AFRL Nonchrome Coatings R&D and Accelerated Testing

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AFRL/MLBT

NASA International Workshop on Pollution Prevention & Sustainable Development

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AFRL

THE AIR FORCE RESEARCH LABORATORY

LEAD I DISCOVER I DEVELOP I DELIVER

AFRL/MLBT Coatings Research Group

- Charter: R&D for advanced protective coatings
  - Corrosion, rapid cure, LO, thermal control, etc.
  - Work closely with AFRL Coatings Technology Integration Office (CTIO) and AF/CPCO for evaluation and transition
- In-House R&D
  - Surface analysis; electrochemistry; formulation; polymer synthesis
  - Initiate and accelerate coating technology development
- External contractual R&D
  - SBIR / STTR
  - CII

Current Facts and Rules of the Game

FROM: ASC/OL-MA, MARIETTA GA
SENT: 17 OCTOBER 2006

TO: F-22A E-MAIL GROUP

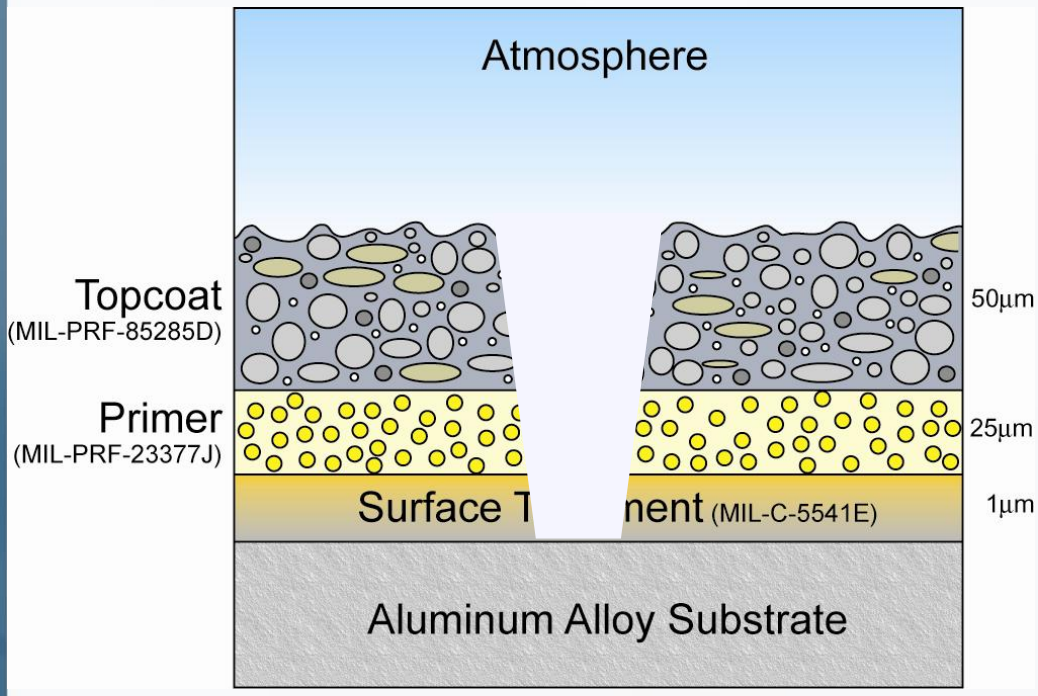
SUBJECT: F-22A: IMMEDIATE USE OF SOLVENT BORNE CHROMATED PRIMER ON ALUMINUM PANELS SKINS, AND STRUCTURE

IMPORTANCE: HIGH

UNCLAS

- Air Force cannot make any sacrifices in corrosion protection for nonchrome technologies
  - Cost of corrosion estimated in the billions annually

Protection Mechanism for AF Coatings

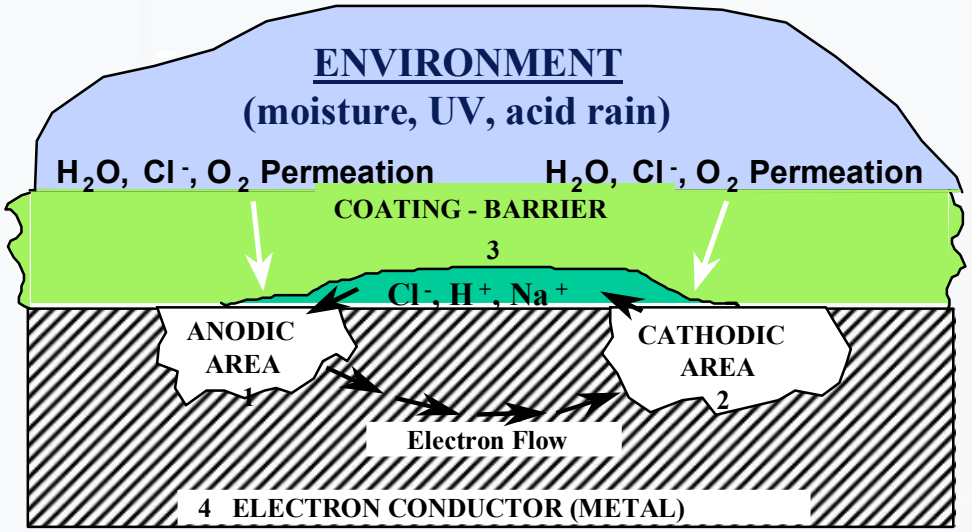


Requires inhibitor pigments to dissolve, migrate to scribe, react with alloy surface

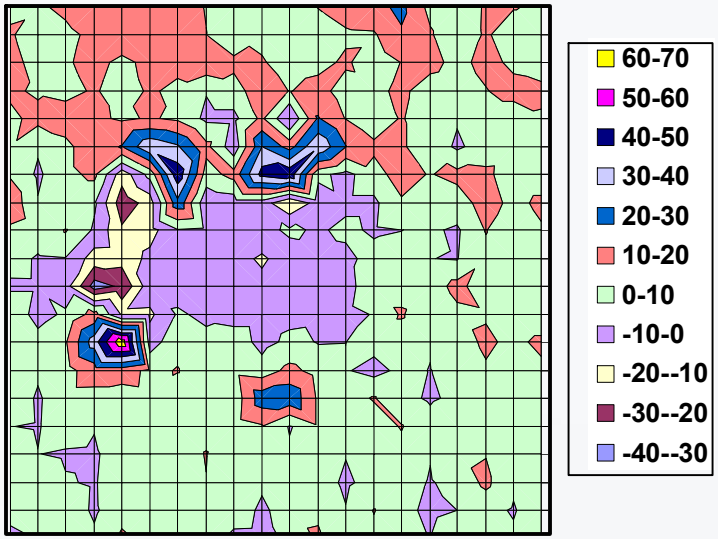
- Passive Protection
  - Develop and maintain a barrier to electrolyte
  - Nonporous coatings (e.g., Defthane ELT APC)
  - Coatings with good adhesion, flexibility & toughness
- Active Protection
  - Rely on inhibitors once barrier properties breached
  - Inhibitors must dissolve (requires water) to be active
  - Inhibitor ions must migrate to exposed substrate and react to passivate the corrosion cell (diffuse through the paint film)

Challenge #1: Identification of effective alternative nonchrome inhibitors

Scanning-Vibrating Probe (SVP) Analysis

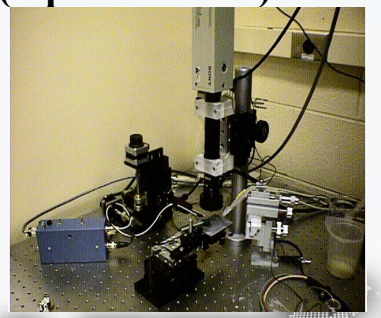


Simplified corrosion cell; copper intermetallic species in the alloy act as cathodic initiation sites

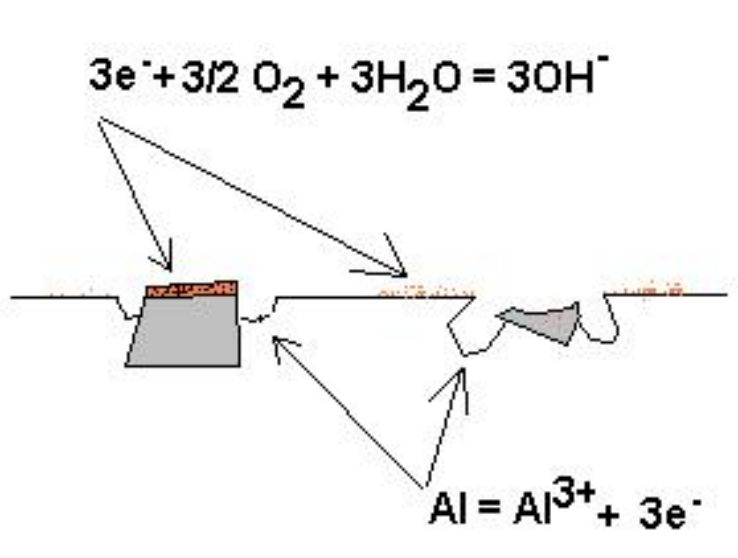


Real time mapping of corrosion sites using SVP (top down view)

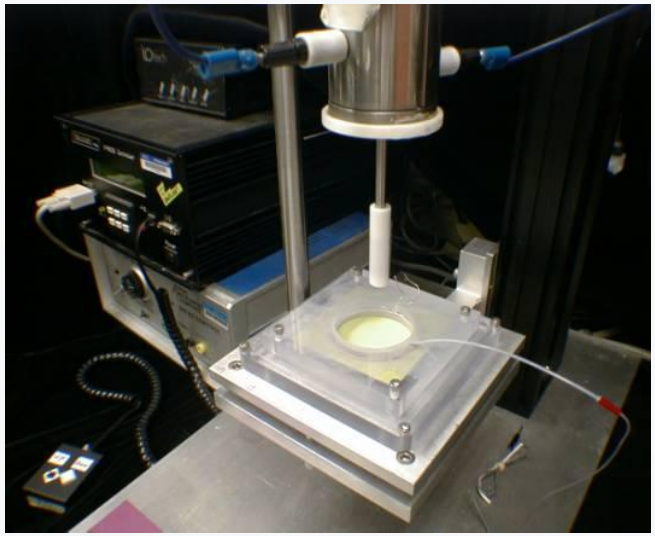
- *Cr(VI) is unique in that it actively suppresses both the cathodic and anodic sites*
- *No single nonchrome inhibitor tested thus far functions in this manner*



Rotating Disk Electrode (RDE) Analysis



Oxygen reduction reaction (ORR) at intermetallic sites is responsible for corrosion initiation and growth



RDE Setup (courtesy of Rockwell Sci.) used to measure inhibitor efficacy and minimum concentration required

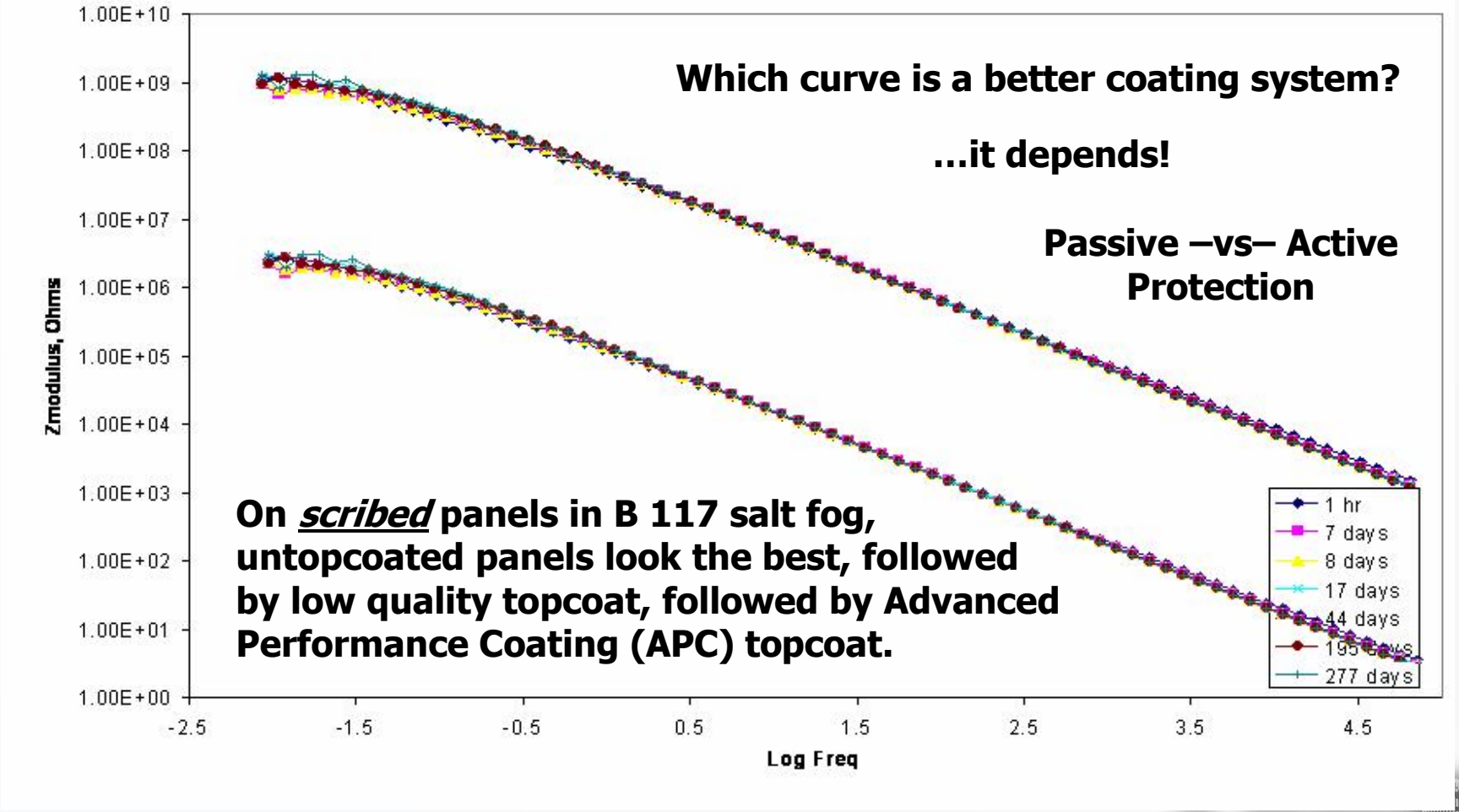
- *Cr(VI) is unique in that it is effective at suppressing the ORR at extremely low ion concentrations*
- *The best nonchrome inhibitors typically require an order of magnitude greater concentration*

Challenge #2: Delivery of the identified nonchrome inhibitor

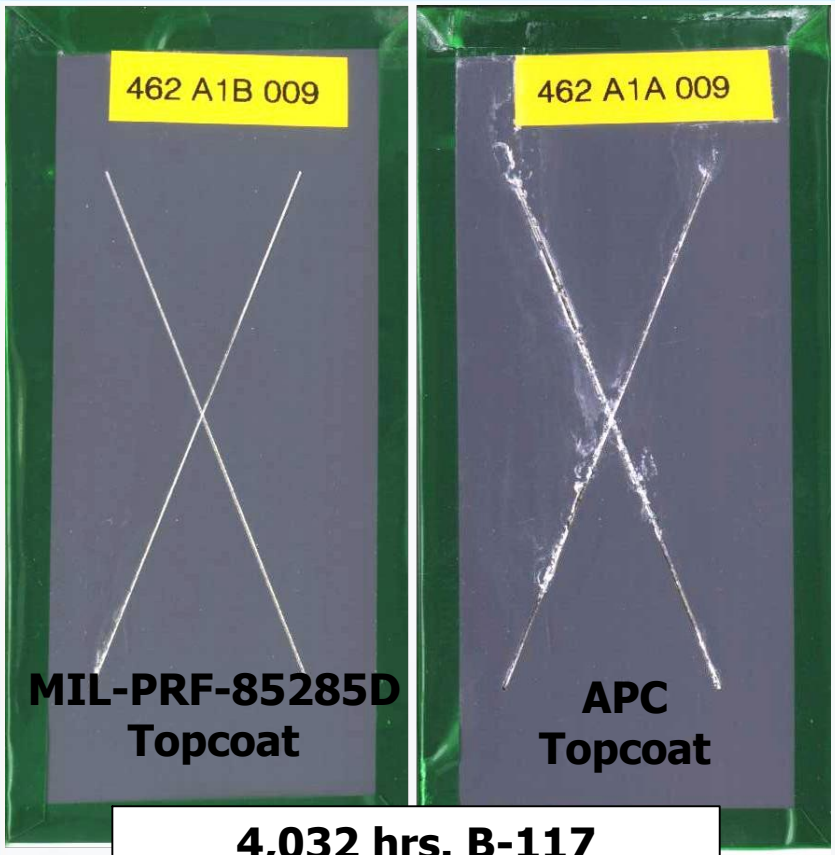
Inhibitor Delivery Mechanism

- Currently there is not enough R&D investment in understanding the optimum delivery method of NC inhibitors
- Inhibitors require water to dissolve and become mobile and effective
  - Inhibitors that are too soluble could flush out or cause blistering
- Water permeability and inhibitor ion mobility performance is dependent upon the coating system (primer + topcoat)
- Virtually no R&D investments being made in tailoring primer resin chemistry to work with a specific inhibitor
- Nonchrome pigments act different!
  - Some more soluble while others are less soluble
  - All require higher ion concentrations for effectiveness

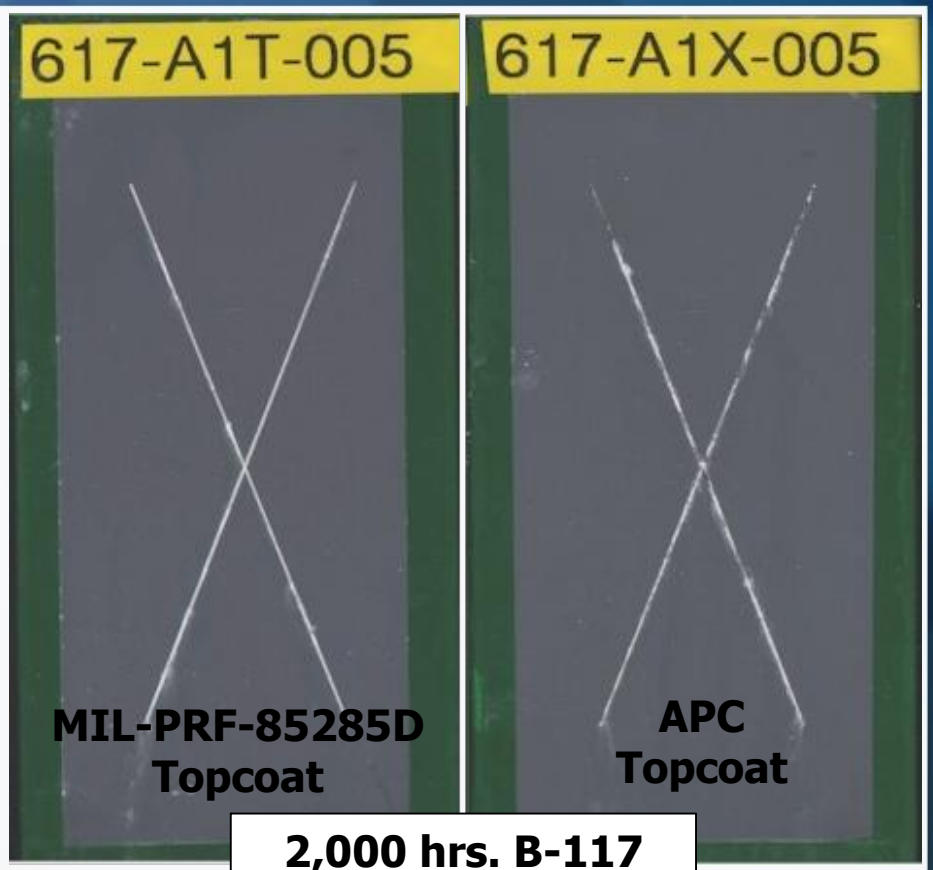
Electrochemical Impedance Spectroscopy (EIS) Analysis



ASTM B 117 Salt Fog Discrepancies due to Polyurethane Topcoat

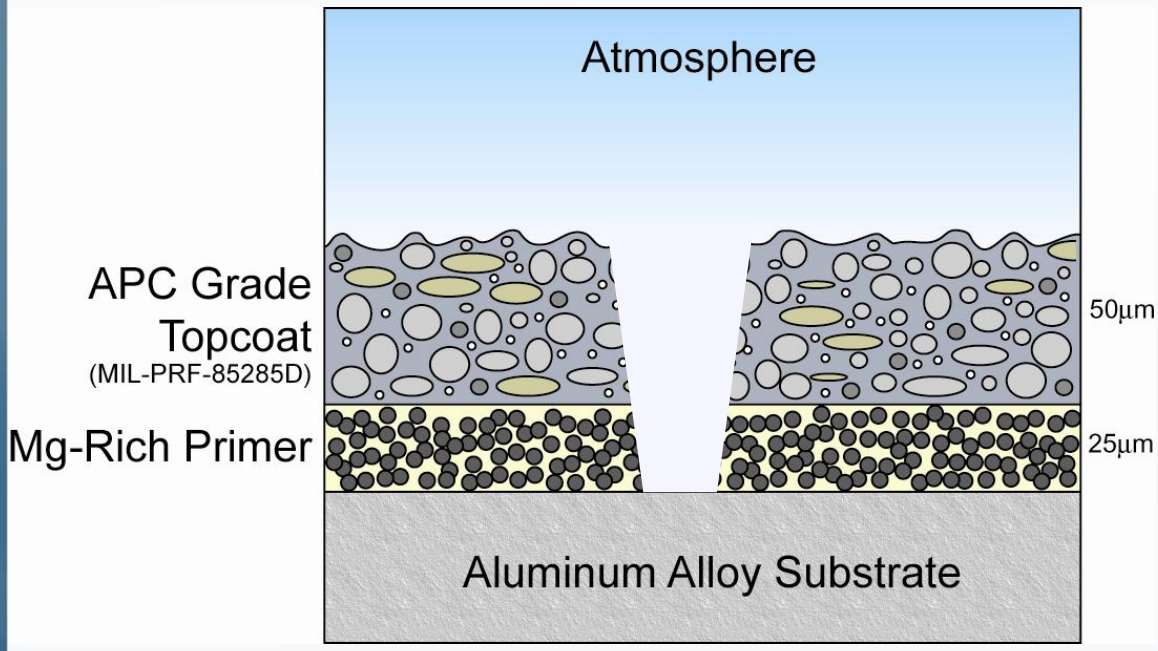


4,032 hrs. B-117
MIL-DTL-81706
MIL-PRF-23377J, Class C2



2,000 hrs. B-117
Alodine 5200™
Sicopoxy™ 577-630

Cathodic Protection of Al Alloys: Magnesium Rich Primer



Cathodic protection allows greater throwing power & should require less water permeability and be less alloy specific

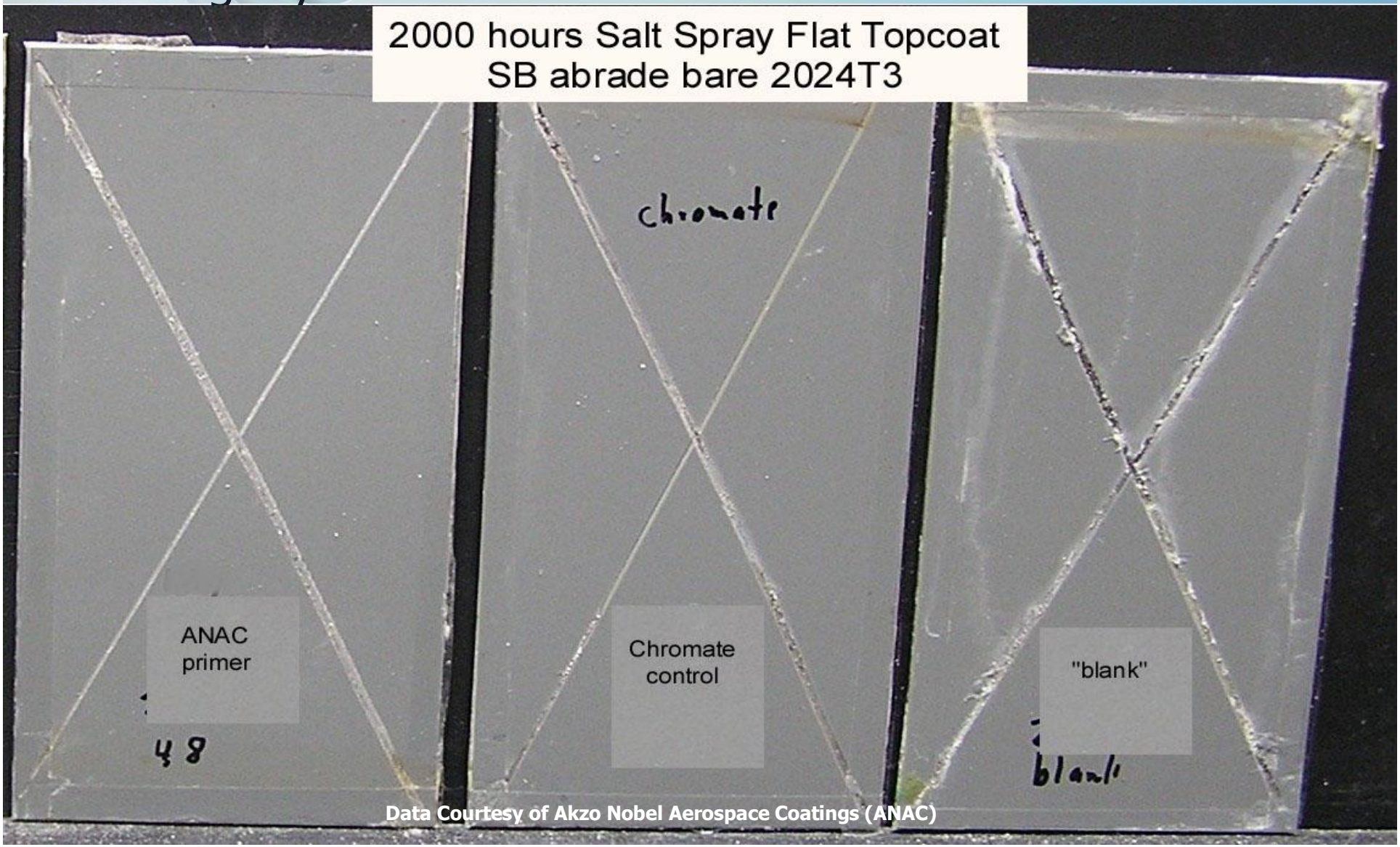
- Concept Developed by NDSU
- Technology Licensed and Product Developed by Akzo Nobel
- Mg-rich primer functions via cathodic protection
  - similar to Zn-rich primers for steel
  - MgO denser than Mg
- Does not use "inhibitors"
- No surface treatment required (or desired)
  - does work with PreKote & AC-131 (Boegel)

Mg-Rich Primer

- MIL-PRF-23377 resin system with Mg substituted for strontium chromate pigment (@ ~50% PVC)
- Essentially all other paint properties similar to conventional primer
- Formulated wet paint has no specific safety concerns with regard to Mg pigment
- Cured paint films are no more flammable than controls
- All samples thus far have passed hydrogen embrittlement testing
- Currently evaluating performance under various conditions and on NASA specialty aluminum alloys

Bare 2024T3 B117:

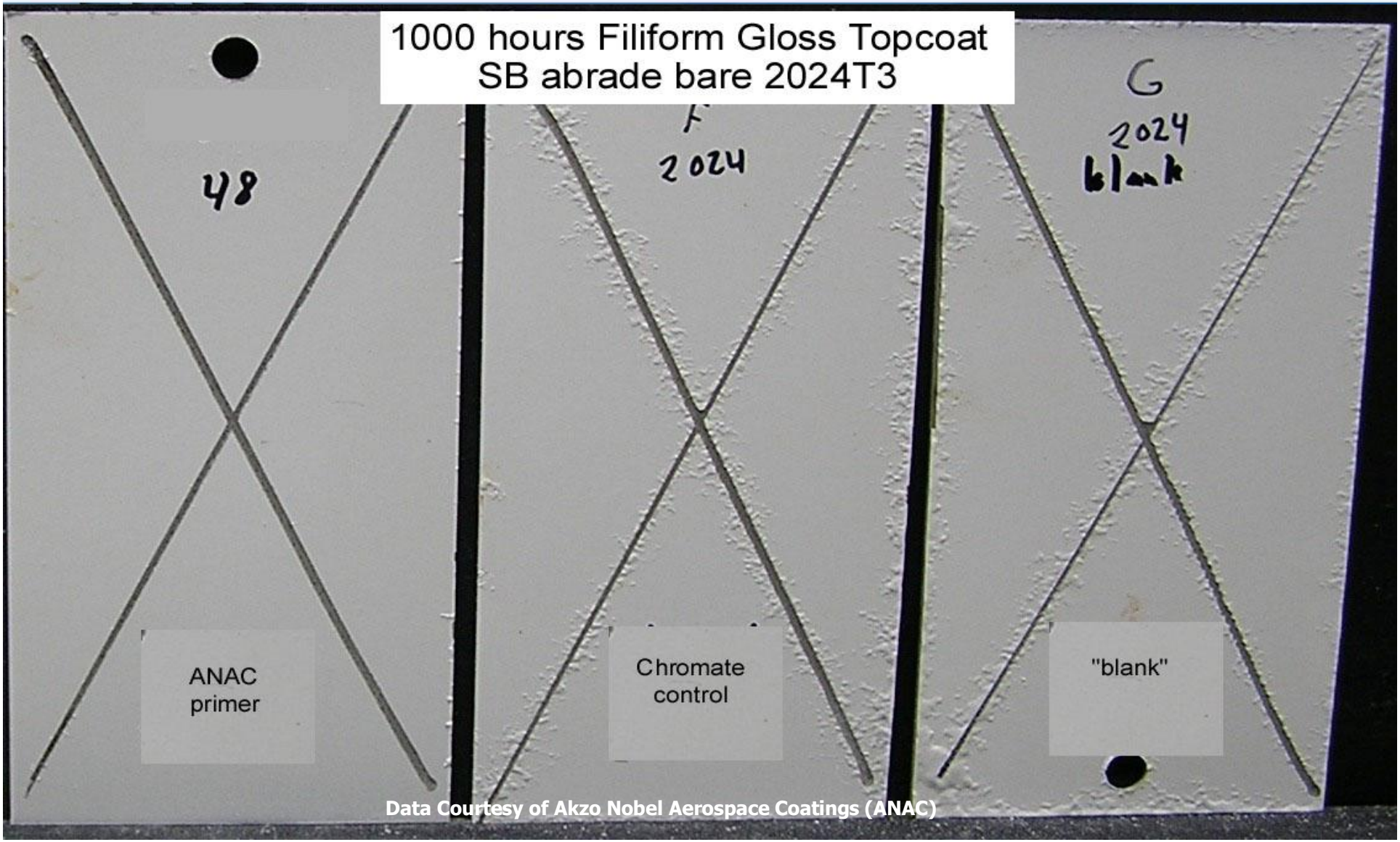
Slightly better than control



Data Courtesy of Akzo Nobel Aerospace Coatings (ANAC)

Bare 2024T3 Filiform:

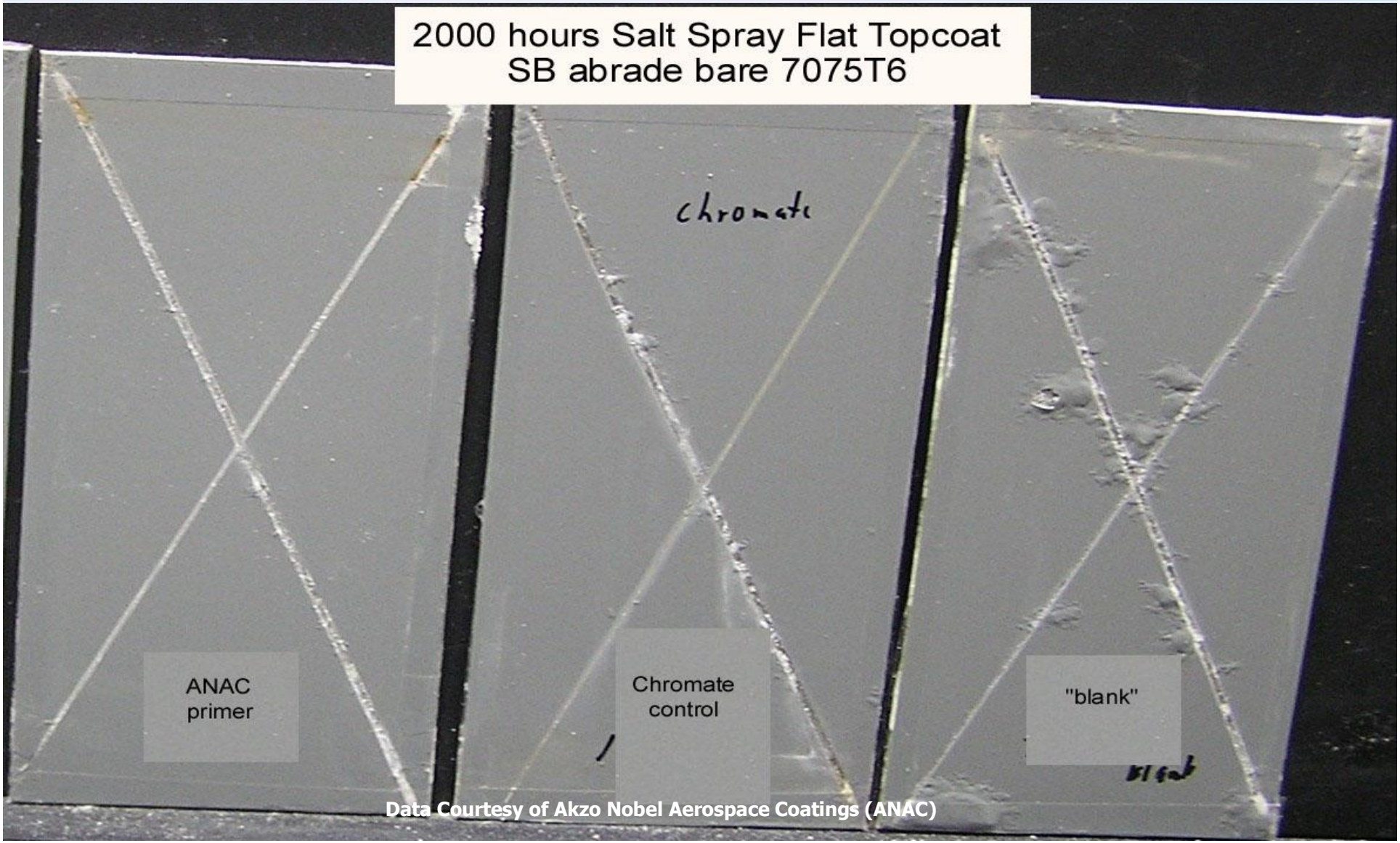
Much better than control



Data Courtesy of Akzo Nobel Aerospace Coatings (ANAC)

Bare 7075T6 B117:

Better than control



Data Courtesy of Akzo Nobel Aerospace Coatings (ANAC)

Perspectives on Nonchrome Inhibitors

- Cr works well because it has ideal solubility (low for strontium chromate) and is effective at extremely low ion concentrations
- We can screen potential Non-Cr inhibitors using electrochemistry for effectiveness but it does not tell the whole story
- R&D needs to be done on how to engineer these inhibitor pigments and coating formulations for proper delivery in films
  - Water permeability into the films must be addressed
  - EIS best for evaluation of barrier component to protection
- Non-Cr inhibitors are therefore much more finicky!
  - Coating "System Level" approval will be crucial
  - Cleaning methods to address Cu intermetallics may be key
  - May need to rely on good flexibility and adhesion to limit dependence on active protection
  - *Non-Cr needs help from the rest of the coating system*

Corrosion R&D Portfolio Snapshot

- 2 SBIR Phase II's to develop aluminum cleaners to selectively remove copper from surfaces
- 2 SBIR Phase II's for non-chrome "unicoat" (used with Alodine)
- CII Program with PPG for non-chrome primer and surface treatment
- Modeling and experimental validation of water, chloride, and inhibitor diffusion in films (in-house)
- Galvanic corrosion of LO materials (in-house)
- Development of advanced accelerated corrosion test methods (in-house)
- Mg-Rich primer validation and integration (OSD)
- Development of high flexibility primer resin systems (in-house)

Qualification and Transition of Nonchrome Technologies

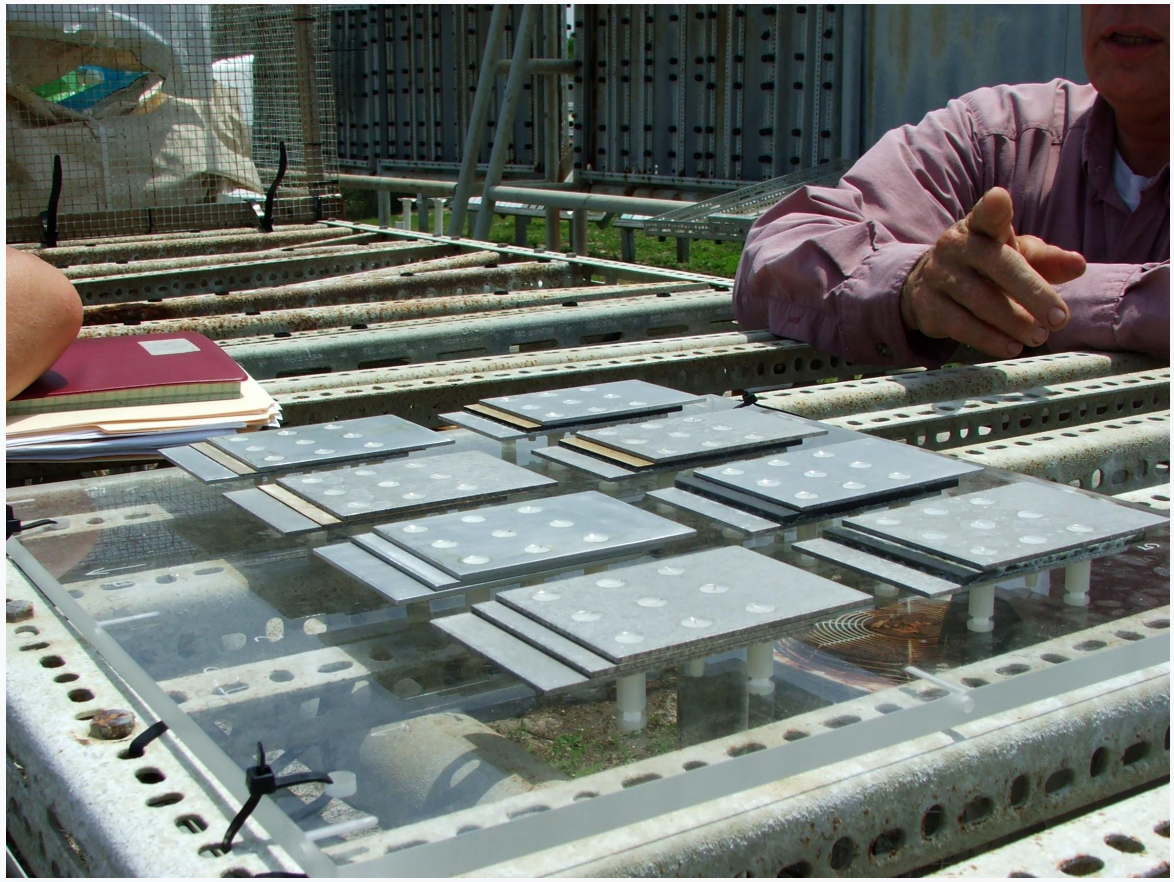
Qualification

- Currently, separate MIL-SPECs for cleaning, surface treatment, primer, topcoat
  - Mixing and matching can cause problems
- CTIO working towards "system level" MIL-SPEC
  - Essential for proper transition of nonchrome
  - Updated performance for weatherability
  - Many potential permutations of material combinations
- But, just because a material is listed on a Qualified Product List (QPL) does not guarantee its successful **transition** and widespread use
- For corrosion, testing beyond pristine lab panels in qualification tests will be essential

Additional Corrosion Testing

- Evaluation on panels with fasteners
  - Evaluation of galvanic induced corrosion
  - Steel (with and without Cd plating), aluminum, titanium fasteners
- Early limited flight demonstrations on non-critical structures
  - C-130 upper wing hatches
- Outdoor testing at Daytona Beach
  - Extremely aggressive corrosion environment
- Artificial lap joints
  - Capable of trapping electrolyte
  - Fabricated with various dissimilar metal sheets and fasteners

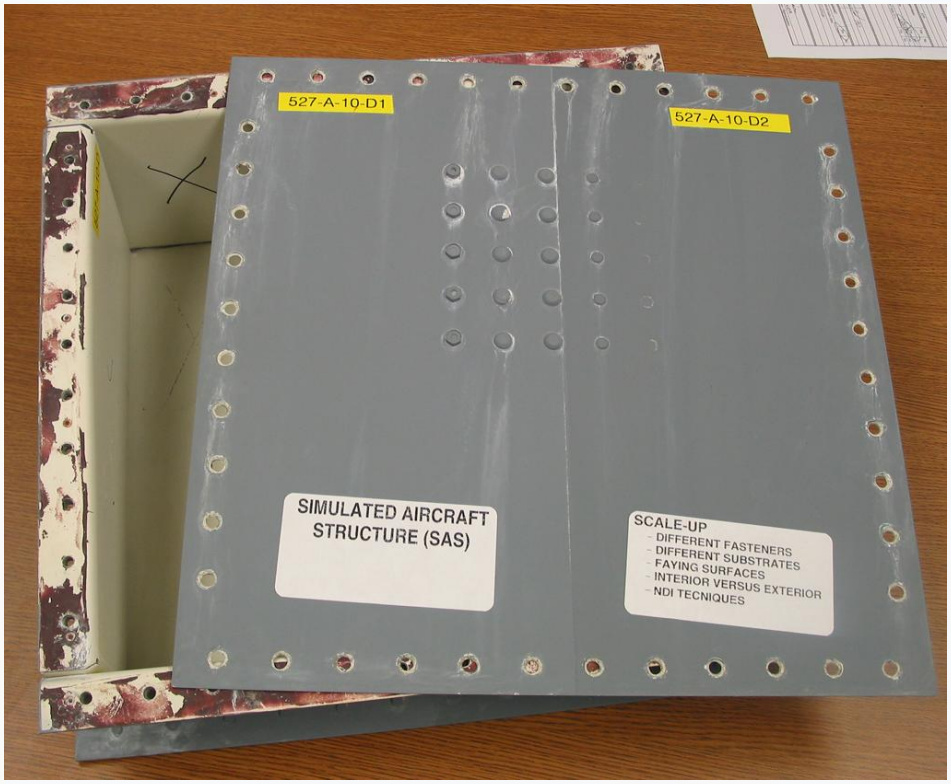
Daytona Beach Testing

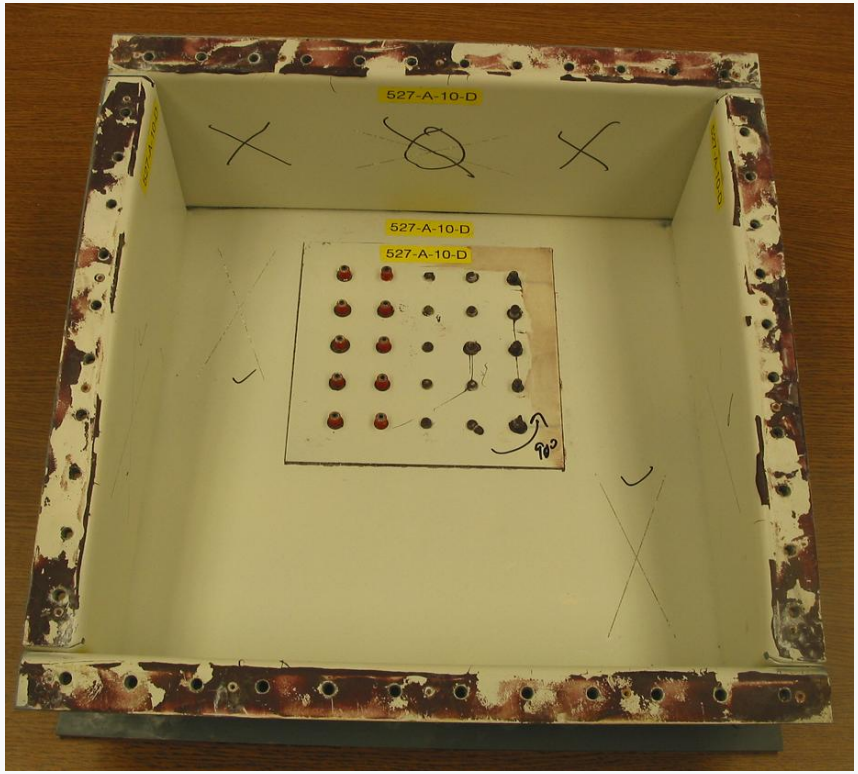


Artificial Lap Joints

Chromate Control after 7 yrs!

Simulated Aircraft Structures (SAS) Boxes

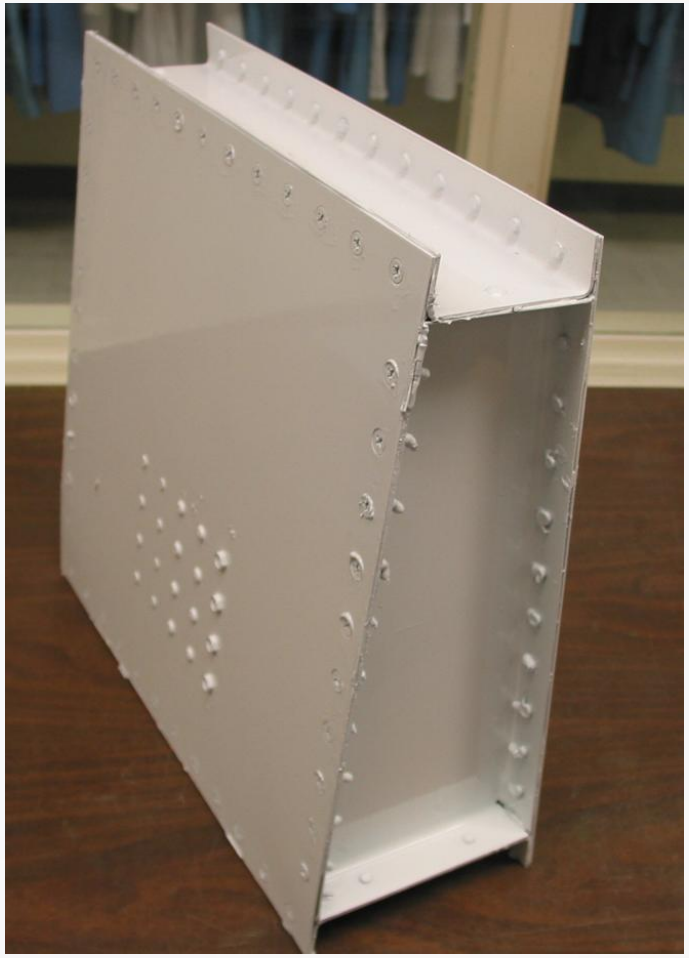




- Miniature version of a wing box
- Capable of evaluating IML and OML coatings
- Can be sealed or unsealed on assembly
- Can have 2024 and 7075 mixed and matched

- Side by side coating evaluations
- Interior and exterior scribes
- Cu sulfate in seams to accelerate corrosion

Simulated Aircraft Structures (SAS) Boxes



AFRL Comprehensive SAS Box Evaluation

- Critically assess the utility of SAS boxes as a tool for accelerated lab testing
- Includes Cr(VI) controls as well as promising reduced Cr and Non-Cr; also includes negative controls
- Includes machined "grindout" areas to simulate prior repairs
- Incorporating NDE through paint evaluation
- All have doublers with 5 different fasteners (half with Cd plating removed)
- Limited use of sealant and Copper sulfate applied to seams to accelerate corrosion
- All raised fastener heads backed out to break the "paint bridge"

SAS Box Test Matrix

		Inner and Outer Mold Line				Interior	Outer Mold Line				
System	Assembly Parameters *	Pre Clean	Clean/Wash	De-Ox	Conversion Coat	Interior Primer DFT per MFG	Exterior Primer DFT per MFG	2nd Coating	3rd Coating	4th Coating	Topcoat DFT per MFG
A	Sealed	CTIO Standard Process			Henkel Alodine 1200S	MIL-PRF-23377 Deft 02-Y-40	MIL-PRF-23377 Deft 02-Y-40				MIL-PRF-85285 Deft 99-GY-001 Color 36173
B	Unsealed										
C	Unsealed							Type I or II Conductive	MIL-PRF-23377 Deft 02-Y-40	RAM carbonyl iron	
D	Unsealed					MIL-PRF-85582 Class N PRC DeSoto EWAE118A/B	PRC DeSoto Chrome Polythioether				
E	Unsealed	CTIO Cleaning Process		MEK Wipe			MIL-PRF-85582 Class N PRC DeSoto EWAE118A/B				
F	Unsealed	CTIO Standard Process			Henkel Alodine 1200S	Deft Non-Chrome Waterborne 44-GN-098	Deft Non-Chrome Waterborne 44-GN-098				Applique

SAS Box Test Matrix – Mg-rich

System	Assembly Parameters *	Pre Clean	Clean/Wash	De-Ox	Conversion Coat	Interior Primer DFT per MFG	Exterior Primer DFT per MFG	2nd Coating	3rd Coating	4th Coating	Topcoat DFT per MFG
G	Unsealed	CTIO Standard Process			Henkel Alodine 1200S	MIL-PRF-23377 Deft 02-Y-40	Akzo/NDSU Mg Primer				Akzo PD-5000 Color 36173
H	Unsealed	CTIO Cleaning Process		MEK Wipe							
I	Unsealed	CTIO Cleaning Process		MEK Wipe							
J	Unsealed	Pantheon PreKote -- 3 Step Process									
K	Unsealed	Pantheon PreKote -- 3 Step Process									
L	Unsealed	CTIO Standard Process			AC Tech Bo-Gel AC-131						
M	Unsealed	CTIO Cleaning Process		MEK Wipe				Type I or II Conductive	Akzo/NDSU Mg Primer	RAM carbonyl iron	
N	Unsealed	Pantheon PreKote -- 3 Step Process									
O	Sealed	Pantheon PreKote -- 3 Step Process									Akzo PD-5000 Color 17925
P	Sealed	CTIO Standard Process			AC Tech Bo-Gel AC-131						
Q	Unsealed	Pantheon PreKote -- 3 Step Process				½ Deft Non-Chrome ½ No Primer					Akzo PD-5000 Color 36173
R	Unsealed	CTIO Cleaning Process		MEK Wipe		Akzo/NDSU Mg Primer with White Topcoat					

Mg-Rich SAS Box Test Matrix

No data yet; only 500 hrs. exposure as of today's date

Mg-Rich SAS Box Test Matrix

One week with simulated LO coating stackup

Galvanic corrosion induced by conductive coating layer

Nonchrome Coatings Strategy

- Near-term chrome reduction through chrome-free conversion coatings and pretreatments
  - Cr is very effective; chromate in primers provide bulk protection
  - Surface treatments which provide superior adhesion can rely on the primer for all of the corrosion protection
  - AC-131 and PreKote good examples (no inhibitors)
- Enhanced chrome reduction through non-chrome primers with chromate conversion coatings (CCC)
  - Must rely on chromate in surface treatment to "bridge the gap"
  - Increasingly "system" dependent; requires proper inhibitor solubility & migration throughout film
- Non-chrome systems are becoming a reality – but must require a coating system specification
  - Inhibitors may be required in both primer and surface treatment
  - Very system dependent on performance (including alloys & topcoats)

Questions yet to be Answered

- Which is more important, barrier properties or active inhibition?
- Is a scribed panel realistic?
- Are there synergistic effects in outdoor exposure?
- Are current Cr(VI) coatings too good?
- How long should we expect our OML coatings to last?

AFRL Nonchrome Summary

- Take home points:
  - There is lots of room for error with Cr(VI); not so for Non-Cr
  - Performance of the coating system is key to Non-Cr qualification and implementation
  - Better and more realistic accelerated test methods are required