SUMMARY OF A3TS CONFERENCE ON LIGHT METAL SURFACE FINISHING

PARIS, DEC 6, 7, 2011

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1. Introduction

This was the second conference, the first one having taken place in November 2010. The intent is that it should now go on to a biannual schedule.

The conference was set up by the A3TS (Association de Traitement Thermique and de Traitement de Surface, Heat Treatment and Surface Treatment Association), which is the French surface engineering society that primarily concentrates on aerospace.

An effort was made this year to incorporate a number of US speakers and the conference was similarly designed so that either the presentation or the overheads (or both) would be in English. This report covers only the European talks, with one or two exceptions.

Chromic acid, sodium dichromate, and most other chromates are in the final stages of entry to REACH Annex XIV

- After about May 2016 they will not be able to be imported, sold or used in the EU without Authorization.
  - Authorization is a very expensive and time-consuming process.
  - Even if authorization is granted, it will be only for a limited period of time (probably a few years), and will be only for those specific uses for which the authorization was sought.
  - This means that these materials cannot be used for any new applications.
- Although they will still be permitted on products imported to Europe, anyone who sells finished products into the EU market will have to inform downstream users of the presence of these materials.
- All European companies, and aerospace companies in particular are therefore moving away from all processes and materials that use chromates:
  - Chromate conversion of Al, chromic acid anodizing, chromate sealing of anodize, Cd or Zn
  - Chromated primers for aircraft
  - Hard chrome plating

European companies and users are following similar routes to alternatives as companies in the US:

- Cr^{3+} pretreatments, sealers and passivates
- Sol-gel coatings with inhibitors
- Sulfuric acid-based anodizing methods
- EN-PTFE for electrical connector shells

2. Agenda

December 6:

Overview of Development and Implementation of Non-Chromate Treatments for Aluminum in the US.
K. LEGG *(ROWAN Technology Group, USA).*

Update on Light Metal Surface Finishing of Boeing Aircraft Parts.
S. P. GAYDOS *(BOEING-Research and Technology Inorganic Finishes and Corrosion).*

Advancements in chrome free anti-corrosive systems for aerospace use, both for airframe and high temperature engine components.
G. ARMSTRONG *(INDESTRUCTIBLE PAINT Ltd)*

Impact de la directive ROHS pour des applications connectiques : présentation de solutions en alternative au Cadmium et au Chrome hexavalent. (Impact of the RoHS Directive on connector applications: presentation of solutions for alternatives to Cd and Cr)
G. TREDAN *(RADIALL).*

Effective Replacements for Hexavalent Chromium Corrosion Inhibitors.
M. JAWOROWSKI *(UNITED TECHNOLOGIES Research Center, UK).*

Aluminium and Aluminium Alloys Treatment: from the Surface Preparation to protection.
B. SOTTIL *(COVENTYA).*

Using Chrome-Free Primer Technology to Develop a Chrome-Free Pretreatment.
E. MORRIS, C. ATHANASOPOULOS, R. ALBERS *(DEFT INC. - US)*
S. BEAN, R. JAFFKE *(NORTHROP GRUMMAN Corporation).*

Bipolar current pulse plasma electrolytic oxydation of light alloys: stakes and limits.
G. HENRION *(INSTITUT JEAN LAMOUR)*, C. ROSSIGNOL *(LIEBHERR-AEROSPACE).*

Projet "SOL-GREEN": recherche et développement de revêtements sol-gel anti-corrosion pour alliages d'aluminium utilisés dans l'industrie aéronautique. ("SOL-GREEN" Project: R&D on sol-gel anti-corrosion treatments for Al alloys used in the aircraft industry)
H. CERDA, J. ESTEBAN, O. JAUBERT, J. GARCIA, J.P. BONINO, P. LENORMAND,
F. ANSART, M. GRASSIER, M.J. MENU *(INSTITUT CARNOT-CIRIMAT Toulouse 3)*
C. GAZEAUX, P. BARES *(MECAPROTEC Industries).*

Essai de faisabilité d'un traitement au SURTEC 650 V par aspersion avec équipement mobile sur une structure mécano-soudée (caisse VBCI), en alliage de la série 7000, en remplacement de l'Alodine 1200. (Feasibility study on a treatment with SURTEC 650 applied with mobile equipment on a tack-welded structure (VBCI hull), in series 7000 Al as a replacement for Alodine 1200)
G. CHOLVY , C. DUCHASSEINT *(NEXTER Systems)*, I. ECOTIERE *(SURTEC France).*

Avenir à court et moyen terme des sol-gels chez Dassault. (Short and medium term future of Sol-gels at Dassault)
P. MICHELIN *(DASSAULT).*

Procédé de conversion des aluminiums sans chrome, sans cobalt INTERLOX 5705. (Non-Cr, non-Co conversion process for Al alloys)
F. ANTOINE *(ATOTECH).*

December 7:

Cr6+ Alternatives for Light Metal Finishing for U.S. Navy Aircraft.

C. MADZDORF *(U.S. NAVY, Naval Air Systems Command, Materials Engineering Division).*

Approaches for Corrosion Protection Based on a Novel Chemical Toolbox.

M. WOLPERS, J. ZIMMERMAN, K. KRAMER, V. WAN, W. OPDYCKE, K. MEAGHER,

B. BAMMEL *(HENKEL).*

Development, Commercialization and Implementation of Hexavalent Chromium-Free Surface Pretreatment. L. ROBERTS *(PANTHEON Enterprises, Inc).*

Electrochemical behaviour of intermetallic phases in aluminium alloys: a chemical strategy in surface treatment processes.

E. ROCCA, J. TARDELLI *(INSTITUT JEAN LAMOUR UMR CNRS 7198 UNIVERSITÉ HENRIPOINCARÉ - NANCY),* M. AUGROS *(MESSIER BUGATTI - SAFRAN).*

Environmentally-Friendly Anodizing of Aluminium Aerospace Alloys.

G. E. THOMPSON, M. CURIONI, P. SELDON, X. ZHOU, E. KOROLEV *(THE UNIVERSITY OF MANCHESTER SCHOOL OF MATERIALS CORROSION & PROTECTION CENTRE - UK).*

OAS new generation to SAFRAN - New generation of sulphuric acid anodizing at Safran : towards performance and eco-awareness.

M. AUGROS *(MESSIER BUGATTI - SAFRAN)*, C. METRAL *(AIRCELLE - SAFRAN).*

Hybrid Nanostructure of the CompCote ® Finish for polymer bonding.

J. RUNGE *(COMPCOTE INTERNATIONAL Inc)*, A. GILBERT *(MERCURY MARINE, Inc)*

G. KRIESCH *(WALGREN Co)*, J. PERNICK *(IHC Corp).*

Nouvelle génération d'anodisation sans chrome pour la protection de pièces aéronautiques. (New generation of non-Cr anodizing for protection of aerospace components)

P. BARES, C. GAZEAU, C. STEPHAN, D. PEDELMAS *(MECAPROTEC)*,

C. ROSSIGNOL, R. BOYER, E. HERAIL *(LIEBHERR AEROSPACE),* O. BRUCELLE (RATIER-FIGEAC), J.J. ROUSSE, K. KLERMAN (DAHER-SOCATA), P. COMBES (GIT SA.), L. ARURAULT,

V. TURQ (INSTITUT CARNOT CIRIMAT, UNIVERSITÉ PAUL SABATIER).

Le remplacement de l'anodisation chromique pour les applications collage. (Replacement of chromic acid anodizing for aerospace joining applications)

S. PETTIER *(EUROCOPTER MARIGNANE)*, P. PEUCH *(EUROCOPTER LA COURNEUVE).*

Advances in chrome free corrosion inhibiting coating technology for the protection of aluminium.

P. VISSER *(AKZONOBEL AEROSPACE COATING B.V.).*

Paint electrode position for aerospace: a new concept of surface protection.

A. TOLZ *(PPG).*

Chrome free paint system.

P.J. LATHIERE *(MAPAERO).*

Non chromate primer industrial testing.

F. FLORIANI *(COMSURTEC).*

3. Interesting developments

3.1. Pretreatments and passivates for Al and anodize

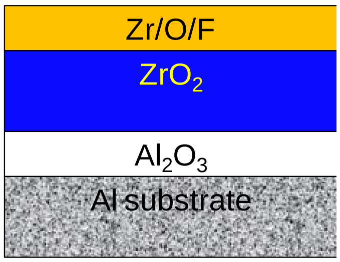

Figure 1. Interlox 5705 schematic.

B. Sottil: Coventya has introduced a trivalent passivate called Lanthane 613.3 which can be used both as a pretreat for Al and a sealer for anodized coatings. As a pretreat it works well in the 5000 and 6000 series Al, but far less well for the 2000 and 7000 series, which contain copper, and the 4000 series which contains silicon.

Anodized coatings on 2000 and 7000 series aluminum are first passivated with Lanthane 613.3 and then hot water sealed. They last longer than 750 hours in B117.

F. Antoine: Atotech has introduced Interlox 5705 as a Cr-free, Zr-inhibited pretreatment for aluminum that is designed to improve painted adhesion by creating a transition layer between the substrate and the paint system (Figure 1).

H. Cerda: Since the original sol-gel adhesion promoters (Boegel, AC-131) do not contain any inhibitors, they provide no corrosion protection themselves, but they improve corrosion protection by enhancing paint system adhesion.

The Institut Carnot has been developing a sol-gel coating of metallic alkoxides, with a Ce inhibitor. This approach appears to work very well (Figure 2) provided the layer thickness exceeds about 0.4µm. They are beginning to incorporate Boehmite clay nanoparticles to act as carriers for the Ce and to create an additional permeation barrier for corrodants. This is a project called "SOL-GREEN".

P. Michelin: Dassault Aviation is considering using sol-gel treatments on Al in place of anodize and seal.

G. Cholvy: Testing is under way to determine whether it is possible to use Surtec 650 TCP for Al-hulled military vehicles (Figure 3). They have done mock-up tests but have

Figure 3. VBCI armor hull infantry vehicle.

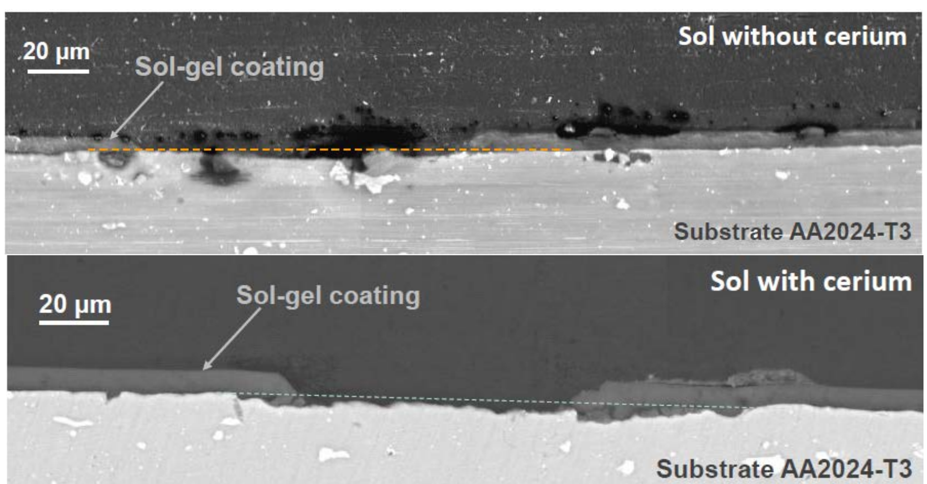

Figure 2. Sol-gel with Ce inhibitor (Inst. Carnot).

not yet tested on actual vehicles. This should be easier than application to steel armored vehicles because, of course, Al-hulls are not subject to flash rust.

M. Wolpers: Henkel is developing various products including a sol-gel for Al with V or Ti inhibition. For steels they are developing a 55% Al-Zn filled organic coating, which is similar to the Zn-rich coatings currently used on USMC vehicles.

3.2. Non-Cr anodizing

G. Thompson: The University of Manchester in the UK runs a center called LATEST (Light Alloys Towards Environmentally Sustainable Transport). George Thompson is a well-known expert on anodizing. He provided a very interesting paper on how one can control the morphology of an anodize layer by proper control of voltage and current.

Standard anodized layers have a porous outer layer and a denser, inner barrier layer. By controlling the voltage and current one can adjust the morphology (Figure 4). This

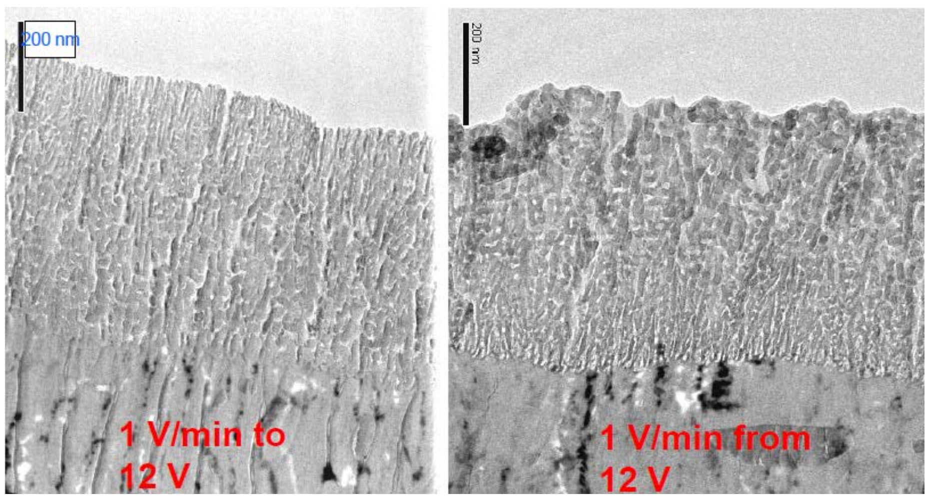

Figure 4. SA Anodized layer structures; left voltage increased through process, right voltage decreased through process.

appears to be a way to use Sulfuric Acid Anodizing to maintain good barrier properties, while providing the paint and bond primer adhesion of CAA. This is important since the primary remaining use for CAA is adhesion of bond primers and paints. It is also possible to tune the process to minimize the energy cost of anodizing, while maintaining the same performance.

S. Pettier: Eurocopter described their approach for eliminating CAA for bonding. Their aim is to eliminate Cd and Cr^{6+} by the end of 2013.

Their approach is to replace cleaning, etching and anodizing (Figure 5). Their preferred replacement for CAA is phosphoric sulfuric acid anodizing (PSAA). Their assessment is that PSAA will be essentially equivalent to CAA in both performance and cost.

They showed a simple, but telling, regulatory timeline (Figure 6).

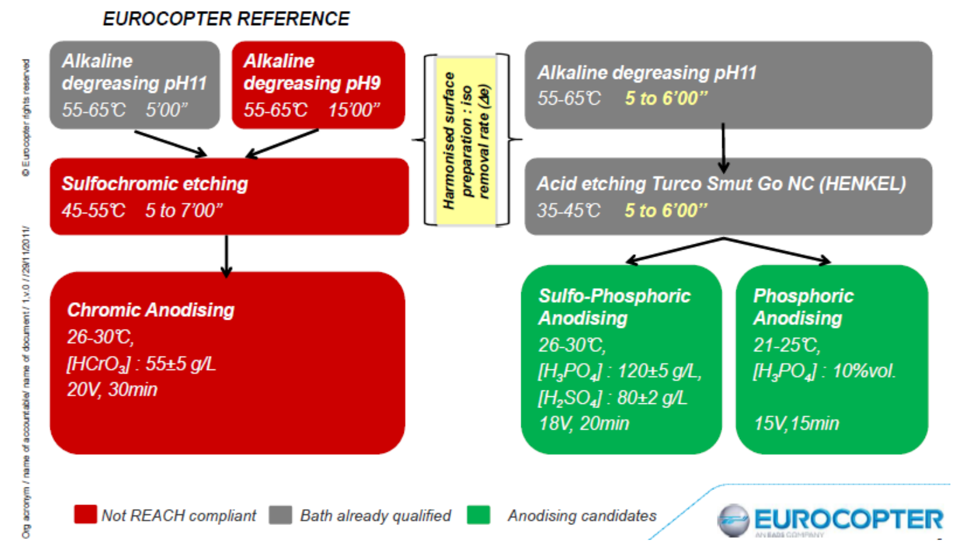

Figure 5. Replacement of current process with non-toxic processes including PSAA.

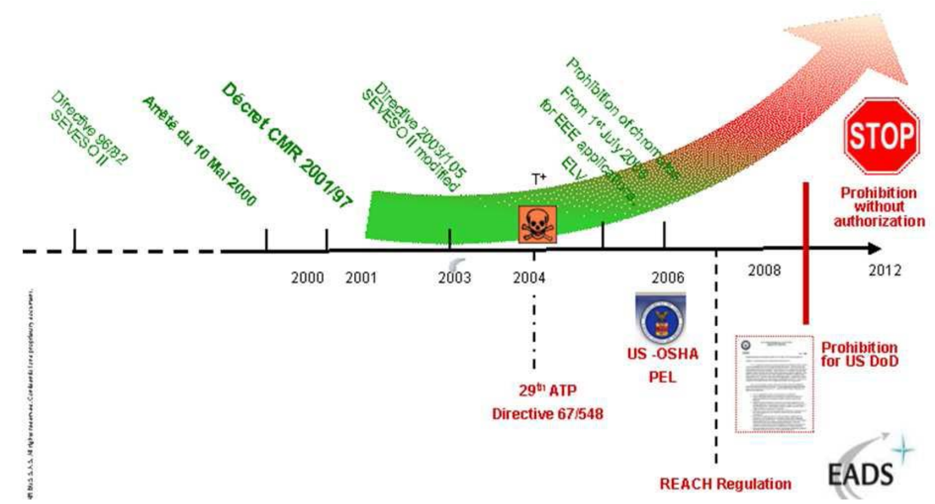

Figure 6. EADS/Eurocopter timeline for hex Cr replacement.

G. Henrion: A small company called Ceratronic is industrializing a very interesting plasma electrolytic oxidation (PEO) coating for Al (similar to Keronite) developed by the University of Lorraine. This approach uses bipolar pulsing rather than DC, which Keronite and Tagnite use. The resulting anodize coating is porous and friable at the surface and can be ground to a smooth finish, but dense and low porosity inside (Figure 7).

This coating has been qualified and implemented quite extensively by Liebherr Aerospace for various production valves, as well as nozzles and turbine wheels. A number of components production coated in this manner are shown in Figure 7.

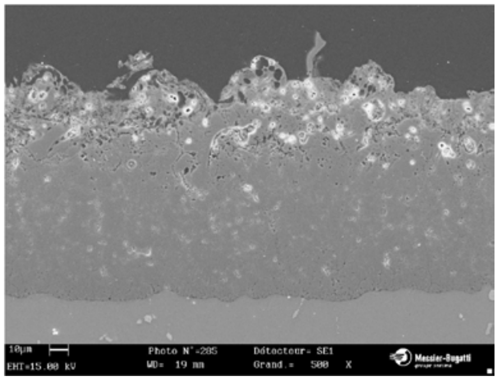

Figure 7. Ceratronic bipolar PEO coating.

J. Runge: Another variation on anodizing was described in a paper by CompCote International of Elmhurst, IL and tested by Mercury Marine in Wisconsin for boat outboard engines. This technology incorporates electroactive polymer into the sulfuric acid anodizing solution. The resulting microstructure did not have the strong columnar pores characteristic of Type III anodize, but was more nanostructured. Two-year beach corrosion testing of actual engine blocks showed no corrosion.

Figure 8. Liebherr components anodized by Ceratronic process. Valve IDs and nozzle (bottom right).

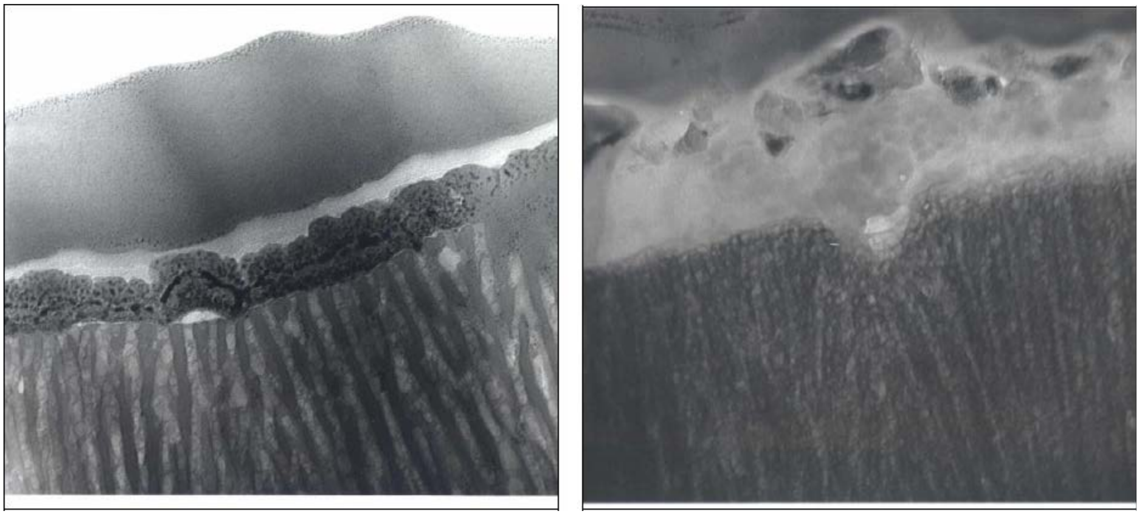

Figure 9. Left - standard Type III anodize with print layer on surface. Right – CompCote layer with ink showing 40nm penetration. Note microstructural differences.

3.3. Non-Cr paint systems

A Tolz: PPG has been developing anodic e-coat paint systems. The results look very good so far, although all the testing has only been done on panels. The paint system is designated as Aerochron. Coating takes 2 mins and curing 30 min at 110°C, thus eliminating the long times "waiting for paint to dry". Corrosion resistance looks good, and the system does not require anodizing prior to painting. However, there is no indication they have tested this on actual components so far.

P. Visser: Akzo-Nobel continues to promote the Aerodur Mg-rich primer. They are also developing a new inhibitor system, but with no indications of what it is based on.

Eric Morris: Eric described Deft's new Cr-free paint system, which uses a rare earth (Pr or Ce) based pretreat matched to their Pr-based primer, for a completely Cr-free paint system. This system is now in production on the F-15 fleet (Figure 10).

Figure 10. F-15 with Deft Rare Earth Cr-free paint system.