Corrosion Investigation in Man-Rated Percussion Ignition Devices

NSWC IHEODTD, E2 CAD/PAD Division
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Outline

- Identification
- Background
- Process Outline
- Analysis / Testing
- Metallurgical Findings
- Progressive Plan
- Long Term Assessment
- Goals
- Lessons Learned
- Questions
- Contact Info
Executive Summary

CAD/PAD Ignition Device (Primer) Program is sole source for the man-rated percussion primers. Recently the program has experience some metallurgical anomalies that have prompted a series of investigations. At no time have any of the metallurgical anomalies created any performance issues or causes of concern in the functioning of the devices. The focus of this presentation is to provide a background, courses of action, results, and a progressive plan moving forward.
Identification of Discoloration

• 2014 - GFM PVU ignition devices reported visual discoloration from vendors – Red
• 2014 – GFM 72M ignition devices reported visual discoloration from vendors – Green
• 2015 – Investigation into PVU series visual discoloration initiated
  – Determine root causes
  – Identify/recommend corrective actions to prevent future discoloration
  – Recommend disposition of discolored items.
Discoloration Examples

Green Discoloration

Red Discoloration
Background – Green Discoloration

- First discovered late 2014 during vendor inspection of GFM
- GFM was returned and replaced. ISE visually inspected for confirmation and documentation.
- Suspect GFM was sent to metallurgist for XRD, EDS, Micrographs, etc..

Results
- Greenish colored areas indicate patina product
  - Patina is an oxidative process
- Patina corrosion becomes a secondary protectant, does not permeate like dezincification
Background – Green Discoloration

Green Patina
Background – Red Discoloration

- First discovered early 2014 during vendor inspection of GFM
- GFM was returned and replaced. ISE visually inspected for confirmation and documentation.
- Suspect GFM was sent to metallurgist for XRD, EDS, Micrographs, etc..
- **Reddish** colored areas indicate de-zincification
  - De-Zincification is selective leaching of zinc
  - Removal of zinc exposes copper in copper-zinc alloy
Background – Red Discoloration

De-Zincification Condition
Metallurgical Corrosion Results

- C26000 series brass cups (70/30) with red colored corrosion product
  - Corrosion product identified at copper oxide.
- Preferential corrosion site (Inside the red circle, high stress area).
  - Chemical / microstructural abnormality may exist in the C26000 series.
• Copper oxide (CU2O) shown as primary corrosion product
Surface Corrosion Micrograph

PVU Cup Surface Pitting: Observed “worst case” magazine condition

- Pits have depth. Measured cross-section 0.0004”, respectively
- Slight surface compromise.
- Pitting type corrosion suggest parts have come in contact with acid/chemical or ammonia type atmosphere
Effects of Surface Pitting

- 2.0% approximate decrease in cup thickness from pitting at the Least Material Condition (LMC)
- Surface Thickness = 0.0166” (approx.)
• **Functional Process Map: PVU Hardware Manufacture and Storage**
• **Highlighted:** Potential acid / chemical area in process
Analysis – Manufacturing Chemicals

• **Formall 2305**: Medium duty deep drawing lubricant
  • pH 5
  • Found to contain chlorine (Potential Issue)
• **Organ TU**: General Purpose Metal Finishing Compound – Brass burnish
  • pH 7
• **BKS-60**: Vibratory finishing compound
  • pH 10
• **Iosso**: Case Cleaner
  • pH 1-2 (Potential Issue)
  • Utilized full strength
• **Sagebrush Tumble Bright**: 
  • pH 4 (Potential Issue)
  • Diluted 1:4
• **Brulin**: Copper Protector
  • pH 14
  • Dilution 1:1000
Corrosion Testing – Diluted Solutions

- Handling contamination was removed via ethanol soak
- Solution of 3 suspect processing chemical were prepared as used in PVU processing
- Series of soak and removal were performed. Results were documented
Corrosion Testing - Results

- Iosso Case Cleaner most corrosive in testing.
- Diluted Sagebrush Tumble Bright had developed green patina.
- Formall 2035 was the least corrosive.
- Brulin Copper Protectant was used as a baseline during the testing.
Progressive Plan

- Determine mitigation strategy for PVU ignition devices
- Determine if any of the parts in inventory are acceptable for use
- Find suitable replacements for hardware manufacturing chemicals
- Return to production of PVU ignition devices and PVU hardware manufacturing.
Mitigation of Assets

- **Mitigation Method – Visual Screening**
- **Discoloration was observed utilizing 1X - 10X Magnification.**
Analysis of Stock (In-House Hardware)

- 70/30 Cartridge Brass (C26000) exists in two phases
  - Alpha (α) phase: Corrosion resistant
  - Beta (β) phase: Corrosion prone
- In theory, C26000 should exist in single α phase below 200°C
- In reality, manufacturing process (annealing, hot/cold rolling, etc.) permit formation of residual stresses prompting β phase formation.
Analysis of Stock (In-House Hardware)

Copper (Cu) / Zinc (Zn) Binary Phase Diagram

C26000
Analysis of Stock (XRD Phase)

• XRD Analysis for corrosion-prone brass phase (β-brass)
  - A strip stock sample used for X-Ray Diffraction (XRD).
• XRD scan was performed within each square marker
  (Bruker D8 Advance Diffractometer)
• A Rietveld analysis was performed on the XRD data to determine if an extraordinarily corrosion-prone brass phase (β-brass) was present in any strip stock samples. If so, the β-brass phase fraction was calculated.
Overlay of raw powder patterns

- Strip stock material lots were designated by letters.
- Samples E through J (PVU Cup Material)
Powder XRD - Analysis

- Brass samples were modeled well using two phases. (main phase \( \text{Cu}_{0.64}\text{Zn}_{0.36} \) and \( \beta \)-brass (CuZn) phase)
- Brass samples were fit with TOPAS software using three models
  - First Model: middle peaks pattern fit
  - Second Model: first and second peak focus
  - Third Model: Preferred orientation along crystallographic plane.
## Powder XRD - Results

<table>
<thead>
<tr>
<th>Strip Stock Lot</th>
<th>wt.% α-brass (Cu_{0.64}Zn_{0.36})</th>
<th>wt.% β-brass (CuZn)</th>
<th>$R_{wp}$</th>
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<tbody>
<tr>
<td>E</td>
<td>35.41</td>
<td>65.49</td>
<td>3.545</td>
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<tr>
<td>F</td>
<td>76.76</td>
<td>23.24</td>
<td>2.713</td>
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<td>G</td>
<td>85.23</td>
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<td>H</td>
<td>68.49</td>
<td>31.51</td>
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<td>J</td>
<td>80.28</td>
<td>19.72</td>
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- **XRD Compiled Results (Three Models)**
- $R_{wp}$ values under 4.00 generally indicate that the analysis is within a tolerable degree of accuracy.
- E, F, and H Strip Stock is identified to have high beta phase.
- E Strip Stock was highlighted due to higher error ($R_{wp}$). Suggest values wt’s may be skewed.
Long Term Assessment

• Accelerated Life Testing (ALT)
• Three concurrent phases
  – Strip Stock Samples
  – Inert PVU Cups
  – Loaded PVU Ignition Devices (Ordnance Assessment)
• Material Properties, Corrosive Degradation, and Performance will be monitored.
  – Coffin-Mansion Model (Arreheinicus & Eyring equations)
• Reliability
  – 99.9% Reliability will be achieved at 99% confidence level at test completion.
## Long – Term Assessment

<table>
<thead>
<tr>
<th>Aging Conditions</th>
<th>Conditioning Time in Months</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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<th>9</th>
<th>10</th>
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<td></td>
<td></td>
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<tr>
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<td>X</td>
<td></td>
<td>a,b</td>
<td>X</td>
<td>a,b,c</td>
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</tbody>
</table>

* X – Withdrawal will contain un-filled inert PVU cups (aged in salt solution)
**Xa – Will contain additional withdrawal of brass sheet stock (aged in salt solution)
***Xb – Will contain additional withdrawal of exposed performance PVU cups (aged at environmental)
****Xc – Will contain additional withdrawal of performance assets (aged at environmental)

### Salt Solution Formulation

<table>
<thead>
<tr>
<th>Aging Conditions</th>
<th>Salt Solution Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>50C</td>
<td>30% Magnesium Chloride in H₂O; Nominal 30.5% RH</td>
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<tr>
<td></td>
<td>60% Potassium Iodide in H₂O; Nominal 64.5% RH</td>
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<tr>
<td></td>
<td>80% Potassium Chloride in H₂O; Nominal 81.2% RH</td>
</tr>
<tr>
<td>60C</td>
<td>30% Magnesium Chloride in H₂O; Nominal 29.3% RH</td>
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<tr>
<td></td>
<td>60% Potassium Iodide in H₂O; Nominal 63.1% RH</td>
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<tr>
<td></td>
<td>80% Potassium Chloride in H₂O; Nominal 80.3% RH</td>
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<tr>
<td>70C</td>
<td>30% Magnesium Chloride in H₂O; Nominal 27.8% RH</td>
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<tr>
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<td>60% Potassium Iodide in H₂O; Nominal 61.9% RH</td>
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<tr>
<td></td>
<td>80% Potassium Chloride in H₂O; Nominal 79.5% RH</td>
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</tbody>
</table>
CAD/PAD Man-Rated Ignition Device Program-Short Term Goals

- Improve processes for hardware manufacture to eliminate selective leaching in PVU series ignition device hardware.
- Return to production utilizing less-susceptible hardware.
- Continue visual screening mitigation strategy
- Complete accelerated aging / life-cycle study on PVU ignition devices and hardware
- Outline surveillance testing of end-items utilizing affected PVU ignition device lots
Lessons Learned

- C26000 series cartridge brass is extremely susceptible to zinc leaching.
- Stresses need to be minimized during manufacturing.
- Processes need to be controlled to prevent over-exposure to chemicals.
- Sufficient cleaning methods should be enforced and strictly maintained at successive iterations during PVU hardware manufacture.
- Chemicals need to be “well balanced” to complete the manufacturing process without detrimental effects to hardware.
QUESTIONS....
CAD/PAD Man-Rated Ignition Device Program

Contact Info

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