NASA and ESA Collaboration on Hexavalent Chrome Free Coatings

NASA Technology Evaluation for
Environmental Risk Mitigation Principal Center
Brian Greene

2017 INTERNATIONAL WORKSHOP ON ENVIRONMENT AND ALTERNATIVE ENERGY
May 30 - June 1, 2017
ESTEC, Noordwijk, Netherlands

Hexavalent Chrome Coating Alternatives

European Space Agency

- Memorandum of Understanding between NASA and ESA Concerning Cooperation in the Field of Space Transportation - signed September 11, 2009
- The National Aeronautics and Space Administration (NASA) and the European Space Agency (ESA) have expressed mutual interest in pursuing cooperation in the areas of evaluating:
  - Hexavalent chrome-free coatings
  - Environmentally-preferable coatings for maintenance of launch facilities and ground support equipment
  - Citric acid as an alternative to nitric acid for passivation of stainless steel alloys

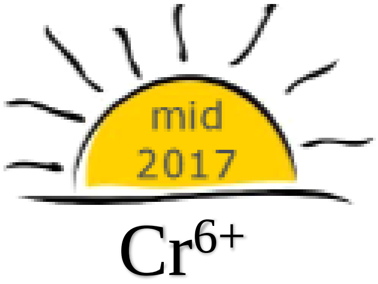
Hexavalent Chrome Coating Alternatives

Team: ESTEC (The Netherlands), NASA (TEERM program, & KSC Corrosion Testing Lab at Kennedy Space Center FL)

Description: Evaluate one or more alternatives to hexavalent chrome (hex-chrome or CrVI) in coatings and plating applications that meet their performance requirements in corrosion protection, cost, operability, and health and safety; while underlining that performance must be equal to or greater than existing systems.

Current Phase: Phase 2 of project, preparing materials for testing

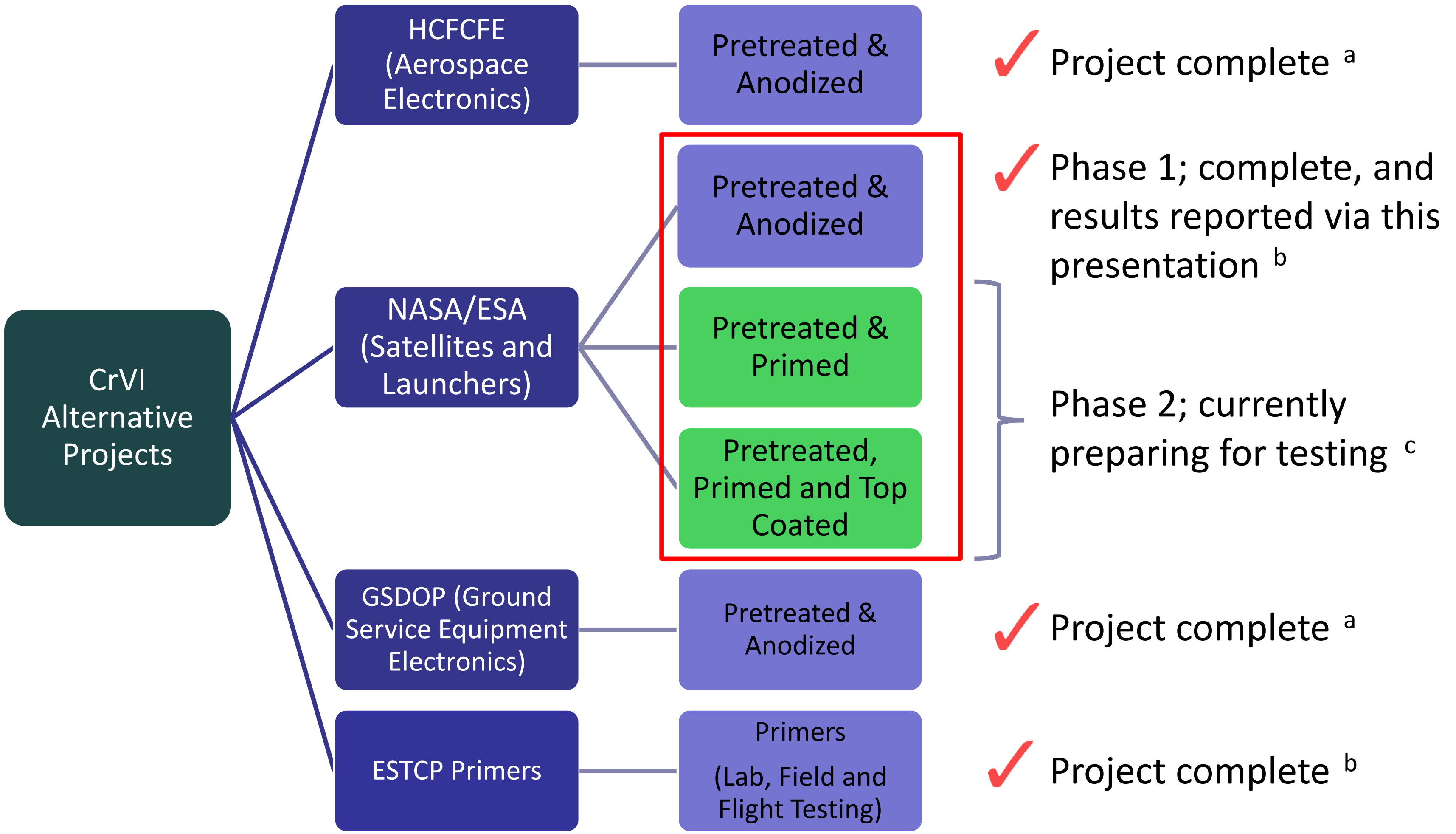
REACH



Hexavalent Chrome Coating Alternatives

Select NASA TEERM Projects History, 2013 - Present

European Space Agency



Footnotes:

a – Findings from pretreatments testing leveraged into NASA-ESA HexCr project

b – Findings from pretreatments and primer testing leveraged into NASA-ESA HexCr Phase 2

c – NASA Space Launch System (SLS) requirements incorporated in Phase 2

Acronyms:

CrVI – hexavalent chromium

HCFCFE – hexavalent chromium free coatings for electronics

GSDOP – Ground Systems Development and Operations Program (NASA Kennedy Space Ctr)

ESTCP - Environmental Security Technology Certification Program (US DoD)

Source: Adapted from M. Rothgeb, NASA/ESA Hex-Chrome Project Phase 1 Results & Overview, 2013 International Workshop on Environment & Alternative Energy, Frascati, Italy, 24 October 2013

European Space Agency

Phase I Test Results

- Pretreatments Only Testing

(pretreatments without primer)

European Space Agency

Pretreatment Only Testing

Alloys

- 2024-T3
- 2024-T8
- 6061-T6
- 7075-T6
- 7075-T73

Pretreatments

Pretreatment	Manufacturer
Metalast TCP HF	Metalast
SurTec 650 V	SurTec
Bonderite M-NT 65000	Henkel
MAPSIL® SILICo (3–5 µm)	MAP

Testing

Test	Test Method	Evaluation Criteria	Location
Salt Spray Resistance	ASTM B 117	MIL-DTL-5541	NASA KSC and ESA ESTEC
Humidity Testing	N/A	MIL-DTL-5541	ESA ESTEC
Thermal Cycle Testing	N/A	MIL-DTL-5541	ESA ESTEC

Hexavalent Chrome Coating Alternatives

European Space Agency

Salt Spray Testing per ASTM B117

Salt Spray Resistance (hours passed)	Metalast TCP HF	SurTec 650V	Bonderite M-NT 65000	MAP Silico {3-5 µm}
2024-T3	0	504[A]	0	0
2024-T8	0	0	0	0
6061-T6	672	672	672	168
7075-T6	168	672	504	168
7075-T73	336	672	504	168

A = 2 of 3 panels passed at 504; 1 panel was still passing at 672

15 or less pits observed on the test panel set (3 panels) (green)

More than 15 pits observed on the test panel set (3 panels) (red)

Salt spray testing produced mixed results

- In general, pretreatments did not perform well on 2024-T3 and 2024-T8 alloys
- Pretreatments performed better on 6061-T6, 7075-T6, and 7075-T73 alloys
- All test panels with SurTec 650V or Bonderite M-NT 65000 met requirements of MIL-DTL 5541 after 504 hours of testing. Several met requirements after 672 hours
- All test panels with Metalast TCP HF met requirements of MIL-DTL-5541 after 168 hours of testing

The reason for the varied results per alloy is due to the fact that resistance to corrosion decreases with increasing copper content

- Alloys 2024-T8 and 2024-T3 have very high copper content making it difficult to protect these alloys from corrosion

Hexavalent Chrome Coating Alternatives

Humidity Testing

Damp Heat[A] (hours of exposure)	Metalast TCP HF	SurTec 650V	Bonderite M-NT 65000	MAP Silico {3-5 µm}
2024-T3	2,500	2,500	2,500	2,500
2024-T8	< 2,300	2,500	2,300	2,500
6061-T6	2,300	2,500	2,300	3,500
7075-T6	2,500	3,200	3,500	3,500
7075-T73	3,200	2,700	2,500	3,500

A = 50°C / 95% RH - no visible signs of corrosion on any panel @ 2,200 hours; temperature was raised to 80°C for rainder of the test

- All of the surface treatments performed well on 2,000, 6,000 and 7,000 series alloys under 50 °C / 95 % RH conditions. No signs of corrosion were visible on any of the test panels at 2,200 hours of testing
- With the temperature increased to 80 °C after 2,200 hours, Metalast TCP-HF begins to show signs of corrosion on 2024-T8. For the 2000 series all other surface treatments reached between 2,300 hours and 2,500 hours
- With the temperature increased to 80 °C after 2,200 hours, MAPSIL® SILICo (thin) performs the best on 6,000 series alloys out of the four different surface treatments investigated, reaching a maximum duration of 3,500 hours with no pits observed on any panel. This is followed by SurTec 650V which starts showing signs of corrosion at around 2,500 hours

Hexavalent Chrome Coating Alternatives

European Space Agency

Thermal Cycling

	Step 1	Step 2	Step 3	Step 4
	10 cycles in vacuum	**80 cycles in ambient**	**10 cycles in vacuum**	**Isothermal step 150 °C in high vacuum for 145 hrs**
T_{max}	100 (+5/-10) °C	100 (+5/-5) °C	100 (+5/-10) °C	
T_{min}	-100 (+5/-5) °C	-100 (+5/-5) °C	-100 (+5/-5) °C	
T_{CR}	<10 °C/min	10 (± 2) °C/min	<10 °C/min	
t_{dwell}	>5 mins for all samples	>5 mins for all samples	>5 mins for all samples	
Samples	All	All	All	MAPSIL® SILICo (thin): One of each alloy Others: One of each 2024-T8 and 7075-T73 alloy

Hexavalent Chrome Coating Alternatives

European Space Agency

Thermal Cycling

Surface treatment	Substrate	Thermal cycling steps + Isothermal step			
		First 10 cycles in vacuum	Next 10 cycles in ambient	Last 10 cycles in vacuum	Isothermal 150 °C
METALAST® TCP-HF	2024-T3	✓	✓	✓	N/A
	2024-T8	✓	✓*	✓*	✓*
	6061-T6	✓	✓	✓	N/A
	7075-T6	✓*	✓*	✓*	N/A
	7075-T73	✓	✓*	✓*	✓*
SurTec 650 V	2024-T3	✓	✓	✓	N/A
	2024-T8	✓	✓	✓	✓
	6061-T6	✓	✓	✓	N/A
	7075-T6	✓	✓	✓	N/A
	7075-T73	✓*	✓*	✓*	✓*
Bonderite M-NT 65000	2024-T3	✓	✓	✓	N/A
	2024-T8	✓	✓*	✓*	✓*
	6061-T6	✓	✓	✓	N/A
	7075-T6	✓	✓	✓	N/A
	7075-T73	✓	✓	✓*	✓*
MAPSIL® SILICo (thin)	2024-T3	✓	✓	✓	×a)
	2024-T8	✓	✓	✓	×a)
	6061-T6	✓	✓	✓	×a)
	7075-T6	✓	✓	✓	×a)
	7075-T73	✓	✓	✓	×a)

Notes

- No changes to microstructure observed
- Small changes to microstructure observed (probably not due to surface treatment itself)
- Major changes to microstructure observed
- Severe changes to microstructure observed

* Cracking around particles containing high number of elements. Number of cracks counted is very low (likely to be substrate itself rather than the surface treatment).

a) Larger gaps in surface treatment after exposure.

- Thermal cycling steps (1 to 3) did not affect the microstructure of 2024-T3 and 6061-T6 alloys in combination with any of the four surface treatments
- In general MAPSIL SILICo (thin) showed no sign of deterioration under an optical microscope during the thermal cycling steps. The gaps in the surface treatment however, appeared larger after the final 150 °C isothermal step
- The other three surface treatments showed cracking around or through "high element" containing particulates under a SEM on 2024-T8, 7075-T6 and 7075-T73 alloys.
  - The quantity of cracks observed was very small and it is important to note that through the course of the thermal cycling process an increased number of cracks was not observed. EDS analysis on the SEM was used to establish around which composition of particulates cracks were forming during the thermal cycling test.

Phase I Test Results

- Pretreatments with Primers Screening

Hexavalent Chrome Coating Alternatives

European Space Agency

Alloy:
- 2024-T3

Pretreatments

Pretreatment	Manufacturer
Metalast TCP HF	Metalast
SurTec 650 V	SurTec
Bonderite M-NT 65000	Henkel
MAPSIL® SILICo (3–5 µm)	MAP

Primers

Primer	Manufacturer
Deft 02GN084	Deft, Inc.
Hentzen 16708	Hentzen Coatings, Inc.
NAVALCOAT	U.S. Navy
MAPSIL® SILICo (14-26 µm)	MAP


Hexavalent Chrome Coating Alternatives

Pretreatment and Primer Screening

Test	Test Method	Evaluation Criteria	Location
Salt Spray Resistance	ASTM B 117	MIL-DTL-5541	NASA KSC / ESA ESTEC
PATTI Pull Test	ASTM D4541	ASTM D4541	NASA KSC

Coating Matrix

Pretreatment	Primer
Metalast TCP HF	Deft 02GN084
	Hentzen 16708
	NAVALCOAT
SurTec 650V	Deft 02GN084
	Hentzen 16708
	NAVALCOAT
Bonderite M-NT 65000	Deft 02GN084
	Hentzen 16708
	NAVALCOAT
MAPSIL® SILICo (14-26 µm)[A]	
A = Applied as a stand alone coating system	

Hexavalent Chrome Coating Alternatives

Salt Spray Testing

Salt Spray Resistance (2,100 hours)	Hentzen	Deft	NAVALCOAT	None
Metalast TCP	[red]	[orange]	[red]	N/A
SurTec 650V	[orange]	[orange]	[orange]	N/A
Bonderite M-NT 65000	[green]	[orange]	[orange]	N/A
MAPSIL® SILICo {14 to 16 μm}[A]	N/A	N/A	N/A	[red]

[green] Good performing combination

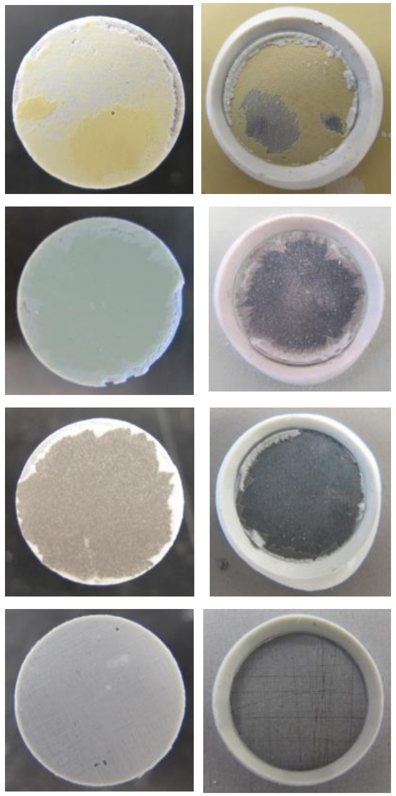
[orange] Moderately performing combination

[red] Poor performing combination

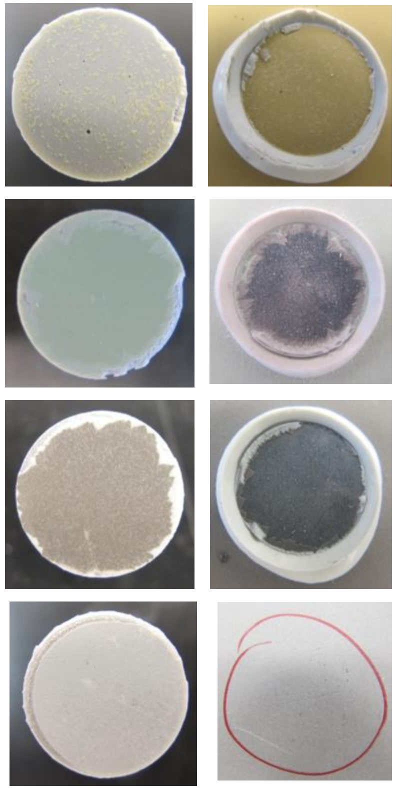
A = Test panels were removed at 1,055 hours

Hexavalent Chrome Coating Alternatives

Coating Adhesion Testing



Conversion Coat	Primer	Average Pull-Off Tensile Strength (psi)
Metalast TCP	Hentzen 16708	3321
	Deft 02GN084	2739
	NAVALCOAT	2381
SurTec 650V	Hentzen 16708	3146
	Deft 02GN084	2438
	NAVALCOAT	3024
Bonderite M-NT 65000	Hentzen 16708	2863
	Deft 02GN084	1793
	NAVALCOAT	3110
MAPSIL® SILICo {12 to 16 µm}		534



MAPSIL® SILICo (thick) had low psi pull-off tensile strength during testing. From previous NASA and ESA project experience, silicon-containing coatings like MAPSIL® SILICo (thick) typically exhibit limited adhesion properties due to the adhesive not being able to adhere to the coatings.

European Space Agency

Phase II Overview

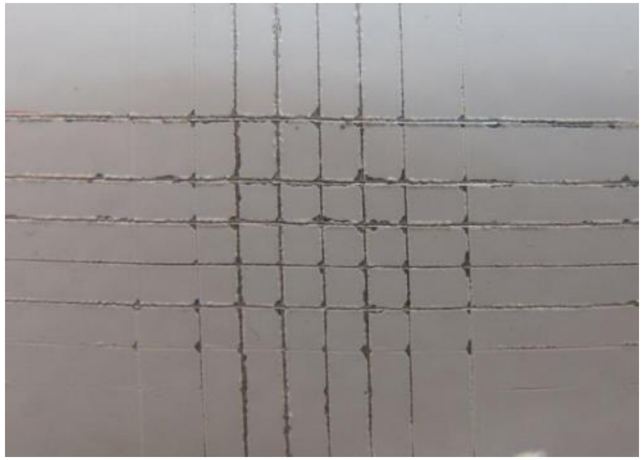
- Pretreatments with Primers Testing
- Pretreatments with Primers and Topcoat Testing

Hexavalent Chrome Coating Alternatives

European Space Agency

Testing

Test	Test Method	Evaluation Criteria	Location
Salt Spray Resistance	ASTM B 117	MIL-PRF-23377	NASA KSC ESA ESTEC
Thermal Cycle / Cross Hatch Adhesion	N/A / ASTM D 3359	ASTM D 3359	ESA ESTEC
Atmospheric Exposure	ASTM D 1014	ASTM D 1654	NASA KSC ESA Kourou



Hexavalent Chrome Coating Alternatives

European Space Agency

Hexavalent Chrome Free Pretreatments & Primers

ESA Selected

Pretreatment	Primer
SurTec 650 / MS 20/15	MAP E'
	MAPSIL® SILICo
Bonderite M-NT 65000	MAP E'
	MAPSIL® SILICo

NASA Selected

Pretreatment	Primer
SurTec 650 / MS 20/15	Deft 02GN084
	Randolph LN4847
Bonderite M-NT 5200 MU	Deft 02GN084
	Randolph
Scotch-Brite / Ardrox 5529	Deft 02GN084
	Randolph LN4847
X-Bond 4000DM	Deft 02GN084
	Randolph LN4847

Alloys

- 2219-T87
- 2024-T8
- 7075-T73

Hexavalent Chrome Coating Alternatives

European Space Agency

Hexavalent Chrome Free Pretreatments, Primers & Topcoat

ESA Selected

Pretreatment	Primer	Topcoat
SurTec 650 / MS 20/15	MAP E'	MAP AQ Static
	MAPSIL® SILICo	
Bonderite M-NT 65000	MAP E'	
	MAPSIL® SILICo	

NASA Selected

Pretreatment	Primer	Topcoat
SurTec 650 / MS 20/15	Deft 02GN084	Hentzen Zenthane Plus
	Randolph LN4847	
Bonderite M-NT 5200 MU	Deft 02GN084	
	Randolph	
Scotch-Brite / Ardrox 5529	Deft 02GN084	
	Randolph LN4847	
X-Bond 4000DM	Deft 02GN084	
	Randolph LN4847	

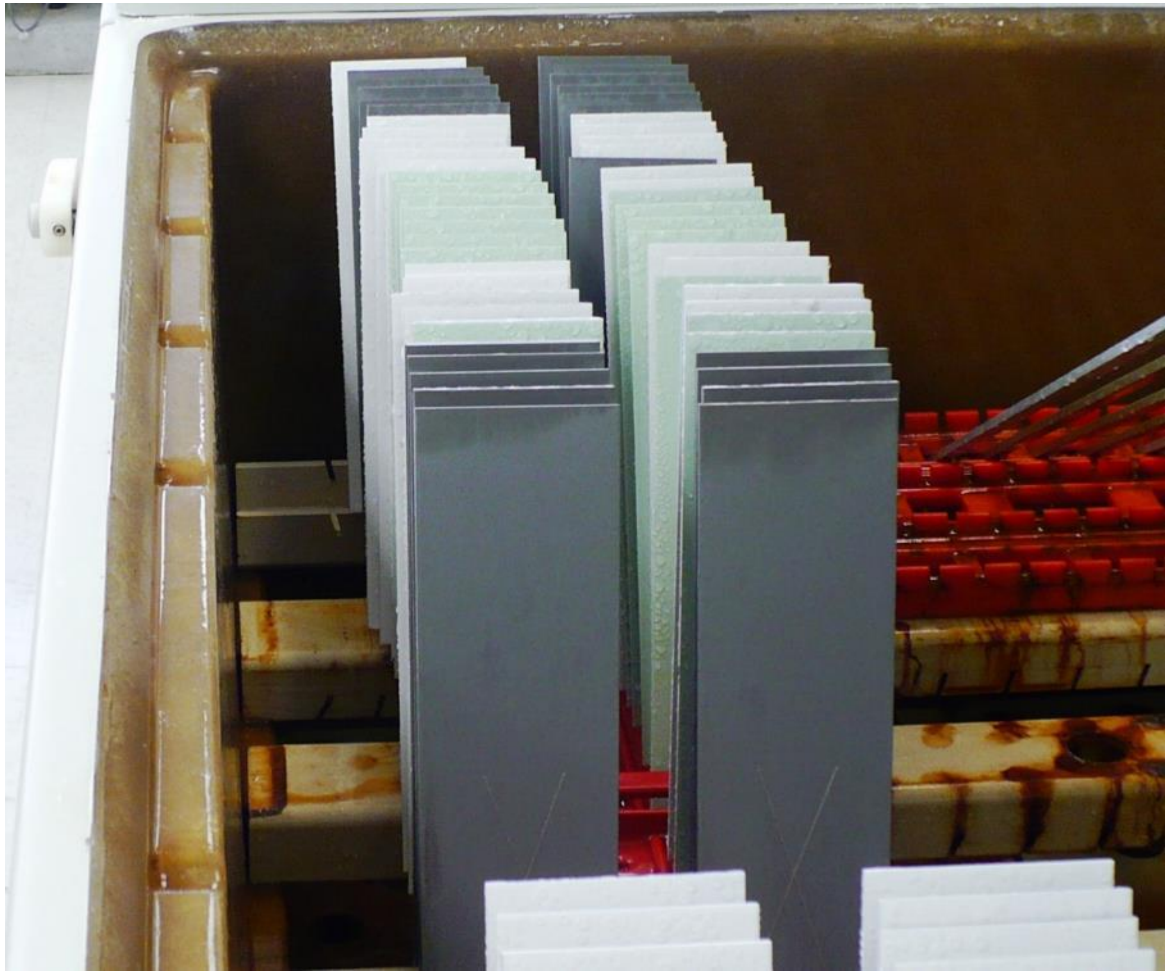
Alloys

- 2219-T87
- 2024-T8
- 7075-T73

Hexavalent Chrome Coating Alternatives

European Space Agency

Salt Spray Testing at KSC Started on 3/27/2017 and is Scheduled to Run for 2,000 Hours



Hexavalent Chrome Coating Alternatives

European Space Agency

Atmospheric Testing at KSC Started on 3/28/2017 and is Scheduled to Run for 12 Months

Acknowledgments

- Thomas Rohr, ESTEC - Thomas.Rohr@esa.int

Questions?