# Effect of Triethanolamine Addition on Sealing Time

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The efficiency of triethanolamine (TEA) and sodium acetate additions in accelerating sealing without detracting from its quality was analyzed. In the presence of TEA, immersion for 1 min ensures compliance with current standards, as measured by the dye spot and acid dissolution tests. This can result in substantial energy and space savings, because a single sealing bath can be used to process the output of two or more anodizing baths. Whether the admittance test requirements are met immediately after sealing is inconsequential, inasmuch as aging of anodic layers ensures their fulfillment within a few days.

Most aluminum used in architectural applications is anodized in sulfuric acid baths, producing a porous oxide layer that covers the metal surface and has highly absorbent properties. As a result, anodized materials are subject to fouling and corrosion in aggressive media; this can be avoided by sealing surface pores. Industrial sealing has traditionally been accomplished by immersion in boiling deionized water, a procedure known as *hydrothermal sealing* (HTS).

The absorbing properties of anodized materials are also exploited for a large variety of architectural purposes, however, because they allow a wide range of colors. Also, the greater hardness of the surface oxide relative to the underlying metal protects the latter from abrasion—one of its few weaknesses.

The temperature required and its long duration (more than  $2 \text{ min}/\mu\text{m}$ )<sup>1,2</sup> make HTS expensive. This shortcoming has been circumvented traditionally by using additives (particularly nickel salts, acetates and triethanolamine [TEA] in the sealing bath.<sup>3-5</sup> Alternative, cold-sealing procedures that are implemented at room temperature and use nickel fluoride solutions were introduced in the early 1980s.<sup>2.6</sup>

This paper assesses the potential of sodium acetate and TEA solutions for shortening the time required for adequate sealing according to standard tests. The results are compared with those provided by traditional boiling in deionized water. The results of the standard tests were contrasted with those obtained with electrochemical impedance spectroscopy (EIS), a proven rationale for deriving new, more detailed information with a view to assessing the rate and completeness of sealing,<sup>7-13</sup> and, accordingly, an effective tool for examining the effect of the presence of additives in the sealing bath on the properties of the barrier and porous layers obtained.

## Experimental Procedure Materials

The material used was aluminum of 99.5 percent purity in the form of 100 x 50 x 1.5 mm sheets. Following the usual degreasing, etching and neutralization, specimens were anodized at a current density of  $1.5 \text{ A/dm}^2$  in an electrolyte containing 180 g/L sulfuric acid, stirred with pressurized air for 45 min. The coating thickness obtained was 18-20  $\mu m.$ 

Specimens were sealed in deionized water containing no additive, 0.5 g/L acetate ion or  $2 \text{ cm}^3/\text{L}$  TEA. The water was maintained at boiling temperature throughout.

## Control Tests

As in previous studies,<sup>10-13</sup> sealing quality was assessed by using standard tests, including the dye spot and (phosphochromic) acid dissolution tests, as well as admittance measurements at 1 kHz.<sup>14,15</sup>



Fig. 1—Simplified equivalent circuit for anodic layers: (a) well-sealed; (b) unsealed. Bode diagrams obtained for layers using the EIS technique (c) and (d). The capacitance of the porous and barrier layers,  $C_p$  and  $C_b$ , were calculated by extrapolation of the straight segments to  $\omega = 1$ .  $R_p$  was taken as the z value corresponding to the minimum  $\theta$ .



Fig. 2—Changes in the dye spot test with sealing time in boiling deionized water containing no additive, 0.5 g/L acetate ion, or  $2 \text{ cm}^3/L$  TEA.



Fig. 3—Variation of mass loss during the acid dissolution test with the sealing time in boiling deionized water containing no additive, 0.5 g/l acetate ion or 2 cm<sup>3</sup>/l TEA.



Fig. 4—Variation of admittance at 1 kHz with sealing time in boiling deionized water containing no additive, 0.5 g/L acetate ion, or 2 cm<sup>3</sup>/L TEA.

## Impedance Tests

In addition to standard control tests, electrochemical impedance spectroscopy (EIS) was used to assess sealing quality. AC impedance measurements were made in unstirred, aerated solutions containing 3.5-percent K<sub>2</sub>SO<sub>4</sub> at  $25 \pm 1$  °C. The surface area of the working electrode used was 1 cm<sup>2</sup>, masked with adhesive tape, for corrosion studies. The EIS cell and experimental set-up used are described in detail elsewhere.<sup>10-</sup>

The typical responses of sealed and unsealed anodic films can be closely approximated by the equivalent circuits in



Fig. 5—Bode diagrams for specimens sealed for 1 ( $\blacksquare$ ), 5 ( $\square$ ), 10 ( $\bigcirc$ ) and 45 min ( $\bullet$ ) in boiling deionized water containing 2 cm<sup>3</sup>/L TEA.

Figs. 1*a* and 1*b*, respectively.<sup>10,11</sup> Figures 1*c* and 1*d* show theimpedance diagrams for both conditions. As can be seen, the parameter values for unsealed and properly sealed films varied by 2-3 orders of magnitude at medium-to-high frequencies. This allows precise assessment of any effects on sealing because the impedance at a given frequency can be used to estimate, virtually error-free, the electrochemical parameter for the oxide film controlling the system's response at such a frequency (Fig. 1*c*). Consequently, EIS is a powerful tool for deriving comprehensive information on the mechanism and quality of sealing.

#### Results

# Behavior in Standard Control Tests

Figures 2-4 compare the changes observed in sealing quality, as estimated by the dye spot, acid dissolution and 1 kHz admittance tests, during sealing in deionized water containing no additive, 0.5 g/L acetate ion and 2 cm<sup>3</sup>/L TEA, respectively, all at boiling temperature.

As can be seen in Figs. 2 and 3, the absorbing capacity of the porous layer and its susceptibility to acid dissolution decreased much more rapidly in the presence of TEA than in



Fig. 6—Bode diagrams for the specimens of Fig. 5 after 1 week of aging in a wet chamber.

deionized water containing no additive. The effect of acetatewas found to be much weaker in both types of test. The action of TEA was much more marked at short, rather than at long times. Beyond 20 min, the responses of the three types of sealing baths were very similar. Although the improvement obtained with TEA was also apparent in the admittance test (Fig. 4), it was much more moderate than in the dye spot and acid dissolution tests. Note that, after one min (a long enough time for the sealing quality level established by these tests to be reached in the TEA solution), the admittance was still about five times higher than the maximum allowed value of 20  $\mu$ S. The time needed for the threshold level to be reached was about 20 min. Again, the effect of the acetate solution was between that of deionized water and the TEA solution.

## Impedance Diagrams

Figure 5 shows changes in the impedance diagrams with immersion time in the TEA solution. As sealing time was extended, the impedance diagram evolved from the typical shape for unsealed anodized materials to adequate sealing.

Figure 6 shows the impedance diagrams for the same



Fig. 7—Impedance for a specimen sealed in a bath containing TEA for 4 min immediately after sealing ( $\bigcirc$ ) and after 1 month ( $\bigcirc$ ), 1 yr ( $\square$ ) and 2 yr ( $\blacksquare$ ) of aging in the atmosphere of Madrid.

specimens in the previous figure after one week of standing in a highly wet atmosphere. As can be seen, sealing quality increased with time; the lower the starting quality, the more marked the improvement. As a result, after one week of aging, the impedance for a specimen sealed for one min was similar to that for one sealed for 45 min. As can be seen from Fig. 7, the favorable effect of aging on sealing quality continued for a long time.

Figure 8 shows changes in the resistance of the porous layer,  $R_p$ , with the sealing time in the three types of media studied. As can be seen,  $R_p$  increased gradually as the typical hydration reactions involved in the sealing process developed within pores; therefore, sealing quality increased with increase in  $R_p$ . This parameter was estimated from the impedance at the lowest phase angle in diagrams such as those of Figs. 5 - 7 ( $\theta$  vs. log  $\omega$ ), where the contribution of resistive control was maximal.<sup>10</sup> Based on this new parameter, the sealing quality obtained with TEA was again clearly superior, especially with short treatment times.

Figure 9 is a compilation of the various parameters studied



Fig. 8—Variation of the resistance of the porous layer with the sealing time in boiling deionized water containing no additive, 0.5 g/L acetate ion or 2 cm<sup>3</sup>/L TEA.



Fig. 9—Comparison of typical results of dye spot, acid dissolution and admittance tests for anodized materials sealed for 1 min in boiling deionized water containing no additive, 0.5 g/L acetate ion, or 2 cm<sup>3</sup>/L TEA.

for a sealing time of one min in deionized boiling water, acetate and TEA solutions. The favorable effect of the additives, particularly of TEA addition, was outstanding in the dye spot and acid dissolution tests, the requirements of which were easily met by the specimens treated with TEA, but hardly in its absence. The accelerating effect of TEA on sealing was also apparent—albeit less clearly—in the admittance tests and  $R_p$  values.

### Discussion

#### Accelerated Sealing

The anodized materials typically used in architectural applications, in thicknesses of about 20  $\mu$ m, require long HTS times (30-60 min or longer). Reducing such times to 1-10 min by using 2 cm<sup>3</sup>/L TEA (Figs. 2, 3 and 9) would result in substantial energy and space savings, because a single sealing bath could be used to process the output of two or more anodizing baths. The addition of sodium acetate also accelerates sealing (see Figs. 2 and 3), but the effect is much less marked than with TEA.

The fact that the effect of TEA takes longer to be reflected in the admittance test (Fig. 4)—about 20 min are needed to reduce the admittance below the allowed 20  $\mu$ S—is a result of the quality tests compared, relying on different properties. Consequently, the dye spot and acid dissolution tests measure surface properties—essentially the degree of pore blocking—whereas the admittance is related to transformations taking place throughout the porous layer, in pore fillings to be precise.

Water absorption and pore filling during sealing take



*Fig. 10—Sealing in TEA solution:* (a) *pore mouths are blocked during immersion in sealing bath;* (b) *hydration continues during aging.* 

longer than passing the dye spot and acid dissolution tests: 1 and 15 min in the presence and absence of TEA (Figs. 2 and 3, respectively). This suggests that TEA catalyzes the formation of bohemite or, through swelling, favors that of another surface compound that expands laterally to block pore mouths, as shown in Fig. 10*a*.

#### Continuation of Sealing

Penetration of the sealing solution into the pores continues until all are filled (Fig. 10*b*). Sealing proceeds through transformations taking place in pore fillings via a complex mechanism involving wall dissolution, gelling, precipitation of hydrated alumina and conversion of some hydrates into more stable forms.<sup>16</sup> These transformations may proceed for minutes during sealing (Fig. 5), weeks, months and years during aging (Figs. 6 and 7), or decades.<sup>12</sup> Well-sealed and incompletely sealed specimens exposed to the atmosphere undergo slow autosealing that results in gradually increasing quality of anodic layers (Figs. 6 and 7), masking the very marked effect of sealing in the early stages (Figs. 1-5). The effects of sealing and aging on the characteristics of anodic layers can readily be quantified from changes in  $R_{a}$  (Fig. 8).

Because aging of inadequately sealed layers gradually improves their sealing quality (Figs. 6-8), it is unimportant whether they meet the requirements of the admittance test for sealing times of 1-10 min in TEA solutions (Fig. 4). In fact, the absorbing capacity of these layers is low enough (Fig. 2) to avoid fouling and their chemical inertness is high enough (Fig. 3) to avoid deterioration of anodic layers until aging eventually lowers the admittance below the established threshold.

# Conclusions

1. The addition of  $2 \text{ cm}^3/\text{L}$  TEA to the sealing bath allows the requirements of the dye spot and acid dissolution tests to be met with a sealing time as short as 1 min.

2. This accelerating effect on sealing can be exploited to save much energy and space because a single sealing bath can be used to process the output of two or more anodizing baths. 3. While the admittance obtained with such short sealing times surpasses the allowed limits, the EIS results reveal that aging of anodic layers ensures fulfillment within a few days. 4. The addition of acetate ion also accelerates sealing, albeit less markedly than that of TEA.

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