Effect of Sealing Agents on the Corrosion Behaviour of Sulphamic acid Anodized Alumina Films

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SUMMARY – AA 1100 Aluminium alloy has been anodized in sulphamic acid electrolyte and sealed in triethanolamine (TEA). Sealing has also been carried out in generally used dichromate and boiling water solutions for comparison. The quality of the sealed aluminium oxide films has been assessed using Electrochemical Impedance Spectroscopy with and without exposure to 3% NaCl solution for 168 hours. From the impedance spectra, the polarisation resistance R_p and the double layer capacitance C_{dl} have been determined. The corrosion resistance behaviour of TEA sealing for various sealing times such as 5, 10 and 15 minutes has been compared with that of dichromate and boiling water sealings. Based on the experimental results, it was concluded that sealing in triethanolamine offered better corrosion resistance indicating it to be the best sealing medium compared to dichromate and boiling water for all sealing times. Also the corrosion resistance of the sealed anodized aluminium decreases with exposure time for all sealings and sealing times. Damage function of the oxide film sealed in different sealing agents and sealing time also confirms that TEA is the best sealing medium compared to dichromate and boiling water sealing.

Keywords: Anodizing, Aluminium, Sulphamic acid, Sealing, Triethanolamine and Electrochemical Impedance Spectroscopy

INTRODUCTION

Most of the aluminium used for architectural applications is often anodized in sulphuric/oxalic/phosphoric acid in order to improve the aesthetic properties and corrosion resistance prior to use. Anodizing of aluminium in these electrolytes produces porous aluminium oxide films, which are highly absorptive in nature. Though these porous oxide films provide adequate protection to the aluminium metal, they can also be a site for corrosion if not properly sealed. So, sealing after anodizing is most essential to prevent staining of the film as well as for enhanced corrosion resistance. Since the above mentioned anodizing electrolytes are highly aggressive in nature, the oxide films formed may undergo dissolution inside the pores even after anodizing. Excess acid electrolyte present in the pores will also affect the quality of sealing. Sulphamic acid is a less aggressive electrolyte, which can also be used for anodizing aluminium and its alloys as an alternative to sulphuric acid. This electrolyte has been recently demonstrated to produce thick and hard oxide films with fewer numbers of pores. Since it can be operated at room temperature without the use of a chilling plant, it can be advantageously used for industrial anodizing. Thus, sulphamic acid has been selected as the anodizing electrolyte for this study. A number of research papers[1-9] has been published on sulphamic acid anodizing wherein the influence of bath composition, anodizing parameters on the surface properties of the oxide film and also their corrosion behaviour has been extensively studied.

In the anodizing industry, sealing is conventionally done in boiling water – hydrothermal sealing. Higher temperature and longer duration of sealing makes the above process expensive. Also, hot water sealing decreases the fatigue strength and leads to stress corrosion. To reduce the temperature and time of sealing, dichromate, acetates and sulphates of nickel, cobalt and other rare earth metals have been added to the sealing bath[10-25]. Room temperature sealing, called cold sealing[26-32], of anodized aluminium has also been reported. Cold sealing using nickel fluoride[33-39] solutions can be used for substantial energy savings but they fail to satisfy the standard tests immediately after sealing, which requires aging. Chromate sealing has to be avoided because chromates are confirmed human carcinogens. Health hazards have also been observed for nickel salts, which can cause allergic contact dermatitis.

In order to overcome the above problem, a new sealing method was introduced by Gonzalez et al.[40-42] who added 2 cm^3 dm^{-3} (ml/l) triethanolamine to the hot water sealing bath and the sealing quality of the oxide films assessed. In our earlier papers[7-9], we have used a special type of sealing bath comprising triethanolamine, nickel acetate and cobalt acetate to seal oxide films formed from sulphamic acid. The reason for selecting triethanolamine as the sealing agent is due to its specific properties. For example, triethanolamine (TEA) is a very good corrosion inhibitor, TEA sealing forms a clean hydrophilic surface on alumina films, and does not produce any fumes as with hot sealing, and finally the colour of the oxide coating will not be altered by TEA sealing. In this paper, the sealing quality and corrosion resistance behaviour of sulphamic acid anodized AA1100 aluminium oxide films sealed in 10 cm^3 dm^{-3} triethanolamine for 5, 10 and 15 minutes has been investigated by using electrochemical impedance spectroscopy and the results compared with those sealed in

boiling water and sodium dichromate for the same times.

EXPERIMENTAL

AA 1100 aluminium panels of size 10 cm x 5 cm x 0.15 cm were used in this study. The panels were degreased with trichloroethylene and etched in 7 wt/v% sodium hydroxide solution for 5 minutes at 45°C. After alkaline etching, the specimens were washed with running tap water and rinsed with deionised water. They were then neutralised with 25 v/v% nitric acid for 2 minutes at room temperature. Again, they were washed with tap water followed by rinsing with deionised water. The specimens were then anodized galvanostatically in 150 g dm^{-3} sulphamic acid electrolyte using graphite electrodes as cathodes at a temperature of 30 ± 5°C; a constant current density of 2 A dm^{-2} was used. The solution was agitated to dissipate the heat evolved around the specimen using pressurised air. Anodizing was carried out for 30 minutes and an oxide coating of 7.5 – 10 μm in thickness was obtained. These specimens were then sealed in different sealing solutions such as boiling deionised water, dichromate and TEA for 5,10 and 15 minutes as described below.

Dichromate sealing bath (DC)
- Sodium dichromate — 15 g dm^{-3}
- Sodium hydroxide — 3 g dm^{-3}
- pH — 6.5 to 7.5
- Temperature — 94 to 98°C

TEA sealing bath (TEA)
- Triethanolamine — 10 cm^3 dm^{-3}
- pH — 7
- Temperature — 70°C

Boiling water bath (BW)
- Boiling deionised water — 100%
- pH — 7
- Temperature — 95 to 98°C

All the processing solutions such as alkaline cleaning, desmutting, anodizing and sealing baths were prepared with double distilled deionised water.

Electrochemical Impedance Spectroscopy measurements
Electrochemical Impedance spectra were recorded using a corrosion cell consisting of a three-electrode system. The anodized and sealed aluminium electrodes were used as working electrode. A platinum electrode and a saturated calomel electrode (SCE) were used as counter and reference electrodes respectively. The reference electrode was placed in a separate cell and was connected to the corrosion cell through a salt bridge with a luggin capillary. The tip of the luggin capillary was set at a distance of 1–2 mm from the surface of the working electrode to minimise errors due to the IR drop in the electrolytes. Corrosion studies were carried out using 3% NaCl solution.

The electrochemical impedance spectra for all the sealed anodized aluminium specimens without exposure (0 hours) and with exposure
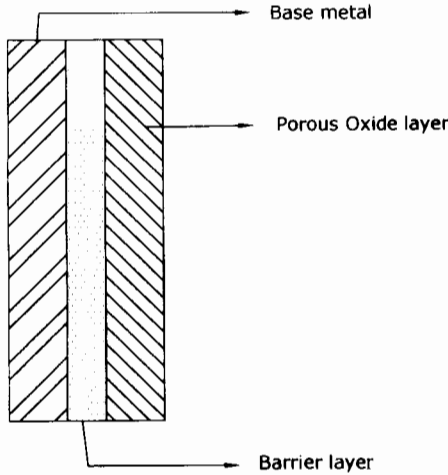

Figure 1. Schematic representation of aluminium oxide layers

to 3 % sodium chloride solution for 168 hours were recorded using Electrochemical Impedance Analyser Model IM6 with THALES software in the frequency range 10 mHz – 100 kHz to evaluate the sealing quality of the oxide films and also to study the influence of triethanolamine on the corrosion resistance behaviour of the sealed oxide coatings.

RESULTS AND DISCUSSION

Electrochemical Impedance spectroscopic studies
The anodized aluminium was found to have a very thin non-porous layer and a thick, porous, partially hydrated outer layer. Figure1 gives the schematic representation of these oxide layers. Electrochemical Impedance Spectra were recorded for all the sulphamic acid anodized aluminium specimens sealed in TEA, BW and DC without and with exposure to 3% NaCl. Figures 2–4 show the impedance spectra as Bode plots obtained for samples anodized in sulphamic acid and sealed in dichromate, TEA and boiling water for sealing times of 5, 10 and 15 minutes respectively. From these spectra, it can be clearly seen that TEA sealing has the maximum impedance compared to dichromate sealing (DCS) and boiling water sealing (BWS) irrespective of the sealing time. From the above results, it can be inferred that TEA offers better corrosion resistance to the anodized aluminium than dichromate and boiling water for all the sealing times.

Figures 5, 6 and 7 are the impedance spectra obtained for the anodized aluminium sealed in the three different sealing agents for 5,10 and 15 minutes respectively after exposure to 3% NaCl solution for 168 hours. From this, it is clear that the anodized samples sealed in TEA show higher impedance than those sealed in dichromate and boiling water which ascertains that TEA sealing offers better corrosion resistance to the anodized aluminium compared to that of BW and DC. The impedance values for all the samples sealed in three different sealing agents increased with increase of the sealing time. From this, it is obvious that the corrosion resistance increases with increase of sealing time and a 15 minutes sealing affords better corrosion protection to the anodized
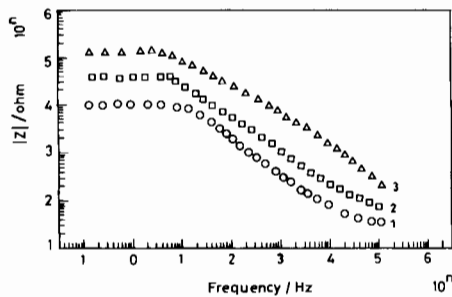

Figure 2. Bode Impedance Plot for different sealings (5 minutes sealing time) without exposure to NaCl
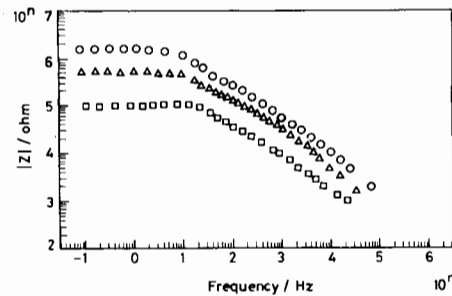ooo – DC sealing □□□ – BW sealing △△△ – TEA sealing

Figure 4. Bode Impedance Plot for different sealings (15 minutes sealing time) without exposure to NaCl
ooo – DC sealing △△△ – BW sealing □□□ – TEA sealing

Figure 3. Bode Impedance Plot for different sealings (10 minutes sealing time) without exposure to NaCl
□□□ – DC sealing △△△ – BW sealing ooo – TEA sealing
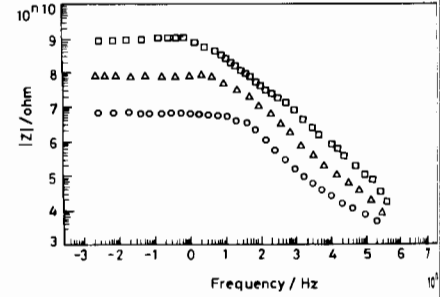

Figure 5. Bode Impedance Plot for different sealings (5 minutes sealing time) with 168 hours of exposure to NaCl
ooo – DC sealing △△△ – BW sealing □□□ – TEA sealing

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Figure 6. Bode Impedance Plot for different sealings (10 minutes sealing time) with 168 hours of exposure to NaCl
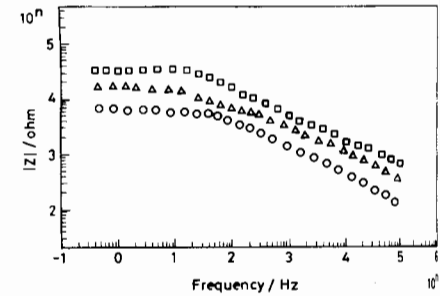ooo – DC sealing △△△ – BW sealing □□□ – TEA sealing

Figure 7. Bode Impedance Plot for different sealings (15 minutes sealing time) with 168 hours of exposure to NaCl
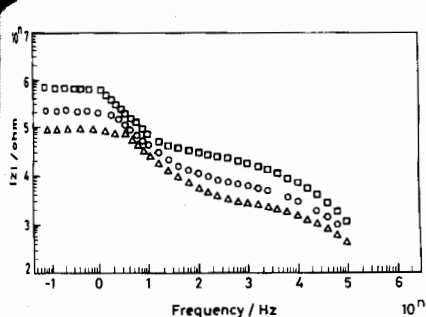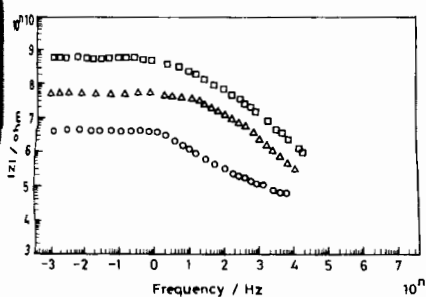ooo – DC sealing △△△ – BW sealing □□□ – TEA sealing

Figure 8. Equivalent circuit describing the impedance behaviour of sealed anodized aluminium

aluminium from corrosive media for all sealings. However, after exposure to 3% NaCl for 168 hours, the impedance values for all sealings and all sealing times, were seen to decrease due to corrosion resulting from chloride ion attack. The decrease in impedance values for TEA sealing is low whereas the difference between the impedance values before and after exposure for DC and BW sealings are greater. This shows that the attack of corrosive species on the samples sealed in TEA is less compared to those sealed in boiling water and dichromate. This decrease in impedance with exposure time is due not only to the dissolution of the oxide film but also to the pit formation by the attack of chloride ions during exposure.

In the case of TEA sealing, the impedance spectra were quite stable with exposure time reflecting its excellent corrosion resistance. For all the 5,10 and 15 minutes sealing operations followed by 168 hours exposure to NaCl, DCS shows low impedance values compared to the other sealings. Large changes in the impedance spectra over the entire frequency region were observed during prolonged exposure to NaCl for all sealings and sealing times which may be attributed to dissolution of the anodized surface and pitting formation as parts of the anodized surface are corroded.

Equivalent Circuit, Resistance and Capacitance values

Hoar and Wood[10] introduced a model for the impedance behaviour of anodized aluminium surface and discussed the changes resulting from sealing in various solutions. Hitzig et al.[15, 17] used a somewhat simpler equivalent circuit which describes the experimental results.
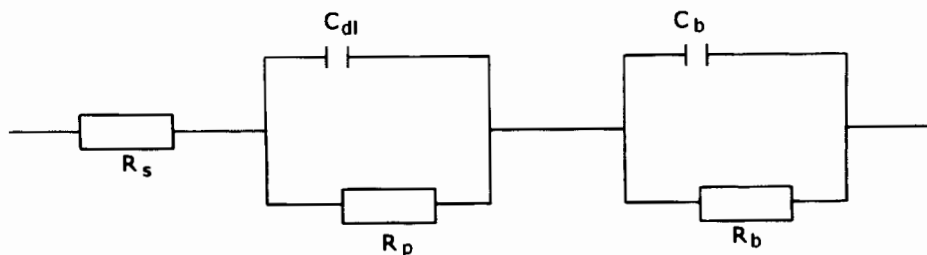
The equivalent circuit model used to explain the impedance behaviour of the sulphamic acid anodized oxide film is given in Figure 8. In this circuit, R_p, R_b and R_s represent the resistance of the porous layer, barrier layer and solution respectively. C_{dl} and C_b represent the double layer capacitance and capacitance of the barrier layer respectively. For simple corrosion systems, the polarisation resistance R_p can be determined from the D.C. limit of the impedance modulus $|Z|$[13],

$$R_P = \lim_{f \to 0} |Z| \qquad (1)$$

Data for R_p and C_{dl} for different sealing agents and sealing times with and without exposure to NaCl are given in Tables I, II and III where R_p is the charge transfer resistance and C_{dl} is the double layer capacitance.

From these data, it is clear that for all the sealing times (5, 10 and 15 minutes) TEA is the best sealing agent.. For a 5 minute sealing time without exposure, however, the values of R_p and C_{dl} for all the three sealings are comparable; TEA sealing has higher R_p values and lower C_{dl} values compared to boiling water and dichromate sealings. There is no appreciable difference in the R_p and C_{dl} values of boiling water and dichromate sealings. After exposure to NaCl for 168 hours, a decrease in R_p values and increase in C_{dl} values was observed for all the sealings, however, the decrease in R_p for TEA sealing was very low compared to BWS and DCS. TEA sealed plates were 15–20% corroded whereas BWS and DCS plates corroded by 40–45 and 70–75% respectively. Similarly, the increase in the C_{dl} value for TEA sealing was much less but the values for BWS and DCS increased by an order of magnitude.

For 10 and 15 minutes sealing time, TEA sealed specimens exhibited maximum impedance compared to that of dichromate and boiling water sealed specimens. The R_p values of boiling water sealing are comparable to TEA sealing but that of dichromate sealing is inferior to that of water

Table I. Polarisation resistance R_p and double layer capacitance C_{dl} values for the anodized alumina films sealed in TEA, DC and BW for 5 minutes with and without exposure to NaCl

Time of Exposure/h	Sealing Medium	R_p /kW	C_{dl} e–6 /F
0	Dichromate	6.82	5.77
0	Triethanolamine	13.43	1.18
0	Boiling Water	7.22	4.50
168	Dichromate	2.36	1.38
168	Triethanolamine	10.63	1.63
168	Boiling water	4.31	1.47

Table II. Polarisation resistance R_p and double layer capacitance C_{dl} values for the anodized alumina films sealed in TEA, DC and BW for 10 minutes with and without exposure to NaCl

Time of Exposure/h	Sealing Medium	R_p /kW	C_{dl} e–6 /F
0	Dichromate	61.9	1.17
0	Triethanolamine	555.4	0.648
0	Boiling Water	311.4	0.651
168	Dichromate	33.8	9.86
168	Triethanolamine	228.0	1.43
168	Boiling water	125.0	3.92

Table III. Polarisation resistance R_p and double layer capacitance C_{dl} values for the anodized alumina films sealed in TEA, DC and BW for 15 minutes with and without exposure to NaCl

Time of Exposure/h	Sealing Medium	R_p /W	C_{dl} e–8 /F
0	Dichromate	473.20 k	9.64
0	Triethanolamine	4.76 M	1.38
0	Boiling Water	4.58 M	5.60
168	Dichromate	138.50 k	71.7
168	Triethanolamine	2.40 M	6.72
168	Boiling water	2.25 M	9.20

sealing. Generally R_p values increased with increase of sealing time and decreased with increase of exposure time. On the other hand, C_{dl} values decreased with sealing time and increased with exposure time. These results point to an important difference in the sealing mechanism for TEA, boiling water and dichromate sealings.

A similar effect was noticed for the samples sealed for 10 minutes, but the samples sealed in all the three sealing agents were 50% corroded after exposure to NaCl for 168 hours. Nevertheless, the R_p values were superior for TEA sealing compared to those found in dichromate and boiling water sealings. For 15 minutes sealing, the R_p and C_{dl} values of TEA sealing were comparable to boiling water sealing but a superior corrosion resistance to that of dichromate sealing was observed. The samples sealed in TEA and boiling water were observed to undergo 50% corrosion after exposure to 168 hours in NaCl but the samples sealed in dichromate underwent 75% corrosion.

A notable increase in R_p values with increase of sealing time was observed as well as an appreciable decrease in R_p with exposure times. Thus, sealing quality increases with sealing time. The R_p values increase gradually as the typical hydration reaction involved in the sealing process developed within the pores of the oxide film. Therefore, sealing quality increases with increase of R_p values. Sealing proceeds through transformations taking place in pore filling via a complex mechanism involving pore wall dissolution, gelling, precipitation of hydrated alumina and conversion of some hydrates into more stable forms. The higher the R_p values, the greater will be the extent to which the hydration reaction was developed within the pores of the oxide film and more effective the sealing.

These tables also demonstrate increases in the capacitance values with increase of exposure time suggesting degradation of the outer oxide layer with time. The value of the capacitance of the oxide layer, which is the outer porous layer, is low in the case of TEA sealing at higher times of sealing and is high for the inner barrier layer in the case of dichromate sealing at all times of sealing. The decrease of R_p values with the increase of exposure time is due to thinning of the oxide resistant layer. Thus, the experimental values of R_p can be used as a measure of the extent of sealing when EIS is used as a quality control test. These parameters can be monitored as a function of exposure time.

Change in the capacitance of the porous oxide layer C_{dl}, which can be derived from the impedance diagram can be used to monitor sealing completeness. If there are unsealed anodic layers, C_{dl} is not initially apparent because the porous layer does not act as an insulator in as much as the hydration is crossed by as many pores of the cells it contains. Above a given degree of hydration, pores are saturated and C_{dl} tends to decrease with increasing sealing quality.

Damage Function
To further confirm the corrosion behaviour, the damage function has been calculated for the

Table IV. Damage function values for anodized aluminium sealed in TEA, DC and BW after exposure to 168 hours

Sealing medium	Sealing Time /min	Damage function
Dichromate	5	0.51
Triethanolamine	5	0.36
Boiling water	5	0.42
Dichromate	10	0.31
Triethanolamine	10	0.20
Boiling Water	10	0.25
Dichromate	15	0.19
Triethanolamine	15	0.10
Boiling Water	15	0.15

sulphamic acid anodized aluminium sealed in TEA, BW and DC using the equation,

$$D = \log (z_o / z_t)_{0.1\ Hz} \qquad (2)$$

where z_o is the impedance at 0 h and z_t is the impedance at 't' hours for a frequency of 0.1 Hz [16,17]. Here t is taken as 140 hours i.e. the specimens have been subjected to the corrosive media for a period of 140 hours.

Table IV gives a summary of the damage function for all sealed anodized aluminium oxide coatings exposed to NaCl for 168 hours. These highlight some of the very important differences in the corrosion behaviour as a function of anodizing process and sealing type. From Table IV, it can be observed that the anodized samples sealed in TEA have lowest damage function after exposure to 3% NaCl for 168 hours. Corrosion resistant anodized aluminium specimens would not show much difference in |Z| values after exposure to the corrosive medium, thereby making the damage function zero or close to zero. Sealing using TEA gives least value of damage function for anodizing in sulphamic acid bath whereas dichromate gives the highest values of damage function in the same bath. Lower damage function values clearly signify the better resistance to localized corrosion attack of the TEA specimen. Table IV also shows that the damage function decreases with increase in sealing time. The damage function values agreed very well with the results reported by Gonzalez et al.[40–42]

A correlation between the experimental values of R_p and C_{dl} with simulated values for the model has been carried out and as seen from Figures 9–11 a good agreement between the simulated and experimental plots is evident.

Sulphamic acid anodizing[1–9] produces thick and hard oxide coatings even at room temperature. Their hardness values are comparable to those formed from sulphuric acid anodizing at low temperatures. The higher the hardness of the oxide coating, the lower will be the porosity, pore density and pore diameter. This is due to the less aggressive nature of the sulphamic acid electrolyte. The lower porosity and pore diameter of the oxide film results in a decreased adsorptive power towards corrosive species compared to sulphuric acid anodizing. Thus, sealing for shorter duration (5, 10 and 15 minutes) is sufficient to close the pores completely and effectively. There is evidence for carrying out

TEA sealing for shorter duration. Lopez et al.[41] showed that the addition of TEA to the hot water sealing bath accelerates or catalyses the hydration reaction within the pores of the alumina coatings. They observed that sealing for one minute at boiling temperature was enough for the spot intensity to decrease to an acceptable level in the dye spot test. The sealing times required at 80 and 50°C were 3 and 45 minutes, both times comparable with industrial practice. Sealing was influenced not only by the temperature but also by the composition of the sealing bath. Consequently the addition of TEA considerably accelerated the hydration kinetics at room temperature and even more markedly at 50°C. They also showed that in TEA sealing, the action of triethanolamine was much more marked at short sealing times. Beyond 20 minutes, the response of the three sealing baths was very similar. One-minute immersion in TEA was sufficient time for the sealing quality level
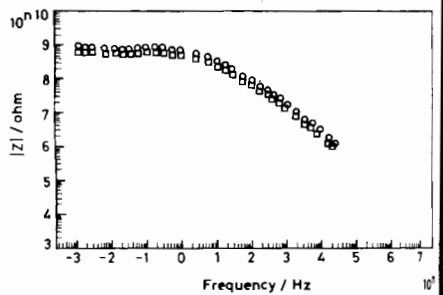

Figure 9. Simulated and Experimental Bode Impedance plot for TEA sealing (15 minutes sealing time) with 168 hours of exposure to NaCl
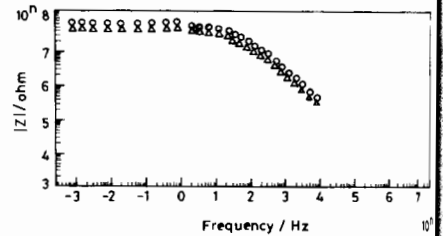ooo – simulated □□□ – experimental

Figure 10. Simulated and Experimental Bode Impedance plot for Boiling Water sealing (15 minutes sealing time) with 168 hours of exposure to NaCl
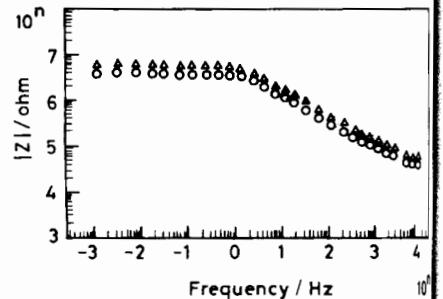ooo – simulated △△△ – experimental

Figure 11. Simulated and Experimental Bode Impedance angle plot for Dichromate sealing (15 minutes sealing time) with 168 hours of exposure to NaCl
△△△ – simulated ooo – experimental

established by the sealing tests to be reached in the TEA solution. Gonzalez[40] reported that TEA takes lesser time to catalyse the formation of a boehmite oxide layer or favour another corrosion inhibitor surface compound that expands laterally to block pores. This behaviour is reflected by the impedance spectra.

The difference in dichromate and hot water sealing has been discussed in detail elsewhere[19]. In dichromate sealing, the R_p values are very low because the pores were not sealed by aluminium hydroxide as in hot water sealing. The R_p in the case of dichromate sealing is therefore a resistance of an aqueous solution assumed to contain chromate ions in the open pores. The increase in capacitance of the outer porous oxide layer with exposure time was the result of the degradation of this layer.

Lopez et al.[41] studied the effect of TEA addition on water sealing at different temperatures and subjected sealed anodic layers to aging. A brief immersion in TEA solution below the boiling temperature has been shown to be enough for perfect sealing. Water continued to be adsorbed in the moist atmosphere very rapidly within the first 24 hours and much more slowly thereafter until a limiting value probably dictated by overall pore volume was reached asymptotically. He found that the dye spot test was very intense immediately after immersion in a TEA solution at 50°C for 30 minutes. It was still too intense if immersion was extended for a further 15 minutes but weak enough to pass the test when immersion was prolonged for a further 15 minutes i.e. a total of 60 minutes.

Mechanism of TEA sealing

The experimental values of polarisation resistance, capacitance and the damage function of the anodized samples sealed in three different sealing agents clearly shows that TEA sealing offers better protection to the anodized aluminium surface towards corrosion. This may be due to the difference in mechanisms of the three sealing systems. The mechanisms of hot water and dichromate sealing have already been explained very well[10]. Although the catalytic effect of TEA in the sealing of anodized aluminium has also been partly discussed no explanation for the improved corrosion resistance offered by TEA sealing or its mechanism has been proposed. A possible explanation for the enhanced effect of TEA may be related to the following.

In TEA sealing, the boehmite oxide layer formation and plugging of pores take place simultaneously with TEA accelerating the hydration reaction at low temperatures. The enhanced corrosion resistance of TEA sealing is due to the special reactions taking place during the sealing of the alumina film using TEA. The interaction of TEA, a model resin compound[45], with the alumina surface is of a specific type. TEA does not adsorb on γ-alumina but does on sulphamic acid anodized aluminium suggesting that the absorption of TEA on alumina is related to its activity as a Bronsted acid. The –OH groups of the TEA

form a trialkoxide covalently bound to the aluminium oxide.

$$Al_2O_3 + 2N(EtOH)_3 \rightarrow 2Al(OEt)_3 + N_2O + O_2 \quad (3)$$
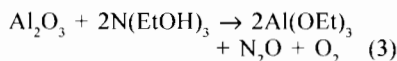
Furthermore, the stronger interaction of TEA with anodic alumina is due to the formation of stable hydrogen bonding between the nitrogen atom of TEA and the oxygen atom of the oxide, Al OOH[45].

$$O=Al–OH + N(EtOH)_3 \rightarrow O=Al–O–H....N(EtOH)_3 \quad (4)$$
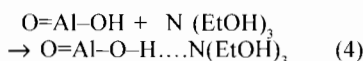
The more stable covalent and hydrogen bonds formed between TEA and alumina films provide excellent protection to the aluminium base metal and so TEA offers excellent corrosion resistance to the sulphamic acid anodized aluminium.

Mechanism of Water sealing

The mechanism of the boiling water sealing and dichromate sealing have been described[10,16,23]. Wafers[43] found that the pH of the water dropped during hydrothermal sealing due to the leaching of the residual acid. The anodic oxide film formed on aluminium in sulphamic acid contains fewer pores because sulphamic acid anodizing produces harder coatings compared to sulphuric acid. The pore sizes and diameters are very small. After anodizing, the pores will contain only very small amounts of acid. The excess of sulphamic acid will not dissolve the oxide film since it is a less aggressive electrolyte and may itself give suitable protection to the oxide film by forming stable hydrogen bonds with the alumina film.

$$Al_2O_3 + NH_2SO_3H \rightarrow Al_2O_2----H-NHSO_3H \quad (5)$$
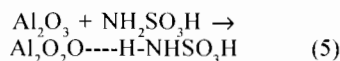
Thus there will be no leaching of this excess of acid during water sealing and hence there is no pH drop which normally occurs in water sealing of sulphuric acid anodized samples and the pH of the sealing bath will be maintained. During water sealing, in addition to the formation of boehmite and bayerite film, there is also an opportunity for the formation of stable hydrogen bonding between aluminium trioxide and water, which also gives protection to the oxide film. Thus, boiling water sealing offers the next best corrosion resistance after TEA sealing.

$$Al_2O_3 + H_2O \rightarrow Al_2O_2 O---H-O-H \quad (6)$$

Mechanism of Dichromate sealing:

Dichromate sealing improves the corrosion resistance behaviour to some extent compared to unsealed surfaces, but a more corrosion resistant surface is obtained by TEA and boiling water sealings. This agrees very well with the results obtained by Hitzig et al.[17] and Mansfeld et al.[16] These authors also reported that the impedance spectrum obtained for the dichromate sealed surface at frequency exceeding 1Hz is almost identical to that of the unsealed surface. Mansfeld[23] also observed that in the dichromate sealing process, the

pores stayed open and were apparently filled with Cr^{6+} ions which act as corrosion inhibitors. During hot water sealing the pores become plugged with oxide and hydroxide.

In the case of dichromate sealing, the discrepancies in the corrosion behaviour can better be explained from the fact that after dichromate sealing, the pores are not filled with a hydrated oxide, but that the dichromate is covering the pore walls and leaving most of the pores open. So the corrosive species, especially chloride ions, can easily penetrate into the pores of the oxide film and attack the underlying metal. This situation would produce low pore resistance. The agreement between the model and experimental data suggests that the dichromate sealing does not plug up the pores in the outer oxide layer as in the case of hot water sealing or nickel acetate sealing but passivates the pores by the adsorption at the pore walls.

According to the Pourbaix[44] potential-pH diagram for aluminium, at low pH the oxide film will dissolve. Therefore, for perfect sealing, the pH of the sealing solution must be in the range of 3.8 to 8.5 where aluminium oxide is stable. For this to occur, the ions in the sealing solution should be able to penetrate deep into the pores. In dichromate sealing, the chromate ions are adsorbed only on the walls of the pores and do not penetrate deep into the pores, and more often most of the pores remain open. Thus, the pH of the sealing solution is not maintained and therefore the sealing carried out in DC may not be perfect. Moreover, there is no reaction between the chromate ions and alumina film and no formation of boehmite or bayerite film over the aluminium oxide surface as in the case of boiling water sealing. So the corrosive species can easily penetrate into the open pores of the oxide film and attack the base metal. Hence, corrosion resistance offered by dichromate sealing is reduced compared to TEA and boiling water sealing. This is well confirmed by the experimental observations.

Advantages of TEA sealing

- Triethanolamine is a very good corrosion inhibitor
- Sealing can be carried out at lower temperatures
- Sealing time can be minimised
- It offers excellent corrosion resistance compared to many other sealings
- TEA accelerates the hydration reaction even at low temperatures
- Boehmite layer formation and plugging of pores take place simultaneously
- It forms a clean hydrophilic surface
- It will not liberate any fumes from hot sealing
- The colour of the oxide film is not changed
- Power, time and cost of the sealing process is minimised
- TEA ensures perfect sealing
- It will not affect the fatigue strength of the film
- It gives protection against stress corrosion
- TEA sealing is an eco-friendly and environmentally viable process

CONCLUSION

It has hence been found conclusively that the corrosion resistance increases with increase of sealing time for all sealing agents. Of the three sealing media evaluated, it has been observed that the TEA medium is most suitable and offers maximum corrosion resistance, and the boiling water medium is more effective than the dichromate sealing. Moreover, it is also true that the corrosion resistance decreases with increase in the exposure time. The same trend is maintained over different sealing times. TEA has been shown to be the best sealing agent for all the above sealing times.

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