Alternative to Nitric Acid Passivation

NASA Corrosion Technology Laboratory (CTL) & NASA Technology Evaluation for Environmental Risk Mitigation (TEERM)

2016 INTERNATIONAL WORKSHOP ON ENVIRONMENT AND ALTERNATIVE ENERGY
October 20, 2016
Background

- Corrosion is an extensive problem that affects the National Aeronautics and Space Administration (NASA) and European Space Agency (ESA).
- The deleterious effects of corrosion result in steep costs, asset downtime affecting mission readiness, and safety risks to personnel.
- It is vital to reduce corrosion costs and risks in a sustainable manner.
Risk

- Nitric acid passivation results in fumes that contain nitrogen dioxide and nitrogen oxide (NOx) emissions which are considered greenhouse gases; Best Available Technology (BAT) to be employed to control nitric acid and NOx emissions.

- Nitric acid passivation requires 25% or 50% concentration of the strong acid.

- Wastewater generated from the passivation process is regulated under the U.S. Environmental Protections Agency’s (EPA) Metal Finishing Categorical Standards.

- Nitric acid can remove beneficial heavy metals (nickel, chromium, etc.) that give stainless steel its desirable properties.
Specification

- Citric acid passivation is allowed per:
  - ASTM A 967 (Standard Specification for Chemical Passivation Treatments for Stainless Steel Parts)
  - AMS 2700 (Passivation Treatments for Corrosion-resistant Steel)

- Citric acid passivation is not a new technology; it was developed (many years ago) for the beverage industry in Germany to process containers that were free of iron which causes an unwanted taste to the beverage.

- While citric acid use has become more prominent in industry in the U.S., there is little evidence that citric acid is a technically sound passivating agent, especially for the unique and critical applications encountered by NASA and ESA.
Benefits of Citric Acid Passivation

- Citric acid is a bio-based material that helps government agencies meet the procurement requirements of the Farm Security and Rural Investment Act of 2002.
- There are no toxic fumes created during the citric acid passivation process making it safer for workers.
- Nitric acid passivation requires 25% or 50% concentrations of the strong acid which are extremely corrosive and hazardous to workers.
- Citric acid removes iron from the surface more efficiently than nitric acid and therefore uses much lower concentrations reducing material costs.
- Citric acid-based processing baths retain their potency for longer periods requiring less frequent refilling and reduced volume and potential toxicity of effluent and rinse water.
Objective

- The primary objective of this effort is to qualify citric acid as an environmentally-preferable alternative to nitric acid for passivation of stainless steel alloys.
Test Specimen Preparation

The NASA Corrosion Technology Lab followed the United Space Alliance (USA) procedure for passivation:

- **Grit Blast** (Iron Media)
- **Degrease - Initial Clean** (Acetone Wipe)
- **Second Degreasing** (Bruhlin 815 GD)
- **Rinse #1** (DI Water)
- **Rinse #2** (Spray Bottle - DI Water)
- **Caustic (Alkaline) Cleaning** (Turco 4090)
- **Rinse #3** (DI Water)
- **Rinse #4** (Spray Bottle - DI Water to Ensure Appropriate Water Break is Present)
- **Citric Acid Passivation** (Parameters Vary)
- **Rinse #5** (DI Water)
- **Rinse #6** (Spray Bottle - DI Water)
- **Check pH of surface** (pH 6.0 to 8.0)
- **Dry** (Gaseous Nitrogen)
- **Check pH of surface** (pH 6.0 to 8.0)
- **Dry** (Gaseous Nitrogen)
Parameter Optimization

Test panels of each stainless steel alloy were prepared using various process parameters

• Citric Acid Concentration: 4% ONLY in this phase
• Immersion Times: 60, 90, and 120 minutes
• Bath Temperatures: 38°C (100°F), 60°C (140°F), and 82°C (180°F)
• Salt Spray Testing per ASTM B 117
• Corrosion Resistance Evaluation every 168 hours up to 504 hours of salt spray testing
• Parameters resulting in the best corrosion resistance shall be used for preparation of that substrate’s test panels for the remainder of the testing
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<tr>
<th>Alloy</th>
<th>Passivation</th>
<th>Concentration (%)</th>
<th>Bath Temperature (°C)</th>
<th>Dwell Time (minutes)</th>
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Note 1 = Citric acid parameters were initially determined by USA
All other citric acid parameters were determined by KSC Corrosion Lab
## Testing

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<tr>
<th>Test</th>
<th>Test Methodology References</th>
<th>Acceptance Criteria</th>
<th>Location</th>
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* = Only one alloy was tested; 17-4PH
** = Test specimens were made of AISI 4340 alloy steel, this is considered worst case
## Overall Test Results

### 4% Citric Acid

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<th>Test</th>
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<td>X-Cut Adhesion by Wet Tape</td>
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<td>Cyclic Corrosion Resistance</td>
<td>Performs as well or better than control process for all alloys</td>
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<td>Atmospheric Exposure Testing^1</td>
<td>Performs as well or better than control process for the majority of alloys</td>
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<td>Hydrogen Embrittlement^3</td>
<td>Performs as well or better than control process for all alloys</td>
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1 = 17-4PH panels processed through the control process performed slightly better
2 = Only one alloy was tested; 17-4PH
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## Expanded Scope to Evaluate 7% and 10% Citric Acid Concentration

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http://www.koslow.com
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9. Citric Acid Passivation (Parameters Vary)
10. Rinse #5 (DI Water)
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12. Check pH of surface (pH 6.0 to 8.0)
13. Dry (Gaseous Nitrogen)
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Test panels of each stainless steel alloy were prepared using various process parameters

- Citric Acid Concentration: 4% (limited alloys), 7% and 10%
- Immersion Times: 60, 90, and 120 minutes
- Bath Temperatures: 38°C (100°F), 60°C (140°F), and 82°C (180°F)
- Salt Spray Testing per ASTM B 117
- Corrosion Resistance Evaluation after 2 hours of salt spray testing
  - SAE AMS 2700 & ASTM A967 = No signs of red rust or staining associated with free iron particles shall be observed
- Salt Spray Testing continued for an additional 166 hours
## Salt Spray Results

- 168 hours of exposure
- 3 panels were tested per parameter set
- **RED** = 1 or more panels showed evidence of rusting
- **GREEN** = all 3 panels showed no signs of rusting

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* Optimization testing completed in a previous project
Conclusions

- Regardless of alloy, higher citric acid concentrations, temperatures, and bath dwell times yielded the best results.
- There is clear evidence that 38°C (100°F) had a significantly greater number of failures than either 60°C (140°F) or 82°C (180°F).
- When differentiating between 60°C and 82°C, there is not enough proof to signify that 82°C is better than 60°C because there is only a 1 percent difference in the failure data.
- Increasing temperature increased difficulty in panel processing.
- When scaled to an industrial process, the 82°C baths would require constant replenishing.
- Longer immersion times showed a positive trend in pass rates; 120 minutes may be the optimal immersion time.
Next Phase – Validation Testing

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<th>Test</th>
<th>Corrosion Protection</th>
<th>Requirement</th>
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Questions?

Kurt Kessel
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