2910 after calibration against indium and zinc standards. The samples were run with a 50ml/min nitrogen purge at heating rates of 5°C/minute. Hermetically sealed aluminum pans were used in these tests. Hermetic pans are used since most
weapon systems are sealed, simulating the worst-case scenario. Only single runs were used. In both cases, there was a <4°C change upon adding the conversion coating to the energetic, so both conversion coatings are considered compatible via DSC.

Summary Table of DSC Compatibility Data at Heating Rate of 5°C/minute.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Exotherm Peak Temperature</th>
<th>Compatible</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanite 19</td>
<td>197.6°C</td>
<td></td>
</tr>
<tr>
<td>Cr (III) coating</td>
<td>No apparent rxn</td>
<td></td>
</tr>
<tr>
<td>Cr (VI) coating</td>
<td>No apparent rxn</td>
<td></td>
</tr>
<tr>
<td>Mechanite 19 + Cr (III) coating</td>
<td>195.6°C</td>
<td>&lt;4°C, Yes</td>
</tr>
<tr>
<td>Mechanite 19 + Cr (VI) coating</td>
<td>197.9°C</td>
<td>&lt;4°C, Yes</td>
</tr>
</tbody>
</table>

4. TGA Analyses

Since two methods of determining compatibility are recommended per reference (d), TGA was also performed. All analyses were performed on the TA Instruments Model 2950. The samples were run with a 50ml/min nitrogen purge at heating rates of 5°C/minute. Pin-holed aluminum pans were used in these tests. In both cases, the first weight loss peaks circa 193°C. The expected contributions from the isolated materials are larger than for the Cr(VI) admixture, so the admixture is compatible. For the Cr(III) admixture, the difference is negligible, so this admixture is deemed compatible as well.

Summary Table of TGA Compatibility Data at Heating Rate of 5°C/minute, 25:75 Ratios.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature Region</th>
<th>% Wt loss</th>
<th>Compatible</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanite 19</td>
<td>50-192.34°C,</td>
<td>45.47%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50-195.33°C</td>
<td>50.26%</td>
<td></td>
</tr>
<tr>
<td>Cr (III) coating</td>
<td>50-195.33°C</td>
<td>0.45%</td>
<td>-</td>
</tr>
<tr>
<td>Cr (VI) coating</td>
<td>50-192.34°C</td>
<td>1.01%</td>
<td>-</td>
</tr>
<tr>
<td>Mechanite 19 + Cr (III) coating</td>
<td>50-195.33°C</td>
<td>-21.99%</td>
<td>Cr. -25.17%, Yes</td>
</tr>
<tr>
<td>Mechanite 19 + Cr (VI) coating</td>
<td>50-192.34°C</td>
<td>-22.7%</td>
<td>Cr. -22.4%, Yes</td>
</tr>
</tbody>
</table>

5. Debra L. Knott assisted with the data collection. Please address any questions to the undersigned at extension 4671.

Daniel N. Sorensen, Ph.D.
Sample: Hexavalent Cr @ 9°C
Size: 0.101 mg
Flow: 0.10 mL/min
Temperature: 50-300°C
Comment: In N₂, Sealed Al max

No significant observable transitions

Heat Flow (W/g)

Temperature (°C)
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