Alternative to Nitric Acid Passivation

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Background

- **Corrosion is expensive**
  - **Financial**
  - **Asset Downtime**
  - **Worker Safety**
  - **Environmental Risks**

- **Passivation**
  - **To treat or coat (a metal) in order to reduce the chemical reactivity of its surface.**
  - **Process forms a shielding metal oxide layer reducing the impact of deleterious environmental factors (i.e. air, water, etc.).**
- **Specification QQ-P-35C**
  - **Details the specific passivating processing conditions for stainless steels using nitric acid.**
  - **Used extensively by the military and industry, but has been cancelled.**

Drawbacks of Nitric Acid

1. Air Pollution

- Nitrogen Oxide (NOx) Emissions are considered Greenhouse Gases (GHGs) and Volatile Organic Compounds (VOCs)
- Subject to Federal and State Regulations

2. Wastewater

- Regulated under Metal Finishing Categorical Standards
- Local wastewater treatment facility may also require permits or pretreatment

3. Worker Safety

- NOx Emissions are toxic to workers
- Passivation tanks require local exhaust ventilation or general area ventilation

4. Operational

- Can remove beneficial heavy metals that give stainless steel its desirable properties

Benefits of Citric Acid

1. **Bio-based Material—meets requirements of**
   - Farm Security and Rural Investment Act of 2002
   - EO 13423
   - EO 13514

2. **No Toxic Fumes**
   - Safer for workers
   - Less required ventilation
3. **Improved Performance**
   - Citric acid removes free iron from the surface more efficiently
   - Requires lower concentrations
   - Processing baths retain potency better requiring less frequent refilling
   - Reduced volume and potential toxicity of effluent and rinse water
4. **Lower Costs**

Experimental Procedure

Stainless Steels Alloys of Interest		
Type	**Alloy**	**UNS Number**
Super Austenitic	AL-6XN	N08367
200 Series Austenitic	A286	S66286
300 Series Austenitic	304	S30400
300 Series Austenitic	316	S31600
300 Series Austenitic	321	S32100
400 Series Martensitic	410	S41000
400 Series Martensitic	440C	S44004
Precipitation-Hardened Martensitic	15-5PH	S15500
Precipitation-Hardened Martensitic	17-4PH	S17400
Precipitation-Hardened Martensitic	17-7PH	S17700

Experimental Procedure

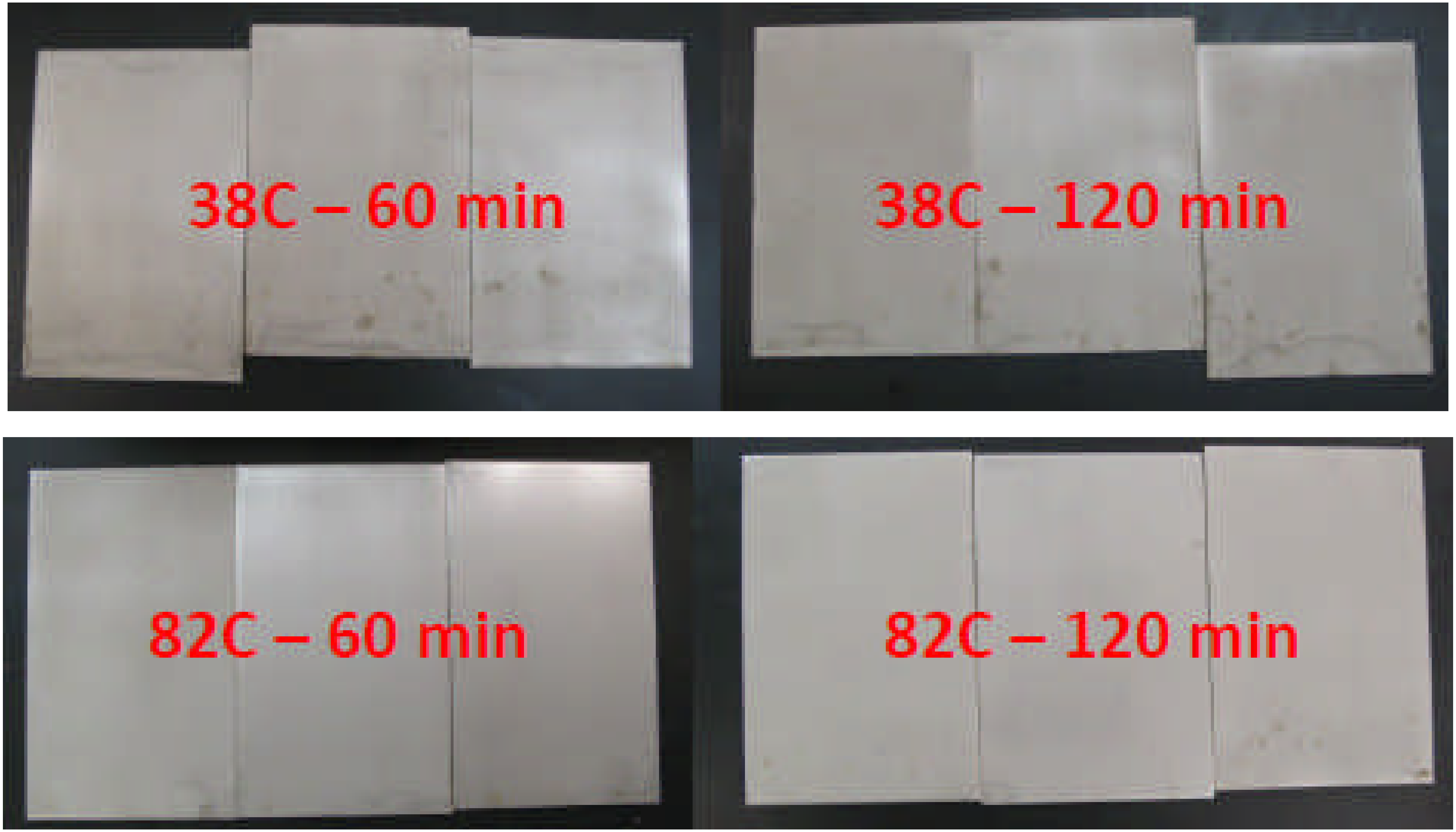
Performance Requirements		
Test	**Acceptance Criteria**	**References**
Parameter Optimization	Best parameters	ASTM B 117 and D 610
Tensile (Pull-off) Adhesion	Alternative performs as well or better than control process	ASTM D 4541
X-Cut Adhesion by Wet Tape		ASTM D 3359
Cyclic Corrosion Resistance		GMW 14872
Atmospheric Exposure Testing		ASTM D 610 and D 714 and NASA-STD-5008
Stress Corrosion Cracking		ASTM E 4, E 8, G 38, G 44 and MSFC-STD-3029
Fatigue		ASTM E 466
Hydrogen Embrittlement		ASTM F 519
Liquid Oxygen (LOX) Compatibility	Twenty samples must not show any reaction when impacted at 98 J.	NASA-STD-6001

Parameter Optimization

- Previous work by United Space Alliance for Ground Operations at NASA John F. Kennedy Space Center showed that process parameters for citric acid affected the corrosion resistance of varying alloys.
- Nitric acid passivation also calls for varying parameters based on the alloy.
- Looked at the following parameters:
  - Bath Temperature: 38°C, 60°C, and 82°C
  - Dwell Time: 60 min, 90 min, and 120 min
- Used a citric acid concentration of 4%

This is an area that we feel more work is necessary in order to implement the citric acid process.

Parameter Optimization – A286



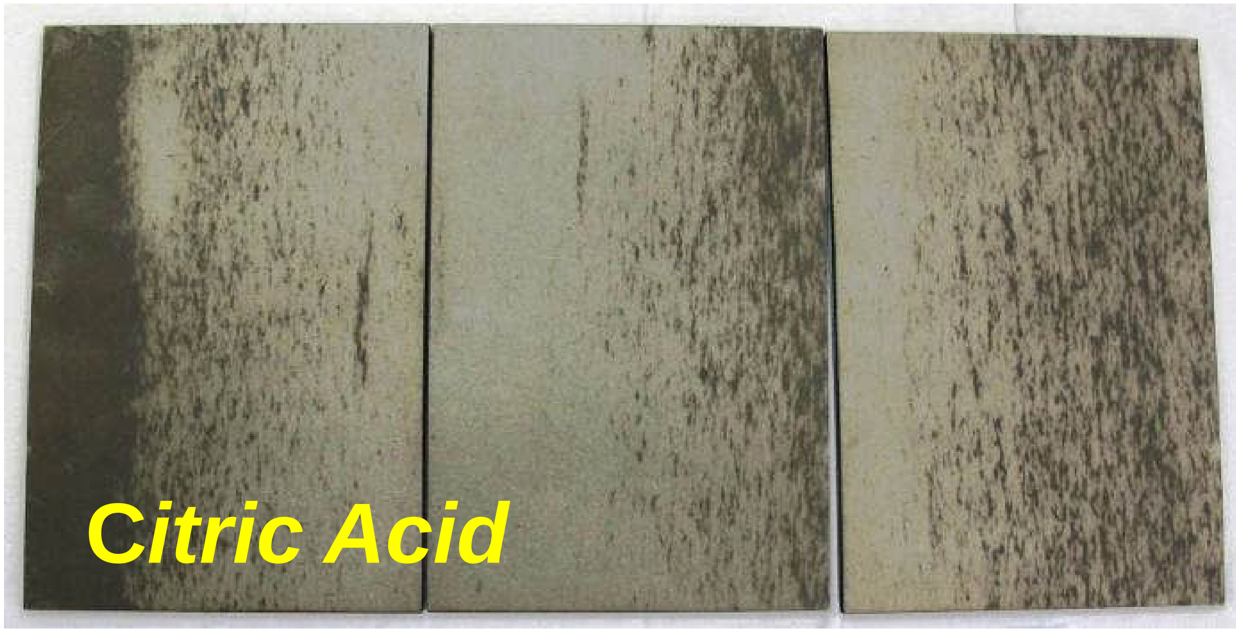
Selected Parameters: *82 °C and 60 minutes*

Parameter Optimization

Alloy	*Passivation*	*Concentration*	*Bath Temperature*	*Dwell Time*
AL6XN	Nitric Acid	22.5%	66° C	20 min
	Citric Acid	4%	38° C	120 min
A286	Nitric Acid	50%	64° C	30 min
	Citric Acid	4%	82° C	60 min
304*	Nitric Acid	22.5%	66° C	20 min
	Citric Acid	4%	49° C	120 min
316	Nitric Acid	22.5%	60° C	20 min
	Citric Acid	4%	60° C	90 min
321	Nitric Acid	22.5	60° C	20 min
	Citric Acid	4%	82° C	60 min
410*	Nitric Acid	50	64° C	30 min
	Citric Acid	4%	82° C	60 min
440C	Nitric Acid	50	60° C	30 min
	Citric Acid	4%	60° C	60 min
15-5PH	Nitric Acid	50	64° C	30 min
	Citric Acid	4%	82° C	60 min
17-4PH*	Nitric Acid	50%	64° C	30 min
	Citric Acid	4%	38° C	30 min
17-7PH	Nitric Acid	50	64° C	30 min
	Citric Acid	4%	82° C	60 min

*** Citric acid processing parameters determined during USA testing**

Parameter Optimization



- The citric acid passivation of the 440C alloy resulted in bath solution discoloration and produced discoloration that was non-uniform over the surface.
- A stakeholder had similar problems during their work and determined the cause to be that the alloy was not fully hardened.

Adhesion

- **Tested for X-cut by Wet Tape Adhesion (per D 3359) and Tensile (Pull-off) Adhesion (per ASTM D 4541).**
- **Coatings from APL in NASA-STD-5008 (*Protective Coating of Carbon Steel, Stainless Steel, and Aluminum on Launch Structures, Facilities, and Ground Support Equipment)***
- **CARC systems: specimens were prepared per**
  - **MIL-DTL-53022, *Primer, Epoxy Coating, Corrosion Inhibiting Lead and Chromate Free,* Type II**
  - **MIL-DTL-53030, *Primer Coating, epoxy, Water Based, Lead and Chromate Free*, Type II**
- **Cadmium plating**
- **Chromium plating**

Conclusion: *There was no evidence that citric acid is detrimental to adhesion.*

NASA Atmospheric Exposure Testing

- **Test panels were placed at the KSC Beachside Atmospheric Test Facility.**
  - Test racks located approximately 150 feet from Atlantic Ocean high tide line.
- **Panels were evaluated according to visual standards in ASTM D 610 and converted from the degree of observation to a rust grade.**
- **Test specimens included:**
  - Nitric/Citric Acid Passivated-only
  - Nitric/Citric Acid Passivated-Coated (primer + topcoat, plating)

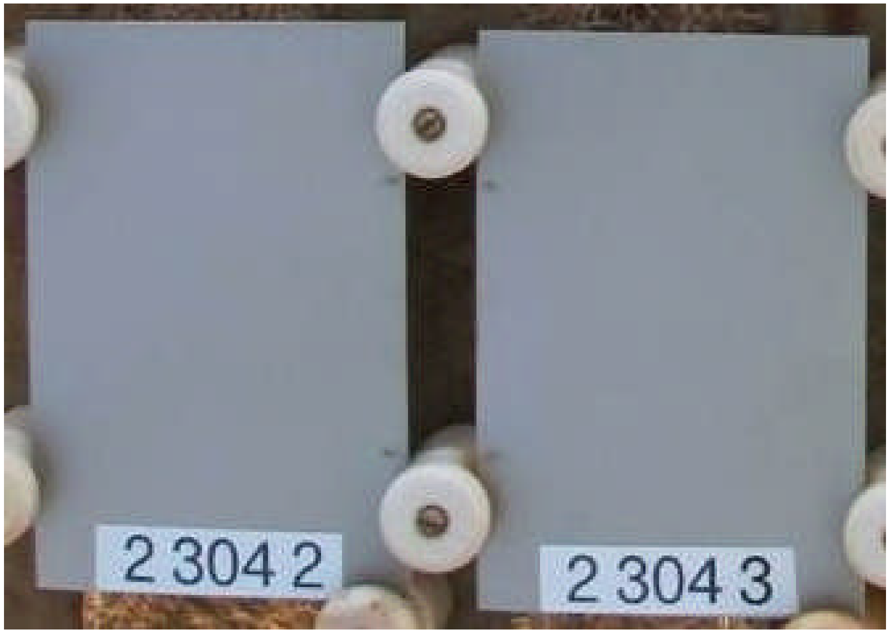
NASA Atmospheric Exposure Testing

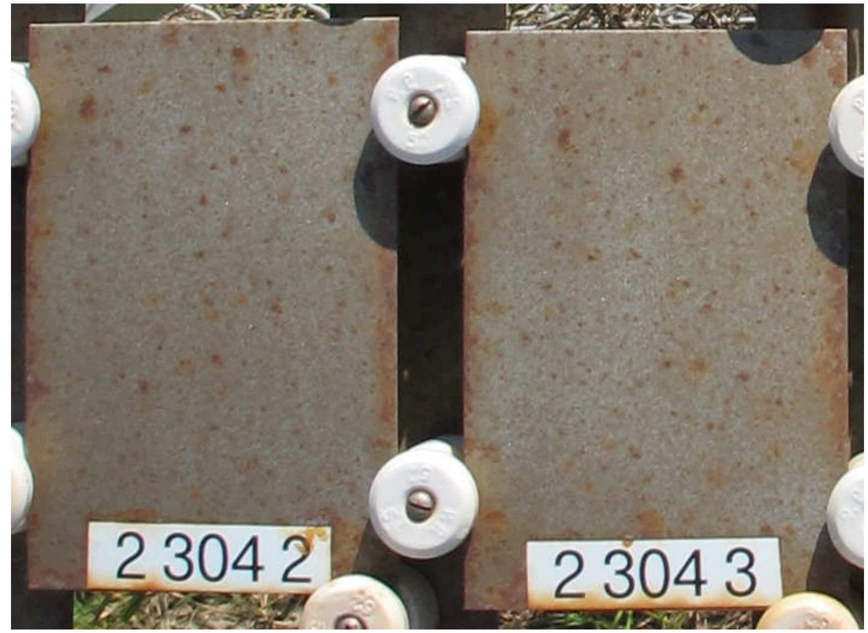
Alloy	Week 1		Week 2		Week 3		Week 4		Week 5		Week 6		Week 7		Week 8	
	Nitric	Citric	Nitric	Citric	Nitric	Citric	Nitric	Citric	Nitric	Citric	Nitric	Citric	Nitric	Citric	Nitric	Citric
AL6XN	10	10	10	10	10	10	10	10	7	10	7	10	6	10	6	10
17-4PH	5	4	4	3	4	3	4	3	4	3	4	3	3	2	3	2
A286	4	6	4	5	4	5	4	5	3	4	3	4	3	4	3	4
304	4	5	3	4	2	4	2	4	2	3	2	3	2	3	2	3
17-7PH	5	5	4	4	4	4	4	4	4	4	4	4	4	4	4	4
410	4	7	3	4	3	4	3	4	2	3	2	3	1	2	1	2
15-5PH	5	5	4	4	4	4	4	4	3	3	3	3	3	3	3	3
321	4	5	3	4	2	4	2	4	2	3	2	3	2	3	2	3
316	4	6	3	5	2	5	2	5	2	4	2	4	2	3	2	3

- **Passivated-only Panels: Citric acid passivated panels exhibited *equal to, or better than, corrosion performance* when compared to the nitric acid passivated panels.**
- **Passivated-Coated Panels: *No signs of corrosion were evident on either* the citric acid passivated or nitric acid passivated panels.**

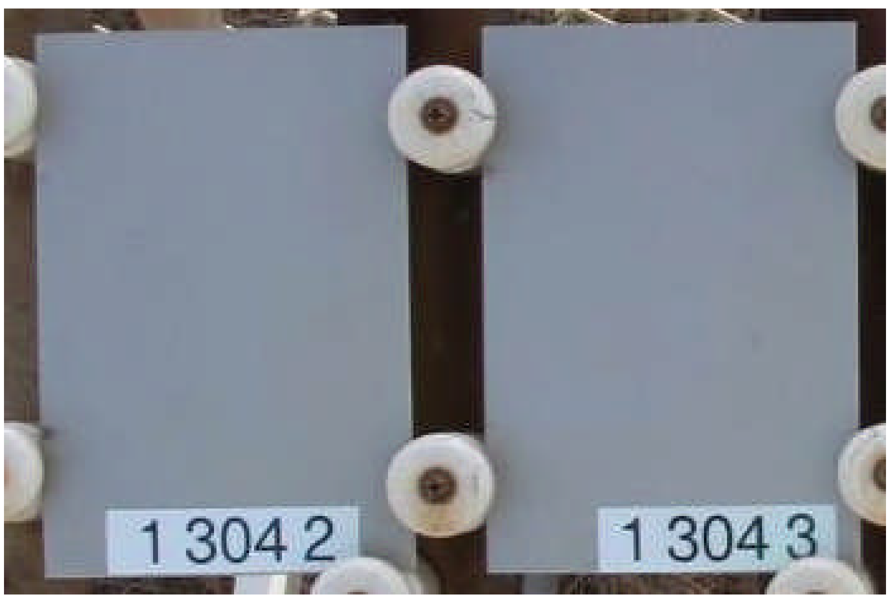
NASA Atmospheric Exposure Testing

304 Citric





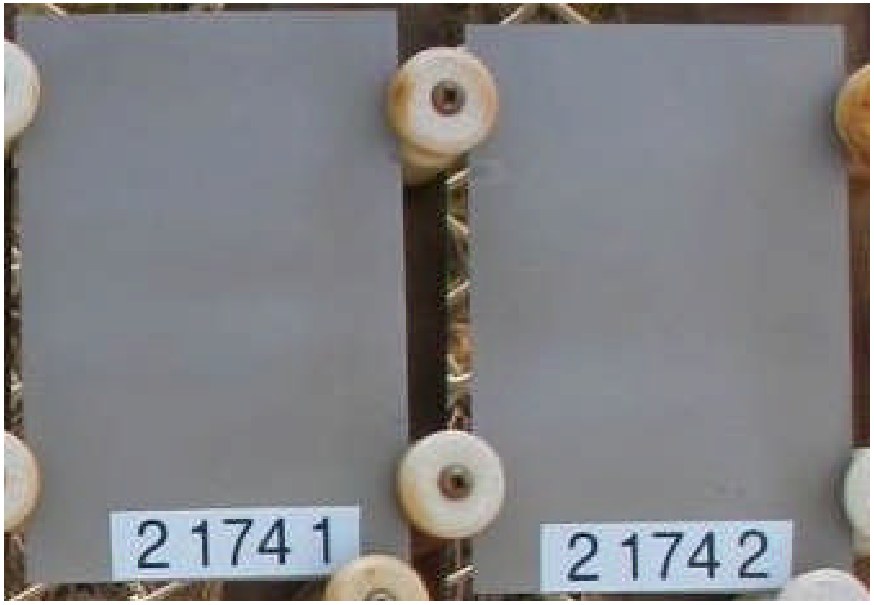
304 Nitric

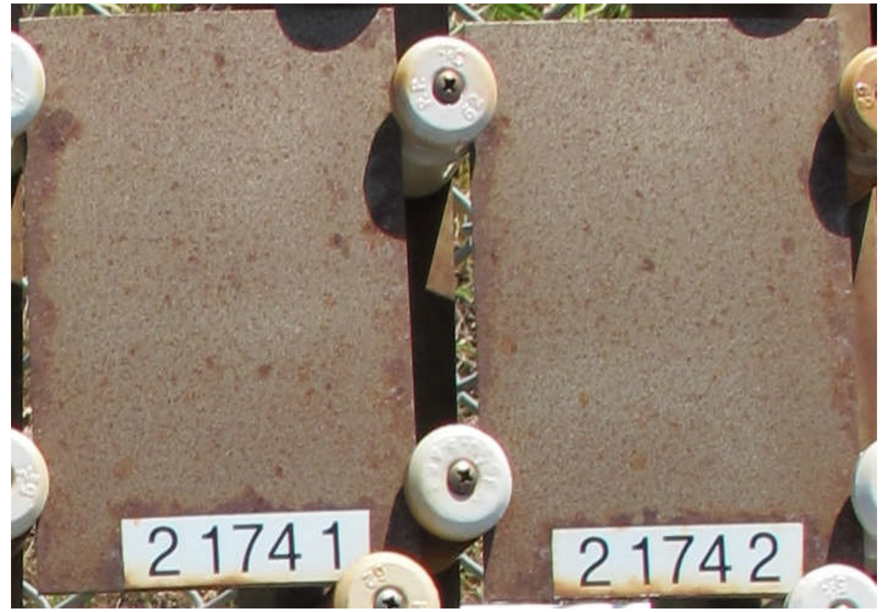


Initial | **After 6 Months**

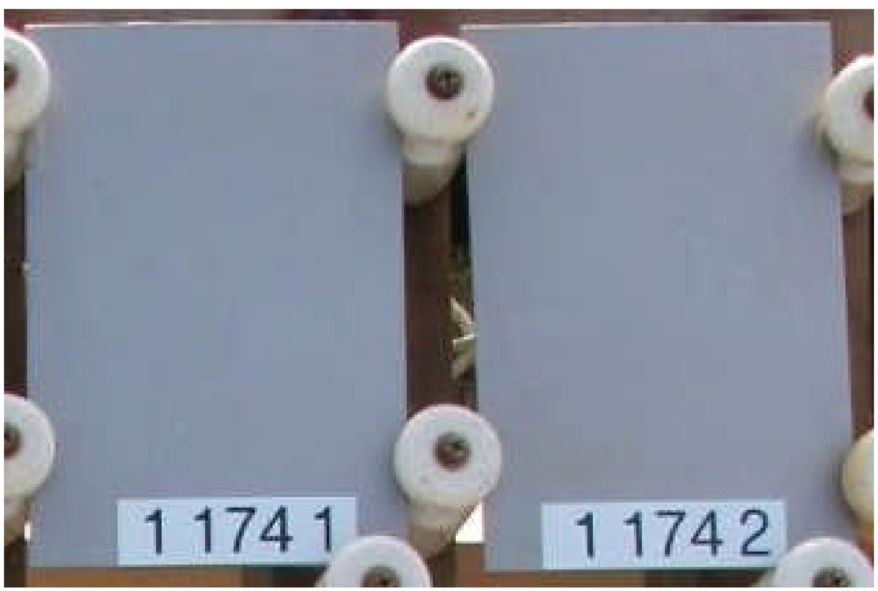
NASA Atmospheric Exposure Testing

17-4 Citric





17-4 Nitric



Initial | **After 6 Months**

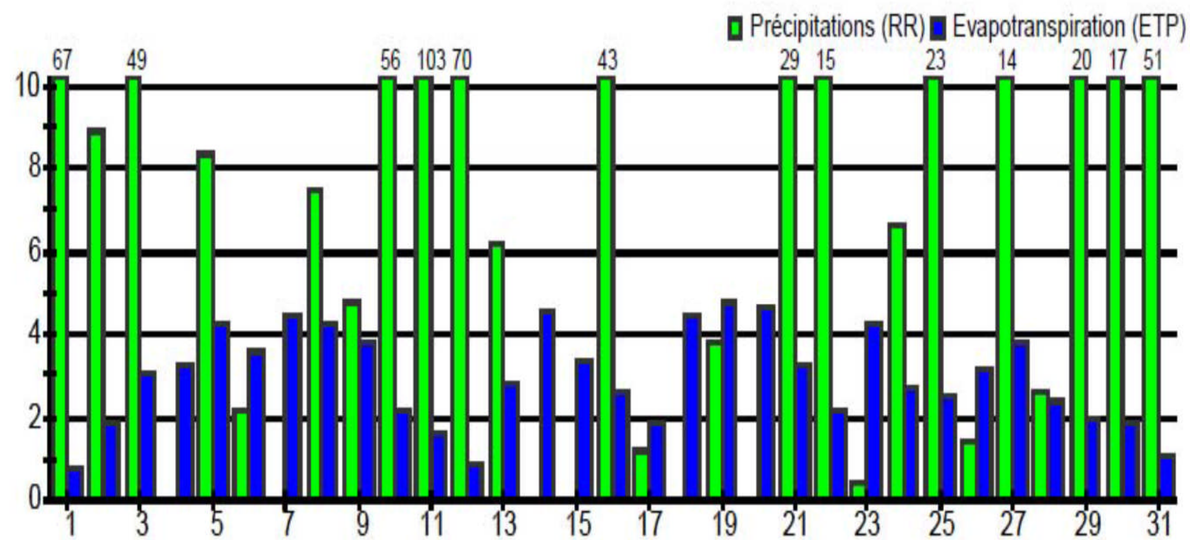
ESA Atmospheric Exposure Testing

- European Space Agency (ESA) also interested in this work, especially for 304 and 316 alloys.
- No matter how alike environments are, there are always differences so decided to conduct comparative atmospheric exposure testing at ESA's Guiana Space Centre, located near Kourou in French Guiana.
- Built test racks that mirrored the height, angle, etc. as the test racks at KSC Beachside Atmospheric Test Facility.

ESA Atmospheric Exposure Testing

ESA Atmospheric Exposure Testing

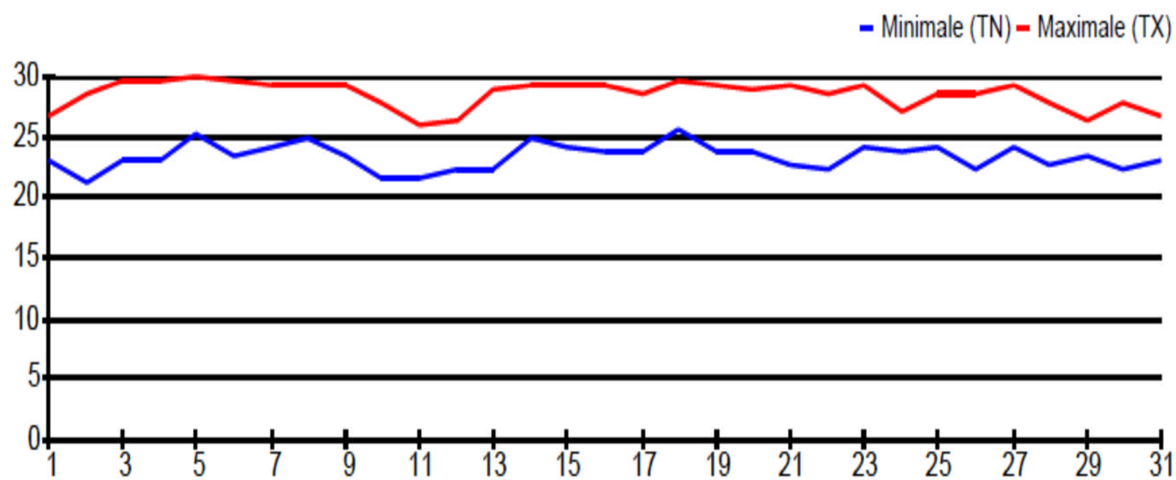
PRECIPITATIONS et EVAPOTRANSPIRATION (mm)



Précipitations	
610.2 mm	
normale :	*358.4 mm*
ETP Penman	
normale :	–

– : donnée manquante

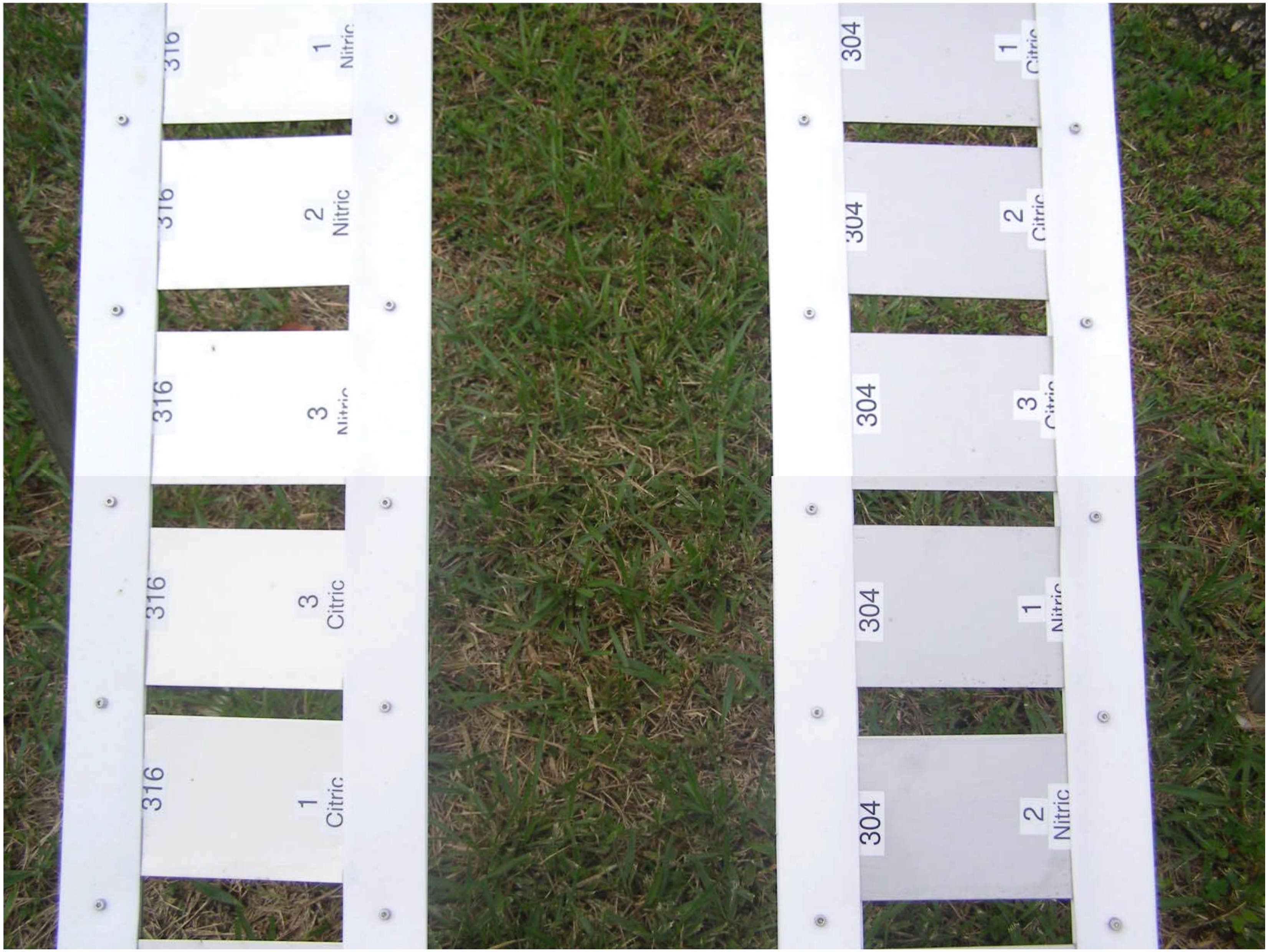
TEMPERATURES (°C)



Moyenne des températures	
maximales	**28.5 °C**
normale :	*29.0 °C*
minimales	**23.3 °C**
normale :	*23.8 °C*
moyennes	**25.9 °C**
normale :	*26.4 °C*

January 2014

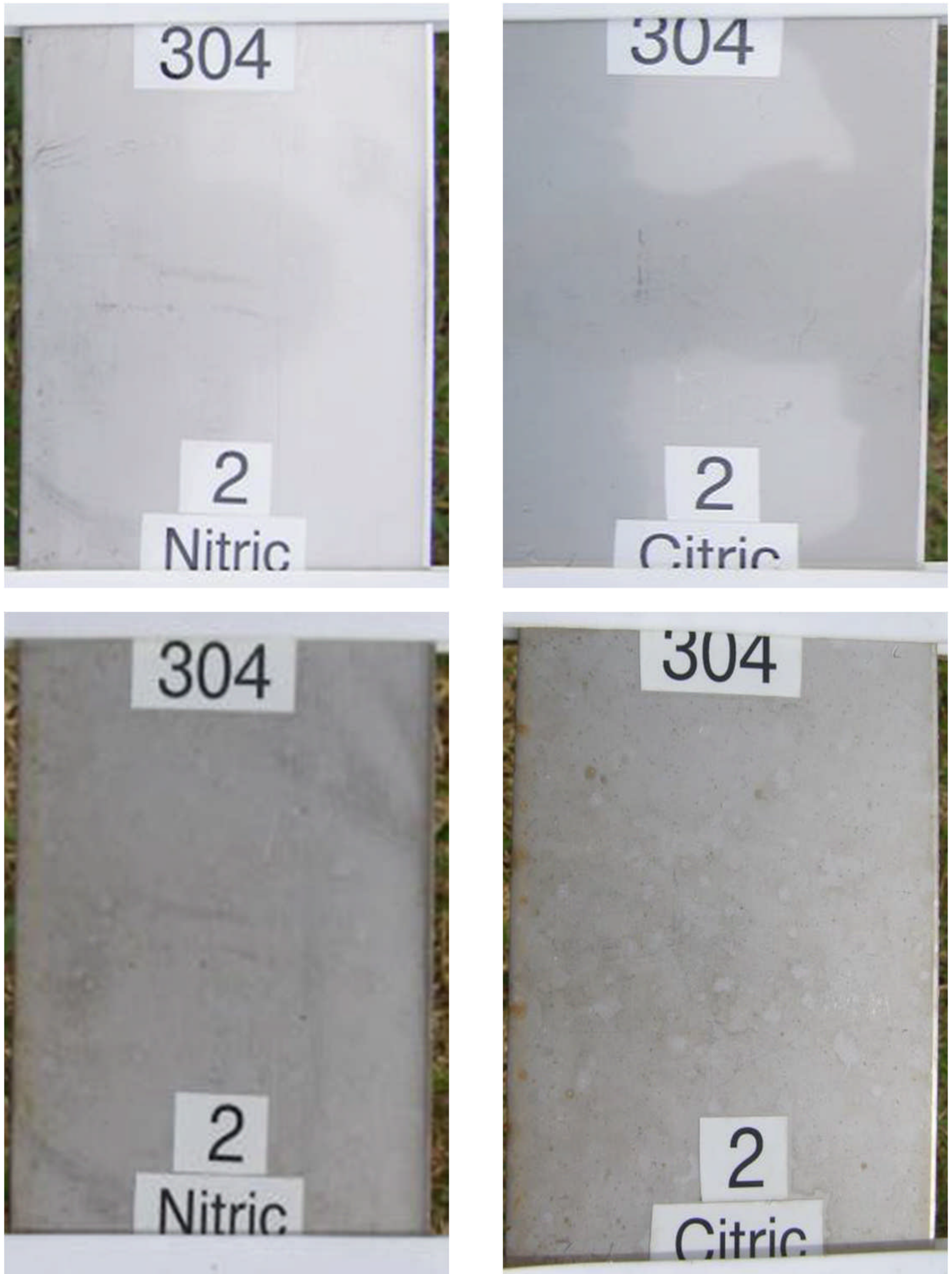
ESA Atmospheric Exposure Testing



ESA Atmospheric Exposure Testing

Initial

After 6 mo.



- **The nitric acid and citric acid test panels show similar conditions after 6 months of exposure.**
- **Will be conducting in-depth analysis of samples at ESTEC.**
- **However, these preliminary results offer further evidence that the citric acid process provides acceptable corrosion protection.**

Future Work

- **Continue to evaluate test panels at the KSC.**
- **Continue to work with ESA and evaluate test panels at Guiana Space Centre.**
- **Stress Corrosion Cracking Testing is underway.**
- **Cyclic Corrosion Testing is underway.**
- **Hydrogen Embrittlement Testing is underway.**
- **Planning for Fatigue Testing.**

At this point, it appears that citric acid passivation performs as well as, or better than, nitric acid passivation.

Project Sponsors

- NASA HQ Environmental Management Division
- NASA Ground Systems Development and Operations (GSDO) Program

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