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# The influence of water when bonding with heat-curing epoxy adhesives on sealed sulphuric acid-anodised aluminium

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ABSTRACT

In this paper, it is demonstrated how the formation of blisters or foaming in a heat-curing epoxy adhesive can be avoided during bonding to sealed sulphuric acid-anodised aluminium. The crucial points to control are the release of water from the anodic film and the total amount of water in the joint. The cure cycle will affect the rate of water release, while the total amount to a large degree depends on the relative humidity in the area of bonding before joint assembly. Besides the adhesive, also the anodic film absorbs water within a short time scale. This behaviour is caused by aluminium sulphate, which is always present in the anodic film after sulphuric acid anodisation. At room temperature the aluminium sulphate is in equilibrium with water vapour at about 30% r.h. It has been experimentally demonstrated that the amount of water stored in the anodic film has a dramatic step change between 30% and 40% r.h. at room temperature. Outside this range up to condensing conditions differences are relatively small. The release of water during the curing of the adhesive can in addition to blistering or gassing also cause a boundary layer with changed properties in between the adhesive and the anodic film.

## 1. Introduction

Sulphuric acid anodising (SAA) is the most widely used anodising procedure for aluminium, due to esthetic appearance and excellent corrosion resistance together with the use of rather low cost and benign chemicals. Especially, architectural products have taken advantage of the good weathering resistance and the decorative colouring options the thick and porous oxide offer.

In addition, it is desirable to use SAA as surface pre-treatment for adhesive bonding. In the aircraft industry it was early discovered that bonded joints with SAA could fracture in the oxide at high-peel loading, resulting in lower joint strength [1,2]. Thick films and low temperatures promote this behaviour. Thinner anodic films with better behaviour had been found earlier with chromic acid as anodising electrolyte; later it was followed by phosphoric acid (PAA). These anodic films have a more open pore structure allowing penetration of high molecular primers/adhesives resulting in superior adhesion and durability [3]. They have therefore become the preferred choice for advanced structural adhesive bonding applications in the aircraft industry.

Minford [4] has shown that thinner SAA films can perform with adequate durability in long-term exposures; the joint strength retention in more aggressive water exposures like soak/freeze/thaw and corrosive salt spray conditions is superb. The morphology of the SAA oxide provides excellent resistance to both pitting corrosion and degradation by harsh-wet environments. This fact has often been foreseen when the initial strength is not amongst the highest ones. Many papers have however reported difficulties in bonding SAA, results with intermediate performance, concerns about poor adhesion, weak boundary layers and glue line defects as voids or blistering in the adhesive, especially in comparison with PAA [5].

Hydro Aluminium did start manufacturing of bonded body structures for Lotus sports cars in 1995, the Elise model; also several Aston Martin models has followed later. Adhesive bonding is the primary joining method, even if mono bolts, self-piercing rivets and Ejot screws are used for mechanical fixation before cure. The bond system in use is a heat-curing epoxy adhesive on sealed SAA anodising with a film thickness of $<10\,\mu m$. The robustness of the bonding process has been successfully proven. A key is to control the water in the system.

It is known that a lot of water will be left in the SAA film after the sealing process. Also reaction products and residuals from the electrolyte will remain in the oxide and the film will roughly contain about 13% sulphate [6]. This paper will show how the content of these reaction products strongly affects how the water is bound in the anodic film. The aims of this study were to gain knowledge on how the water is bound to the SAA oxide film, the

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dynamics of water transportation and also a better understanding of how water will interact with the adhesive during the bonding process.

Although the work done and the results generated are of quantitative value only to users of the specific system employed, the generic implications are of importance also to other adhesive bonding systems involving sealed sulphuric acid-anodised aluminium.

Details on materials and equipment are given in Appendix A.

## 2. Dynamics of water transport out of and into sealed anodised films on aluminium

### *2.1. Experimental determination of the amount of water in sealed anodised films*

Anodised films on aluminium are porous and therefore prone to contain water. In addition, the film will contain some impurities and aluminium compounds like sulphate that also might bind water as hydrate.

In an attempt to determine the state of the water in the films, reflection infrared molecular spectroscopy was applied. There are distinct differences between such absorption spectra from aluminium oxide, aluminium hydroxide and water. However, no differences were observed between the spectra from the surface of 'as-anodised' samples and from 'as-anodised' samples a short time after they had been heated to 100 °C in air to degas the films. Both spectra clearly show the presence of water on the surface of the samples, while indications of hydroxide were not seen. This observation was interpreted as an indication that the water was present as bound or adsorbed water, and that it was either never completely removed from the film during the degassing or that it was very quickly re-adsorbed on the surface of the anodised films. A limitation to this technique is that it does not directly allow for quantification of the amount of water on the surface, but only its presence above a certain detection limit.

In an attempt to get further information on the dynamics of the removal and re-adsorption of water, the electric leakage current through the anodised film was measured with an electrode area of about 10 $cm^2$ with varying applied voltage up to 45 V, both polarities. The aluminium substrate formed one electrode and the other electrode was made of electrically conductive porous polymer as used for packing electronic components. This technique allows measurement of the leakage current in real time under varying environmental conditions. The basic assumption behind these measurements is that the leakage current increases with increasing water content. It was found that the leakage current was not dependant on polarity of applied voltage and that the measurements were reversible and reproducible under stationary conditions. It was further demonstrated that the leakage current was reduced by more than a decade by degassing the anodic film at temperatures above 140 °C, but when exposed to room conditions after the degassing the current increased again in a short time to a new fixed level. These measurements indicated that the water content of the anodised films adapts to the environment within less than 1 h, but the technique does not allow for quantification of the amount of water.

In an attempt to quantify the amount of water released on heating of the anodised aluminium sample, a vacuum condensation procedure was applied. These experiments showed that a large fraction of the water is released during the first hour of degassing at 180 °C. The experiments further showed that after about an hour at room temperature and humidity an appreciable fraction of the water was reabsorbed and that after a couple of days at room temperature and humidity the water released on repeated heating is just the same as before the first degassing. To get an indication on how the degassing temperature influences the degassing rate, a set of data were collected, where the temperature was increased stepwise after some time at selected temperatures. The results from these experiments indicated that the amount of water that was released increased with increasing temperature. These results further demonstrated that the amount of water released and re-adsorbed was in the order of 50 $\mu g/cm^2$, or equivalent to a continuous water layer of about 0.5 μm thickness.

The amount of water transported into and out of the anodised films was found to be so large that a simple gravimetric technique could be applied for further investigations. The samples used were anodised panels of size $125 \times 80 \times 2\ mm^3$. Before the investigation started, all samples were heated to 180 °C for 70 h in an oven to condition the samples. After this conditioning, the samples were rapidly transferred to containers with controlled humidity. The wanted humidities were obtained according to ASTM E104-85, Standard Practice for Maintaining Constant Humidity by Means of Aqueous Solutions. Salt slush of LiCl and KCl were applied to represent low and high humidities (11% r.h. for LiCl and 84% r.h. for KCl, respectively, at 25 °C). A separate measuring instrument regularly controlled the humidity in the containers during the experiments. To expose the samples to intermediate humidity, they were left open in the laboratory and the humidity registered.

After the exposure, the samples were transferred back to the degassing oven and weighted at different times while being degassed. Since the change in weight (a few mg) is small compared to the sample weight (~50 g for the aluminium samples), the samples were handled with lint-free gloves and the samples were not marked with ink etc., but by scribing. During degassing, the samples were weighted by hanging them by a thin metal string that went through the top of the oven and were attached to a sensitive laboratory scale with a resolution of 0.1 mg. When weighting the samples at elevated temperatures, the weight change must be corrected for the change with temperature of buoyancy in air.

In the following measurements of weight changes at exposure and degassing, it is assumed that this is due to water transport in and out of anodised films. This assumption is based on general knowledge to the systems involved.

The weight change from degassing and exposure at 84% r.h. (oversaturated solution of KCl) and ~40% r.h. (open in the laboratory) is shown in Table 1.

The same samples were then re-exposed, some to 11% r.h. (oversaturated solution of LiCl) and some to ~47% r.h. The results are shown in Table 2.

All these data are shown graphically in Fig. 1.

Samples 1A, 2A and 3A are repeated tests as are samples 4B, 5B and 6B. This indicates that the repeatability of the measurements is within ~10 $\mu g/cm^2$ and significantly smaller than the difference between these two groups of samples after re-exposure at 11% r.h. and 85% r.h., respectively, which is ~40 $\mu g/cm^2$. When comparing parallels in Fig. 1 it should be kept in mind that the change in weight is small compared to the total weight of the samples. The spread in data is therefore probably solely due to random weighting errors. The data in Fig. 1 do not give reason to other conclusions than that all the water released during conditioning is re-adsorbed during exposure to ~40% r.h. and 84% r.h. and released again on degassing, while exposure to 11% r.h. gives only about 1/3 re-adsorption.

It might also be concluded that the samples exposed to controlled humidity after repeated cycles end up somewhat lighter than the samples exposed only to open laboratory air. Before taking this observation further, it should be remembered that the difference is only a few mg on 50 g samples.