Technical Leaflet

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Anticorrosive Conversion Coatings Replacing Chromium (VI)

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Introduction

Corrosion of ferrous metal and aluminium costs society about US$2.5 trillion/an, which is equivalent to 3.4% of the global Gross Domestic Product, according to NACE international, a worldwide corrosion authority. Particularly concerning are railways, oil platforms, vessels, metal constructions, pipelines and all sort of vehicles. While ferrous metals are more affected by corrosion than aluminium, the latter also needs protection as pitting, crevice and especially galvanic corrosion may take place. Aluminium is a metal increasingly used in airplanes and car manufacturing as it is both light and strong. In this report we will specifically look into prevention of aluminium corrosion.

While corrosion is problematic it can be mitigated by the use of coatings. A crucial part of the corrosion prevention is with the pre-primer, often referred to as the conversion coating. It is called conversion coating as the first layer ought to convert the metal surface into an inert layer. Until recently hexavalent chromium primers have prevailed but since their ban in 2017 in most of the western hemisphere for the majority of industrial applications, the paint industry has been looking for suitable replacements.

Conversion coatings are typically part of a total system, built up on the conversion coating, which is overcoated with an epoxy primer and finished off with a polyurethane (PU) or fluoropolymer (FP) topcoat. However some conversion coatings can be used as a single layer in direct to metal applications or as a wash primer as initial protection of the metal.

Sol-gel based conversion coatings have been promising as technology to replace hexavalent chromium as they act in a similar way by converting the metal surface to a very thin metal oxide layer. In this report we present EXOCOAT AC which is a sol-gel system, specifically targeted to protect the metal in a total system build up of Sol-gel/epoxy primer/PU topcoat. EXOCOAT ACX-W is targeted to direct to metal applications and performs especially well as a stand alone coating.

A new technology presented here and especially effective as conversion coating is EXOCOAT 161, a preceramic polymer. Similar to sol-gel-technology a key action of preceramic polymers is the conversion to a metal oxide barrier layer. The conversion rate, measured in % metal oxide, is crucial to the effectivity of the barrier and is typically higher in the case of preceramic polymers compared to sol-gel systems. Higher conversion rates generally result in increased barrier properties and better corrosion protection.

In this report we have tested 3 EXOCOAT products which are compared to a competitive product known in industry, which are shown in Table 1.

	Type	Medium
EXOCOAT AC*	Sol-gel hybrid	ethanol
EXOCOAT ACX-W	Sol-gel hybrid	water
EXOCOAT 161	Preceramic polymer	ether
Reference 1	Sol-gel	water

*Table 1. Products used. *used as 2K (AC/APTES 2:1 (APTES = Amino propyl triethoxy silane)).*

The aluminium types chosen were Al2024 and Al7075, predominately used as aircraft alloy due to their excellent strength and toughness. Downside of Al2024, which includes about 4.5% copper, is its sensitivity to corrosion.

Experimental setup

The aluminium plates (2024 and 7075) were coated with the three conversion coatings and subjected to water immersion and anticorossion tests. The coatings were tested as monolayer (ML) and part of aerospace compliant paint system based on epoxy primer and polyurethane topcoat, designated as total system (TS) (Table 2). The prescribed primer and topcoat were AKZO NOBEL Epoxy Primer 37076 / Hardener 92133 and ECL-C-101 / Hardener PC-233.

		Alu 2024		Alu 7075	
EXOCOAT AC		ML	TS	ML	TS
EXOCOAT ACX-W		ML	TS	ML	TS
EXOCOAT 161		ML	TS	ML	TS
Reference 1		ML	TS	ML	TS
Cyclic tests	**Norm**	**Test hours**			
Water immersion	ISO 2812-2	500		500	
Neutral SS	ISO 7253	500	3000/4000	500	3000/4000

Table 2: Experimental Setup, ML= monolayer; TS = Total System, ML overcoated with epoxy and PU

Water immersion test (500h)

The water immersion test (ISO 2812-2) was performed on the monolayer systems, based on both aluminium 2024 and aluminium 7075 substrates according to following parameters:

- Demineralized water
- Temperature: 40°C ± 1°C
- ¾ of samples are immersed
- Panels were visually inspected and tested for adhesion after 500h

Neutral salt spray test

Neutral salt spray test (ISO 7253) was performed according to following parameters:

- NaCl concentration: 5% ± 1%
- Temperature: 35°C ± 2°C
- Demineralized water
- pH : 6.5 - 7.2

Substrates were pre-cleaned with Acetone + NaOH (60°C, 60g/L), rinsed with water and HNO_3 (room temperature, 20%), again rinsed with water and dried with compressed air.
Panels with monolayers were tested up to 500hrs; the total system went for a 3000hrs saltspray test with one exception that went to 4000hrs.

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Results

Water immersion test (ML, direct to metal)

The panels were inspected visually after the water immersion test and the adhesion was determined following the normative cross-cut test ISO 2409. After the test, the cross-hatched area was examined with a magnifier and recorded as a function of the classified results grid (C=0 is good, 5 is bad).

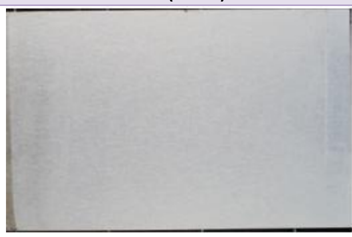
	Cross cut adhesion 500hrs	
Conversion primer	Al 2024	Al 7075
EXOCOAT AC (2K)	 Some cracks Adhesion OK (C=0) after 500h	 Some cracks Adhesion OK (C=0) after 500h
EXOCOAT ACX-W	 Whitening of some areas Adhesion OK (C=0) after 500h	 Whitening of some areas Adhesion OK (C=0) after 500h
EXOCOAT 161	 No defect Adhesion OK (C=0) after 500h	 No defect Adhesion OK (C=0) after 500h
Reference 1	 Whitish aspect Adhesion OK (C=0) after 500h	 Whitish aspect Adhesion OK (C=0) after 500h

Table 3. Water immersion test

The water immersion test shows some surface whitening effect on the coatings in the case of EXOCOAT AC and EXOCOAT ACX-W, strong whitening in the case of Reference 1 and no effect in the case of EXOCOAT 161 (Table 3). In all cases the coatings passed the cross cut adhesion test.

Neutral salt spray test (ML, direct to metal)

The coated panels were inspected visually after neutral salt spray test, after 300hrs and 500hrs for Al 2024 and Al 7075 respectively.

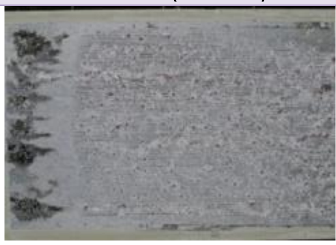
	Salt spray results	
Conversion primer	Al 2024 (300hrs)	Al 7075 (500hrs)
EXOCOAT AC	 Servere pitting	 Servere pitting
EXOCOAT ACX-W	 Presence of pitting	 Presence of pitting
EXOCOAT 161	 Presence of a white fog	 Presence of a white fog
Reference 1	 Generalised corrosion	 Generalised corrosion after 300hrs (test stopped)

Table 4. Neutral salt spray test of monolayer (direct to metal)

Neutral salt spray test (total system)

A monolayer of the test product was overcoated with Epoxy Primer and PU topcoat in the exact same way for the all four conversion coatings. A scribe had been etched on each sample with a scratching tool before the sample was put in the salt spray cabine. The -end of test- pictures are presented in Table 5.

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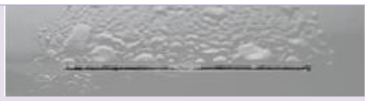
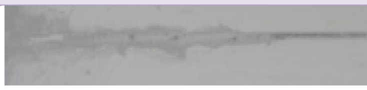
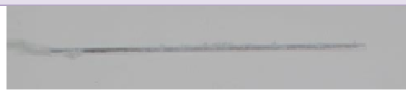
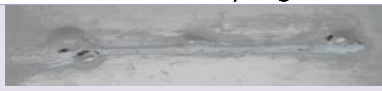
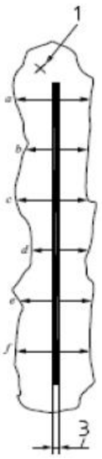
Conversion Coating	Hours	Salt Spray Results Al 2024	Al 7075
EXOCOAT AC	3000	 Grade 3 – Moderate	 Grade 3 – Moderate
EXOCOAT ACX-W	500	 Grade 5 – Severe	 Grade 5 – Severe
EXOCOAT 161	4000!	 Grade 1 - Very Slight	 Grade 1 - Very Slight
Reference 1	3000	 Grade 3 - Moderate	 Grade 3 – Moderate

Table 5. Salt spray test of total system: conversion coating/epoxy/PU coating

Scribe analysis EXOCOAT 161

During the test, some panels have been removed to perform an assessment of the delamination area around the scratch. The measurement of width of delamination is done following the procedure below:



1 corroded or delaminated area

3 width of original scribe, w

Determine, to the nearest 0,5 mm, the mean overall width of delamination, d_1, using Formula (1):

$$d_1 = \frac{a+b+c+d+e+f}{6} \quad (1)$$

Calculate the delamination, d, in millimetres, using Formula (2):

$$d = \frac{d_1 - w}{2} \quad (2)$$

where

d_1	is the mean overall width of delamination, in millimetres;
w	is the width of the original scribe or other artificial defect, in millimetres;
a, b, c, d, e, f	are individual delamination measurements

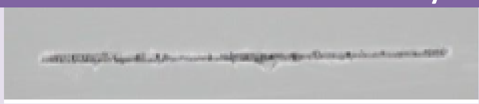
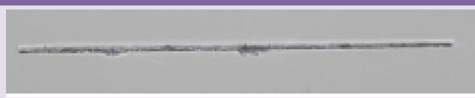
Scribe analysis after 4000hrs NSS		
EXOCOAT 161	 Scribe width: 1mm	 Scribe width: 1mm

Table 6. Scribe analysis EXOCOAT 161 after 4000hrs of neutral salt spray

While EXOCOAT AC shows pitting in the direct to metal test after 300 and 500hrs salt spray on Al 2024 and 7075 respectively (Table 4), the test of the total systems went relatively well with moderate corrosion results after 3000hrs of salt spray testing (Table 5). The opposite effect was noticed in case of EXOCOAT ACX-W with a strong performance in the direct to metal test but worse performance as part of a coating system which may be related to an intercoat adhesion issue. A particularly bad performance

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was seen with Reference 1 that showed generalised corrosion in the case of the monolayer. The results of Reference 1 were comparable to EXOCOAT AC in the total system.

A strong performance may be attributed to EXOCOAT 161, while showing no pitting in the direct to metal salt spray test the performance in the total system was overwhelming. After 4000hrs! in the salt spray cabinet the total system with EXOCOAT 161 as conversion primer showed very slight corrosion (Table 5) and scribe creep does not surpass more than 1mm (Table 6).

Conclusion

In this report 3 EXOCOAT products were compared to a market reference (Reference 1) on their anticorrosion performance as conversion coatings. EXOCOAT AC when used as conversion coating in a total coating system led to enduring corrosion protection after 3000hrs salt spray. EXOCOAT ACX-W performs adequately for direct to metal protection of aluminium up to 500 hrs of salt spray testing. Reference 1 which is seen as market reference performed particularly poorly in case of direct to metal (generalised corrosion) and similar to EXOCOAT AC in case of total system (moderate corrosion after 3000hrs).

The premium solution for direct to metal and as conversion coating as part of a total system in including an epoxy based primer and PU based topcoating is EXOCOAT 161. This product established on a preceramic polymer is able to protect the metal as single layer and can pass 4000hrs of salt spray exposure when used as a conversion primer as part of a coating system.

About Axcentive:

Axcentive develops and promotes sol-gel and preceramic nanotechnology for the coatings industry.

This technology base allows for chemical modifications on nano level to suite to a certain performance need. Smart and functional coatings with specific properties such as self-cleaning, easy to clean, anticorrosive, superhydrophobic or superhydrophilic properties can be formulated with this nanotechnology.

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