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.

http://commons.wikimedia.org

http://www.offshoreenergytoday.com

http://www.theguardian.com
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:

1. Grit Blast (Iron Media)
2. Degrease - Initial Clean (Acetone Wipe)
3. Second Degreasing (Bruhlin 815 GD)
4. Rinse #1 (DI Water)
5. Rinse #2 (Spray Bottle - DI Water)
6. Caustic (Alkaline) Cleaning (Turco 4090)
7. Rinse #3 (DI Water)
8. Rinse #4 (Spray Bottle - DI Water to Ensure Appropriate Water Break is Present)
9. Citric Acid Passivation (Parameters Vary)
10. Rinse #5 (DI Water)
11. Rinse #6 (Spray Bottle - DI Water)
12. Check pH of surface (pH 6.0 to 8.0)
13. Dry (Gaseous Nitrogen)
14. Check pH of surface (pH 6.0 to 8.0)
15. 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: \(38^\circ\text{C} (100^\circ\text{F})\), \(60^\circ\text{C} (140^\circ\text{F})\), and \(82^\circ\text{C} (180^\circ\text{F})\)
- 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
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Passivation</th>
<th>Concentration (%)</th>
<th>Bath Temperature (°C)</th>
<th>Dwell Time (minutes)</th>
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<td>4</td>
<td>82</td>
<td>60</td>
</tr>
</tbody>
</table>

Note 1 = Citric acid parameters were initially determined by USA
All other citric acid parameters were determined by KSC Corrosion Lab

AL6XN @ 504 Hours of ASTM B117 Exposure

A286 @ 504 Hours of ASTM B117 Exposure
### Testing

<table>
<thead>
<tr>
<th>Test</th>
<th>Test Methodology References</th>
<th>Acceptance Criteria</th>
<th>Location</th>
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<tr>
<td>X-Cut Adhesion by Wet Tape</td>
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<td>Tensile (Pull-off) Adhesion</td>
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<td>Atmospheric Exposure Testing</td>
<td>ASTM D 610</td>
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<td>NASA Corrosion Technology Lab Atmospheric Exposure Site</td>
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<td>Hydrogen Embrittlement**</td>
<td>ASTM F 519</td>
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</table>

* = 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**

<table>
<thead>
<tr>
<th>Test</th>
<th>Citric Acid Performance</th>
</tr>
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<tbody>
<tr>
<td>X-Cut Adhesion by Wet Tape</td>
<td>Performs as well or better than control process for all alloys</td>
</tr>
<tr>
<td>Tensile (Pull-off) Adhesion</td>
<td>Performs as well or better than control process for all alloys</td>
</tr>
<tr>
<td>Cyclic Corrosion Resistance</td>
<td>Performs as well or better than control process for all alloys</td>
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<tr>
<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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<tr>
<td>Stress Corrosion Cracking</td>
<td>Performs as well or better than control process for all alloys</td>
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<tr>
<td>Fatigue(^2)</td>
<td>Performs as well or better than control process for all alloys</td>
</tr>
<tr>
<td>Hydrogen Embrittlement(^3)</td>
<td>Performs as well or better than control process for all alloys</td>
</tr>
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1 = 17-4PH panels processed through the control process performed slightly better  
2 = Only one alloy was tested; 17-4PH  
3 = Test specimens were made of AISI 4340 alloy steel, this is considered worst case
Expanded Scope to Evaluate 7% and 10% Citric Acid Concentration

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<td></td>
<td>4 7 10</td>
<td>38 60 82</td>
<td>60 90 120</td>
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<tr>
<td>316</td>
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* Optimization testing completed in a previous project
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- **Second Degreasing** (Bruhlin 815 GD)
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- **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)
Parameter Optimization

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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<tr>
<th>Test</th>
<th>Corrosion Protection</th>
<th>Requirement</th>
<th>Test Methodology</th>
<th>Evaluation</th>
<th>Acceptance Criteria</th>
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Questions?

Kurt Kessel
Kurt.r.kessel@nasa.gov
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