Environmentally-preferable Corrosion Protection

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Why Corrosion is Such a Concern

1. **Facility Locations**
   - Typically in coastal areas
   - Extreme launch environments
2. **Financial**
   - The estimated cost of corrosion to the U.S. is $276 billion/year (includes direct and indirect costs)
3. **Worker Safety**
   - Exposure to hazardous materials
   - Corrosion can result in accidents
4. **Environmental Risks**
   - Increasing regulations
   - Public perception
5. **Asset Downtime**
   - Can cause delays in missions

Alternative to Nitric Acid Passivation

Qualify citric acid as a greener alternative to nitric acid for passivation of stainless steel alloys

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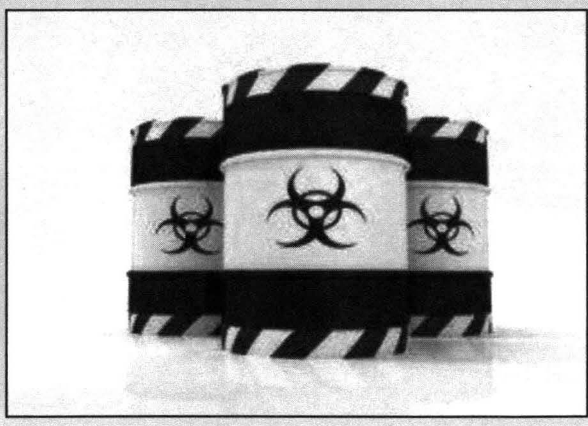

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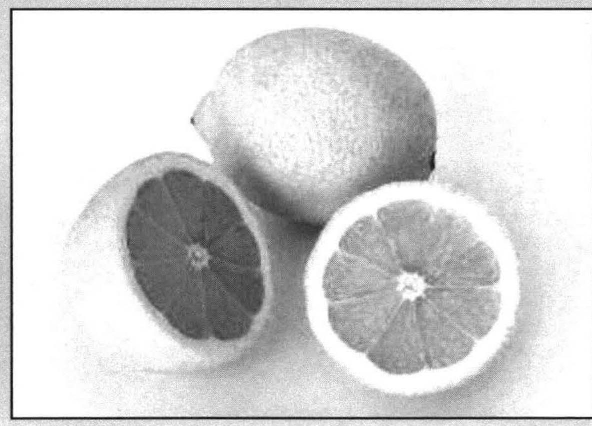


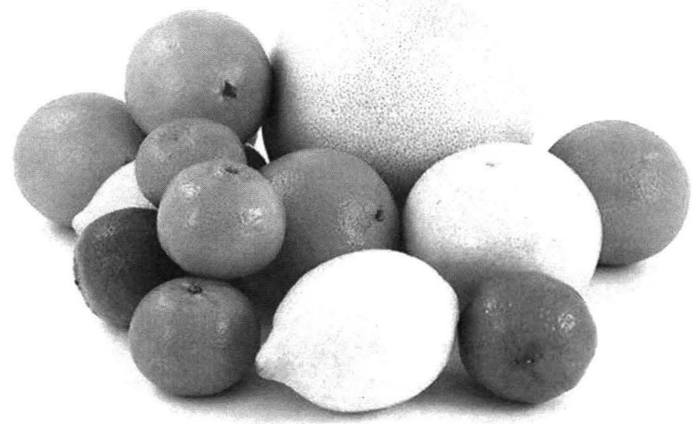
Drawbacks of Nitric Acid

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

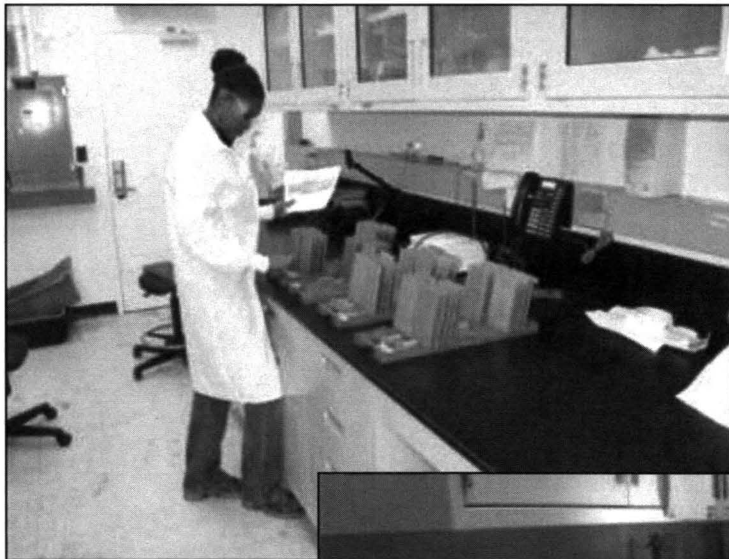
Stainless Steels Alloys of Interest		
Type	**Alloy**	**UNS Number**
Super Austenitic	AL-6XN	N08367
200 Series Austenitic	A286	S66286
300 Series Austenitic	304	S30400
300 Series Austenitic	316	S31600
300 Series Austenitic	321	S32100
400 Series Martensitic	410	S41000
400 Series Martensitic	440C	S44004
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

Testing Summary

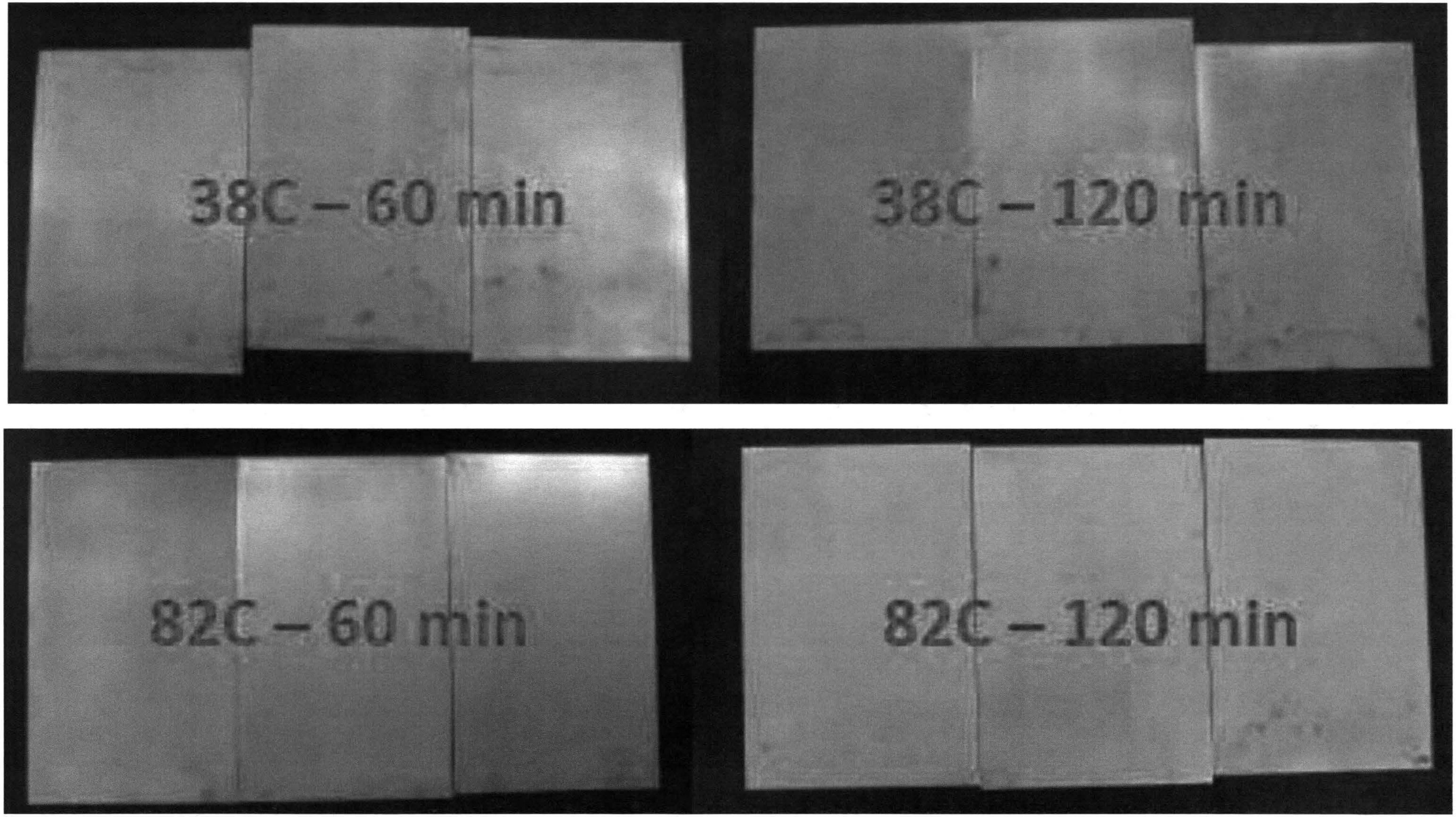
- **Stage 1 Testing is currently underway.**
- **Stage 1 Alloys:**
  - UNS N08367
  - UNS S66286
  - UNS S30400
  - UNS S17400
- **Stage 1 Tests:**
  - Parameter Optimization
  - Tensile (Pull-off) Adhesion
  - Atmospheric Exposure
  - Stress Corrosion Cracking
- **Results presented are to-date**



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%

Parameter Optimization – UNS S66286



Selected Parameters: *82 °C and 60 minutes*

Parameter Optimization

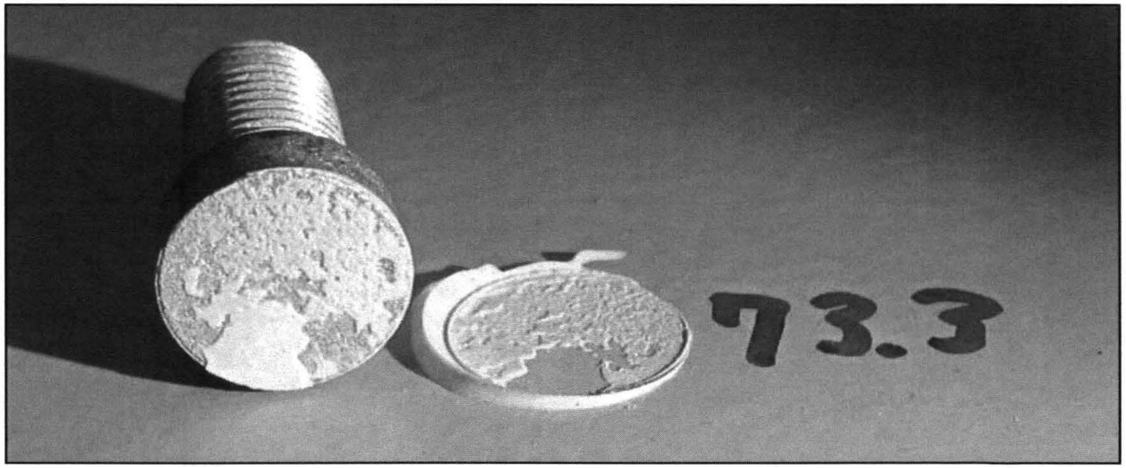
The following parameters were used for the preparation of Stage 1 test specimens.

Alloy	Passivation	Concentration (%)	Bath Temperature (°C)	Time (minutes)
UNS N08367	Nitric Acid	22.5	66	20
	Citric Acid	4	38	120
UNS S66286	Nitric Acid	50	64	30
	Citric Acid	4	82	60
UNS S30400*	Nitric Acid	22.5	66	20
	Citric Acid	4	49	120
UNS S17400*	Nitric Acid	50	64	30
	Citric Acid	4	38	30

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

Tensile Adhesion

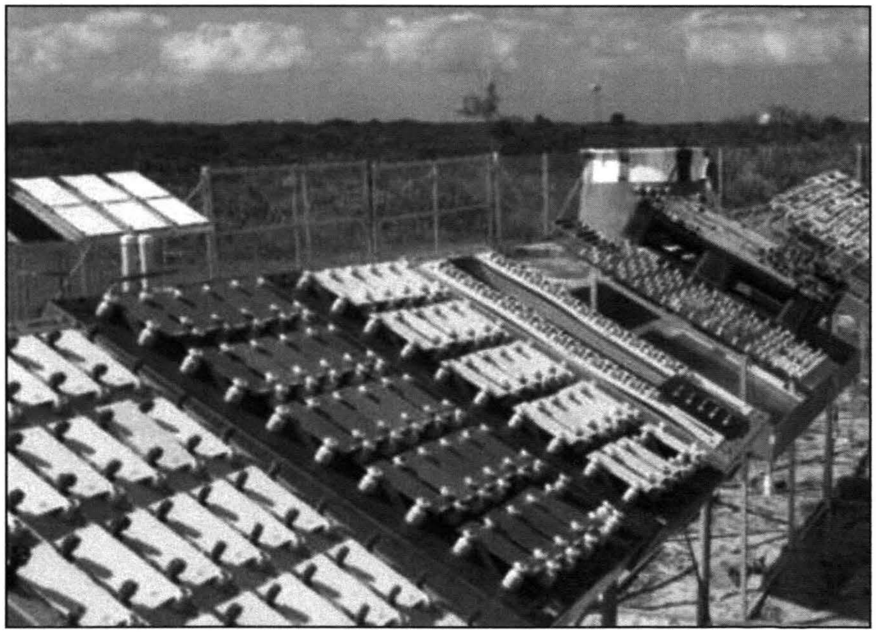
- Adhesion values were determined using a PATTI adhesion tester per ASTM D 4541.
- Except for 2 nitric acid passivated panels, all pull-off values were strictly related to the epoxy adhesive.



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

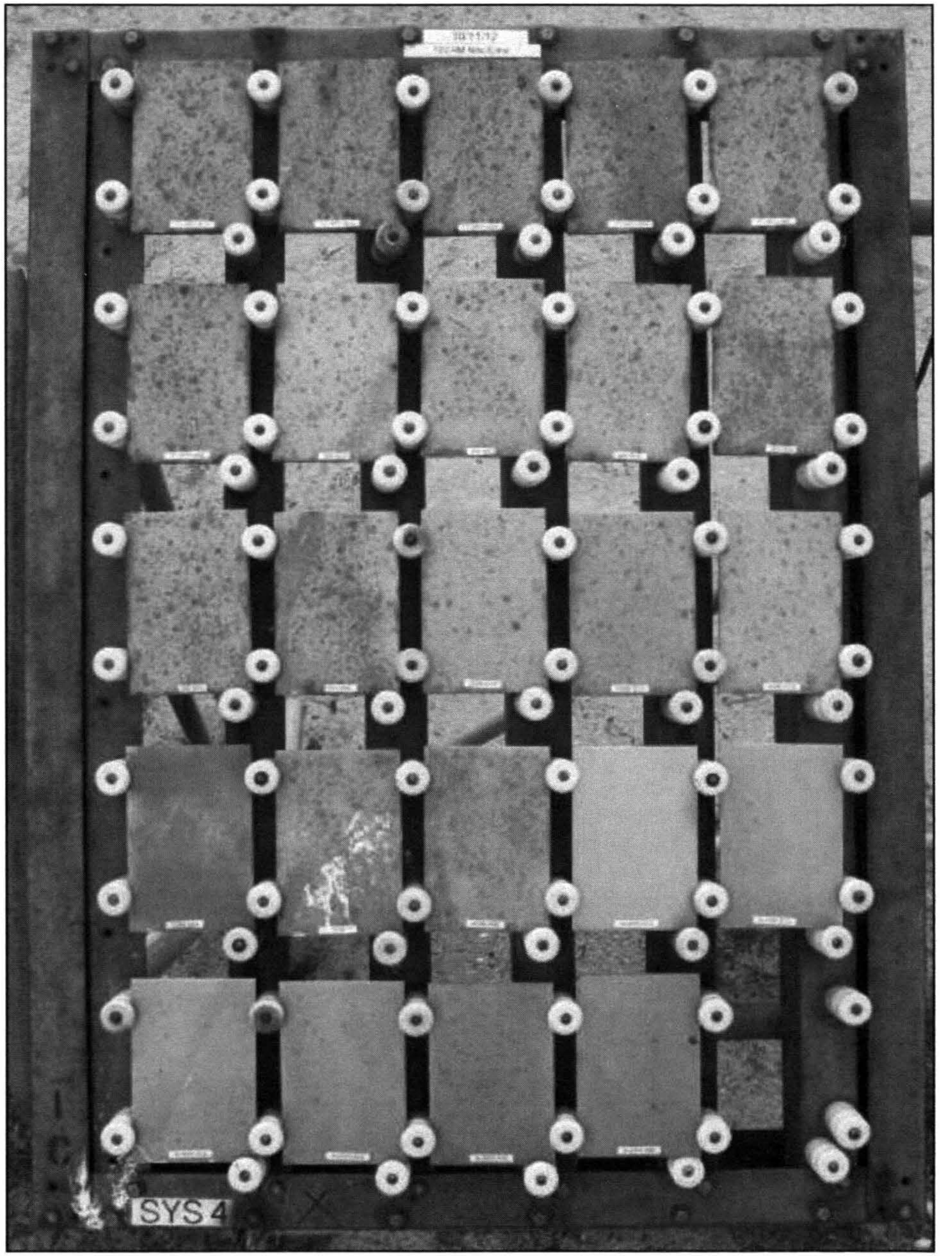
Atmospheric Exposure Testing

- **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)
- **Exposure was initiated on 10/11/12.**



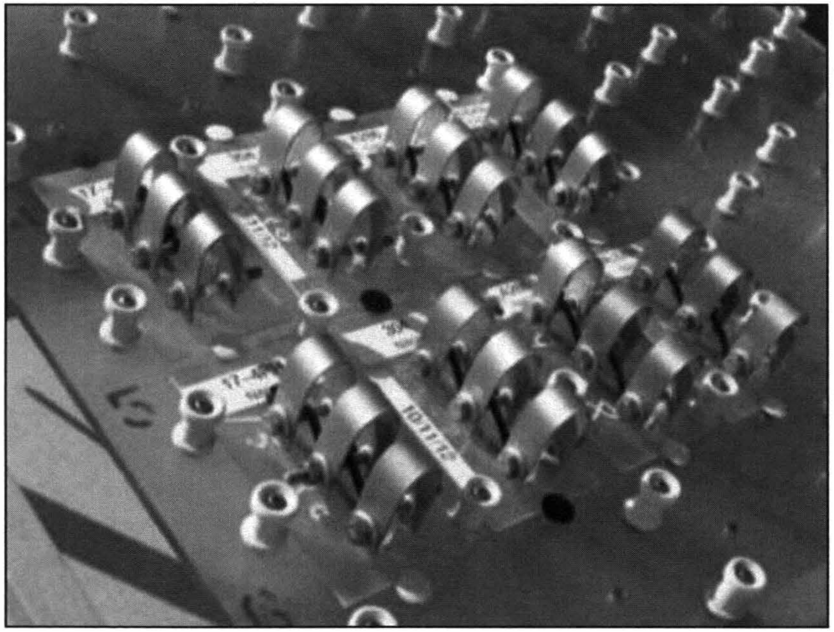
Atmospheric Exposure Testing

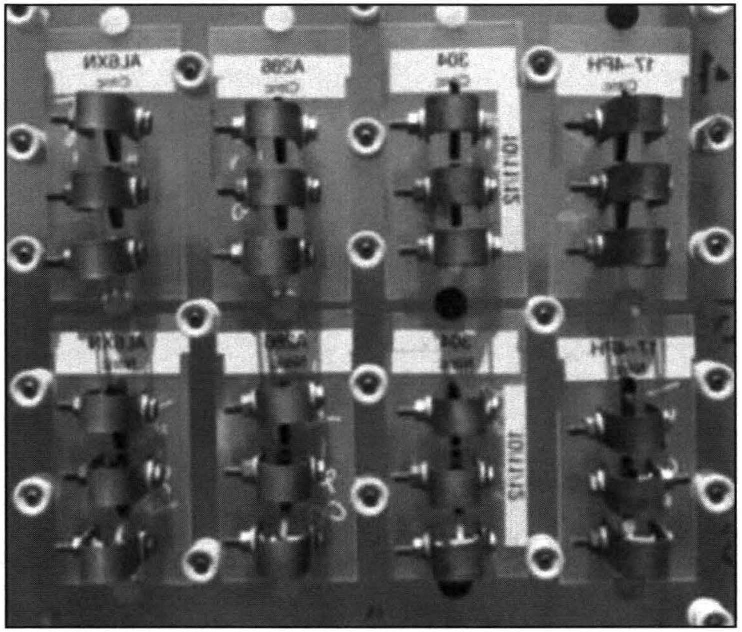
- Test panels were evaluated at 1, 3, and 6 months.
- Passivated-Coated Panels: *No signs of corrosion were evident on either* the citric acid passivated or nitric acid passivated panels.
- Passivated-only Panels: Citric acid passivated panels exhibited *equal to, or better than, corrosion performance* when compared to the nitric acid passivated panels.

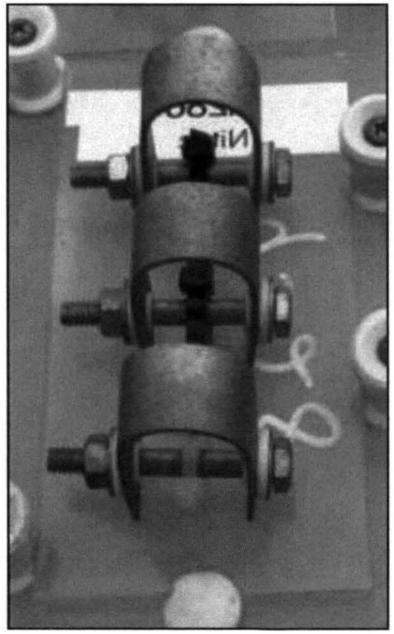


Stress Corrosion Cracking

- Stress corrosion cracking can lead to sudden failure of normally ductile metals subjected to a tensile stress.
- Exposure was initiated on 10/11/12.







After 6 months of exposure, there has been no evidence of cracking on any specimens.

Conclusions

- **Parameter Optimization**
  - Process parameters were determined for Stage 1 alloys not included in the USA study.
- **Tensile (Pull-off) Adhesion**
  - The citric acid passivation had no derogatory effect on the adhesion of a subsequently applied liquid primer.
- **Atmospheric Exposure (after 6 months)**
  - There is no evidence of corrosion on any of the Passivated-Coated panels.
  - The citric acid passivated-only panels had <u>an equal or lesser</u> degree of corrosion when compared to the nitric acid passivated-only panels.
- **Stress Corrosion Cracking**
  - No samples have cracked after 6 months of exposure.

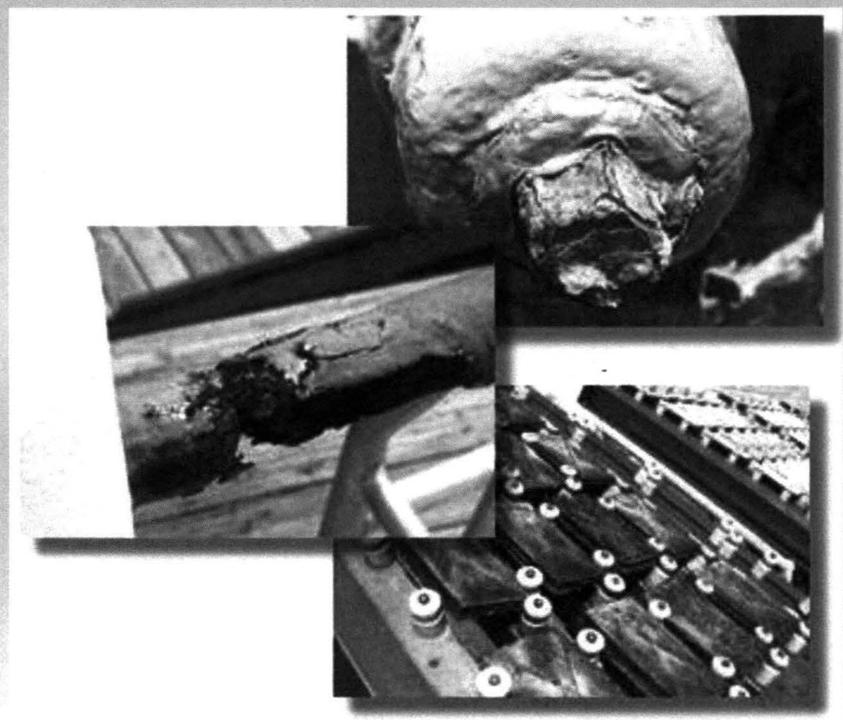
At this point, it appears that citric acid performs as well as, or better than, nitric acid.

Future Work

- **Stage 1 Testing continues.**
- **Remaining testing has recently started and includes the other identified alloys and additional tests:**
  - X-Cut Adhesion by Wet Tape
  - Cyclic Corrosion Resistance
  - Fatigue Testing (selected alloys)
  - Hydrogen Embrittlement
- **Place test panels at Guiana Space Centre for comparative atmospheric exposure testing of the 304 and 316 alloys.**

Environmentally-preferable Coatings for Launch Facilities

Validate greener coating systems for protection of structural steel launch facilities and ground support equipment



Specification NASA-STD-5008B *Protective Coating of Carbon Steel, Stainless Steel, and Aluminum on Launch Structures, Facilities, and Ground Support Equipment*

- Governs maintenance at John F. Kennedy Space Center and other NASA Centers.
- Establishes practices for the protective coating of ground support equipment and related facilities.
- Zones of Exposure are established to define coating system requirements for specific environments.
  - ***Zone 4a.*** Surfaces not located in the launch environment, but located in a neutral pH corrosive marine industrial environment or other chloride-containing environments.
  - ***Zone 4b.*** Surfaces located in neutral pH exterior environments in any geographical area.
  - ***Zone 4c.*** Surfaces located in indoor environments that are not air-conditioned.

Phase 1 Performance Requirements

Test	*Acceptance Criteria*	*Test References*
Pot Life	Equal to or better than control coating based upon Applicator Evaluation.	None
Ease of Application	Based on Applicator Evaluation: Smooth coat, with acceptable appearance, no runs, bubbles or sags; Ability to cover the properly prepared/primed substrate with a single coat (one-coat hiding ability); Dry Film Thickness Measurements.	SSPC-PA-2
Surface Appearance	Based on Applicator Evaluation: No streaks, blistering, voids, air bubbles, cratering, lifting, blushing, or other surface defects/irregularities.	ASTM D 523; ASTM D 2244
Atmospheric Exposure	Gloss/color change and panel condition of candidate coating rated equal to or better than control coatings.	ASTM D 610; ASTM D 714; ASTM D 523; NASA-STD-5008B
Heat Adhesion	No loss of adhesion after heating.	ASTM D 4541; NASA-STD-5008B

Phase 2 Performance Requirements

Test	*Acceptance Criteria*	*Test References*
Hypergol Compatibility	Slight to Moderate Reactivity Observed	KSC MTB-175-88; NASA-STD-6001
LOX Compatibility	Twenty samples must not react when impacted at 72 ft-lbs or 98 J. If one sample out of 20 reacts, 40 additional samples must be tested without any reactions.	ASTM D 2512; NASA-STD-6001
Cure Time (MEK Solvent Rub)	Coating will be tested every 2 days for a total of 14 days; No effect on surface or coating on the cloth (Resistance Rating 5).	ASTM D 4752
Removability	Less than one minute to penetrate substrate.	ASTM G 155
Reparability	Ease of removal and replacement of damaged areas of the test coatings, color matching of aged versus new material; Acceptable surface appearance, No peel away of the repaired coating during the dry tape adhesion test.	ASTM D 523; ASTM D 2244; ASTM D 3359
Mandrel Bend Flexibility	No peeling or delamination from the substrate and no cracking greater than ¼-inch from the edges.	ASTM D 522

Potential Alternative Evaluation

1. Commercially Availability
2. Technical Feasibility
3. Volatile Organic Compound (VOC) Content <200 g/L
4. Hazardous Air Pollutants (HAPs) Content
5. Other Hazardous Constituents
6. Isocyanates
7. Heavy Metals
   - Lead
   - Chromium
   - Cadmium
   - Zinc

Round 1 Selection of Alternatives

- **Identified 21 commercially available potential alternatives**
- **Project stakeholders reviewed information and discussed advantages and disadvantages to down-select those to include in testing**
- **Selected 10 alternative coating systems:**
  - Four (4) zinc-free and isocyanate-free systems
  - Three (3) isocyanate-free systems (contain zinc)
  - Two (2) zinc-free systems (contain isocyanates)
  - One (1) isocyanate-free and reduced zinc content system

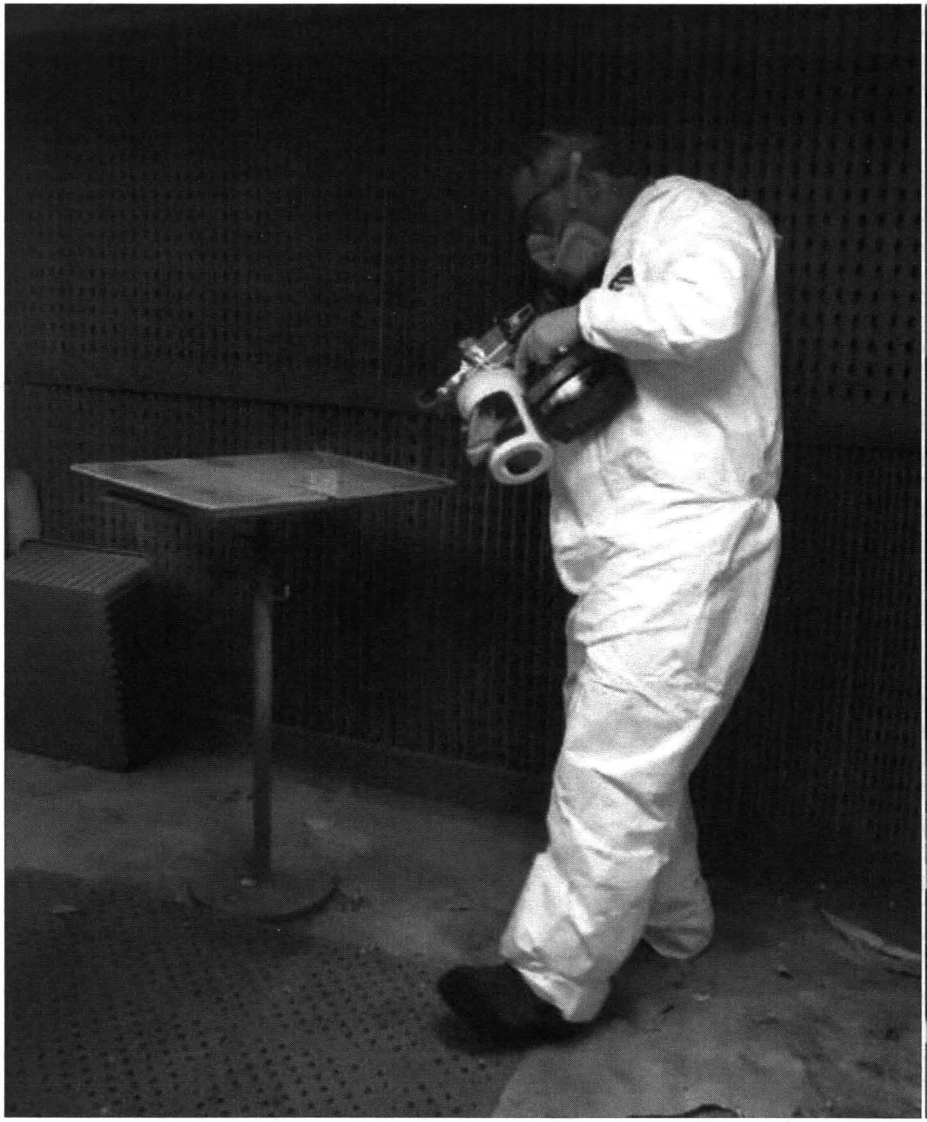
Round 1 Testing Summary

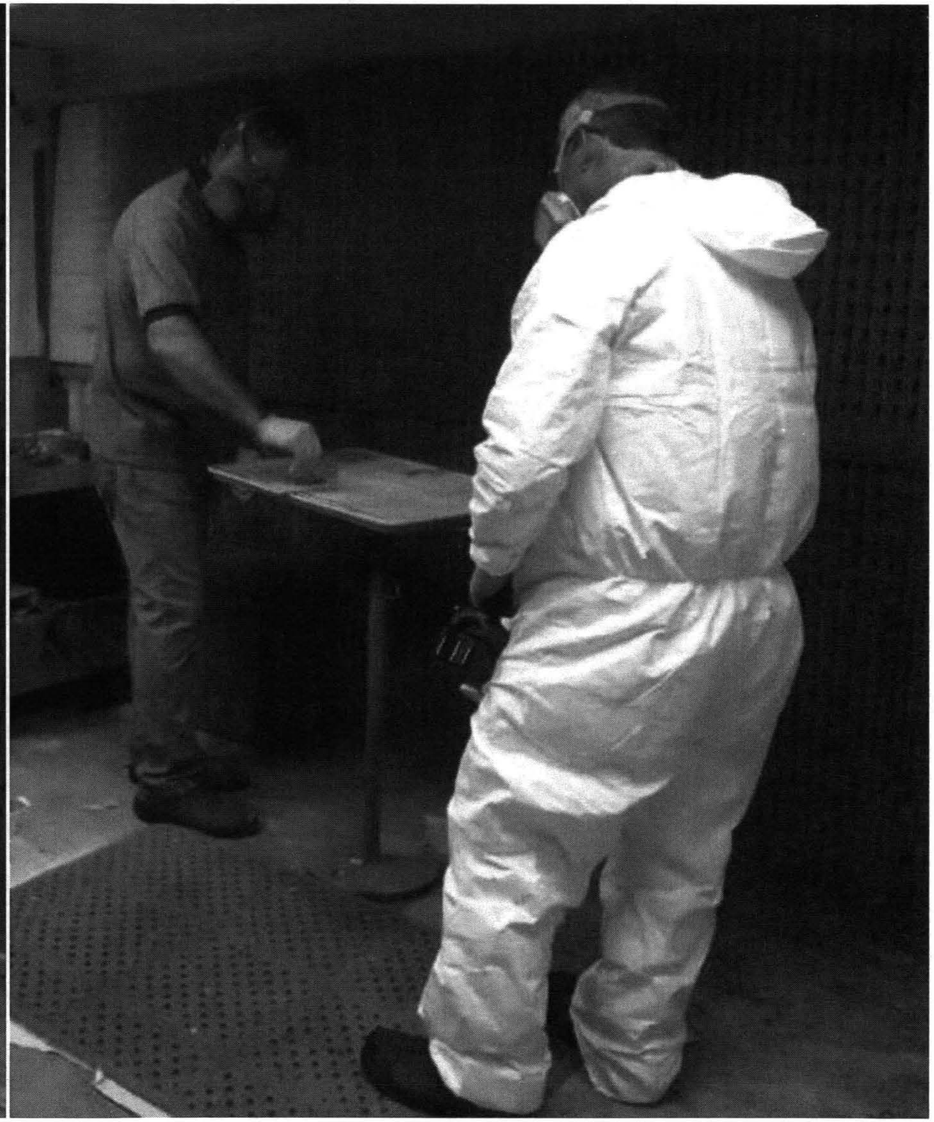
- **Completed test panel preparation**
- **Completed the following tests:**
  - Pot Life
  - Ease of Application
  - Surface Appearance
  - Heat Adhesion Testing
- **Atmospheric Exposure Testing currently underway**
- **Determining which alternatives are showing acceptable performance and will be subjected to Phase 2 Tests**

Test Panel Preparation

- 4 inches x 6 inches x 3/16 inches
- ASTM A 36 (*Standard Specification for Carbon Structural Steel*) hot rolled carbon steel
- Composite panels have 1" channel welded on the front face
- Panels were abrasive blasted to a white metal per SSPC-SP-5 (*White Blast Cleaning*) to remove any mill scale and weld slag
- Anchor profile created by the abrasive blasting was measured ranging from 2.5 to 3.0 mils (1 mil = 0.001 inches)

Test Panel Preparation

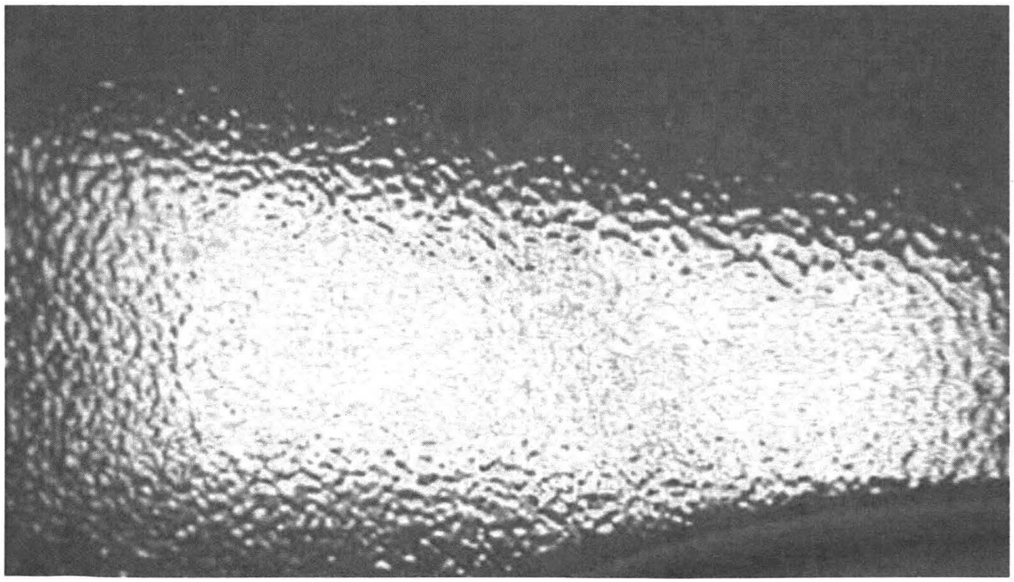


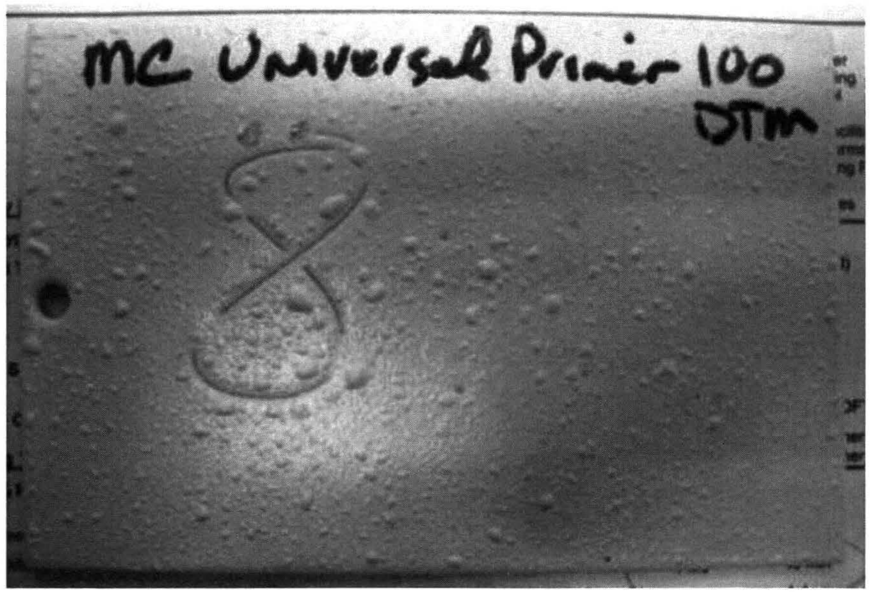


Preparation of Test Panels and Quality Control Check

Pot Life, Ease of Application and Surface Appearance

- Pot Life Test provides data to characterize the pot life envelope.
- Ease of Application determines how easily a coating system may be applied.
- Surface Appearance examines the surface for coating defects.





Heat Adhesion Testing

- Evaluates the performance of primers after exposure to prolonged heat as required by NASA-STD-5008B.
- Purpose is to identify a coating's resilience after exposure to high temperatures
- Flat primer-only coated panels will be tested for tensile adhesion using ASTM D 4541 (*Standard Test Method for Pull-off Strength of Coatings Using Portable Adhesion Testers*).
- The same primer-only coated panels are then be exposed in a high temperature oven to a temperature of 750° F for 24 hours and allowed to cool at room temperature.
- The coating is then be re-tested for tensile adhesion to check for adhesion loss or film deterioration caused by the heating.

Round 1 Completed Testing Results as Compared to Baseline System

System	*Pot Life*	*Ease of Application*	*Surface Appearance*	*Heat Adhesion*
1 (Iso-free)	✗	✗	✓	✗
2 (Iso-free)	✓	✓	✓	=
3 (Zinc-free)	✓	✓	✓	✗
4 (Iso-free)	✓	✓	✓	=
5 (Iso-free + Zinc-free)	✓	✓	✓	✗
6 (Iso-free + Zinc-free)	✓	✓	✓	✗
7 (Iso-free + Zinc-free)	✓	✓	✓	✗
8 (Iso-free + Red. Zinc)	✓	✓	✓	✗
9 (Iso-free + Zinc-free)	✓	✓	✓	✗
10 (Zinc-free)	✗	✗	✓	✗

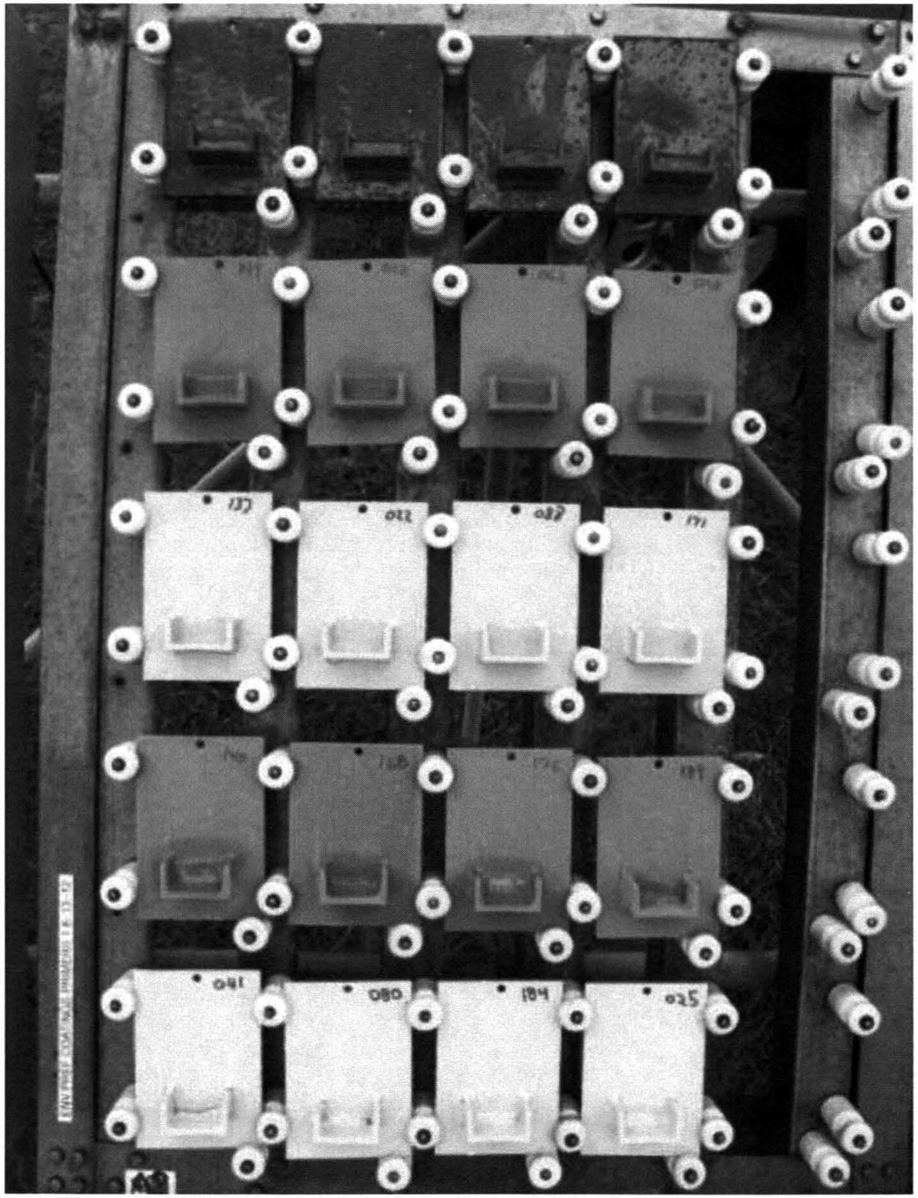
Atmospheric Exposure Testing

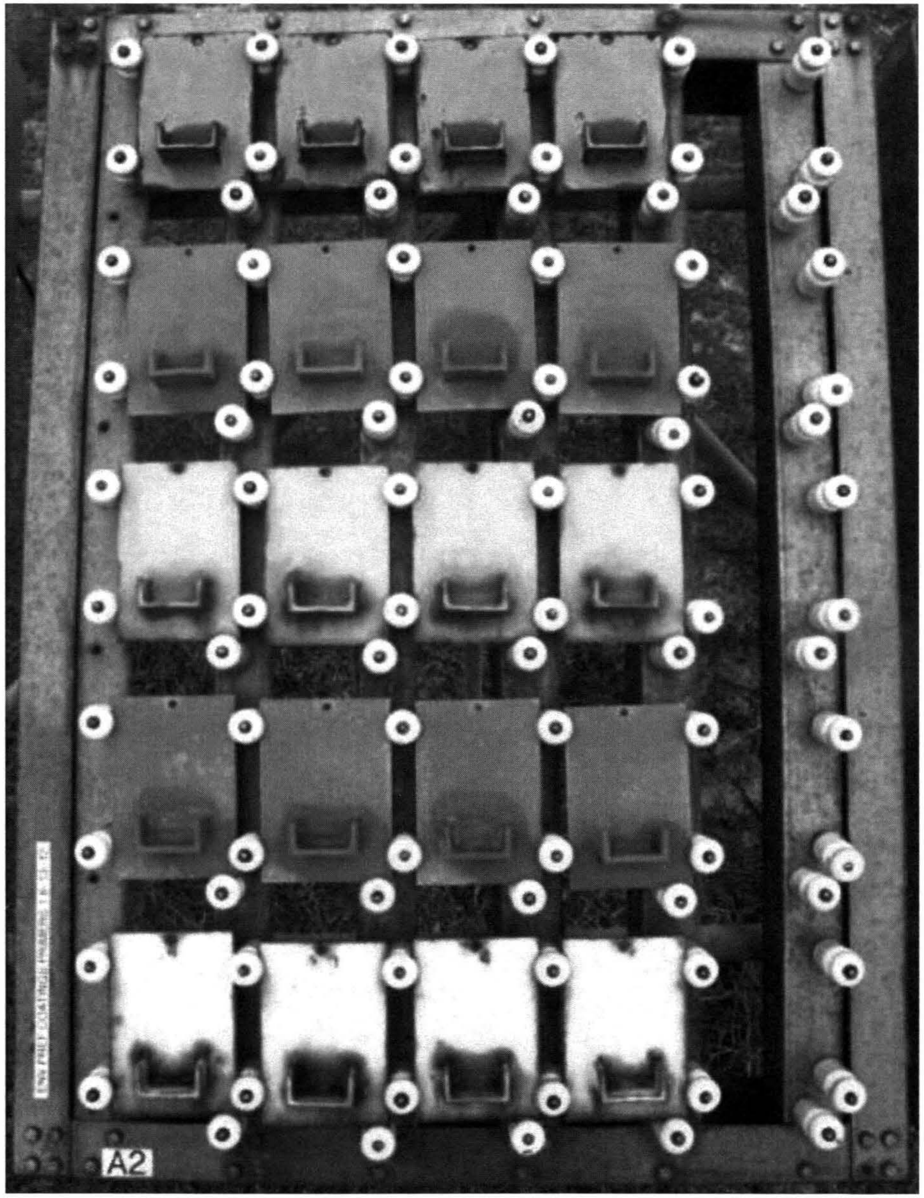
- **Test panels were placed at the KSC Beachside Atmospheric Test Facility.**
  - Test racks located approximately 150 feet from Atlantic Ocean high tide line.
- **Panels evaluated for:**
  - Color Changes
  - Gloss Retention
  - Corrosion Ratings
- **Round 1 exposure initiated on 08/23/12.**

Atmospheric Exposure Testing

System	*Atmospheric Exposure Testing as Compared to Baseline System (after 12 months)*			
	Corrosion	*Scribe*	*Color*	*Gloss*
1 (Isocyanate-free)	✗	✗	✗	✗
2 (Isocyanate-free)	✓	✓	✓	✓
3 (Zinc-free)	=	✗	=	✓
4 (Isocyanate-free)	✓	✓	=	✗
5 (Isocyanate- + Zinc-free)	✗	✗	✗	✗
6 (Isocyanate- + Zinc-free)	=	✗	=	✗
7 (Isocyanate- + Zinc-free)	✗	✗	=	✓
8 (Isocyanate-free + Red. Zinc)	=	✗	=	✗
9 (Isocyanate- and Zinc-free)	✓	✓	✗	✗
10 (Zinc-free)	=	✗	=	=

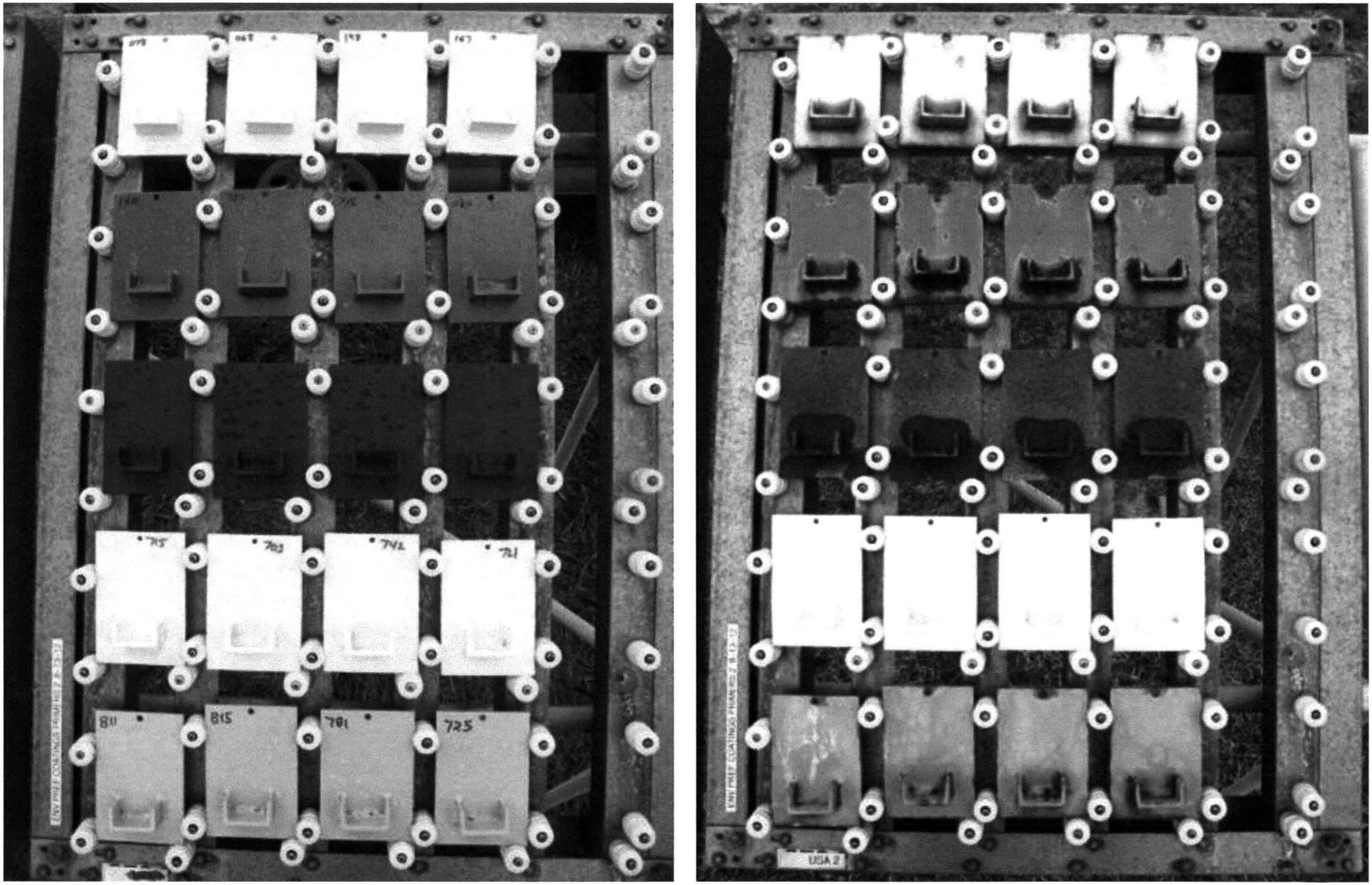
Atmospheric Exposure Testing





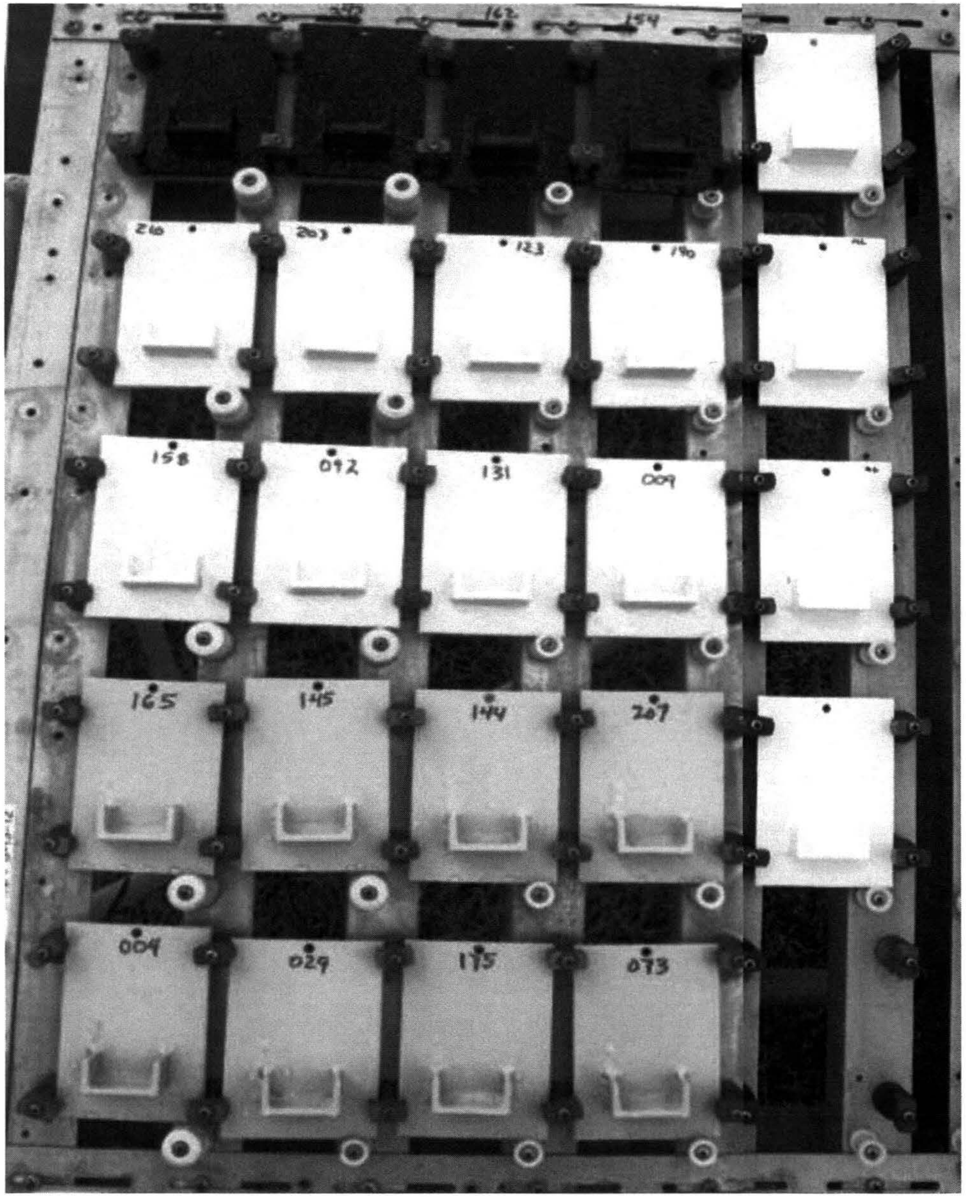
Primers-only Rack 1 – Initial and after 12 months

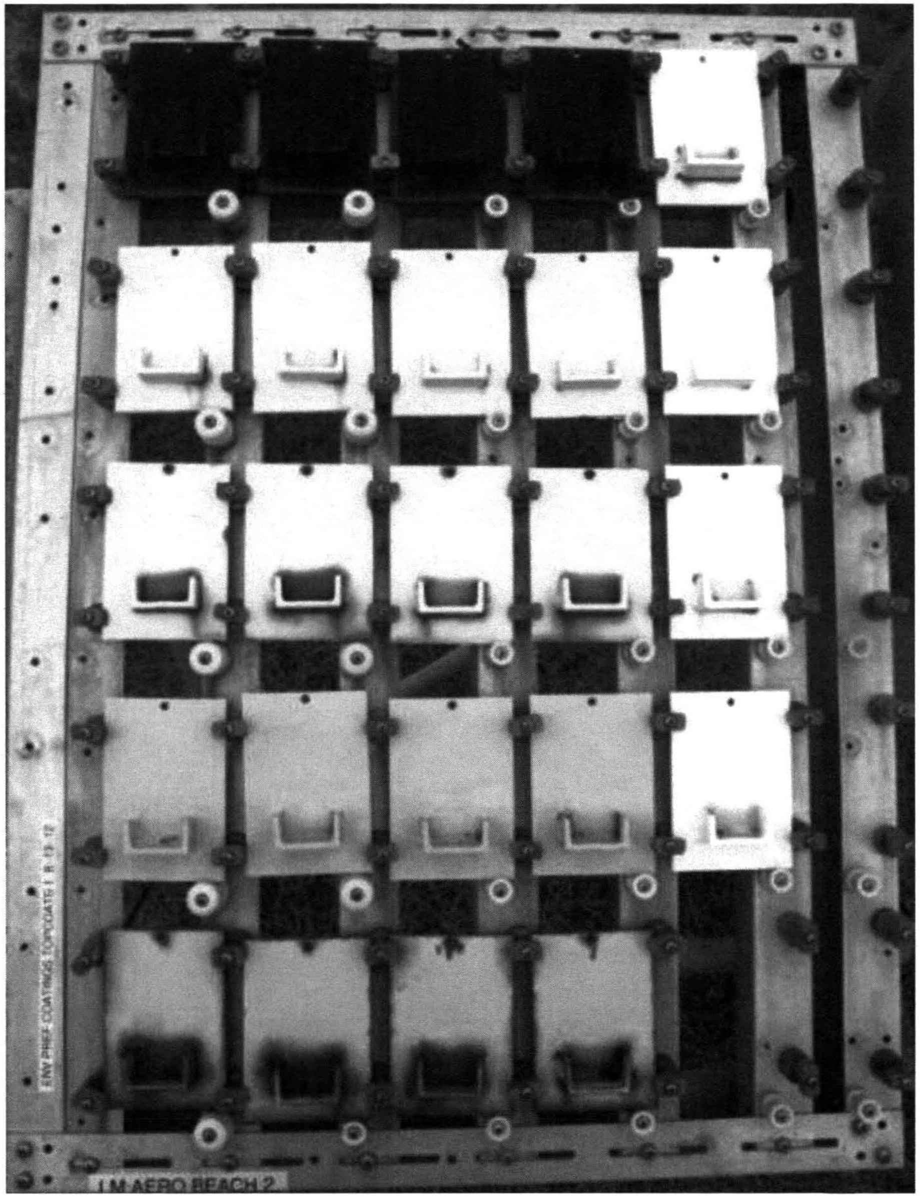
Atmospheric Exposure Testing



Primers-only Rack 2 – Initial and after 12 months

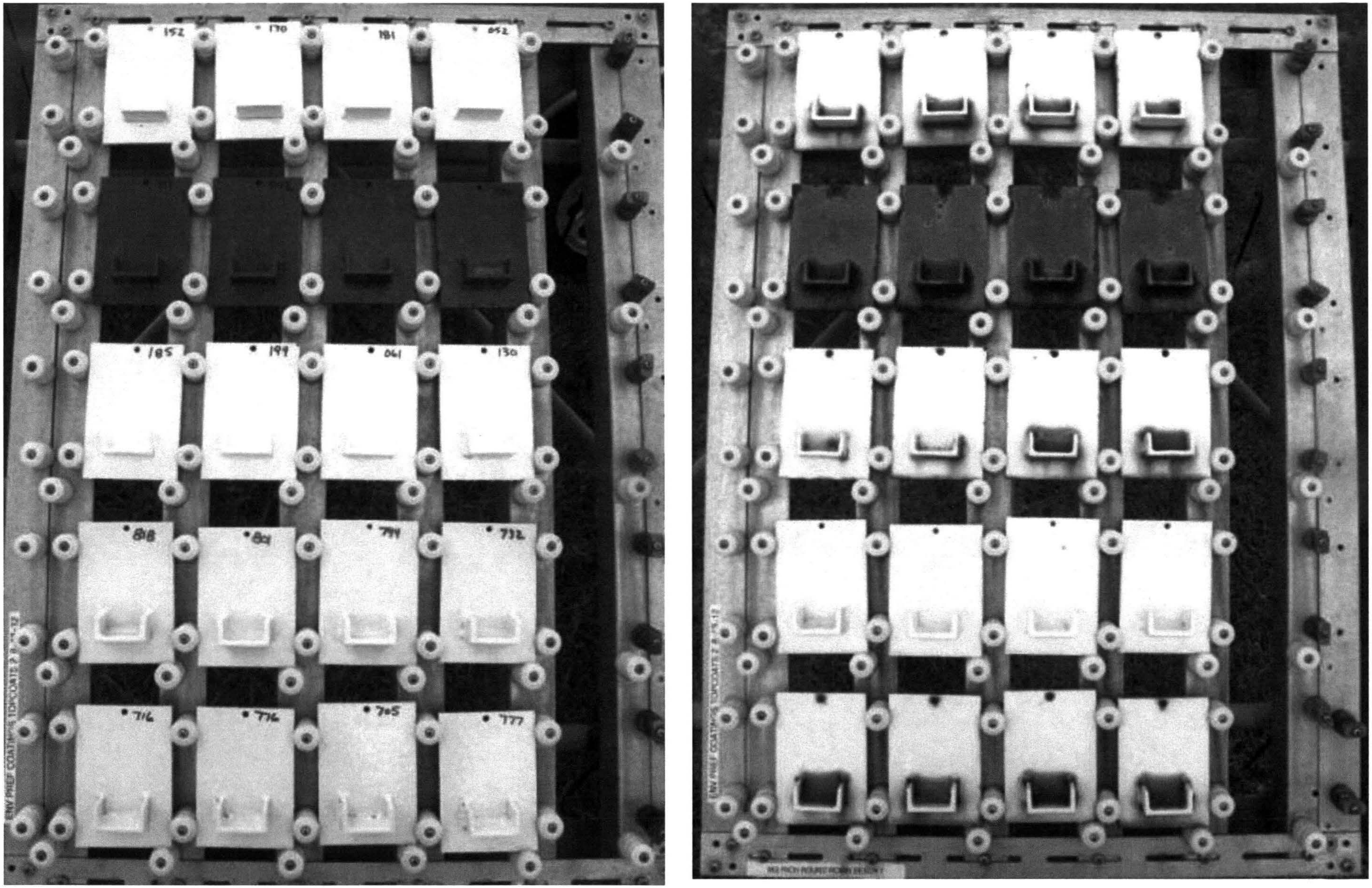
Atmospheric Exposure Testing





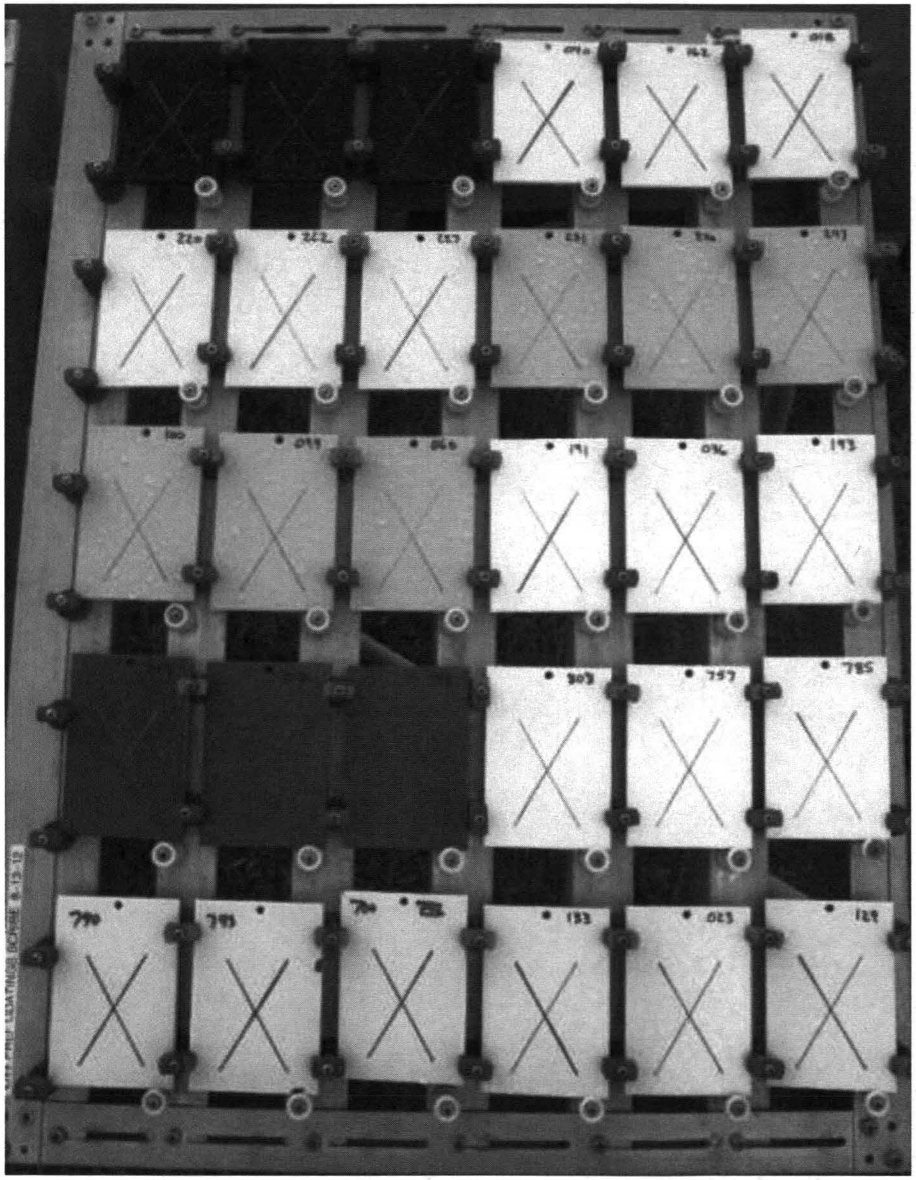
Full Systems Rack 1 – Initial and after 12 months

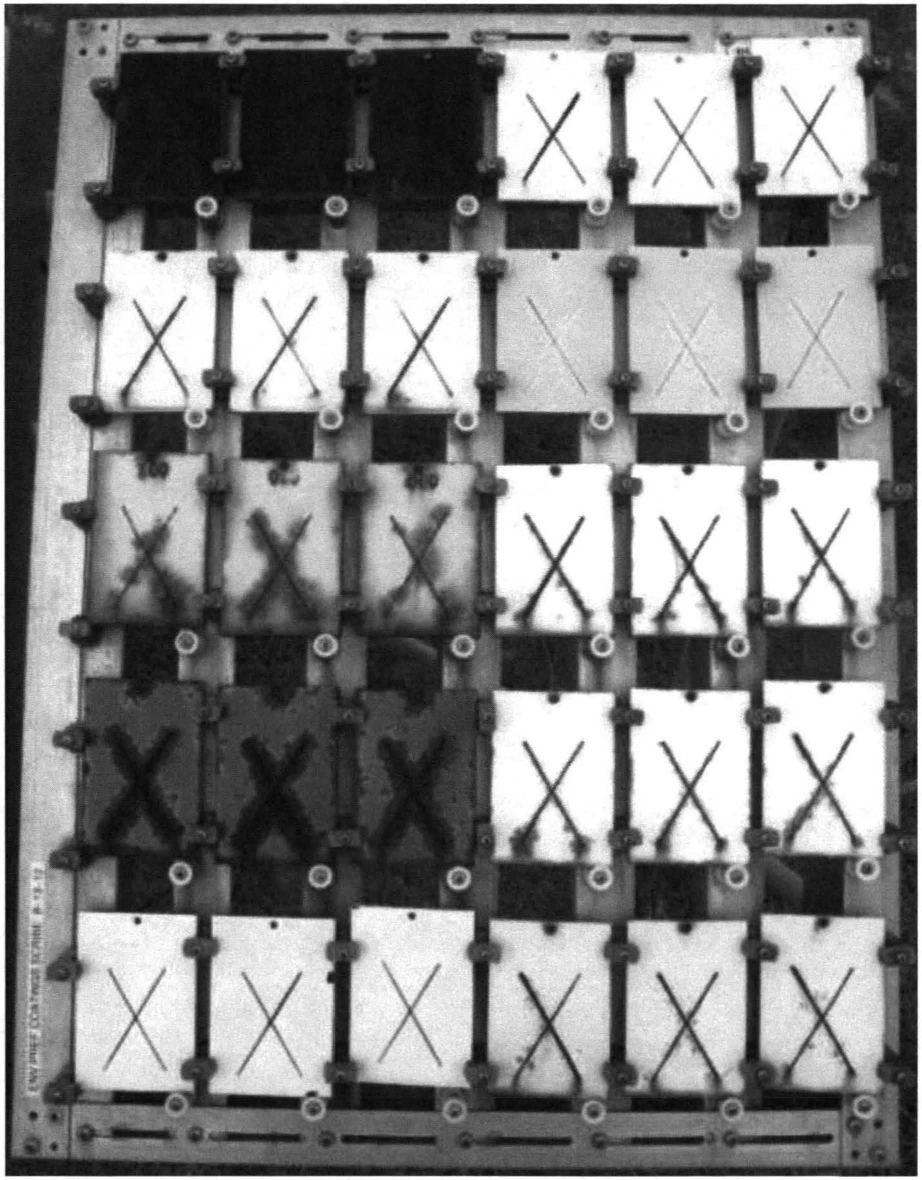
Atmospheric Exposure Testing



Full Systems Rack 2 – Initial and after 12 months

Atmospheric Exposure Testing





Full Systems Scribed – Initial and after 12 months

Round 2 Selection of Alternatives

- **Identified 23 commercially available potential alternatives**
- **Project stakeholders reviewed information and discussed advantages and disadvantages to down-select those to include in testing**
- **Selected nine (9) alternative coating systems:**
  - Two (2) zinc-free and isocyanate-free systems
  - Two (2) isocyanate-free systems (contain zinc)
  - Three (3) zinc-free systems (contain isocyanates)
  - Two (2) systems containing zinc and isocyanates

For more information visit the NASA TEERM Website:

http://www.teerm.nasa.gov/AltNitricAcidPassivation.htm

http://www.teerm.nasa.gov/EnvPrefLaunchCoatings.htm

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