Document n°	JTI-CS-2011-3-ECO-01-033 - SAA-Seal—Corrosion protection of Aluminum unpainted parts: development of an appropriated Cr free sealing process on thin SAA layer (≤5 μm)
	Final report SAA
Issue date	30/04/2014

ECO-DESIGN ITD

Grant Agreement n° 307834:

JTI-CS-2011-3-ECO-01-033

Document Title	Approval sheet for ECO-DESIGN ITD Grant Agreement for Partners (GAP) Final Report
Issue date	April 30 2014

Eco-Design for Airframe	
GAP n.	307834
Acronym	SAA-Seal
Title	Corrosion protection of Aluminum unpainted parts: development of an appropriated Cr free sealing process on thin SAA layer (≤5 μm)
Starting date	1.05.2012
End date	30.04.2014
Project Period	1.05.2012-30.04.2014
Deliverable id	D9.3 Final report
Deliverable due date	30.04.2014
Deliverable submission date	30.04.2014
ED task n° :	9

Author(s)	Partner:	Date and Signature
Norica Godja/Erich Kny	CEST GmbH	28.04.2014 [signature]
Approval	Topic Manager:	Date and Signature
Nadia Vialas	Liebherr Toulouse	07/05/2014 [signature]

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Partners involved in the document

No	Member name	Short name	Check if involved
1	**CENTRE OF ELECTROCHEMICAL SURFACE TECHNOLOGY**	**CEST**	**X**
2	**LIEBHERR-AEROSPACE TOULOUSE SAS**	**LTS**	**X**

Document Change Record

Version	Date	Author	Comments
01	28/03/14	N. Godja / E. Kny	Document layout and structure
02	01/04/14	N. Godja / A. I. Stoica	Document structure revision & content
03	30/04/14	N. Godja, A. I. Stoica, E. Kny (SAA Coordinator)	Final version

PROJECT FINAL REPORT

Grant Agreement number: 307834

Project acronym: SAA-SEAL

Project title: Corrosion protection of Aluminium unpainted parts: development of an appropriated Cr free sealing process on thin SAA layer (≤ 5 µm)

Funding Scheme: Clean Sky THEME [JTI-CS-2011-3-ECO-01-033]

Date of latest version of Annex I against which the assessment will be made: 29.02.2012

Periodic report: **Final Report**

Period covered: **from 05.2012** **to 04.2014**

Name, title and organisation of the scientific representative of the project's coordinator[1]:

Dr. Erich Kny CEST GmbH

Tel: 0043 664 39 34 459

Fax: 0043 2622 22266 50

E-mail: Erich.Kny@cest.at

Project start: 01 05 2012

Project end: 30 04 2014

Report information

SAA-Seal Final Report	
Due date of final report	30.04.2014
Date of issue	30.04.2014
Reporting period	Month 1-24
Version	1.0
Remarks	RE

[1] Usually the contact person of the coordinator as specified in Art. 8.1. of the Grant Agreement.

Table of content

ACRONYMS LIST

Acronym	Definition
R	Report
RE	Restricted to a group specified by the consortium (including the Commission Services)
SEM	Scanning Electron Microscopy
FIB	Focused Ion Beam
EIS	Electric Impedance Spectroscopy
SAA	Sulphuric Acid Anodizing
RT	Room temperature
DI	Di ionized water
HWS	Hot water sealing
Lib-SAA	Liebherr Sulphuric Acid Anodizing
CEST-SAA	CEST Sulphuric Acid Anodizing
Lit-SAA	Sulphuric Acid Anodizing from literature
TSA	Tartaric Sulphuric Acid Anodizing

Temp. 1 > Temp. 2 > Temp. 3 > Temp. 4

Time 3 < Time 1< Time 4 < Time 2

1. DECLARATION BY THE SCIENTIFIC REPRESENTATIVE OF THE PROJECT COORDINATOR

I as scientific representative of the coordinator of this project and in line with the obligations as stated in Article II.2.3 of the Grant Agreement declare that:

- The final report represents an accurate description of the work carried out in this project for this reporting period;
- The final report (tick as appropriate):

  X has fully achieved its objectives and technical goals of the project;

  ☐ has achieved most of its objectives and technical goals for the project with relatively minor deviations.

  ☐ has failed to achieve critical objectives and/or is not at all on schedule.

- To my best knowledge the financial statements which are being submitted as part of this report are in line with the actual work carried out and are consistent with the report on the resources used for the project (section 3.4) and if applicable with the certificate on financial statement.
- All beneficiaries, in particular non-profit public bodies, secondary and higher education establishments, research organizations and SMEs, have declared to have verified their legal status. Any changes have been reported under section 3.2.3 (Project Management) in accordance with Article II.3.f of the Grant Agreement.

Name of scientific representative of the coordinator: Dr. Erich Kny

Date: 30.04.2014

2. PUBLISHABLE SUMMARY

First anodizing the Al components and applying further protective coatings can counteract corrosion of Al very effectively. During anodizing, Al reacts with the electrolyte and a layer of aluminium oxide is formed, which is highly porous and is subject to corrosive attack. Therefore, anodized Al is normally further processed with a sealing as a final step. Sealed SAA (sulphuric acid anodizing) industrial processes providing thicker layers (~10 µm) are already on the market, but the missing step is to develop a well-suited process for thin layers (≤ 5 µm) that meets the corrosion resistance requirements. Hot water sealing is one of the widely used methods. However in order to close (seal) the pores in the anodized layer for corrosion protection a process involving boiling water containing chromate is still commonly used. Cr(VI)-based sealing solutions (CCC) have been employed for several decades, and remain one of the most effective and commonly-used methods to improve corrosion resistance of anodized Al despite the very toxic properties of Cr(VI). There is an urgent need to replace the toxic Cr(VI) with less harmful alternatives. Alternative sealing methods have been proposed, e.g. with Ni(II), Co(II), Ni(II) + Co(II), rare earth salts, alkali metal fluorides, alkanolamine phosphonates, Cr(III), fatty acids, silicates, etc. It should be noted that Ni(II), Co(II) and fluorides are not without health implications, whereas most organic molecules would be expected to have limited lifetimes under the extreme conditions (UV radiation, low pressure, large temperature range) experienced by commercial aircraft during operation.

In the project anodized AA 2024 samples (sheet and machined) were conversion treated with Sealing 1, with a combination of two silanes or by using of different additives in the sealing bath. The investigated variants provided appropriate corrosion protection after 750 h SST at least comparable to commercially available variants. An adapted version of the electrical SAA cycle for improved corrosion resistance has been developed and tested in the project as well with good and promising success. Conversion with Sealing 1+ additive 2 at low temperature and few minutes treatment time provides the best result in SST (750 h-1176 h) with maximum 1 corrosion pit/dm². The starting material influence (sheet and machined sample) as well as the pre-treatment influence (cleaning, etching etc.) were analysed and the results supported the better understanding of the promising sealing results obtained. Finally the sealing parameters have been optimized with respect to improved corrosion resistance and minimized energy consumption during processing.

3. PROJECT OBJECTIVES

An important objective for the industrial usability is to reduce or eliminate potentially environmentally hazardous effluents from aluminium finishing processes. Particular interest is focused on development of Cr(VI)-, cobalt- and nickel-free aqueous sealant compositions for sealing thin aluminium oxide coatings, with similar or even better results as the ones obtained by an SAA process (Sulphuric Acid Anodizing). Therefore, the main objectives of the SAA-Seal project are:

1. The sealing process on thin (≤ 5 µm) anodized layers obtained by a SAA process has to be carried out by environmental friendly REACH compliant processes and products avoiding Chromium(VI), with optimized process parameters in order to minimize energy consumption.
2. The sealing process on thin layer SAA has to show sufficient corrosion protection in order to meet the corrosion resistance requirements in a 750 hours salt spray test.
3. The effect of the substrate composition (2024, 2618, AS7G06, Au5NKZR) and the effect of the production process (e.g.: cast, laminated, forged) on the corrosion resistance of the sealed SAA layers has to be investigated.
4. Finally, a successful technology transfer towards a supplier selected by the topic manager has to be performed.

In accordance with the topic manager (results of a teleconference on 6.03.2013) the objective 3 was modified:

It has been decided that in **WP5 (D5.1, MS6**) CEST will focus its work on AA 2024 sheet and machined samples only and will not investigate other substrates.

The following processes were undertaking in WP5:

A Optimization of the sealing process with Sealing 1 and with 5 different additives on thin SAA (LTS- LIEBHERR-AEROSPACE TOULOUSE SAS)

B Improved understanding of the differences between machined and sheet samples

The following investigations of the SAA (LTS) surfaces sealed with hot water were performed:
- cross-sections,
- layer thickness and microstructures,
- cracks, etc.

The results helped in understanding and optimizing the reproducibility of anodizing and sealing on both AA 2024 sheet and machined samples.

3.1 QUANTIFIED OBJECTIVES OF SAA-SEAL WORK PACKAGES IN RELATION TO MILESTONES

Work package/ Related Milestone	**Process**	**Objective in SAA-Seal 750 h salt spray test**	**Results achieved**
WP2/MS2	Reference SAA	To provide standard thin SAA reference for comparison	Thin SAA layers provided state of the art were produced on AA 2024 sheet and machined samples.
WP2	Reference CAA	Standard CAA reference for comparison	Standard reference for comparison was provided.
WP3/MS3	SAA + hot water additives	5-10 pits	The objectives (5 to 10 pits) were surpassed on sheet and machined samples: Sealing 1 = 2-3 pits/dm^2; Sealing 2 = 5 pits/dm^2
WP4/MS4	SAA + conversion layer	5-10 pits	1-7 pits/dm^2 have been obtained with Conversion 1 and silane combination (double layers)
WP5/WP6	Optimized process	3-5 pits	Max 1 pit/dm^2 with Sealing 1+ additive 2 at low temperature, few min. for sheet and machined samples

* pits (smaller than 0.8 mm diameter) / 100 cm^2, no pits larger than 0.8 mm.

4 HIGHLIGHTING OF CLEARLY SIGNIFICANT RESULTS

***Significant result 1 - WP3/WP4*: Good results with Sealing 1 treatments obtained**

A good corrosion protection (less than 5 pits/dm² after 750 h SST) using different sealing treatments could be obtained by: Sealing 1 and Conversion 1.

For sheet samples the best results obtained after 750 h in SST are summarized in Table 1 and for machined samples in Table 2.

Table 1 Results for 750 h SST for AA 2024 sheet samples

Time 1 < Time 2; Temp. 1 > Temp. 2 > Temp.4

No.	Sample treatment	SST 750 h (pits/dm²)
1.	HWS, as reference	> 10
2.	Sealing 1 (Temp. 2, Time 2)	2
3	Sealing 2 (Temp. 2, Time 2)	5
4.	Sealing 3 (Temp. 1, Time 2)	8
5.	Conversion 1 (Temp. 4, Time 1)	1

Table 2 Results for 750 h SST for AA 2024 machined samples

No.	Sample treatment	SST 750 h (pits/dm²)
1.	HWS, as reference	>>>
2.	Sealing 2 (Temp. 2, Time 1 or Time 2)	5
3	Sealing 1 (Temp. 2, Time 2)	3
4.	Conversion 1 (Temp. 4, Time 1)	3

Significant result 2 - WP 5/WP6: Reasons for different behaviour of sheet and machined samples elucidated, cause of cracking in coatings explored, excellent results with new conversion coatings obtained

Differences between sheet and machined samples consist in different number and size of particles (containing mainly alloying elements) near to the surface. Particles high in Cu near to the surface of machined samples are bigger than the ones found on sheet samples and will have increased influence on the pore orientation formation during anodizing. A more columnar orientation was found in the case of sheet samples.

A more uniform surface morphology is observed with a supplementary pretreatment step such as alkaline etching (TSAA –pretreatment). There is some evidence by SEM investigations that by TSAA-pretreatment the Cu particles are more completely removed and the resulting mass loss is much higher (15.52 g/m² for sheet and 16.73 g/m² for machined samples) in comparison with standard SAA pretreatment with a resulting mass loss of 1.48 g/m² for sheet and 1.09 g/m² for machined samples.

To further clarify the influence on the occurrence of cracking by layer morphology, thickness, and vacuum exposure (10^{-6} mbar in SEM characterization) for samples treated with a sealing temperature of 98°C and for 40 minutes, the reasons for cracking were investigated more systematically and in greater detail with the following results: the cracks appear only in samples of SAA layer thicknesses > 4 µm induced by the exposure of the samples to vacuum (10^{-6} mbar) during SEM inspection. No such cracks were found by LOM observation.

The best corrosion protection (SST 750 h and 1176 h) was obtained by: Solution 1+ additive 2 treatment at low temperature (Temp. 4) and a few minutes (Time 1) with max 1 pit/dm² for sheet and machines samples (with reproducible results). The same results for sheet samples were obtained by using the solution 1 + additive 3 at Temp.3 and Time 2 sealing.

Table 3 Results for 750 h/1176 h SST for AA 2024 sheet samples

Pre-	Solution no.	Sealing sheet samples	Layer thickness	SST 750 h	SST 1176 h
treatment	Composition based on		(µm)	Pits/dm²	Pits/dm²
Liebherr	Sealing 1 + additive 2	Temp. 4, Time 1	5.3/5.5/5.4	1 / 1 /1	1 / 1 /1
		Temp. 4, Time 1 (reproducibility test)	6.3/6.2/5.6	1 / 1 /1	1 / 1 /1
Liebherr	Sealing 1 + Additive 3	Temp. 3, Time 2	4.3/4.4/4.4	0/0/0	0/0/0
		Temp. 3, Time 2 (reproducibility test)	4.4/5.1/4.6	1 / 0 / 1	1 / 0 / 1

Table 4 Results for 750 h/1176 h SST for AA 2024 machined samples

Pre-	Solution no.	Sealing machined samples	Layer thickness	SST 750 h	SST 1176 h
treatment	Composition based on		(µm)	Pits/dm²	Pits/dm²
Liebherr	Sealing 1 + additive 2	Temp. 4, Time 1	5.2/5.3/5.2	1 / 1 /1	1 / 1 /1
Liebherr	Sealing 1 + additive 2 New samples from February 2014 (thicker)	Temp. 4, Time 1	7.2/7.4/7.4	1 / 1 /1	1 / 1 /1

Time 1 < Time 2; Temp. 2 > Temp. 3 > Temp. 4

Significant result 3 – WP3/WP4/WP 5/WP6: Improved corrosion protection obtained with modified sealing solutions further investigated and explained

The following solutions based on Solution 1 + different additives and on organic compounds were tested in WP4-WP6 with the aim of the replacement of Cr(VI) conversion coatings. These solutions are based on different mixtures and were used for sheet and machined AA 2024 surface treatment to yield a coating equivalent or superior in comparison to a chromate coating.

The tendency of corrosion protection of the sealing layers tested in WP2-WP8 is decreasing in the following order:

Sealing 1+ additive 2 > Conversion 1 > Sealing 1+ additive 3 > Sealing 1+ additive 1 ≥ Sealing 1 > Sealing 2 ≥ Sealing 3 ≥ Sealing 6

5 DETAILED RESULTS OF WP'S

WP1 detailed progress report in ***Annex 1 (deliverable 1.2 uploaded at 31.05.2012, deliverable 1.1 uploaded at 29.10.2012)***

WP2 detailed progress report in ***Annex 2 (deliverable 2.1 uploaded at 17.09.2012)***

WP3 detailed progress report in ***Annex 3 (deliverable 3.1 uploaded at 30.08.2013)***

WP4 detailed progress report in ***Annex 4 (deliverable 4.1 uploaded at 30.08.2013)***

WP5 detailed progress report in ***Annex 5 (deliverable 5.1 uploaded at 31.10.2013)***

WP6 detailed progress report in ***Annex 6 (deliverable 6.1 uploaded at 30.04.2014)***

WP7 detailed progress report in ***Annex 7 (deliverable 7.1 uploaded at 30.04.2014)***

WP8 detailed progress report in ***Annex 8 (deliverable 8.1 uploaded at 30.04.2014)***

WP9 detailed progress report in ***Annex 6 (deliverable 9.1 uploaded at 31.05.2012, deliverable 9.2 uploaded at 11.07.2013, D9.3 uploaded at 30.04.2014)***

6 PROJECT MANAGEMENT DURING THE PERIOD

- *Consortium management tasks and achievements:* coordinating the project, organizing meetings and teleconferences, checking and verifying deliverables and reports.
- *Problems which have occurred and how they were solved or envisaged solutions*: no problems have been encountered
- *Changes in the consortium:* no changes of partners
- *List of project meetings, dates and venues:*

Review number	Tentative timing	Planned venue of rewiew	Comments, if any	Meeting date
RV1	1	Toulouse	Kick Off meeting	05.05.2012
RV2	7	Vienna	6 month report and 6 month meeting	26.11.2012
RV3	13	Toulouse	12 month report and 12 month meeting	13.06.2013
RV4	19	Vienna	18 month report and 18 month meeting	04.02.2014
RV5	21	Toulouse	Final report and Final meeting	07.05.2014

- *Project planning and status:* The objective of work package 5 was changed in accordance with the Topic manager (details to be found in chapter 3 “Project Objectives: Changes in WP5 objectives”)
- *Impact of possible deviations from the planned milestones and deliverables:* deliverables and milestones have been performed as planned; therefore no necessary deviations from the work plan were required.
- *Any changes to the legal status of any of the beneficiaries, in particular non-profit public bodies, secondary and higher education establishments, research organisations and SMEs:* no changes have happened.
- *Deviations from DOW and their impact on other tasks as well as on available resources and planning:* No deviations from DOW have been taking place in the project period for WP 1. 2. 3 and 4. The objectives of WP 5 were modified in accordance with the topic manager and the content of the deliverable D5.1 and the MS6 has been changed accordingly. All other deliverables, milestones and tasks are on schedule and unchanged. The modification of WP5 has however no influence on budget and resources.
- *Use of resources:* No deviations from planned work have happened.

7 DELIVERABLES AND MILESTONES TABLES

TABLE 5. DELIVERABLES

Del. no.	Deliverable name	Ver-sion	WP no.	Lead beneficiary	Natu-re	Dissemina-tion level	Delivery date from Annex I (proj month)	Actual delivery date Dd/mm/yyyy	Status Not Sub-mitted/ Submitted	Contractual Yes/No	Comments
D9.1	Kick Off Meeting	1	9	CEST	CO	RE	1	29/05/2012	Submitted	Yes	
D1.2	Agreed and detailed test program	1	1	CEST	R	RE	1	29/05/2012	Submitted	Yes	
D2.1	Implementation of SAA process as reference	1	2	CEST	R	RE	3	17/09/2012	Submitted	Yes	
D1.1	Bibliography od SAA sealing	1	1	CEST	R	RE	6	30/10/2012	Submitted	Yes	
D3.1	SAA sealing process	1	3	CEST		RE	16	30.08/2013	Submitted	Yes	

D4.1	Alternative sealing process developed	1	4	CEST	R	RE	16	30.08/2013	Submitted	Yes	
D5.1	Study on substrate variation effect	1	5	CEST	R	RE	18	31/10/2013	Submitted	Yes	In agreement with the Topic manager. the objective was changed in favour of intensified studying of conversion layers based on Mn/Zr/F/Ce for AA 2024 sheet and machined
D6.1	Samples. results of combined measures	1	6	CEST	R	RE	24	30/04/2014	Submitted	Yes	
D7.1	Results of characterizati on will be provided to the corresponding	1	7	CEST	R	PP	24	30/04/2014	Submitted	Yes	

	work packages										
D8.1	Optimized process parameters	1	8	CEST	R	RE	24	30/04/2014			
D9.2	Midterm progress report	1	9	CEST	R	RE	13	11.07.2013	Submitted	Yes	Deliverable date was changed in accordance with the topic manager
D9.3	Final meeting and final report	1	9	CEST	R	RE	24	07/05/2014	Submitted	Yes	

TABLE 6. MILESTONES

Milestone no.	Milestone name	Work package no	Lead beneficiary	Delivery date from Annex I Project month	Achieved Yes/No	Actual achievement date dd/mm/yyyy	Comments
MS1	Agreed and detailed Test Program	1	CEST	1 (31/05/2012)	Yes	31/05/2012	
MS2	SAA process implemented and characterized as reference	2	CEST	3(31/07/2012)	Yes	17/09/2012	
MS3	Preliminary identification of optimal hot water sealing additives	3	CEST	10(28/02/2013)	Yes	06/03/2013	
MS4	Final identification of optimal hot water sealing additives optimized	3	CEST	16(31/08/2013)	Yes	30/08/2013	

MS5	Identification of optimal alternative cold sealing procedure	4	CEST	16(31/08/2013)	Yes	30/08/2013	
MS6	Study on substrate variation effect completed	5	CEST	18(31/10/2013)	Yes	18/10/2013	In agreement with the topic manager the objective of WP5 was modified in favour of intensified studies of conversion layers based on Mn/Mo/V//Zr/F/Ce for AA 2024 laminated and machined samples.
MS7	Identification of optimal combined process parameters	6	CEST	24(30/04/2014)	Yes	30/04/2014	

MS8	Final report on characterization results	7	CEST	24(30/04/2014)	Yes	30/04/2014	
MS9	Optimized sealing procedure	8	CEST	24(30/04/2014)	Yes	30/04/2014	
MS10	Final report. Presentation. discussion and benchmarking of all results	9	CEST	24(30/04/2014)	Yes	7/05/2014	

8 LIST OF ANNEXES

- Annex 1 WP1 Results Report
- Annex 2 WP2 Results Report
- Annex 3 WP3 Results Report
- Annex 4 WP4 Results Report
- Annex 5 WP5 Results Report
- Annex 6 WP6 Results Report
- Annex 7 WP7 Results Report
- Annex 8 WP8 Results Report
- Annex 9 WP9 Results Report

ANNEX 1 WP1 RESULTS REPORT

WP1: Bibliography of SAA sealing

Objectives of WP1: Definition of detailed test program based on bibliography report of SAA

Description of Work according to DOW: *to perform a bibliographic study on SAA and sealing.* The state on the art on anodizing processes will be described in great detail; other anodizing processes such as BSAA, TSAA will be included in order to be exhaustive. A suitable detailed test matrix will be worked out based on the bibliographic survey, on previous experience and on exploration of commercially available sealing solutions and those reported in the literature and patents. The matrix will then be employed in WP2. Main focus of literature search: SAA Anodization / Sealing.

Deliverables:

D1.1 Bibliography of SAA sealing (fulfilled and uploaded on 10.10.2012- bibliography gradually included in report until October 2012)
D1.2 Agreed and detailed test program: Agreed and detailed tests to be performed, proposal for analytics and methods to monitor and optimize the performance of the processes (fulfilled and uploaded on 29.05.2012)

Milestone MS1: Agreed and detailed Test Program: was discussed in detail at the SAA Kick-off meeting at 5.05.2012 in Toulouse and described in D.1.2: Agreed and detailed test program.

Results achieved in WP1

The finished literature report (D1.1) describes the effect of anodizing conditions like voltage, temperature, composition and acid concentration of the bath, on the anodizing current density, on the porosity and on the diameter of the pores of the anodic oxide. It can be concluded that potentiodynamic anodizing is a powerful tool for fundamental and practical investigations of anodizing processes. When applied to alloys, potentiodynamic anodizing enables rapid identification of the potentials required for the oxidation of additional secondary phases present on the surface of alloys, for a given electrolyte-material combination.
A hot water (usually including other ingredients as well) sealing process is one of the widely used methods. In this process the aluminum oxide reacts with water to form aluminum hydroxide, which fills the pores in the coating and seals the surface. However in order to close very effectively (seal) the pores in the aluminum oxide anodized layer for corrosion protection a process involving boiling water containing chromate is still commonly used.
By hot water sealing (HWS), the hydration of the aluminum oxide results in a volume expansion of the films and closes the pores. Additives in the sealing bath are sometimes used to increase the efficiency of treatment. The differences in thermal expansion between the substrate and the film can lead to the cracking of the film when thermally loaded.
Cold sealing techniques of anodic films via CCC may offer advantages concerning the integrity of the anodized coating. A number of promising “green” alternatives have been studied, with the objective of replacing chromates, such silane (water-based and alcohol based) with and without corrosion inhibitors (e.g. cerium salts), monocarboxylic acids, Mn/Mo oxyanions.
Based on the literature study and on previous experiences of CEST a test matrix was established in D1.2 in agreement with the topic manager.

All detailed results of WP1 have been uploaded on 10.10.2012 in deliverable D 1.1

ANNEX 2 WP2 RESULTS REPORT

WP2: SAA implementation as reference

Objectives of WP2: SAA implementation as reference

Description of Work according to DOW: Aluminium (AA 2024 sheet) will be anodised according to the SAA process to prepare standard “reference” samples. The performance of such samples will be tested in corrosion tests. This will provide a baseline from which to judge the sealing procedures. A further comparison with SAA sealed with hot water will be established as an alternative and additional reference. The SAA process will later be performed in the scope of later work packages for in-line-preparation of specimens for subsequent sealing process.

Deliverables:

D2.1 Implementation of SAA process as reference, specimens and results (report) delivered to the topic manager.

Milestone MS2: SAA process implemented and characterized as reference.

Results achieved in WP2

Aluminium substrates (AA 2024 sheet and machined) were anodised according to the SAA process to prepare standard “reference” samples. The performances of such samples were tested in corrosion tests: impedance measurements and salt spray tests. These results have provided a baseline from which to judge the performance of sealing procedures. Furthermore, a comparison with SAA sealed with hot water results was done and based on this a reference was established. The SAA process will be applied afterwards in the later work packages for in-line-preparation of specimens for subsequent sealing process.

The samples are AA 2024, sheet and machined, with a size of 25x100x3 mm, while for SST samples with a dimension of 150x80x3 mm were used for characterization. The surface of all the samples was treated (anodized and hot water sealed) at laboratory scale at CEST. Three different anodizing procedures have been compared:

- The standard SAA anodizing process of Liebherr
- The anodizing process established at CEST
- An anodizing process adapted from literature

AA 2024 sheet

- Layer thickness (obtained from FIB measurements): for the anodizing methods Liebherr and CEST the measured layer thicknesses are around 5 µm and the layer thickness for the process derived from Literature was around 3.5 µm.

- Pore diameter (on surface and anodic layer): for anodizing method CEST and Liebherr the pores (ranked equal) are smaller than for Literature. The pores for anodizing method Literature are the largest ones and are not uniformly distributed.

- Contact angle: after performing the sealing process an increase of the contact angle by about 10° was obtained for all the anodizing methods.

- Layer morphology investigation by FIB and SEM: for the anodizing methods Liebherr and CEST after HWS and FIB preparation many cracks are visible. A larger amount of cracks were detected for the anodizing method Liebherr compared to the CEST method. For the anodizing method Literature, no cracks are visible after sealing (this method generates a thinner anodic layer). However, this is assumed to be a preparation artifact caused by the FIB preparation method. After performing the sealing process the surface was covered with a typical layer of acicular boehmite crystals and for all anodizing methods the presence of closed pores is evident.

- Agreement of EIS and SST results: SST results of samples obtained by using the CEST and Liebherr anodization procedure are in full agreement with results obtained by EIS measurements. For SST results of samples anodized with the method from Literature there is no agreement with EIS measurements. A tentative explanation for this behavior might be that the pore distribution on the surface of such samples is not uniform and the pore diameter is twice as large as for the samples anodized by CEST and Liebherr methods.

- SST corrosion testing: for samples at 840 h SST the anodizing methods CEST and Liebherr ranked equally followed by anodizing method Literature.

Based on the above results, the SAA process to be defined as a reference for the next working package could therefore be either the CEST-anodizing or the Liebherr-anodizing process. The obtained results were discussed on November 28th 2012 at a meeting in Wiener Neustadt, and it was decided that the anodizing reference for both alloys machined and sheet would be the Liebherr-anodizing process.

AA 2024 machined

- Layer thickness (obtained from FIB investigations): the results shows that for the samples anodized with Liebherr and CEST methods the layer thicknesses are higher than for the ones obtained with the Literature method.

- Pore diameter (on surface): no substantial differences were found between anodizing methods Liebherr, CEST and Literature.

- Pore diameter (of anodic layer): larger values of pore diameter were determined for anodizing method Literature (but pores are not uniformly distributed) compared to anodizing methods CEST and Liebherr. The pore diameters of the samples obtained with the latter methods are in the same range.

- Contact angle: no significant difference for anodizing methods CEST (± 6°) and Liebherr (± 2°) could be found after sealing in comparison to values before sealing. For the anodizing method Literature the contact angle values after sealing are approximately 10° higher than the ones recorded before this process.

- Morphology by SEM/FIB: for all anodizing methods (Liebherr, CEST and Literature) remaining grooves of the machined surface are visible on the anodized surface before sealing. After performing the sealing process the surface was covered with a typical layer of acicular boehmite crystals.

750 h SST results –variation in anodizing methods

To identify the best working conditions, the samples anodized with Liebherr, CEST and Literature methods and hot water sealed at 98 °C for 40 min were salt spray tested for 750 h. To simulate the aging effect of Al ions $Al_2(SO_4)_3$ (8 g/l) were added to the anodizing baths. The SST results show no significant differences for the samples anodized with the Liebherr method with and without Al(III) in the bath.

All detailed results of WP2 have been uploaded on 17.09.2012 as deliverable D2.1

ANNEX 3 WP3 RESULTS REPORT

WP3: Hot and cold water sealing

Objective of WP3: Hot and cold water sealing with REACH compliant sealing additives

Description of Work according to DOW: commercially-available, REACH-compliant sealing additives and related chemicals will be sourced. Aluminium will then be anodised according to the SAA process and the oxide layer sealed in hot and cold water with said additives. The suggested additives are based on additions of rare earth elements, and/or carboxylic acid and/or silane.

Deliverables:

D3.1 SAA sealing process: SAA sealing process development performed. SAA-coated and sealed samples delivered and documented in Report [month 16; 31.08.2013]

Milestones:

Milestone MS3 Preliminary identification of optimal hot water sealing additives [month 10; 28.02.2013]

Milestone MS4 Final identification of optimal hot water sealing additives optimized [month 16; 31.08.2013]

Results achieved in WP3

AA 2024 sheet and machined (Temp. 1 > Temp. 2)

With Sealing 2, the pores are partially filled, an organic layer (thickness depending on sealing temperature) is deposited onto the SAA layers, and the contact angle is increased to values of >100° for sheet samples (120°at Temp. 2 and 106° at Temp. 1) and to > 45° for machined samples (45° at Temp. 2 and 63° at Temp. 1).

With Sealing 5 and Sealing 6 the pores are partially filled in case of using of Sealing 6 and the contact angle was about 90° (temperature dependent). The sealing layers were very thin and could not be determined by FIB because FIB was not enough sensitive for layer thicknesses measurement.
The pores are not filled in case of using of sealing 5 and the contact angle was for sheet samples 79° at Temp. and 97° at Temp. 1 and 84° for machined samples at Temp. 2 and Temp. 1. The sealing layers were about 300 nm thick for sheet samples and about 150 nm for machined samples.

With Sealing 1: the pores are filled (at Temp. 1 and Temp. 2), the contact angles were 55 ° at Temp. 1 and 54 ° at Temp. 2 for sheet samples and 65 ° at Temp. 1 and 51 ° at Temp. 2 for machined samples.

With Sealing 3: the pores are partially filled and the contact angle was between 43° (Temp. 2) and 63° (Temp. 1). The contact angles for machined samples were about 37°.

The best results (green) from 750 h SST are presented in the table 3.1

Table 3.1 750 h SST results for AA 2024 sheet and machined samples anodized with Liebherr process and sealed with different additives (hot sealing with additives, Time 2)

	Temperature	AA 2024 sheet	AA 2024 machined
		Pits/dm^2	Pits/dm^2
HWS		> 10	>>
Sealing 2	Temp. 1	10	5
	Temp. 2	5	5
Sealing 5	Temp. 1	20	>>>>
	Temp. 2	20	>>>>
Sealing 6	Temp. 1	10	>>>>
	Temp. 2	10	>>>>
Sealing 1	Temp. 1	5	10
	Temp. 2	2	3
Sealing 3	Temp. 1	12	>>
	Temp. 2	10	>>>

Note:
Temp.1 > Temp. 2 > Temp. 3 > Temp. 4
Time 1< Time 2

All detailed results of WP3 have been uploaded on 30.08.2013 as deliverable D3.1

ANNEX 4 WP4 RESULTS REPORT

WP4: Investigation of alternative sealing processes via conversion coatings

Objectives of WP4: To seal aluminium according via alternative chromate-free conversion coatings

Description of Work according to DOW: Aluminium samples will be anodised by the SAA process. A range of alternative, chromate-free conversion coatings will be applied according to the test program defined in WP1. Ideally these processes should operate at room temperature, with low-cost, permitted chemicals and therefore represent a safe and energy-efficient alternative to existing sealing processes. Alternatives will for example include Cr(III), silanes, or aluminium salts with alkoxy silanes or rare earth elements containing coatings (e.g. CeO_2 2 H_2O).

Deliverables

D4.1 Alternative sealing process developed: Alternative sealing process developed and documented [delivery date month 16 (31.08.2013)]

Milestone MS5 Identification of optimal alternative cold sealing procedure

Results achieved in WP4

Conversion 1 at low temperatures, for a few minutes treatment time, increased the corrosion resistance for sheet and machined samples (max. 3 pits/dm² at 750 h SST). With all the proposed conversion coatings such as Sealing 5 and Sealing 6, the SST results were not satisfactory (large number of pits) and the layer characterisation was not included in this report (D4.1). Another CEST idea (not included in the initial proposed test matrix) was to use a double silane layer and with this procedure encouraging results could be obtained, but the economical point of view (chemicals costs, treatment time) has to be taken into account too. The best results for 750 h SST of conversion layer are presented in table 4.1.

Table 4.1 750 h results for AA 2024 sheet and machined
Temp. 2 > Temp. 4; Time 1 > Time 3

Anodizing Liebherr	Time	AA 2024 sheet	AA 2024 machined
	minutes	Pits/dm²	Pits/dm²
Conversion 1	Time 3	2	3
	Time 1	1	3
Silane double layers	Time 2 (Temp. 2) + Time 4 (Temp.4) +	6	7

All detailed results of WP4 have been uploaded on 30.08.2013 as deliverable D4.1

ANNEX 5 WP5 RESULTS REPORT

WP5: Investigating the effects of the substrate and working conditions

The original objective of WP5 was: investigating the effects of the substrate composition (2024, 2618, AS7G06, AU5NKZR) and working conditions (cast, laminated, forged) on the performance of the SAA/sealing processes.

This work package was modified in accordance with the Topic manager.

It has been decided by the topic manager that the investigations of CEST in WP5 will be focused on AA 2024 samples (sheet and machined) for more detailed investigations and not as **previously planned to** use different substrates composition.

The new objectives are:

A Optimization of the sealing process by Sealing 1 with different additives on thin SAA (Liebherr- LTS)

B Improved understanding of the differences observed between machined and sheet samples

To understand the differences between machined and sheet samples, a more extended characterization of the samples has to be done. Investigation (of SAA Liebherr samples sealed with hot water) of the surfaces, cross-sections, layers, microstructures, cracks, thickness etc. which could help in understanding and optimizing reproducibility of results for both AA 2024 sheet and machined samples will be performed.

New Deliverable D5.1: Optimal sealing process based on Sealing 1 + additive 2 and identification of differences observed between sheet and machined samples [to be delivered in month 18, 31.10.2013]

New Milestone M5: Identification of optimal sealing process based on Sealing 1+ additive 2 on thin SAA for AA 2024 sheet and machined samples and identification of differences between sheet and machined samples.

Results achieved in WP5, Objective A

A Optimization of the sealing process by Sealing 1 + different additives on thin SAA (LTS)

- The best result in SST (750h) for sheets samples was obtained for the sample treated with Sealing 1 + additive 3 (Temp. 3, Time 2) with 0 pits for all 3 parallel samples with a SAA layer thickness of about 4.4 µm and with Sealing 1 + additive 2 (Temp. 4, Time 1) with 1 pit/dm² for all parallel samples with a SAA layer thickness of about 5.3 µm.
- The potentiodynamic measurements cannot predict the corrosion resistance in SST, probably because of a heterogeneous distribution of intermetallic phase on the surface and due to

localized heterogeneity of the sealing layers. The results (chapter 2.2.1.8- pit analysis by SEM- in D5.1 uploaded on 31.10.2013) and also mentioned in the literature suggests that these particles are electrochemically active with respect to the matrix phase and subject to de-alloying which leaves Cu-rich remnants after exposure to aggressive solutions. The potentiodynamic measurements in 5 different spots on the same sample show differing results as well.

- The grazing incidence X-ray measurements for all sheet and machined samples treated with Sealing 1 + additive 1 revealed the presence of different crystalline phase regardless of temperature and time.
- Generally better results in SST were obtained for the sheet samples in comparison to machined samples treated with comparable anodizing and sealing conditions.

B Understanding of the differences observed between machined and sheet samples

The objective B was the improved understanding of the differences observed between machined and sheet samples.

Results achieved in WP5, Objective B

Sheet and machined samples with different SAA layer thicknesses (between 1.6 µm and 6.6 µm) obtained by variation of the anodizing time have been characterized.

The results show:

- The cracks appear only in samples of SAA layer thicknesses > 4 µm after SEM inspection exposed to high vacuum. No cracks were found by LOM characterization.
- Good sealing quality (SEM surface analysis and tests with Sanodal Blue G) were obtained for thin SAA layers (2-2.5 µm)
- SST results (750 h) show good results only for SAA layer thickness >4 µm for sheet samples (10 pits) but not for the machined samples (>>>> pits / whole surface covered with pits) for all SAA thicknesses.
- Two pre-treatment types: SAA and TSAA were tested and the surface of sheet and machined sample was characterised with SEM/EDX. A mass loss of 1.48 g/m² resulted for sheet samples and 1.09 g/m² for machined samples after SAA pretreatment, alkaline decreasing and acid pickling. A mass loss of 15.52 g/m² for sheet samples and of 16.73 g/m² for machined samples resulted after TSA pretreatment, after alkaline decreasing, alkaline etching and acid pickling. A more uniform surface morphology is observed for the TSAA treatment. There is some evidence by SEM investigations that by the TSAA treatment Cu particles are more completely removed. It could also be shown that in the pit region appearing after SST a Cu particle is the probable cause.
- For the same SAA layer thicknesses (~ 5 µm) on both sheet and machined AA 2024 samples, the pore diameters (of anodic layer) were between 16 nm and 29 nm. For both sheet and machined samples the Cu content on the surface was ~ 4.5 wt% and the Mg concentration was ~ 1.7 wt% (EDX – measurement). Big differences were found in particles (alloying elements) size and content. For example for machined samples the biggest particles (14 µm - 29 µm) contained Cu and the small particles (3 µm - 11 µm) contained Cu/Mn/Fe/Mg phases, while for sheet samples the biggest particles (6 mm - 17 µm) contained Cu/Mn/Fe/Mg phases and the small particles (0.5 µm - 0.8 µm) contained Cu.

The results concerning surface characterization were presented in the Midterm report (uploaded on 11.07.2013) and D5.1 (uploaded on 31.10.2013).

The summarising SST results are presented in the next table 5.1 and 5.2

Table 5.1. Samples for SST on aluminium AA 2024 sheet. Sample dimension 150x80x2 mm, pretreatment and anodization with Liebherr method.
Time 1 < Time 2
Temp. 2 > Temp. 3 > Temp. 4

Sample No.	AA 2024	Sealing	SST 750h (Pits/dm²) 3 parallel samples
S152-S 154	sheet	Sealing 1 + additive 1, Temp. 3, Time 2	10 / 12 / 12
S155-S157	sheet	Sealing 1 + additive 1, Temp. 4, Time 1	3 / 5 / 5
S158-S160	sheet	Sealing 1 + additive 2, Temp. 3, Time 1	6 / 7 / 7
S161-S163	sheet	Sealing 1 + additive 2, Temp. 4, Time 1	1 / 1 / 1
S164-S166	sheet	Sealing 1 + additive 3, Temp. 3, Time 2	1 / 0 / 1
S167-S169	sheet	Sealing 1 + additive 3, Temp. 4, Time 1	1 / 5 / 4
S170-S172	sheet	Sealing 1 + additive 4, Temp. 3, Time 1	8 / 6 / 6
S173-S175	sheet	Sealing 1 + additive 4, Temp. 2, Time 1	10 / 9 / 10
S176-S178	sheet	Sealing 1 + additive 5, Temp. 2, Time 1	12 / 10 / 10
S179-S181	sheet	Sealing 1 + additive 5, Temp. 3, Time 2	8 / 9 / 8

Table 5.2 Samples for SST on aluminium AA 2024 machined. Sample dimension 150x80x2 mm, pretreatment and anodization with Liebherr method.
Time 1 < Time 2
Temp. 2 > Temp. 3 > Temp. 4

Sample No.	**AA 2024**	**Sealing**	**SST 750 h (Pits/dm²) 3 parallel samples**
SM142-SM144	machined	Sealing 1 + additive 1, Temp. 2, Time 2	5 / 4 / 6
SM145-SM147	machined	Sealing 1 + additive 1, Temp. 3, Time 1	0 / 0 / 1
SM148-SM150	machined	Sealing 1 + additive 2, Temp. 3, Time 2	3 / 5 / 3
SM151-SM153	machined	Sealing 1 + additive 2, Temp. 2, Time 2	>>>
SM154-SM156	machined	Sealing 1 + additive 3, Temp. 2, Time 2	>>>
SM157-SM159	machined	Sealing 1 + additive 3, Temp. 4, Time 1	6 / 6 / 7
SM160-SM162	machined	Sealing 1 + additive 4, Temp. 2, Time 2	6 / 6 /6
SM163-SM165	machined	Sealing 1 + additive 4, Temp. 3, Time 2	4 / 7 / 8
SM166-SM168	machined	Sealing 1 + additive 5, Temp. 2, Time 1	5 / 5 / 7
SM169-SM171	machined	Sealing 1 + additive 5, Temp. 3, Time 1	6/ 11 / 7

ANNEX 6 WP6 RESULTS REPORT

The content of WP 6 according to DOW is: Combination of individual measures.

Objectives: Combination of individual measures to optimize the corrosion resistance of sealed SAA samples further.

Description of work and role of partners:

The SAA treatment may be performed with different electrical profiles (e.g. continuous, pulsed, pulsed with offset, and so on). It is well known that the potential profile can have a significant effect on the resulting oxide layer. In this WP the effect of the potential / current profile on the thin anodic layer properties will be investigated.
The optimised SAA samples will be sealed with the sealing processes obtained in WP3 and WP4 and their corrosion resistance will be determined. Also the cleaning steps of the Al samples before the SAA process will be closely investigated and optimized in order to optimize the corrosion resistance of resulting anodized and sealed samples. The optimization of the SAA process parameters to improve corrosion resistance will be performed in close accordance with the topic manager since the topic manager and its supplier have already defined SAA and cleaning parameters.

Related Milestone MS7: Identification of optimal combined process parameters [month 24; 30.04.2014]

The effect of the potential / current profile on the thin anodic layer properties was investigated and the results were presented in the Deliverable D2.1. The cleaning steps of the Al samples before the SAA process were investigated and optimized in order to optimize the corrosion resistance of resulting anodized samples. In order to evaluate the pre-treatment procedure it was decided in accordance with the Topic Manager to test in comparison to Liebherr pretreatment the standard AIRBUS pretreatment procedure (AIPI_02-01-003_2010-06_3), see Chapter 2, D6.1. The Mn/Mo conversions coating developed in WP 3 (with the best corrosion results in WP3 for sheet and machined samples) was optimized in WP 5 with different additives addition. The new objective of WP 5, part A was: optimization of the sealing process by solution 1 + additives on the thin SAA (Liebherr-LTS). Based on D2.1 results, the SAA process to be defined as reference for the next work packages: WP 3, WP4 could be either CEST anodizing or Liebherr-anodizing. The decision based on these results was discussed in the meeting on 28. November 2012 in Wiener Neustadt and so for all next work packages the SAA cycles remain SAA-Liebherr. On the teleconference from 18 December 2013 it was decided to test the reproducibility of the sealing quality for the best results obtained after SST in WP 5 in comparison with the conversion 1 (best results in WP4). The effect HWS treatment after sealing with the previous Sealing solutions was studied.

For the identification of optimal combined process parameters, a text matrix was established and the results are presented in the table 6.1 and 6.2.

Results achieved in WP6

The reproducibility of only the best results obtained for both samples type sheet and machined respectively, are for sheet samples in Sealing 1+ additive 2 and Sealing 1 + additive 3 and for machined samples in Sealing 1 + additive 1 and Sealing 1 + additive 2. The reproducibility in SST was found to be good (difference of only 0-1 pit) for sheet samples for both solutions. The reproducibility of machined samples was only found to be good for Sealing 1 + additive 2.

The best sealing processes (carried out after Liebherr-Anodization cycle) are Sealing 1+ additive 2, Temp. 4, Time 1 and Sealing 1+ additive 3, Temp.3, Time 2 for sheet samples (with 0-1 pits after 1176 h (7 weeks) SST) and Sealing 1 + additive 2, Temp. 4, Time 1 (1 pit after 1176 h SST) for machined samples.

The combined SST results (WP5 + WP6) are presented in the table 6.1 (sheet samples) and table 6.2 (machined samples).

Table 6.1 750 h SST/1176 h SST results for sheet samples (WP5/WP6)

Temp. 2 > Temp. 3 > Temp. 4; Time 1 < Time 2

Pre-treatment	Solution no. Composition based on	Sealing sheet samples	Layer thickness (µm)	SST 750 h Pits/dm²	SST 1176 h Pits/dm²
Liebherr	Sealing 1 + additive 1	Temp. 4, Time 1	7.5 / 7.5 / 7.3	3/5/5	5/6/6
		Temp.3, Time 1	6.5 / 6.4 /6.1	12/11/10	-------
		Temp.3, Time 2	5.7 / 6.8 / 7.0	10/12/12	-------
		Temp. 3, Time 1 + HWS	4.0 / 4.5 / 4.3	30 / 30 / 30	-------
Liebherr	Sealing 1 + additive 2	Temp. 4, Time 1	5.3 / 5.5 /5.4	1 / 1 /1	1 / 1 /1
		Temp. 4, Time 1 (reproducibility)	6.3 / 6.2 / 5.6	1 / 1 /1	1 / 2 /2
		Temp. 3, Time 1	6.0 / 6.2 / 6.1	6/7/7	10/6/10
		Temp. 4, Time 1, HWS	5.5 / 5.0 / 5.4	10/10/10	-------
Liebherr	Sealing 1 + additive 3	Temp. 4, Time 1	4.4 / 5.1 / 4.8	1/5/4	1/5/4
		Temp.3, Time 2	4.3 / 4.4 /4.4	0/0/0	0/0/0
		Temp.3, Time 2 (reproducibility)	4.4 / 5.1 / 4.6	1 / 0 / 1	1 / 0 / 1
		Temp.3, Time 2 + HWS	5.7 / 5.8 / 5.9	0/ 1 / 1	0 / 1 / 1 black staining
Liebherr	Sealing 1 + additive 4	Temp. 3, Time 1	6.1 / 6.3 / 6.5	8/6/6	-------
		Temp. 2, Time 1	7.9 / 7.9 / 8	10/9/10	-------
Liebherr	Sealing 1 + additive 5	Temp. 3, Time 2	6.0 / 5.9 / 5.7	8/9/8	-------
		Temp. 2, Time 1	6.8 / 6.9 / 6.3	12/10/10	-------
TSA	Sealing 1 + additive 1	Temp.3, Time 1 (reproducibility)	5.4 / 5.7 / 5.8	12/10/10	12/10/10
TSA	Sealing 1 + additive 2	Temp. 4, Time 1 (reproducibility)	6.1 / 5.7 / 6.3	1 / 1 / 0	1 / 1 / 1
TSA	Sealing 1 + additive 3	Temp. 3, Time 2 (reproducibility)	5.1 / 5.6 / 5.5	0/0/0	0 / 0 / 0 black staining
Liebherr	Conversion 1	Temp. 4, Time 1	4.2 / 3.0 / 2.5	1/1/0	-------

Table 6.2 750 h SST/1176 h SST results for machined samples (WP5/WP6)

Temp. 2 > Temp. 3 > Temp. 4; Time 1 < Time 2

Pre-treatment	**Solution no. Composition based on**	**Sealing machined samples**	**Layer thickness (µm)**	**SST 750 h Pits/dm²**	**SST 1176 h Pits/dm²**
Liebherr	Sealing 1 + additive 1	Temp. 2, Time 2	4.7 / 5.5 / 4.8	5/4/6	8/5/10
		Temp. 3, Time 1	5.6 / 3.8 /3.5	0/0/1	0/1/3
		Temp. 3, Time 1 (reproducibility)	8.2 / 7.9 / 7.6	10/8/10	10/8/10
		Temp. 3, Time 1 + HWS	3.3 / 3.0 / 3.0	>>> />>> />>>	--------
Liebherr	Sealing 1 + additive 2	Temp. 4, Time 1	5.2 / 5.3 / 5.2	1 / 1 /1	1 / 1 /1
		Temp. 3, Time 2	5.9 / 6.3 /5.8	3/5/3	10/5/>10
		Temp. 2, Time 2	6.5 / 8.3 / 6.6	>>>	--------
		Temp. 4, Time 1 + HWS	4.4 / 4.8 / 4.7	>>	--------
Liebherr	Sealing 1 + additive 3	Temp. 4, Time 1	4.6 / 4.5 / 4.1	6/6/7	--------
		Temp. 2, Time 2	4.4 / 4.0 /4.2	>>>	--------
		Temp. 3, Time 2	3.8 / 3.8 / 4.2	>>>	--------
		Temp. 3, Time 2 + HWS	5.5 / 5.8 / 4.9	4/5/7	>> black staining
Liebherr	Sealing 1 + additive 4	Temp. 3, Time 2	5.7 / 4.9 /7.7	4/7/8	4/10/12
		Temp. 2, Time 2	6.1 / 5.3 / 6.5	6/6/6	--------
Liebherr	Sealing 1 + additive 5	Temp. 3, Time 1	5.4 / 3.6 / 2.8	7/11/7	--------
		Temp. 2, Time 1	4.4 / 4.0 /3.5	5/5/7	--------
TSA	Solution 1 Mn/Mo/Zr	Temp. 3, Time 1	5.5 / 5.7 / 5.1	18 / 20 / 20	--------
TSA	Sealing 1 + additive 2	Temp. 4, Time 1	4.2 /4.8 / 4.9	>>>>	--------
TSA	Sealing 1 + additive 3	Temp. 3, Time 2	6.1 / 5.8 / 5.5	>>	--------
Liebherr	Conversion 1	Temp. 4, Time 1	4.6 / 4.9 / 5.9	3/3/3	--------
Liebherr	Sealing 1 + additive 2 new samples from February 2014 (thicker)	Temp. 4, Time 1 (reproducibility)	7.2 / 7.4 /7.4	1 / 1 /1	1 / 1 /1
Liebherr	Sealing 1 + additive 2	Temp. 4, Time 1 + rinsing with Di water after sealing	6.1 / 5.5 / 5.5	2 / 5 / 4	2 / 5 / 4

All detailed results of WP6 have been uploaded on 30.04.2014 as deliverable D6.1

ANNEX 7 WP7 RESULTS REPORT

The objective of Deliverable D7.1 Characterisation of the anodic and sealed layers obtained from WP3 - 6.

The content of WP 7 according to DOW is: Results of characterization will be provided to the corresponding work packages.

Objectives: Characterisation of the anodic and sealed layers obtained from WP3 – 6.

Description of work and role of partners:

The assessment of the sealing options will be justified with the required standard salt spray test, but also with additional investigations like impedance spectroscopy (EIS), to get detailed information about the resistance of the generated films. Further aim is to correlate SST values and EIS data, so that EIS can be used as an additional very fast method for quality control of the sealed films in case of production problems. SEM will be used to investigate the morphology of the surface and in cross sections (prepared by FIB) after the sealing process and as a pre-assessment for selection if sealed coatings were suitable for paint application as alternative option for the post local sealing procedure. Aim is to meet the performance of the CAA (chromic acid anodization) film in combination with dichromate hot water sealing, which is usually 750 h salt spray test (SST) and more. Thickness measurements will be performed by eddy current method with a “Fisher Dualscope MP40E-S”. Additional thickness measurements will be done as a by-product of SEM-investigations in FIB-cross-sections of the layer.

Related Milestone MS8: Final report on characterization results [month 24; 30.04.2014]

The main objective of the project SAA-Seal is:

- The sealing process on thin (≤ 5 µm) anodized layers obtained by a SAA process has to be carried out by environmental friendly REACH compliant processes and products avoiding Chromium(VI) with optimized process parameters in order to minimize energy consumption.
- The sealing process on thin layer SAA has to show sufficient corrosion protection in order to meet the corrosion resistance requirements in a 750-hour salt spray test.
- The effect of the substrate composition (2024, 2618, AS7G06, Au5NKZR) and the effect of the production process (e.g.: cast, laminated, forged) on the corrosion resistance of the sealed SAA layers have to be investigated. In accordance with the topic manager this objective was modified. It has been decided that in WP 5 CEST will focus its work on AA 2024 samples only and will not investigate other substrates. The results will help in understanding of the differences between machined and sheet samples.
- Finally, a successful technology transfer towards a supplier selected by the Topic Manager has to be performed.

The Quantified Objectives of SAA-seal (from DOW) are present in the next table 7.1

WP/Milestone	Process	Objective in SAA-Seal (750 h SST)
WP2/MS2	Reference SAA	To provide standard thin SAA reference for comparison
WP2	Reference CAA	Standard CAA reference for comparison
WP3/MS3	SAA + hot water + additives	5-10 pits
WP4/MS4	SAA + conversion layer	5-10 pits
WP5/WP6	Optimized process	3-5 pits

In order to achieve this objective a sample matrix for each work package was planned and systematic investigation of the influence of raw material, pre-treatment, anodizing and sealing was performed.

Results achieved in WP7

- Raw material influence: the dissolution characteristics of alloy 2024-T3 lead to deposition corrosion and overall poor corrosion performance. It was found for the machined 2024-T3 samples particles with large size max. 29 µm with higher Cu content and for sheet 2014-T3 samples the Cu containing particles were max. 0.8 µm. SEM analysis in the pit area show higher Cu/Cl concentration.
- Pre-treatment influence: a more uniform surface morphology is observed for the TSAA pre-treatment. There is some evidence by SEM investigations that by the TSAA treatment Cu particles are more completely removed. A mass loss of 1.48 g/m² resulted for sheet samples and 1.09 g/m² for machined samples after SAA pre-treatment (alkaline decreasing and acid pickling). A mass loss of 15.52 g/m² for sheet samples and of 16.73 g/m² for machined samples resulted after TSAA pre-treatment. The pre-treatment for sheet samples not influence the SST results after conversion with the optimized process. A big influence have the pre-treatment for machined samples, the best results in SST was obtained with SAA standard pre-treatment.
- Anodic layer: for the corrosion protection the minimal anodic layer thickness shall be 4 µm. The cracks appear only in samples of SAA layer thicknesses > 4 µm after SEM inspection exposed to high vacuum. No cracks were found by LOM characterization.
- Sealing: the objectives were achieved and the results are presented in the following table 7.2

Table 7.2 Objectives achieved in WP 2-WP6

WP/Milestone	Process	Objective in SAA-Seal (750 h SST)	Comments
WP2/MS2	Reference SAA	To provide standard thin SAA reference for comparison	State of art estimate according to previous CEST experiments. Thin SAA layers were produced on AA 2024 sheet and machines samples.
WP2	Reference CAA	Standard CAA reference for comparison	To provide standard reference for comparison.
WP3/MS3	SAA + hot water + additives	5-10 pits	Sheet and machined samples: Sealing 1 = 2-3 pits/dm^2; Sealing 2 = 5 pits/dm^2
WP4/MS4	SAA + conversion layer	5-10 pits	1-7 pits/dm^2 Conversion 1 and silane combination (double layers)
WP5/WP6	Optimized process	3-5 pits	Max. 1 pit/dm² with Sealing 1 + additive 2 at low temperature, a few minutes, for sheet and machined samples

* pits (smaller than 0.8 mm diameter) / 100 cm^2, no pits larger than 0.8 mm.

Results of WP7 have been uploaded on 30.04.2014 as deliverable D7.1

ANNEX 8 WP8 RESULTS REPORT

The objective of Deliverable D8.1 is Optimisation of process parameters to minimize energy consumption to minimize the effort for corrosion resistance characterization.

The content of WP 8 according to DOW is: Optimisation of process parameters.

Objectives: Optimisation of process parameters to minimize energy consumption to minimize the effort for corrosion resistance characterization.

Description of work and role of partners:

Data and results gained in work packages 5 and 7 (characterization of anodic and sealed layers) will lead to a more detailed understanding of the influence of the process parameters and thus will allow to optimize the sealing process.

Related Milestone MS9: Optimized sealing procedure.

Results achieved in D8.1

More uniform surface morphology is observed for TSAA pre-treatment (see D6.1, table 1) with higher mass loss of 15.52 g/m² for sheet and 16.72 g/m² for machined samples in comparison with SAA pre-treatment with a mass loss of 1.48 g/m² for sheet and 1.09 g/m² for machined samples. The detailed surface characterization was presented in D6.1 and the influence of pre-treatment on corrosion resistance was presented in D7.1. So we conclude that the most effective pre-treatment method for both sheet and machined samples is **SAA pre-treatment.**

Regarding anodization methods and parameters, for 750 h SST the anodizing method Liebher and CEST ranked equal. The difference between electrolyte composition is 20 g/l more sulphuric acid for Liebherr method, the differences between anodizing parameters are for Liebherr method: higher voltage (+ 2V), lower temperature (-2 °C), short anodization time (-4.5 min) for the same layer thickness. Detailed results were presented in D2.1.
It was decided in accordance with the Topic Manager to use the standard **SAA-Liebherr anodization** (see D6.1, table 13) before all further sealing methods.

Regarding the optimised process parameters to minimize energy consumption (to minimize the effort for corrosion resistance) were identified:

Conversion 1 (Temp. 4, Time 1) assure a good corrosion resistance for sheet (max. 1 pit/dm²) and machined samples (max. 3 pits/dm²) after 750 h SST.

Better results as with Conversion 1 were obtained by using of **Sealing 1 + additive 2 (Temp. 4, Time 1)** for sheet and machined (max. 1 pit/dm²) samples after 750 h SST. The corrosion protection obtained with Sealing 1 + additive 2 remains unchanged until the 1176 SST. The pretreatments procedure has a big influence only for the machined samples (see D.6.1, Table 18).

Optimized sealing process

RESULTS: optimized sealing process from max. 12 pits/dm^2 to 1 pit/dm^2 at 750 h SST – sheet samples AA2024.

Temp. 4 < Temp. 3 < Temp 2 < Temp. 1
Time 1 < Time 2

Max 12 pits/dm^2
HWS, Sealing 1+ additive 1 (Temp. 3, Time 2), Sealing 1+ additive 1 (Temp. 3, Time 1), Sealing 1+ additive 5 (Temp. 2, Time 1)

Max 10 pits/dm^2
Sealing 1+ additive 4 (Temp. 2, Time 1),

Max 9 pits/dm^2
Sealing 1+ additive 5 (Temp. 3, Time 2)

Max 8 pits/dm^2
Sealing 3 (Temp. 1, Time 2), Sealing 1+ additive 4 (Temp. 3, Time 1)

Max 7 pits/dm^2
Sealing 1 + additive 2 (Temp. 3, Time 1)

Max 5 pits/dm^2
Sealing 2 (Temp. 2, Time 2), Sealing 1 + additive 1 (Temp. 4, Time 1)

Max 4 pits/dm^2
Sealing 1+ additive 3 (Temp. 4, Time 1)

Max. 2 pits/dm^2
Sealing 1 (Temp. 2, Time 2)

Max. 1 pit/dm^2
Conversion 1 (Temp. 4, Time 1), Solution 1+ additive 3 (Temp. 3, Time 2), Sealing 1 + additive 2 (Temp. 4, Time 1)

RESULTS: optimized sealing process from max. >>> pits/dm^2 to 1 pit/dm^2 at 750 h SST – machined samples AA2024.

>>> pits/dm^2
HWS

Max 11 pits/dm^2
Sealing 1+ additive 5 (Temp. 3, Time 1)

Max 10 pits/dm^2
Sealing 1+ additive 1 (Temp. 3, Time 1)

Max 8 pits/dm^2
Sealing 1+ additive 4 (Temp. 3, Time 2)

Max 7 pits/dm²
Sealing 1+ additive 5 (Temp. 2, Time 1)

Max 6 pits/dm²
Sealing 1 + additive 4 (Temp. 2, Time 2), Sealing 1+ additive 1 (Temp. 2, Time 2), Sealing 1 + additive 3 (Temp. 4, Time 1)

Max 5 pits/dm²
Sealing 2 (Temp. 1 or Temp. 2, Time 2)

Max 3 pits/dm²
Conversion 1 (Temp. 4, time 1), Sealing 1 (Temp. 1, Time 2), Sealing 1 + additive 1 (Temp. 4, Time 1)

Max 1 pit/dm²
Sealing 1 + additive 2 (Temp. 4, Time 1)

Detailed results of WP8 have been uploaded on 30.04.2014 in deliverable D8.1