Citric Acid Passivation of Stainless Steel

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Materials & Processes Engineering

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Contents

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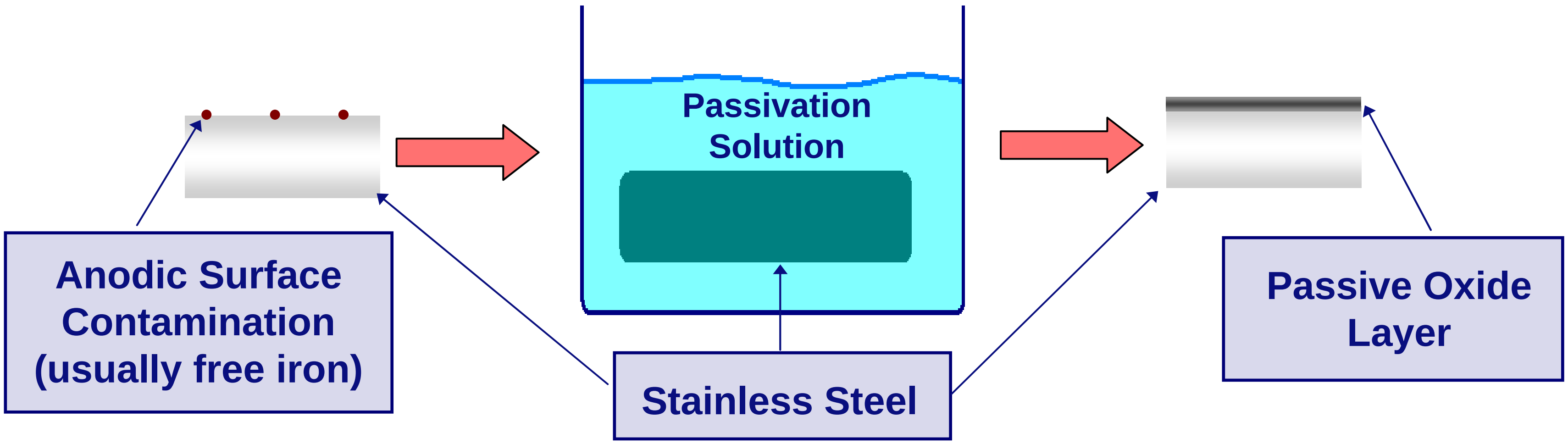
What is Passivation?

- Generation of a chemically passive oxide layer on certain metals.
- In terms of metal treatments, passivation is a chemical cleaning process to improve the corrosion resistance of stainless steel.
  - Removes free iron from the surface.
  - Stimulates growth of a passive oxide layer on the surface which will protect the substrate from corrosion.
  - Many solutions (e.g. H_2SO_4, HNO_3, methanol) have been studied.



How Passivation Solutions Work

- **The active surface of stainless steel is exposed to the passivation solution.**
- **Several phenomena occur during passivation *[A. Pardo et al], [S. Bera et al], [Westin], [Schmucki]*:**
  - **Surface contamination dissolved.**
  - **Oxidation proceeds by nucleation and diffusion-controlled growth.**
  - **Surface stoichiometry changes based on solubility of metals and metal oxide species in passivation solution.**

- **In literature, passive layers are characterized in several ways *[Bera, Pardo, Capobianco]*:**
  - **Composition, i.e. enrichment of passive Cr_2O_3 species (XPS, AES-ICP).**
  - **Thickness (XPS, Sputtering).**
  - **Electrochemical Properties (IES, Open-circuit potential).**

It is generally accepted that thick, Cr_2O_3-rich layers are desirable, however these properties have not been reliably correlated with atmospheric corrosion rates.

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NASA Specifications Concerning Passivation

Flight Hardware

NASA 6016

MSFC-SPEC-250

Ground Hardware

KSC-DE-512-SM

MIL-STD-171

QQ-P-35
(Federal Specification)
CANCELLED IN 1997

SAE-QQ-P-35
(AMS Specification)
CANCELLED IN 2005

SAE-AMS-2700

ASTM A-967

- **The active passivation specifications are AMS-2700 and ASTM A-967 – *both allow the use either Nitric Acid or Citric Acid*.**

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Environmental Concerns with Nitric Acid Passivation

- **In addition to free iron, it also can remove nickel, chromium or other heavy metals from alloy surfaces.**

  [Control Electropolishing Corporation, 2002]

- **Hazardous waste removal required.**

- **The metal finishing industry releases ~200,000 lbs of nitric acid annually.**

  [www.scorecard.org]

- **Releases nitrogen oxide (NO_X) gasses into the atmosphere during processing.**

  [Control Electropolishing Corporation, 2002]

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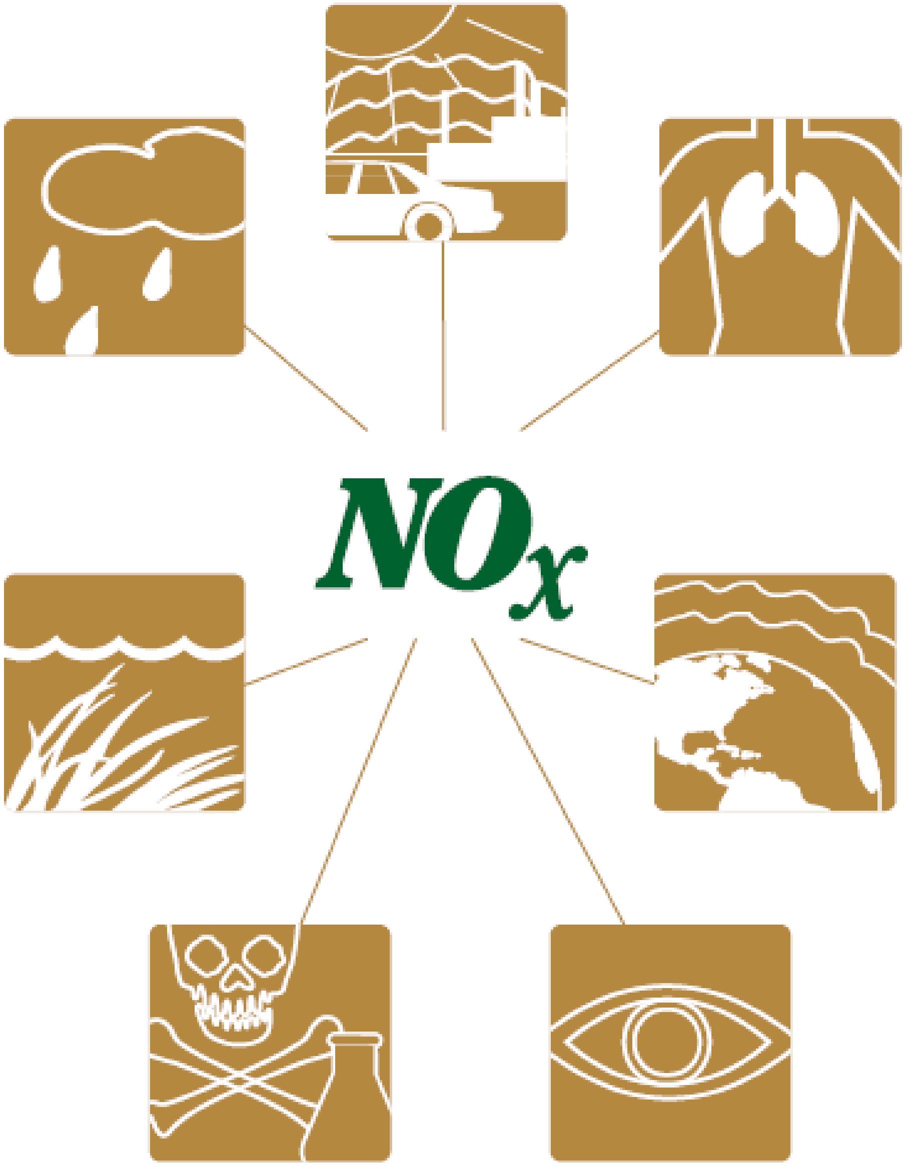
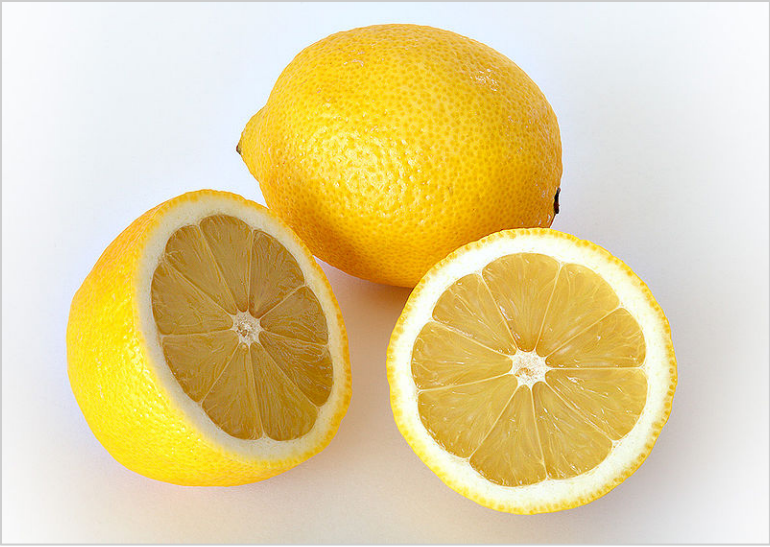
Environmental Concerns with NO_X Release *[EPA, 2008]*



- Contributes to acid rain.
- Increases nitrogen loading (oxygen depletion) in bodies of water.
- NO_X vapors react with volatile organic compounds (VOCs), sunlight and heat to make smog.
- NO_X vapors react with many common organic chemicals to form toxic chemicals.
- Nitrous oxide (N_2O) is a greenhouse gas and contributes to global warming.
- NO_X gasses are able to be carried over long distances.
- **In short, NO_X attacks our air, our land, our water, our planet and our bodies.**

Environmental Benefits of Citric Acid

- **Citric acid is biodegradable.**
- **Naturally occurs in citrus fruits.**
- **Hazardous waste removal not necessarily needed.**
- **Removes only free iron and iron oxides from surface; no heavy metals are removed during the passivation process.**
  [Control Electropolishing Corporation, 2002]
- **No toxic fumes or byproducts are created from its use or reactions during the passivation process.**
  [Control Electropolishing Corporation, 2002]



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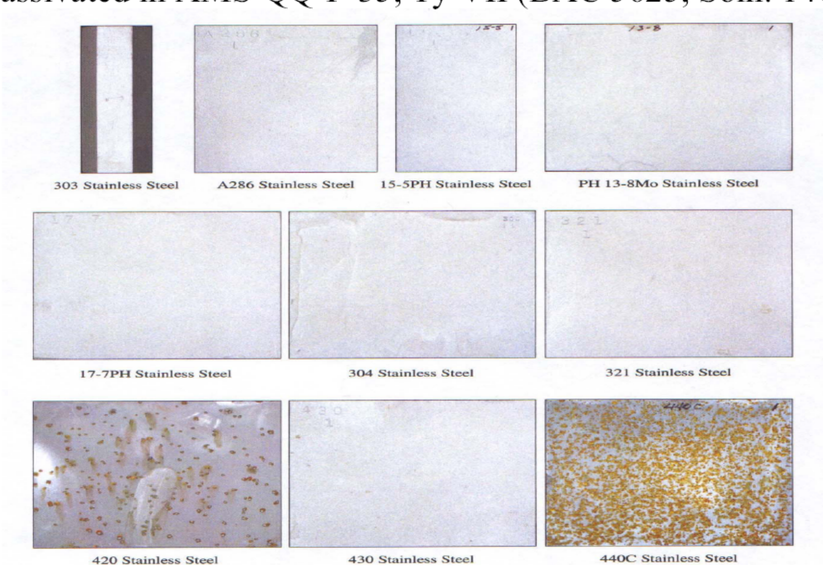
Citric Acid Studies in Industry *[Stephen Gaydos, Boeing, 2003]*

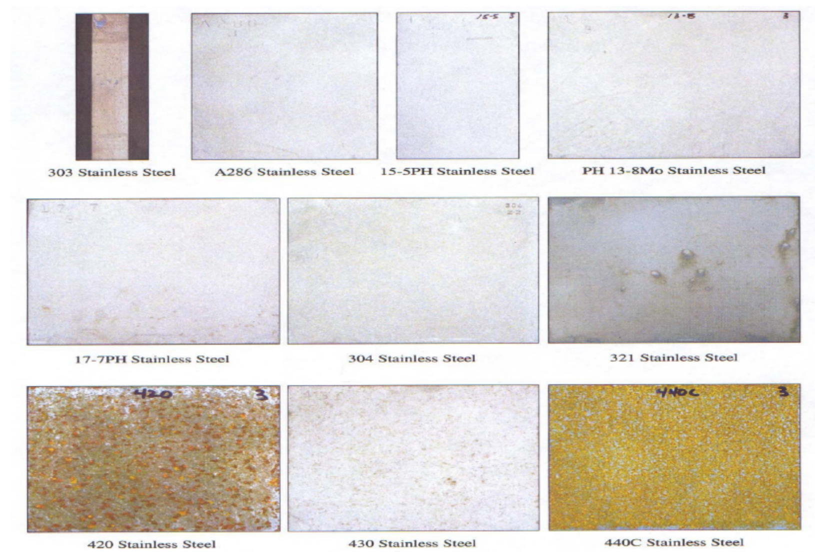
- **Boeing compared citric to nitric on 10 stainless steel alloys.**
- **Conclusion: citric acid passivation is as effective as nitric acid passivation.**

Passivation Solution	303	A286	15-5PH	PH13-8Mo	17-7PH	304	321	420	430	440C
AMS-QQ-P-35, Ty VII (22% HNO_3, $130^{\circ}F$)	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Fail	Pass	Fail
Optimized Nitric Acid (20% HNO_3, Ambient)	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Fail	Pass	Fail
AMS-QQ-P-35, Ty II (22.5% HNO_3+Dichromate, $120^{\circ}F$)	Fail	Fail	Pass	Pass	Fail	Fail	Fail	Fail	Fail	Fail
Optimized Citric Acid (15% Citric Acid, Ambient)	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Fail	Pass	Fail
Commercially Available Citric Acid Cleaner (12.5%, $155^{\circ}F$)	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Fail	Pass	Fail

Salt Spray Test Results for Contaminated Test Specimens Passivated in AMS-QQ-P-35, Ty VII (BAC 5625, Soln. 14C)

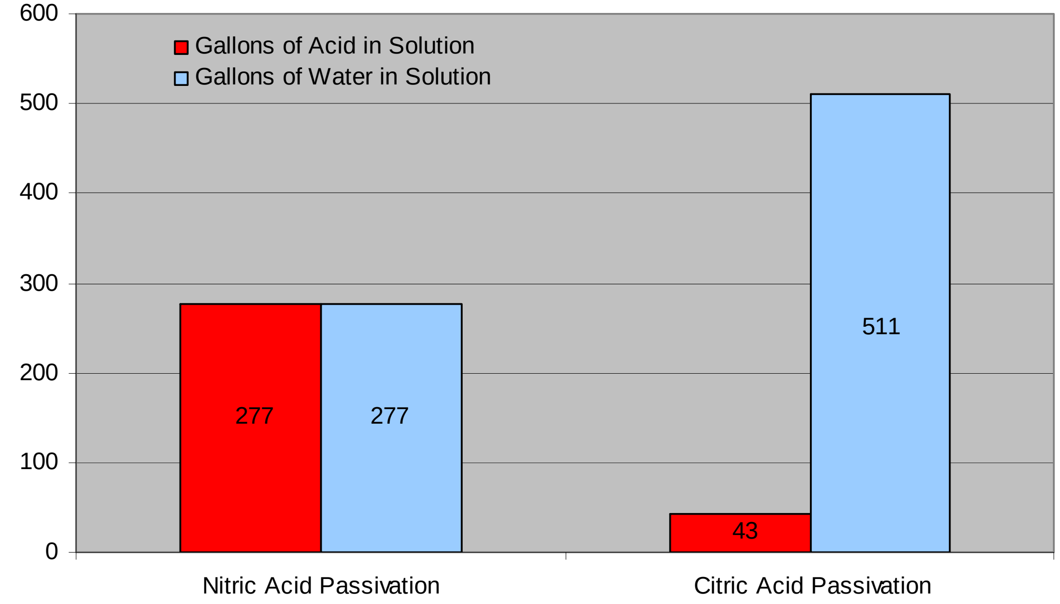


Salt Spray Test Results for Contaminated Test Specimens Passivated in Optimized Citric Acid



Citric Acid Studies in Industry *[Control Electropolishing Corporation, 2002]*

- **Control Electropolishing Corporation of Brooklyn, New York conducted a thorough study in 2002, exploring the effects of citric acid vs. nitric acid as well as studying acid consumption.**
  - **Like Boeing, they found citric acid performed on par with nitric acid.**
  - **Citric acid passivation solutions were 4% to 10% citric acid as opposed to ~50% nitric acid while still yielding the same results.**
    - **Lower concentration results in more neutral pH of ultimate rinse stream.**
  - **Immersion time in citric acid bath was decreased from a nitric acid bath.**
    - **Requires less batch refill.**
    - **Decreases consumption and disposal of acid.**
    - **Decreases operating costs.**



Passivation at Kennedy Space Center

- KSC disposes of approximately 125 gallons of concentrated nitric acid per year, and receives many passivated parts from vendors.
- Passivated parts are used on both Shuttle and ground support equipment; mostly fasteners and welded joints.

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Passivation at Kennedy Space Center

- **Currently, only nitric acid is permitted for use to passivate parts at KSC laboratories.**
- **Only nitric acid passivated parts are acceptable from vendors per NASA specifications.**
- **Industry studies are promising, but not conclusive for NASA at KSC.**
  - **No atmospheric corrosion evaluation.**
  - **Examination of corrosion resistance lacks quantitative analysis.**
  - **Lack of articles published in peer-reviewed journals.**
- ***In 2007, NASA's Materials Advisory Working Group (MAWG) requested the evaluation of a procedure that employs citric acid in place of nitric.***
- **Citric acid may improve the cost, safety, and environmental friendliness associated with passivation.**

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Goal and Scope

GOALS:

- To optimize a citric acid passivation procedure.
- To compare citric acid passivation to nitric acid passivation in terms of corrosion protection.

IF CITRIC ACID IS EFFECTIVE…

- To reduce nitric acid waste stream at Kennedy Space Center by 125gal/yr.
- To disseminate results to other organizations to reduce nitric acid disposal.

SCOPE:

- Optimize citric acid passivation on three types of steel commonly used at Kennedy Space Center: UNS S30400, S41000, and S17400.
- Compare severity of corrosion using citric acid vs. nitric acid for passivation.
  - Expose coupons to artificial (salt fog chamber) and natural (KSC Beach Site) corrosive environments.
- Evaluate side effects of citric acid passivation, e.g. LOX/GOX compatibility, performance on welds, and effects of entrapment.

High Level Test Plan

Phase 1

- Preliminary Optimization
- ASTM B-117 - Salt Fog Chamber exposure
- RESULTS: Important process variables for successful passivation

Phase 2

- Refined Optimization
- ASTM G-50 - Atmospheric Exposure
- RESULTS: Optimized Citric Acid Passivation Procedure (Time, Temperature, Concentration)

Phase 3

- Comparison between citric and nitric
- Analysis of the effects of citric acid
- RESULTS: Statistical comparison between citric and nitric, and an understanding of its "side effects"

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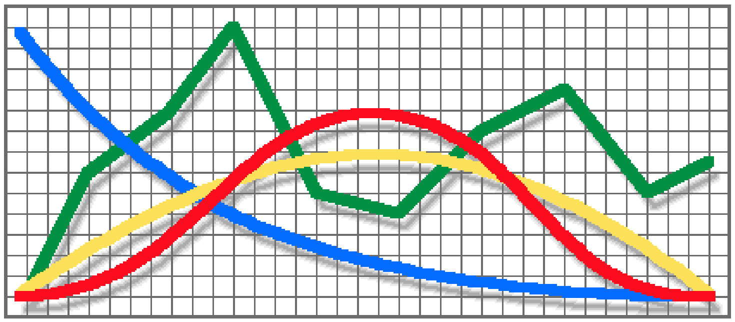
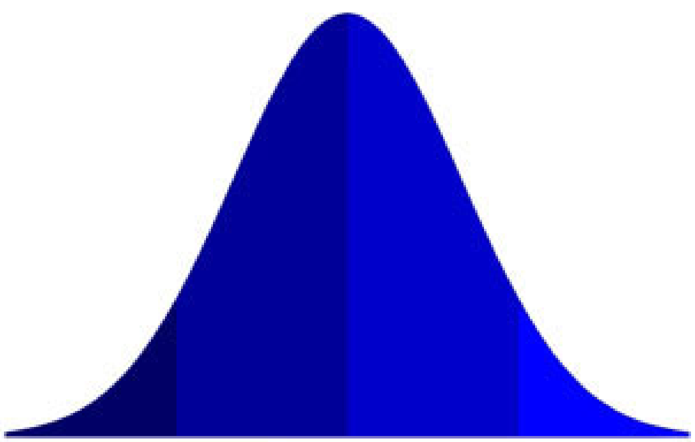
Statistical Tools



- **Design of Experiments (DoE) Analysis:**
  - **Analyzes multiple test parameters simultaneously.**
  - **Exposes interactions between variables.**
  - **Delivers optimized combination of variables.**
  - **Used in phases 1 and 2 to optimize the citric acid treatment.**



- **Analysis of Variance (ANOVA):**
  - **Compares the output of two or more processes.**
  - **Confirms whether or not two processes differ.**
  - **Used in phase three to compare nitric and citric acid treatments.**

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Test Parameters and Materials

- Citric Acid Test Parameters:
  - Immersion Time (4 – 120 Minutes)
  - Solution Temperature (21 – 82 °C)
  - Citric Acid Concentration (4 – 40 % Citric Acid by weight)

- Material Test Coupons:
  - UNS S30400 (304 austenitic stainless steel, 0.33cm thick)
  - UNS S41000 (410 martenisitic stainless steel, 0.23cm thick)
  - UNS S17400 (17-4 precipitation hardened steel, 0.23cm thick)
  - 10cm x 15cm
  - Representative of parts at KSC

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Phase 1 (Screening DoE)

Test 9 citric acid treatments on each material (304, 410, and 17-4).

Evaluate Corrosion resistance per ASTM B-117, Salt Spray Chamber Testing.

Include control samples:

- Nitric acid passivated
- Non-passivated

Refine citric acid treatment parameters.

Phase 1 DoE Schedule

Run #	Time (min)	Temp. (°C)	Conc. Citric Acid (wt%)
1	4	21	4
2	120	21	4
3	4	82	4
4	120	82	4
5	4	21	40
6	120	21	40
7	4	82	40
8	120	82	40
9	62	52	22

Phase 2 (Optimization DoE)

Test 9 citric treatments for each material based on Phase 1 data analysis.

Evaluate corrosion resistance per ASTM G-50 - Conducting Atmospheric Corrosion Tests on Metals (6 months).

Include control samples:

- Nitric acid passivated
- Non-passivated

Choose optimized citric acid passivation procedure for each material.

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Phase 3 (Citric Acid vs. Nitric Acid)

Develop optimized citric acid procedure from Phase 2 results.

Passivate all three metals with optimized procedure AND the current nitric acid procedure.

Expose coupons at the Corrosion Beach Facility for 6 months.

Compare corrosion on the passivation coupons.

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Phase 3 (Special Cases)

Special Cases

Test LOX/GOX compatibility of residual anhydrous citric acid per NASA-STD-(I)-6001.

Evaluate corrosion caused by citric acid solution entrapped between two parts.

Test corrosion resistance of passivated welds.

Entrapment and weld corrosion will be studied at Corrosion Beach Facility.

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Passivation Processing – High Level Process

Initial Degrease to Remove Machining Contamination.

Grit blast coupons with carbon steel to eliminate passive layer and introduce free iron.

Degrease per NASA approved Flight Hardware Process.

Passivate

Citric Acid

- Acid Concentration (4 - 40 pbw)
- Solution Temperature (21 – 82 °C)
- Passivation Time (4 - 120 minutes)

Nitric Acid

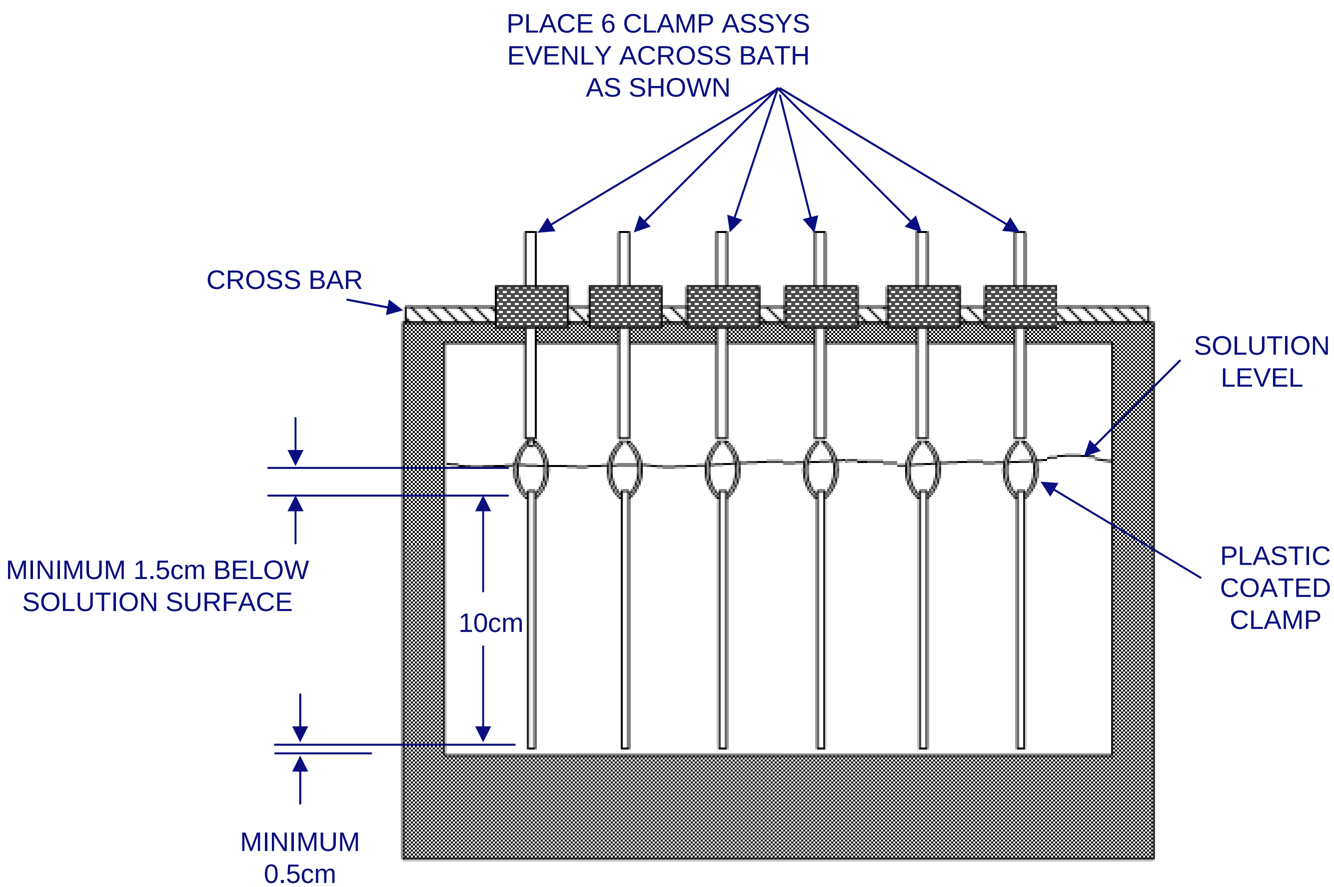
- NASA approved Flight Hardware Process
- 25°C, 40 % by volume

Rinse Coupons with DI Water to neutral pH.

Blow Dry with Filtered GN_2.

Store in clean, soft, low lint cloth in controlled environment.

Passivation Processing – Coupon Immersion



LINDBERG/BLUE M WATERBATH
MODEL # WB11OA
SECTION VIEW

Coupon Exposure Methods

Phases 2 & 3 - ASTM G-50 - Conducting Atmospheric Corrosion Tests on Metals – 6 months for each exposure.

Phase 1 - ASTM B-117 – Salt Spray Chamber Testing – 2+ days.

Corrosion Evaluation Plan

- Evaluation of general corrosion per *ASTM G-1 - Preparing, Cleaning, and Evaluation of Corrosion Test Specimens*: Weighing and measuring per 6.5, chemical cleaning per 7.2, corrosion rate per 8.
- Evaluation of Pitting corrosion per *ASTM G-46 - Inspection and Evaluation of Pitting Corrosion*: Pit density, pit depth per 5.2.3 (Micrometer or depth Gage) or 5.2.4 (Microscopical), pitting factor, and pitting probability (calculated from all coupons).
- *ASTM D-610 - Evaluation of Degree of Rusting on Painted Steel Surfaces* for evaluation of general corrosion. This specification assigns an index number to a coupon based on the % of the surface that has corroded.

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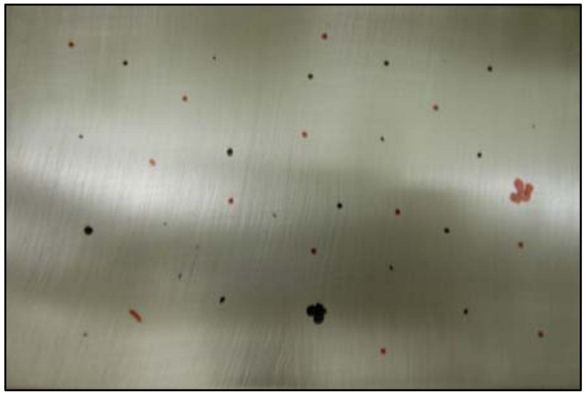
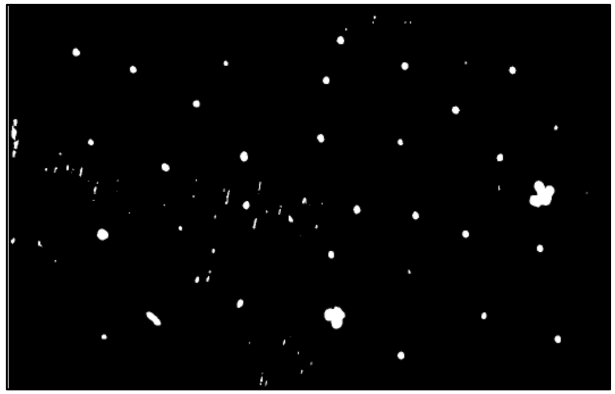
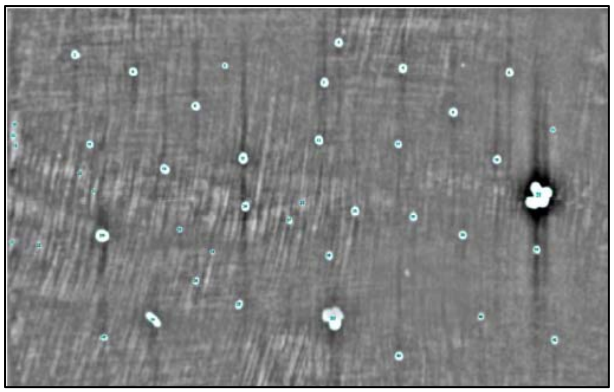
Corrosion Evaluation Plan

- **Pit Count, Pit Diameter, and General Corrosion evaluated by image analysis software.**
- **Computer software uses a number of techniques to remove photographic "noise" and isolate surface irregularities (corrosion).**



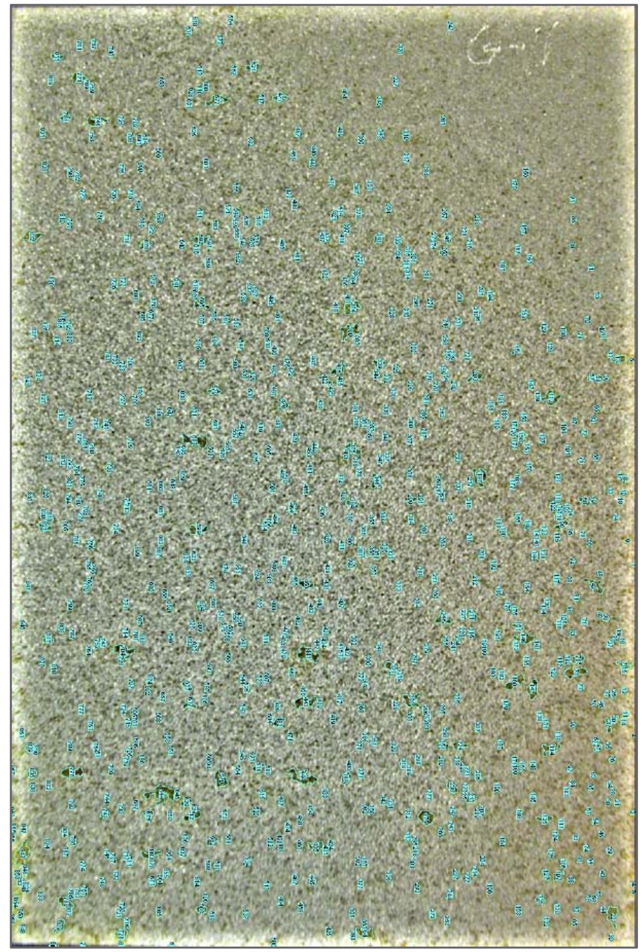




43 Pits were Identified

Corrosion Evaluation Plan

- **General corrosion can be evaluated with software by distinguishing colors.**



Approximately 3% of the surface covered with corrosion

Project Status

- The team has begun phase 1, optimization of the citric acid treatment.
- Estimated completion date: Early 2011
  - This date is due in part to the slow nature of atmospheric corrosion tests.

IF CITRIC ACID IS EFFECTIVE:

- NASA specifications will be revised to permit citric acid passivation.
- Final results will be shared with other government organizations (Army, Navy, Air Force, Marines) and government contractors.
- Nitric acid waste stream will be reduced.

FURTHER STUDY:

- Characterize surface produced by citric acid (AES-ICP, XPS, IES).
- Citric acid logistics.
  - Maintenance costs.
  - Storage, mixing requirements, ease of use.

Acknowledgements

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- **Eric Burke, United Space Alliance, LLC**
- **Pattie Lewis Burford, ITB, Inc.**
- **J. Michael Johnson, WilTech Laboratory**
- **NASA TEERM**
- **C3P**

-Please contact the presenter for references-

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Questions?

Back-up

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Corrosion Evaluation Plan

Corrosion Type	Method	Location and Equipment	Reported Metrics	Measurement System Analysis
General/ Uniform Corrosion	1. Coupon cleaning and weight loss per ASTM G1 2. Visual Inspection	Scales Equipment available at Hanger M Annex	Coupon weight loss.	Scales calibrated
Pit Depth	1. Optical Microscopy 2. Interferometry 3. Mold impressions	1. Stereoscope 2. Interferometer 3. Mold impression material (orange) Stereoscope available from M&P Ground Ops, All other equipment and methods available from MIT	Max depth and average of deepest pits (3 per coupon).	Interferometer calibrated Reproducibility study during screening DoE
Pit Count	1. Pit count per G46, 4.1.4.2, covering the coupon with a plastic grid for systematic counting. 2. Pit count using photographs and image analysis software.	1. Plastic grid 2. Digital Camera, image analysis software, 10X lens Camera, lens, and grid available from USA M&P Ground Ops, software available from USA NDE (Hanger N).	Pit count total, pit count density (pits/unit area).	Software calibrated Reproducibility study during screening DoE
Pit Diameter	1. Measure diameter using photographs and image analysis software	1. Digital Camera, image analysis software Camera available from USA M&P Ground Ops, software available from USA NDE (Hanger N).	Max diameter and average of largest pits (3 per coupon).	Software calibrated Reproducibility study during screening DoE

Requirements Per QQ-P-35

- Passivation is for the final cleaning of corrosion resistant steels.
- Nitric Acid in accordance with O-N-350
  - O-N-350 has been cancelled and redirects to Commercial Item Description A-A-59105
    - Vendors do not certify to CID
- 4 Types; 70-150°F Bath Temperature, 20-55% Nitric Acid
  - Type II - Medium (120-130°F) temperature 20-25% nitric acid solution with 2-2.5 wt% sodium dichromate additive
  - Type VI - Low (70-90°F) temperature 25-45% nitric acid solution
  - Type VII – Medium (120-150°F) temperature 20-25% nitric acid solution
  - Type VIII - Medium (120-130°F) temperature high concentration 45-55% nitric acid solution
- Optional Chromate post-treatment
- Lot Testing

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Requirements Per ASTM A-967

- Passivation is defined as the chemical treatment of stainless steel with a mild oxidant for the purpose of the removal of free iron (or sulfides or other foreign matter)
- Nitric Acid Treatment
  - 5 different solutions; 70-140°F Bath Temperature, 20-55% Nitric Acid
  - 4 of the 5 solutions are essentially equivalent to QQ-P-35 Types
    - Nitric 1 => Type II
    - Nitric 2 => Type VI
    - Nitric 3 => Type VII
    - Nitric 4 => Type VIII
  - 5th solution is a catch-all for any combination of temperature, time, concentration, chemical additives that results in an acceptable part.
- Citric Acid Treatment
  - 5 different solutions; 70-160°F Bath Temperature, 4-10% Citric Acid
  - 2 of the 5 solutions are catch-alls for any combination of temperature, time, concentration, chemical additives that results in an acceptable part. The difference between the two solutions is control of the immersion tank pH.
  - 3 of the 5 solutions vary by temperature and time but require 4-10% citric acid.
- Other Chemical Solution (including Electrochemical) Treatments
  - Allows for any other media which produces an acceptable product
- Optional chromate post-treatment
- Lot testing when specified on purchase order
- When not explicitly stated on purchase order, the processor may select any passivation treatment.

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ASTM A-967 Parameters

	Nitric Acid	Citric Acid
Concentration	20-55vol%	4-10wt%
Temperature	70-130ºF	70-160ºF
Processing Time	20-30min.	4-20min.

- Per this specification, any combination of concentration of the primary specie, temperature, and time, with or without accelerants, inhibitors, etc. that produces parts capable of passing corrosion resistance tests is acceptable (provided that a specific procedure is not called out)

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Requirements Per AMS 2700B

- Passivation is used to remove metallic contaminants from the surface of corrosion resistant steels using chemically oxidizing methods to prevent bulk degradation.
- Method 1, Nitric Acid
  - 8 Types; 70-155°F Bath Temperature, 20-55% Nitric Acid
  - 5 of the 8 types require the dichromate additive
  - AMS 2700 Type 2, 6, 7, and 8 are essentially equivalent to respective QQ-P-35 Types
  - Optional Additives
    - 2-6wt% sodium dichromate dihydrate ($Na_2Cr_2O_7{:}2H_2O$), an oxidizer, if $[HNO_3] < 35\%$
    - Up to 6wt% copper sulfate ($CuSO_4{:}5H_2O$) for extra oxidation potential (in lieu of $Na_2Cr_2O_7{:}2H_2O$)
    - Up to 0.35wt% molybdic acid ($HMoO_3$) for Pb removal
    - 2-5 volts may be applied to prevent etching and reduce process time
- Method 2, Citric Acid
  - 0 Types; 70-160°F Bath Temperature, 4-10% Citric Acid
  - Optional Additives
    - Inhibitors
    - Wetting agent
- Class 1 – statistical sampling frequency
- Class 2 – lot testing
- Class 3 – periodic testing
- Post Treatment is in 2-5% NaOH unless chromate treatment specified
- When not explicitly stated on purchase order, Method 1, any Type, Class 2 is implied.

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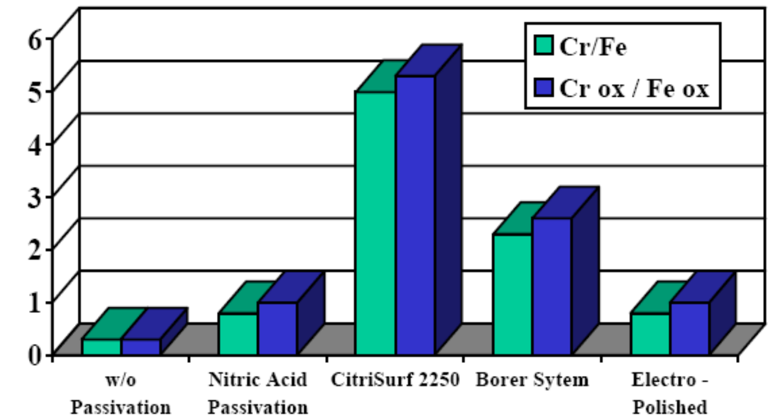
Secondary NASA Specifications

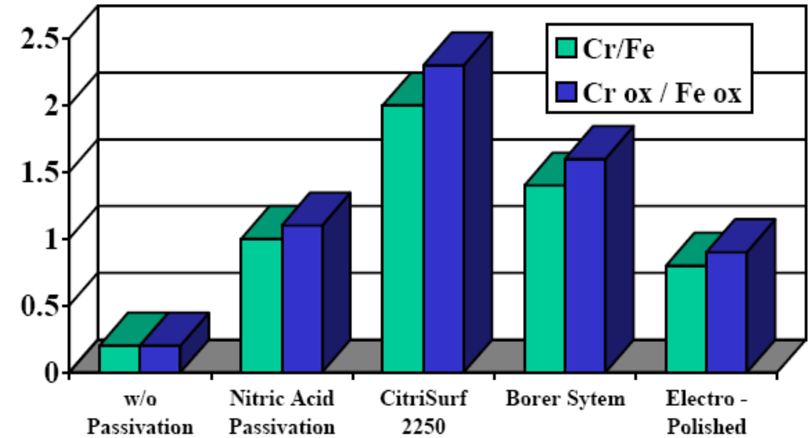
- NASA-STD-5008 *(Protective Coating Of Launch Structures, Facilities, And GSE)*
  - Clean parts per SSPC SP-1
  - No specific passivation methods mentioned
- TM-584C (*Corrosion Control and Treatment Manual)*
  - Clean parts per SSPC SP-1
  - Acid clean parts
    - HNO_3 (42°Bé): 225 to 375 kilograms per cubic meter (kg/m3) [30 to 50 ounces per gallon (oz/gal) weight]
    - HF (ammonium bifluoride, NH_4HF_2 may be used in lieu of HF): 9 to 52 kg/m3 (1.2 to 7.0 oz/gal)
    - Bath temperature 140°F
  - No specific passivation methods mentioned

NMI Report (cont.)

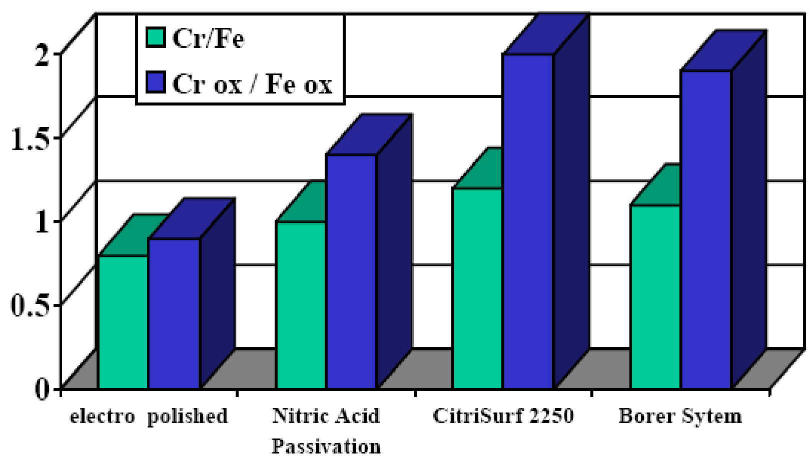
SS 1.4034 - 3M brushed finish



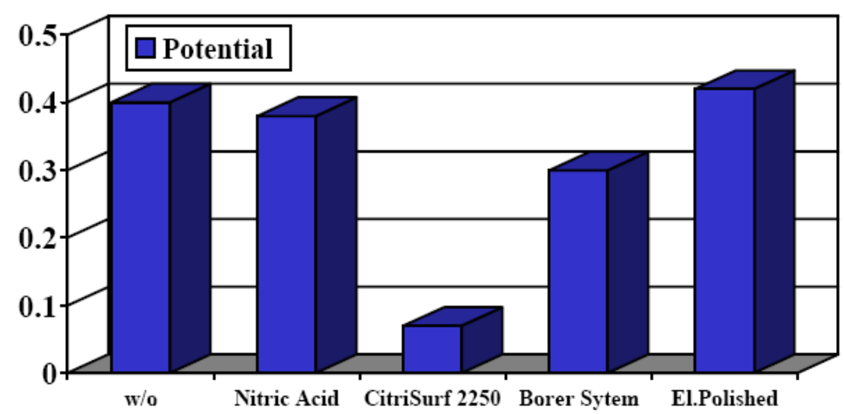
SS 1.4021 - 3M brushed finish



SS 1.4021 - 3M brushed finish & electro polished



SS 1.4021 - 3M brushed finish



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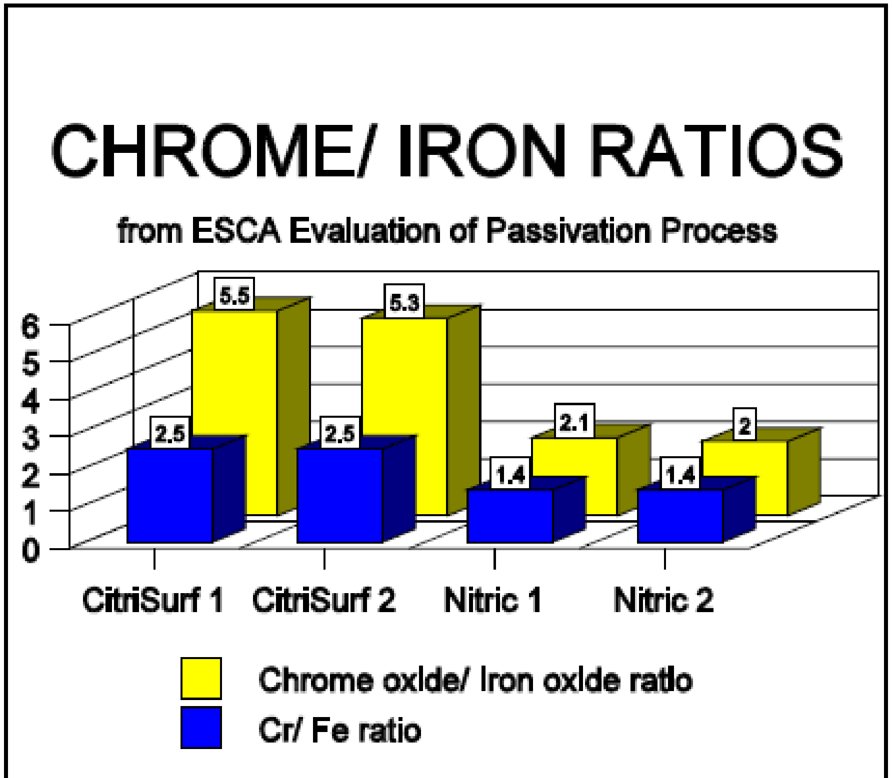
NMI Report - Conclusions

- Citric acid passivated surfaces produced higher Fe/Cr and higher Fe ox/Cr ox ratios than nitric acid, electro-polishing, and a sequestering agent
- Low potential values indicate the highest surface resistance, thus citric acid produces most electrically resistant surface

Semiconductor Equipment and Materials International (SEMI) Report



Chrome oxide	5.5	5.3	2.1	2
Cr/ Fe ratio	2.5	2.5	1.4	1.4

- **Carried out by SEMI on 316L coupons**
- **Samples passivated with citric acid per ASTM A-967 Citric 4 (proprietary solution, CitriSurf 2050 in this case)**
- **Samples passivated with nitric acid per ASTM A-967 Nitric 2 (20-45vol% acid, 70-90°F bath, 30 minutes)**

SEMI Report (cont.)

AES Depth Profile Results

Sample	Oxide thickness	Max. Depth of Enrichment	Depth of Enrichment
CitriSurf 1	27.0 Å	18.0 Å	17.0 Å
CitriSurf 2	28.0 Å	19.0 Å	17.0 Å
Average	**27.5** Å	**18.5** Å	**17.0** Å
Nitric 1	21.0Å	13.0 Å	12.0 Å
Nitric 2	17.0 Å	11.0 Å	11.0 Å
Average	**19.0** Å	**12.0** Å	**11.5** Å

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SEMI Report - Conclusions

- On 316L coupons, CitriSurf 2050 produced higher Fe/Cr and higher Fe ox/Cr ox ratios than nitric acid
- CitriSurf produced oxide thicknesses about 50% thicker than those produced with nitric acid.

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