Citric Acid Passivation of Stainless Steel

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Contents

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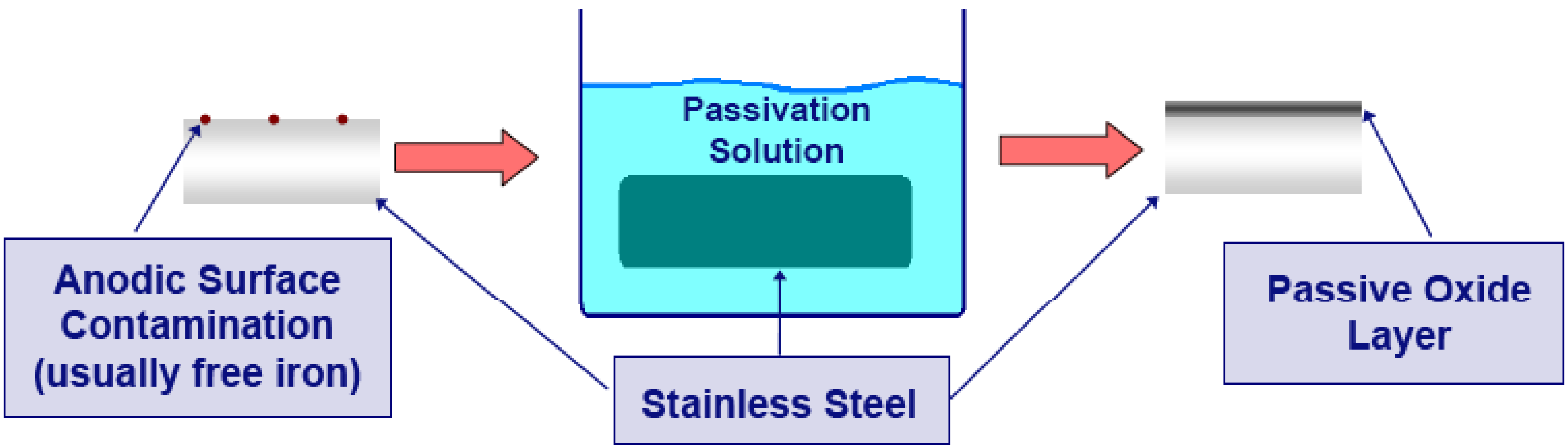
Introduction - Passivation

- Passivation is a chemical cleaning process to improve the corrosion resistance of stainless steel.
  - Removes anodic surface contamination, e.g. free iron particles.
  - Induces the formation of a passive oxide layer.
- Nitric Acid is the most widely used passivation agent.
  - This solution is currently used on KSC.
  - Recently, some alternative passivating agents, including citric acid, have been studied.



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Introduction - 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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Problem Statement - NASA Specifications

Flight Hardware

Ground Hardware

NASA 6016

MSFC-SPEC-250

KSC-DE-512-SM

MIL-STD-171

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

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

ASTM A967

SAE AMS 2700

- **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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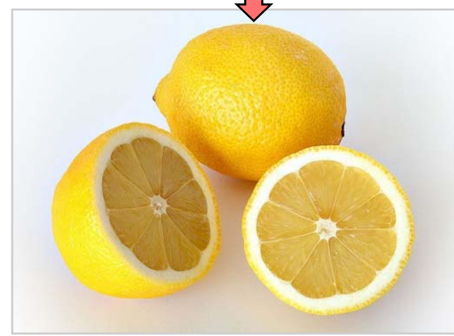
Problem Statement and Goal



- **Using citric acid as the passivating agent has numerous benefits.**
  - **Citric acid is a biodegradable, safe alternative to the hazardous nitric acid waste stream.**
  - **Some organizations report cost savings.**

<u>THE PROBLEM</u>: Although the benefits are well-established, evidence for citric acid as a technically sound passivation method is scarce.

  - **In 2008, NASA's Materials Advisory Working Group (MAWG) requested the evaluation of a procedure that employs Citric Acid in place of Nitric Acid to address the specification issue**

<u>THE GOAL</u>: to determine whether or not citric acid passivation is an adequate substitute for nitric acid passivation and update NASA specifications accordingly.

Test Plan

Optimize

- Optimize passivation to determine the best results that citric acid is capability of producing.
- ASTM B117 - Salt Fog Chamber.

Compare

- Compare citric acid to the current passivation process see if it is capable of providing equal or better corrosion protection.
- ASTM B117 - Salt Fog Chamber and ASTM G50 - Atmospheric Corrosion.

Address Special Cases

- Passivation of Welds.
- Effects of Citric Acid Entrapment.
- ASTM G50 - Atmospheric Corrosion.

Material Test Coupons:

- UNS30400 (304 austenitic stainless steel)
- UNS41000 (410 martensitic stainless steel)
- UNS17400 (17-4 precipitation hardened steel)
- 10cm x 15cm
- Representative of parts at KSC

Test Plan – Passivation Parameters

Phase 1

- ASTM B117 - Salt Fog Chamber
- Parameters:
  - Acid Conc: 4 - 40%
  - Temp: 72 – 180°F
  - Time: 4 – 120min.
- RESULTS: Concentration has a small effect; higher values of time and temperature are more effective.

These results drove parameter selection for phases 2 and 3

Phase 2

- ASTM B117 – Salt Fog Chamber
- Parameters:
  - Acid Conc: 4%
  - Temp. 100 – 180°F
  - Time: 30 – 120min.
- RESULTS: Optimized Processing Parameters and Nitric Acid Comparison

Phase 3

- ASTM G50 – Atmospheric Exposure
- Parameters:
  - Acid Conc: 4%
  - Temp: 100 – 180°F
  - Time: 30 – 120min.
- RESULTS: Optimized Processing Parameters and Nitric Acid Comparison

Weld and Entrapment coupons included in this phase

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Procedures - Passivation Processing

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
- Solution Temperature
- Passivation Time

OR

Nitric Acid

- NASA approved Flight Hardware Process
- QQ-P-35B

OR

Non-passivated

Rinse Coupons with DI Water to neutral pH.

Blow Dry with Filtered GN_2.

Store in clean PE bags in controlled environment.

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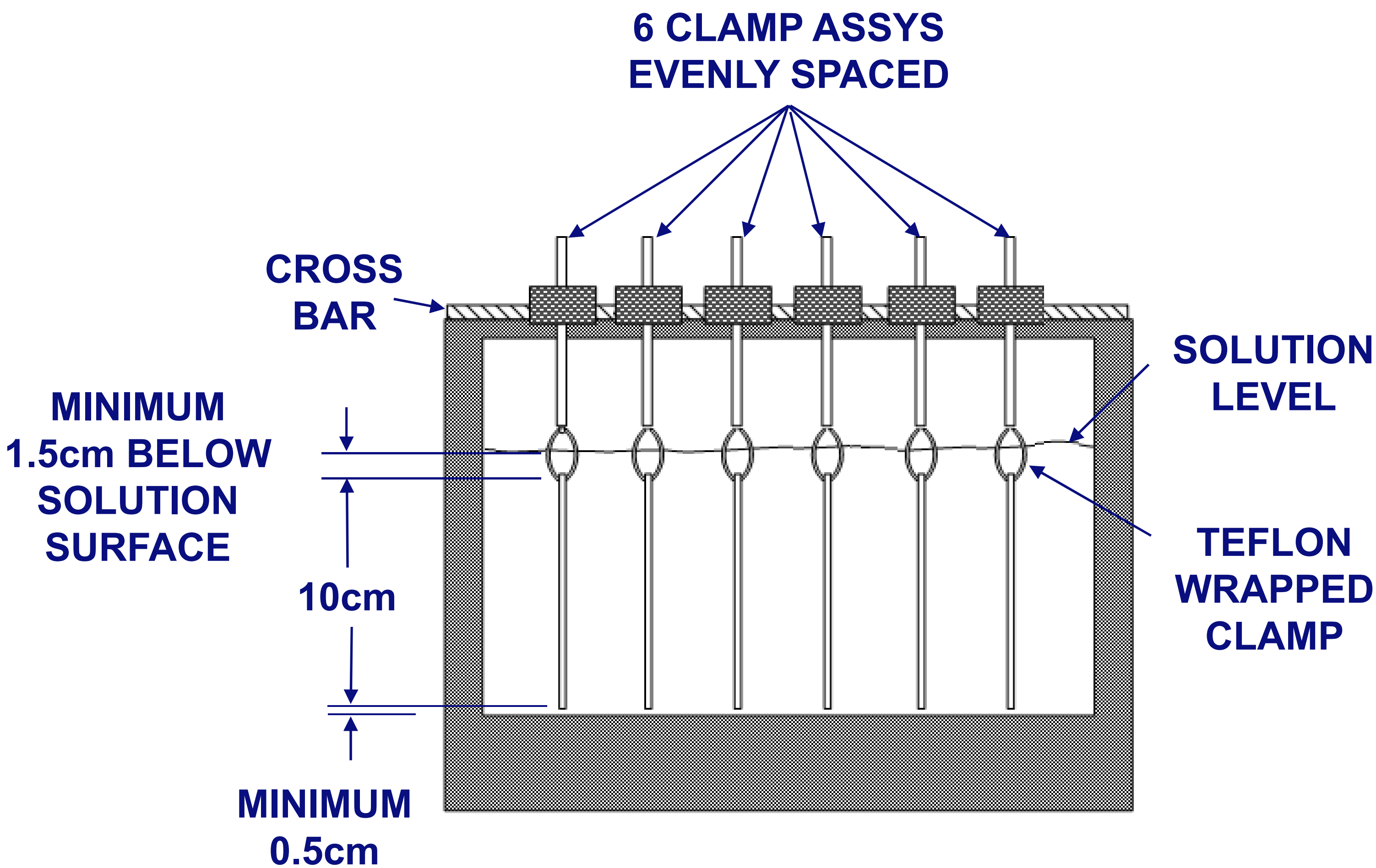
Procedures – Citric Acid Tank

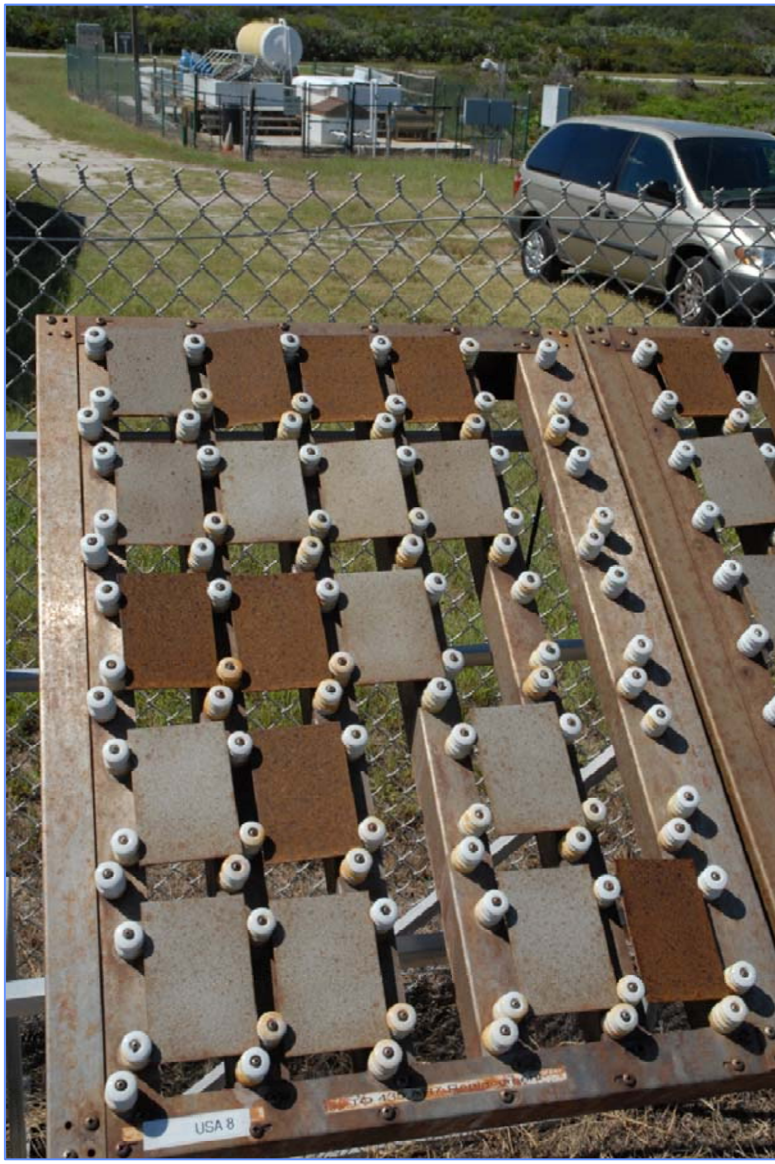
- LINDBERG/BLUE M
  Waterbath
  Model # WB11OA
- 10L Capacity
- Controls temperature up to 212°F
- Up to 6 coupons per run
- Constant agitation

Procedures – Citric Acid Tank



LINDBERG/BLUE M WATERBATH
MODEL # WB11OA
SECTION VIEW

Procedures - Coupon Exposure



- **Phase 3 - ASTM G50 - *Conducting Atmospheric Corrosion Tests on Metals* - 6 months**

- **Phases 1 & 2 - ASTM B117 – *Salt Spray Chamber Testing* – 2+ days**

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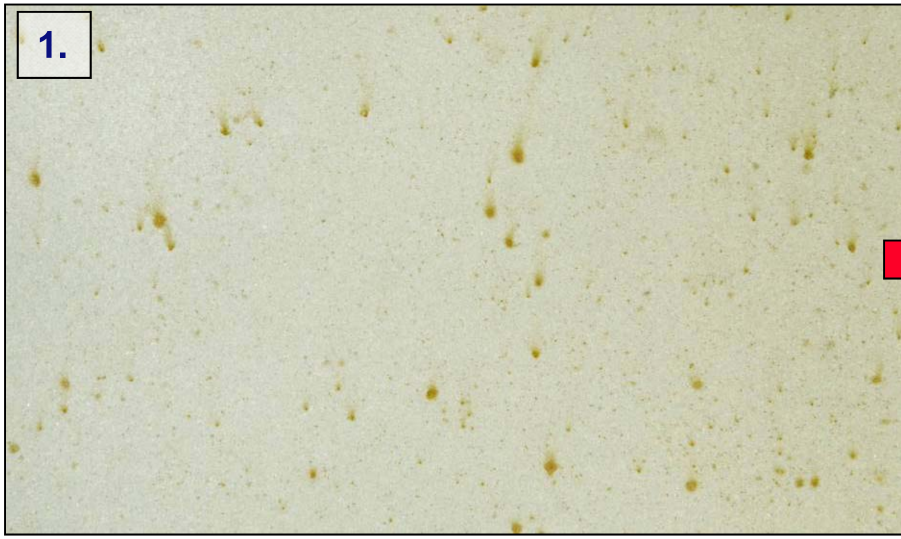
Procedures - Corrosion Evaluation

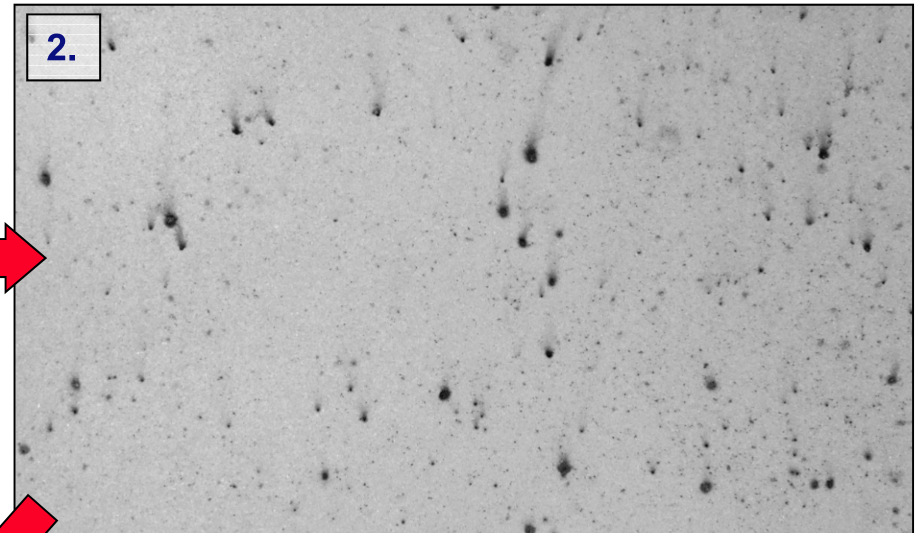
- Corrosion measurements designed to be enhanced, quantitative versions of passivation process verification testing per ASTM A967 and ASM SAE 2700
  - Pass/Fail based on the presence of superficial rust.
- If coupons corroded sufficiently, weight loss was measured.
  - Only alloy 410 coupons corroded enough to measure sizeable weight loss.
  - Scale resolution 0.1mg
- If coupons only exhibited superficial staining, image analysis was used to quantify the amount of staining.
  - Images were analyzed with ImageJ[1], image analysis software developed by the National Institutes of Health for academic applications.
  - Corrosion quantified as the percent of the area covered with corrosion.
  - All images within a group taken under the same studio conditions and analyzed with the same parameters (threshold value, region of interest).
- Due to the small extent of corrosion on most coupons and the surface texture produced by grit blasting, pitting was not distinguishable on the coupons.

1 - Rasband, W.S., ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, http://imagej.nih.gov/ij/, 1997-2011.

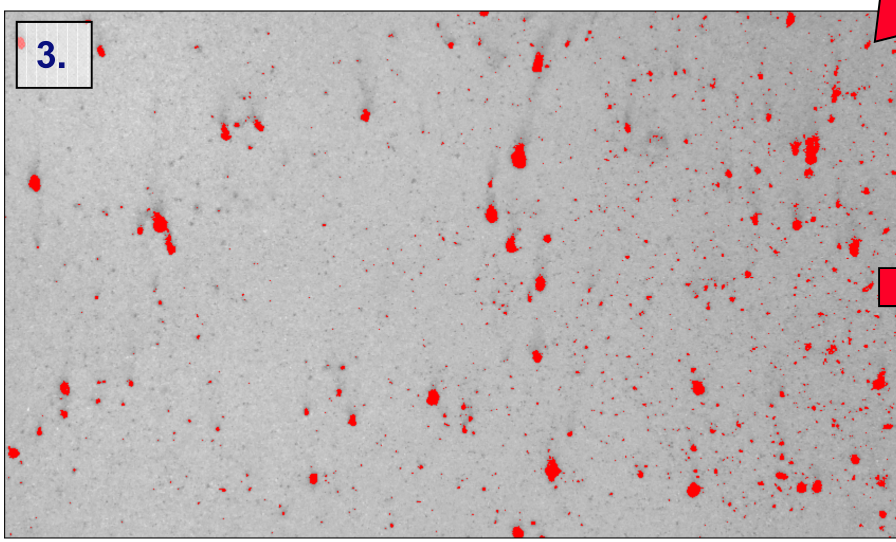
Procedures - Image Analysis Example 1



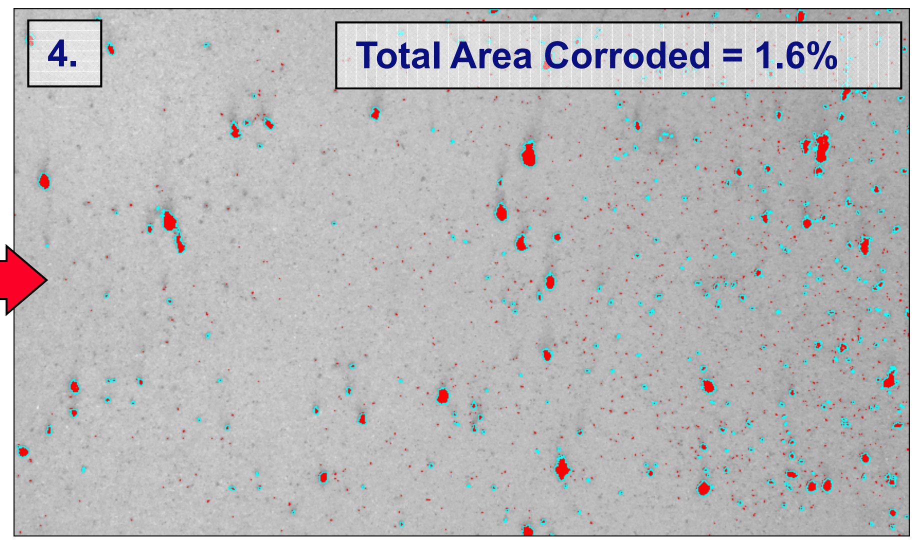
Crop Region of Interest



Isolate Blue Image

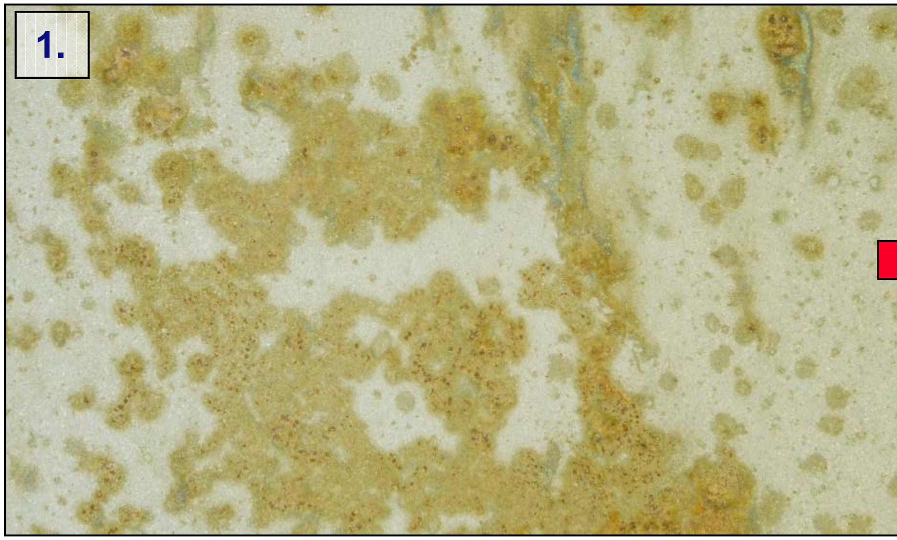


Apply Threshold

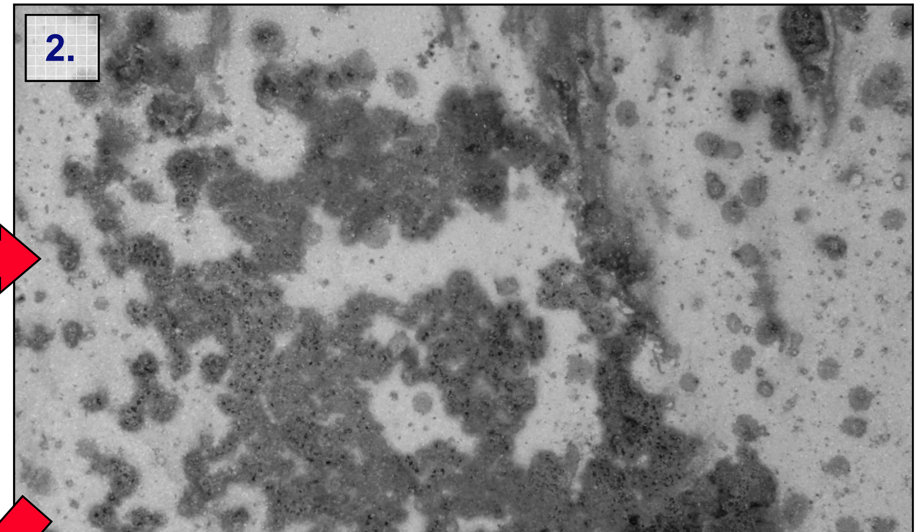


Sum Threshold Area

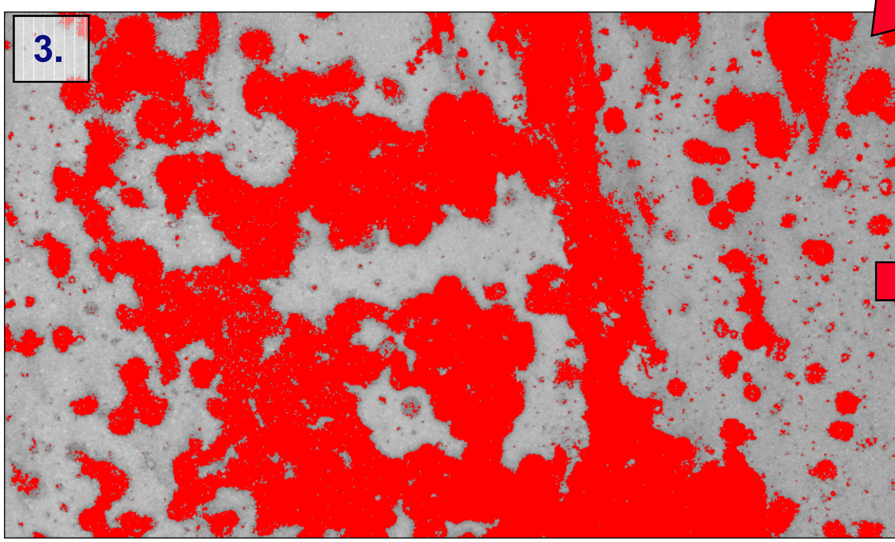
Procedures - Image Analysis Example 2



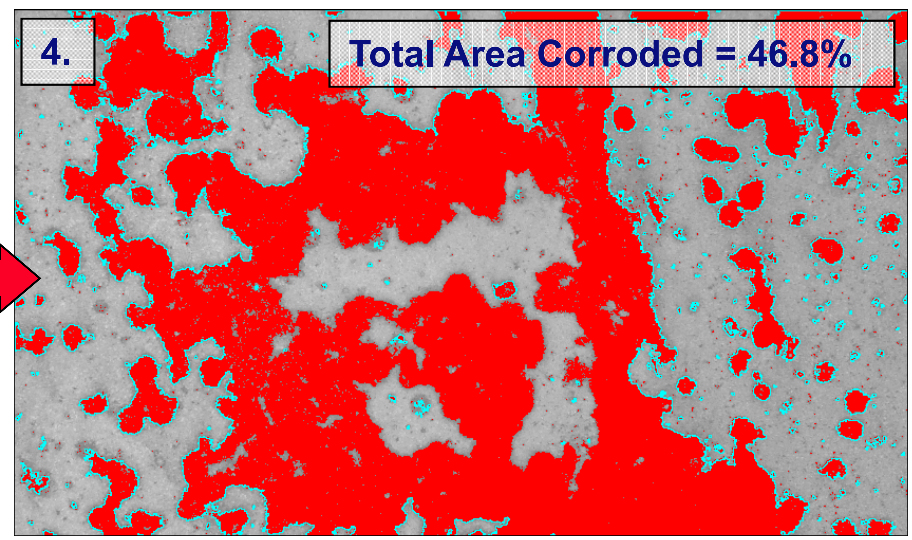
Crop Region of Interest



Isolate Blue Image



Apply Threshold



Sum Threshold Area

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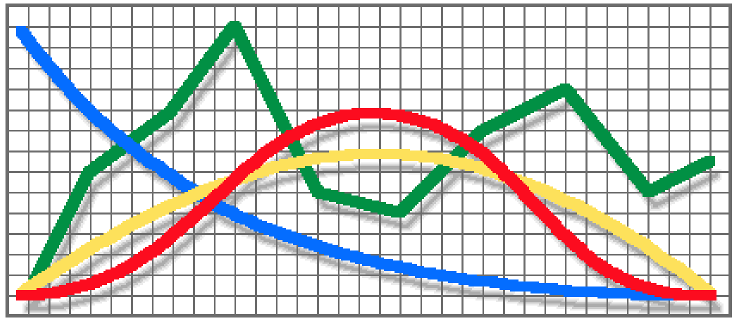
Optimization - Statistical Tools

- Design of Experiments (DoE) Analysis.
  - Analyzes multiple test parameters simultaneously.
  - Exposes interactions between variables.
  - Delivers optimized combination of variables.



- Factorial DoE in Phase 1.
  - Finds 1st order relationships and interactions.
- Central Composite Design in Phases 2 and 3.
  - Finds 1st and 2nd order relationships and interactions.

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Optimization – DoE Interpretation

- The DoE identifies significant factors through p-values.
  - p-values describe how certain we are that a factor is actually affecting the output of a process.
  - p-values are calculated for linear relationships with the factors (e.g. time t and temperature T), the interaction between variables (e.g. $t \times T$), and in the central composite designs (CCDs), the 2nd order relationships with factors (e.g. t^2 or T^2)
  - The p-value can be interpreted as the probability that a factor is *not* significant.
  - In research, a factor with a $p\text{-value} < 0.10$ is generally accepted as significant.
- The model as a whole can be evaluated through the R^2_{adj}-value.
  - This value can be interpreted as the amount of variation in the model that is explained by the factors (Time, Temperature, Concentration)
  - A model with an R^2_{adj}-value > 80% is generally regarded as conclusive.
  - A model with an R^2_{adj}-value > 50-79% is regarded in this study as noteworthy but not conclusive

Optimization - Phase 1

Phase 1

- ASTM B117 - Salt Fog Chamber
- Parameters:
  - Acid Conc: 4 - 40%
  - Temp: 72 – 180°F
  - Time: 4 – 120min.
- RESULTS: Concentration has a small effect; higher values of time and temperature are more effective.

Phase 2

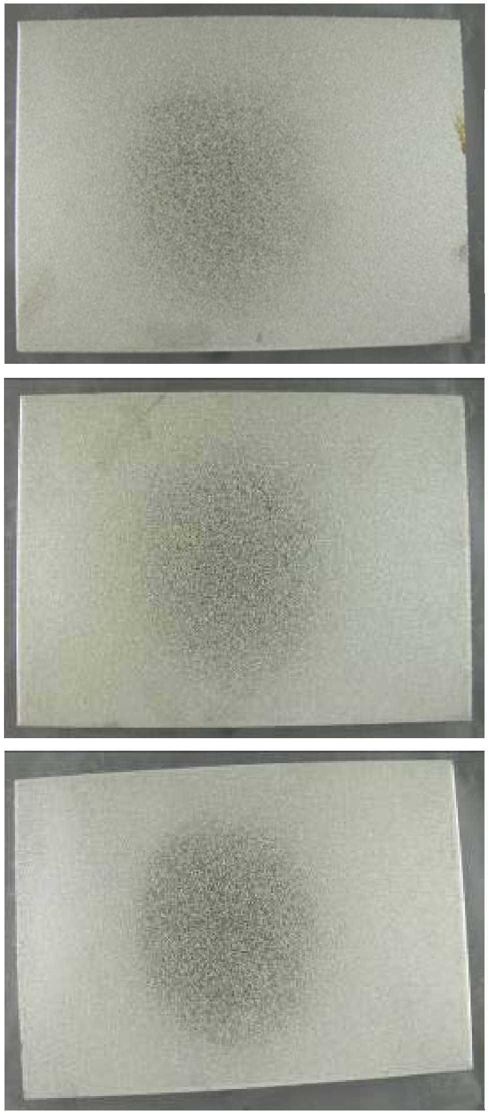
- ASTM B117 – Salt Fog Chamber
- Parameters:
  - Acid Conc: 4%
  - Temp. 100 – 180°F
  - Time: 30 – 120min.
- RESULTS: Optimized Processing Parameters and Nitric Acid Comparison

Phase 3

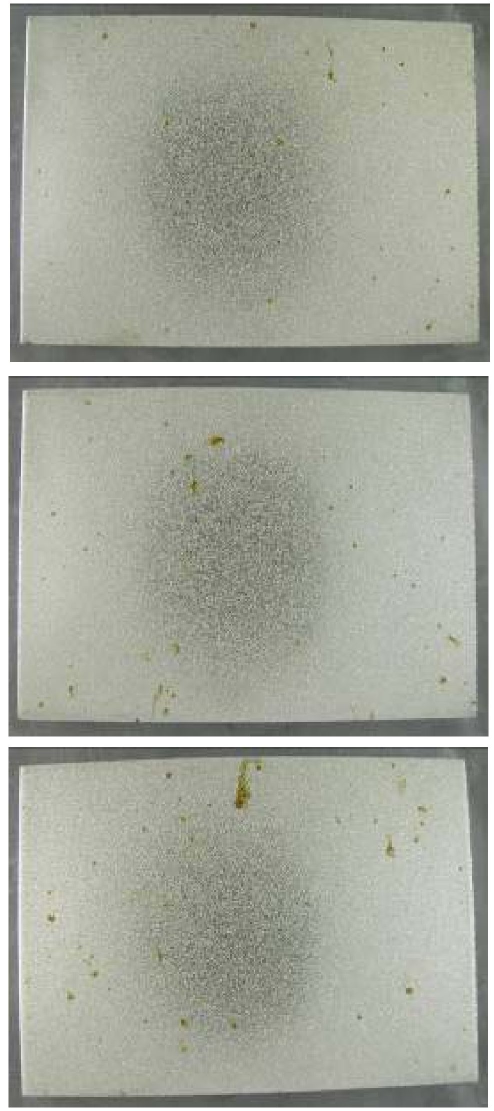
- ASTM G50 – Atmospheric Exposure
- Parameters:
  - Acid Conc: 4%
  - Temp: 100 – 180°F
  - Time: 30 – 120min.
- RESULTS: Optimized Processing Parameters and Nitric Acid Comparison

Optimization Phase 1 - 304 – CA vs. NA vs. Un-passivated

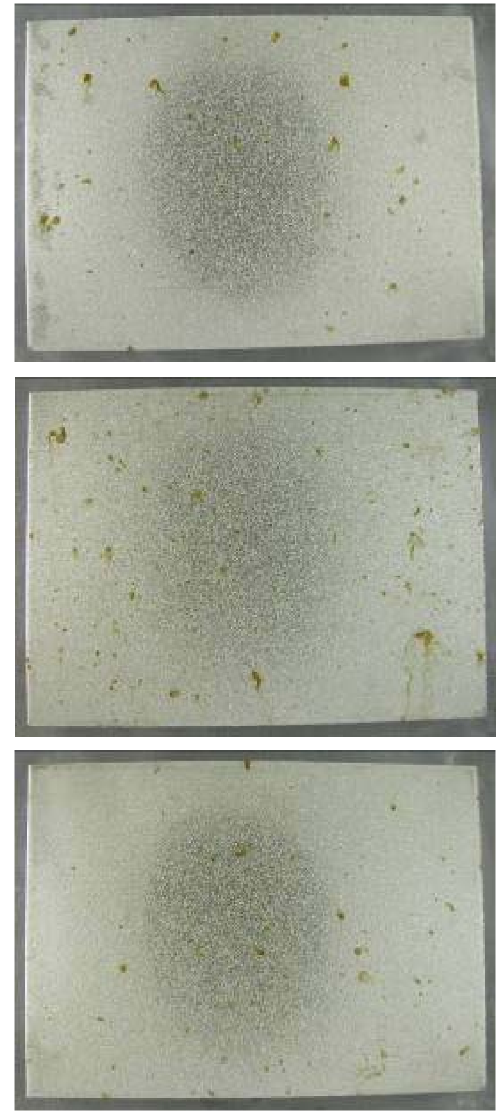
Citric Acid 120m, 180F, 4%
(Best Performing CA Treatment)



Nitric Acid 60m, 77F, 32%

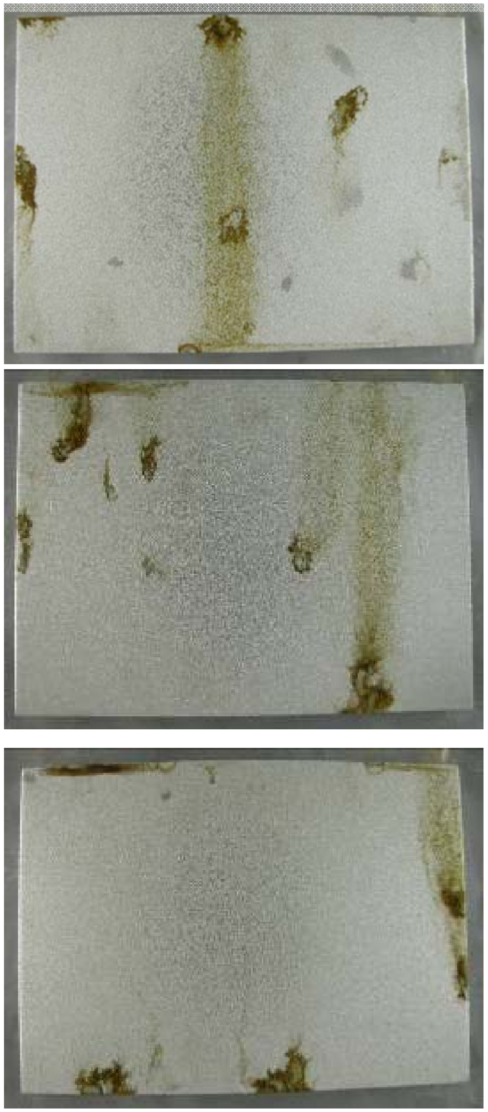


Unpassivated

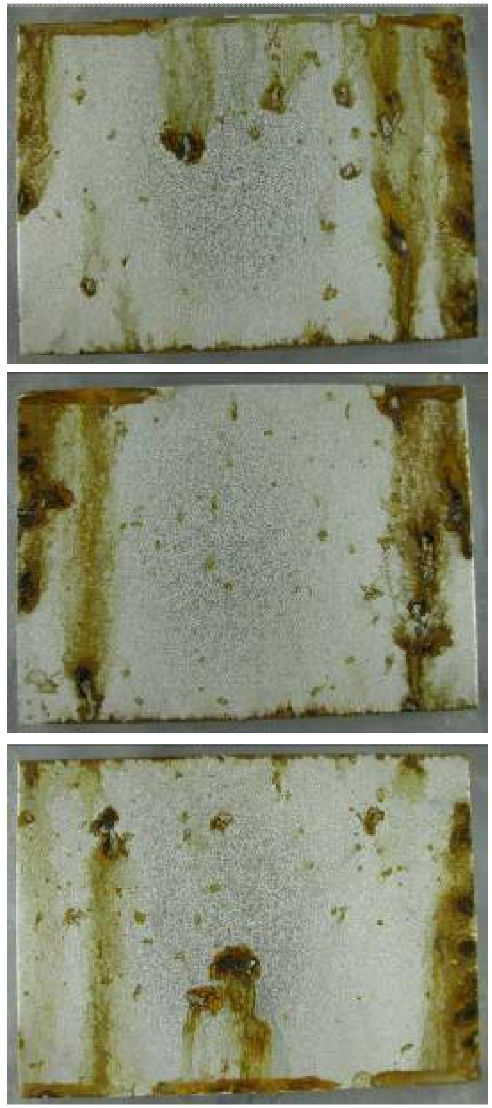


Optimization Phase 1 - 410 - CA vs. NA vs. Un-passivated

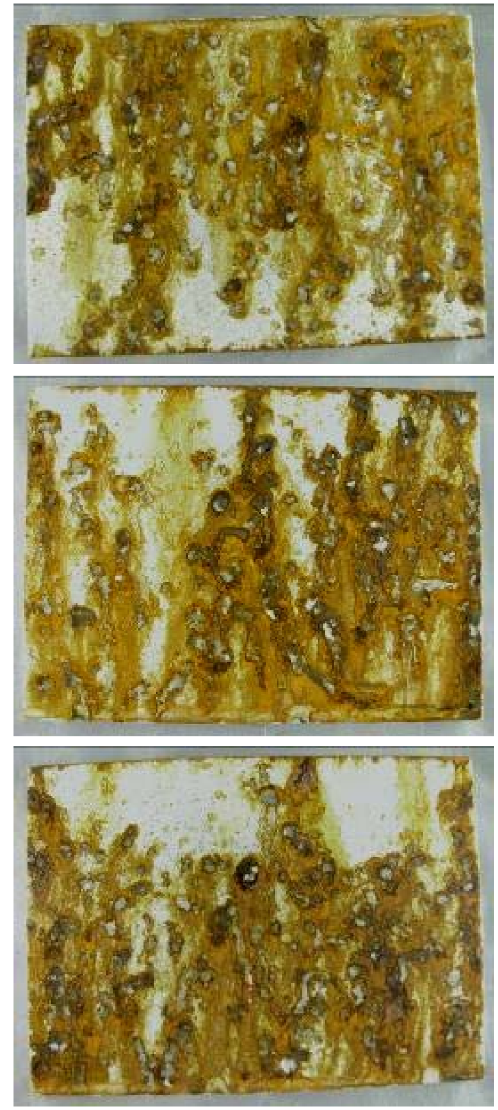
Citric Acid 120m, 180F, 4%
(Best Performing CA Treatment)



Nitric Acid, 20-25vol%+2-3wt%
$Na_2Cr_2O_7 \cdot 2H_2O$, RT, 75min.



Unpassivated



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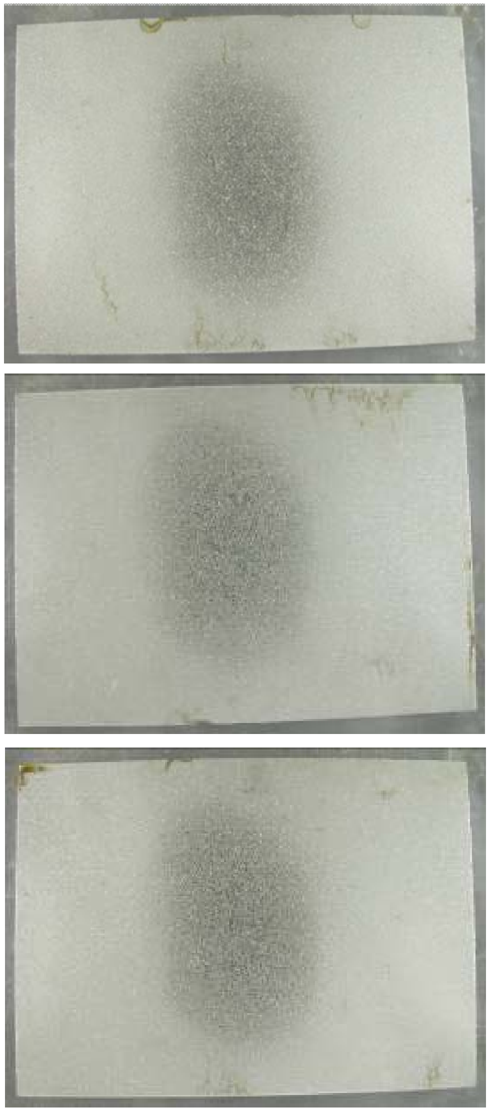
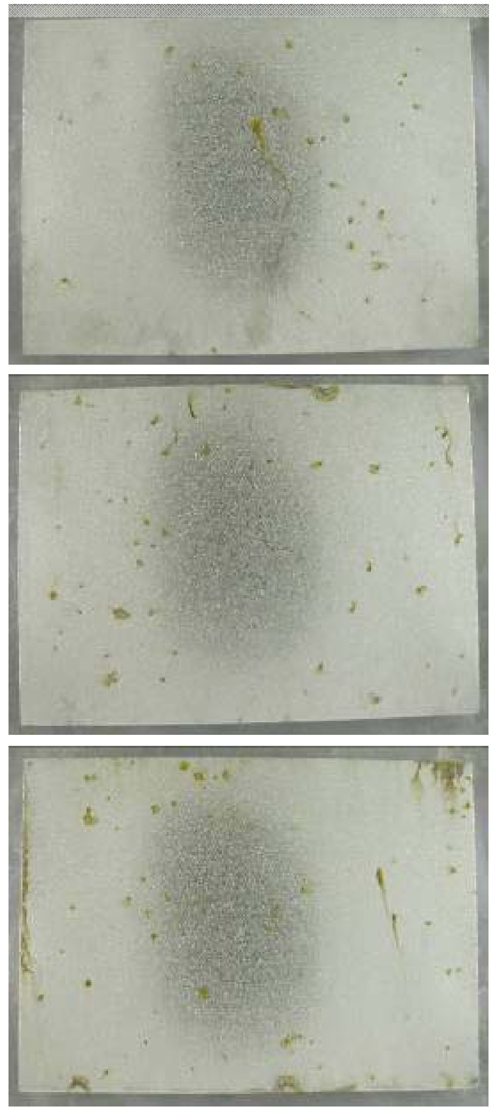
Optimization Phase 1 - 17-4 - CA vs. NA vs. Un-passivated

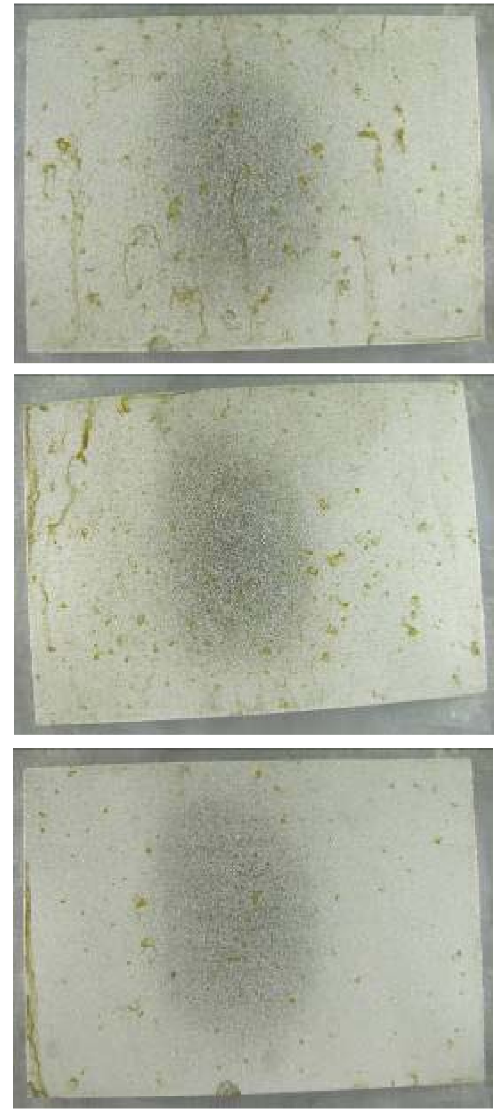
Citric Acid 120m, 180F, 4%
(Best Performing CA Treatment)



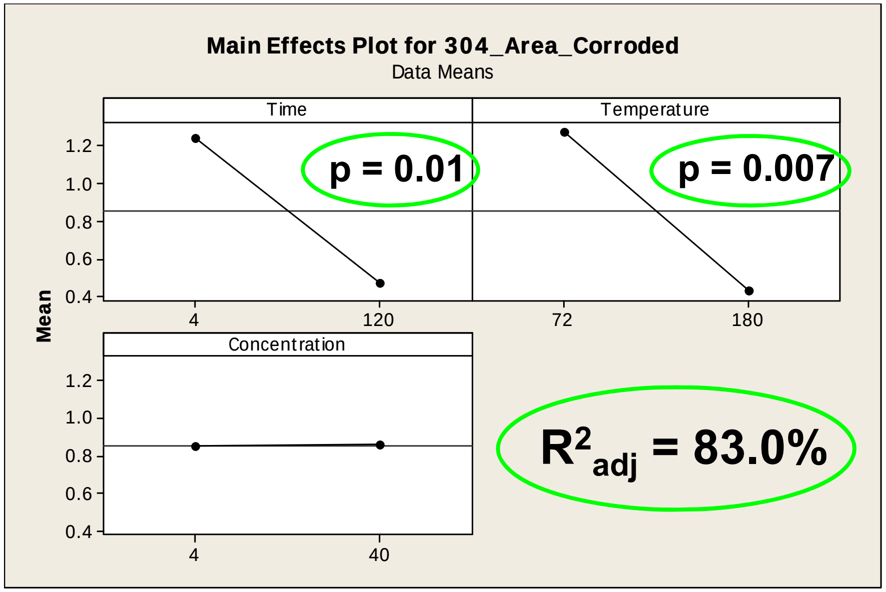
Nitric Acid, 20-25vol%+2-3wt%
$Na_2Cr_2O_7 \cdot 2H_2O$, RT, 75min.

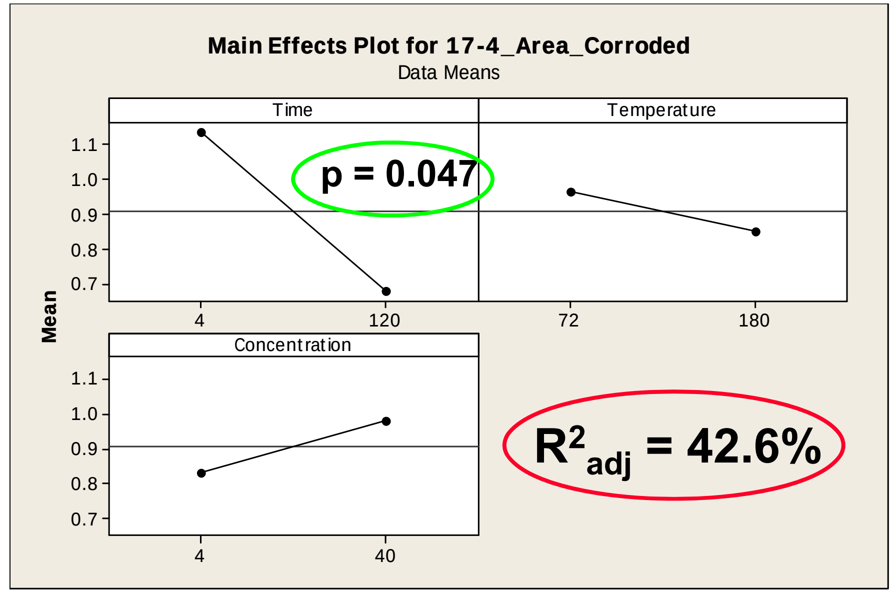


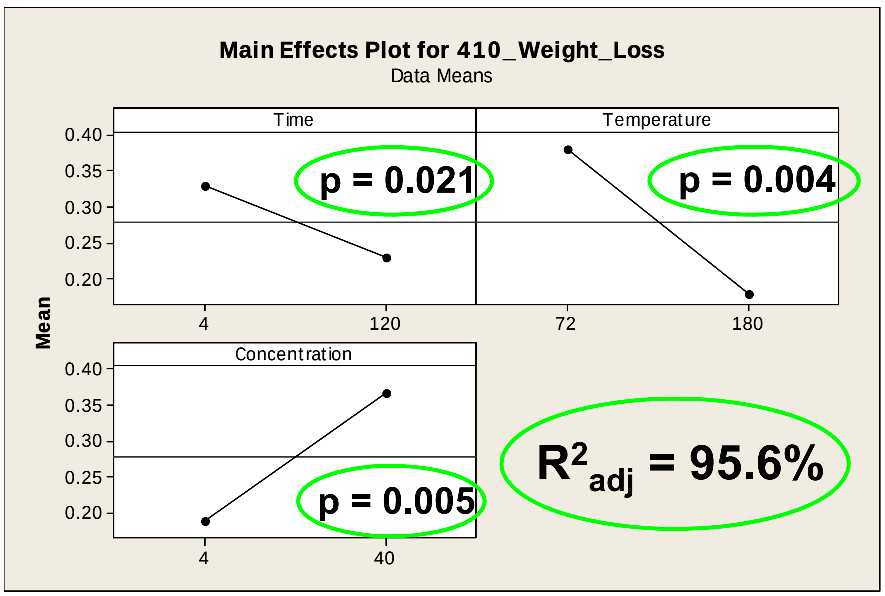
Unpassivated



Optimization Phase 1 – DoE Results







Significant Effects and Optimal Settings

- 304 – Time (high) and Temperature (high).
- 410 – Time (high), Temperature (high), and Concentration (low).
- 17-4 – Inconclusive.

Optimization Phase 1 - Conclusions

- In general, high temperature, low concentration, and longer processing time provide more corrosion resistance.
  - Temperature and processing time have larger effects than concentration. This finding agrees with testing performed by Boeing.
  - For 410, high concentration had a detrimental effect on corrosion resistance. For 304, concentration had almost no effect at all.

- From the preliminary results citric acid is capable of providing acceptable results compared with nitric acid.
  - The best citric acid treatment (180F, 120min, 4% citric acid) performed better than the typical nitric acid passivation treatment for flight hardware.
  - HOWEVER, several citric acid treatments, especially those at room temperature, performed worse than no passivation treatment.

Optimization - Phase 2

Phase 1

- ASTM B117 - Salt Fog Chamber
- Parameters:
  - Acid Conc: 4 - 40%
  - Temp: 72 – 180°F
  - Time: 4 – 120min.
- RESULTS: Concentration has a small effect; higher values of time and temperature are more effective.

Phase 2

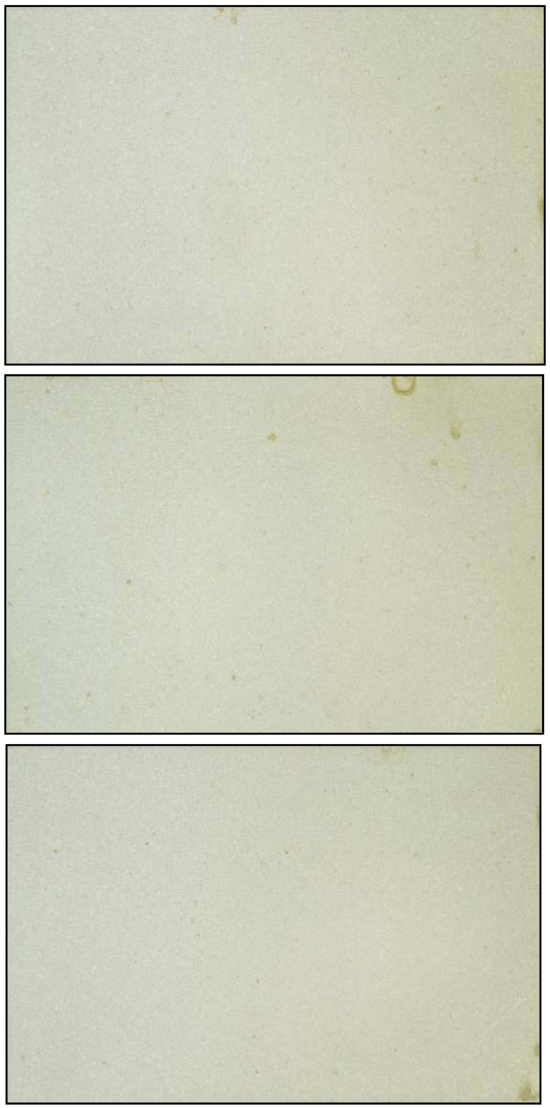
- ASTM B117 – Salt Fog Chamber
- Parameters:
  - Acid Conc: 4%
  - Temp. 100 – 180°F
  - Time: 30 – 120min.
- RESULTS: Optimized Processing Parameters and Nitric Acid Comparison

Phase 3

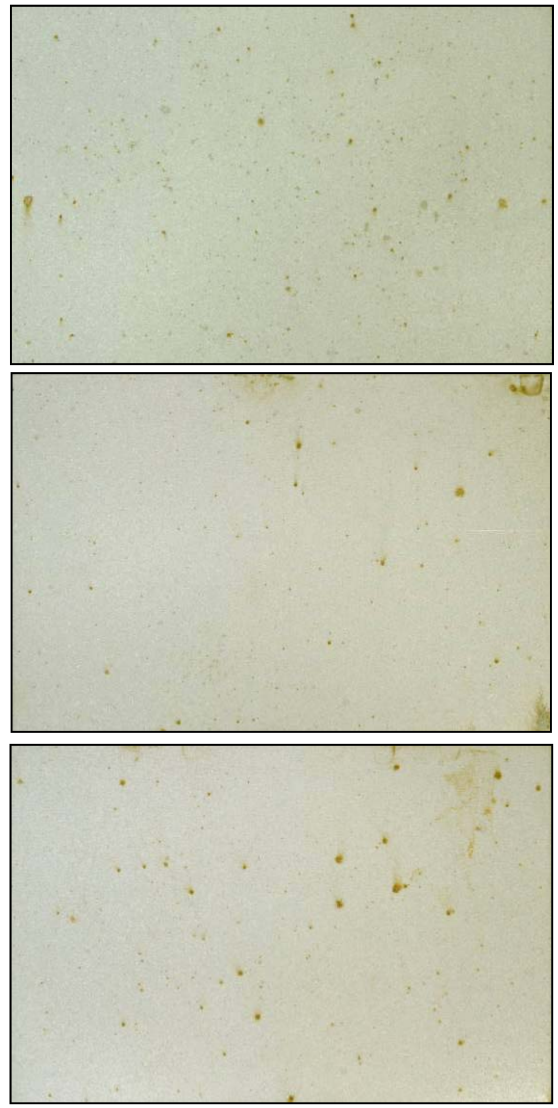
- ASTM G50 – Atmospheric Exposure
- Parameters:
  - Acid Conc: 4%
  - Temp: 100 – 180°F
  - Time: 30 – 120min.
- RESULTS: Optimized Processing Parameters and Nitric Acid Comparison

Optimization Phase 2 - 304 - CA vs. NA vs. Unpassivated

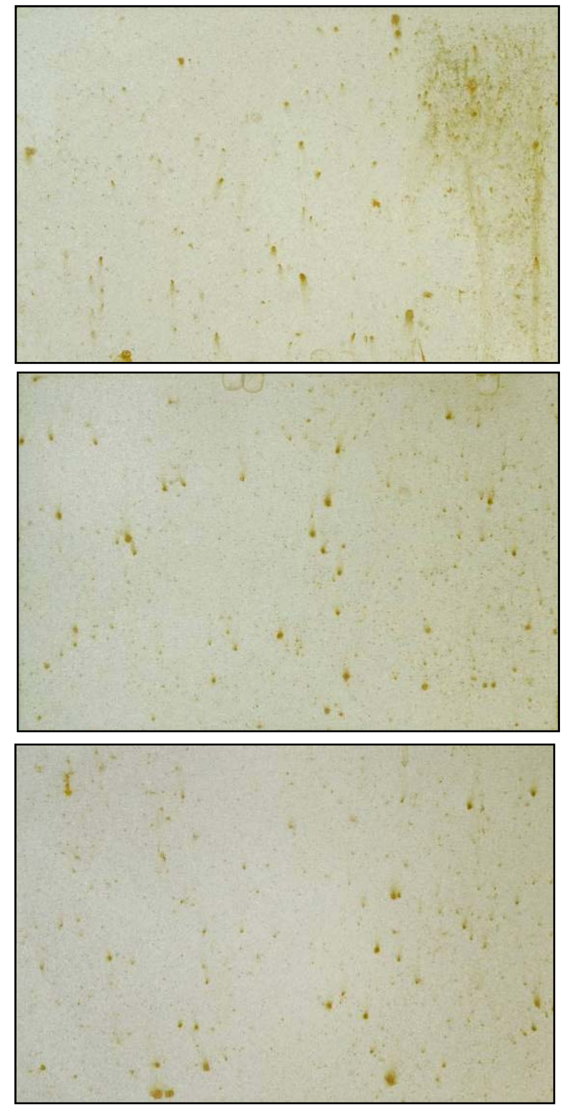
Citric Acid, 4%, 140°F, 30min.
(Best Performing CA Treatment)



Nitric Acid, 20-25vol%, RT, 60min.



Unpassivated



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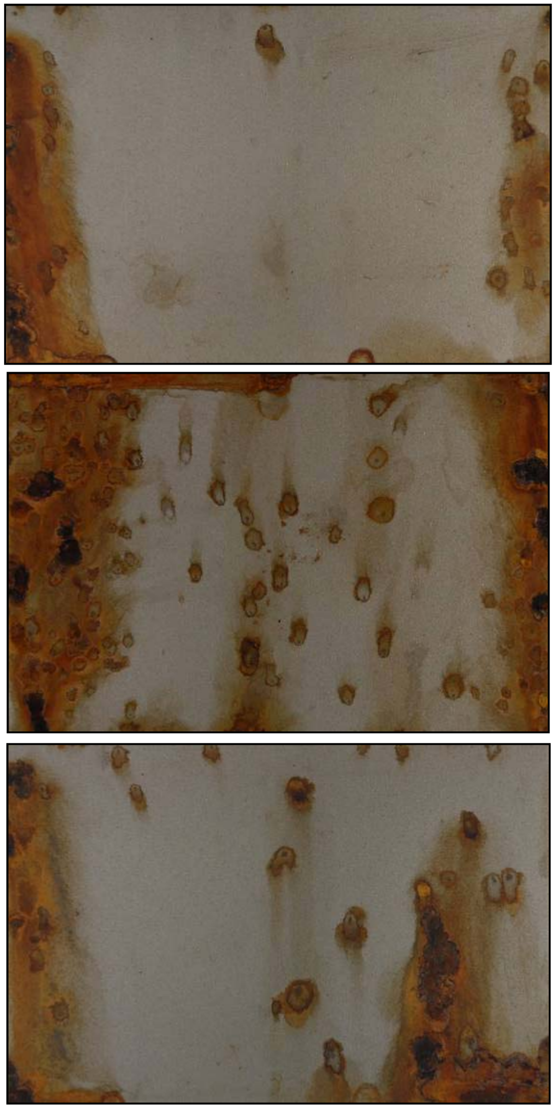
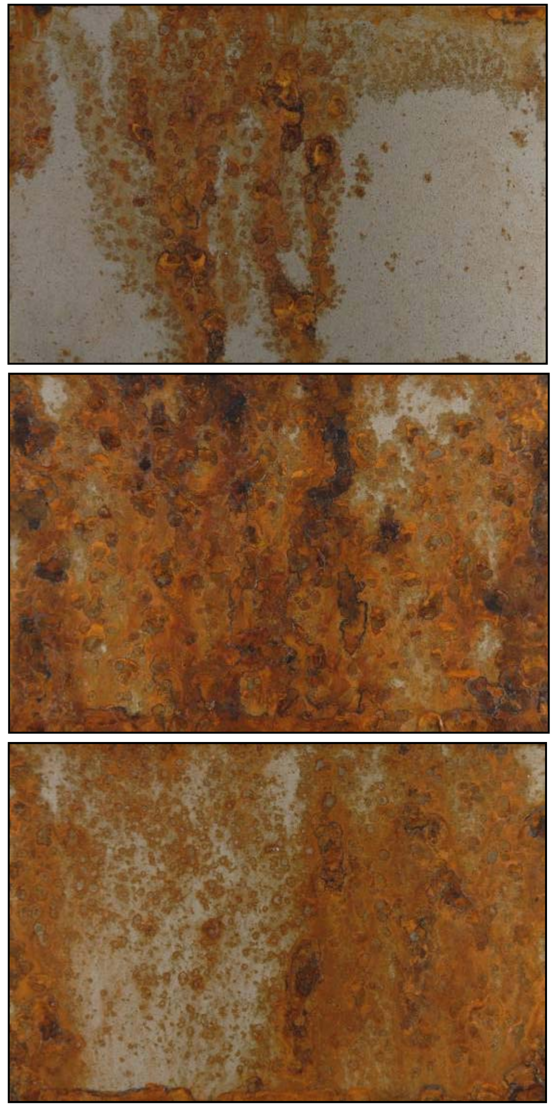
Optimization Phase 2 - 410 - CA vs. NA vs. Unpassivated

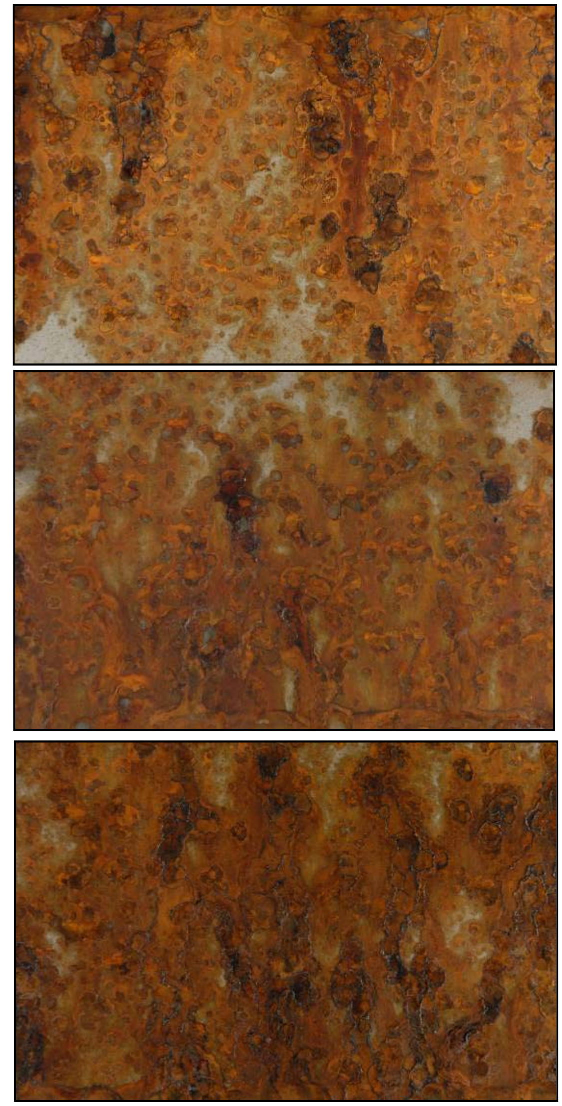
Citric Acid, 4%, 140°F, 75min.
(Best Performing CA Treatment)



Nitric Acid, 20-25vol% + 2-3wt%
$Na_2Cr_2O_7 \cdot 2H_2O$, RT, 75min.



Unpassivated



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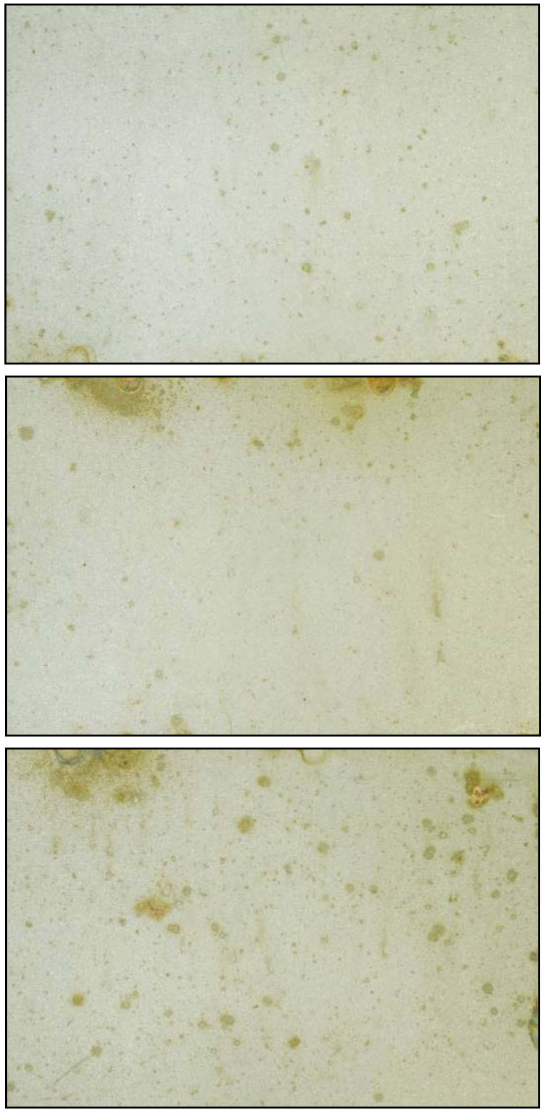
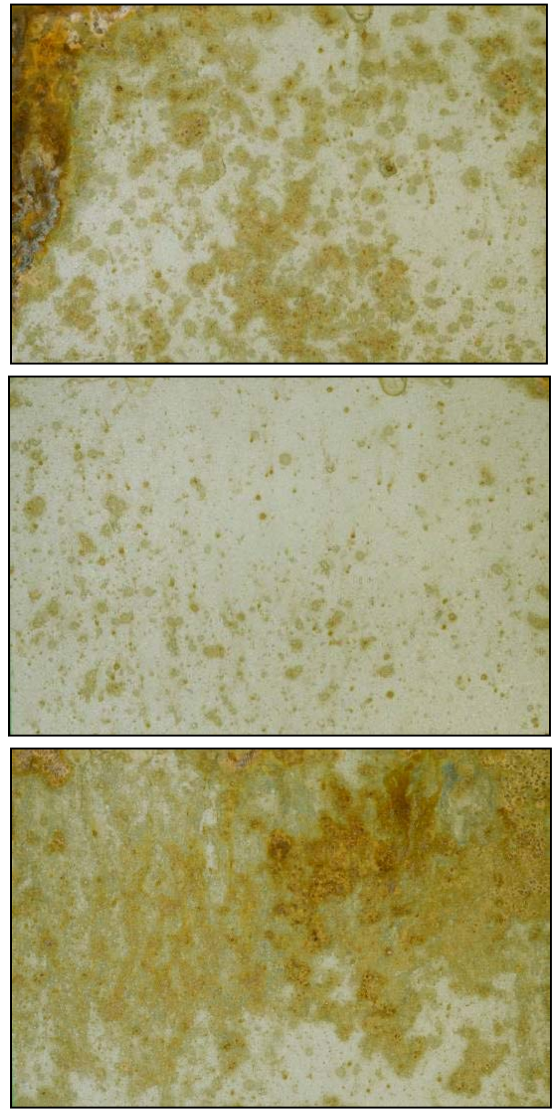
Optimization Phase 2 - 17-4 - CA vs. NA vs. Unpassivated

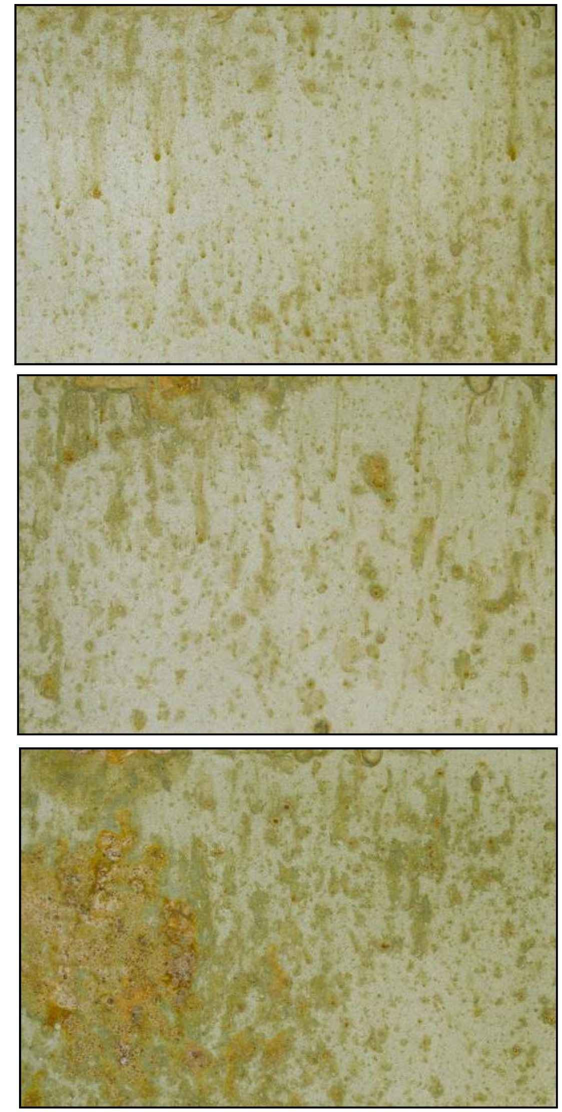
Citric Acid, 4%, 100°F, 75min.
(Best Performing CA Treatment)



Nitric Acid, 20-25vol%,RT, 60min.

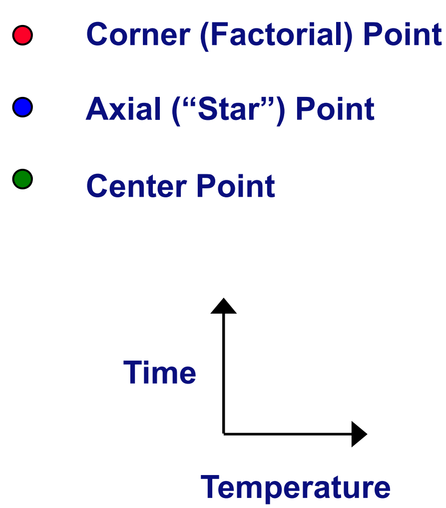


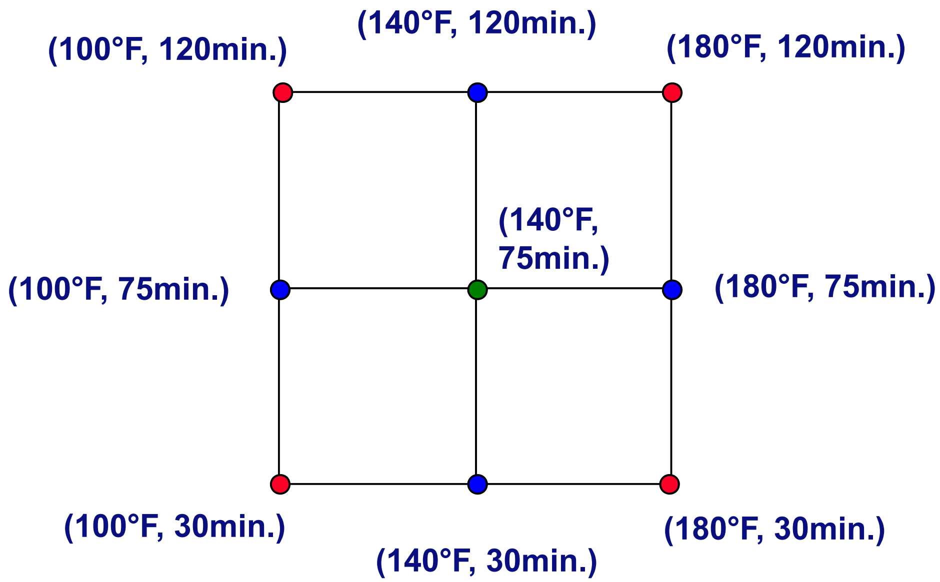
Unpassivated



Optimization - Central Composite Design (CCD)

- Attempts to explain the relationship between input variables on output variables in such a way that the response can be optimized (ref. “Response Surface Methodology” by Myers and Montgomery).
  - Input variables: submersion time and temperature.
  - Output variable: amount of corrosion on a passivated coupon.
    - For stainless steel 410 coupons, this was measured through coupon weight loss
    - For stainless steel 304 and 17-4 coupons, this was measured through image analysis (see next page).
  - Qualifies output with statistical significance based on ANOVA.
- A Cubic Central Composite Design was used in this phase.
  - Provides a more in depth analysis than a factorial DoE.
  - Accounts for curvature in response.





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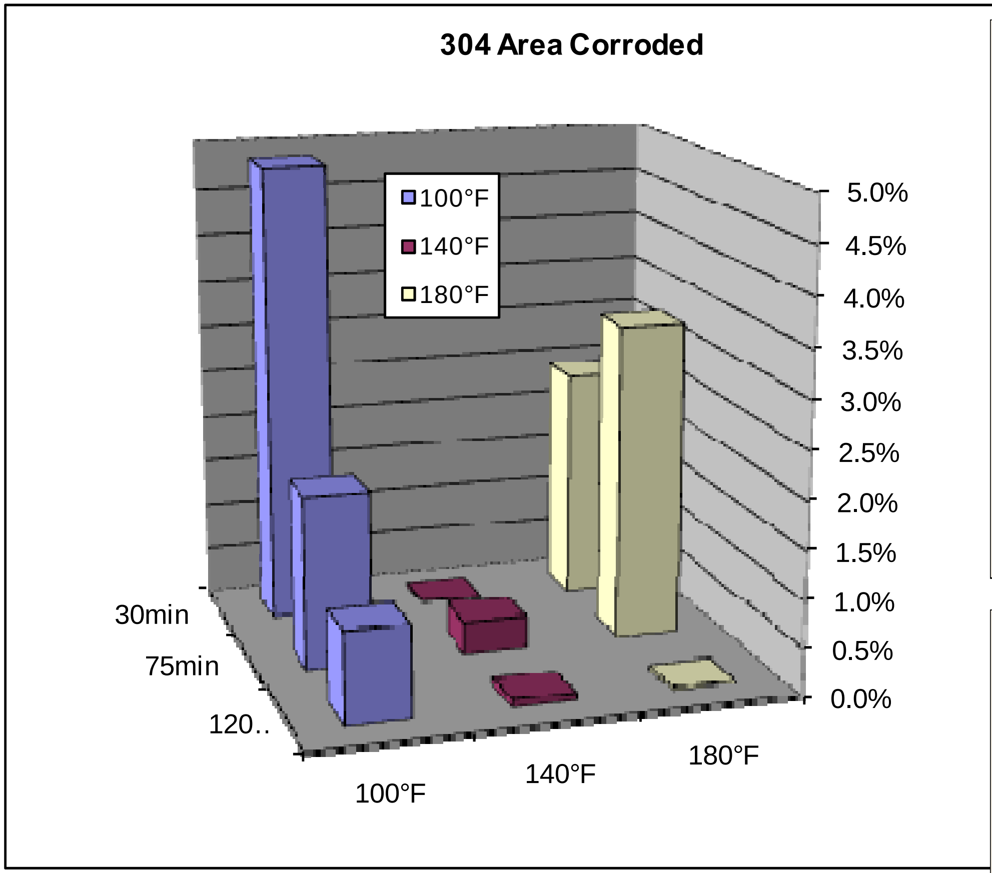
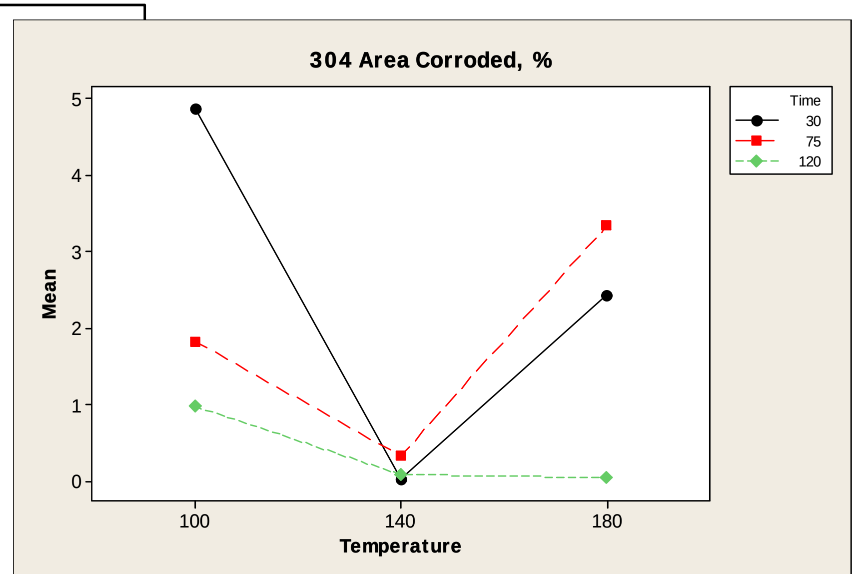
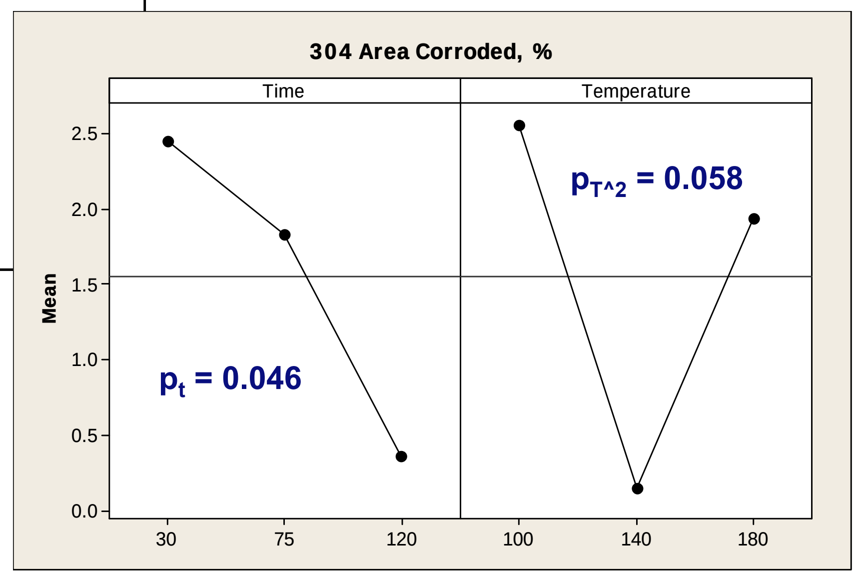
Optimization Phase 2 – 304 DoE Results







Time (t) p-values

$p_t = 0.046$

Temperature (T) p-values

$p_{T^\wedge 2} = 0.058$

$R^2_{adj} = 59.37\%$

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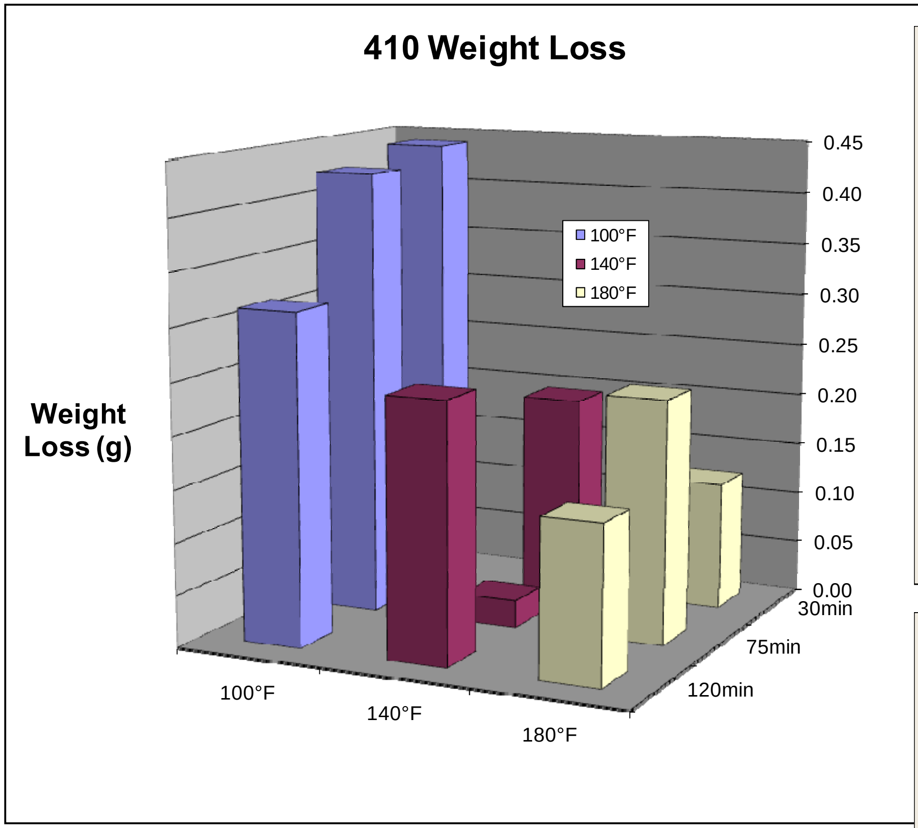
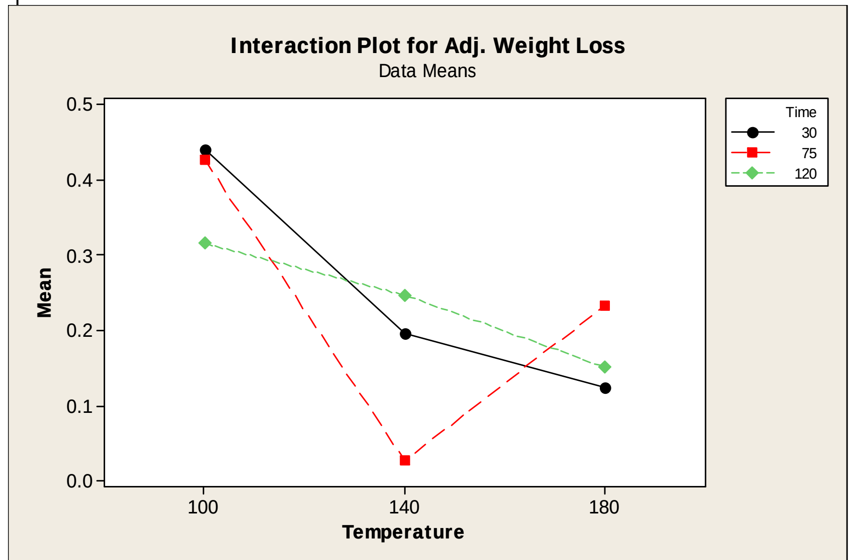
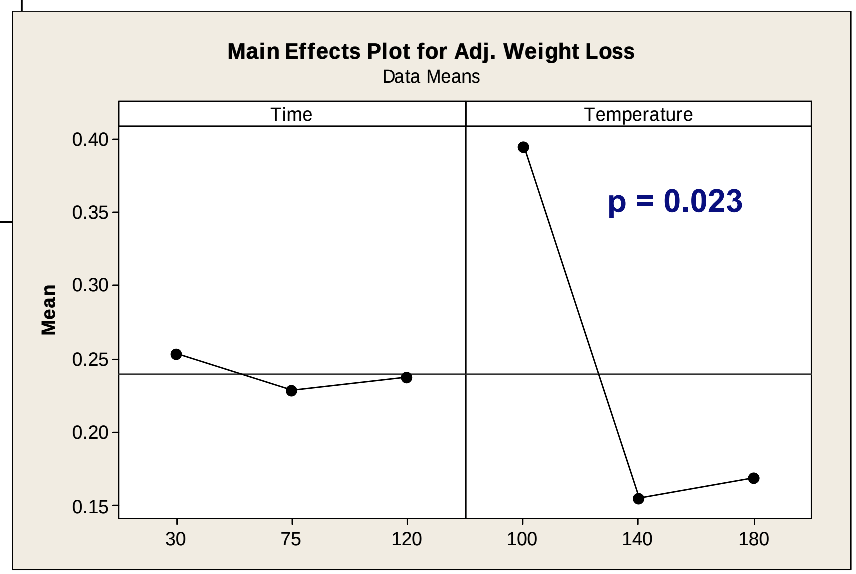
Optimization Phase 2 – 410 DoE Results







Time (t) not significant

Temperature (T) p-values

$p_T = 0.023$

$p_{T\wedge 2} = 0.079$

$R^2_{adj} = 62.27\%$

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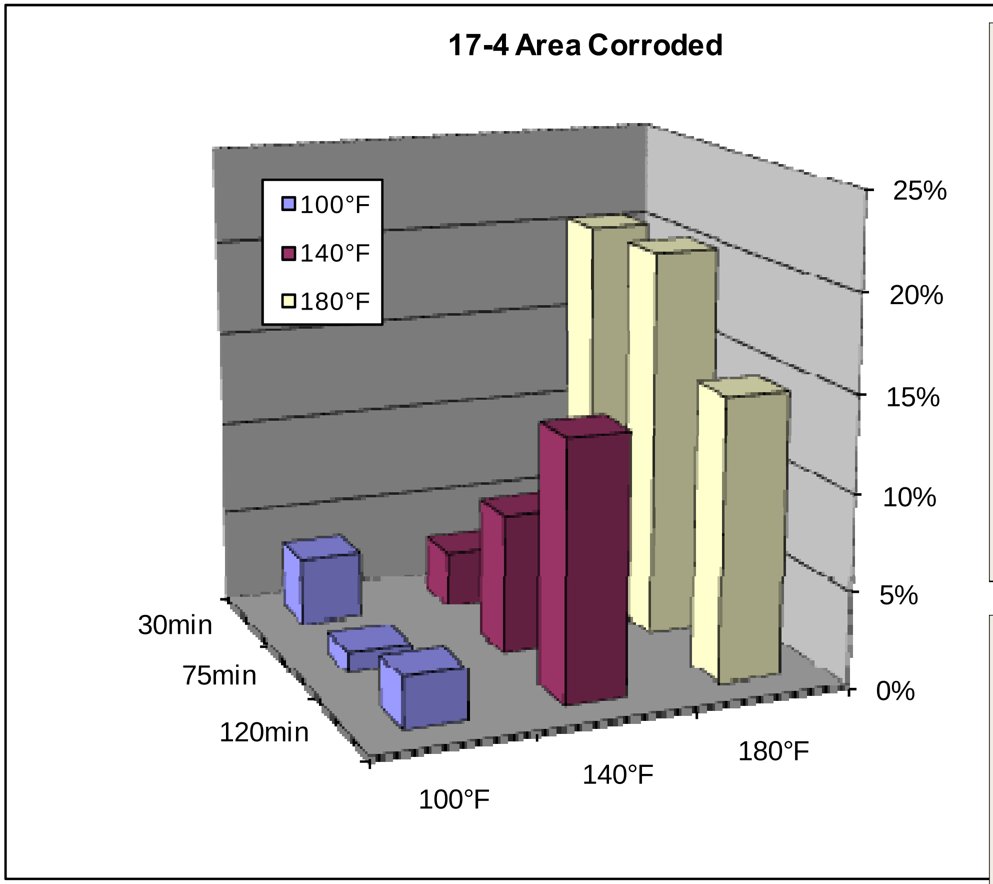
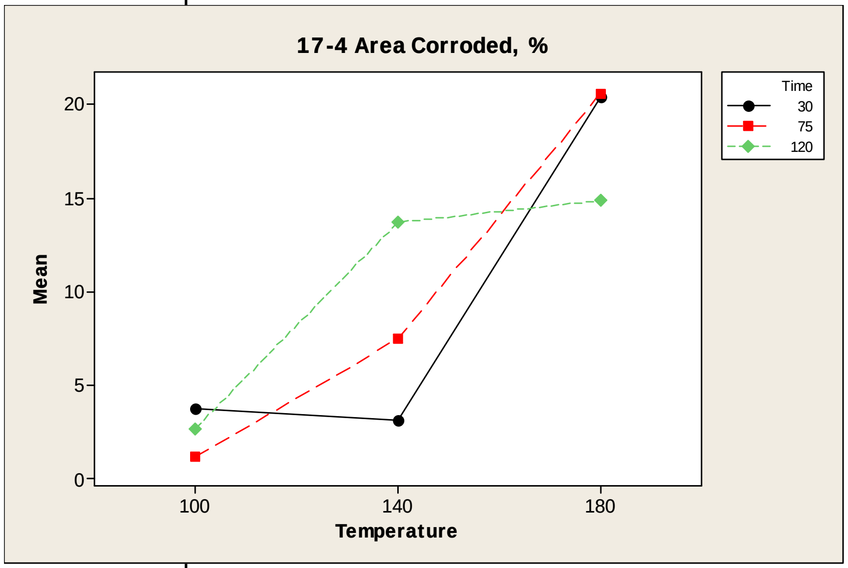
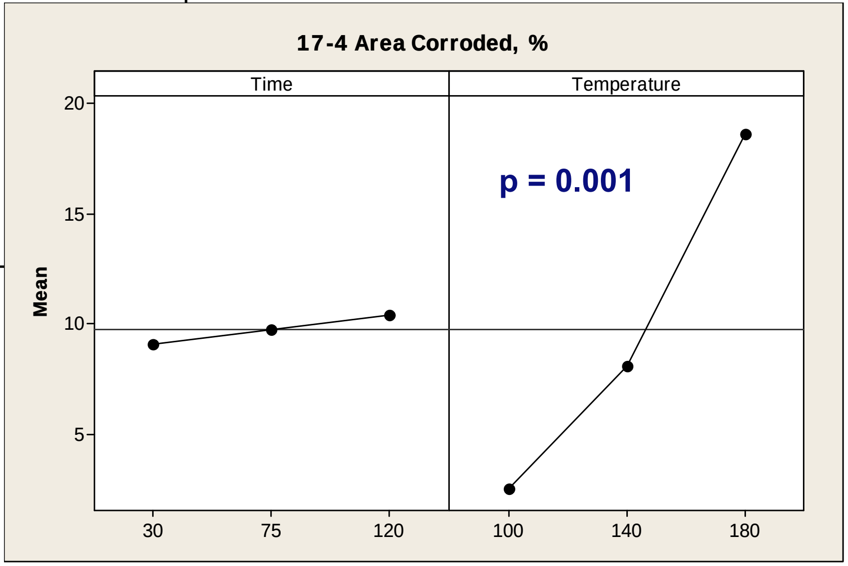
Optimization Phase 2 - 17-4 DoE Results







Time (t) not significant

Temperature (T) p-values
$p_T = 0.001$

$R^2_{adj} = 78.39\%$

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Optimization - Phase 3

Phase 1

- ASTM B117 - Salt Fog Chamber
- Parameters:
  - Acid Conc: 4 - 40%
  - Temp: 72 – 180°F
  - Time: 4 – 120min.
- RESULTS: Concentration has a small effect; higher values of time and temperature are more effective.

Phase 2

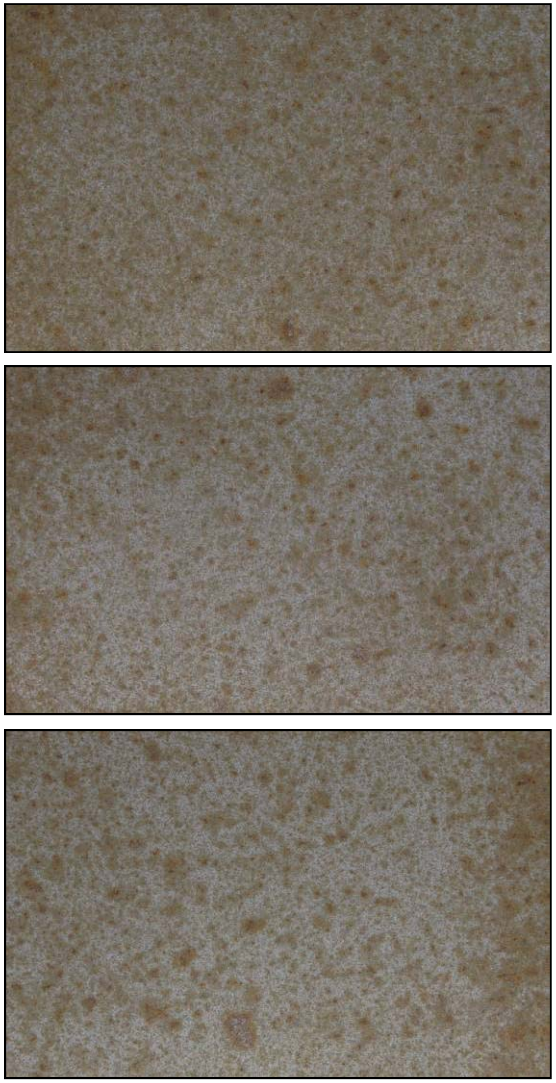
- ASTM B117 – Salt Fog Chamber
- Parameters:
  - Acid Conc: 4%
  - Temp. 100 – 180°F
  - Time: 30 – 120min.
- RESULTS: Optimized Processing Parameters and Nitric Acid Comparison

Phase 3

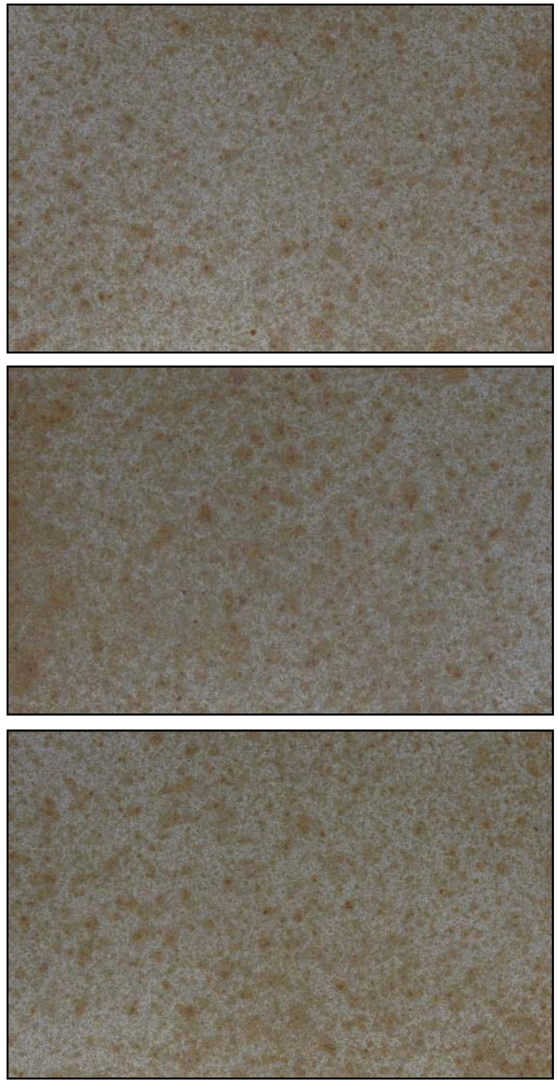
- ASTM G50 – Atmospheric Exposure
- Parameters:
  - Acid Conc: 4%
  - Temp: 100 – 180°F
  - Time: 30 – 120min.
- RESULTS: Optimized Processing Parameters and Nitric Acid Comparison

Optimization Phase 3 - 304 - CA vs. NA vs. Unpassivated

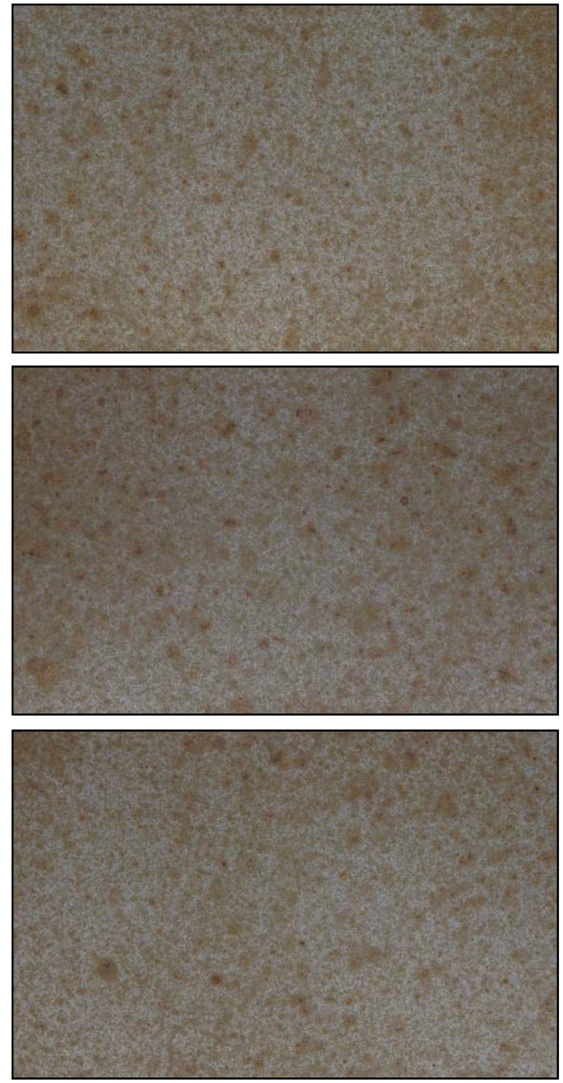
Citric Acid, 4%, 140°F, 75min.
(Best Performing CA Treatment)



Nitric Acid, 30-32vol%, RT, 75min.



Unpassivated



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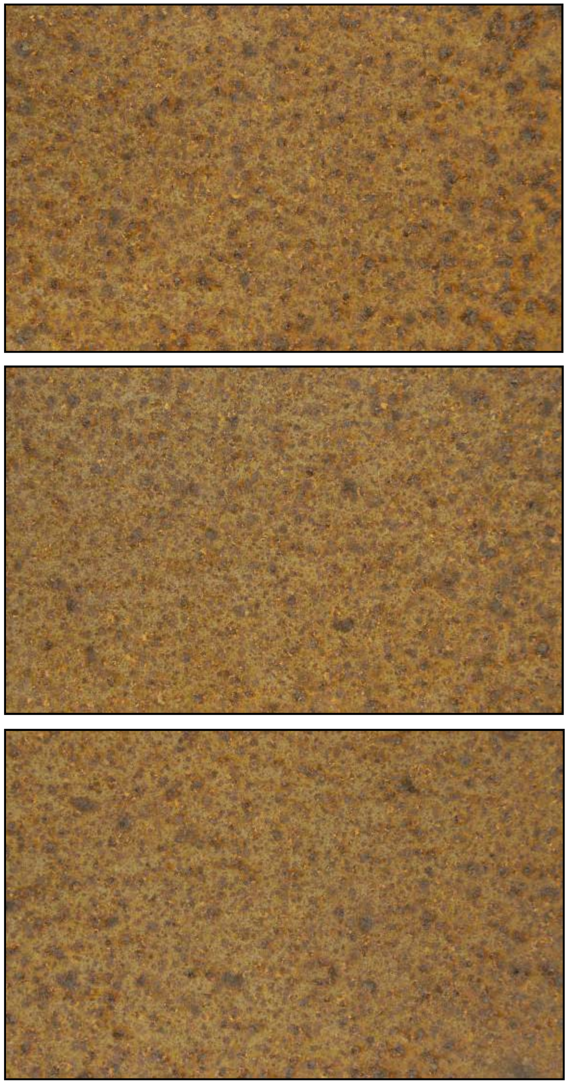
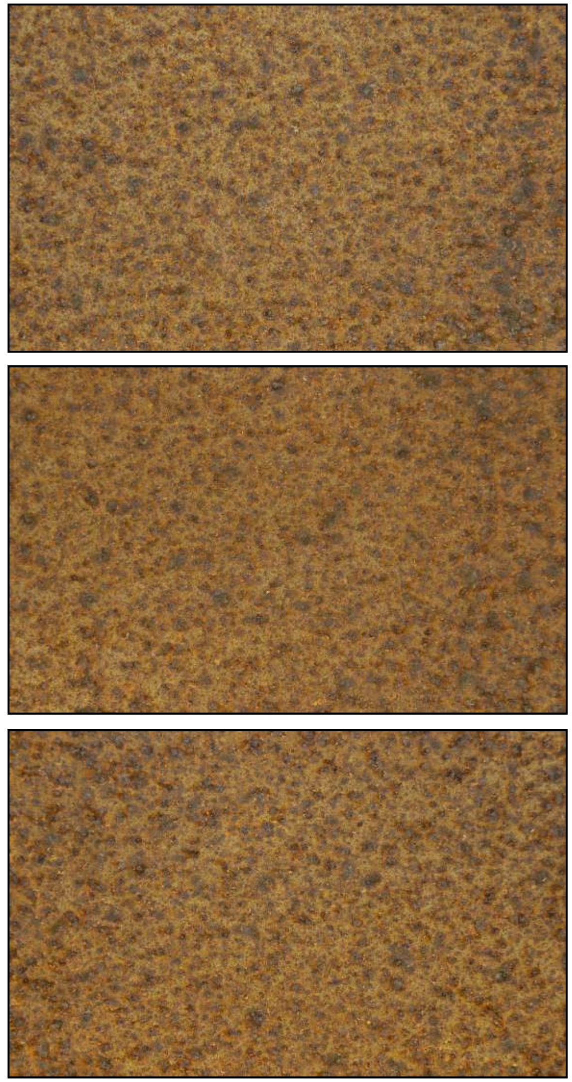
Optimization Phase 3 - 410 - CA vs. NA vs. Unpassivated

Citric Acid, 4%, 140°F, 75min.
(Best Performing CA Treatment)



Nitric Acid, 20-25vol% + 2-3wt%
$Na_2Cr_2O_7 \cdot 2H_2O$, RT, 75min.



Unpassivated

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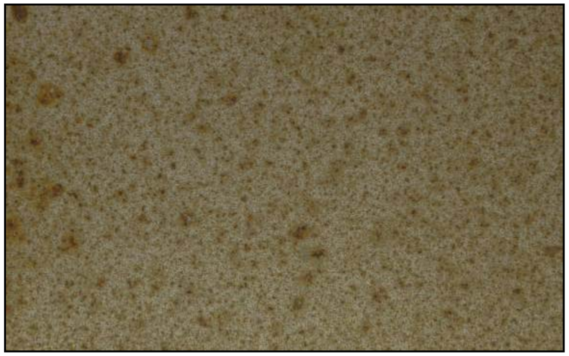
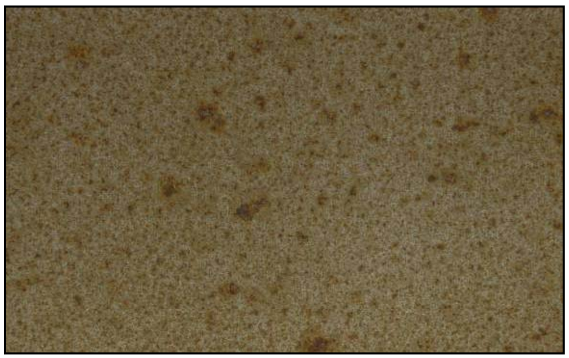
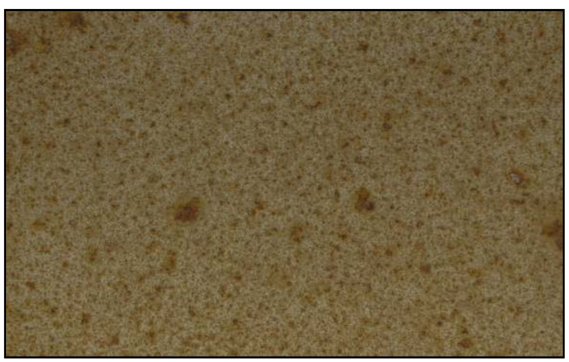
Optimization Phase 3 - 17-4 - CA vs. NA vs. Unpassivated

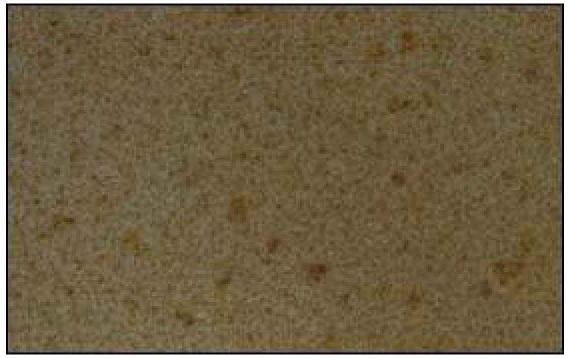
Citric Acid, 4%, 140°F, 75min.
(Best Performing CA Treatment)

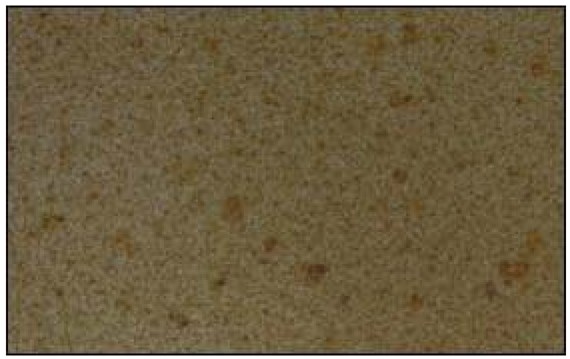


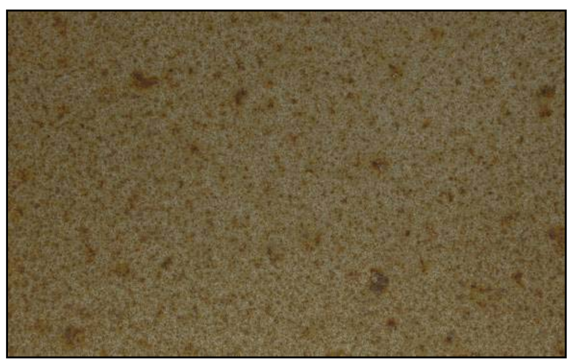




Nitric Acid, 20-25vol% + 2-3wt%
$Na_2Cr_2O_7 \cdot 2H_2O$, RT, 75min.

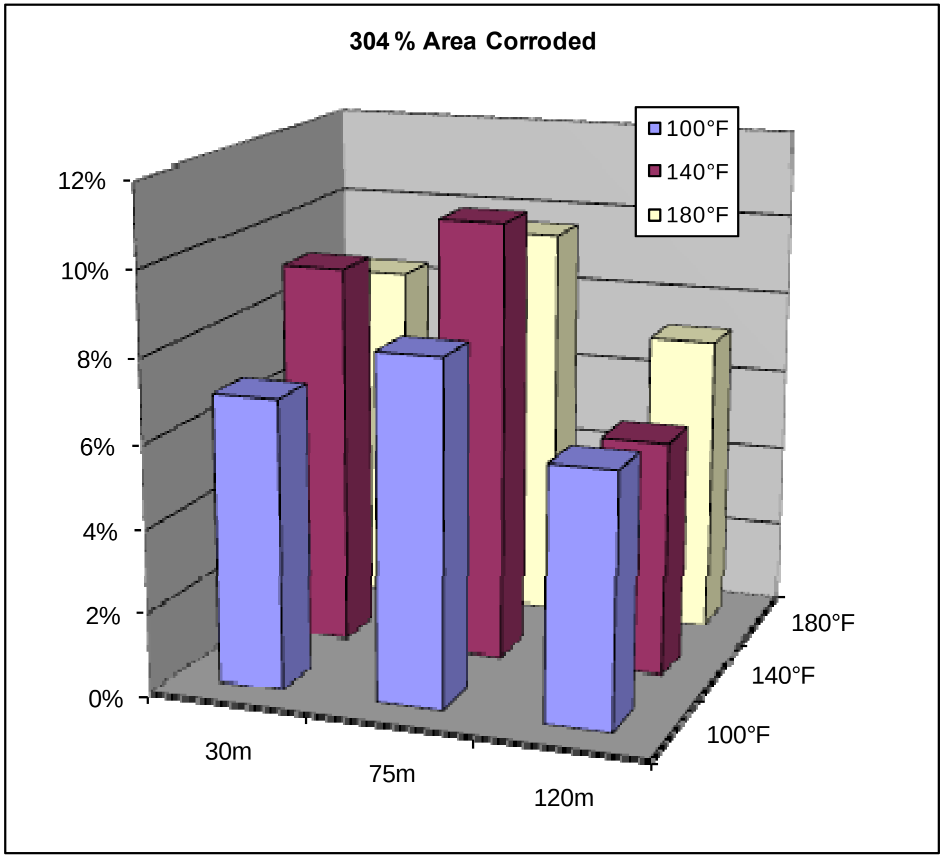


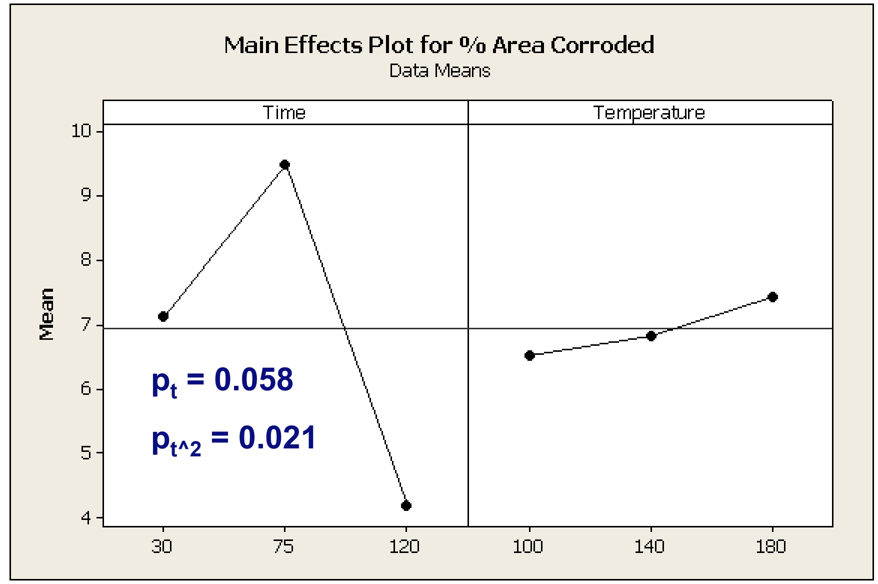


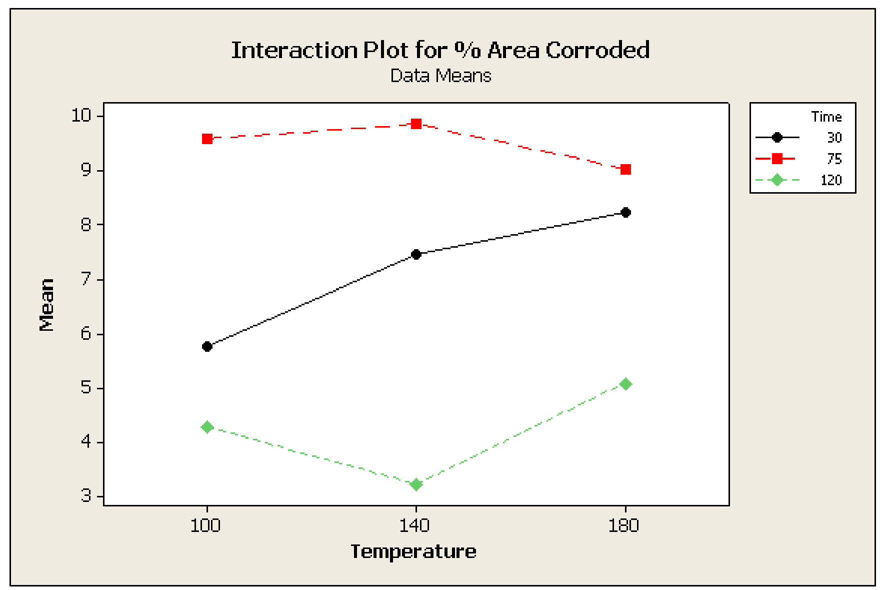


Unpassivated

Optimization Phase 3 - 304 Results







Time (t) p-values

$p_t = 0.058$

$p_{t^2} = 0.021$

Temperature (T) not significant

$R^2_{adj} = 72.70\%$

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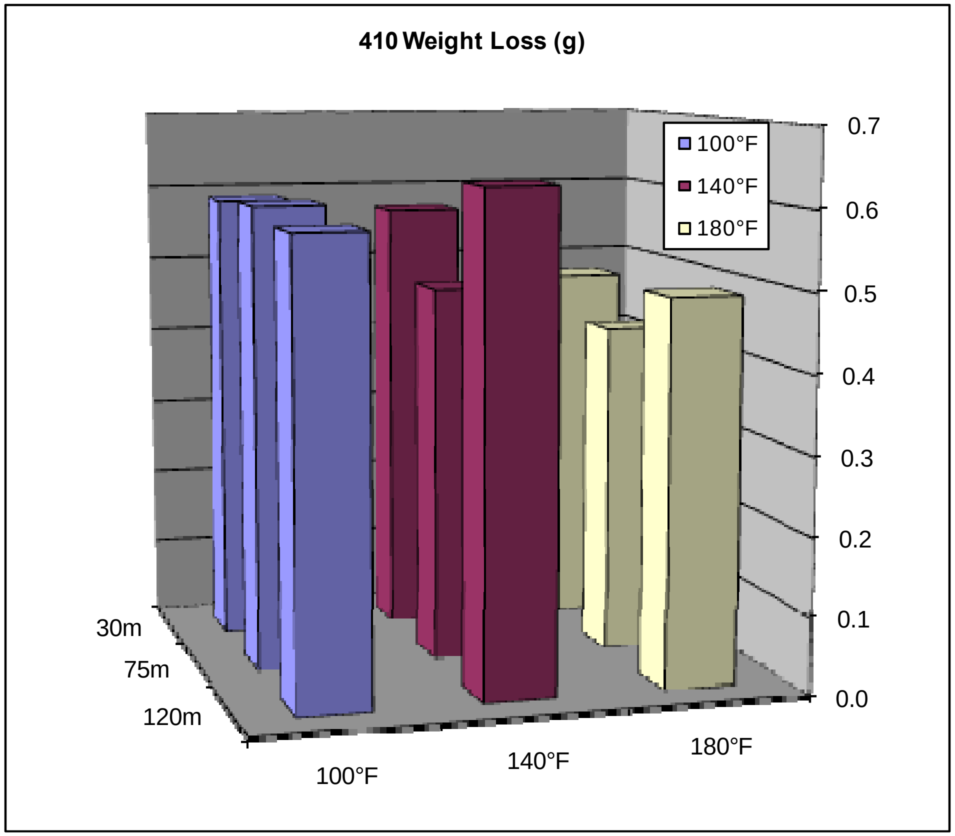
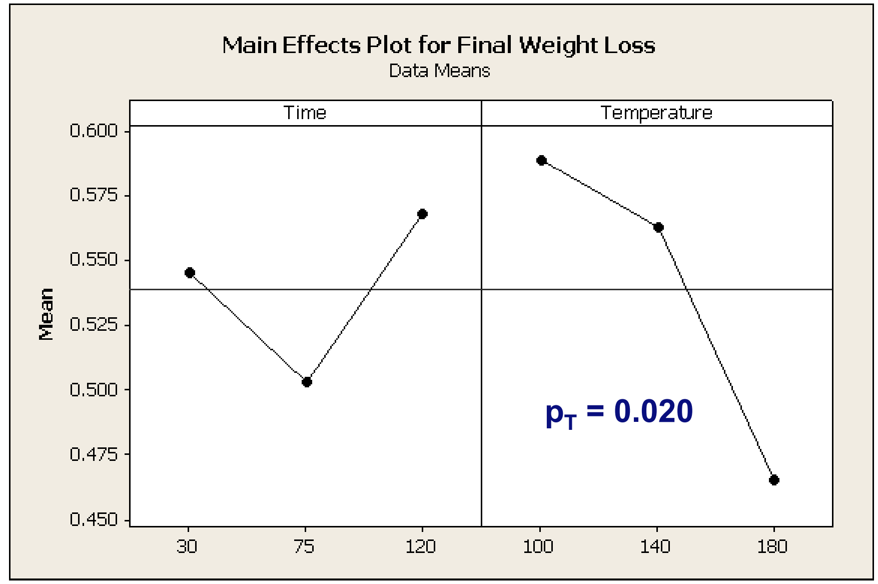
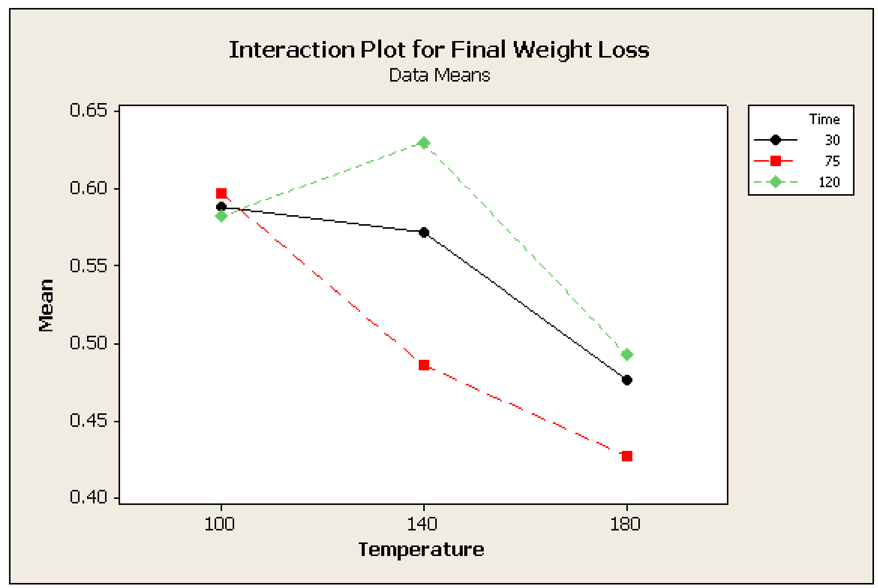
Optimization Phase 3 - 410 Results







Time (t) not significant

Temperature (T) p-values

$p_T = 0.020$

$R^2_{adj} = 66.46\%$

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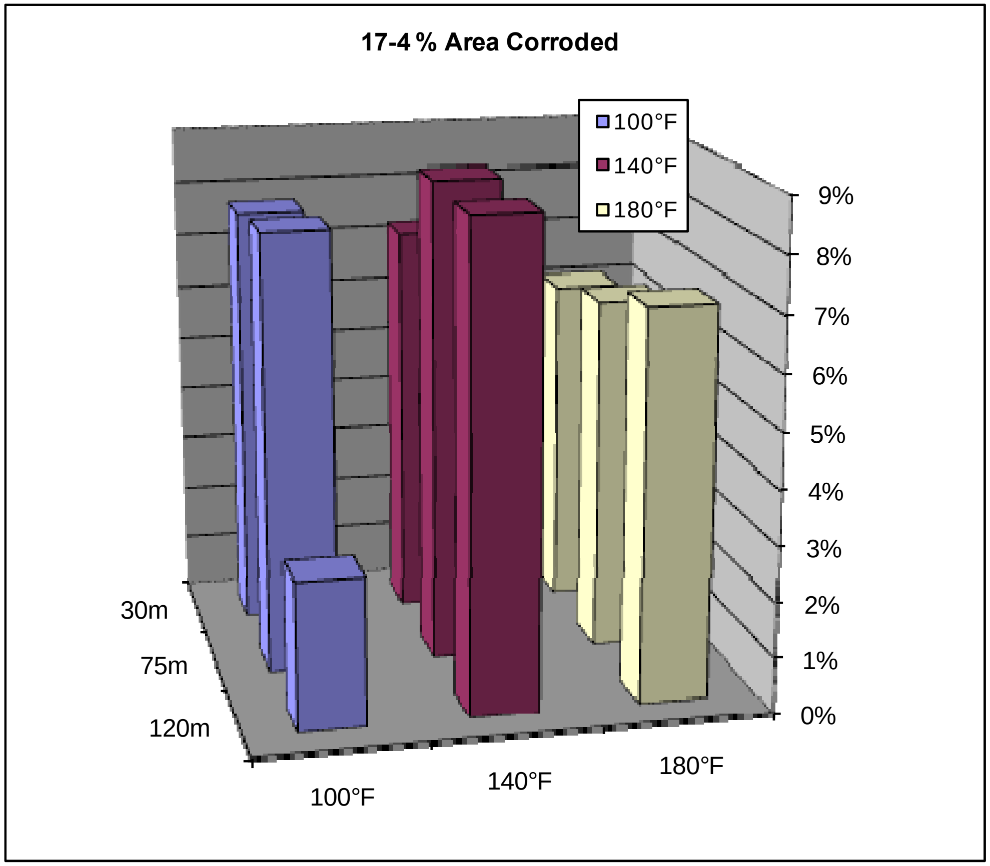
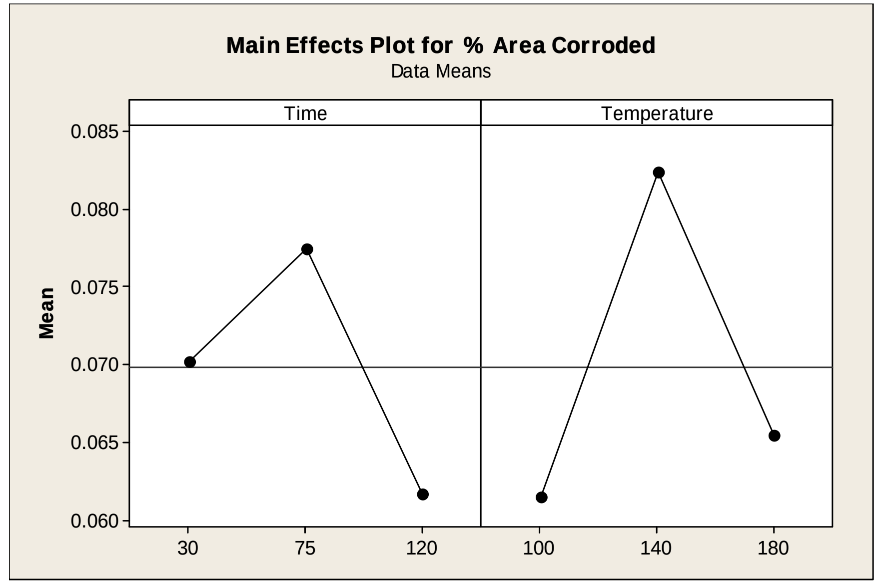
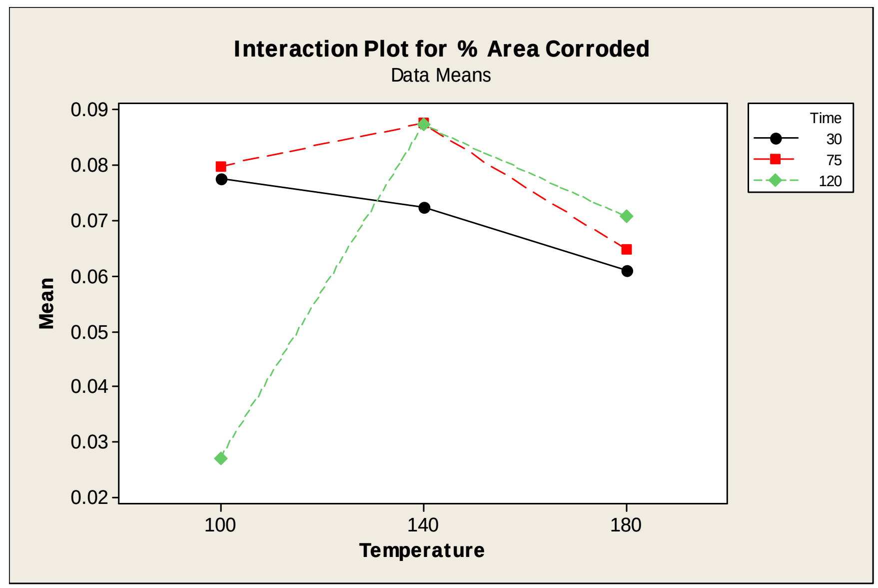
Optimization Phase 3 - 17-4 Results







Time (t) not significant

Temperature (T) not significant

$R^2_{adj} = 31.45\%$

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Optimization - Results Summary

		Optimal Treatment from DoE		Best Performing Treatment	
		Time (minutes)	Temperature (°F)	Time (minutes)	Temperature (°F)
Phase 2	304	120	143	30	140
	410	30*	158	75	140
	17-4	30*	100	75	100
Phase 3	304	120	100*	120	140
	410	30*	180	75	180
	17-4	30*	100*	120	100

*No value predicted by DoE. Values were chosen as optimal for practical reasons.

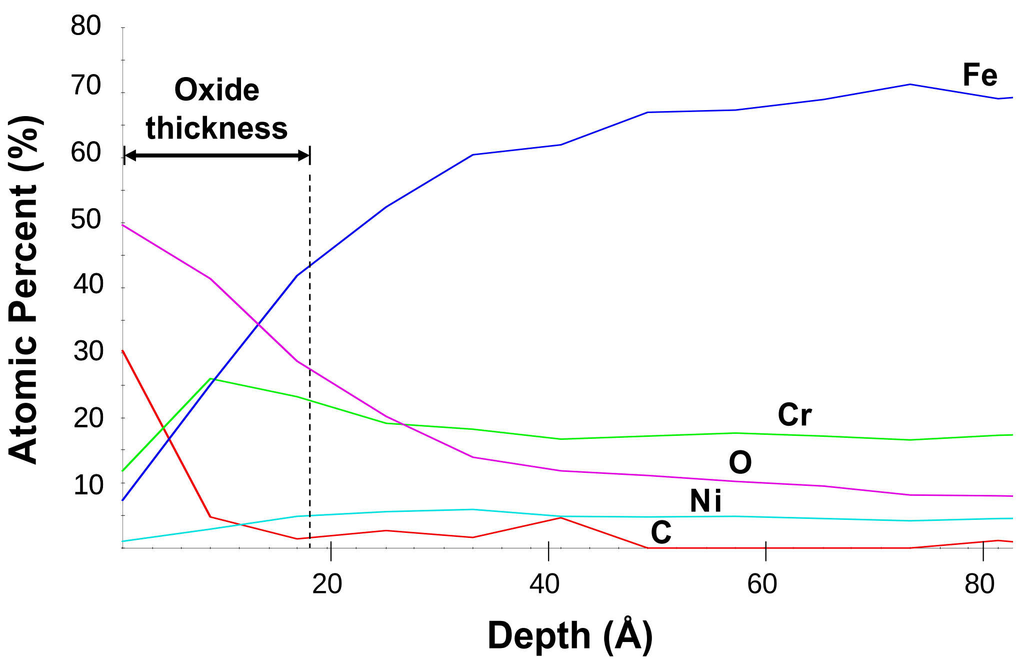
- The left side of the table displays optimal treatment parameters.
  - If a factor was insignificant, the lowest setting was chosen as optimal.
  - All other values were dictated by RSA results.
- The right side of the table displays treatment parameters that resulted in the least amount of corrosion.
  - In all cases but 1, the value predicted by RSA matches well with actual best performing treatment.
  - For insignificant factors (starred values), the best performing value is not expected to correlate to the optimal treatment.

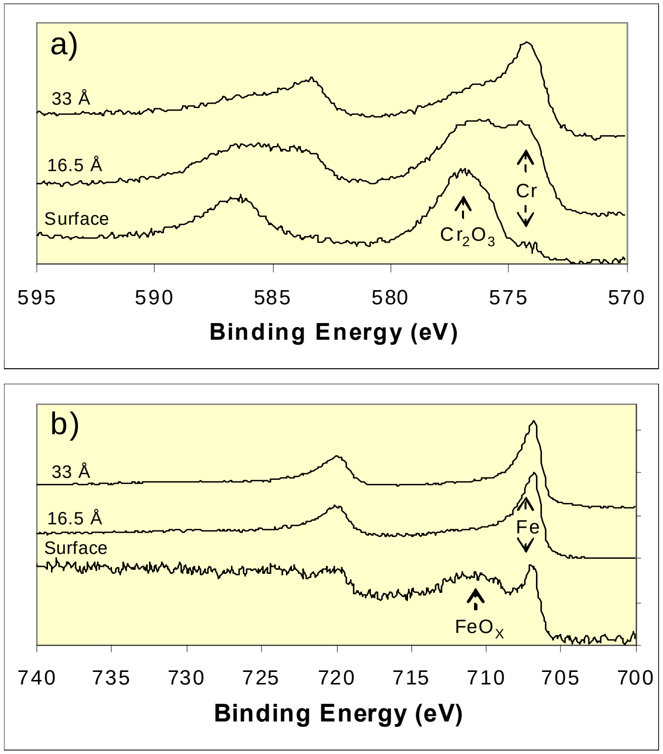
Optimization Phases 2 and 3 - Conclusions

- Temperature in the region studied (100°F ≤ T ≤ 180°F) is a significant factor for all alloys.
  - For 304, corrosion protection improves with temperature up to ~140°F and then diminishes.
  - For 410, corrosion protection improves with higher temperature, but doesn't appear to benefit past ~140°F.
  - For 17-4, corrosion protection diminishes with higher temperatures.
- Time in the region studied (30min ≤ t ≤ 120min) is significant for 304, but does not appear to affect passivation of 410 and 17-4.
  - For 304, corrosion protection improves with time.
  - Beyond 30 minutes, time appears to have no effect on 410 and 17-4.

Comparison - X-ray Photoelectron Spectroscopy

- X-ray Photoelectron Spectroscopy (XPS) was performed on 4 specimens of each material: Non-passivated, nitric, citric 1 (best performing treatment from Phase 2), and citric 2 (treatment closest to that recommended by RSA).
- Specimens were scuffed, pre-cleaned, and passivated as designated.
- XPS performed at NASA's Life Sciences facility.
- Cr / Fe and Cr_2O_3 / FeOx ratios were calculated using SEMISPEC Technical Transfer 90120403-STD.
- Typical resulting data shown below.





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Comparison - XPS Results

- The Cr_2O_3 / FeOx ratios improve with passivation, sometime dramatically, in almost every case.
- Cr / Fe ratios appear to be unaffected by passivation with no discernable trend. The ratios also appear to be correlated with Cr_2O_3 / FeOx ratios or oxide layer thickness.
- FWHM analysis of the O 1s photoelectron spectra was used to estimate the oxide depth on each specimen (see Table 8). The oxide depths range from 16.5 Å to 22 Å, and follow no discernable trend.
- Citric acid appears to provide more Cr_2O_3 enrichment than nitric acid on 304 and 410, and less than nitric on 17-4.
- The Ni concentration in the film was negligible on the 304 and 17-4 stainless steel specimens.

Specimen		Treatment	Oxide Thickness (± 2 Å)	Cr / Fe Ratio (± 5%)	Cr_2O_3 / FeOx Ratio (± 5%)
304	Unpassivated	No passivation	16.5	0.28	1.87
	Nitric	QQ-P-35B Type VI	20.4	0.23	2.61
	Citric 1	4 wt.%, 140 °F, 120 min	16.5	0.17	2.69
	Citric 2	4 wt.%, 140 °F, 30 min	18.7	0.17	2.98
410	Unpassivated	No passivation	18.4	0.12	1.12
	Nitric	QQ-P-35B Type II	17.9	0.12	0.6
	Citric 1	4 wt.%, 140 °F, 30 min	16.5	0.21	0.9
	Citric 2	4 wt.%, 140 °F, 75 min	22	0.1	1.4
17-4	Unpassivated	No passivation	19.8	0.14	1.42
	Nitric	QQ-P-35B Type II	21.2	0.15	2.3
	Citric 1	4 wt.%, 100 °F, 75 min	18.4	0.15	1.7
	Citric 2	4 wt.%, 100 °F, 30 min	17.6	0.17	1.61

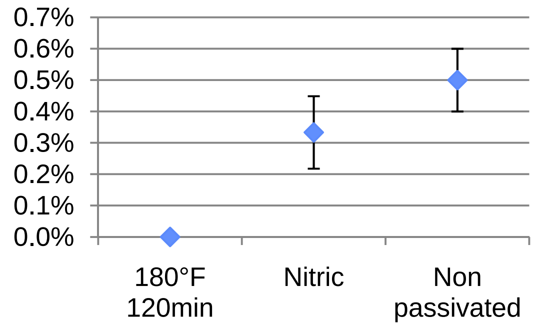
Comparison - XPS Conclusions

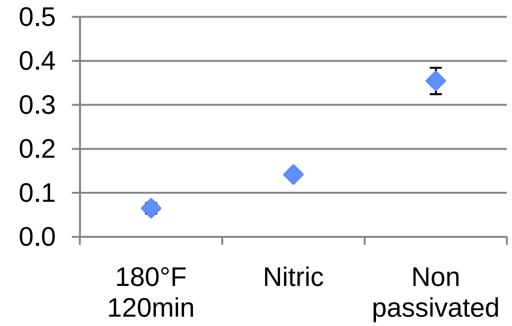
- **Nitric and citric acid passivation treatments produced comparable surface films (16.5-22 Å) containing primarily Cr_2O_3 with smaller quantities of FeOx.**
- **The elemental Cr/Fe ratios and oxide thicknesses remained relatively unaffected by citric acid and nitric acid passivation treatments.**
- **Cr_2O_3 surface enrichment is a leading factor affecting the corrosion resistance of stainless steels.**

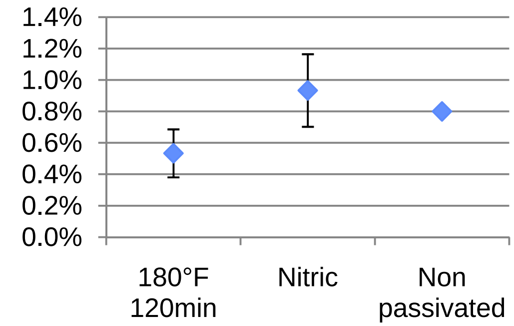
Comparison - Results

304 (% Area Corroded) | **410 (Weight Loss, mg)** | **17-4 (% Area Corroded)**

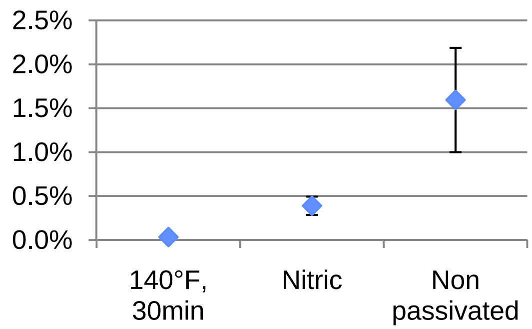
Phase 1

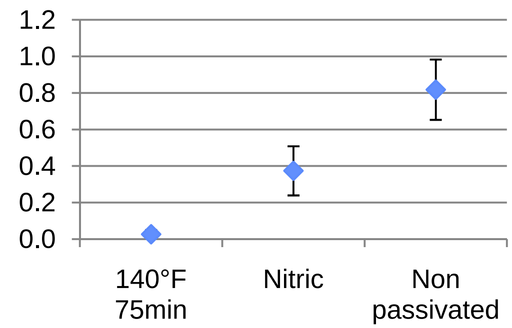


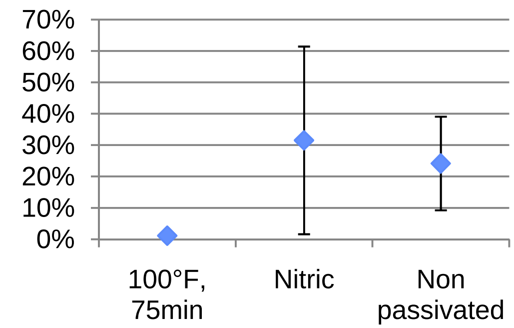




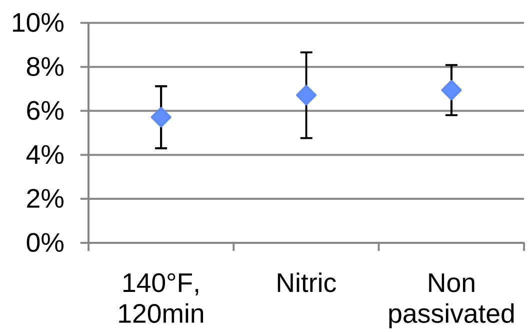
Phase 2

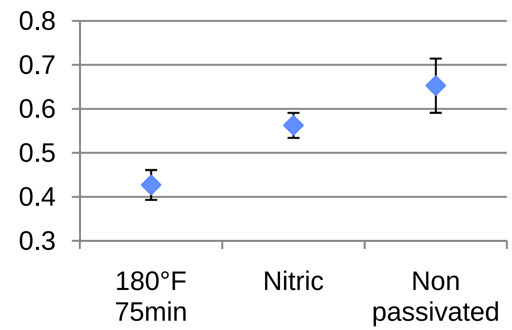


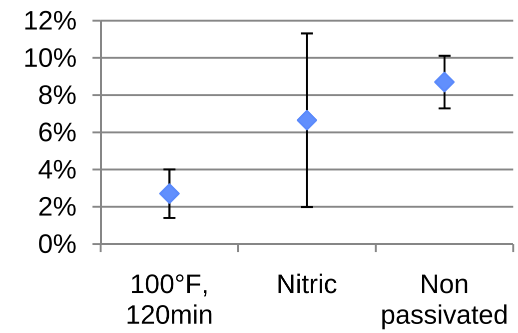




Phase 3







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Comparison - Conclusions

- **A hypothesis test was performed to compare the best citric acid treatments to nitric acid treatments.**
  - **Each value represents the probability that the citric acid performs as well as *or* better than nitric acid.**
  - **E.g. for 304 in a ASTM B117 salt fog chamber, there is a 98.5% chance that the best citric acid treatment performs at least as well as nitric acid and only a 1.5% chance that nitric performs better.**

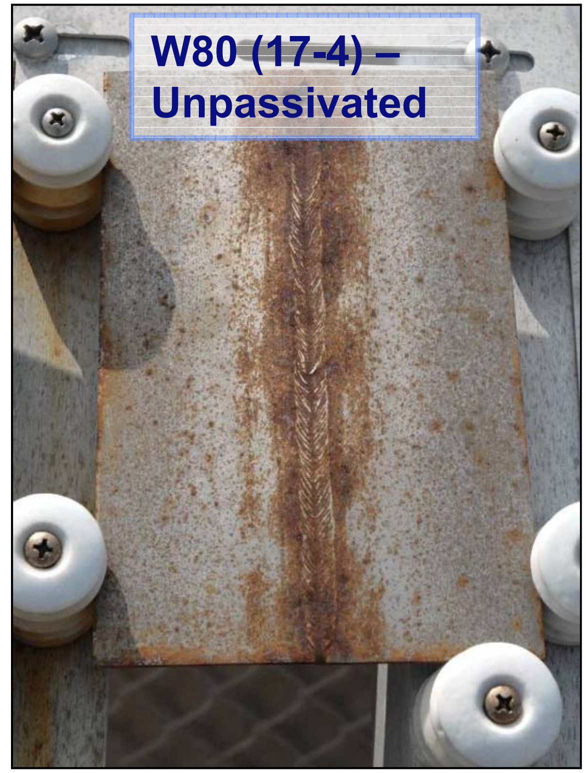
Probability that Citric Acid is Able to Perform As Well or Better than Nitric Acid

Material	Phase 1 (ASTM B117)	Phase 2 (ASTM B117)	Phase 3 (ASTM G1)
304	97.0%	98.5%	83.3%
410	99.6%	97.6%	99.9%
17-4	95.6%	89.0%	94.9%

- **Conclude that citric acid most likely performs as well or better than nitric acid**

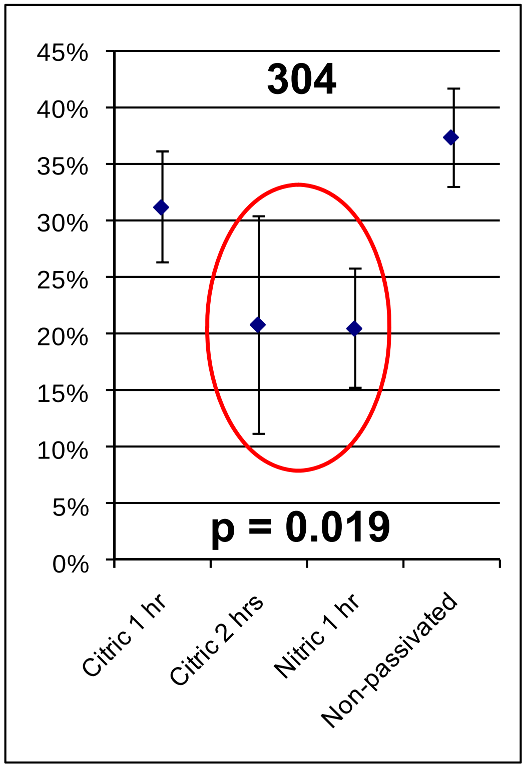
Weld Passivation - Procedure

- Welded per GSS-DIR-017 (NASA-5004), Scuffed, Passivated
  - Nitric acid (32vol%, 1 hour)
  - Citric acid (4wt%, 1 hour and 2 hours)
  - Unpassivated
- Exposed at Beach Facility for 26 weeks
- Measured with image analysis

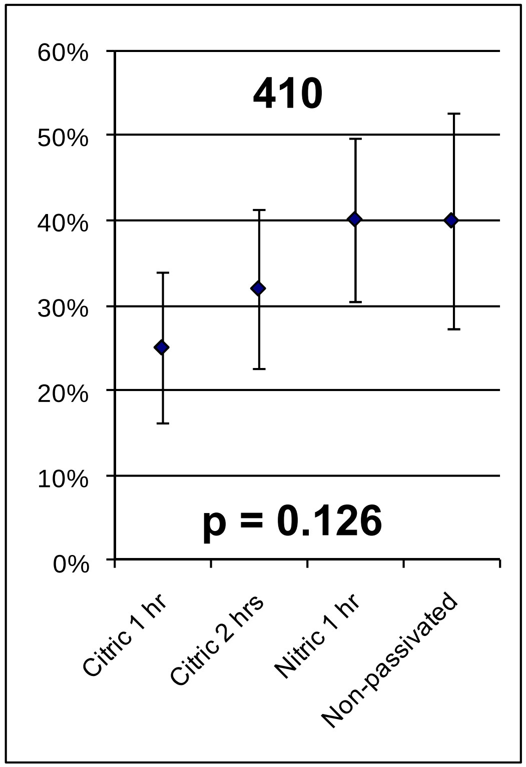


Weld Passivation - Results

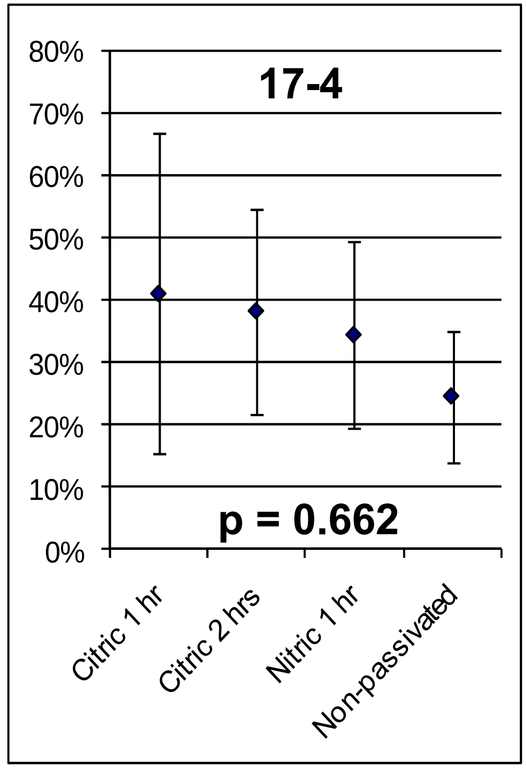
- Statistical comparisons were made using 1-way ANOVA.
- Comparisons between individual treatments made using Fisher's comparison.



Citric Acid, 2hrs performed on par with Nitric, 1hr



No significant differences detected



No significant differences detected

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Entrapment Effects - Procedure

- Citric acid, 4%, entrapped between two coupons for 3 days, then air dried (no rinse).
- Exposed at NASA's Beach Corrosion Facility for 26 weeks.
- Corrosion measured with image analysis.

E01 – Citric Acid Entrapment

E12 – No Entrapment

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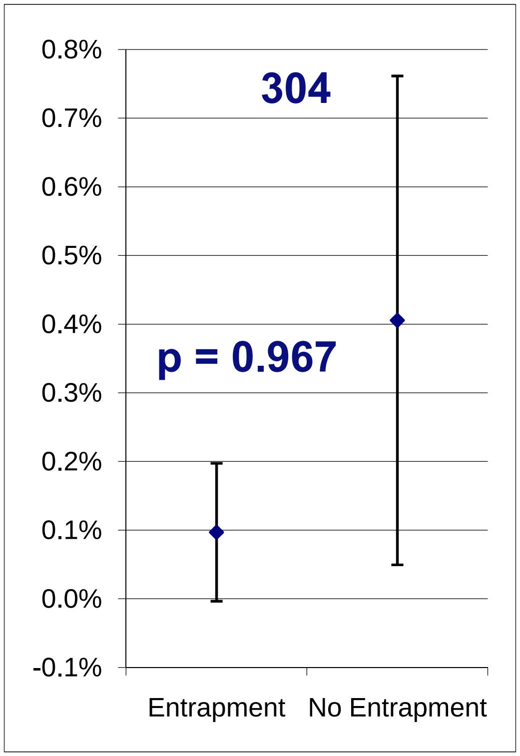
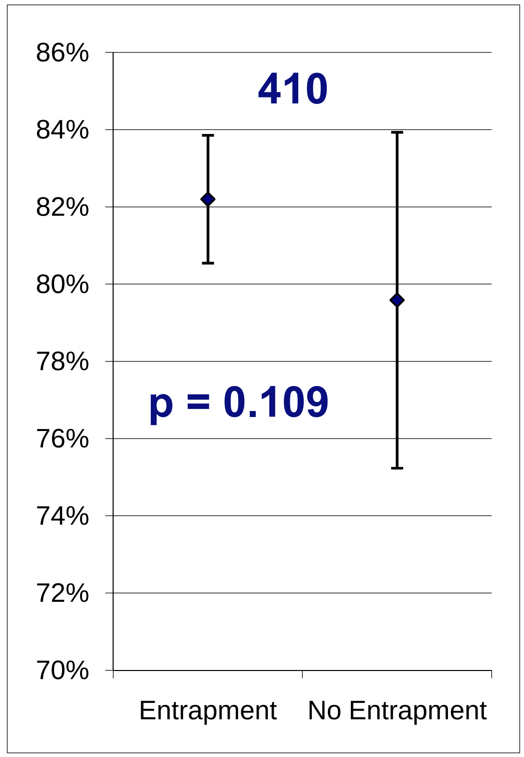
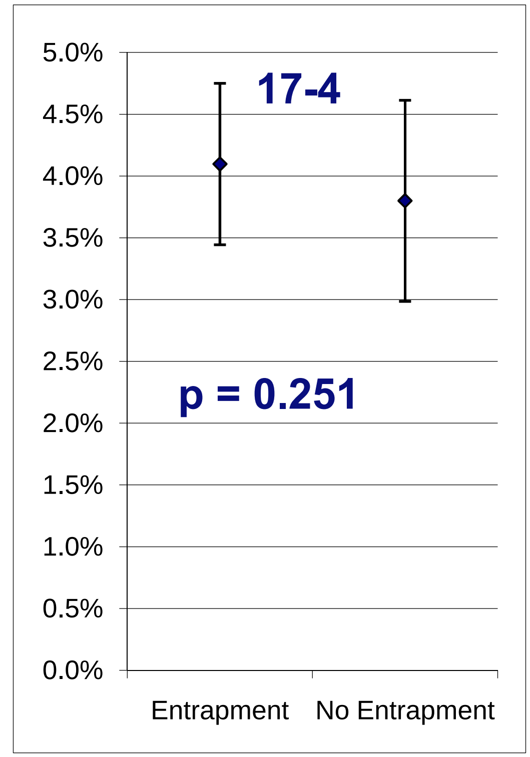
Entrapment Effects - Results

- 2-sample t-test used to compare H_0: $\mu_{entrap} \leq \mu_{no\_entrap}$ to H_a: $\mu_{entrap} > \mu_{no\_entrap}$.
- No statistical differences were detected between corrosion on samples exposed to citric acid entrapment and control samples.







- Cannot conclude that entrapment compromises corrosion protection.
- Agrees with testing performed by Boeing *[Gaydos, 2003]* concluding that citric acid does not etch the surface.

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Conclusions – Citric Acid Optimization

- Treatments with elevated temperature and longer submersion times (T > 100°F and t > 30 minutes) provide significantly better corrosion protection than treatments at ambient temperature or shorter submersion times (T ≈ 100°F and t ≈ 30 minutes). Several treatments at ambient temperature appeared to worsen corrosion protection.
- Concentration of citric acid has little effect on corrosion protection beyond 4% for 304, 410, and 17-4 stainless steels.
- Different types of stainless steel may have different ideal passivation parameters.
- According to testing per ASTM B117 and ASTM G50 at NASA's Beach Site Corrosion Facility at the Kennedy Space Center:
  - For 304, temperatures of 100-140°F and submersion times of 120 minutes provided the best corrosion protection.
  - For 410, temperatures of 140-180°F and submersion times of 30-75 minutes provided the best corrosion protection.
  - For 17-4, no increase in corrosion protection was observed for temperatures above 100°F and submersion times greater than 30 minutes.

Conclusions – Comparison, Welds, Entrapment

- In each atmosphere (ASTM B117 and KSC per ASTM G50), and for each material (304, 410, and 17-4), citric acid was able to provide corrosion resistance similar to or superior to nitric acid passivation.
- Cr_2O_3 enrichment appears to be the main contributor to corrosion protection for passivation. Both nitric and citric acid passivation treatments produced surface films (16.5-22Å) and increased Cr_2O_3 / FeOx ratios. Elemental Cr/Fe ratios seem to be unrelated to passivation.
- Passivating with 4 wt. % citric acid produced slightly greater Cr_2O_3 surface enrichment than nitric acid on 304 stainless steel, and slightly less than nitric acid on 17-4 stainless steel. The Cr_2O_3/FeOx ratios for 410 stainless steel were inconclusive.
- No evidence to reject citric acid passivation of welds on 304, 410, and 17-4 for processes used on KSC. 304 required a longer residence time than nitric acid to achieve the same corrosion resistance. For 410 and 17-4, there was no statistical difference between passivated and non-passivated samples.
- Entrapment of citric acid does not adversely affect corrosion resistance of 304, 410, or 17-4.

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Recommendations

- USA M&P recommend approving standards that include provisions for citric acid passivation.
  - All evidence suggests that citric acid is capable of providing corrosion protection as well as the methods in QQ-P-35B currently in use.
  - Due to the sensitive nature of the treatment and the broad language used in the industry standard specifications (i.e. ASTM A967 and AMS 2700), vendors' passivation process qualification should be examined.
- When implementing an in-house procedure for citric acid passivation and using generic citric acid solutions with no additives, the processing parameters in this report should be referenced.
  - In general, elevated temperatures, ~100°F or higher, and processing times longer than 4 minutes are usually required to provide the same corrosion resistance afforded by passivating with nitric acid per QQ-P-35B.

Acknowledgements

The authors would like to acknowledge:

- Jennie Ward and NASA's Materials Advisory Working Group at Kennedy Space Center for their commission, council, and providing funding for this project.
- Mike Johnson and Don Kahn at WilTech Laboratories for their accommodation and extensive work in their laboratories.
- Bonnie Hauge and USA's Lean Six Sigma organization for their guidance with experimental designs and data analysis.
- Jerry Curran and Mark Kolody of ASRC for arranging and assisting with corrosion testing at NASA's Beach Corrosion Facility.
- Mike Zelinsky and Kenny Bukowski of USA's Materials and Processes Laboratory for conducting salt fog chamber testing.
- EG&G for performing grit blasting.
- Steven Trigwell at ASRC for performing XRF Analysis.

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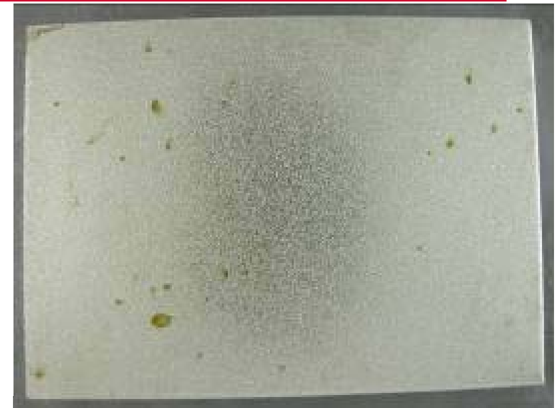
Back-up

Phase 1 - Stainless Steel 304 – CA Treatments

4m
70F
4%

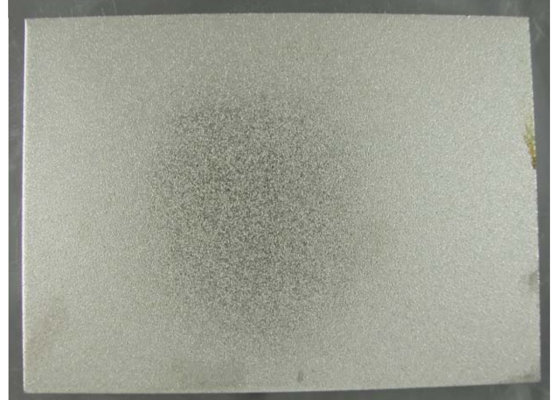
120m
70F
4%

4m
180F
4%



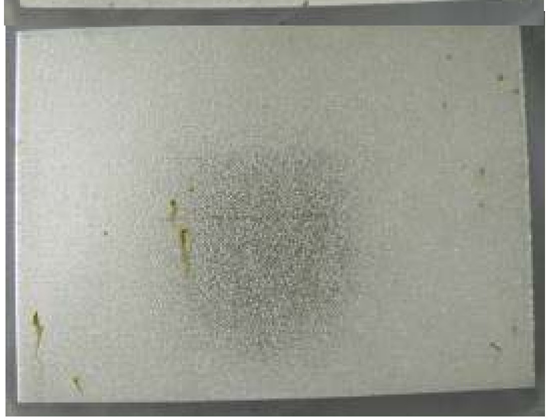
4m
70F
40%

120m
180F
4%



120m
70F
40%

4m
180F
40%



120m
180F
40%

Red – High Setting

Blue – Low Setting

United Space Alliance

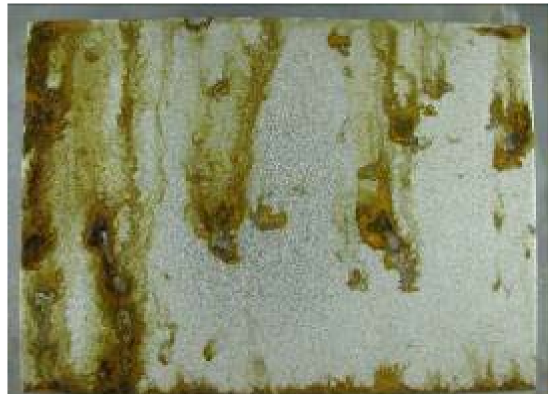
Phase 1 - Stainless Steel 410 – CA Treatments

4m
70F
4%

4m
70F
40%

4m
180F
40%

120m
70F
4%



120m
180F
4%

120m
180F
40%

4m
180F
4%

120m
70F
40%

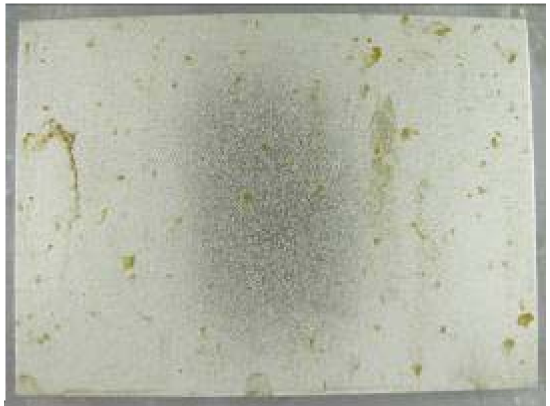
Red – High Setting

Blue – Low Setting

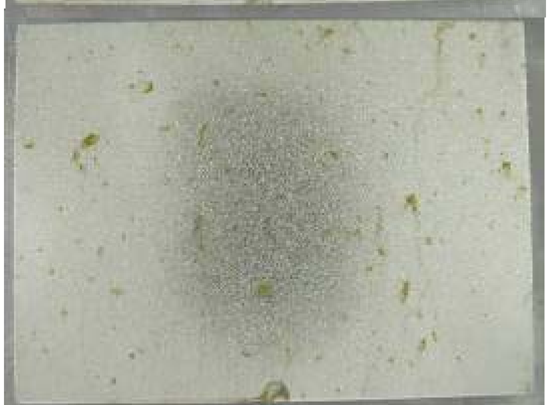
USA United Space Alliance

Phase 1 - Stainless Steel 17-4 – CA Treatments

4m
70F
4%

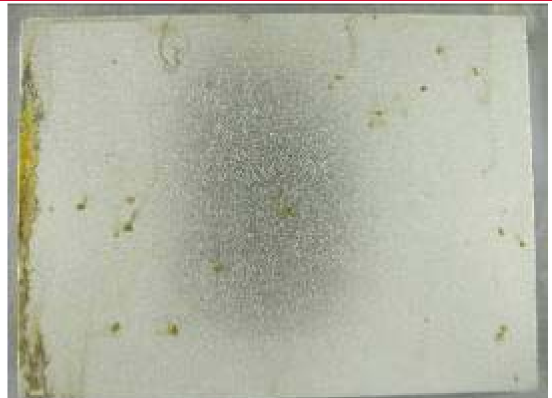


4m
70F
40%

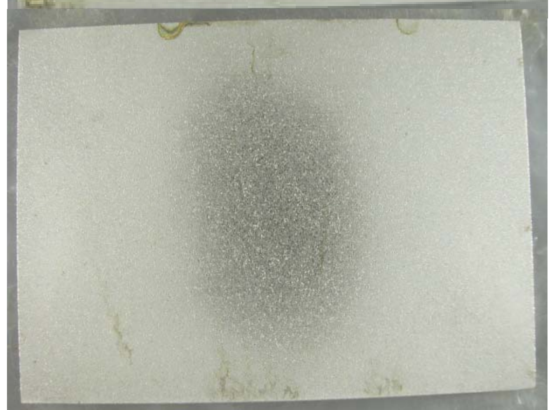


4m
180F
40%

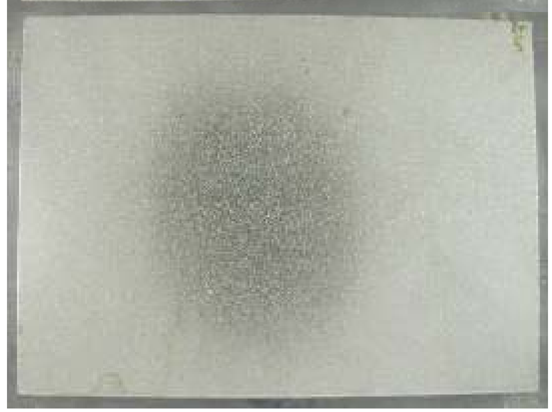
120m
70F
4%



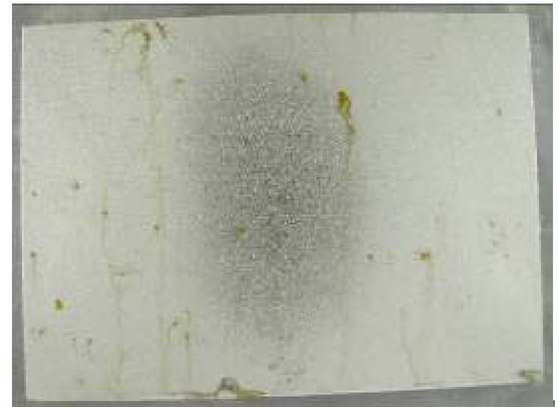
120m
180F
4%



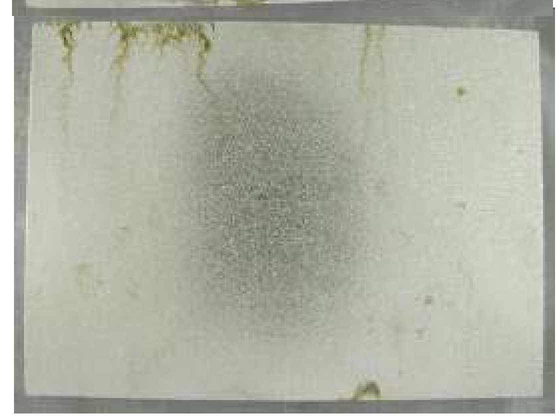
120m
180F
40%



4m
180F
4%



120m
70F
40%



Red – High Setting

Blue – Low Setting

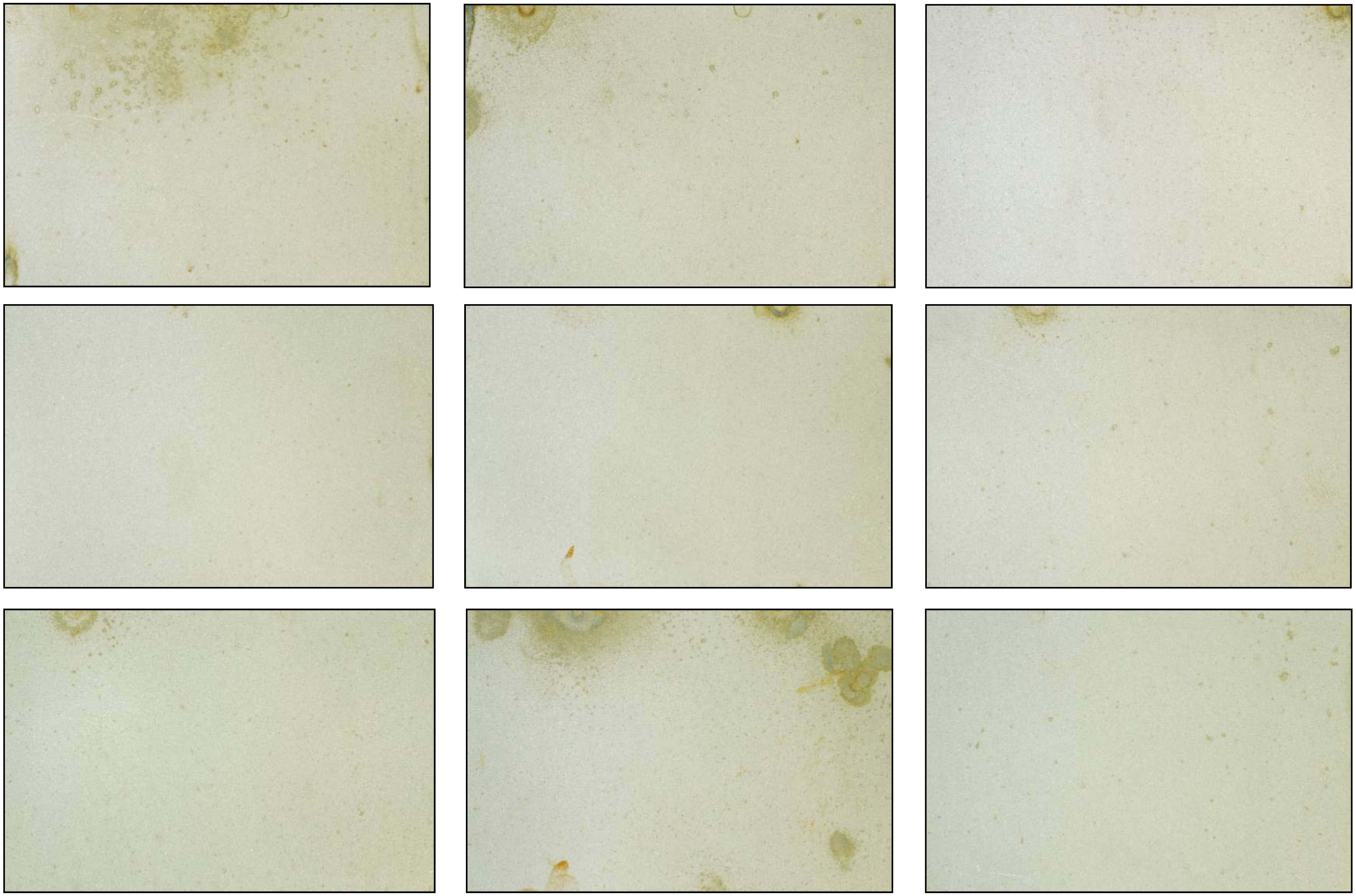
Phase 2 - 304 CA Treatments (Representative Samples)

30min. 75min. 120min.

100°F

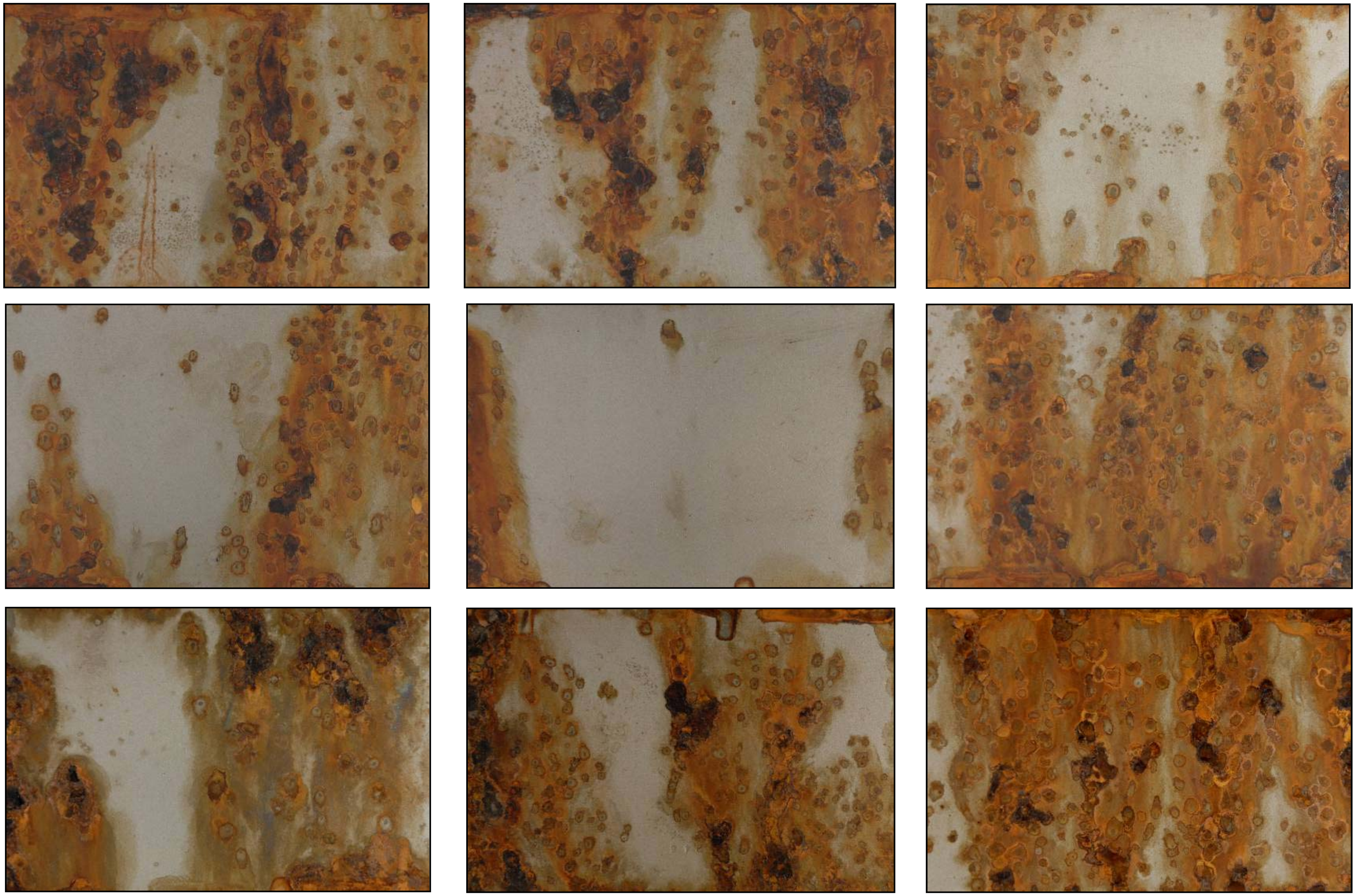
140°F

180°F



Phase 2 - 410 CA Treatments (Representative Samples)

	30min.	75min.	120min.
100°F			
140°F			
180°F			



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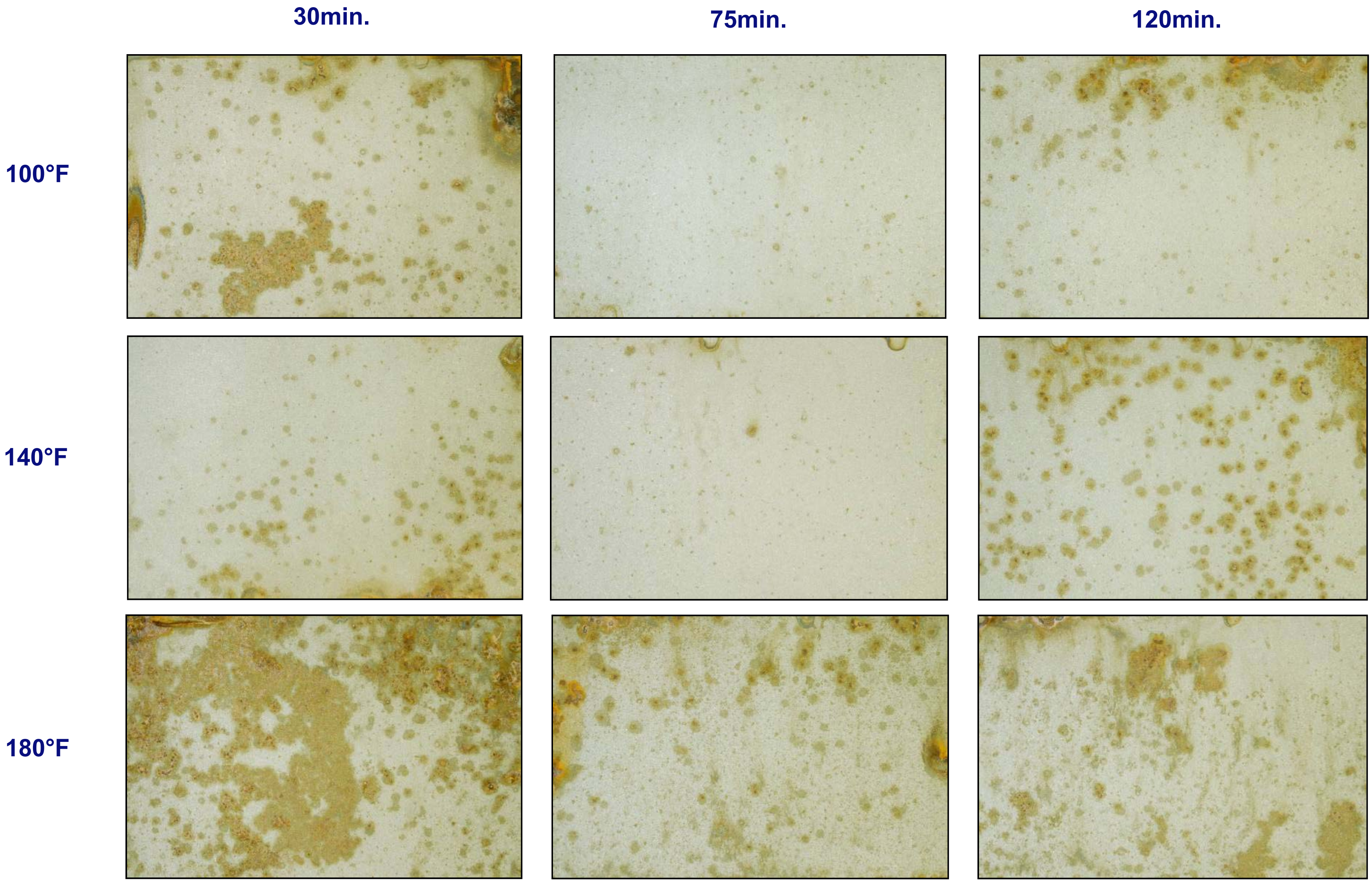
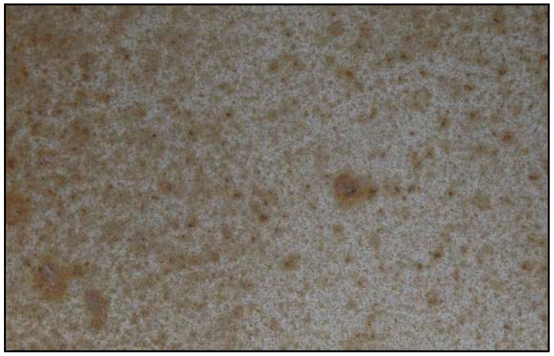
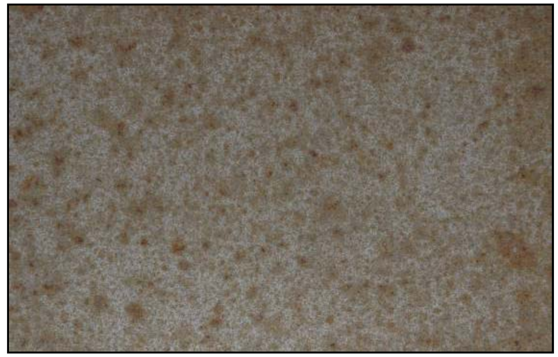
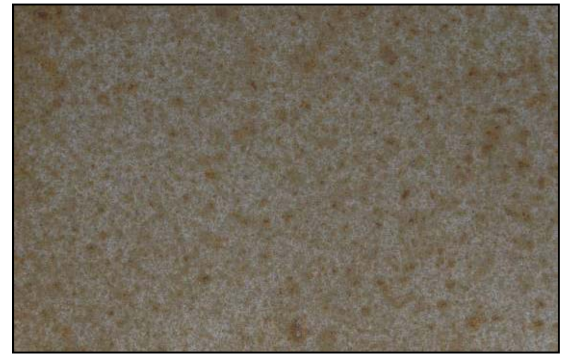
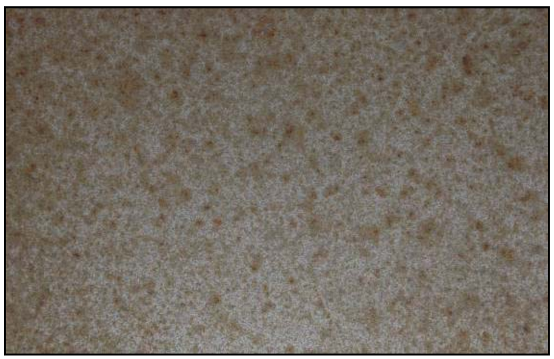
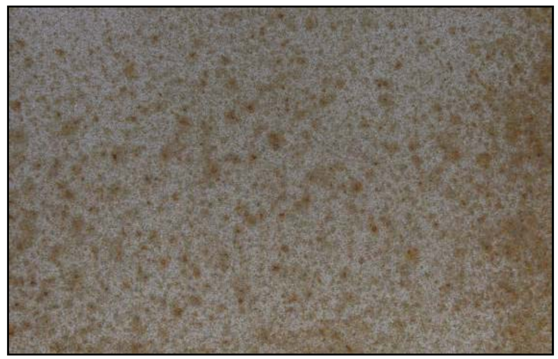
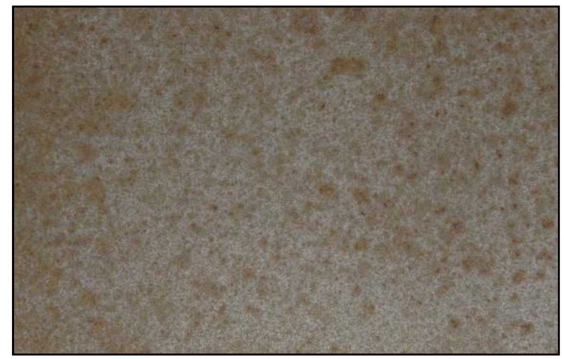
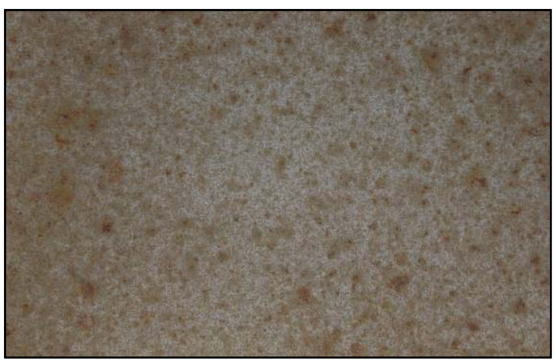
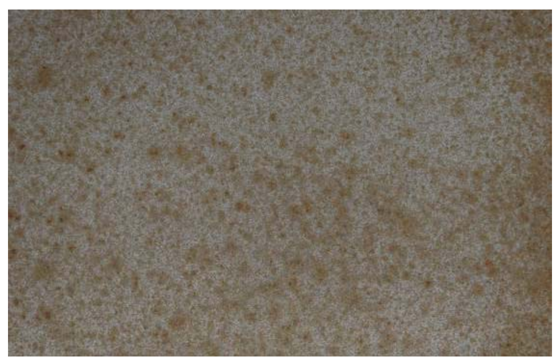
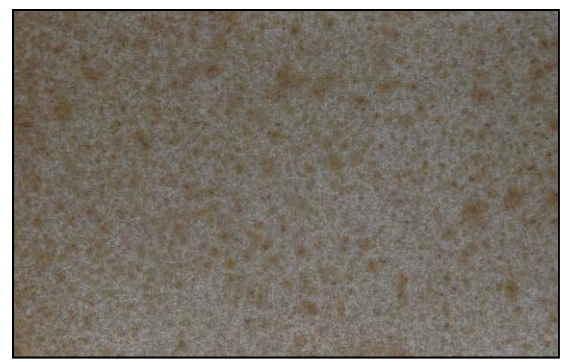
Phase 2 - 17-4 CA Treatments (Representative Samples)



Phase 3 - 304 CA Treatments (Representative Samples)

	30min.	75min.	120min.
100°F			
140°F			
180°F			

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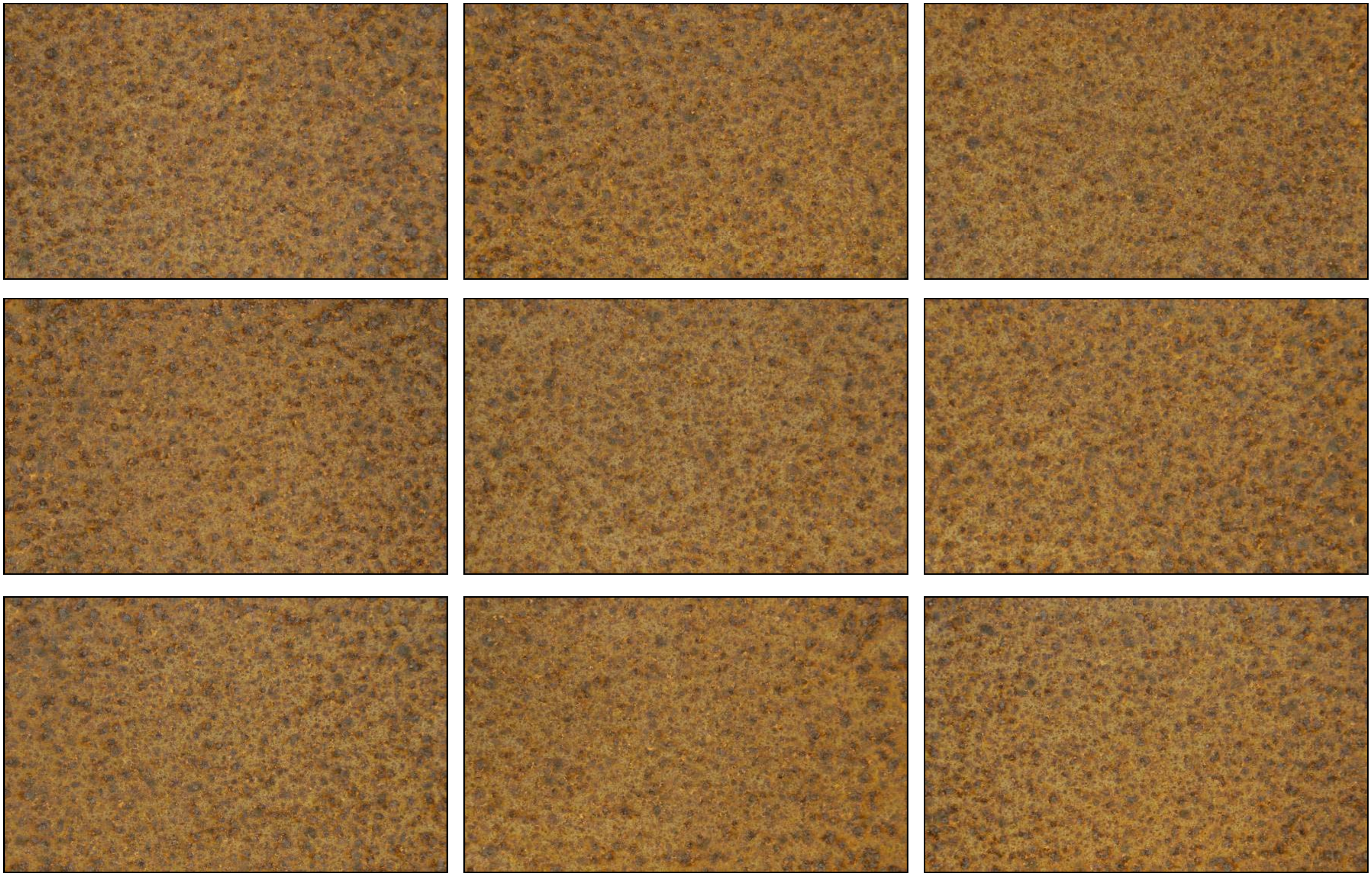
Phase 2 - 304 CA Treatments (Representative Samples)

30min. | 75min. | 120min.

100°F

140°F

180°F



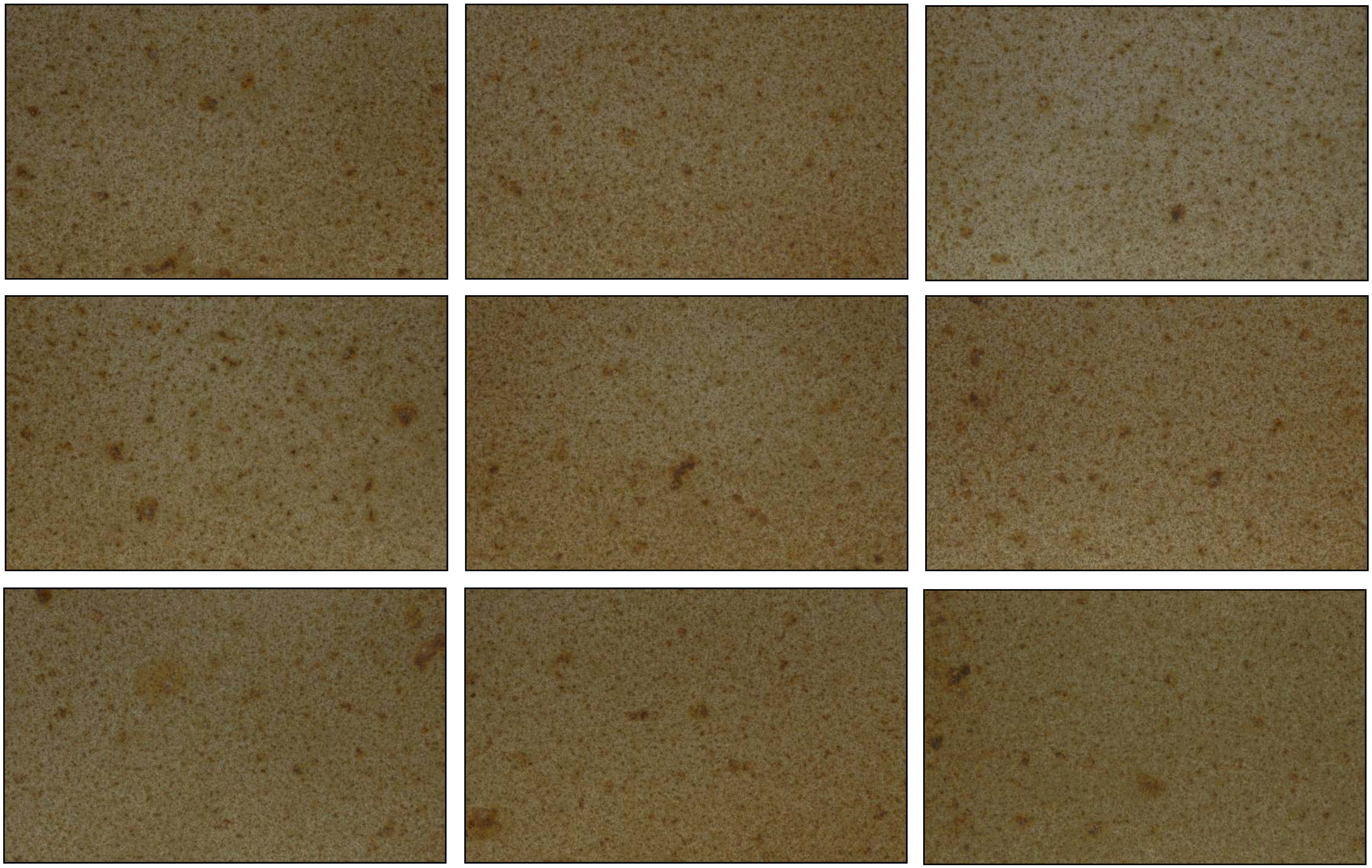
Phase 2 - 17-4 CA Treatments (Representative Samples)

30min. | 75min. | 120min.

100°F

140°F

180°F



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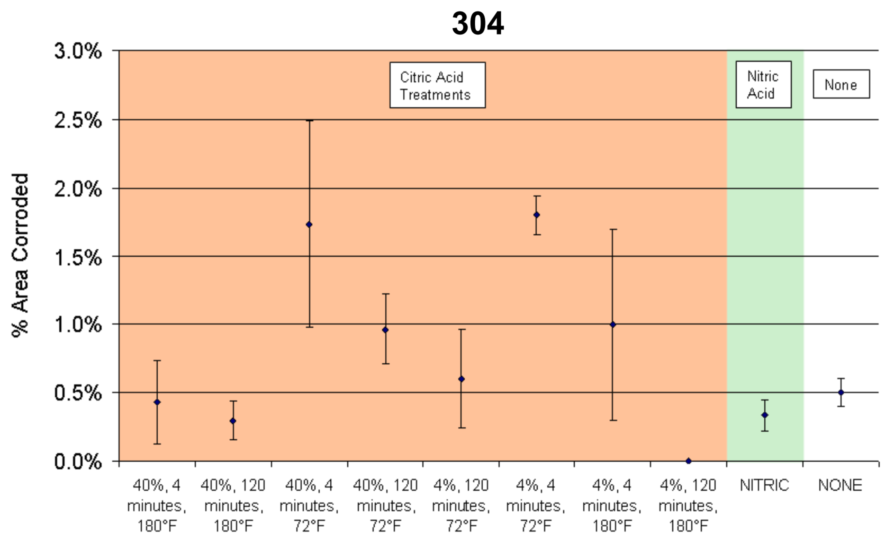
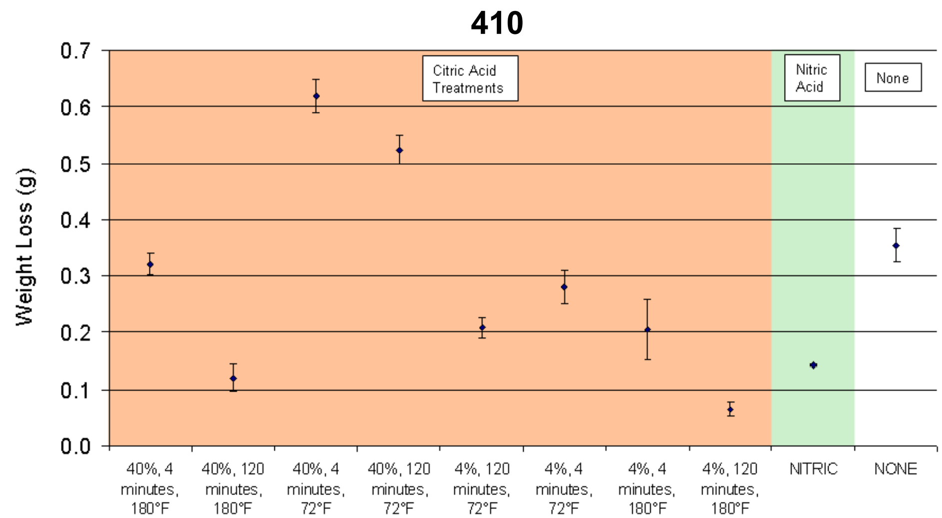
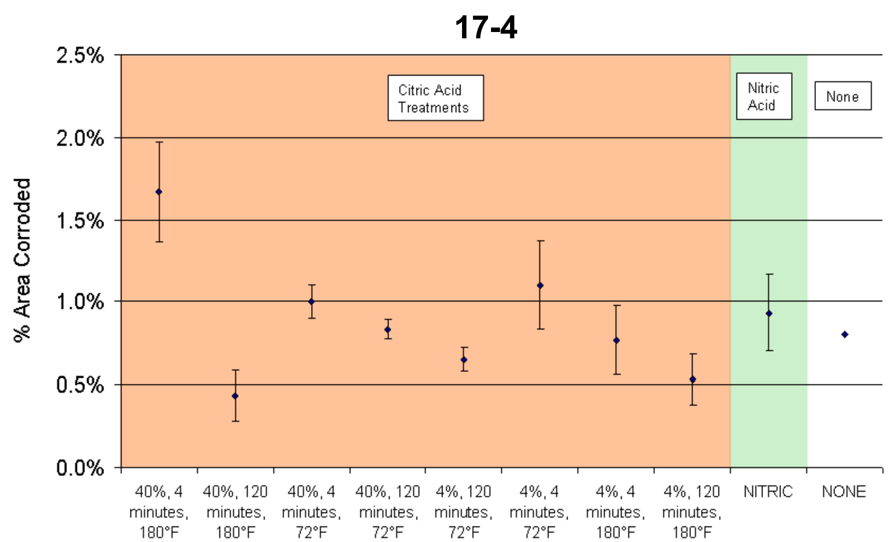
Optimization - Phase 1 Data







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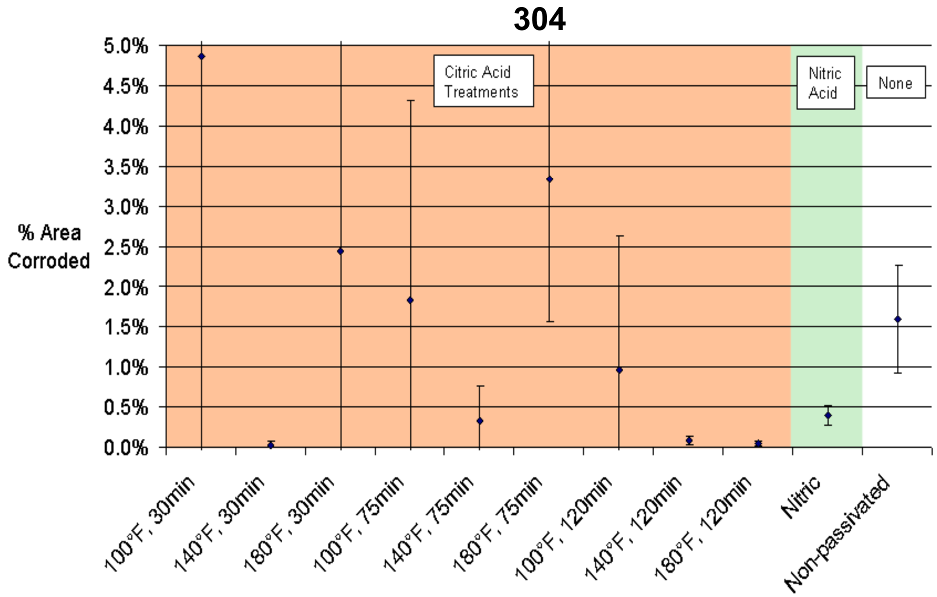
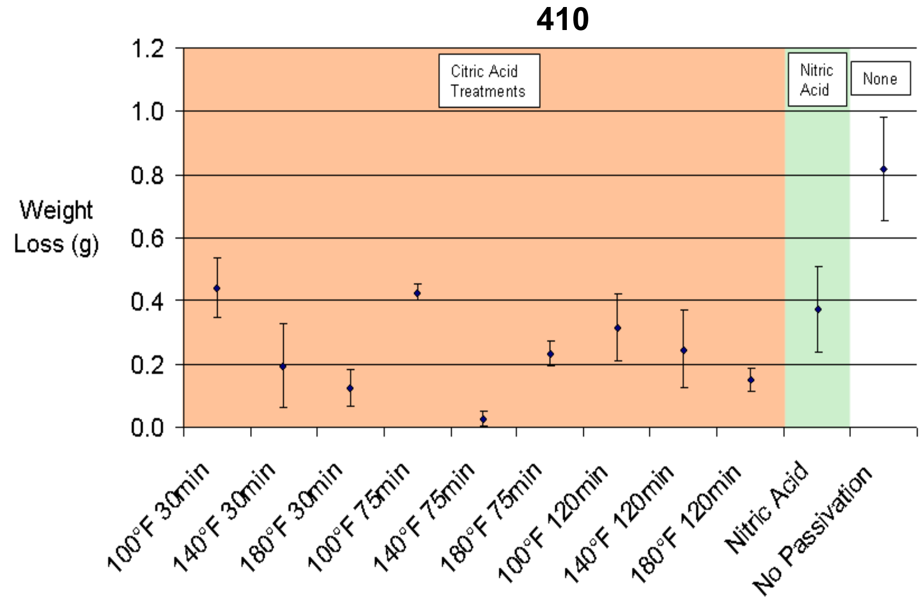
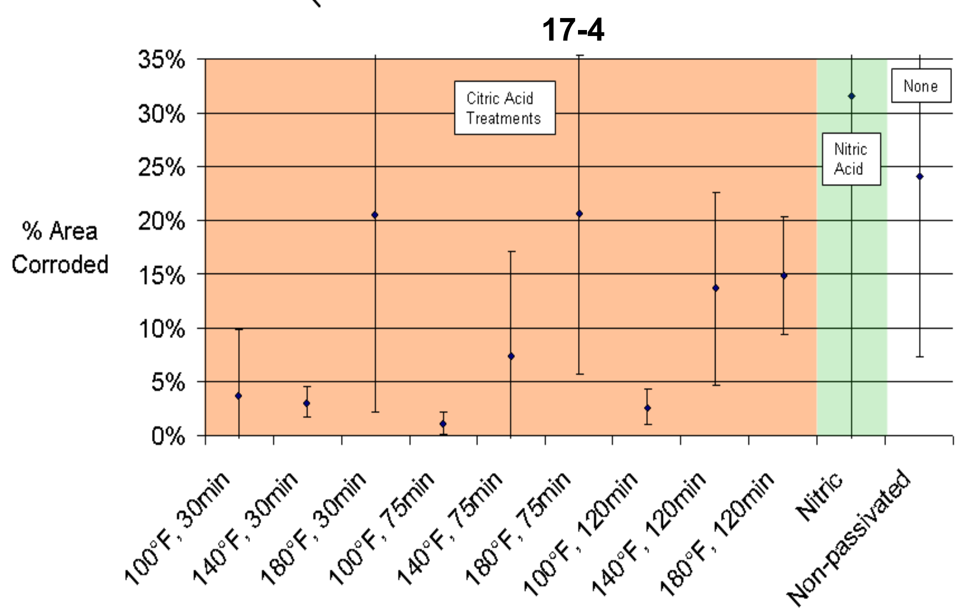
Optimization - Phase 2 Data







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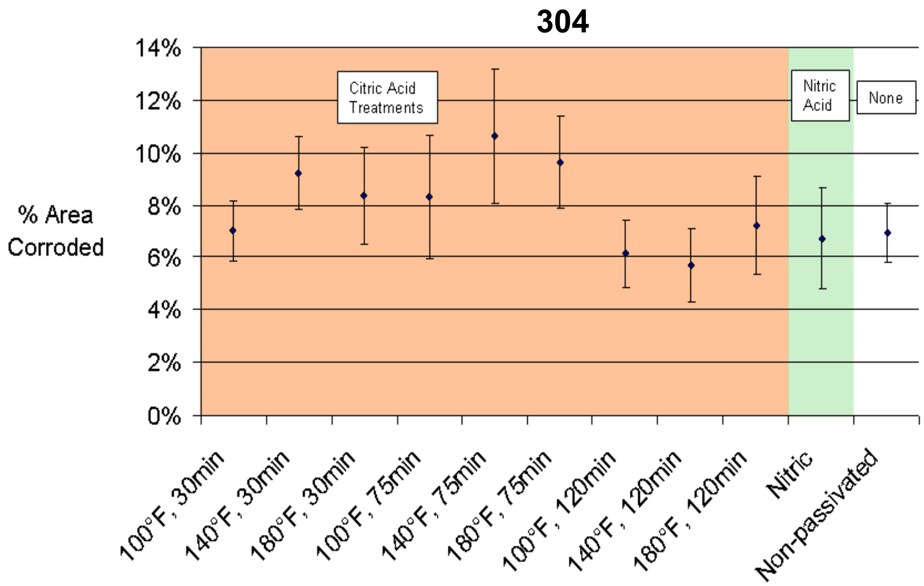
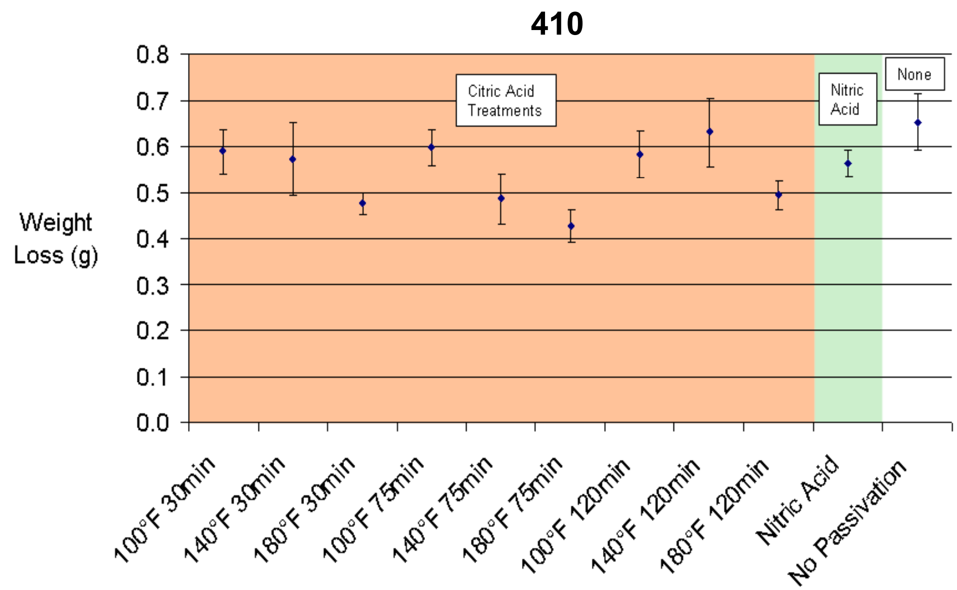
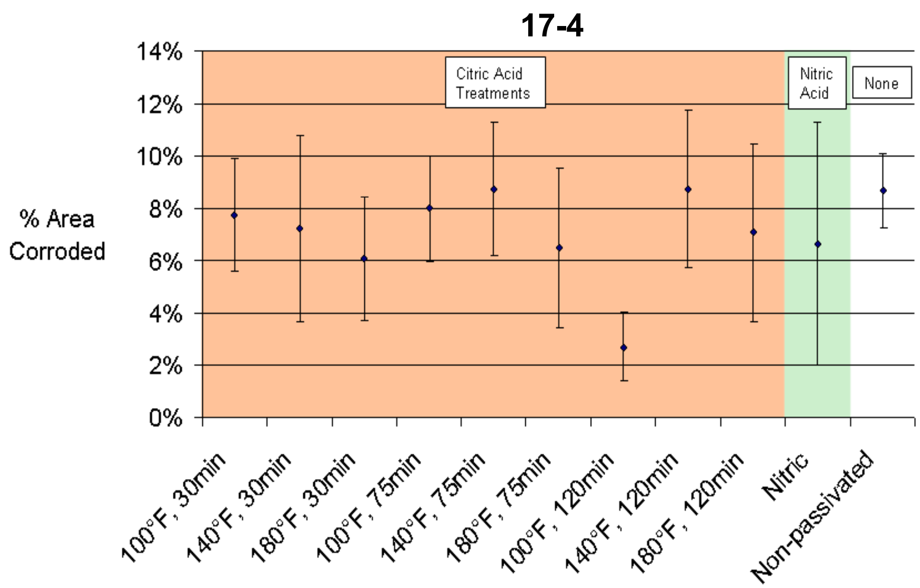
Optimization - Phase 3 Data







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Results – Citric vs. Nitric vs. Unpassivated

- Comparing Phase 1 to Phase 2 (both ASTM B117), more treatments in Phase 2 performed better than nitric acid and no passivation.
  - Raising the minimum temperature and submersion time in the DoE improved the performance of all treatments.
  - As in Phase 1, the best citric acid treatments provided comparable or better corrosion protection than nitric acid or no passivation.
- In Phase 3, the citric acid treatments did not perform as well against nitric acid as in Phase 2 despite the treatment parameters being equal.
  - The atmosphere in Phase 3 was far more complex and varied.
  - As in Phases 1 and 2, the best citric acid treatments provided comparable or better corrosion protection than nitric acid or no passivation.

Number of Citric Acid Treatments Outperforming Nitric Acid or Non-Passivation

Material	Phase 1 (ASTM B117)		Phase 2 (ASTM B117)		Phase 3 (ASTM G1)	
	Non-passivated	Nitric Acid	Non-passivated	Nitric Acid	Non-passivated	Nitric Acid
304	3	2	5	4	2	1
410	6	2	9	7	9	4
17-4	3	4	9	9	7	3

DoE CCD Summary

Phase 1

		SS30400	SS41000	SS17400
p-value	t	0.010	0.021	0.047
	T	0.007	0.004	-
	C	-	0.005	-
	t×T	-	-	-
	t×C	-	-	-
	T×C	-	0.024	-
R^2_{adj}		83.00%	95.60%	42.50%

Phase 2

		SS30400	SS41000	SS17400
p-value	t	0.046	-	-
	T	-	0.023	0.001
	t^2	-	-	-
	T^2	0.058	0.079	-
	t×T	-	-	-
R^2_{adj}		59.37%	62.27%	78.39%

Phase 3

		SS30400	SS41000	SS17400
p-value	t	0.058	0.521	0.542
	T	0.148	0.020	0.771
	t^2	0.021	0.132	0.367
	T^2	0.219	0.279	0.178
	t×T	-	-	0.143
R^2_{adj}		72.70%	66.46%	31.45%

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

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**

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.

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.

Citric Acid Passivation of Stainless Steel

David Yasensky

United Space Alliance, LLC

Materials & Processes Engineering

May 12, 2010

United Space Alliance

Outline

- Introduction
- Background
- Phase 1 Test Plan
- Phase 1 Results
- Phase 1 Conclusions
- Phases 2 and 3 Test Plans
- Transition and Implementation
- Summary
- Acknowledgements

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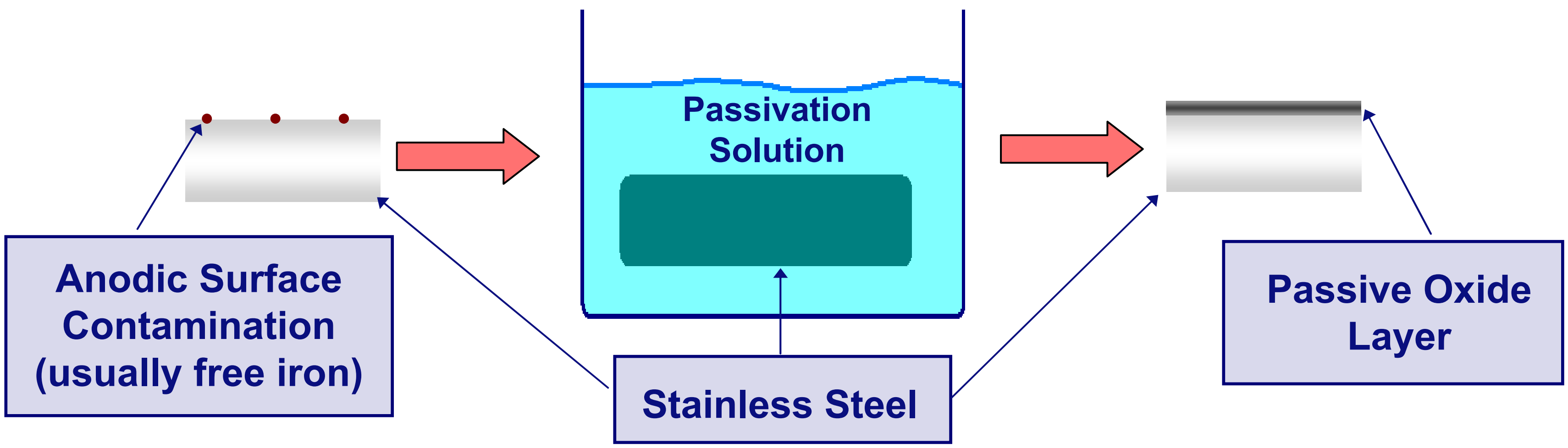
Introduction to Passivation – What is it?

- 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.



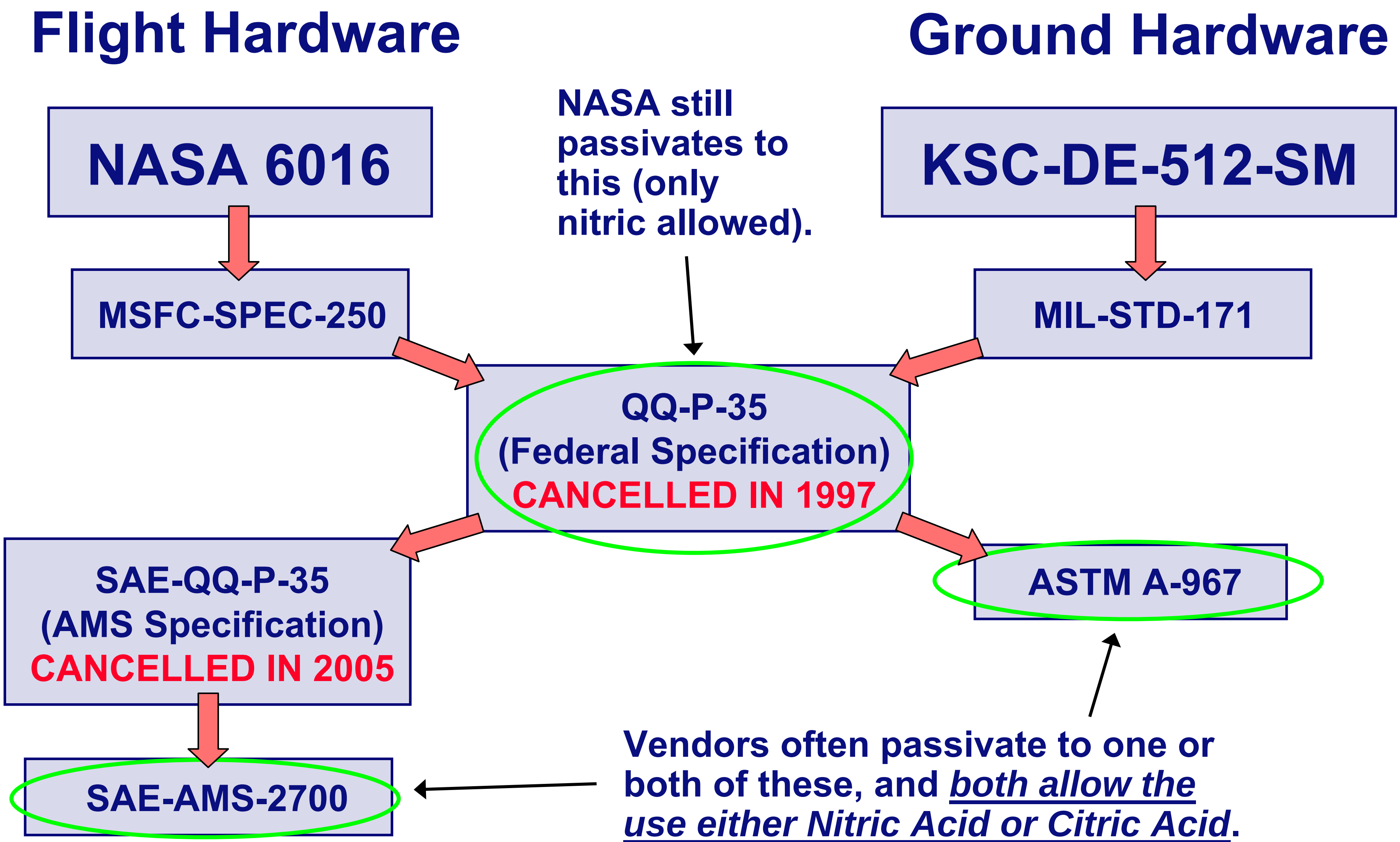
Introduction to Passivation – How it Works

- **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).**

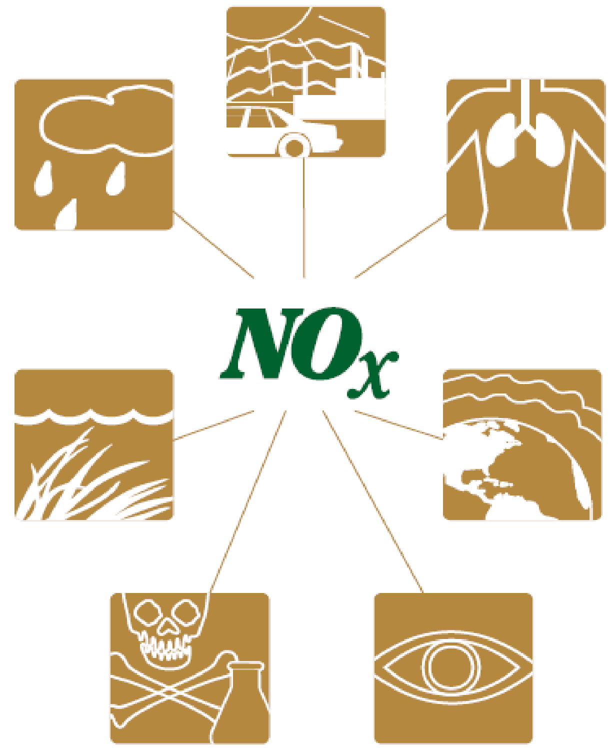
It is generally accepted that thick, Cr_2O_3-rich layers are desirable, however these properties have not been reliably correlated with atmospheric corrosion rates.

Background – NASA Specs Governing Passivation



Background – The Opportunity for Improvement

- Currently, HNO_3 (nitric acid, NA) is used to passivate parts on KSC at WilTech and the NSLD, and only NA passivated parts are acceptable from vendors per NASA specifications.
- KSC disposes of ~125gal of concentrated NA per year, and receives many parts from vendors.
- Unfortunately, NA poses health and environmental concerns. Using $C_6H_8O_7$ (citric acid, CA) in lieu of nitric would alleviate many of these concerns.
- Before CA can be used, the effectiveness of the acid as a passivation agent must be evaluated.
- In 2008, NASA's Materials Advisory Working Group (MAWG) requested the evaluation of CA in place of NA.



HEALTH	4
FIRE	0
REACTIVITY	0

NA NFPA

HEALTH	1
FIRE	0
REACTIVITY	0

CA NFPA

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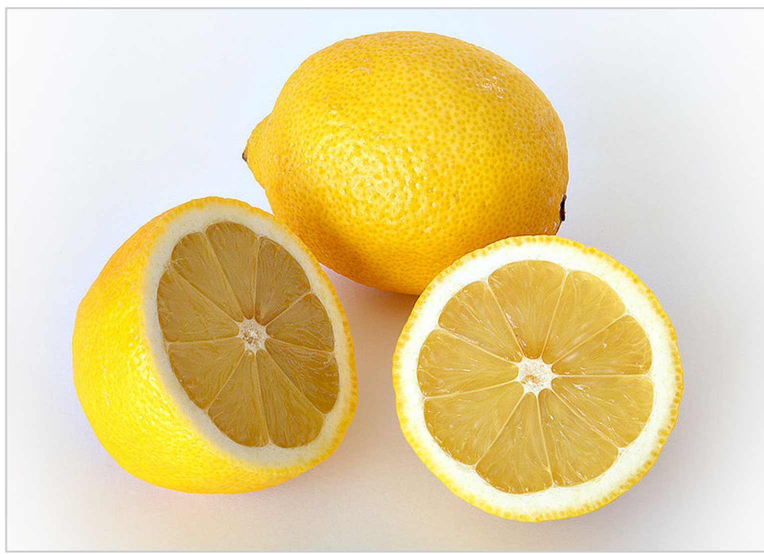
Test Plan - Goals

- Reduce hazardous waste and improve safety.
  - This can be achieved by evaluating CA passivation. If accepted, the change will reduce hazardous waste and improve safety.
- Making the switch may also yield cost savings.



Test Plan - Scope

- Citric acid passivation will be optimized and compared on three commonly used stainless steels.
- The optimized citric acid solution will be compared to nitric acid to see if it is capable of passivating as well or better.
- The following questions will also be addressed:
  - Will the solution effectively passivate welds?
  - If entrapped, will the solution etch or corrode steel?
  - How does citric acid affect the surface of stainless steel?

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Test Plan - Overview

Phase 1

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

Phase 2

- Refined Optimization
- ASTM B-117 - Salt Fog Chamber 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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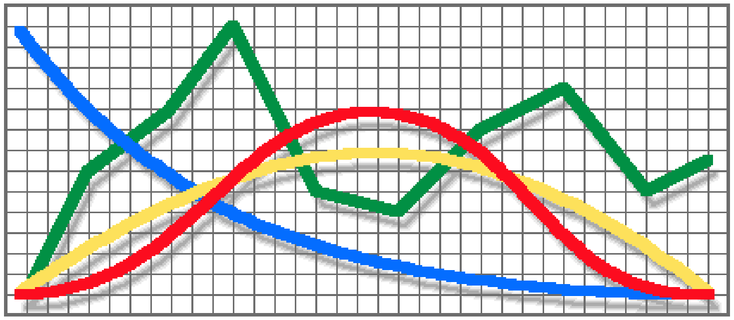
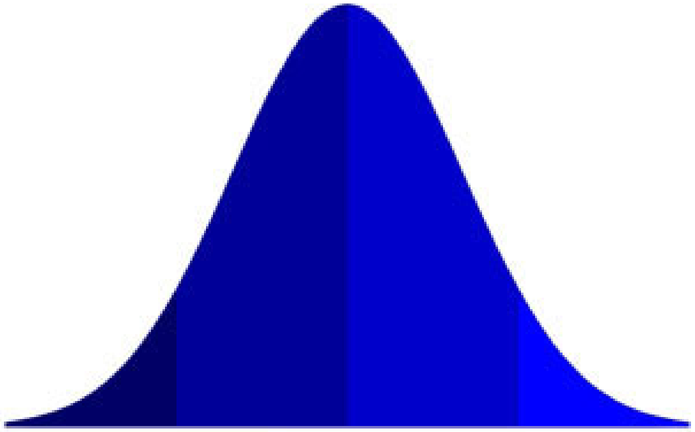
Test Plan - Statistical Tools

- Design of Experiments (DoE) Analysis
  – Analyzes multiple test parameters simultaneously.
  – Exposes interactions between variables.
  – Delivers optimized combination of variables.
- 2-sample T-test
  – Compare the results of two processes
  – Determines whether the output is significantly different





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Test Plan – DoE Schedule

- Explore time, temperature, and concentration at 2 values
  - Time – 4min, 120min
  - Temperature – 72°F, 180°F
  - Concentration – 4%-40%
  - Include control samples (nitric and unpassivated)
- Material Test Coupons:
  - UNS S30400 (304 austenitic stainless steel)
  - UNS S41000 (410 martenisitic stainless steel)
  - UNS S17400 (17-4 precipitation hardened steel)
  - 10cm x 15cm
  - Representative of parts at KSC
- 33 samples per metal
  - 3 repeats per treatment in salt fog chamber

Phase 1 DoE Schedule

Run #	Time (min) (+/- 5 sec)	Temp. (°F) (+/- 2°F)	Conc. Citric Acid (wt%) (+/- 5%)
1	4	72	4
2	120	72	4
3	4	180	4
4	120	180	4
5	4	72	40
6	120	72	40
7	4	180	40
8	120	180	40

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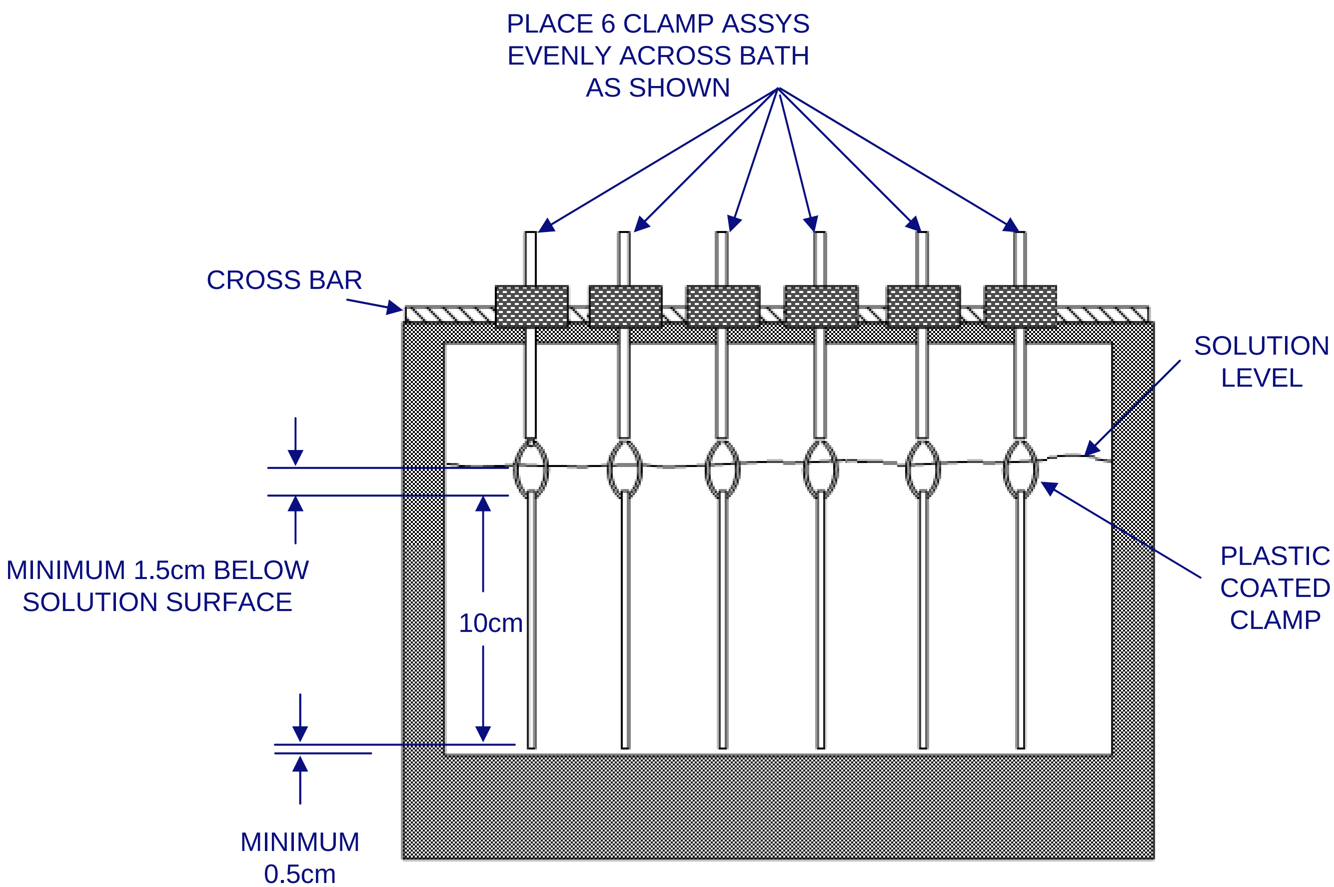
Test Plan - Processing

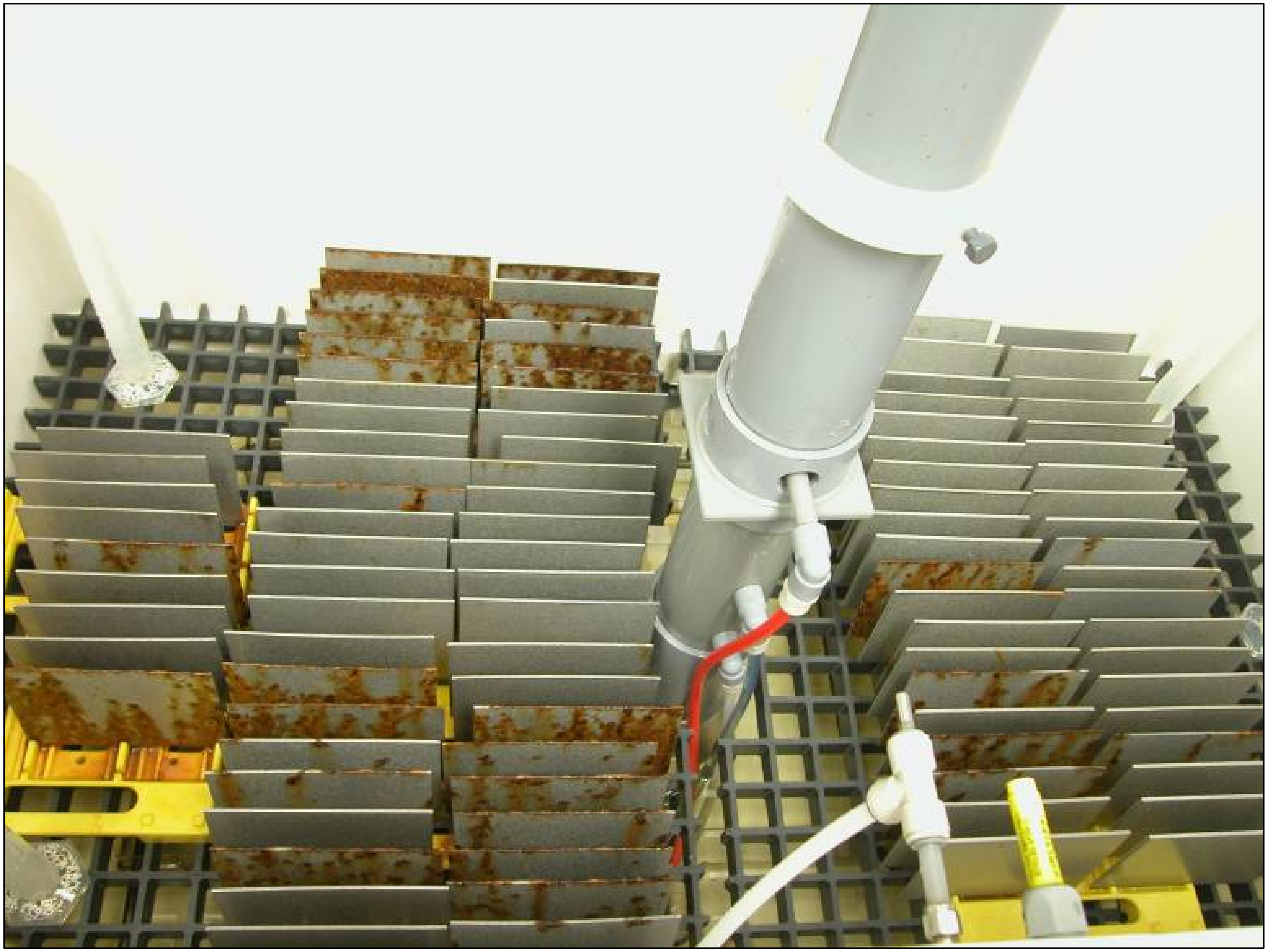
1. Initial Degrease to Remove Machining Contamination.
2. Grit blast coupons with carbon steel to eliminate passive layer and introduce free iron.
3. Degrease per NASA approved Flight Hardware Process.
4. Passivation.
5. Rinse Coupons with DI Water to neutral pH.
6. Blow Dry with Filtered GN_2.
7. Salt Fog or Beach exposure.
8. Photograph coupons.
9. Image analysis or weight loss measurement.
10. Data Analysis.

Test Plan – Processing Equipment



LINDBERG/BLUE M WATERBATH
MODEL # WB11OA
SECTION VIEW

Coupons In Salt Fog Chamber



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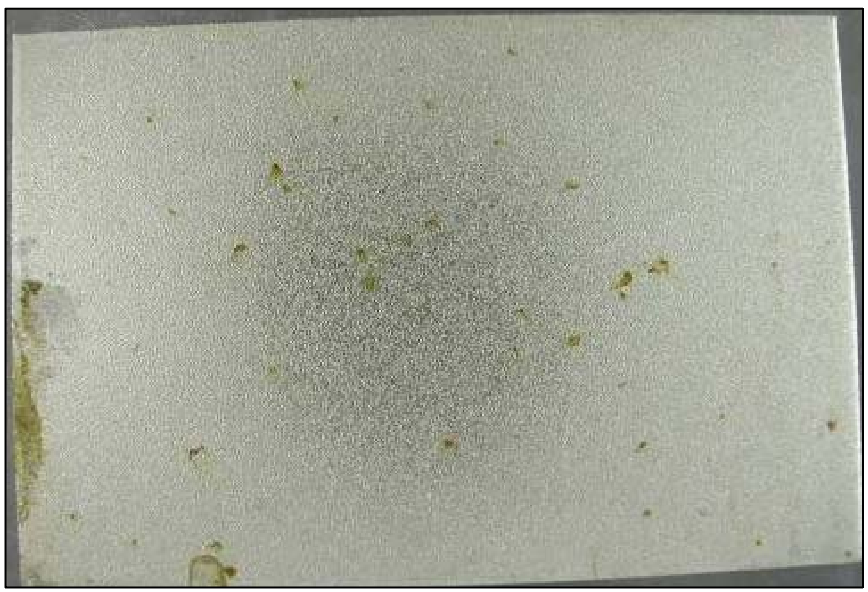
Corrosion Evaluation Plan – Weight Loss

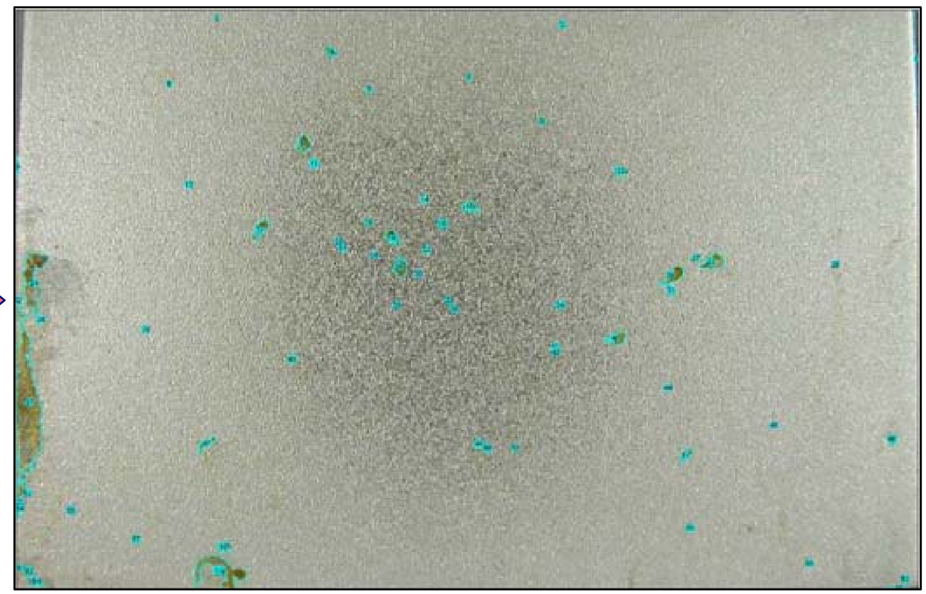
- **Weight loss of heavily corroded parts (410 Steels)**
  - **Soaked in IPA and brushed for 20 seconds to remove loose particles.**
  - **Treated in NaOH solution for 60 minutes to remove remaining corrosion.**
  - **Untreated, uncorroded witness samples to gauge base metal loss.**

Unpassivated 410 coupon, sample #65

Corrosion Evaluation Plan – Image Analysis

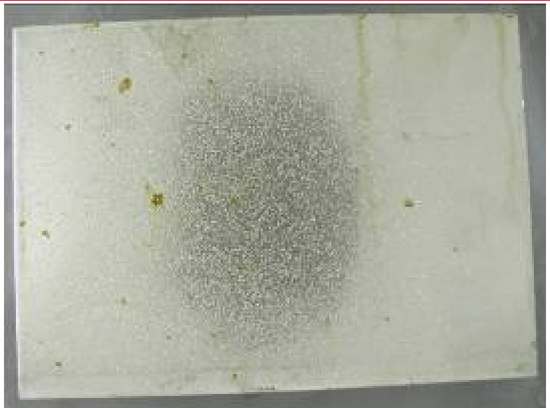
- Image Analysis software for light corrosion (seen on 304, 17-4 coupons)
  - Presents % of area containing corrosion
  - Used when not enough corrosion for weight loss measurements
- Software distinguishes colors in digital images.





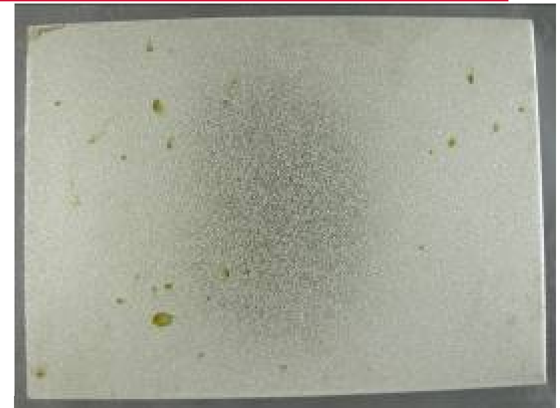
Phase 1 Results – 304 CA Treatments

4m
70°F
4%



120m
70°F
4%

4m
180°F
4%



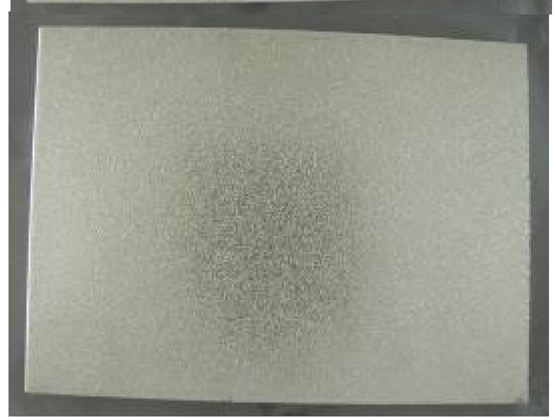
4m
70°F
40%

120m
180°F
4%

120m
70°F
40%

4m
180°F
40%

120m
180°F
40%

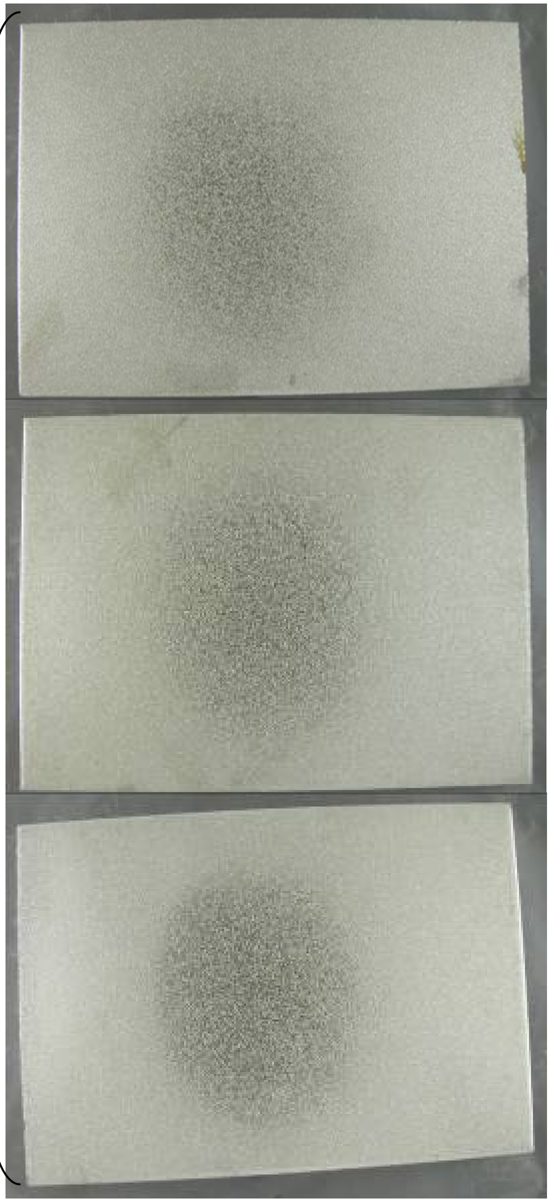


Red – High Setting

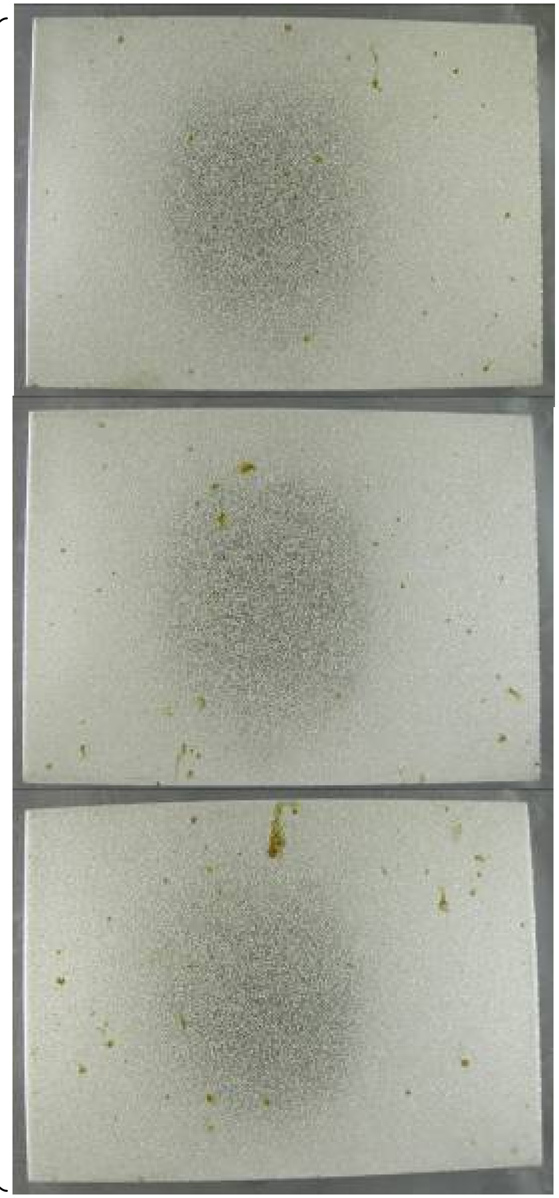
Blue – Low Setting

Phase 1 Results - 304 CA vs. NA vs. Un-passivated

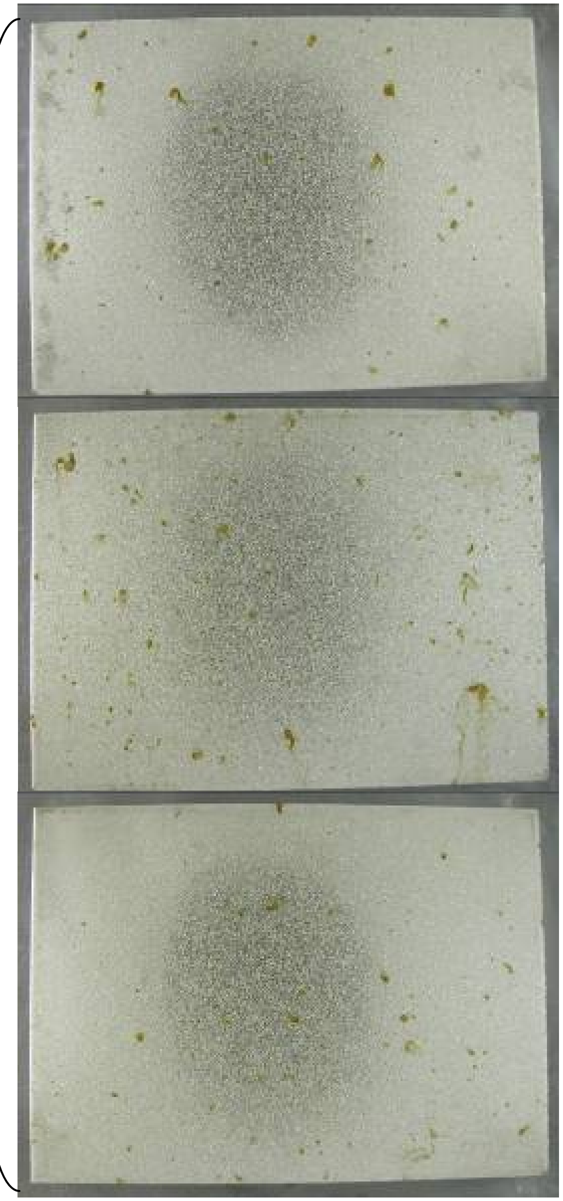
Citric Acid 120m, 180F, 4%



Nitric Acid 30m, 77F, 32%



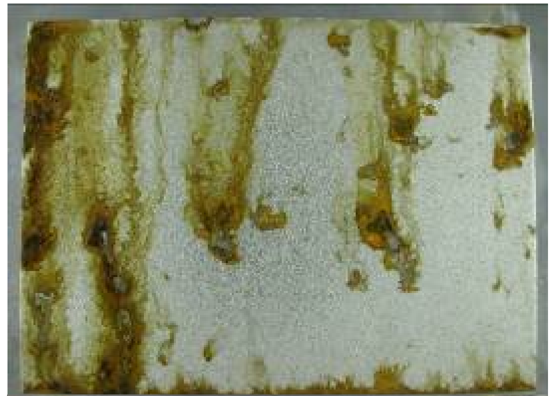
No Treatment



Phase 1 Results – 410 CA Treatments

4m
70°F
4%

120m
70°F
4%



4m
180°F
4%

4m
70°F
40%

120m
180°F
4%

120m
70°F
40%

4m
180°F
40%

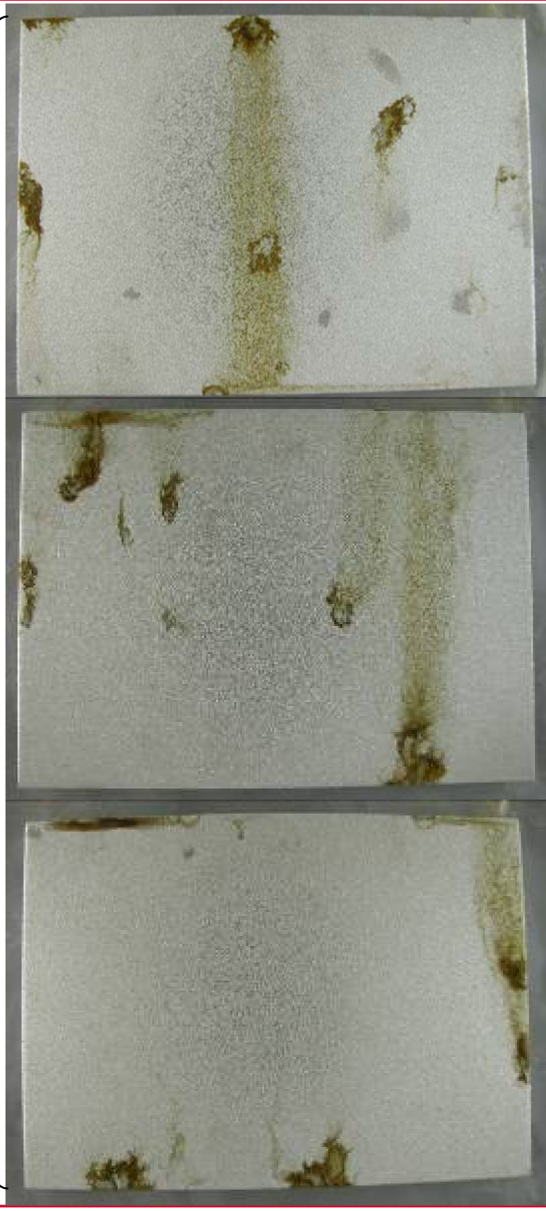
120m
180°F
40%

Red – High Setting

Blue – Low Setting

Phase 1 Results - 410 CA vs. NA vs. Un-passivated

Citric Acid 120m, 180F, 4%



Nitric Acid 30m, 77F, 32%

No Treatment

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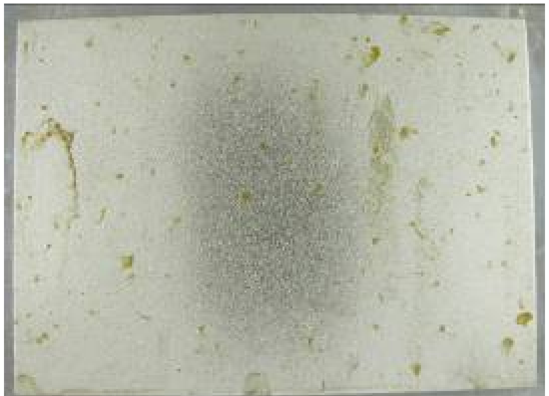
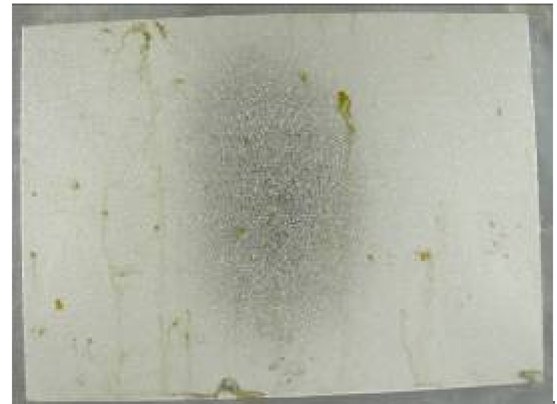
Phase 1 Results – 17-4 CA Treatments

4m
70°F
4%

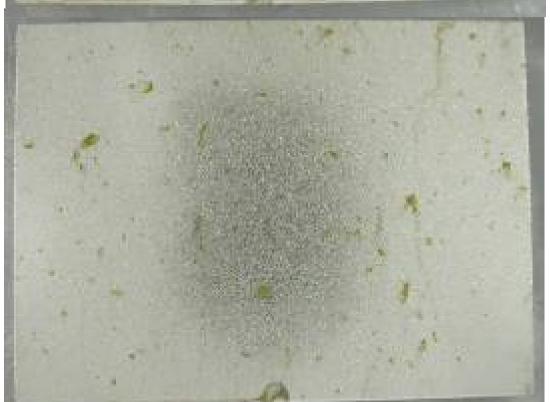


120m
70°F
4%

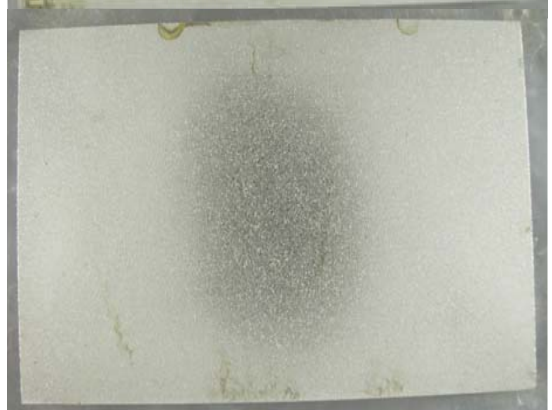
4m
180°F
4%



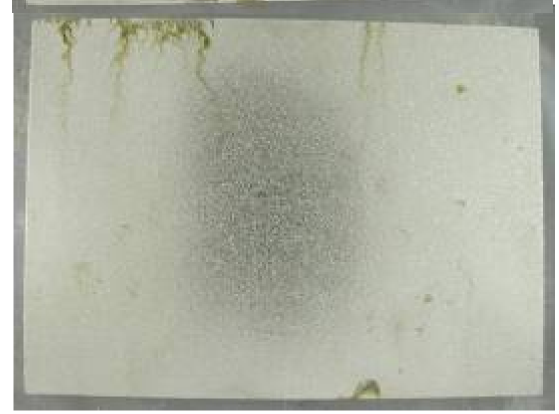
4m
70°F
40%



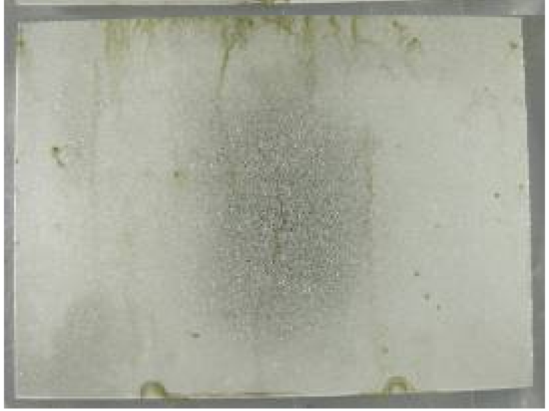
120m
180°F
4%



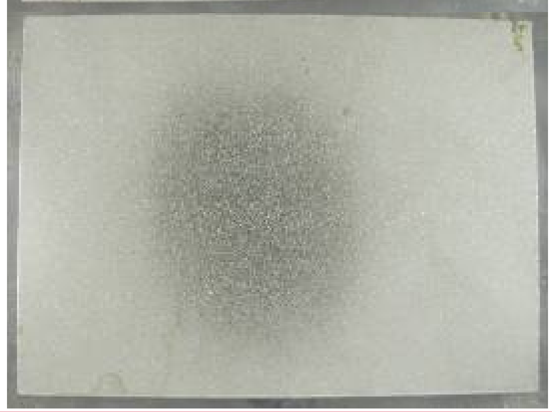
120m
70°F
40%



4m
180°F
40%



120m
180°F
40%

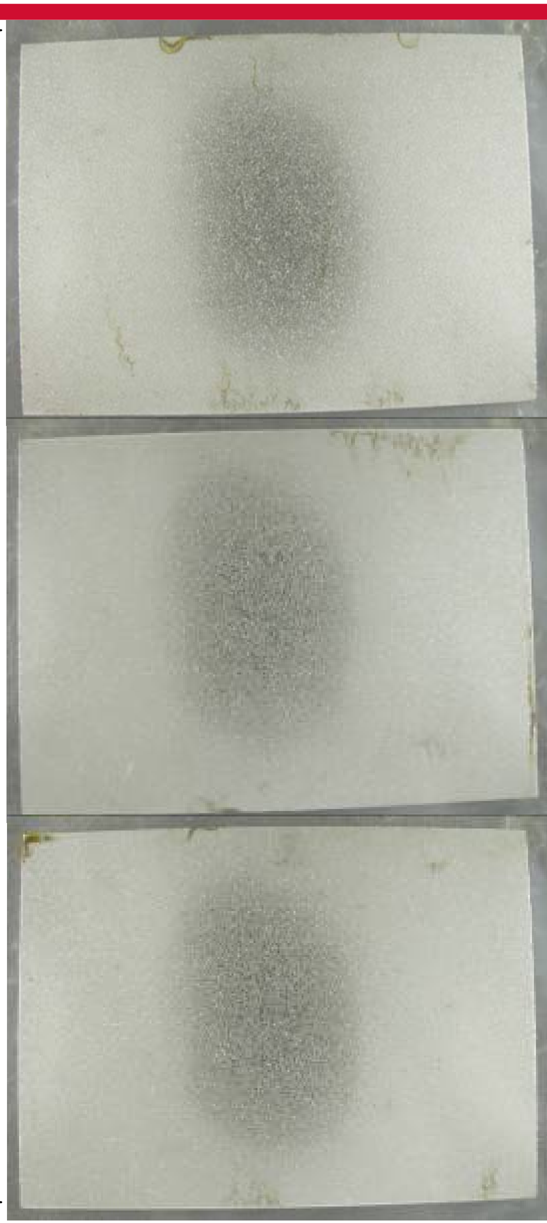


Red – High Setting

Blue – Low Setting

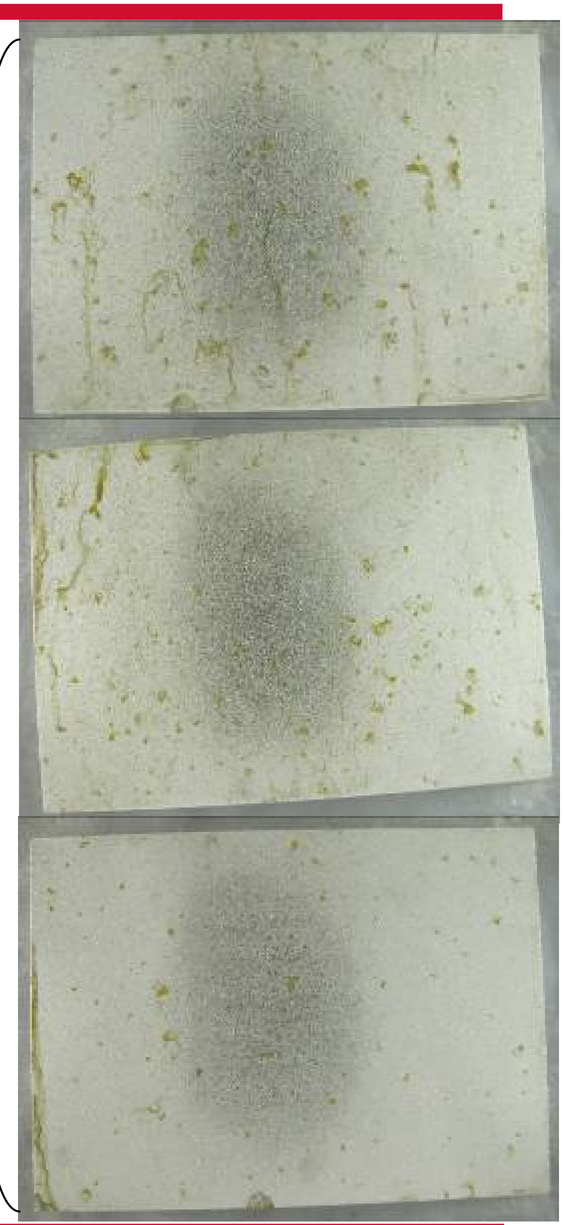
Phase 1 Results – 17-4 CA vs. NA vs. Un-passivated

Citric Acid 120m, 180F, 4%



Nitric Acid 30m, 77F, 32%

No Treatment



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Phase 1 Results - Data

	40%, 4 minutes, 180°F	40%, 120 minutes, 180°F	40%, 4 minutes, 72°F	40%, 120 minutes, 72°F	4%, 120 minutes, 72°F	4%, 4 minutes, 72°F	4%, 4 minutes, 180°F	4%, 120 minutes, 180°F	NITRIC	NONE
410 Weight Loss										
Coupon #1	0.2993	0.0917	*	0.5482	0.1866	0.2976	0.1908	0.0779	0.1401	0.3218
Coupon #2	0.3366	0.1306	0.6393	0.4983	0.2223	0.2469	0.2626	0.0624	0.1433	0.3805
Coupon #3	0.3272	0.1367	0.5978	0.523	0.2161	0.2965	0.158	0.0545	0.1414	0.3612
Average	0.3210	0.1197	0.6185	0.5232	0.2083	0.2803	0.2038	0.0649	0.1416	0.3545
St. Dev.	0.0194	0.0244	0.0293	0.0250	0.0191	0.0290	0.0535	0.0119	0.0016	0.0299
Outlier			0.2845							
304 Area Corroded										
Coupon #1	0.1	0.2	1.2	1.2	0.3	*	0.7	0	0.2	0.6
Coupon #2	0.5	0.4	1.4	0.7	0.5	1.9	1.8	0	0.4	0.5
Coupon #3	0.7	*	2.6	1	1	1.7	0.5	0	0.4	0.4
Average	0.43	0.30	1.73	0.97	0.60	1.80	1.00	0.00	0.33	0.50
St. Dev.	0.31	0.14	0.76	0.25	0.36	0.14	0.70	0.00	0.12	0.10
Outliers		4.9				0.7				
17-4 Area Corroded										
Coupon #1	1.4	0.3	1	0.8	*	0.8	0.7	0.7	0.8	0.8
Coupon #2	1.6	0.4	0.9	0.8	0.7	1.2	1	0.5	0.8	0.8
Coupon #3	2	0.6	1.1	0.9	0.6	1.3	0.6	0.4	1.2	0.8
Average	1.67	0.43	1.00	0.83	0.65	1.10	0.77	0.53	0.93	0.80
St. Dev.	0.31	0.15	0.10	0.06	0.07	0.26	0.21	0.15	0.23	0.00
Outlier					1.5					

- **Some outliers appear to be caused by insufficient grit blasting.**
- **One 410 coupon was corrupted due to aggressive cleaning.**

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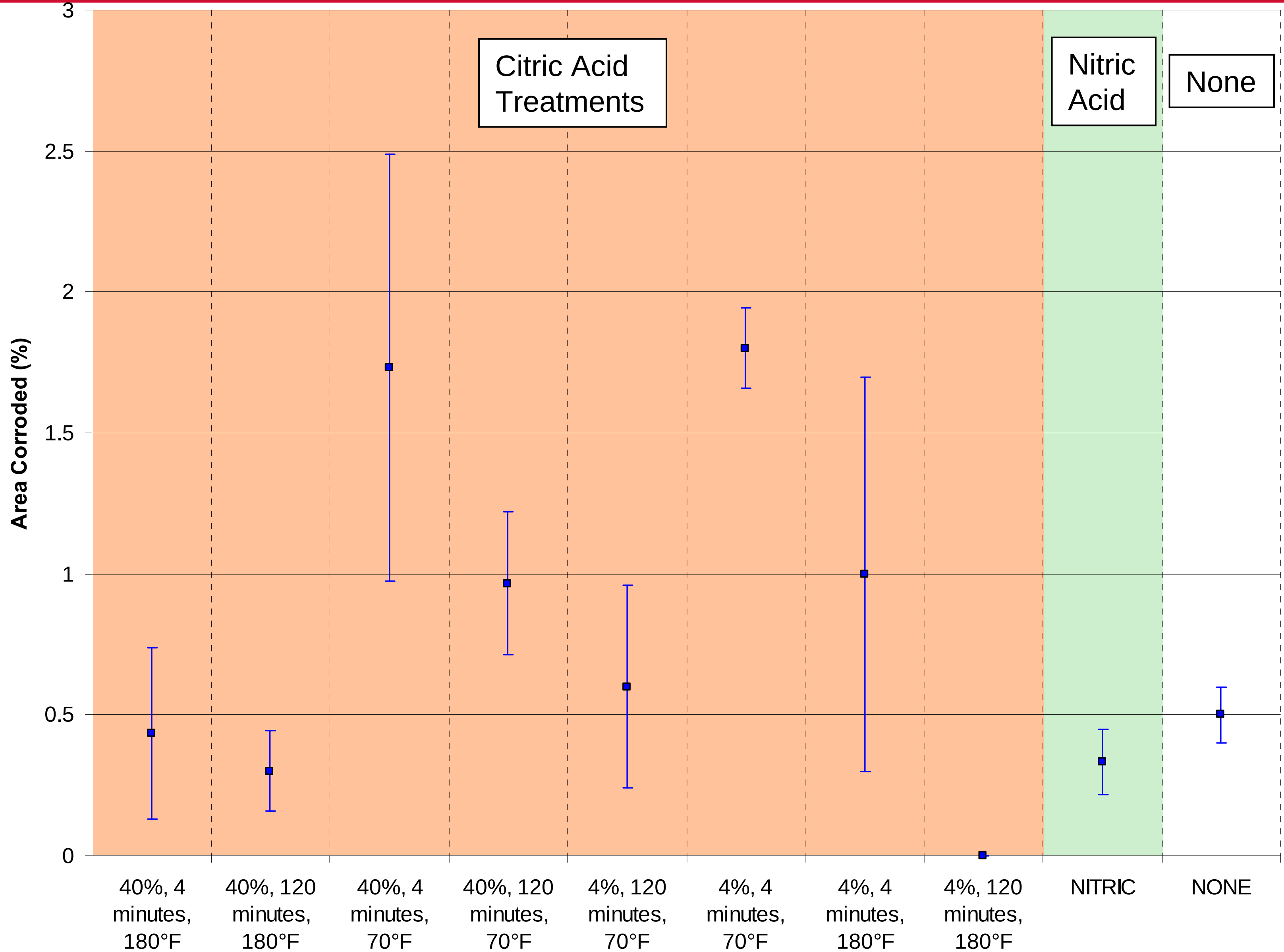
Phase 1 Results - 304 Plotted



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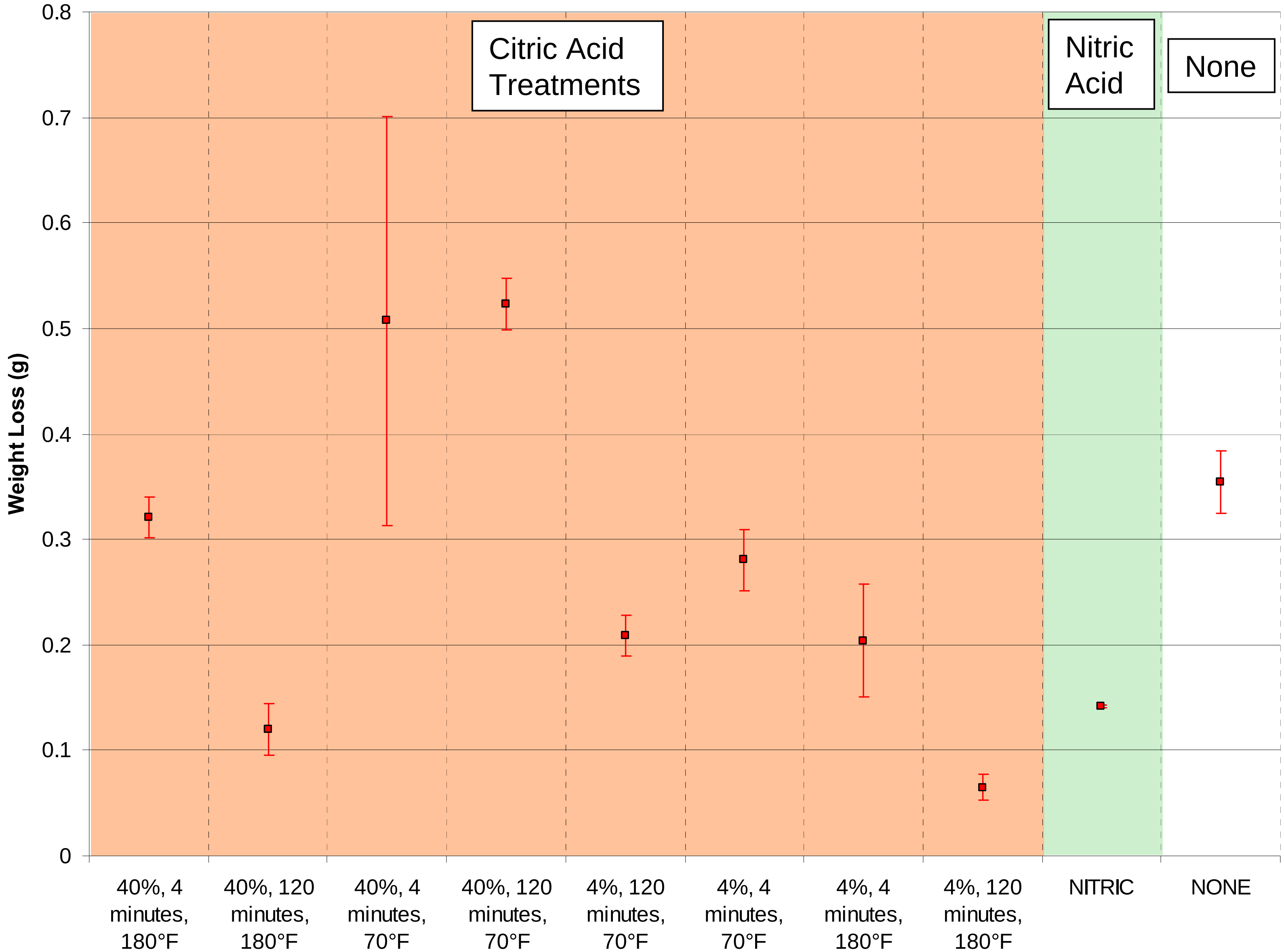
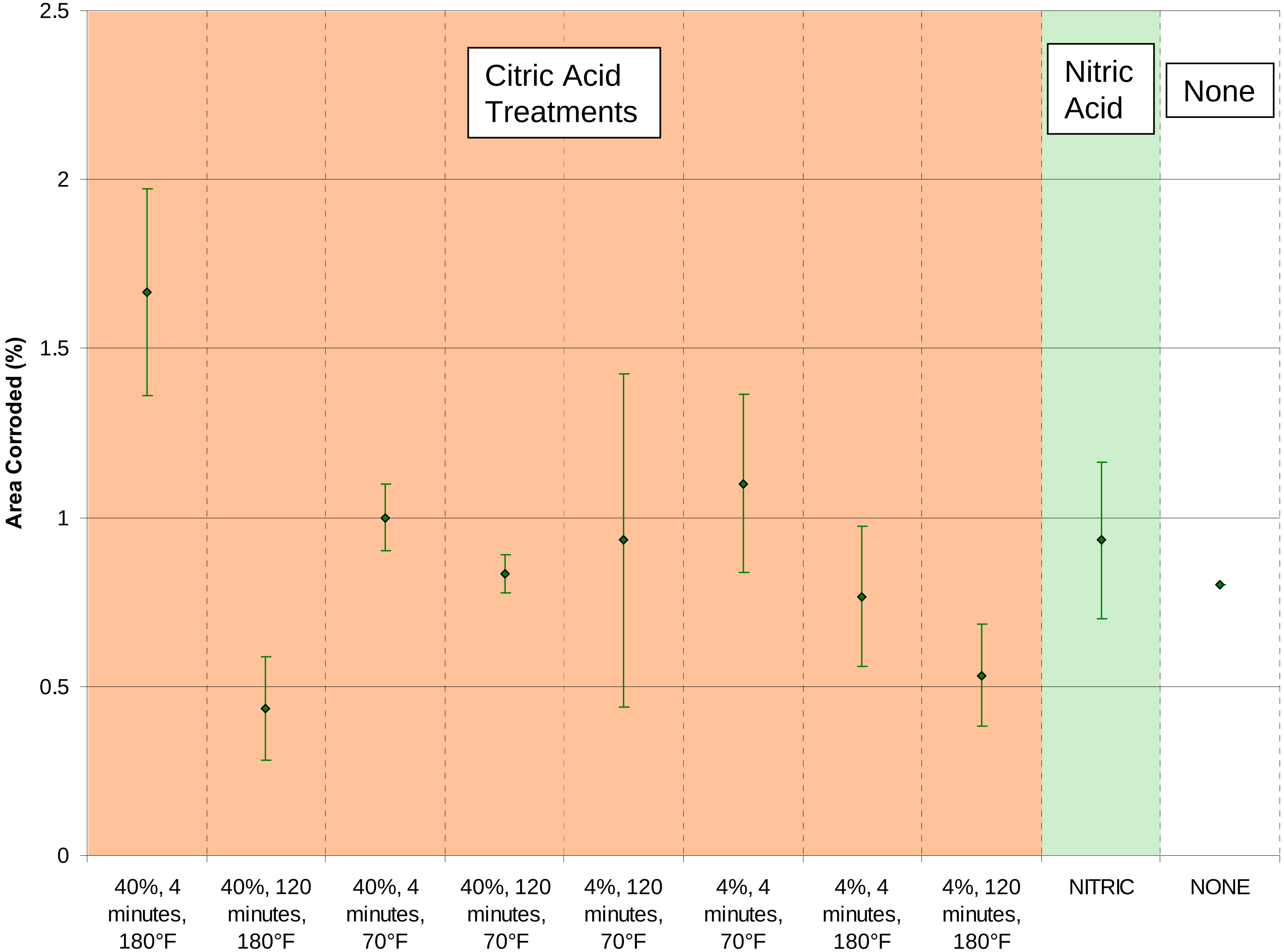
Phase 1 Results - 410 Plotted



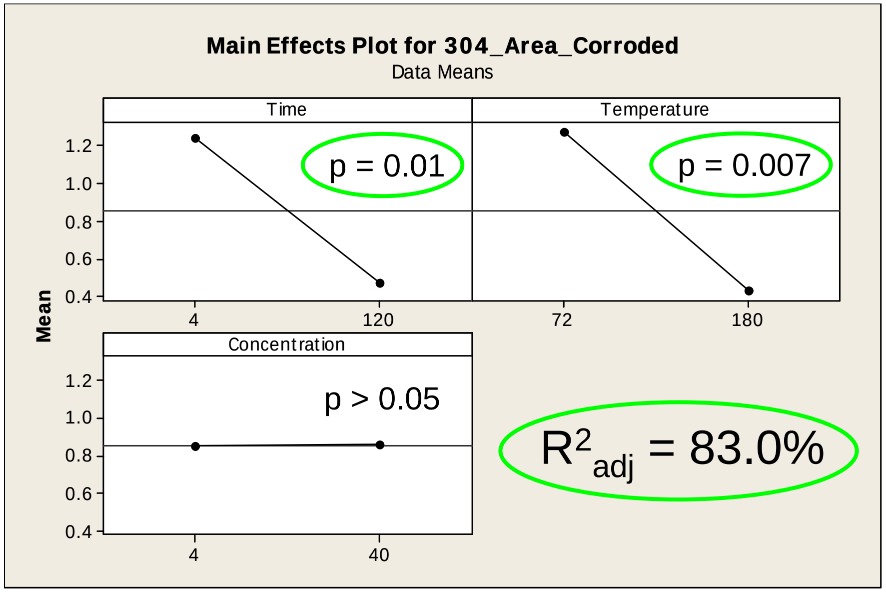
Phase 1 Results - 17-4 Plotted

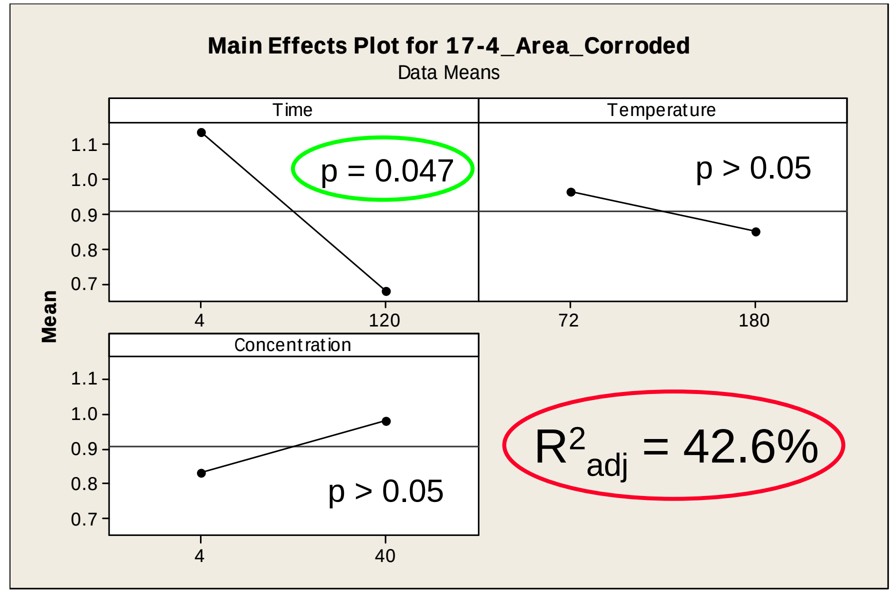


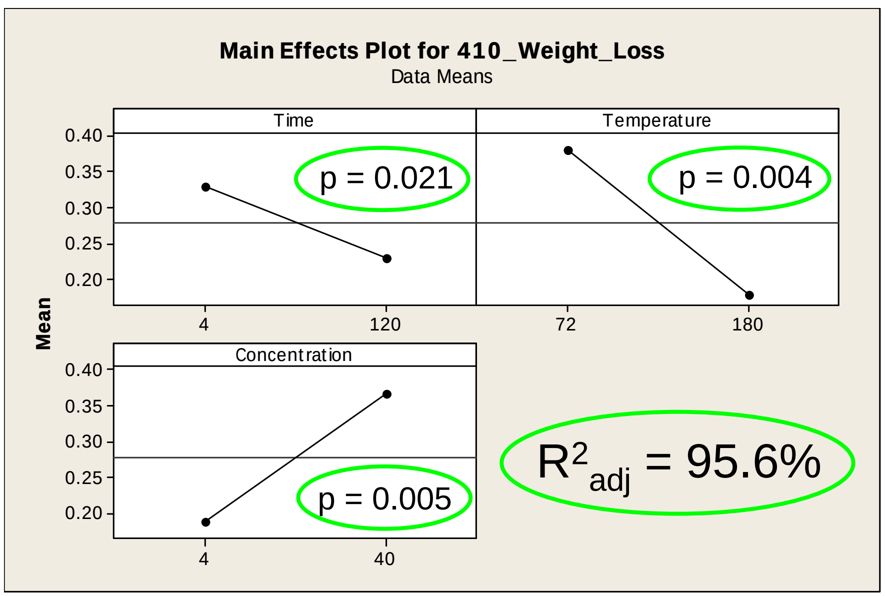
Phase 1 Results – ANOVA Method

- For each material, the results of the DoE were analyzed using ANOVA.
- Significant effects were determined using the following process.
  - Remove the most insignificant effect.
    - Generate Pareto chart to rank variables and interactions' effects on corrosion.
    - Remove the most insignificant effect according to the chart.
    - This must be done first to increase the degrees of freedom high enough to calculate p-values during ANOVA.
  - Analyze the DoE using ANOVA.
  - Again, remove the most insignificant effect and re-analyze using ANOVA.
  - Continue removing insignificant effects until only significant ones are left.
- $\alpha = 5\%$.
- R^2-adjusted > 80% is considered acceptable.

Phase 1 Results – ANOVA Results







Significant Effects

- **304 – Time and Temperature.**
- **410 – Time, Temperature, and Concentration.**
- **17-4 – Inconclusive.**

Phase 1 Results - Nitric vs. Citric

- In order to accept citric acid (CA) as a replacement for nitric acid (NA), CA must perform as well as or better than NA.
  - The comparison can be made using a series of 2 hypothesis tests.
    - The first test can be expressed as:
      - H_0: $\mu_{CA} \leq \mu_{NA}$
      - H_a: $\mu_{CA} > \mu_{NA}$
      - $P \geq 0.10$ indicates that we cannot conclude that NA is better than CA.
    - If CA passes the first test, a second, more rigorous test can be run. This test can be expressed as:
      - H_0: $\mu_{CA} \geq \mu_{NA}$
      - H_a: $\mu_{CA} < \mu_{NA}$
      - $P \leq 0.05$ indicates that CA passivates better than NA.
    - μ is the average amount of corrosion on a passivated part.
- 2-sample t-tests were used to compare the best citric acid method (180°F, 120m, 4%) with nitric acid for all three metals.

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Phase 1 Results - Nitric vs. Citric on 304

- 1st Hypothesis Test
  - Difference = mu (304 Citric) - mu (304 Nitric)
    Estimate for difference: -0.2833
    95% lower bound for difference: -0.4955
    T-Test of difference = 0 (vs >): T-Value = -3.90 P-Value = 0.970 DF = 2
  - The p-value is very high, 0.97, thus the null hypothesis is not rejected.
  - We cannot conclude that NA is better than CA.
- 2nd Hypothesis Test
  - Difference = mu (304 Citric) - mu (304 Nitric)
    Estimate for difference: -0.2833
    95% upper bound for difference: -0.0712
    T-Test of difference = 0 (vs <): T-Value = -3.90 P-Value = 0.030 DF = 2
  - The p-value is 0.03, thus the null hypothesis is rejected.
  - We conclude that CA is better than NA.

Phase 1 Results - Nitric vs. Citric on 410

- 1st Hypothesis Test
  - Difference = mu (410 Citric) - mu (410 Nitric)
    Estimate for difference: -0.07667
    95% lower bound for difference: -0.09692
    T-Test of difference = 0 (vs >): T-Value = -11.05 P-Value = 0.996 DF = 2
  - The p-value is very high, 0.996, thus the null hypothesis is not rejected.
  - We cannot conclude that NA is better than CA.
- 2nd Hypothesis Test
  - Difference = mu (410 Citric) - mu (410 Nitric)
    Estimate for difference: -0.07667
    95% upper bound for difference: -0.05642
    T-Test of difference = 0 (vs <): T-Value = -11.05 P-Value = 0.004 DF = 2
  - The p-value is 0.004, thus the null hypothesis is rejected.
  - We conclude that CA is better than NA.

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Phase 1 Results - Nitric vs. Citric on 17-4

- 1st Hypothesis Test
  - Difference = mu (17-4 Citric) - mu (17-4 Nitric)
    Estimate for difference: -0.400
    95% lower bound for difference: -0.776
    T-Test of difference = 0 (vs >): T-Value = -2.50 P-Value = 0.956 DF = 3
  - The p-value is very high, 0.956, thus the null hypothesis is not rejected.
  - We cannot conclude that NA is better than CA.
- 2nd Hypothesis Test
  - Difference = mu (17-4 Citric) - mu (17-4 Nitric)
    Estimate for difference: -0.400
    95% upper bound for difference: -0.024
    T-Test of difference = 0 (vs <): T-Value = -2.50 P-Value = 0.044 DF = 3
  - The p-value is 0.044, thus the null hypothesis is rejected.
  - We conclude that CA is better than NA.

Phase 1 Conclusions – DoE (ANOVA)

- In general, the DoE showed that ***high temperature, low concentration, and longer processing time are the optimal passivation variable settings.***
  - For 410 and 304, temperature and processing time have larger effects than concentration. This agrees with testing performed by Boeing.
  - For 410, high concentration had a detrimental effect on corrosion resistance. For 304, concentration had almost no effect at all.
  - The standard deviation was not related to the factors for either 304 or 410.
  - Although DoE results for 17-4 were inconclusive, the comparison with nitric acid showed promising results.
  - Tighter controls on variables and more corrosion exposure should provide more conclusive results in Phases 2 and 3.

Phase 1 Conclusions – Nitric vs. Citric vs. Control

- A preliminary comparison indicates that ***citric acid is capable of providing acceptable results compared with nitric acid on all three metals.***
  - The best citric acid treatment (180°F, 120min, 4% citric acid) performed better than the typical nitric acid passivation treatment for flight hardware (ambient temp, 30min, 32% nitric acid).
  - Hypothesis testing showed that most likely, citric acid is capable of providing equal or better passivation than nitric acid.
  - Several citric acid treatments performed worse than the control coupons that received no treatment at all.
    - Some citric treatments may be detrimental.
    - Citric acid passivation needs to be well-understood
  - Although results are promising, more data is needed for a more conclusive comparison.
    - Phases 2 and 3 will provide more data points.
    - Data will provide stronger DoE and Hypothesis test results.

Test Plan – Phases 2 and 3

Phase 1

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

Phase 2

- Refined Optimization
- ASTM B-117 - Salt Fog Chamber 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"

Test Plan – Phases 2 and 3 - Goals

- The new plan builds off of results from phase 1.
  - Concentration either has a negligible effect OR provides better passivation when set low.
  - Citric acid is capable of meeting or exceeding performance of the current nitric acid method.

- Two goals:
  - Establish optimized treatment, i.e. find “point of diminishing returns” for temperature and time.
  - Answer the following questions:
    - Is citric acid capable of passivating welds in-situ?
    - Will entrapment damage parts?
    - What is the composition/structure/depth of the passive layer created through citric acid passivation?

Test Plan – Phase 2 and 3 - Optimizing DoE

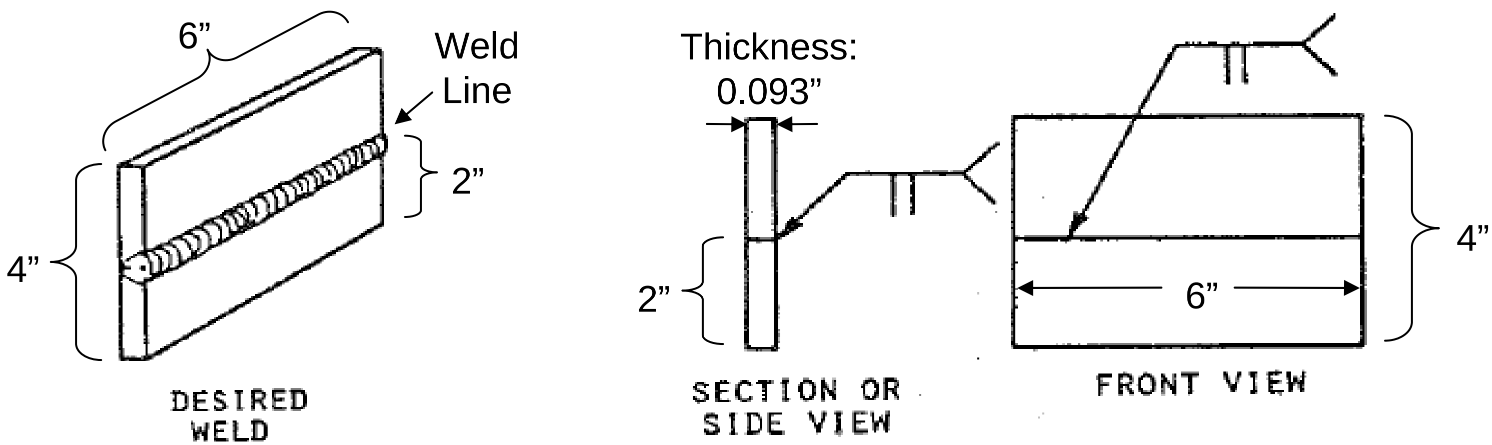
- Fix Concentration at 4%
  - Results indicate that concentration has little effect OR that lower is better
- Explore time and temperature at 3 values
  - Time – 30min, 75min, 120min
  - Temperature – 100°F, 140°F, 180°F
  - Include control samples (nitric and unpassivated)
- 99 samples per metal
  - 3 repeats per treatment in salt fog chamber
  - 6 repeats per treatment at Beach Facility

Phases 2 & 3 DoE

Run #	Time (min)	Temp. (°F)	Conc. (wt%)
	(+/- 5s)	(+/- 2°F)	(+/- 0.2wt%)
1	30	100	4
2	30	140	4
3	30	180	4
4	75	100	4
5	75	140	4
6	75	180	4
7	120	100	4
8	120	140	4
9	120	180	4

Test Plans – Phase 3 - Welded Samples

- **6”×4” coupons cut into two 6”×2” pieces, welded together, then passivated.**
  - **Ambient temperature (since weld passivation is usually done in the field *in-situ*, temperature is uncontrolled).**
  - **Two values for passivation time: 60 minutes and 120 minutes.**
  - **Concentration fixed at 4%.**
  - **Weld kept wet with fresh solution for the duration of passivation.**



- **24 samples per metal.**
  - **6 citric passivated at ambient temperature, 60 minutes, 4%.**
  - **6 citric passivated at ambient temperature, 120 minutes, 4%.**
  - **6 nitric passivated at ambient temperature, 60 minutes, 32%.**
  - **6 cleaned, degreased, but not passivated.**

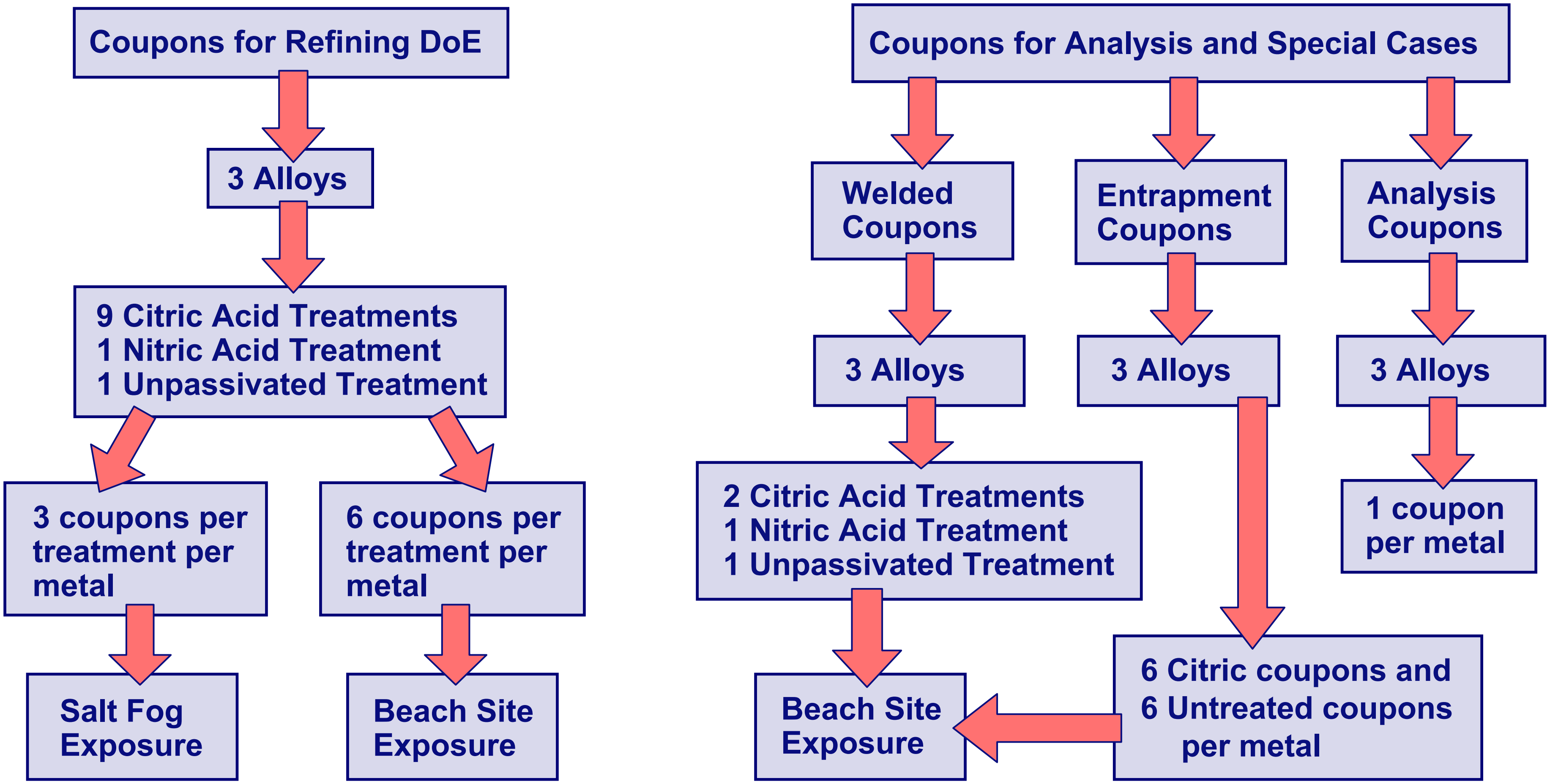
Test Plans – Phase 3 - Entrapment Effects

- The goal of the test is to determine any detrimental effects of citric acid entrapment.
- Test procedure:
  - Create entrapment test coupons.
    - Citric acid, 4%, introduced between two coupons.
    - Coupons clamped together with acid between them to simulate entrapment.
    - Coupons left in laboratory until acid dries (several days, most likely).
  - Expose coupons to beach site.
  - Compare corrosion on entrapment coupons with corrosion on control coupons to determine if entrapment makes a surface sensitive to corrosion.
- 12 samples per metal.
  - 6 citric.
  - 6 unpassivated.

Test Plans – Phase 3 - Characterization

Technique	Function	Comments
XPS	Surface characterization	Oxide/hydroxide layered surface structure, Cr/Cr_2O_3 and Fe/Fe_xO_y ratios.
EIS	Surface stability	Breakdown voltage of passive layer.
EDS, XRF, ICP	Material characterization	Quantitative analysis of alloy composition.
FTIR	Residual characterization	Confirm the presence or absence of a residual organic film caused by passivation with an organic acid.
ICP	Passivation agent waste analysis	Heavy metal content of acid waste, determination of environmental friendliness of waste.

Test Plan – Phases 2 and 3 - Summary



Phase II Total: 297 Coupons

Phase III Total: 111 Coupons

Phases II and III Total: 408 Coupons

Transition and Implementation

- After the specifications are changed, users would be urged to switch to passivation to take advantage of its benefits
- In order to maximize the benefits of this research, users must be aware of the work done. USA and NASA have taken steps to spread the information.
  - NASA Environmental Group Teleconferences
    - Designed to determine requirements of users to accept citric acid.
    - Intends to find funding to perform follow-on work to meet requirements of a wider range of users.
    - Participants include U.S. Military and several NASA centers.
  - Presentations
    - Environmental Workshop, C3P and NASA (Nov. 2009)
    - Hill AFB (March 2010)
    - Aircraft Airworthiness and Sustainment (May 2010)
  - AMS Committee B (SAE 2700)

Summary

- NASA is interested in using citric acid as a passivation agent in lieu of nitric acid for safety and environmental benefits.
- USA created a test plan to evaluate the viability of citric acid passivation.
- Higher temperatures and longer processing times correlate strongly with corrosion resistance. Citric acid at 4% passivated better than 40%, but concentration was not correlated as distinctly as time or temperature.
- Preliminary results indicated that pure citric acid is capable of passivating as well as nitric acid, but may require longer processing times, higher temperatures, and lower concentration (higher, more neutral pH).
- In some cases, citric acid passivated coupons performed worse than untreated test panels, thus indicating that improper citric treatments can be detrimental to corrosion resistance.
- Coupons for the next phases of testing have been fabricated and passivated, and are currently in corrosive environmental exposure.
- Results are expected December 2010.

Acknowledgements

The presenter would like to thank the following individuals for their effort and support on this project:

- Chad Carl, NASA
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- John Reali, United Space Alliance, LLC
- Christopher Larson, United Space Alliance, LLC
- J. Michael Johnson, WilTech Laboratory
- Eric Burke, United Space Alliance, LLC
- Pattie Lewis Burford, ITB, Inc.
- NASA TEERM

United Space Alliance

Questions?

Back-up

Phase 1 Results – 304 ANOVA Analysis

Factorial Fit: Mean versus Time, Temperature

Estimated Effects and Coefficients for Mean (coded units)

Term	Effect	Coef	SE Coef	T	P
Constant		0.8542	0.09511	8.98	0.000
Time	-0.7750	-0.3875	0.09511	-4.07	0.010
Temperature	-0.8417	-0.4208	0.09511	-4.42	0.007

Statistically significant effects ($p < 5\%$)

S = 0.269000   PRESS = 0.926222
R-Sq = 87.86%   R-Sq(pred) = 68.92%   R-Sq(adj) = 83.00%

High R^2 (adj) value indicates high correlation between the model and results

Analysis of Variance for Mean (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	2.61806	2.61806	1.30903	18.09	0.005
Residual Error	5	0.36181	0.36181	0.07236		
Lack of Fit	1	0.08681	0.08681	0.08681	1.26	0.324
Pure Error	4	0.27500	0.27500	0.06875		
Total	7	2.97986				

Phase 1 Results – 410 ANOVA Analysis

Factorial Fit: Mean versus Time, Temperature, Concentration

Estimated Effects and Coefficients for Mean (coded units)

Term	Effect	Coef	SE Coef	T	P
Constant		0.2925	0.01421	20.58	0.000
Time	-0.1269	-0.0635	0.01421	-4.46	0.021
Temperature	-0.2302	-0.1151	0.01421	-8.10	0.004
Concentration	0.2063	0.1031	0.01421	7.26	0.005
Temperature*Concentration	-0.1203	-0.0601	0.01421	-4.23	0.024

Statistically significant effects (p < 5%)

S = 0.0401991   PRESS = 0.0344739
R-Sq = 98.11%   R-Sq(pred) = 86.59%   R-Sq(adj) = 95.60%

High R^2 (adj) value indicates high correlation between the model and results

Analysis of Variance for Mean (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.223310	0.223310	0.074437	46.06	0.005
2-Way Interactions	1	0.028930	0.028930	0.028930	17.90	0.024
Residual Error	3	0.004848	0.004848	0.001616		
Total	7	0.257088				

Phase 1 Results – 17-4 ANOVA Analysis

Factorial Fit: Mean versus Time

Estimated Effects and Coefficients for Mean (coded units)

Term	Effect	Coef	SE Coef	T	P
Constant		0.8729	0.1047	8.34	0.000
Time	-0.5208	-0.2604	0.1047	-2.49	0.047

Statistically significant effect ($p < 5\%$)

S = 0.296175 PRESS = 0.935679
R-Sq = 50.76% R-Sq(pred) = 12.46% R-Sq(adj) = 42.55%

Low R^2 (adj) value indicates low correlation between the model and results

Analysis of Variance for Mean (coded units)

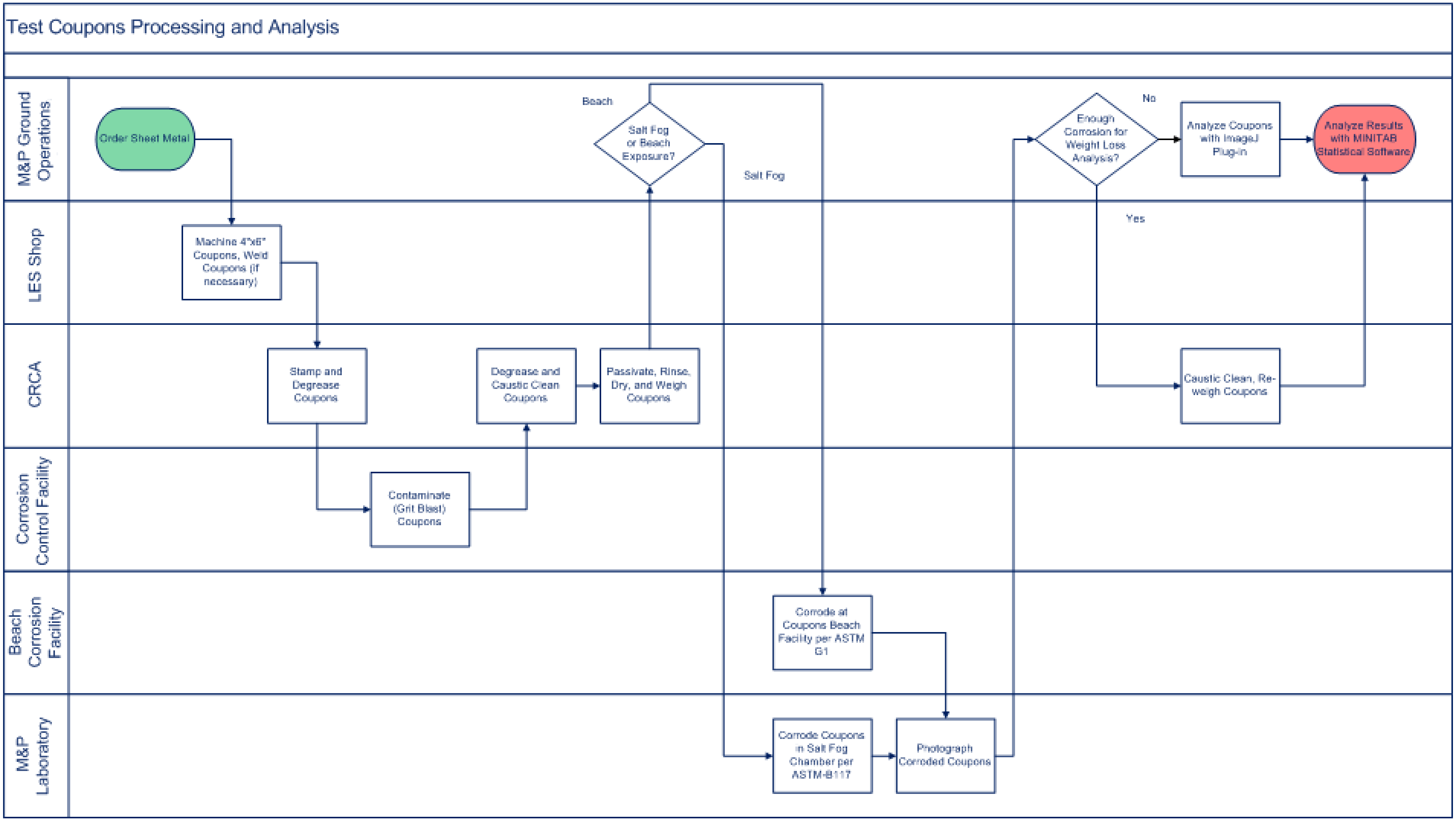
Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	1	0.54253	0.542535	0.54253	6.18	0.047
Residual Error	6	0.52632	0.526319	0.08772		
Pure Error	6	0.52632	0.526319	0.08772		
Total	7	1.06885				

Control Plan

Item	Specified Requirements	Measurement Technique	Responsible Party	Control Method	Trigger	Reaction Plan
Contamination (grit blasting)	Surface finish uniformity on all samples	Visual Inspection	CAP Team, EG&G (performs blasting)	Blast extra coupons as spares to replace failed samples	3% or more coupons have irregular blasting	Investigate blasting facility and process
Passivation Bath Temperature	Target temperature +/- 2°F	Thermocouples at the top and bottom of bath	CAP Team	Lindberg PID temperature controller, temperature monitoring by operator	Monitor observes temperature outside specified limits	Verify correct settings, ID cause of temperature change
Passivation Bath Citric Acid Concentration	In-situ: target surface level +/- 0.3in	In-situ: Surface level height using graduated markings	CAP Team, WilTech (performs sample analysis)	Add water, ~25ml every 3 minutes, to maintain surface level, surface level monitoring by operator	In-situ: Monitor detects bath surface level outside specified limits	Adjust frequency of water additions, replace water bath, add CA powder
	Between baths: target concentration +/- 0.2wt%,	Between baths: Titration			Between baths: analysis returns concentration outside specified limits	
Photography	Equivalent framing and lighting in each coupon photograph	Photograph inspection	CAP Team	Build studio to fix coupon placement, mount camera, provide fixed light sources dedicated to studio	Photograph appears misaligned, blurry, or lighter/darker than similar photos	Adjust equipment and lighting, Re-take photo

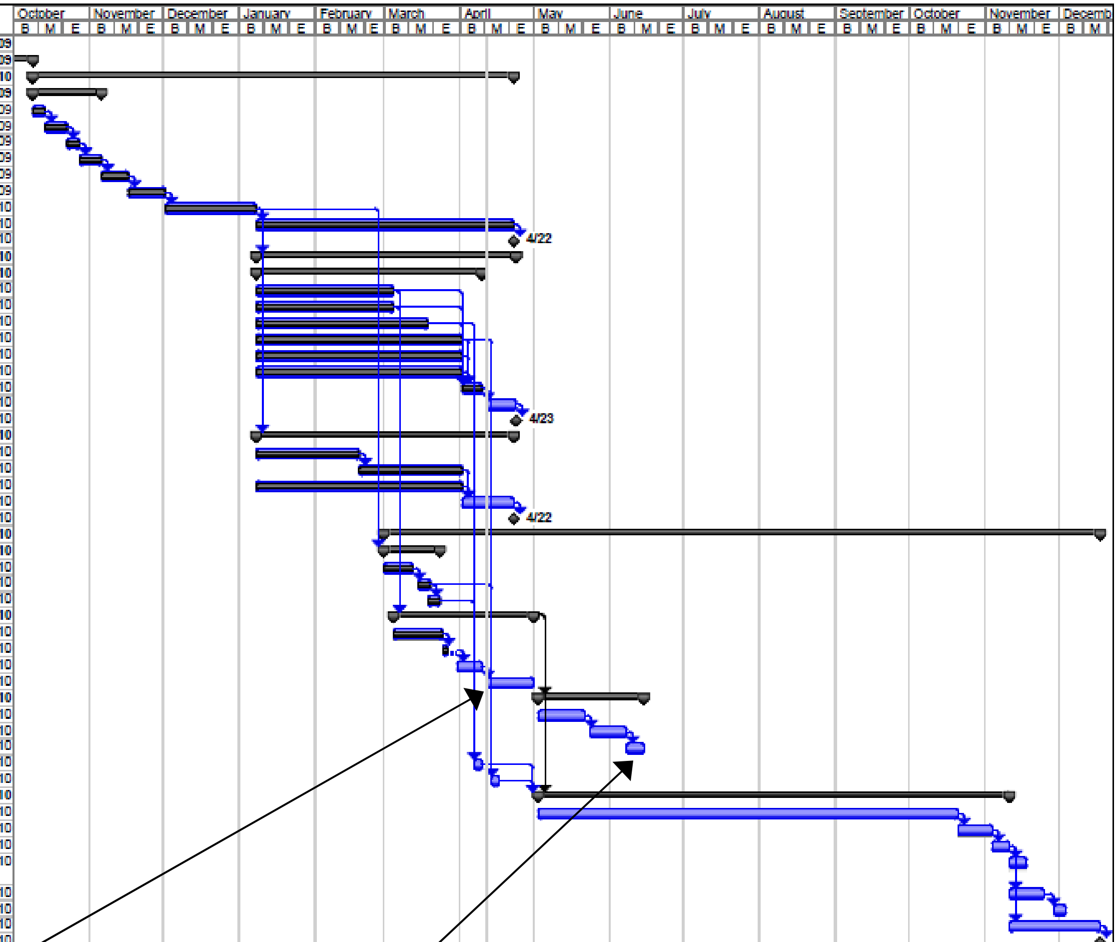
- **In addition to the control plan, established procedures will control other processes used to make coupons**
  - **Nitric acid passivation – WilTech's Procedure (meets MA0110-302)**
  - **Welding – GSS-DIR-17 (meets NASA-5004)**
  - **Corrosion test exposures – ASTM B117 and ASTM G1**
  - **Degreasing – WilTech's Procedure**
  - **Caustic Cleaning – WilTech's Procedure**

Test Plan - Processing



Schedule and Status

ID		Task Name	Duration	Start	Finish
1	✓	**DEFINE Phase**	**24 days**	**Mon 5/18/09**	**Fri 6/19/09**
10	✓	**MEASURE Phase**	**77 days**	**Mon 6/22/09**	**Thu 10/8/09**
17		**ANALYZE Phase**	**131 days**	**Fri 10/9/09**	**Thu 4/22/10**
18	✓	**Perform Passivation Process**	**20 days**	**Fri 10/9/09**	**Thu 11/5/09**
19	✓	Degrease Samples	3 days	Fri 10/9/09	Tue 10/13/09
20	✓	Contaminate Samples	7 days	Wed 10/14/09	Thu 10/22/09
21	✓	Degrease Samples (2nd time) and Caustic Clean	3 days	Fri 10/23/09	Tue 10/27/09
22	✓	Perform the Screening DoE Passivation Process	7 days	Wed 10/28/09	Thu 11/5/09
23	✓	Photograph and Weigh Coupons	7 days	Fri 11/6/09	Mon 11/16/09
24	✓	Place in Exposure Location (Salt Fog Chamber per B-117)	9 days	Tue 11/17/09	Tue 12/1/09
25	✓	Collect and Analyze exposed coupons	20 days	Wed 12/2/09	Thu 1/7/10
26	✓	Develop Analyze Gate package	75 days	Fri 1/8/10	Thu 4/22/10
27		Analyze Gate Review	0 days	Thu 4/22/10	Thu 4/22/10
28		**IMPROVE Phase**	**76 days**	**Fri 1/8/10**	**Fri 4/23/10**
29	✓	**Develop final CA Test Plan**	**66 days**	**Fri 1/8/10**	**Fri 4/9/10**
30	✓	Draft DoE Test Plan (Phase 2)	40 days	Fri 1/8/10	Thu 3/4/10
31	✓	Draft Hypothesis Test Plan (Phase 3)	40 days	Fri 1/8/10	Thu 3/4/10
32	✓	Draft Weld Passivation Test Plan (Phase 3)	50 days	Fri 1/8/10	Thu 3/18/10
33	✓	Draft Entrapment Test Plan (Phase 3)	60 days	Fri 1/8/10	Thu 4/1/10
34	✓	Draft Characterization and Analysis Test Plan	60 days	Fri 1/8/10	Thu 4/1/10
35	✓	Secure Facilities, Funding, and POCs for all Testing	60 days	Fri 1/8/10	Thu 4/1/10
36	✓	Insert Final Test Plans into Passivation Work Document	6 days	Fri 4/2/10	Fri 4/9/10
37		Develop Improve Gate Review	10 days	Mon 4/12/10	Fri 4/23/10
38		Improve Gate Review	0 days	Fri 4/23/10	Fri 4/23/10
39		**CONTROL Phase**	**75 days**	**Fri 1/8/10**	**Thu 4/22/10**
40	✓	Identify Lessons Learned	30 days	Fri 1/8/10	Thu 2/18/10
41	✓	Develop Control Plan	30 days	Fri 2/19/10	Thu 4/1/10
42	✓	Identify Opportunities for Implementation Beyond KSC	60 days	Fri 1/8/10	Thu 4/1/10
43		Develop Control Gate package	15 days	Fri 4/2/10	Thu 4/22/10
44		Control Gate Review	0 days	Thu 4/22/10	Thu 4/22/10
45		**Savings and Validation Phase**	**205 days**	**Mon 3/1/10**	**Fri 12/17/10**
46	✓	**Fabricate Test Coupons**	**17 days**	**Mon 3/1/10**	**Tue 3/23/10**
47	✓	Order Coupon Raw Material	10 days	Mon 3/1/10	Fri 3/12/10
48	✓	Machine Coupons	5 days	Mon 3/15/10	Fri 3/19/10
49	✓	Fabricate Welded Coupons	3 days	Fri 3/19/10	Tue 3/23/10
50		**Perform Passivation for DoE and Hypothesis Test Plans (Phase**	**41 days**	**Fri 3/5/10**	**Fri 4/30/10**
51	✓	Degrease Samples	14 days	Fri 3/5/10	Wed 3/24/10
52	✓	Contaminate Samples	4 days	Thu 3/25/10	Tue 3/30/10
53		Degrease Samples (2nd time)	8 days	Wed 3/31/10	Fri 4/9/10
54		Perform Passivation Process	15 days	Mon 4/12/10	Fri 4/30/10
55		**Salt Fog Evaluation (Phase 2)**	**30 days**	**Mon 5/3/10**	**Mon 6/14/10**
56		Expose Coupons in Salt Fog Chamber	15 days	Mon 5/3/10	Fri 5/21/10
57		Measure Corrosion	10 days	Mon 5/24/10	Mon 6/7/10
58		Analyze Data	5 days	Tue 6/8/10	Mon 6/14/10
59		Perform Passivation of Welded Samples (Phase 3)	3 days	Wed 4/7/10	Fri 4/9/10
60		Perform Entrapment (Phase 3)	3 days	Wed 4/14/10	Fri 4/16/10
61		**Beach Corrosion Facility Evaluation (Phase 3)**	**135 days**	**Mon 5/3/10**	**Wed 11/10/10**
62		Expose Coupons at Corrosion Beach Facility	6 mons	Mon 5/3/10	Wed 10/20/10
63		Measure Corrosion	10 days	Thu 10/21/10	Wed 11/3/10
64		Analyze Data	5 days	Thu 11/4/10	Wed 11/10/10
65		Recommend changes SOP's, Training Plan & Process Controls	5 days	Thu 11/11/10	Wed 11/17/10
66		Implement Changes	10 days	Thu 11/11/10	Wed 11/24/10
67		Develop Final Savings BOE	5 days	Mon 11/29/10	Fri 12/3/10
68		Develop Savings/Validation Gate package and Final Report	25 days	Thu 11/11/10	Fri 12/17/10
69		Savings/Validation Gate Review	0 days	Fri 12/17/10	Fri 12/17/10



- **Currently passivating samples.**
- **Second salt fog exposure results in June 2010.**
- **Project completion anticipated mid-December 2010**

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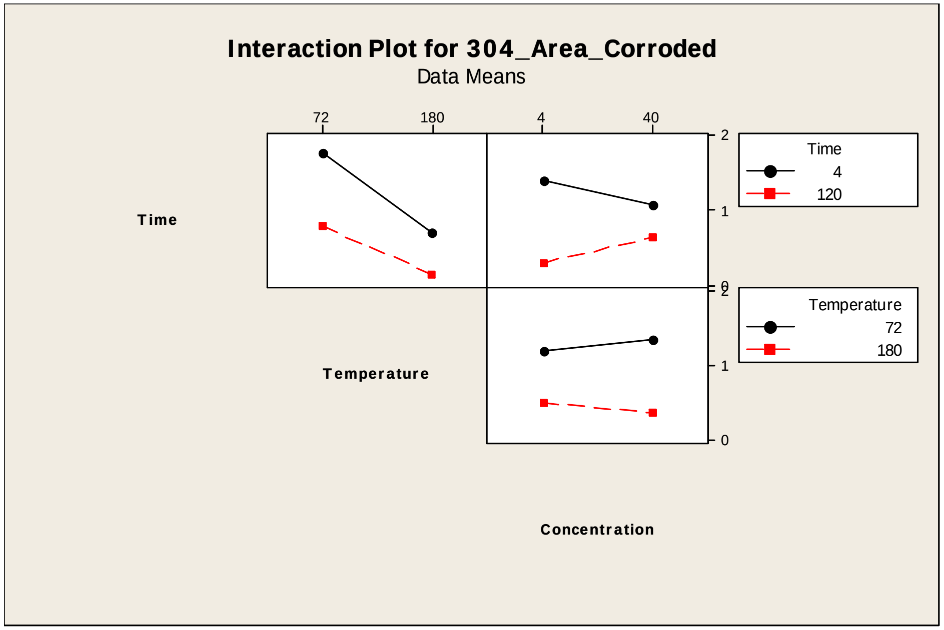
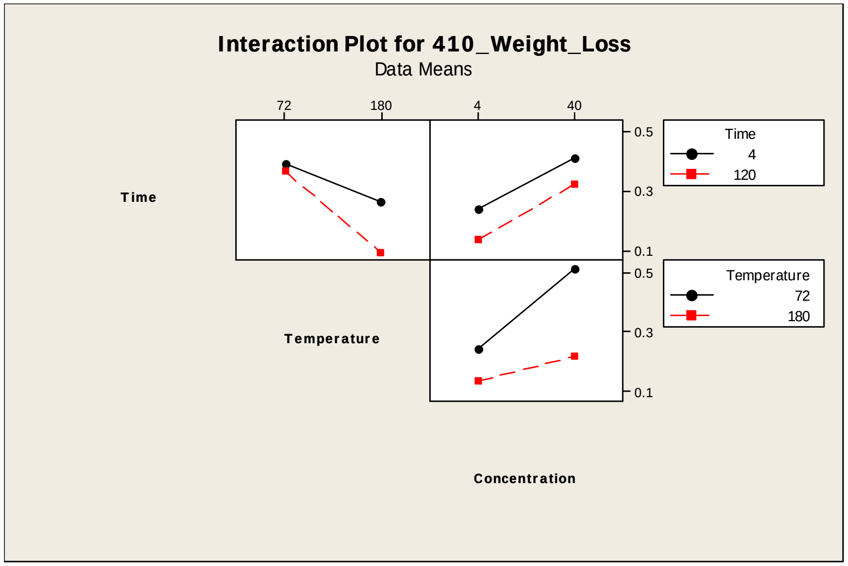
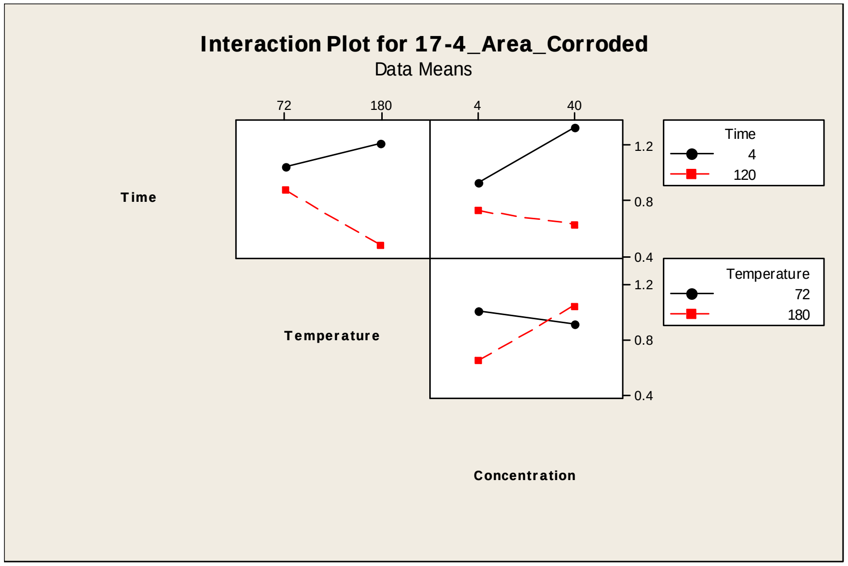
Phase 1 Results







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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

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

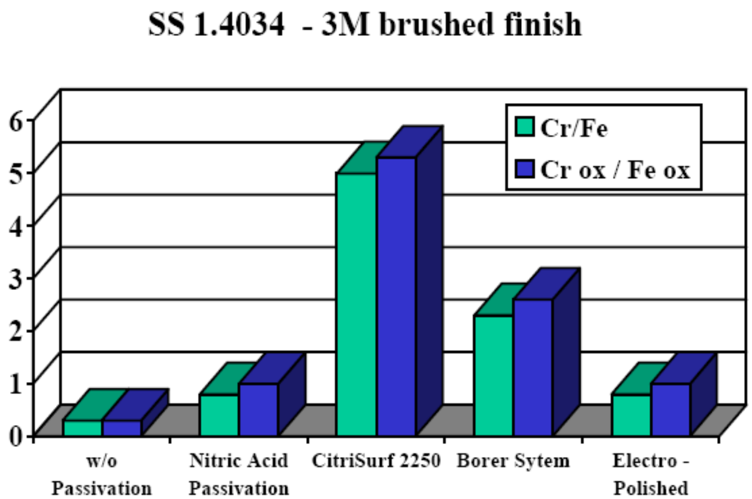
Requirements Per ASTM A-967

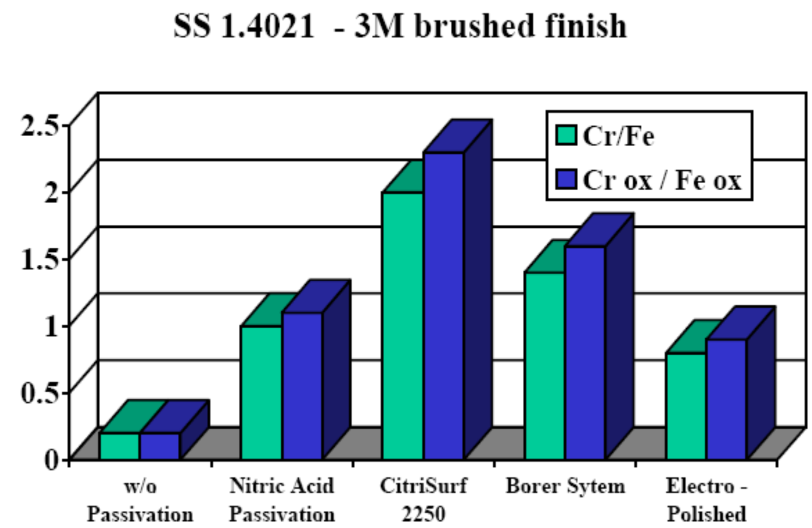
- Passivation is defined as the chemical treatment of stainless steel with a mild oxidant for the purpose of the removal of free iron (or sulfides or other foreign matter)
- Nitric Acid Treatment
  - 5 different solutions; 70-140°F Bath Temperature, 20-55% Nitric Acid
  - 4 of the 5 solutions are essentially 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.

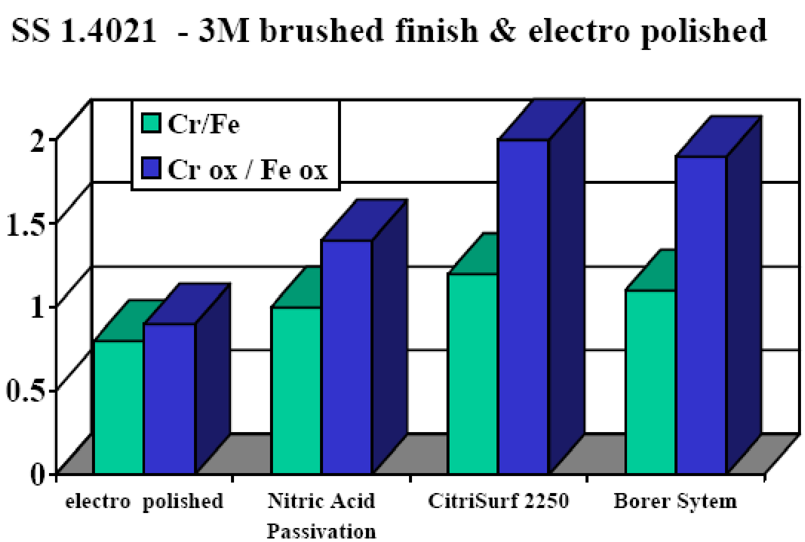
Requirements Per AMS 2700B

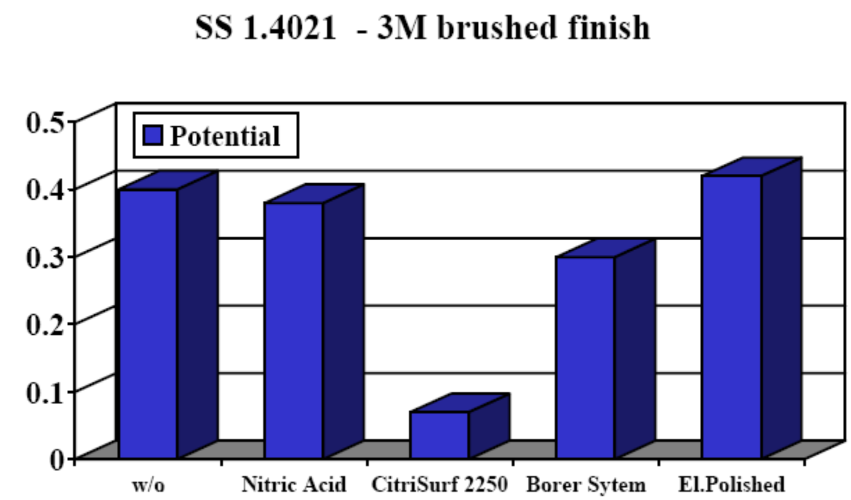
- Passivation is used to remove metallic contaminants from the surface of corrosion resistant steels using chemically oxidizing methods to prevent bulk degradation.
- Method 1, Nitric Acid
  - 8 Types; 70-155°F Bath Temperature, 20-55% Nitric Acid
  - 5 of the 8 types require the dichromate additive
  - 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.

NMI Report









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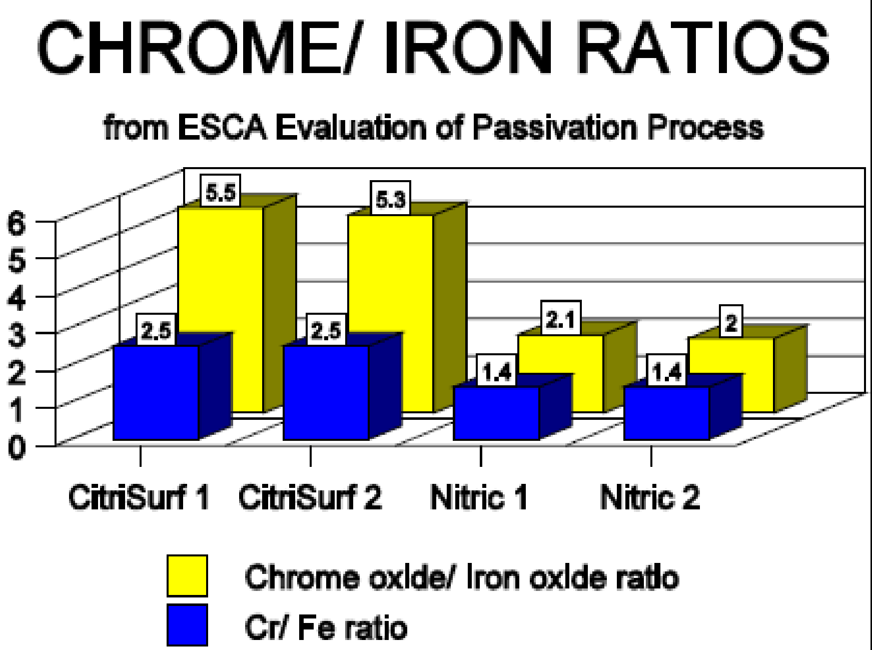
NMI Report - Conclusions

- 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)**

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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

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.

Citric Acid Passivation of Stainless Steel

David Yasensky

United Space Alliance, LLC

Materials & Processes Engineering

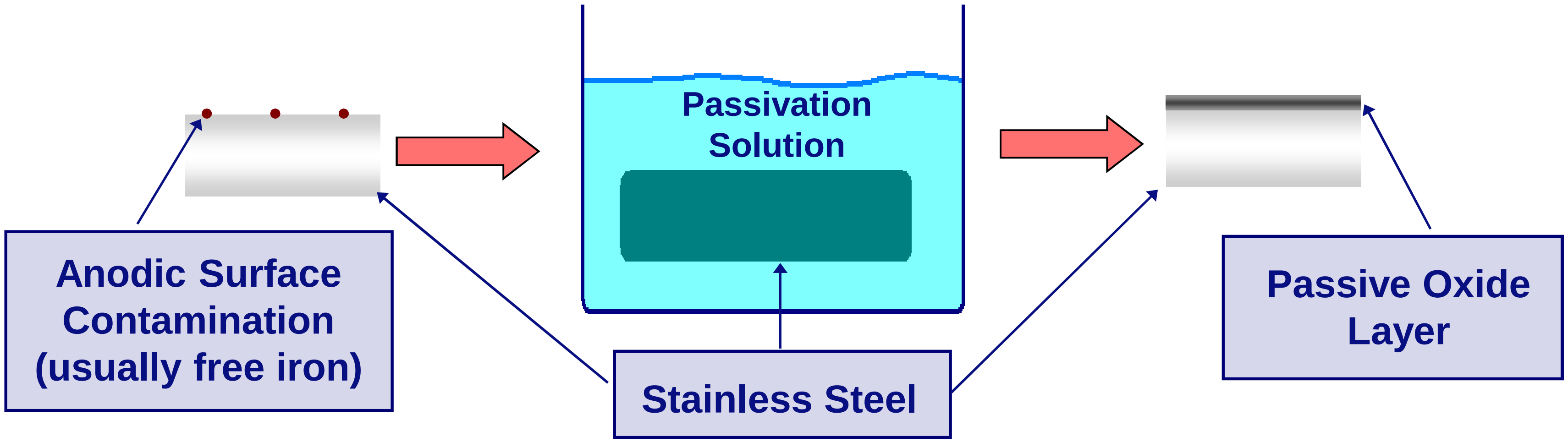
November 11th, 2009

Contents

- What is Passivation?
- Environmental Issues with Passivation
- Previous Industry Studies
- Passivation at Kennedy Space Center
- Our Study – Exploring an Alternative to Nitric Acid Passivation

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 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

- **Before passivation, 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.

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 A967 – *both allow the use either Nitric Acid or Citric Acid*.**

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]

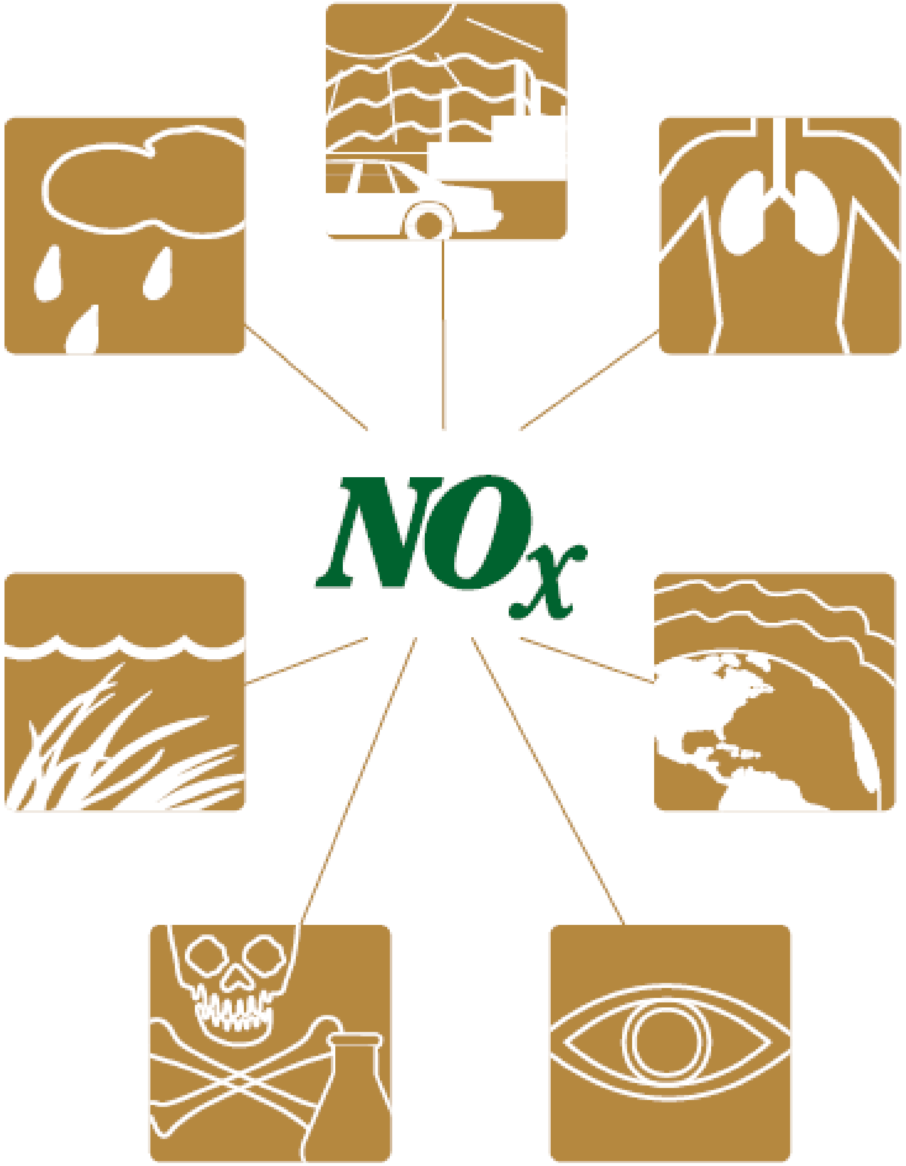
- **Hazardous waste removal required.**

- **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.**

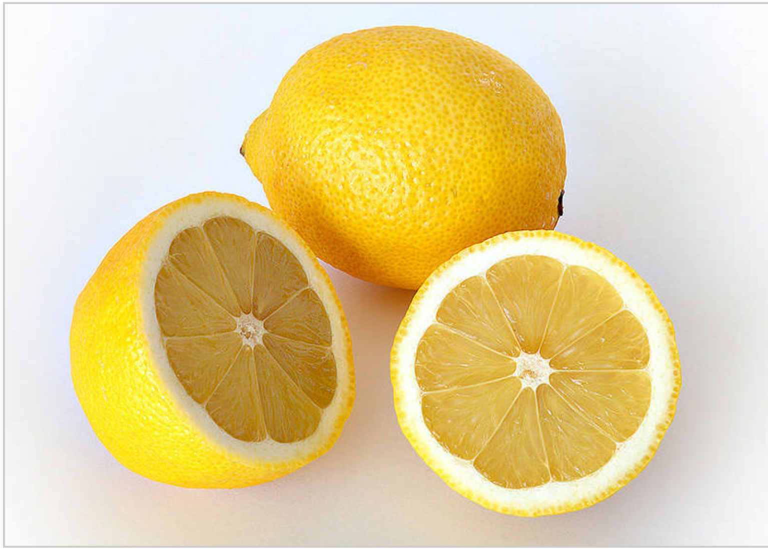
Environmental Concerns with NO_X Release *[EPA, 2008]*



- 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 (iron content).**
- **Removes only free irons 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]

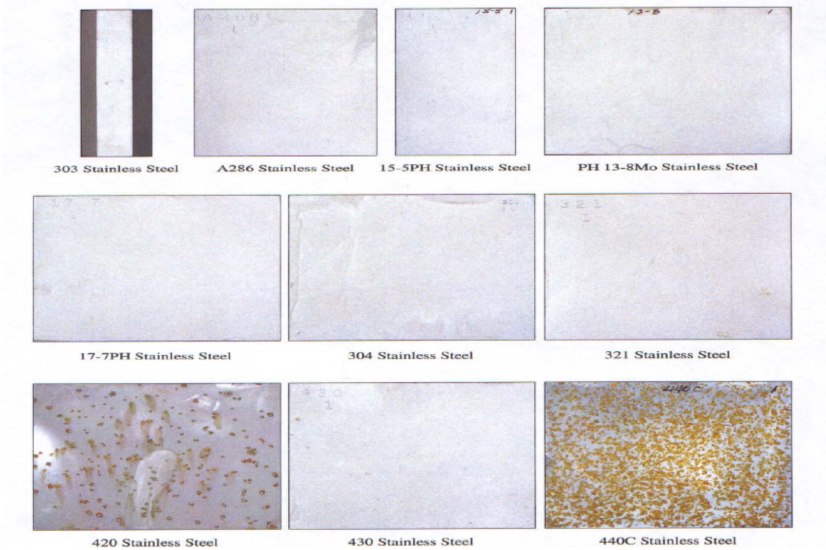


Citric Acid Studies in Industry *[Stephen Gaydos, Boeing, 2003]*

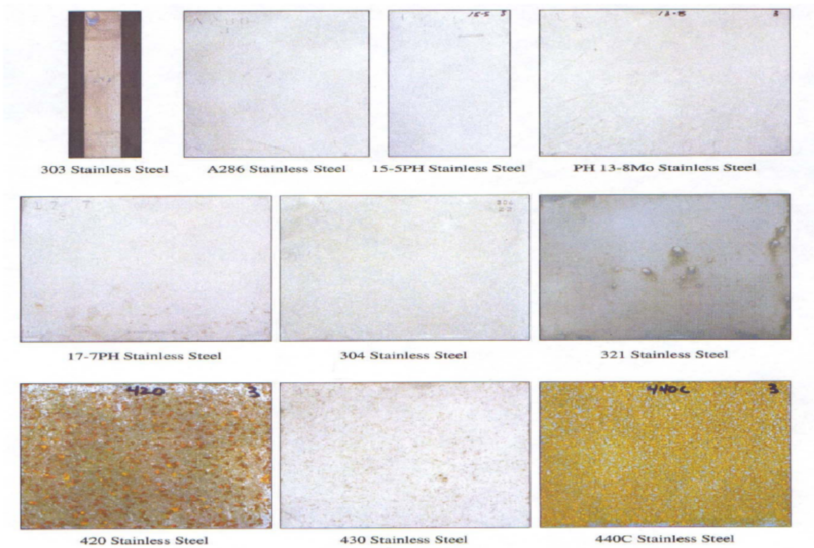
- **Boeing compared citric to nitric on 10 stainless steel alloys.**
- **Conclusion: citric acid passivation is as effective as nitric acid passivation.**

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)

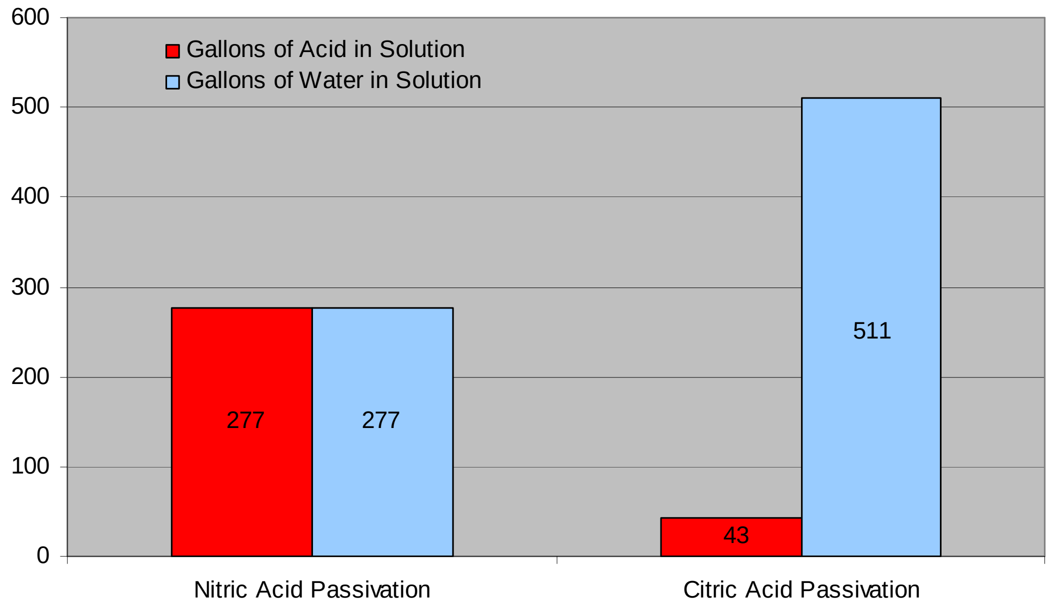


Salt Spray Test Results for Contaminated Test Specimens Passivated in Optimized Citric Acid



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.**

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

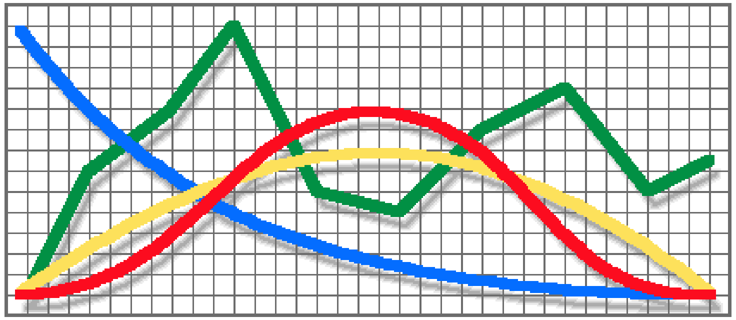
Phase 2

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

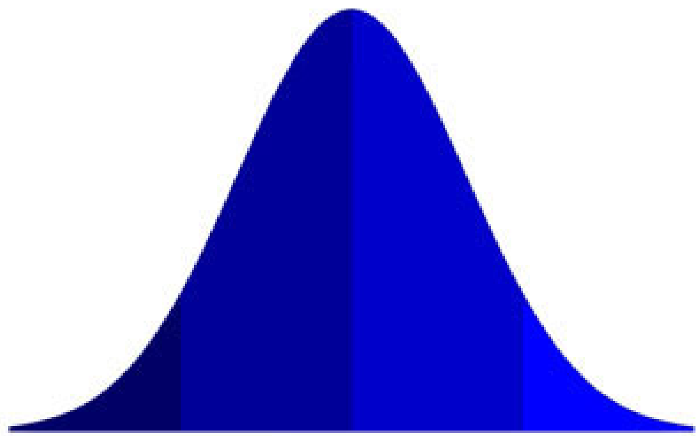
Phase 3

- 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”

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.

Test Parameters and Materials

- Citric Acid Test Parameters:
  - Immersion Time (4 – 120 Minutes)
  - Solution Temperature (70 – 180 °F)
  - Citric Acid Concentration (4 – 40 % Citric Acid by weight)

- Material Test Coupons:
  - UNS30400 (304 austenitic stainless steel, 0.05cm thick)
  - UNS41000 (410 martenisitic stainless steel, 0.035cm thick)
  - UNS17400 (17-4 precipitation hardened steel, 0.035cm thick)
  - 10cm x 15cm
  - Representative of parts at KSC

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 Fog Exposure.

Include control samples:

- Nitric acid passivated
- Non-passivated

Refine citric acid treatment parameters.

Phase 1 DoE Schedule

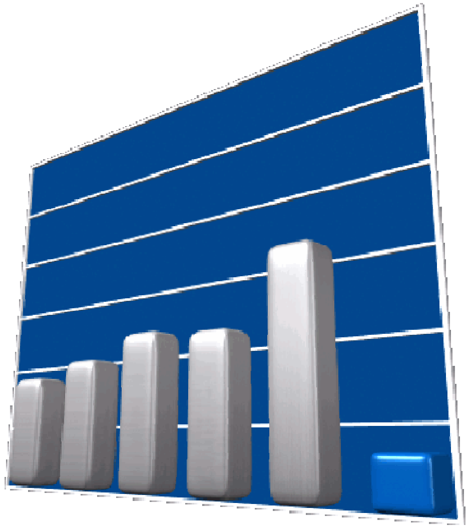
Run #	Time (min)	Temp. (°C)	Conc. Citric Acid (wt%)
1	4	21	4
2	120	21	4
3	4	82	4
4	120	82	4
5	4	21	40
6	120	21	40
7	4	82	40
8	120	82	40
9	62	52	22

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 passivation
  - Non-passivated



Choose optimized citric acid passivation procedure for each material.

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.

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 occur at Corrosion Beach Facility and analyzed similar to Phase 1 and 2.

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 (70 - 180 °F)
- Passivation Time (4 - 120 minutes)

Nitric Acid

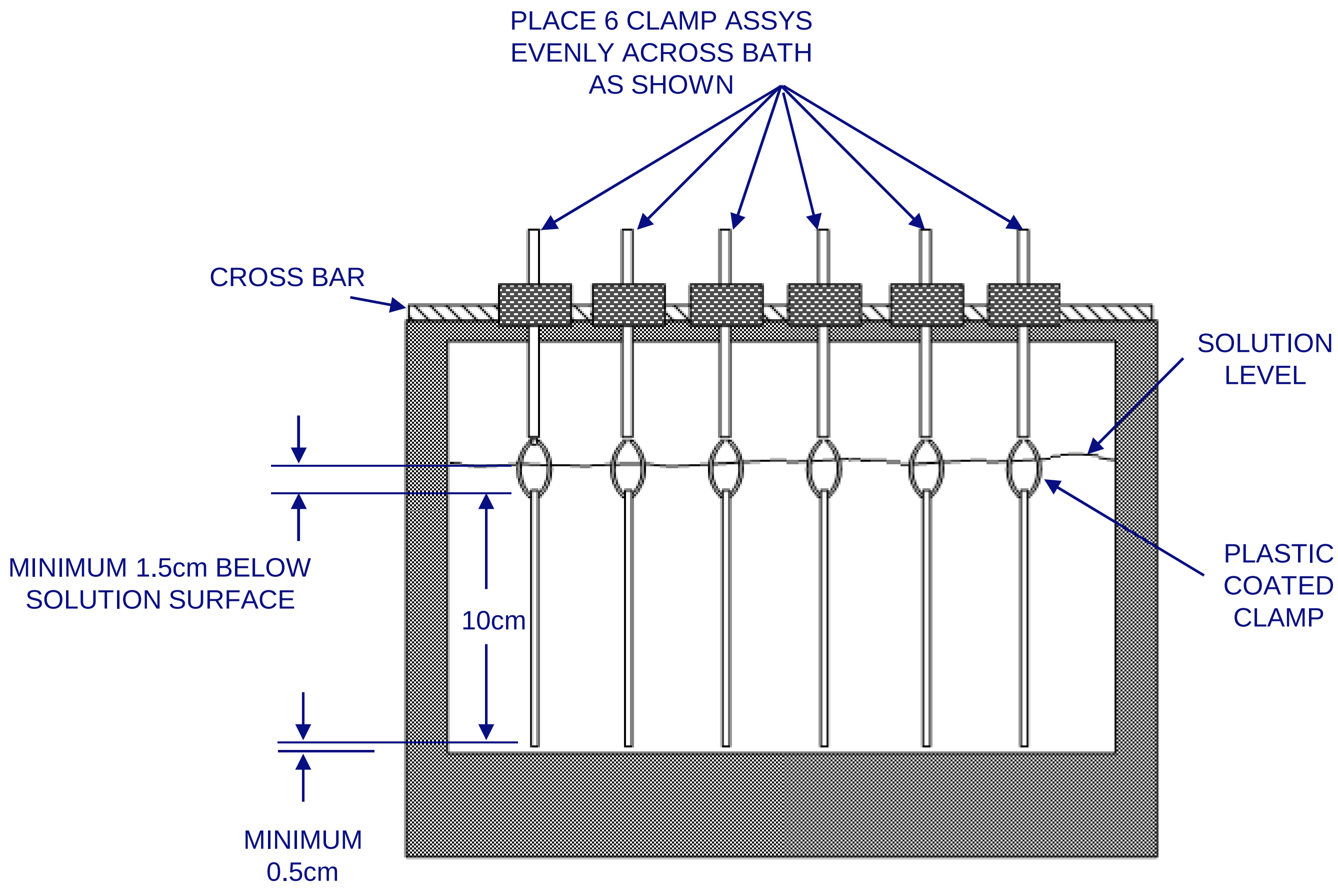
- NASA approved Flight Hardware Process
- 25 °C, 40% by volume

Rinse Coupons with DI Water to neutral pH.

Blow Dry with Filtered GN_2.

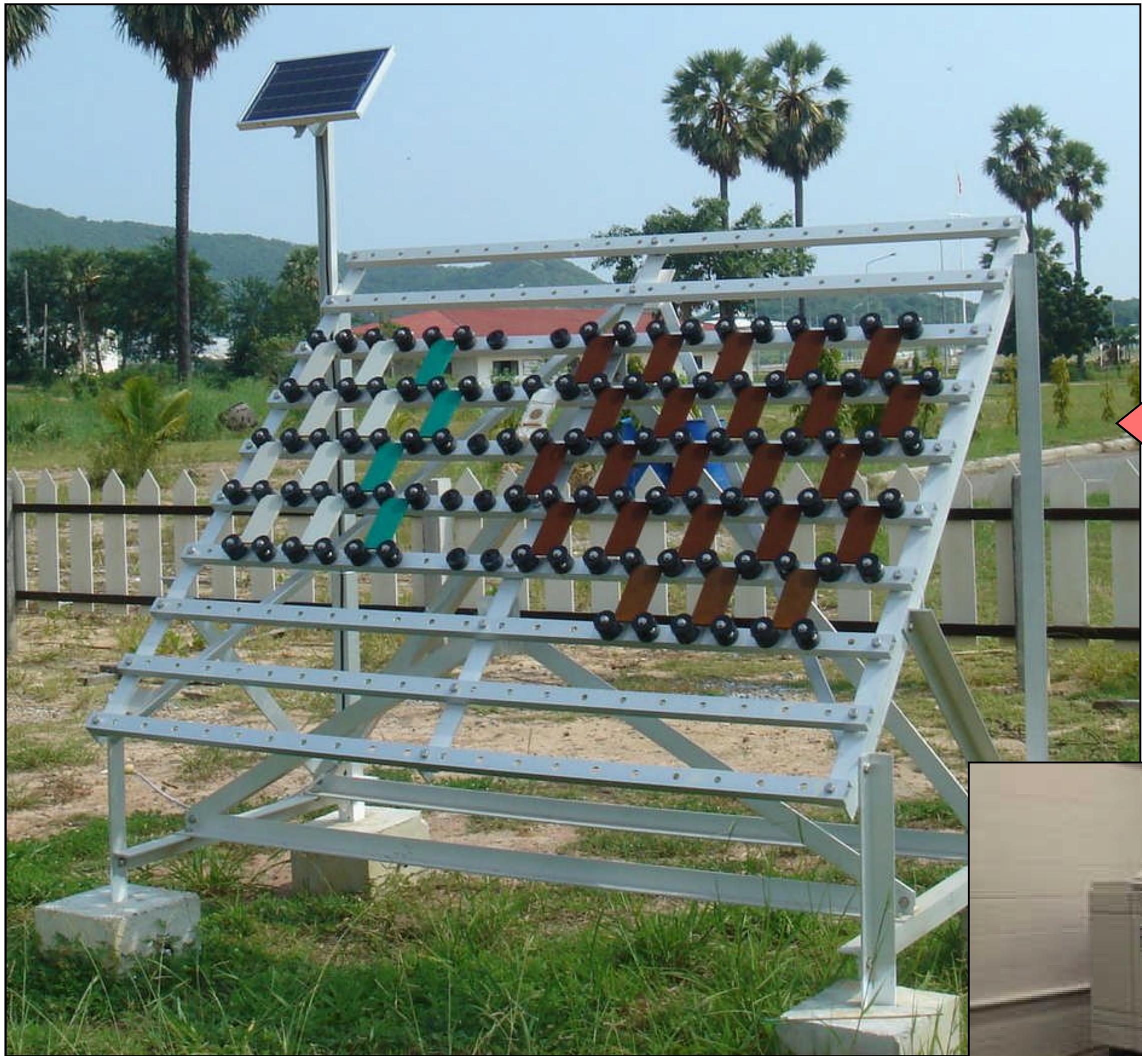
Store in clean, soft, low lint cloth in controlled environment.

Passivation Processing – Coupon Immersion



LINDBERG/BLUE M WATERBATH
MODEL # WB11OA
SECTION VIEW

Coupon Exposure Methods

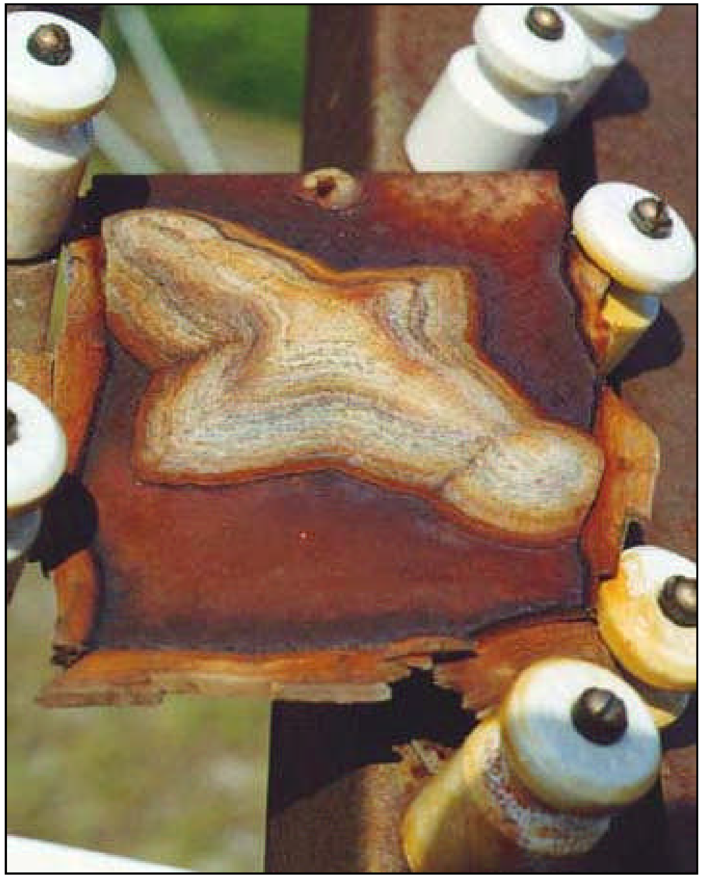


Phases 2 & 3 - ASTM G50 - Conducting Atmospheric Corrosion Tests on Metals – 6 months for each exposure.

Phase 1 - ASTM B117 – Salt Spray Chamber Testing – 2+ days.

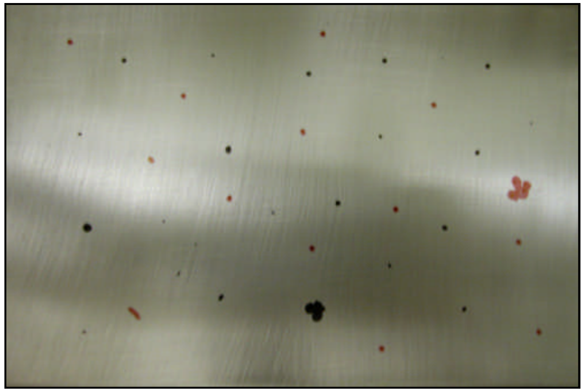
Corrosion Evaluation Plan

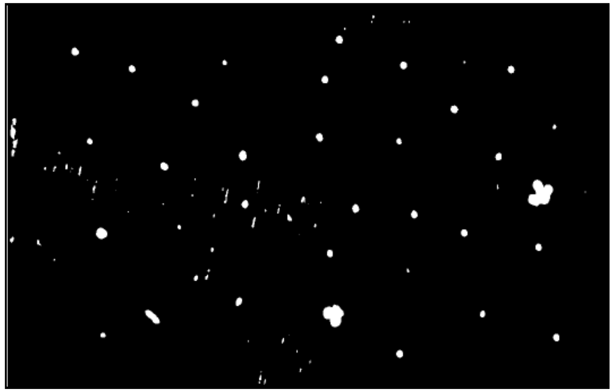
- Evaluation of general corrosion per *ASTM G1 - Preparing, Cleaning, and Evaluation of Corrosion Test Specimens*: Weighing and measuring per 6.5, chemical cleaning per 7.2, corrosion rate per 8.
- Evaluation of Pitting corrosion per *ASTM G46 - Inspection and Evaluation of Pitting Corrosion*: Pit density, 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 D610 - 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.

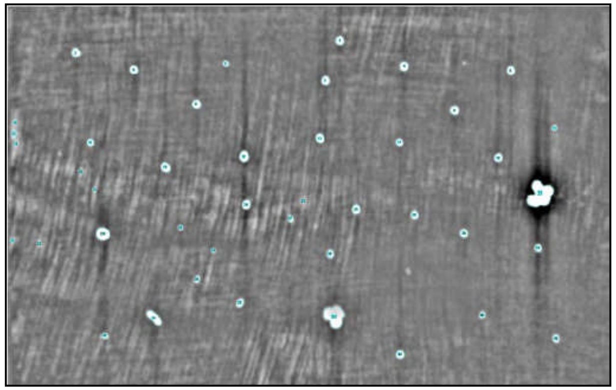


Corrosion Evaluation Plan

- 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).



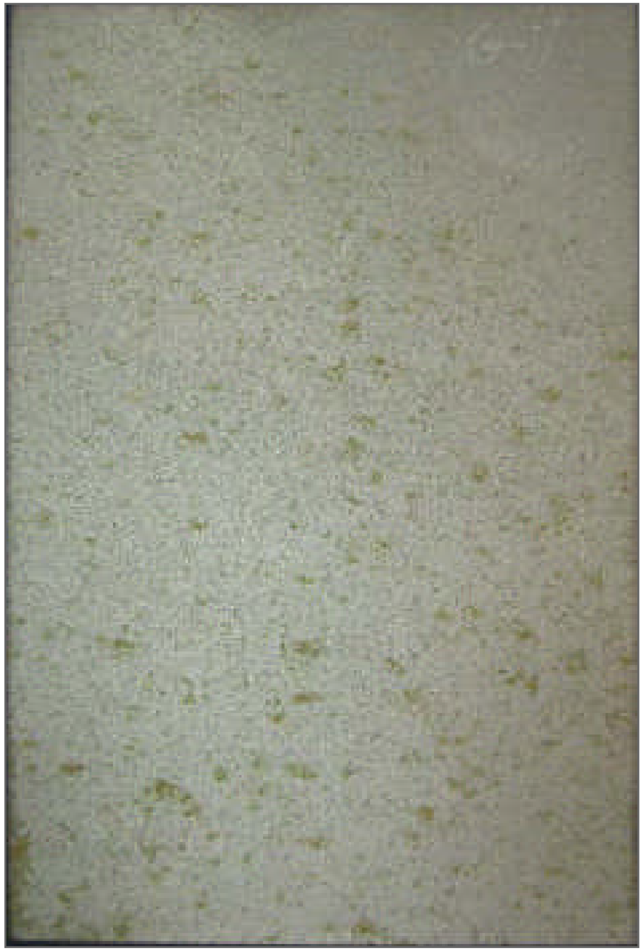




43 Pits were Identified

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.

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Acknowledgements

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- Pattie Lewis Burford, ITB, Inc.
- J. Michael Johnson, WilTech Laboratory
- NASA TEERM
- C3P

Questions?

Back-up

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.

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)

Requirements Per AMS 2700B

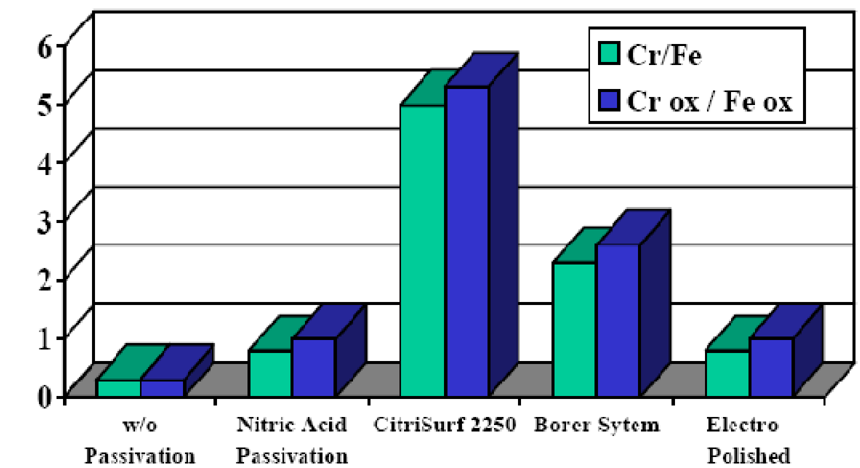
- Passivation is used to remove metallic contaminants from the surface of corrosion resistant steels using chemically oxidizing methods to prevent bulk degradation.
- Method 1, Nitric Acid
  - 8 Types; 70-155°F Bath Temperature, 20-55% Nitric Acid
  - 5 of the 8 types require the dichromate additive
  - 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.

Secondary NASA Specifications

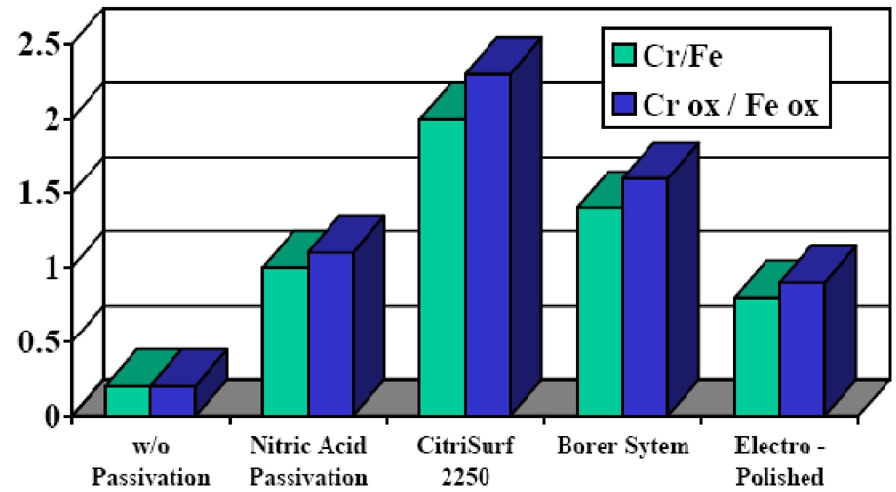
- NASA-STD-5008 *(Protective Coating Of Launch Structures, Facilities, And GSE)*
  - Clean parts per SSPC SP-1
  - No specific passivation methods mentioned
- TM-584C (*Corrosion Control and Treatment Manual)*
  - Clean parts per SSPC SP-1
  - Acid clean parts
    - HNO_3 (42°Bé): 225 to 375 kilograms 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.)

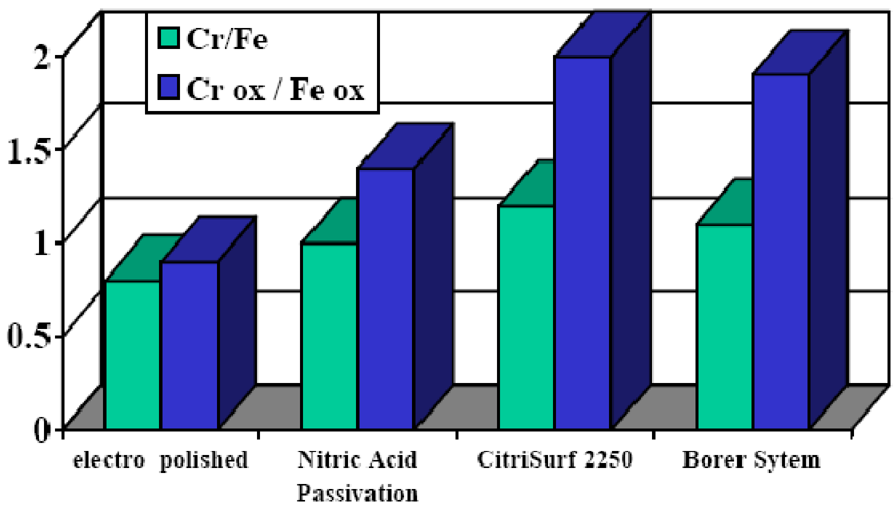
SS 1.4034 - 3M brushed finish



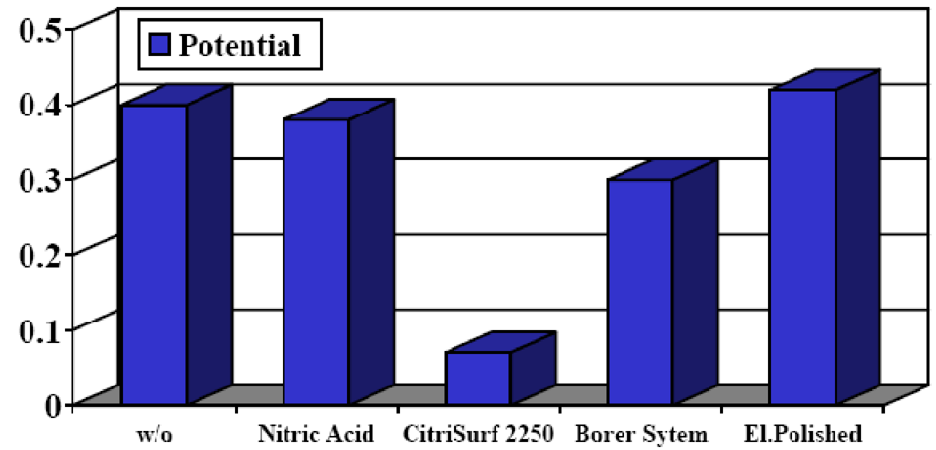
SS 1.4021 - 3M brushed finish



SS 1.4021 - 3M brushed finish & electro polished



SS 1.4021 - 3M brushed finish



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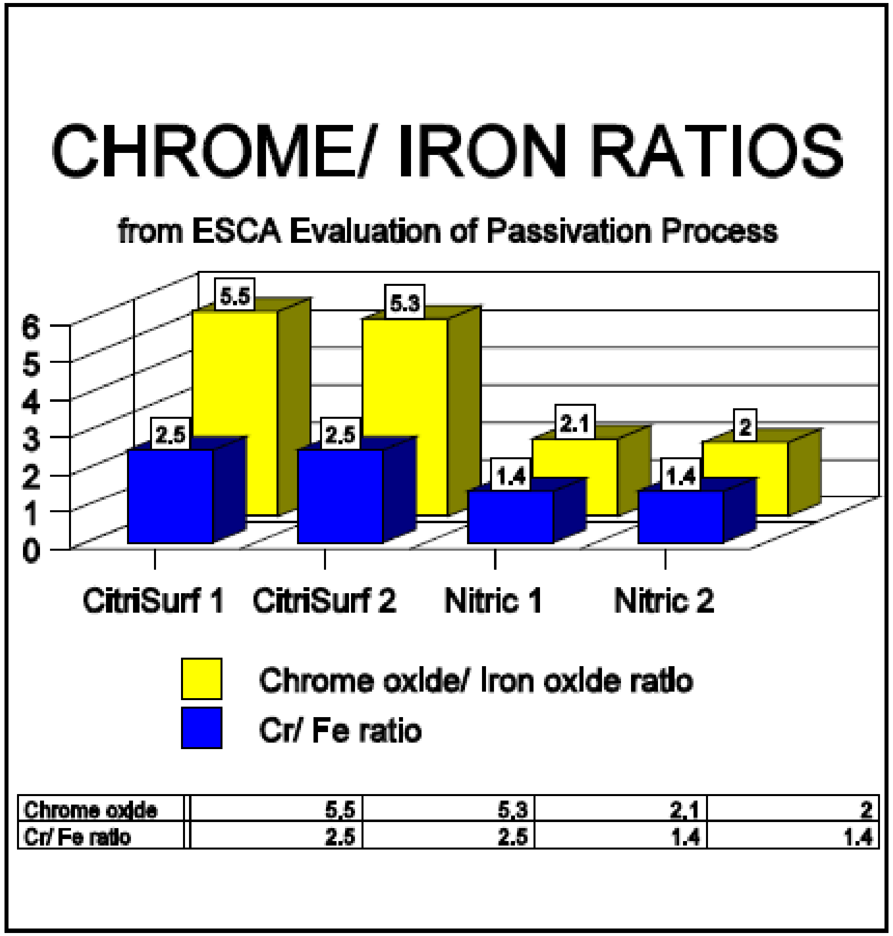
NMI Report - Conclusions

- 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



- **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**

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.