# Effect of Temperature & Triethanolamine Addition on The Kinetics of Sealing Anodized Aluminum

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Electrochemical impedance spectroscopy (EIS) and standard sealing quality control tests were used to examine the accelerating effect on hydration reactions of the addition of 2 cm<sup>3</sup>/L TEA to the sealing bath. The presence of TEA was found to shorten the critical times required for the acid dissolution test to be passed by a factor of 5 at boiling temperature and by almost 100 times at 50 °C. The effect of TEA was reflected similarly in the dye drop and acid dissolution tests, and somewhat less markedly in the admittance test.

The porous nature of anodic layers in architectural aluminum entails their sealing in order to improve the aesthetic appearance and corrosion resistance of the material. The high cost of hydrothermal sealing (HTS), however, has fostered the search for additives intended to preserve the formation of sealing bloom or smut,<sup>1</sup> prevent or minimize dye leaching,<sup>2</sup> stabilize the pH of the sealing bath and cut maintenance costs, and, especially, save energy,<sup>3</sup> whether by reducing the sealing time<sup>4–7</sup> or by lowering the treatment temperature (*i.e.*, by using a cold sealing procedure).<sup>8–11</sup>

In recent work,<sup>12</sup> the ability of triethanolamine to substantially shorten the sealing time needed at boiling temperature to meet the quality requirements for award of the EWWA– EURAS quality label was demonstrated.

In this study, the effect of adding TEA at a 2 cm<sup>3</sup>/L concentration to a sealing bath below boiling temperature (down to 50 °C) was analyzed to ascertain whether the catalytic capacity of the bath was preserved at temperatures between that of traditional HTS and those of modern cold sealing methods.



Fig. 2—Variation of mass loss during the acid dissolution test as a function of the temperature of the sealing bath and immersion time in a solution containing  $2 \text{ cm}^3/L$  TEA.



Fig. 1—Changes in the dye spot test with temperature of the sealing bath and immersion time in a solution containing  $2 \text{ cm}^3/L$  TEA.



Temperature	Sealing time (min)
Boiling	1, 2, 5, 10, 20 & 45
80 °C	2, 5, 10, 30, 60 & 300
50 °C	10, 30, 45, 60, 120, 300,
	600, 960, 1440 & 2400



Fig. 3—Variation of admittance at 1 kHz with temperature of the sealing bath and immersion time in deionized water and a solution containing 2  $cm^3/L$  TEA.

# Experimental Procedure

The specimens used were 5 X 10 cm plates of 99.5 percent pure aluminum, anodized under technical conditions in 18percent  $H_2SO_4$  at 20 °C and 1.5 A/dm<sup>2</sup>, to obtain oxide layers 20 ±1 µm thick. Sealed specimens were obtained from them by dipping in de-ionized water containing 2 cm<sup>3</sup>/L TEA under the temperature and time conditions given in the table. Occasionally, specimens were also sealed in deionized water containing no additives or 0.8 g/L sodium acetate (0.5 g/L acetate ion).

Sealing quality was assessed from the response to the dye spot test, admittance measurements at 1 kHz and resistance to chemical dissolution in a phosphochromic acid medium.<sup>13,14</sup> Also, electrochemical impedance spectroscopy (EIS) was used as a supplement to the standard sealing quality control tests because it provides a quantitative measure of the extent of sealing similar to those obtained with the acid dissolution and admittance tests. It lacks the destructive effect of the former, however, and provides much more information than the latter. The cell used in EIS tests, and the experimental set-up and operating conditions employed, are described in detail elsewhere.<sup>15-17</sup>

### Results

Figures 1–3 show changes in the dye spot, acid dissolution and admittance tests, respectively, as a function of sealing time at three different temperatures: boiling, 80 °C and 50 °C. As can be seen from Fig. 1, sealing for one min at boiling temperature was enough for the spot intensity to decrease to acceptable levels in the dye spot test. The sealing times required at 80 °C and 50 °C were 3 min and 45 min; both times are compatible with industrial practice.

The results of the acid dissolution test were similar. As can be seen in Fig. 2, 1 and 10 min were sufficient to bring weight losses in the phosphochromic medium below the established threshold (30 mg/dm<sup>2</sup>) at boiling temperature and 80 °C, respectively. On the other hand, the time needed at 50 °C was five hr—exceedingly long for chain processing and about five times longer than the anodizing time and consequently calling for several sealing baths per anodizing bath.

The admittance test took longer to be passed in TEA solutions, *viz.*, about 20, 120 and 800 min at boiling temperature, 80 °C and 50 °C, respectively (Fig. 3). The process is accordingly much too slow by industrial standards, not only at 50 °C but also at 80 °C. Figure 3 also compares changes in admittance with time during sealing in deionized water and in the TEA solution (at both boiling temperature and 50 °C). As can be seen in the figure, the temperature had a marked effect, whatever the composition of the sealing solution. Sealing was influenced not only by the temperature, but by the composition of the sealing bath as well; consequently, the addition of TEA considerably accelerated the hydration kinetics at boiling temperature and, even more markedly, at 50 °C. Additions of acetate resulted in more modest accelerating effects.

Let us establish a minimum value for the resistance of the porous layer,  $R_p$ , as a quantitative measure of sealing quality. This threshold is not a part of any established standard; however, in the light of the results obtained for industrial sealing in boiling water, it would be about 100–200 k $\Omega \cdot \text{cm}^2$  for an anodized layer of 20 µm thickness, coating a material



Fig. 4—Variation of resistance of the porous layer with temperature of the sealing bath and immersion time in a solution containing 2 cm<sup>3</sup>/L TEA.



Fig. 5—Impedance diagrams obtained as a function of sealing time in a 2 cm<sup>3</sup>/L TEA solution at 80 °C: ( $\bullet$ ) 10 min, ( $\bigcirc$ ) 30 min, ( $\blacksquare$ ) 60 min and ( $\Box$ ) 300 min.

of the type studied in this work.<sup>15</sup> As can be seen in Fig. 4, the sealing times obtained would be very similar to those of the admittance test, with the advantage that impedance diagrams provide valuable additional information on the characteristics of the barrier and porous layers.

 $R_p$  can be estimated from impedance diagrams, such as those of Figs. 5 and 6. As can be seen from the former, sealing quality increased as the immersion time in the TEA solution at 80 °C was increased. Also, Fig. 6 reveals the beneficial effect of atmospheric aging at ambient temperature of an anodized specimen previously immersed in the TEA solution at 50 °C for one hr. As can be seen in the figure, the starting sealing quality was inadequate; however, provided pores were filled up with a hydrating solution, meeting the required quality standards was only a matter of time.

Figures 1–3 allow one to estimate the minimum sealing times required to meet the requirements of each test under each set of conditions: type of test, treatment temperature and



Fig. 6—Impedance diagrams for a specimen sealed in a 2 cm<sup>3</sup>/L TEA solution at 50 °C for 1 hr, obtained after variable times of atmospheric exposure: ( $\bullet$ ) immediately after sealing, and after 1 week ( $\bigcirc$ ), 1 month ( $\blacksquare$ ) and 3 months ( $\Box$ ) of exposure.

sealing solution. The logarithm of such critical times decreased linearly with increasing temperature in the three sealing solutions tested in the acid dissolution test (Fig. 7). The admittance test led to kinetic laws of the same type and even to similar critical times (Fig. 8), even though the accelerating effect of TEA was less marked at low temperatures.

#### Discussion

Fortunately, the accelerating effect on sealing of TEA additions at boiling temperature<sup>12</sup> is preserved at lower temperatures, as reflected in the results of the standard control tests (Figs. 1–3). Interestingly, the sealing quality achieved at 80 °C passed the dye spot (Fig. 1) and acid dissolution tests (Fig. 2) within 10 min, with anodic layers of  $20 \pm 1 \mu m$  thick, as those here utilized, resulting in similar sealing quality as that achieved with deionized water containing no additives at boiling temperature. In practice, this would result in substantial energy savings and avoidance of disturbing plant condensation. Raising the temperature to the water boiling point leads to acceptable sealing quality in even shorter times (Figs. 1 and 2), so much so that a single bath containing TEA can be used to process the output of several anodizing baths.<sup>12</sup>

Lowering the admittance below the threshold of the standard test, 20  $\mu$ S, would certainly entail extending immersion at 80 °C to about 120 min (Fig. 3), which is too long a time for a production line. Because the admittance continues to decrease (and the impedance to increase), however, during aging of inadequately sealed layers (Fig. 6), the requirements for this quality index are also eventually fulfilled after a few days.

The minimum sealing times needed to meet the quality requirements of the dye spot, acid dissolution and admittance tests at 50 °C would be 45, 300 and 800 min, the last two of which are incompatible with industrial practices. Alternatively, materials can be subjected to pre-sealing at a low temperature for a short time, followed by aging under appropriate conditions; this operating procedure will be examined in future work.

Impedance diagrams allow quantification of changes in sealing quality from capacitance and porous layer resistance measurements,  $C_p$  and  $R_p$  respectively, with much higher sensitivity than do standard control tests. Let us consider



Fig. 7—Minimum sealing times required to pass acid dissolution test as a function of temperature and composition of the sealing bath (water without additives, with 2 cm<sup>3</sup>/L TEA or 0.5 g/L acetate ion).



Fig. 8—Minimum sealing times required to pass admittance test as a function of temperature and composition of the sealing bath.

changes in  $R_p$  (Fig. 4), estimated from impedance diagrams, such as those of Figs. 5 and 6, as the *Z* value corresponding to the minimum dephase angle, where the contribution of resistive control is maximal.<sup>17</sup> The variation of  $R_p$  allows assessment of hydration reactions within the pores (the foundation of sealing) via a quantitative index that avoids the subjectiveness involved in visually assessing the spot intensity in the dye spot test, as well as the destructive effect of the acid dissolution test and the constraints of the admittance test, which involves measuring the impedance at a fixed frequency of 1 kHz.

All the conditions considered in Fig. 5, for example, which can readily be distinguished in terms of  $R_p$  (Fig. 4), correspond to level zero in the dye spot test (Fig. 1) and to acid dissolution values virtually coinciding for sealing times of 10, 30 and 60 min at a temperature of 80 °C (Fig. 2).

Increasing the temperature accelerates hydration, both in the traditional deionized bath and in the presence of additives. Many compounds inhibit the hydration process, but few accelerate it (*e.g.*, TEA, as shown by Fig. 3). As can be seen, the accelerating effect of TEA is also exerted—even more markedly in relative terms—at lower temperatures.

As can be inferred from Figs. 7 and 8, the minimum times required to pass the standard tests conform to exponential functions of temperature:

$$\begin{array}{l} log \; T_{_{b}} = log \; T_{_{t}} \text{-} b(\Delta t^{a}) \\ R = 10^{b(\Delta ta)} \end{array}$$

where  $R = T_t/T_b$  is the ratio between the minimum times at the test and boiling temperatures.

These minimum times or critical values can be used to quantitatively assess the effect of additives or temperature on the sealing kinetics. Actually,  $1/T_t$  can be considered as a measure of the rate of hydration processes and, plotting  $1/T_t$  vs.  $1/^{\circ}$ K, an Arrhenius-type graph is obtained (Fig. 9). The accelerating effect of the TEA additions on the kinetics of sealing is reflected in a decreased critical time at boiling temperature ( $T_b$ ) and an also decreased exponent *b* (the slope of the lines in the semi-logarithmic plots of Figs. 7, 8 and 9), which can be correlated to a decrease in the energy of activation of hydration reactions by the effect of the additive.

As can be seen from Fig. 7, the critical times for the acid dissolution test at boiling temperature were about 10 times



*Fig.* 9—*Arrhenius diagram, variation of*  $1/T_t$  (*hydration rate*) *as a function of the reciprocal of the absolute temperature.* 

lower in the TEA solution than in deionized water, the difference increasing with decreasing temperature (to nearly two orders of magnitude at 50 °C). The accelerating effect on sealing seems appealing enough to renew the traditional interest<sup>4,5</sup> in using TEA as an additive, though under new working conditions. Acetates also have a beneficial effect, though less marked than that of TEA (Figs. 7 and 8).

## Conclusions

- 1. The addition of 2 cm<sup>3</sup>/L TEA to a sealing bath decreases the time needed to pass the acid dissolution test by a factor of 10 at boiling temperature and by almost 100 at 50 °C.
- 2. For equal sealing times, the presence of TEA in a bath at 80 °C results in sealing quality similar to that achieved with deionized water containing no additive at boiling temperature.
- 3. The favorable effect of TEA reflects similarly in the dye spot and acid dissolution tests, and somewhat less markedly in the admittance test.
- 4. Acetates also have an accelerating effect on sealing, but less strongly than that of TEA.

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