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# Development and certification of chromic acid-free anodizing process for aircraft grade aluminium alloys

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Chromic acid ($Cr^{6+}$) anodization process is widely used for the corrosion protection of aircraft aluminium alloys. Hexavalent chromium being toxic in nature need to be phased out by eco-friendly alternatives. In the present study modified tartaric-sulphuric acid (TSA) process has been developed followed by sealing in permanganate based bath to obtain 4 to 6 µm thick anodic oxide layer on 2024-T3, 6061-T6 and 7075-T6 aluminium alloys. The process was carried out using a pilot scale anodizing plant. The anodized specimens were characterized for visual observation, thickness, adhesion, electrical breakdown voltage, corrosion resistance and tensile behaviour. All the tests were carried out as per MIL-A-8625F specifications. The specimens were also subjected for about 800 hrs to real time corrosion testing, 200 metres away from sea shore at Mandapam Camp, Rameshwaram, India. The performance of the permanganate sealed TSA anodized aluminium alloys are comparable with that of the conventional chromic acid anodized coatings. This chromic acid-free anodization process has been qualified to airworthiness regulating standards by Indian military certification authorities. Efforts are in progress to commercialize this technology for use on aero platforms.

**Keywords:** TSA process, Anodization, Chromic acid-free, Certification

## 1 Introduction

Aluminium alloys (2XXX, 6XXX and 7XXX) are widely used in aircraft industry due to their light weight and excellent strength. In general, a three-layer coating system comprising of anodized first layer followed by aircraft grade primer and polyurethane top coat is used to impede the corrosion in aggressive chloride environment. Chromic Acid Anodization (CAA) is a widely used process for aircraft structures as a pre-treatment because of its unique corrosion inhibition and adhesion promoting behaviour. However, as per the strict environmental regulations (RoHS and REACH) the usage of hexavalent chromium [Cr (VI)] is restricted due to its carcinogenic behaviour. Efforts have been made by various researchers in developing an alternate to CAA process with similar or enhanced corrosion resistance property for aircraft grade aluminium alloys[1-5]. One of the alternates to CAA process is the TSA anodization and this process is being used by Airbus. However, the sealing process being used by Airbus involves dichromate ($Cr^{6+}$)/ boiling water sealing[6]. The sealing process used by the authors is eco-friendly and also provides additional self-healing property.

The available literature is limited to laboratory testing of alternate CAA process and are primarily focused on 2XXX aluminium alloys in terms of adhesion, thickness, corrosion resistance behaviour etc.[7-11]. It is mandatory that the alternate process should undergo a detailed certification program for airworthiness in a larger scale before it is inducted for actual aircraft programs.

The objective of the present study is to establish anodizing pilot plant (400 ltrs) to develop chromic acid-free, permanganate sealed tartaric sulphuric acid anodization (TSA) process on large size (2'X2') aluminium alloys and complex geometries for certification. Various documents related to material specification, process parameters, functional tests etc., had been prepared and inspected by Indian certifying agency for aircraft applications RCMA (F&F-FOL), CEMILAC and DGAQA qualified personnel. It is

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also essential to qualify the test coupons in real time testing conditions i.e., actual sea shore environment. In this regard, various test coupons (AA 2024, 6061 and 7075) have been prepared using chromic acid-free permanganate sealed TSA process to qualify for thickness, adhesion, breakdown voltage, continuous salt spray tests as per MIL-A-8625 F specification.

## 2 Experimental

A pilot scale anodizing plant with a volume 400 ltrs was established and the layout is described in Fig. 1. The elaborate details of the process parameters and the anodization process has been discussed in detail elsewhere[12]. During the upscaling of the process from laboratory to the pilot plant, several challenges were addressed like prevention of fungal growth in the TSA bath by inclusion of UV disinfection system along with continuous activated carbon filtration system and proper jigging of the large specimen to ensure the uniformity in the thickness of the anodic oxide layer. Also, anode and cathode geometry and dimensions were optimized. The cathode used in the pilot plant was SS 316 sheets of dimensions 2' X 2'. The anode to cathode area ratio was varied from 1:2 to 1:10. Aluminium alloy (2024-T3, 6061-T6 and 7075-T6) specimens of dimensions 10"X3" were prepared for visual observation, thickness, electrical breakdown voltage, corrosion resistance and tensile testing. The thickness of the coatings was measured using Electro Physik make tester based on eddy current principle. Adhesion of the coating was examined using ELCOMETER 107 X-Hatch, peel-off test method. The continuity of the coatings was determined at > 50 V using HPS 2682, HELPASS make High Resistance Meter.

The corrosion test was performed in continuous salt fog chamber Ascott make. The tensile strength of the coated Al alloys was determined using 25 kN servo hydraulic test machine. The test matrix comprising of the standards adopted for carrying out various evaluations is described in Table 1.

The real time corrosion test has been carried out in severe tropical marine conditions at Corrosion testing centre, Mandapam Camp, Rameshwaram, India for about 800 hrs with periodic inspection. The exposure limits of this place are mentioned elsewhere[13] indicating highly corrosive atmosphere. A large scale 2'X2' AA 2024 panel and an aircraft stepdown model has also been anodized using the pilot scale facility.

## 3 Testing and Evaluation

### 3.1 Visual examination

The visual appearance of the permanganate sealed TSA anodized 2024, 6061 and 7075 aluminium alloys are displayed in Fig. 2. It is observed from the figure that the colour of the anodized and permanganate sealed specimens varies from golden yellow to light yellow depending upon the alloy composition.

### 3.2 Coating thickness

The coating thickness measured using eddy current method was found to be in the range of 5.5 ± 0.5 µm for all the aluminium alloy specimens. The obtained thickness is comparable with that of the conventional CAA process in conformance with MIL-A-8625F specification. However, a maximum thickness of 15 µm can also be obtained for other applications by slightly varying the process parameters.

### 3.3 Adhesion test

The adhesion of the anodized coatings was tested by peel-off method. No delamination of the coating was observed during the test thereby indicating good adhesion with the substrate (Fig. 3). The adhesion of the sealed anodic oxide layer with the aircraft grade primer and polyurethane top coat was also found to be excellent. This shows that the chromic acid-free anodization treatment exhibited good adhesion not only with the substrate but also with next layers i.e., primer and top coat.

### 3.4 Electrical breakdown voltage test

All the three anodized and sealed aluminium alloys exhibited >100 V as a breakdown voltage and no


Fig. 1 — Chromic acid-free permanganate sealed TSA process layout.

Table 1 — Test matrix comprising of the reference standards used for various evaluations.

| Test | Reference Standard | Acceptance Criteria |
|---|---|---|
| Visual Examination | --- | Before sealing, the anodic film should be continuous, free from defects. The colour of film varies from transparent to grey depending upon the composition of alloy.<br>After sealing, the anodic film should be continuous, free from defects and sealed properly. The colour of film varies from light yellow to golden yellow depending upon the composition of alloy. |
| Coating thickness measurement | ASTM B244 | > 3 µm |
| Adhesion test<br>3.1 Anodic layer to substrate<br>3.2 Anodic layer to primer | ASTM D3359 | No peeling off from the base metal |
| Electrical breakdown test | IS 1868:1996/ RPS54 | Low voltage continuity check at 50 V |
| Salt spray corrosion test | ASTM B-117 | Specimen shall withstand minimum 336 hours without indication of corrosion products |
| Tensile Strength | ASTM E 8/E8M | Should meet values as per respective material specification |
| Continuity and freedom from porosity | --- | --- |

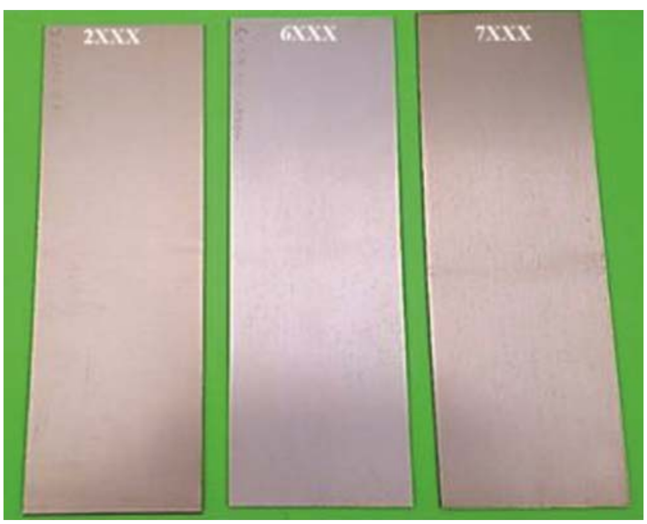


Fig. 2 — Photographic images of anodized and sealed aluminium alloys.

indication of conductivity or any other deterioration of the coating was observed. As per the MIL-A-8625F specifications, breakdown voltage should be > 50 V.

### 3.5 Corrosion test

#### *3.5.1 Salt spray test*

The sealed and anodized specimens were subjected to continuous salt spray exposure test in 5% NaCl salt fog medium. The photographic image of the salt fog exposed specimens are shown in Fig. 4. It is seen from the figure that apart from slight discoloration; no corrosion pits or products were observed after 336 hours of salt fog exposure. As per the MIL-A-8625F specifications the discoloration of the anodic oxide coating is acceptable. This implies that the corrosion resistance of the permanganate sealed TSA anodized specimens is satisfactory.

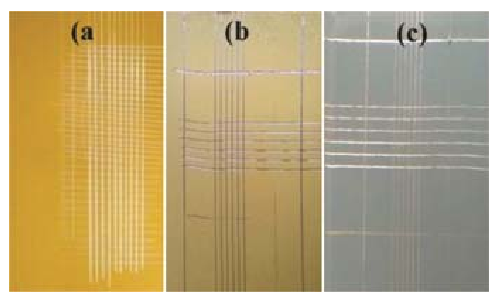


Fig. 3 — Pull-off adhesion test performed on (a) anodized and sealed AA 2024 sheet (as-coated), (b) as-coated with primer and (c) as-coated with primer and polyurethane top coat.

#### *3.5.2 Real time test*

The real time corrosion test has been performed at Corrosion Testing Centre for about 800 hours. The photographic images of the bare and anodized aluminium alloys (2024, 6061 and 7075) are shown in Fig. 5.


Fig. 4 — Photographic images of the anodized and sealed aluminium alloy specimens after 336 h of salt fog exposure.

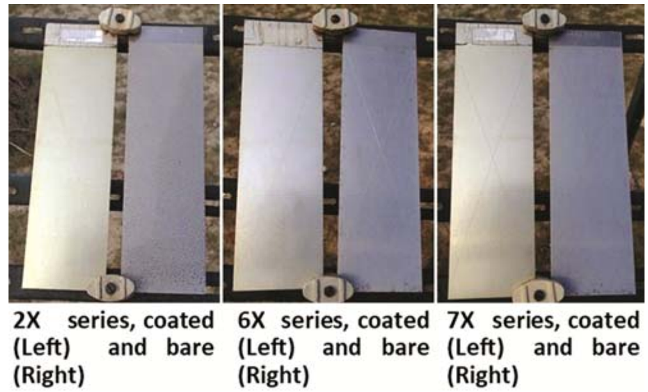


Fig. 5 — Photographic images of real time corrosion tested aluminium alloys.

It is observed from the above figure that even after 800 hours of exposure at sea shore environment there were no sign of corrosion pits or products seen on the surfaces of anodized specimens apart from slight discoloration which is acceptable as per MIL-A-8625F specifications. However, all the bare aluminium alloys specimens displayed the presence of corrosion pits/ products. From the above it is evident that anodized aluminium alloys exhibited excellent corrosion resistance in harsh real time environment.

### 3.6 Tensile strength

The tensile strength of the anodized and sealed aluminium alloys were compared with that of the uncoated specimens.The tensile strength of bare 2024, 6061 and 7075 specimens are 498, 342 and 574 MPa, respectively. The values of the anodized and sealed 2024, 6061 and 7075 specimens are 489±5, 342±1 and 588±2 MPa, respectively. From the above it is evident that there is no effect of anodization and sealing on the tensile strength of the aluminium alloys.

### 3.7 Continuity and freedom from porosity

The continuity and porosity test was performed on TSA anodized and permanganate sealed AA 2024, 6061 and 7075 alloy specimens with anodized layer thickness of 4 to 6 microns using copper sulphate solution of composition: copper sulphate: 20-25 g/L; HCl: 18-22 ml/L; DM water: 1 litre; RT and 5-10 minutes. The anodized specimens were immersed in the copper sulphate solution and after 5 min. of immersion no brown deposit appeared on the test specimens indicating it is free from porosity (Fig. 6).

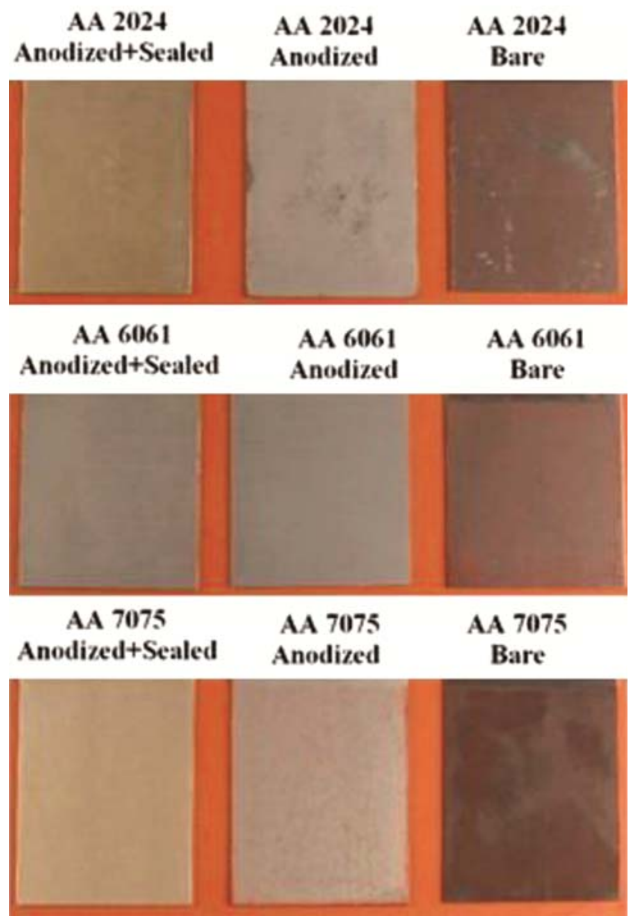


Fig. 6 — Al alloys test specimens tested for porosity test.

In the case of bare and anodized test specimens copper deposit is clearly seen as shown in the figure.

### 3.8 Sealing Test

The sealing test was performed on TSA anodized and permanganate sealed AA 2024, 6061 and 7075 specimens with a anodized coating of thickness 4 to 6 microns. After the application of few drops of

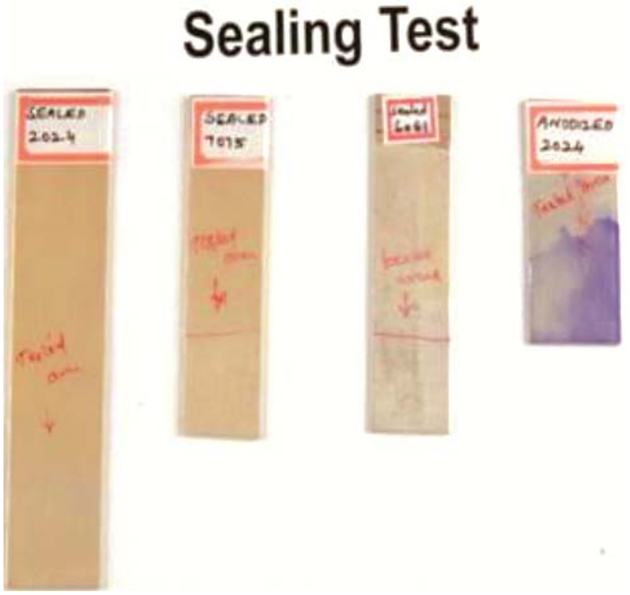


Fig. 7 — Al alloy test specimens tested for sealing.

nitric acid (35 to 45% by mass) followed by applying a drop of methyl violet dye, the specimen is cleaned by rubbing with pumice powder followed by rinsing with DI water. Absence of methyl violet dye stain on the test specimen indicates defect free sealing (Fig. 7). These tests were carried out as per ASTM B136-84. In the case of only anodized test specimen (without sealing), the presence of methyl violet dye stain is visible.

**3.9 Anodization of AA2024 sheet and aircraft model**

Anodization and sealing of 2'X2' AA 2024 sheet was performed in the pilot scale plant and its photographic image is displayed in Fig. 8 (a). It is seen from the figure that the coating is uniform in its appearance and colour. The thickness is found to be 4±1 μm. Anodization and sealing was also carried out on step down aircraft model made of AA2024. The image of the anodized model is shown in Fig. 8 (b). It can be seen that both larger size sheet and also complex geometries have been successfully anodized using the pilot plant facility.

**3.10 Document preparation for airworthiness process clearance**

Documentation is essential for process clearance. The documents prepared to obtain clearance for the chromic acid-free TSA process includes technical specifications comprising of the bath composition, process parameters and test standards adopted for evaluation of the anodized coatings on aluminium alloys. The other document is the process document which comprises of (i) raw materials – aluminium alloy composition and its source, details of the

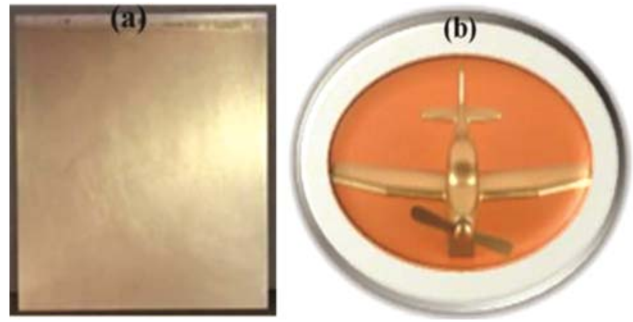


Fig. 8 — (a) Anodized and sealed AA 2024 sheet and (b) aircraft step down model.

chemicals used like composition, source, safety data sheet, details of tank material used for pre-treatment, anodization and sealing processes, (ii) The details of the equipments used during anodization and sealing processes like power supply, temperature controllers along with sensors, pH indicators, heaters, agitation/ filtration system and UV system are included along with operating procedures. Similarly, the details about instruments used for characterization/evaluation like adhesion, thickness, peel-off, electrical breakdown voltage, corrosion and tensile strength testing are included. These instruments need periodic calibration and maintenance and the records of these have been made, (iii) The performance of the anodized and sealed coatings has been evaluated based on the quality checks – the thickness uniformity, adhesion of the sealed anodic oxide layer with the substrate and the primer, electrical breakdown voltage resistance of the oxide layer, corrosion resistance in 5% NaCl fog, real time corrosion testing for 800 hrs at Mandapam camp and the effect of the formed oxide layer on the tensile strength of the aluminium alloys.

Procedure has been established to strip the defective anodic oxide layer and re-anodization of the aluminium alloys. Upon continuous usage of the anodizing and sealing baths, a variation in the composition of the baths is likely to occur. Procedures have been established to analyse the various constituents of the baths and replenish them at regular intervals. The TSA process has been developed as an alternate to CAA process wherein the effluent treatment is a major concern due to the release of toxic $Cr^{6+}$ ions. Although there are no toxic elements involved in the present developed TSA process, procedures have been arrived out for the safe disposal of the chemicals used. It is important to adopt appropriate safety measures during the execution of the anodization process. The details of which have

Table 2 — Test results of the anodized samples demonstrated in presence of RCMA representative and DGAQA approved QC.

| Test description | Reference Standard | Sample ID | Acceptance Criteria | Test Results | Compliance Status/Remarks |
|---|---|---|---|---|---|
| Visual examination | NA | 2X08021802<br>6X08021809<br>7X08021814 | Sealed anodic film free from defects and colour varies from light yellow to golden yellow | Golden yellow<br>Light yellow<br>Light yellow | Complied |
| Coating thickness | ASTM B 244 | 2X08021802<br>6X08021809<br>7X08021814 | > 3 µm | 5.87 µm<br>5.00 µm<br>5.36 µm | Complied |
| Adhesion test | ASTMD3359 | 2X08021802<br>6X08021809<br>7X08021814 | No peeling off from the base metal | Excellent Adhesion No delamination observed | Complied |
| Electrical breakdown test | IS 1868: 1996/RPS 54 | 2X08021802<br>6X08021809<br>7X08021814 | Low voltage continuity check at 50 V | All the specimens withstood up to 100 V. No failure of the coating observed | Complied |
| Salt spray corrosion test | ASTMB117 | 2X08021803<br>6X08021808<br>7X08021815 | Specimen shall withstand minimum 336 hours without indication of corrosion products | No pit formation/corrosion products observed after 336 h of salt spray test | Complied |
| Tensile test / To be comparable with bare specimens | ASTM E 8/E8M | 2X080021806<br>2X<br>6X08021811<br>6X<br>7X08021827<br>7X | Should meet values as per respective material specification | 494 MPa (±5)<br>498 MPa<br>341 MPa (±3)<br>342 MPa<br>586 MPa (±4)<br>574 MPa | Complied |

also been included. Traceability of the samples is vital specifically during the airworthiness certification hence, proper documentation has been done. A detailed test report as shown in Table 2 has been prepared for the process certification comprising the demonstration of the process, evaluation and testing of anodized and sealed coatings on 2024, 6061 and 7075 alloys in presence of the airworthiness certifying agency in India, RCMA (F&F-FOL), CEMILAC and DGAQA approved quality personnel.

## 4 Conclusions

It is observed from the above test results that the coated surfaces appeared light yellow to golden yellow colour and were free of defects. The coating thickness obtained was >3 µm (in the range 5 -6 µm). The adhesion of the coating with the substrate was found to be excellent as no delamination was observed. The electrical breakdown voltage of the coating was found to be > 50 V and was satisfactory. The salt spray test showed absence of corrosion pits or products on the coated specimens after 336 hours. The real time corrosion test confirmed these results even after 800 hrs of exposure. The tensile strength of 2024, 6061 and 7075 aluminium alloys was unaffected by the anodization. The process demonstration, coating evaluation and document preparation in the presence of airworthiness certifying agency has resulted in obtaining the process clearance for the chromic acid-free permanganate sealed tartaric sulphuric acid anodization on aircraft aluminium alloys (2XXX, 6XXX and 7XXX).

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