Collaborative Research with Aerospace/Defense Industry for Hexavalent Chromium Solutions

Greg Morose
November 9, 2021

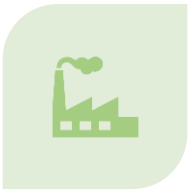
TURI
TOXICS USE REDUCTION INSTITUTE
UMASS LOWELL

Outline

COLLABORATIVE RESEARCH PROCESS

SEALANTS

BOND PRIMERS



CONVERSION COATINGS

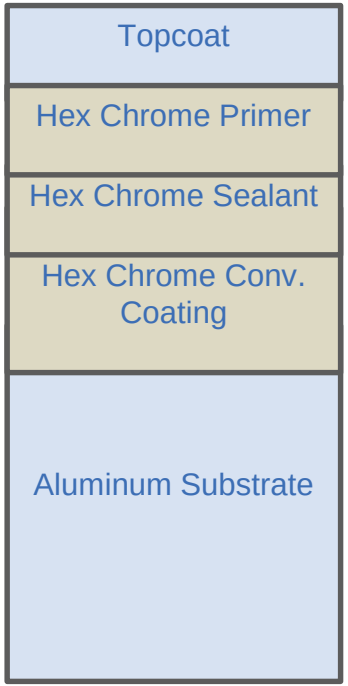
RESULTS

Hex Chrome Free Applications Investigated

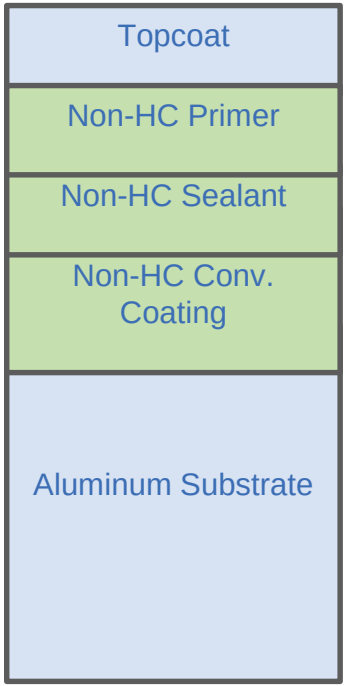
Coating Application	Phase	Timeframe
Sealants	1	2012 - 2014
Bond primers	2	2015 - 2017
Conversion coatings	3	2018 - 2021

Hexavalent Chromium (HC) Coating Stack up

Past/Current State



Hex Chrome Free



Government

Aviation & Missile Command Safety Office

NAVAIR Naval Air Systems Command

AFRL The Air Force Research Laboratory Lead | Discover | Develop | Deliver

NASA

Industry

LOCKHEED MARTIN

NORTHROP GRUMMAN

BOMBARDIER the evolution of mobility

Raytheon

TEXTRON AVIATION

BOEING

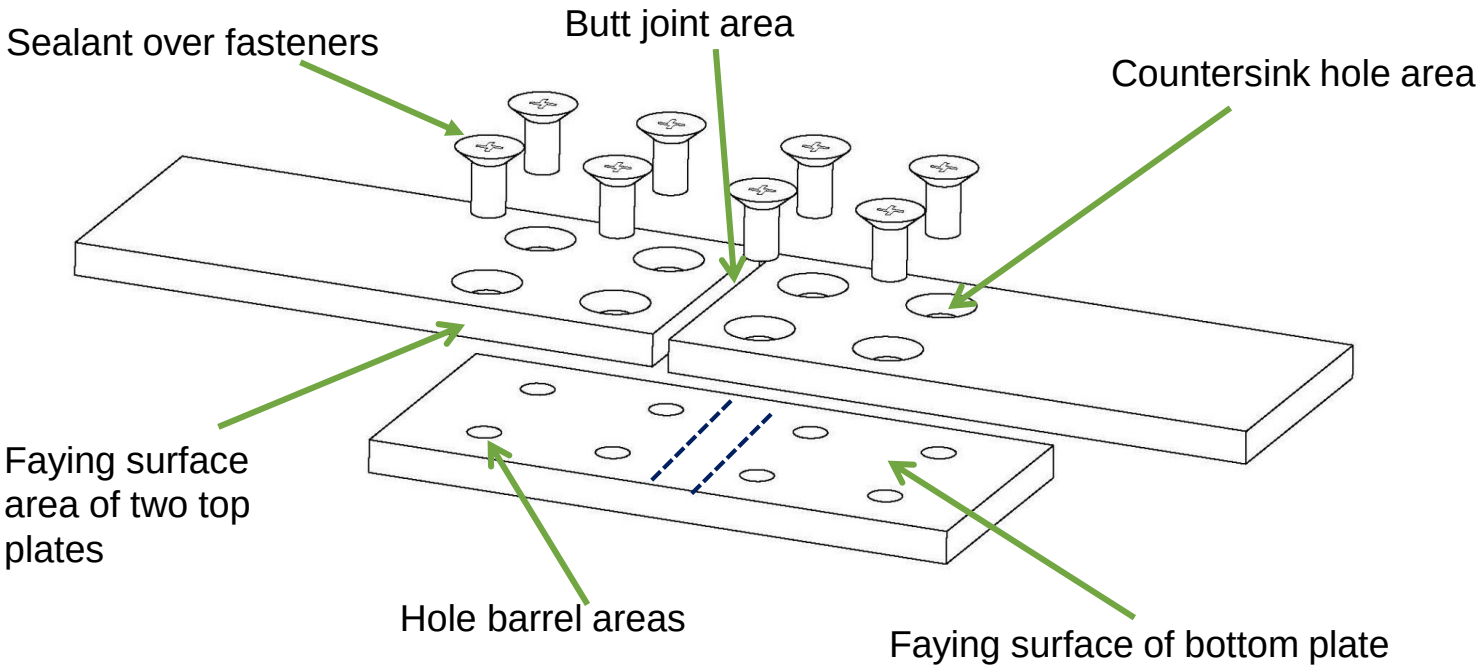
BLUE ORIGIN

Sealants

Sealants Evaluated

Vendor	Vendor PN	Specification	Purpose	Chemical Class	Corrosion Inhibitor
PPG Aerospace	PS-870	MIL-PRF-81733 Type II Class 1 Grade A	Baseline	Polysulfide	Hexavalent chromium
3M	AC-735	MIL-PRF-81733 Type II Class 1 Grade B and AMS 3265 Class B	Alternative Sealant	Polysulfide	Zinc phosphate
PPG Aerospace	PR-1775	AMS 3265 Class B	Alternative Sealant	Polysulfide	Phosphite salt Second chemical TBD
PPG Aerospace	PR-2870	MIL-PRF-81733 Type II Class 2 Grade B	Alternative Sealant	Polythioether	Non Hex chrome (proprietary)
Flame Master	CS 5500N CI	Not yet qualified	Alternative Sealant	Polysulfide	Molybdates
PPG Aerospace	PR-1440	AMS-S-8802 Type 2 Class B	Negative Control	Polysulfide	None

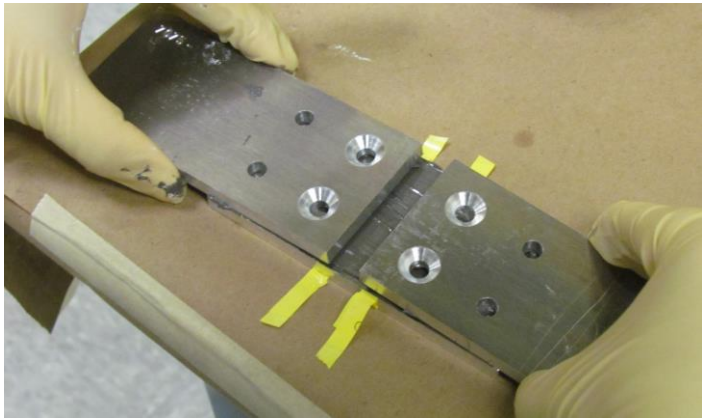
Test Vehicle



Plates: Aluminum alloy 7075, stainless steel bolts and nuts

Research Process

Conversion Coating
MIL-DTL5541
(MacDermid Iridite 14-2)
Northrop Grumman
Maryland



Test Vehicle Assembly,
Prime, Paint, Scribe
Raytheon
Arizona

Thermal and Mechanical Preconditioning
(MIL-PRF-81733D, Section 4.8.9.3.1 Cyclic Loading for Class 1 Materials)
U.S. Navy – NAVAIR
Maryland

30 test vehicles = 6 sealants x 5 replicates

*Fasteners for the test vehicle provided by **Bombardier.**

Research Process

Accelerated Corrosion Test
1,000 hours
SO_2 Salt Fog, ASTM G85 Annex 4
pH 2.5 – 3.2
(24 Test Vehicles)
Lockheed Martin
Texas

Long-term Corrosion Test
1 year duration
(6 Test Vehicles)
NASA
Beachside Atmospheric Test Facility,
Kennedy Space Center, Florida

Image: commons.Wikimedia.org

Conclusions

Faying surface/butt joint areas:

Four alternative sealants containing non-hex chrome corrosion inhibitors (AC-735, CS 5500N CI, PR-1775, and PR-2870) provided comparable corrosion prevention performance to the baseline sealant PS-870.

Fastener holes and fastener areas:

Three alternative sealants containing non-hex chrome corrosion inhibitors (AC-735, PR-1775, and PR-2870) provided comparable corrosion prevention performance to the baseline sealant PS-870.

Corrosion in countersunk hole for fastener

Further Information

https://www.turi.org/Our_Work/Business/Industry_Sectors/Aerospace_and_Defense/Collaborative_Research_Hex_Chrome_Free_Sealants

PF PLATING

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Sailors assigned to the Saberhawks of Helicopter Maritime Strike Squadron 77 perform maintenance on the propellers of an MH-60R Sea Hawk helicopter. *(U.S. Navy photo by Mass Communication Specialist 3rd Class Travis K.*

It also prohibits the use or removal of hex chrome-containing materials during subsequent phases of the deliverable, unless an exception or approval applies. Sealant applications that contain hex chrome are not an exception.

Hex Chromium-Free Sealants for Defense and Aerospace

Results of second phase of research conducted by top defense contractors.

BY GREGORY MOROSE, DAYNA LAMB, KENT DEFRANCO AND CURTIS LEMIEUX

Collaborative Project

To address the challenges of adopting hex chrome-free alternatives, TURI, the Toxics Use Reduction Institute at the University of Massachusetts Lowell, reached out to companies in the aerospace and defense industry that were interested in participating in a collaborative project.

In 2012, a Hexavalent Chromium-Free Sealant Evaluation Team was established with representatives from TURI, Lockheed Martin, Raytheon, Northrop Grumman, Bombardier, NASA, Naval Air Systems Command, Air Force Research Laboratory and Army Aviation and Missile Command (AMCOM). This article presents the results of the second phase of research conducted by the evaluation team.

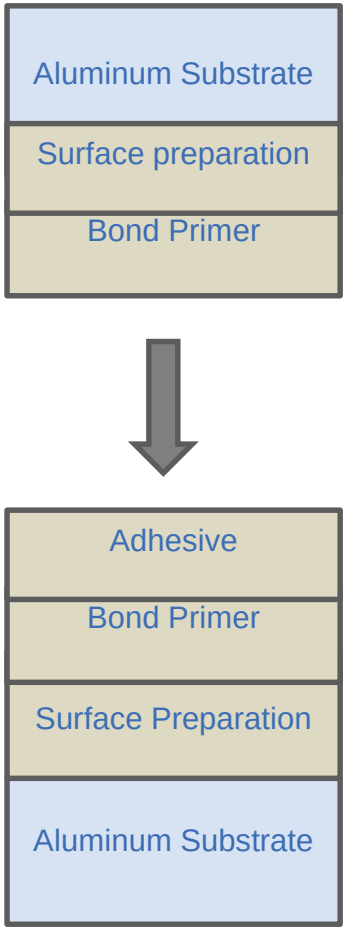
Sealants industry spec test procedures don't

Bond Primers

Bond Primers

Bond primers are used to improve the adhesion of structural bonds and historically have included hexavalent chromium as a corrosion inhibitor.

Bond primers are being used in aerospace manufacturing with several different combinations of surface preparations, substrates, and adhesives.



Bond Primers Evaluated

Vendor	Product	Primer Type	Corrosion Inhibition
Cytec	BR 127	Baseline – Solvent Based	Strontium Chromate
Cytec	BR 127NC	Solvent Based	No Corrosion Inhibitor
Cytec	BR 252	Water Based	Non-Chromate Corrosion Inhibitor (zinc oxide, zinc phosphate)
Cytec	BR 6747-1NC	Water Based	No Corrosion Inhibitor
3M	EW-5000 ET	Water Based	Non-Chromated Corrosion Inhibitor (zinc molybdate)
3M	EW-5005	Water Based	Non-Chromate Corrosion Inhibitor (zinc and aluminum phosphates)

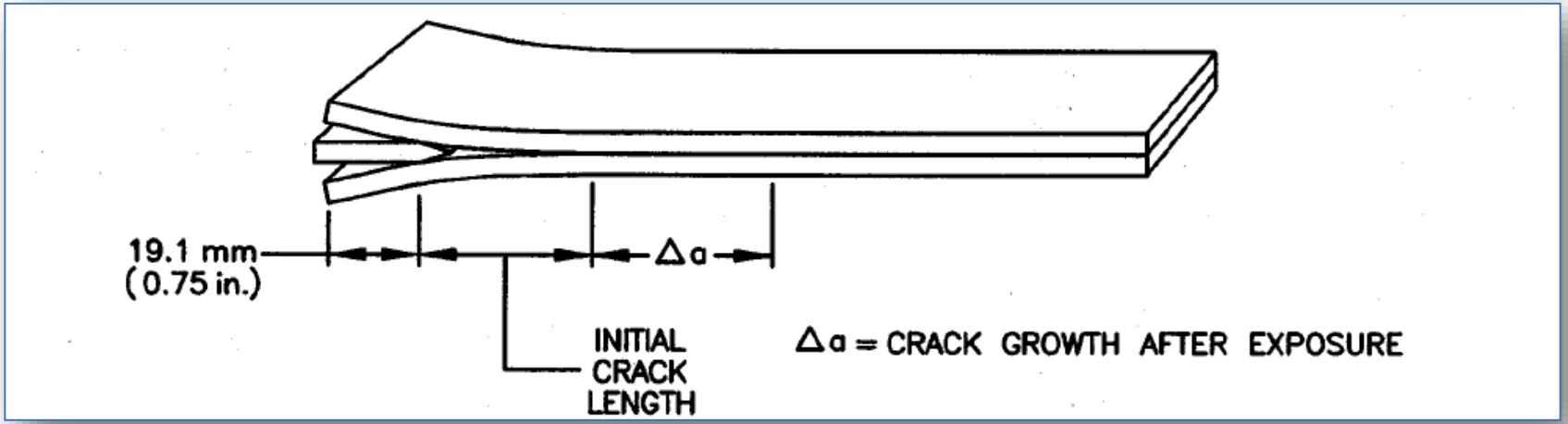
Test Panels

Aluminum Alloys	2024-T3
	7075-T6
Test Panel	3” x 10” x 0.125”
	Test panels will be scribed (3 on bottom half; 1 on top half)
Surface Preparation	Phosphoric Acid Anodize (PAA) - ASTM D3933
	Aluminum Oxide Grit Blast
	Aluminum Oxide Grit Blast followed by Sol-Gel AC130-2
Adhesives	Cytec FM73
	3M AF163-2M

Hexavalent Chromium Free Bond Primers Testing

- Neutral Salt Fog (NSF) Corrosion Testing
  - ASTM B 117 spray
  - 4 replicates for each combination
  - *Requirement*: 960 hours with no corrosion outside of the scribe
- Wedge Crack Extension Testing (WCET) - ASTM D 3762
  - After NSF and elevated temperature and humidity/wet environment (ETW)
  - 3 replicates for each combination

Wedge Crack Extension Testing (WCET)



ASTM D3762: Crack Extension Specimen Configuration

Results

Panels with a PAA surface treatment had the best corrosion resistance results and had the lowest crack lengths.

3

Three alternative non hex chrome bond primers (EW-5000-ET, EW-5005, and BR 6747-1NC) with PAA had lower average crack length after 9 weeks than the baseline bond primer with hex chrome (BR-127).

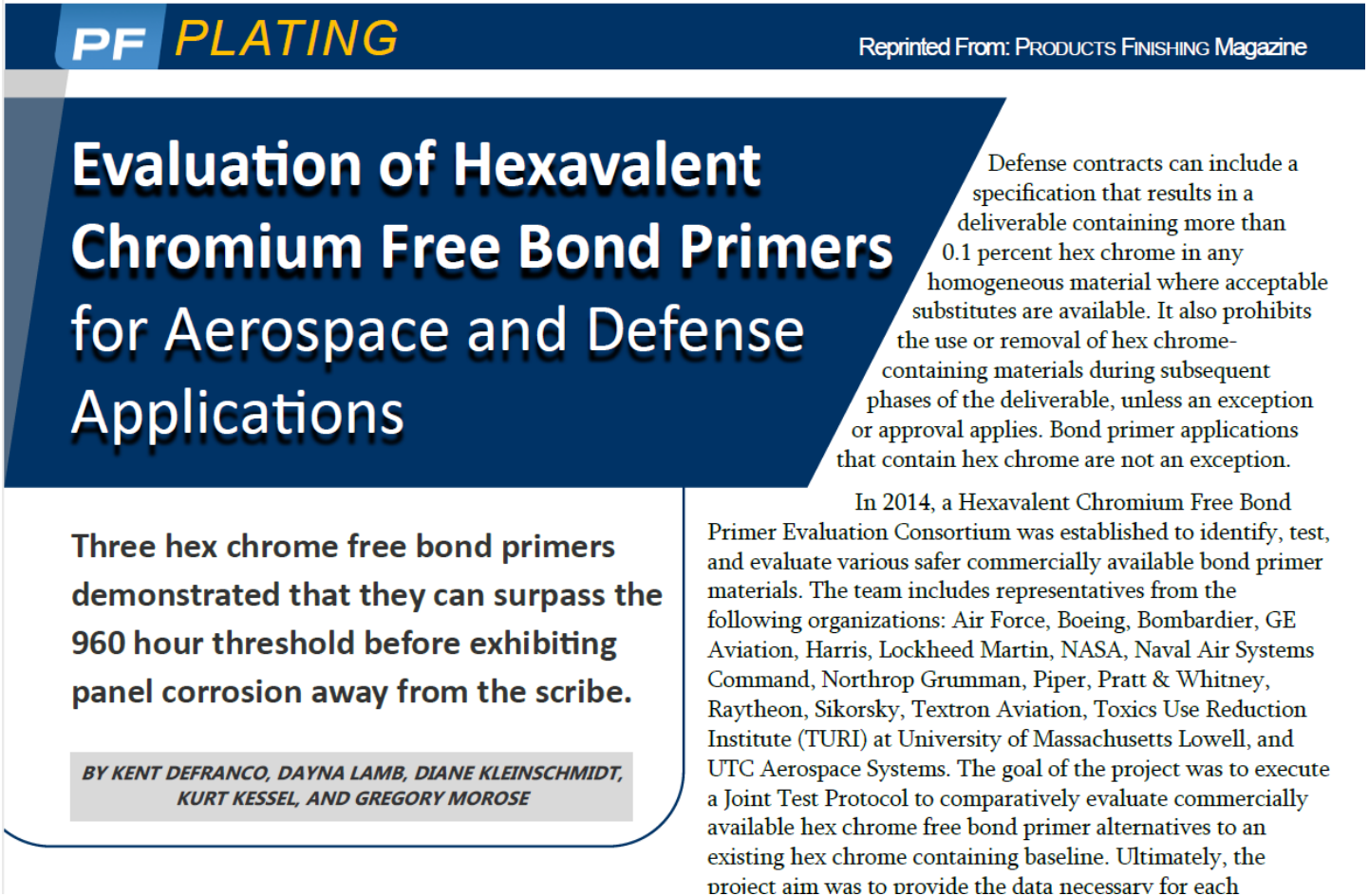
2

Two alternative non hex chrome bond primers (EW-5000-ET and EW-5005) with PAA had a greater passing rate for the 960 hour corrosion test than the baseline bond primer with hex chrome (BR-127).

With a PAA surface treatment: EW-5000-ET and EW-5005 are viable alternative bond primers achieving both the required corrosion resistance and adhesion strength.

Further Details

https://www.turi.org/Our_Work/Business/Industry_Sectors/Aerospace_and_Defense/Collaborative_Research_Hex_Chrome_Free_Bond_Primers



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Evaluation of Hexavalent Chromium Free Bond Primers for Aerospace and Defense Applications

Three hex chrome free bond primers demonstrated that they can surpass the 960 hour threshold before exhibiting panel corrosion away from the scribe.

BY KENT DEFRANCO, DAYNA LAMB, DIANE KLEINSCHMIDT, KURT KESSEL, AND GREGORY MOROSE

Defense contracts can include a specification that results in a deliverable containing more than 0.1 percent hex chrome in any homogeneous material where acceptable substitutes are available. It also prohibits the use or removal of hex chrome-containing materials during subsequent phases of the deliverable, unless an exception or approval applies. Bond primer applications that contain hex chrome are not an exception.

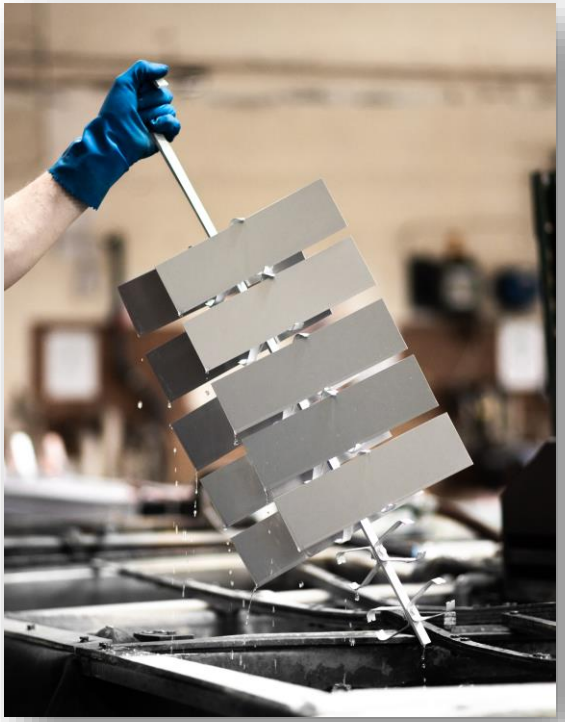
In 2014, a Hexavalent Chromium Free Bond Primer Evaluation Consortium was established to identify, test, and evaluate various safer commercially available bond primer materials. The team includes representatives from the following organizations: Air Force, Boeing, Bombardier, GE Aviation, Harris, Lockheed Martin, NASA, Naval Air Systems Command, Northrop Grumman, Piper, Pratt & Whitney, Raytheon, Sikorsky, Textron Aviation, Toxics Use Reduction Institute (TURI) at University of Massachusetts Lowell, and UTC Aerospace Systems. The goal of the project was to execute a Joint Test Protocol to comparatively evaluate commercially available hex chrome free bond primer alternatives to an existing hex chrome containing baseline. Ultimately, the project aim was to provide the data necessary for each

Conversion Coatings

Conversion Coating Materials and Corrosion Inhibitors

Supplier	Product	Corrosion Inhibitor
Henkel	Alodine 1200S	Hexavalent chromium (baseline for comparison)
Chemeon	eTCP	Trivalent chromium
PPG	Desoprep 4000	Zirconate
PPG	PPG TCP	Trivalent chromium
Socomore	Socosurf TCS/PACS	Trivalent chromium

Conversion Coating



eTCP conversion coating applied at Polymetal

Conversion Coating

- Chemical tanks were prepared as recommended by the coating Technical Data Sheet and applied based on the MIL-DTL-5541 standard.

Coating Weight Measurement

- MIL-DTL-81706 Para 4.5.4

Applicators

- Polymetal (Springfield, MA): eTCP, Alodine 1200S
- International Hardcoat (Michigan): Socosurf TCS/PACS
- PPG (Pennsylvania) DesoPrep 4000, PPG TCP

Aluminum substrates: 6061, 7075, 2024, and 2219

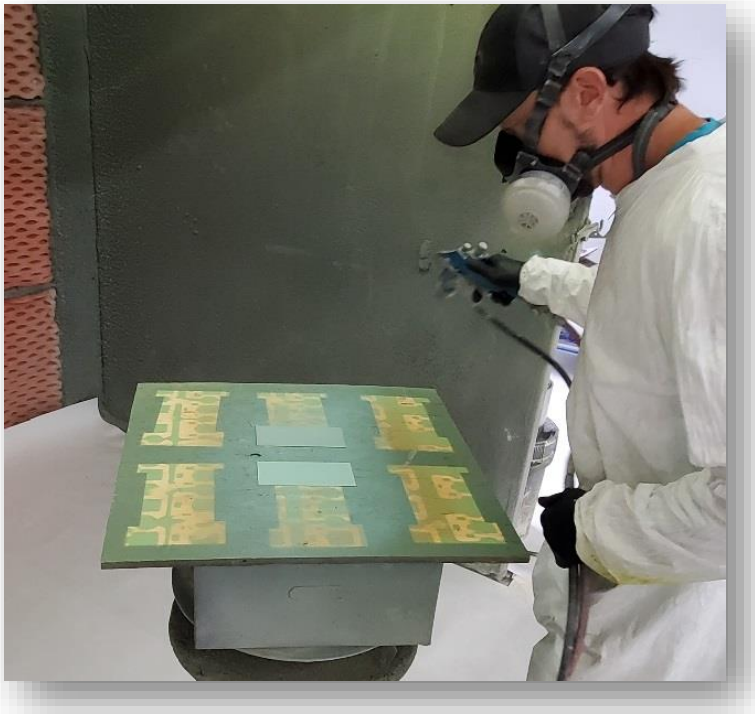
Primer and Topcoat

The non-hex chrome primer

- PPG 02GN097 that may be a future candidate to qualify to MIL-PRF-23377 Type 1 Class N
- Chosen based on previous testing by consortium members

The non-hex chrome topcoat

- PPG 03W127BF urethane color 17925 White that meets MIL-PRF-85285 Type 1 Class H



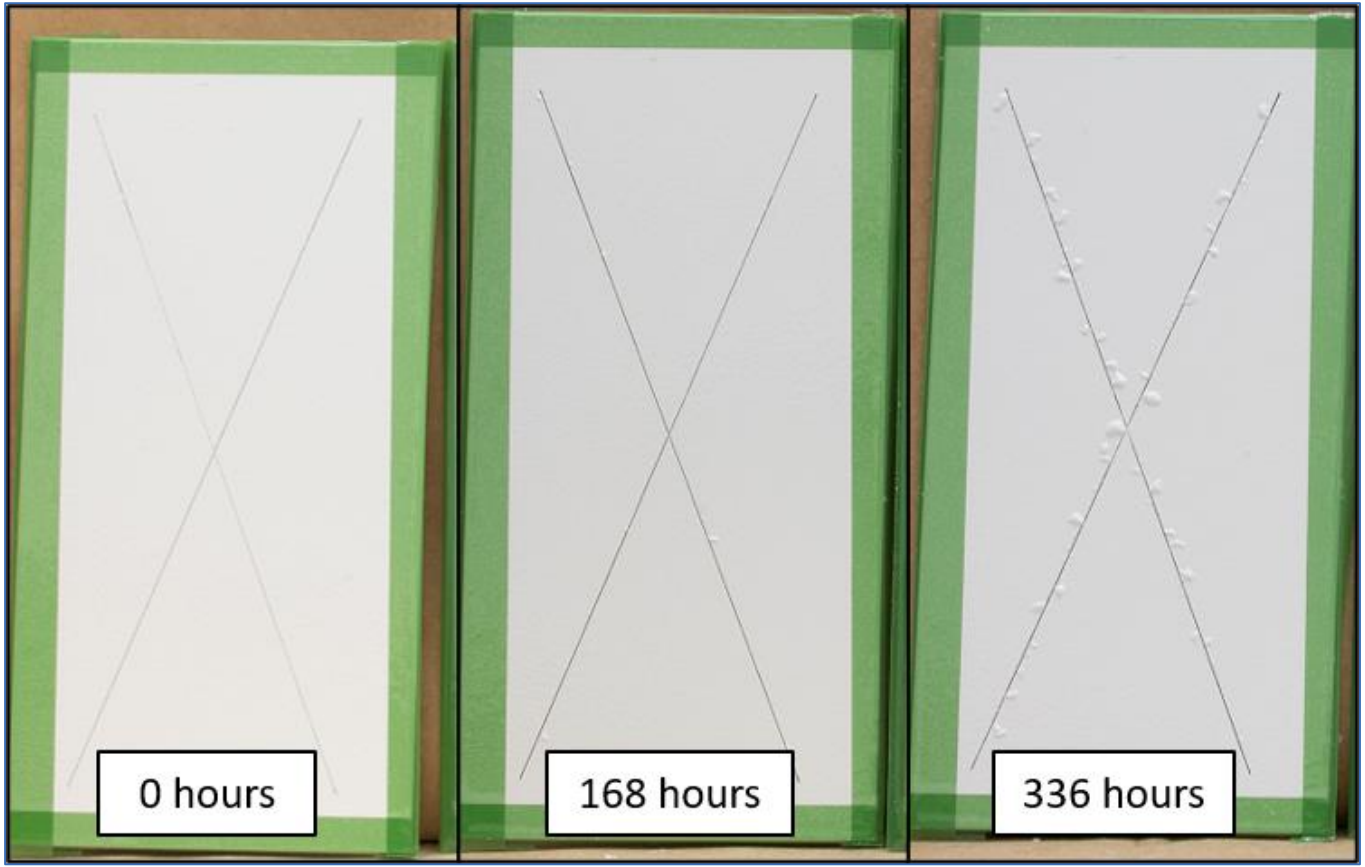
Primer and topcoat being applied at CIL (Lawrence, MA)

Conversion Coating Tests

Test	Specification
Paint adhesion	MIL-DTL-5541, MIL-DTL-81706, and ASTM D3359
Electrical Contact Resistance	MIL-DTL-5541 and MIL-DTL-81706
Neutral Salt Fog – Bare Aluminum	ASTM B117, MIL-DTL-81706, and MIL-DTL-5541
Neutral Salt Fog – Painted Panels	ASTM B117
SO_2 Salt Fog	ASTM G85 A4
Beachfront (started Dec. 2020, minimum one year testing)	ASTM D1654 Procedure A for corrosion measurement

Salt fog testing at Lockheed Martin in Fort Worth, Texas

Conversion Coatings – Test Panel



Test Panels after SO2 Salt Fog Corrosion Testing (Desoprep on 2219 Alloy)

1) 0.032” thick x 3.0” wide x 10.0” long, and 2) 0.020” thick x 3.0” wide x 6.0” long

Results

- Overall, the Socosurf TCS/PACS was the best performing hexavalent chromium free conversion coating across all four types of aluminum alloys.
- For the 2024 alloy, Socosurf TCS/PACS passed requirements including coating weight, paint adhesion, NSF bare aluminum corrosion test, SO_2 painted corrosion test, and beachfront corrosion test.
- For the 2219 alloy, Socosurf TCS/PACS passed the coating weight, paint adhesion, and NSF bare aluminum corrosion test.

No single evaluation will completely resolve the long-standing issue of replacing hexavalent chromium in conversion coatings with a safer alternative. However, the results of this evaluation provide significant progress to achieving that goal since numerous hexavalent chromium free conversion coatings passed several qualification tests for various aluminum alloys.

Further Details

Journal of Aerospace Technology and Management - Currently under peer review

Evaluation of Conversion Coatings Without Hexavalent Chromium for Aerospace and Defense Applications

***Gregory Morose[1], David Pinsky[2], Chandler Humphrey[3], and Kent DeFranco[3]**

[1] Toxics Use Reduction Institute, University of Massachusetts Lowell. Lowell, Massachusetts, USA

[2] Raytheon Technologies, Andover, Massachusetts, USA

[3] Lockheed Martin Aeronautics, Fort Worth, Texas, USA

The Massachusetts Toxics Use Reduction Institute

www.turi.org

126 John Street, Suite 14
Boott Mills West
Lowell, MA 01852

Greg Morose
Research Manager
Gregory_Morose@uml.edu