ESA – Frame Contract on Materials Testing

Alternative pre-treatments to aluminium

Replacements for Hexavalent Chromate Conversion Coatings

www.isq-group.com

Clean Space Industrial Days

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PROJECT BACKGROUND

- High strength aluminium alloys are widely employed in aerospace applications for both structural and non-structural applications. Key structural components such as launcher stages and sandwich panels are examples of applications. Aluminium alloys are selected for their high strength-to-weight ratios but the improved strength usually compromises the corrosion resistance of the material.

- Specific environmental conditions may trigger corrosion and therefore these alloys require additional protection.

- Chromium-VI based coatings have been really an effective solution but their use has been prohibited by EU since 2007 due to their carcinogenicity and negative environmental impact.

PROJECT BACKGROUND

- In the European automotive and electrical engineering industry, replacement of classical chromate process by chromium (VI)-free alternatives has been finished.

- In the aeronautic and space industry a sunset date of September 21st-2017 has been set for hexavalent chromium. The Cr-VI based process is maintained in full scale in aerospace and military industry[1].

- Significant research has been conducted to replace the Chromium (VI) based surface treatments and some commercial substitute systems are now available and needs to be tested to evaluate their performance and to know how they comply with the required specifications.

[1]**POKORNY, P. TEJ, P. SZELAG, CHROMATE CONVERSION COATINGS AND THEIR CURRENT APPLICATION,** ISSN 0543-5846, METABK 55(2) 253-256 (2016), UDC – UDK 669.268:621.793:542.8:669.715:615.372=111

PROJECT BACKGROUND

- ESA contracted ISQ to conduct a study focusing on a selection of alternative surface treatments which are sourced from European vendors.

- The objective is to select the most suitable pre-treatment for the required applications and to determine their relative performance and efficiency.

- Alodine 1200 samples will be used for baseline in all tests.

- The candidate surface treatments have been evaluated in terms of protection when used alone on different aluminium alloy substrates. In the last phase primer and topcoat will be also applied onto the conversion coating.

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Table 1 – Aluminium alloys, temper condition and alloying elements.

Aluminium Alloy	Temper	Specifications	Major alloying elements
AA2024	T3	AMS-QQA250/4, AMS4037	Cu
AA2024	T81	AMS-QQA250/4	Cu
AA6061	T6	AMS-QQA250/11, AMS4027	Mg, Si
AA7075	T73	AMS-QQA250/12, AMS4078	Zn
AA5083	H111	AMS- QQ-A-250/6 5083, AMS 4056	Mg

Table 2 – Summary of chromium (VI)-free conversion coatings.

Conversion Coating	PreCoat A32	ALUPRET 300	Nabural 33	SOCOSURF TCS / PACS	SURTEC 650V	Pre-treatment based on Vanadate	Bonderite M-NT 65000
Chemistry (from MSDSs)	Trivalent chromium	Trivalent chromium	Trivalent chromium	Trivalent chromium	Trivalent chromium	Sodium vanadate	Trivalent chromium
Supplier	AD International B.V., The Netherlands	SPCB, France	NABU Oferflachen-technik, Germany	Socomore, FRANCE	SurTec, FRANCE	SmallMaTek, Portugal	HENKEL, Germany

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Phase 1 – Pre-Screening

Pre-screening of selected pre-treatments on five different substrates with special attention to AA2024
(Salt spray testing (ASTM B 117) for 168 hours)

Phase 2 – Extended Testing

Four surface treatments (that performed better in Phase 1) were tested:

- Metallurgical coating evaluation
- Salt spray testing (ASTM B 117) for 168 hours + 336 hours duration
- Resistivity Check (e. g. MIL-DTL-81706)
- Humidity testing (ASTM D2247)
- Thermal cycling (ECSS-Q-ST-70-04C)

Phase 3 - Long Term Environmental Test Programme

Based on the results of Phase 2, three surface treatments will be exposed, alone and with primer/topcoat in ESA facilities in Kourou, French Guiana

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✓ **Phase 1 – Pre-Screening -** (Salt Spray testing (ASTM B 117) for 168 hours)

- Only **Precoat A32** and **Socosurf TCS/PACS** passed the minimum 168 hrs requirement for all the alloys including both AA2024 T3 and T81.
- **Surtec 650V** and **Bonderite M-NT 65000** passed the minimum 168 hrs requirements for AA7075- T73, AA6061-T6 and AA5083-H111 and failed for both AA2024-T3 and T81.
- The T81 showed more intense corrosion signs than the T3 in all the pretreatments, for AA2024.

⇒ **Precoat A32** and **Socosurf TCS/PACS** are the most promising chemical conversion alternatives for all the aluminium alloys, including AA2024.

⇒ **Surtec 650V** and **Bonderite M-NT 65000** could be also candidates for replacement if submitted to optimization for the AA2024.

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IN PROGRESS → **Phase 2 - Extended Testing**

- The four best surface treatment options, **PreCoat A32**, **Socosurf TCS/PACS**, **Surtec 650V** and **Bonderite M-NT 65000**, were applied on five substrates;

Table 3 -Test methods and evaluation criteria.

Test	Conditions	Test Method	Evaluation criteria
Salt Spray	504 h	ASTM B117	MIL-DTL-5541
Resistivity Check	Before and after SST	MIL- DTL-81706	MIL-DTL-5541
Humidity	3500 h	ASTM D2247	MIL-DTL-5541
Thermal Cycling	4 Steps in specific conditions	ECSS Q ST 70 04C	Acceptance criteria shall be defined (beforehand)
Metallurgical coating evaluation	Optical Microscopy, SEM and EDS observations before and after testing		

PHASE 2 – EXTENDED TESTING

Table 4 - Test Plan.

Test	Test duration (hrs)	Samples dimension (cm)	Number of samples for each combination alloy / conversion coating
Salt spray	504*	25.4 x 7.62	5
Resistivity Check	N/A	Resistivity checked in the same panels for salt spray, before and after testing	
Humidity	3500**	25.4 x 7.62	5
Thermal Cycling	Minimum 100 thermal cycles***	25.4 x 7.62	5

Notes:

* test panels will be inspected every 168 hours

** Test panels will be inspected every 168 hours (or every 336 hrs towards the end of testing, depending on the results).

*** To be defined with ESA

PHASE 2 – EXTENDED TESTING

Panel Processing

All the substrate panels have been submitted to the following sequence:

- Cleaning
- Water rinsing
- Deoxidizing
- Water rinse
- Treating with the conversion coating solution
- Water rinsing
- Drying

The products (cleaner, deoxidizing, desmutting and conversion solution) and the respective application parameters (concentration, temperature, time, etc.) were specified by each one of the vendors that applied the complete sequence in their own facilities.

Note: Alodine 1200 and Bonderite M-NT 65000 (supplied by HENKEL) were applied by ISQ, according to the respective application instructions.

PHASE 2 – EXTENDED TESTING – Salt Spray Test

- 5 test panels in each configuration subjected to a 5% NaCl neutral salt spray test (ASTM B117) with a pH between 6.5 and 7.5 for 504 hrs.
- Panels inspected every 168 hrs (number of spots or pits recorded).
- Areas within 5 mm from the edges, identification markings and holding points were excluded from inspection and loss of colour was not a cause for rejection.

Evaluation criteria for all tests taken from MIL-DTL-5541 [1] as follows:

"After 168 hrs of exposure there should be no more than 5 isolated spots or pits, none larger than 800 µm in diameter, per test specimen."

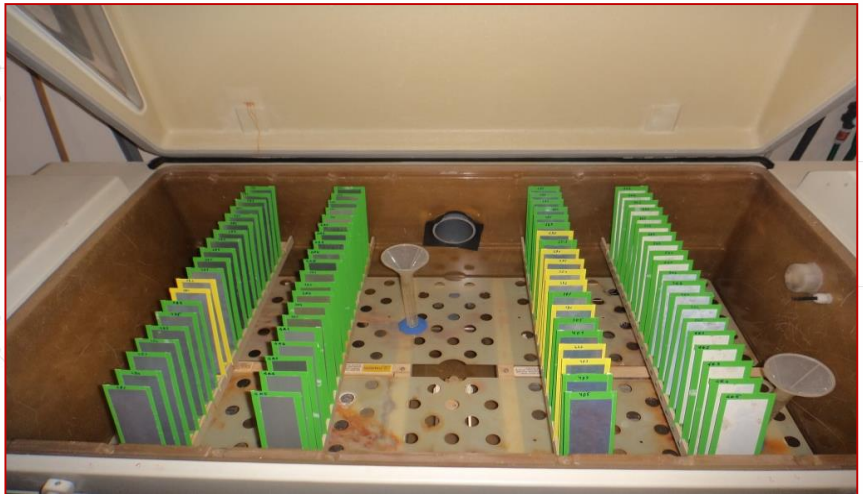


Figure 1 – Salt spray chamber, *Q-FOG*.

PHASE 2 – EXTENDED TESTING – Salt Spray Test results

		Pit count hours after NSS		
Pre-treatment	**Substrate**	**168h**	**336h**	**504h**
Alodine 1200	AA2024-T3	2-3	3-4	4-6
	AA2024-T81	3-4	4-5	5-8
	AA6061-T6	0-3	2-3	3-4
	AA7075-T73	0-0	1-2	2-3
	AA5083-H111	0-1	0-1	1-3
Precoat A32	AA2024-T3	2-4	5-7	10-15
	AA2024-T81	3-5	6-8	10-15
	AA6061-T6	0-0	1-4	2-4
	AA7075-T73	0-0	1-2	2-3
	AA5083-H111	2-3	3-4	3-5
Socosurf TCS/PACS	AA2024-T3	1-3	2-4	5-6
	AA2024-T81	2-4	3-5	5-7
	AA6061-T6	0-0	1-2	2-3
	AA7075-T73	0-0	1-2	2-3
	AA5083-H111	0-1	1-2	3-5
Surtec 650V	AA2024-T3	4-6	6-10	10-13
	AA2024-T81	4-6	5-7	10-13
	AA6061-T6	0-0	1-3	2-4
	AA7075-T73	0-3	2-4	3-7
	AA5083-H111	1-2	2-3	5-7
Bonderite M-NT 65000	AA2024-T3	10-13	15-20	21-25
	AA2024-T81	15-18	21-27	25 - 35+
	AA6061-T6	0-1	4-7	5-8
	AA7075-T73	0-3	4-5	5-6
	AA5083-H111	1-3	2-5	5-8

No corrosion

Few corrosion

Medium corrosion

High corrosion

Table 5 – Summarised pit count (**minimum and maximum**) after 168, 336 and 504 hours of salt spray test on all substrates with every pre-treatments.

PHASE 2 – EXTENDED TESTING – Salt Spray Test results

Table 6 – Summarised results obtained after 504h of salt spray test .

Aluminium Alloy	Chemical Conversion Coating Pre-treatments				
	Alodine 1200	Precoat A32	Socosurf TCS/PACS	Surtec 650 V	Bonderite M-NT 65000
AA2024-T3	No/ little evidence of corrosion	Few density corrosion spots/pits	Few density corrosion spots/pits, barely visible to eye	Medium density corrosion spots/pits	Few-medium density corrosion spots/pits; evidence of pre-treatment breakdown
AA2024-T81	No/ little evidence of corrosion	Few-medium density corrosion spots/pits	Few density corrosion spots/pits, barely visible to eye	Medium density corrosion spots/pits	Medium-high density corrosion spots/pits; evidence of pre-treatment breakdown
AA6061-T6	No/ little evidence of corrosion	No/ little evidence of corrosion	No/ little evidence of corrosion	Few density corrosion spots/pits	Few density corrosion spots/pits; evidence of pre-treatment breakdown
AA7075-T73	No/ little evidence of corrosion	No/ little evidence of corrosion	No/ little evidence of corrosion	Few density corrosion spots/pits	Few density corrosion spots/pits; evidence of pre-treatment breakdown
AA5083-H111	No/ little evidence of corrosion	No/ little evidence of corrosion	No/ little evidence of corrosion	Few density corrosion spots/pits;	Few density corrosion spots/pits

PHASE 2 – EXTENDED TESTING – Thermal Cycling Test

- Panels exposed to number of thermal cycles under vacuum conditions, oscillating within a defined temperature range to evaluate the resistance to effects such as cracking or fracture of materials and/or surface treatments.

Table 7 – Thermal cycling test parameters.

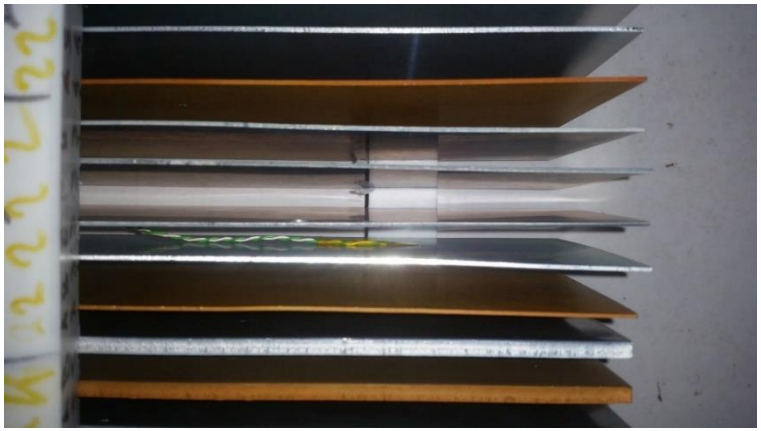
	Step 1	Step 2	Step 3	Step 4
	10 cycles in vacuum	80 cycles in ambient	10 cycles in vacuum	Isothermal step 150ºC in high vacuum for 145 hrs
T_{max}	100 (+5/-10) ºC	100 (+5/-5) ºC	100 (+5/-10) ºC	
T_{min}	-100 (+5/-5) ºC	-100 (+5/-5) ºC	-100 (+5/-5) ºC	
T_{CR}	1 ºC/min	5 ºC/min	1 ºC/min	
T_{dwell}	>5 min	>5 min	>5 min	

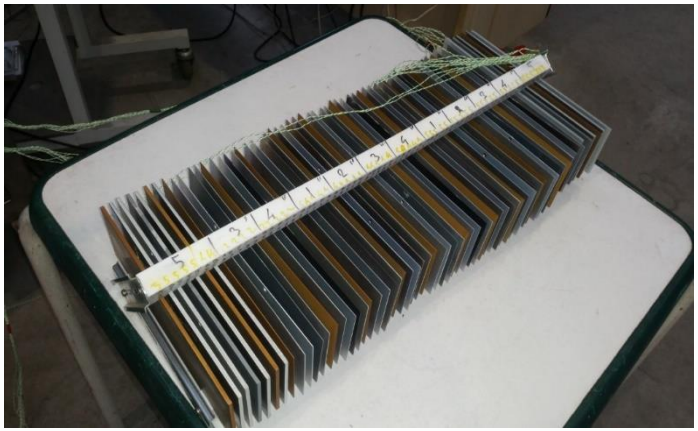
- The method is adapted to the steps included in Table 4, according to ESA requirements and due to limitations in achieving a higher vacuum than 10^{-3} Pa.
- Step 4 in additional finish on some samples to get an indication of the surface treatments resistance to high temperature in high vacuum condition.

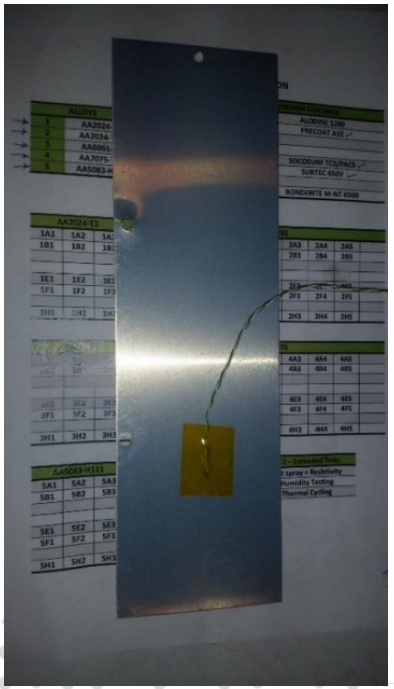
PHASE 2 – EXTENDED TESTING – Thermal Cycling Test

Figure 8 – Thermal Cycling chamber.

PHASE 2 – EXTENDED TESTING – Thermal Cycling Test







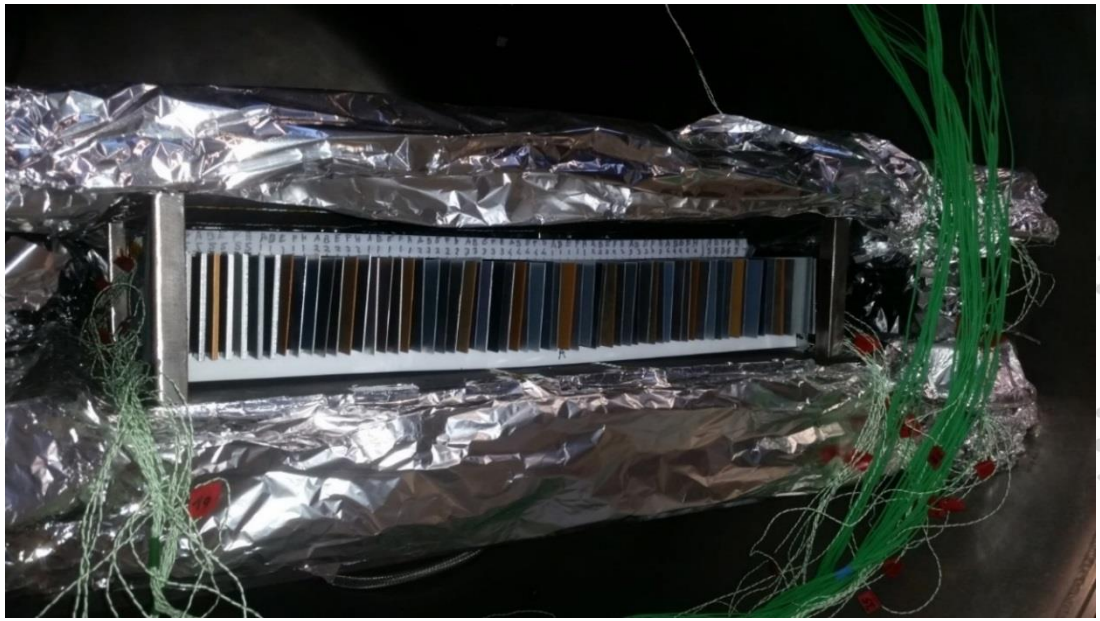


Figure 9 – Details of the test panels submitted to Thermal Cycling.

PHASE 2 – EXTENDED TESTING – Thermal Cycling Test results

Table 8 – Summarised results obtained after thermal cycling test (visual analysis).

STEPS	Aluminium Alloy	Chemical Conversion Coating Pre-treatments				
		Alodine 1200	Precoat A32	Socosurf TCS/PACS	Surtec 650 V	Bonderite M-NT 65000
STEP 1	AA2024-T3	No evidence of corrosion	No evidence of corrosion	No evidence of corrosion	No evidence of corrosion	No evidence of corrosion
	AA2024-T81					
	AA6061-T6					
	AA7075-T73					
	AA5083-H111					
STEP 2	AA2024-T3	No evidence of corrosion; visible areas of discoloration	No evidence of corrosion	No evidence of corrosion	No evidence of corrosion; visible areas of discoloration	No evidence of corrosion
	AA2024-T81					
	AA6061-T6					
	AA7075-T73					
	AA5083-H111					
STEP 3	AA2024-T3	No/ little evidence of corrosion; visible areas of discoloration	No/ little evidence of corrosion	Few density corrosion spots/pits, barely visible to the eye	Few density corrosion spots/pits; visible areas of discoloration	Few density corrosion spots/pits; visible areas of discoloration
	AA2024-T81					
	AA6061-T6					
	AA7075-T73					
	AA5083-H111					
STEP 4	AA2024-T3	No/ little evidence of corrosion; visible areas of discoloration	No/ little evidence of corrosion	Few density corrosion spots/pits	Few density corrosion spots/pits; visible areas of discoloration	Few density corrosion spots/pits; visible areas of discoloration
	AA2024-T81					
	AA6061-T6					
	AA7075-T73					
	AA5083-H111					

PHASE 2 – EXTENDED TESTING – Resistivity Check

- The determination of the resistivity consists on measuring the resistance considering the geometry of the samples.
- The Resistivity Check was carried out in accordance with MIL-DTL-81706, in coated samples before and after the salt spray testing.
- 5 test panels in each configuration were tested 10 times each.

The evaluation criteria for resistivity check, taken from MIL-DTL-5541 are as follows:

"When under a nominal electrode pressure of 200 psi, class 3 coatings are qualified under MIL-DTL-81706 to have a resistance not greater than 5,000 microhms per square inch as supplied and 10,000 microhms per square inch after 168 hours of salt spray exposure".

Figure 15 - Apparatus for connection to the aluminium sheets, detail and micro-ohmmeter.

PHASE 2 – EXTENDED TESTING – Resistivity Check results

ALLOYS	CONVERSION COATINGS	Average Resistivity (mΩ/in²)
AA2024-T3	ALODINE 1200	0.48
	PRECOAT A32	0.45
	SOCOSURF TCS/PACS	0.59
	SURTEC 650V	0.60
	BONDERITE M-NT 6500	0.52
AA2024-T81	ALODINE 1200	1.65
	PRECOAT A32	0.48
	SOCOSURF TCS/PACS	1.45
	SURTEC 650V	1.42
	BONDERITE M-NT 6500	0.87
AA6061-T6	ALODINE 1200	3.80
	PRECOAT A32	1.61
	SOCOSURF TCS/PACS	1.69
	SURTEC 650V	1.91
	BONDERITE M-NT 6500	2.34
AA7075-T73	ALODINE 1200	2.30
	PRECOAT A32	1.35
	SOCOSURF TCS/PACS	1.83
	SURTEC 650V	2.49
	BONDERITE M-NT 6500	1.94
AA5083-H111	ALODINE 1200	2.54
	PRECOAT A32	2.35
	SOCOSURF TCS/PACS	2.97
	SURTEC 650V	2.90
	BONDERITE M-NT 6500	3.00

Table 9 – Resistivity check values before salt spray tests for all tested alloys.

Note: all values not greater than 5 mΩ/in²)

PHASE 2 – EXTENDED TESTING – Resistivity Check results

Resistivity Check After Salt Spray Testing:

- The high number of corrosion points and salt residues present in the samples surface after salt spray testing have make difficult the resistivity check measurements.
- It was agreed to make resistivity measurements on samples submitted to thermal cycling, after the 4 steps.
- All obtained values are greater than 10 $m\Omega/in^2$
- It will be necessary more tests to validate the results and get more knowledge concerning this measurements.

PHASE 2 – EXTENDED TESTING – Humidity Test

- Evaluates the performance of a coating at how well it prevents corrosion under damp heat environments (provides a milder, long term atmosphere in comparison to salt spray tests).
- Humidity exposure and corrosion resistance is a requirement of MIL-PRF-5541.
- 5 test panels in each configuration subjected to an 0 ºC / 90 % R.H. environment, in accordance with ASTM D 2247.
- Test panels were tested altogether for **3500 hrs**. Were inspected every 168 hrs (or every 336 hrs towards the end of testing, depending on the results).
- Areas within 5 mm from the edges, identification markings and holding points during processing were excluded from inspection and loss of colour was not a cause for rejection.

Status: Tests in progress (results after 3321 hours – Table 15).

PHASE 2 – EXTENDED TESTING – Humidity Test

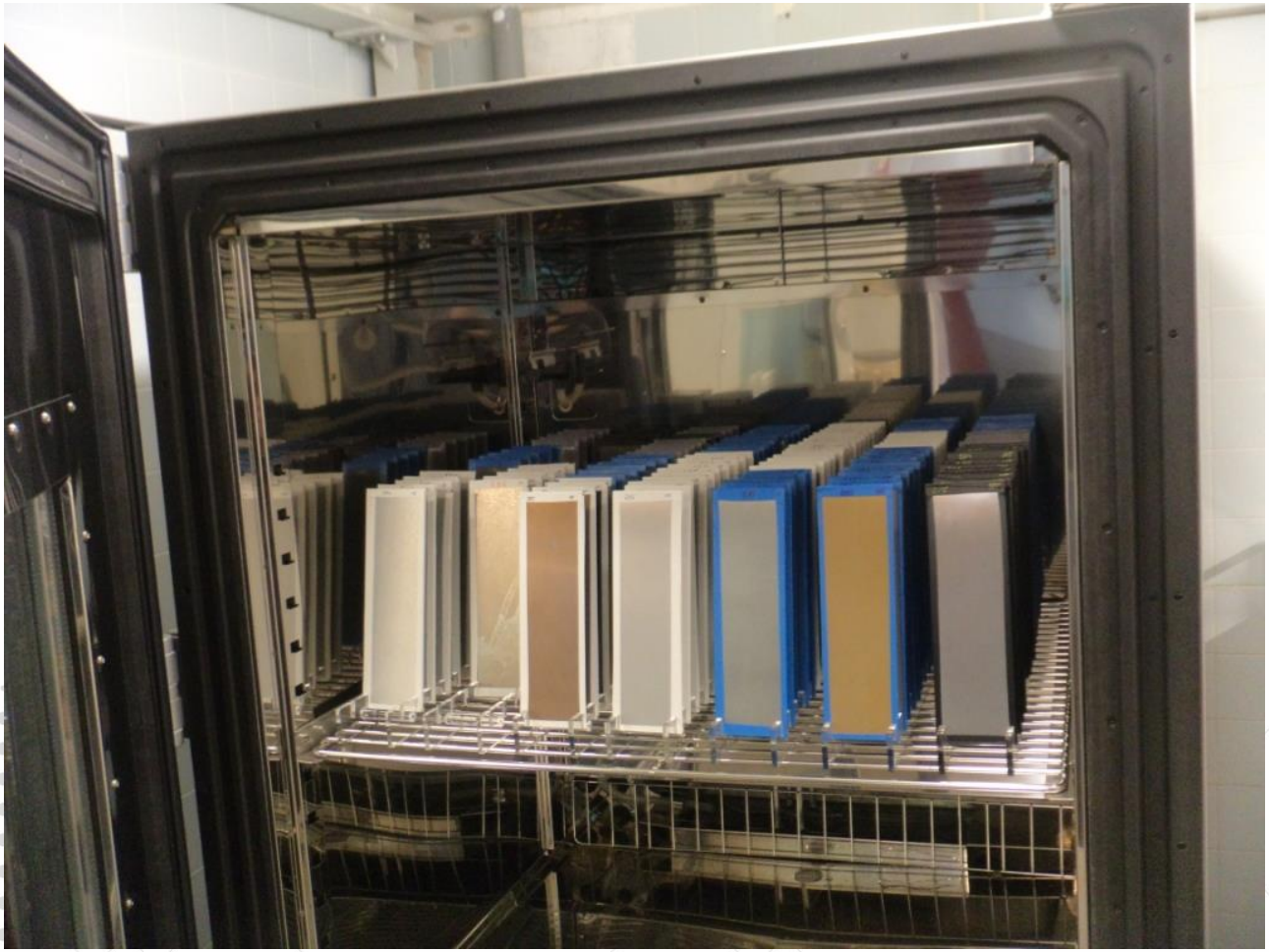


Figure 16 - Humidity and Temperature chamber: ESPEC, MODEL ARL – panels before testing.

PHASE 2 – EXTENDED TESTING – Humidity Test results

Table 15 – Summarised results obtained after 3321h of humidity test .

Aluminium Alloy	Chemical Conversion Coating Pre-treatments				
	Alodine 1200	Precoat A32	Socosurf TCS/PACS	Surtec 650 V	Bonderite M-NT 65000
AA2024-T3	No evidence of corrosion; visible areas of discoloration	No/ little evidence of corrosion	Few density corrosion spots/pits, barely visible to the eye	Few-medium density corrosion spots/pits; visible areas of discoloration	Few-medium density corrosion spots/pits; visible areas of discoloration
AA2024-T81	No evidence of corrosion; visible areas of discoloration	No/ little evidence of corrosion	Few density corrosion spots/pits, barely visible to the eye	Few-medium density corrosion spots/pits; visible areas of discoloration	Few-medium density corrosion spots/pits; visible areas of discoloration
AA6061-T6	No evidence of corrosion; visible areas of discoloration	No/ little evidence of corrosion	No/ little evidence of corrosion	No/ little evidence of corrosion; visible areas of discoloration	No/ little evidence of corrosion; visible areas of discoloration
AA7075-T73	No evidence of corrosion; visible areas of discoloration	No/ little evidence of corrosion	No/ little evidence of corrosion	No/ little evidence of corrosion; visible areas of discoloration	No/ little evidence of corrosion; visible areas of discoloration
AA5083-H111	No evidence of corrosion; visible areas of discoloration	No/ little evidence of corrosion	No/ little evidence of corrosion	No/ little evidence of corrosion; visible areas of discoloration	Few-medium density corrosion spots/pits; visible areas of discoloration

CONCLUSIONS

➢ Test results have shown that after **Salt Spray testing** (504 h), only one pre-treatment (Precoat A32) passed the minimum requirement for all the alloys excepted AA2024 T81.
Socosurf TCS/PACS, Surtec 650V and Bonderite M-NT 65000 passed the minimum requirements for AA7075-T73, AA6061-T6 and AA5083-H111 and failed for both AA2024 T3 and T81.
In all the cases it was noticed that on AA2024 more intense corrosion signs are visible for the T81 treatment than for the T3.

➢ **Resistivity Check** values measured before salt spray tests are bellow 5 $m\Omega/in^2$ for all the pre-treatments and substrates. The average values obtained on samples submitted to thermal cycling are all higher than 10 $m\Omega/in^2$.

CONCLUSIONS

- **Thermal Cycling** results showed that Precoat A32 had good results for all the alloys, after the 4 steps and Socosurf TCS/PACS, Surtec 650V and Bonderite M-NT 65000 showed corrosion and discoloration after step 3 and 4 for all the alloys.

- **Humidity Testing** results (after 3321 h) showed that Precoat A32 performs better on all the substrates. Socosurf TCS/PACS and Surtec 650V showed good performance on all alloys , except on AA2024 alloys. Finally Bonderite M-NT 65000 showed good performance on AA7075-T73 and AA6061-T6.

- The results obtained until now in the extended testing phase have indicated that Precoat A32 and Socosurf TCS/PACS are the most promising chemical conversion alternatives for all the aluminium alloys, including AA2024.

- These two pre-treatments and SURTEC 650V will be included in the **Long Term Environmental Test Programme (Phase 3)** that is now in preparation.

REMARKS

- Current investigations, on a laboratory level, suggest that Cr (III) formulations are the preferred alternative candidates. They do not, however, fully meet the desired requirements e.g. corrosion resistance on high strength alloys. Additionally, the technology maturity of these candidates is low (TRL 3-4 after 10 years of development) for many space applications.

- For the space sector, no other candidate formulations investigated are deemed suitable at this time; however investigations are on-going.[2]

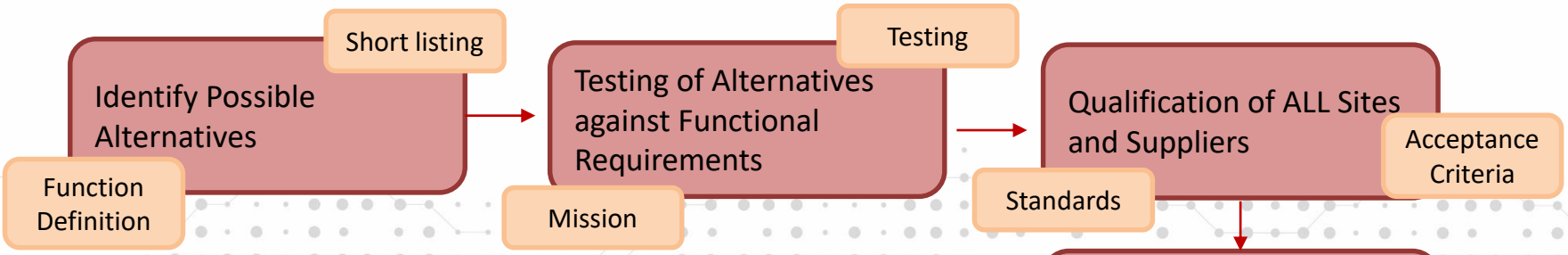


Figure 22 – Key steps in the implementation of new technologies in the Space Sector

[2] Comments on the CTAC(Sub) application for authorisation in public consultation, STF-2015-01 - 6.10.2015

Thank you for your attention!