Pre-Sealing of Anodized Aluminum in a Triethanolamine Solution at 50 °C-Effect of Aging at Ambient & Moderately High Temperatures

By V. López, A. Bautista, E. Otero & J.A. González

Traditional standard quality control tests and electrochemical impedance spectroscopy (EIS) were used to demonstrate that brief pre-sealing in a triethanolamine solution at 50 °C, followed by aging in a highly moist atmosphere, lead to results similar to those of cold-sealing procedures. In both cases, standard quality requirements are not fulfilled immediately after sealing, but are easily met after aging for a short period. The time needed for the standard tests to be passed is two weeks if aging takes place at ambient temperature, but only 24 hr if the temperature is raised to 50 °C.

Anodic oxidation of aluminum is most often performed by using a phosphoric, oxalic or, especially, sulfuric acid solution that gives rise to a porous coating separated from the underlying metal by a very thin, highly compact film known as the barrier layer.^{1–4} The high cost of classical hydrothermal sealing (HTS) procedures in boiling deionized water, which are required to ensure preservation of the aesthetics and durability of anodized materials—threatened by their porous nature—has fostered the exploration of a variety of additives for the sealing bath, intended to reduce the treatment time or temperature. Prominent among such additives are nickel acetate, cobalt salts and triethanolamine (TEA).³

The accelerating effect of TEA addition on sealing at different temperatures^{5.6} and the improved quality for sealed anodic layers provided by aging, whatever the sealing conditions, have been demonstrated.⁷⁻¹¹ It seems logical, therefore, to explore the potential of brief immersions in a TEA solution below boiling temperature, followed by aging under different conditions. This was the chief purpose of the present study.

Experimental Procedure

The specimens used were of the same type employed in previous work,^{5.6} viz., 5 x 10 cm plates of 99.5-percent pure aluminum, anodized under technical conditions in 18-percent H_2SO_4 at 20 °C and 1.5 A/dm² until coatings of $20\pm1\,\mu$ m thickness were obtained.

The coatings were pre-sealed in a 2 cm³/L TEA solution in deionized water at 50 °C for 30, 45 or 60 min. In this way, pores were partially filled with the sealing solution in times similar to those required in HTS, but at a substantially lower temperature. These pre-sealed anodic layers were subsequently allowed to age in a wet chamber at ambient temperature or 50 °C over variable intervals from 1 to 14 days.

Sealing quality was assessed by using the dye spot and (phosphochromic) acid dissolution tests, as well as admittance measurements at 1 kHz.¹² Measurements were made immediately after pre-sealing and after 1, 2, 4, 7, 10 and 14 days of aging.

Routine quality control tests were complemented by obtaining impedance diagrams for the anodic coatings under each set of experimental conditions studied. The cell and experimental set-up used were described in detail elsewhere.⁹⁻¹¹

Results

As can be seen from Figs. 1 and 2, the amount of water absorbed during immersion in the sealing bath ranged from about 12 to 23 mg, depending on the duration of sealing. Water continued to be absorbed in the moist atmosphere, very rapidly within the first 24 hr and much more slowly thereafter until a limiting value, probably dictated by the overall pore



Fig. 1—Changes in the amount of water absorbed by specimens pre-sealed in a 2-cm³/L TEA solution at 50 °C for 30, 45 and 60 min as a function of the time of aging in a wet chamber at ambient temperature.



Fig. 2—Changes in the amount of water absorbed by specimens such as those of Fig. 1, aged in a wet chamber at 50 $^{\circ}$ C.



Fig. 3—Changes in the dye spot test of the specimens pre-sealed in a 2-cm³/ L TEA solution at 50 °C for 30, 45 and 60 min as a function of the time of aging at ambient temperature.

volume, was reached asymptotically. There were no significant differences in absorption at ambient temperature (Fig. 1) and 50 $^{\circ}$ C (Fig. 2).

The dye spot (#4) was very intense immediately after immersion in a TEA solution at 50 °C for 30 min. It was still too intense if immersion was extended for a further 15 min and weak enough to pass the test when immersion was prolonged for another 15 min for an overall time of 60 min



Fig. 5—Changes in the acid dissolution test of specimens pre-sealed 60 min in a 2-cm³/LTEA solution at 50 °C as a function of the time of aging in a wet chamber.



Fig. 6—Changes in the admittance of specimens pre-sealed in a 2-cm³/L TEA solution at 50 °C for 30, 45 and 60 min, and unsealed specimens as a function of the time of aging in a wet chamber at ambient temperature.



Fig. 4—Changes in the dye spot test of the specimens pre-sealed in a $2 \text{-cm}^3/L$ TEA solution at 50 °C for 30, 45 and 60 min as a function of the time of aging at 50 °C.

(Fig. 3). After two days of aging at ambient temperature, the specimens passed the test—those that were immersed in the sealing bath for 30 min included. After 10 days of aging, the spot intensity was close to level 1.

If aging took place at 50 °C, the absorbing capacity was much lower than that established by the standards at the end of the first day (Fig. 4). Absorption virtually stopped after two days, whether pre-sealing in the TEA solution lasted 60, 45 or only 30 min.

Figure 5 illustrates the behavior in an acid dissolution test of specimens pre-sealed in a TEA solution and allowed to age at 50 °C. All this suggests that brief pre-sealing, which is compatible with chain production practices, suffices to meet the requirements of the acid dissolution test, provided the materials are allowed to age at 50 °C for 24 hr.

As can be seen from Fig. 6, the demands of the admittance test are stricter. The admittance measured immediately after immersion in the bath was about $300 \,\mu$ S. To bring it below the $20 \,\mu$ S threshold imposed by the standard, the pre-sealed material must be allowed to age for 10 days (up to 12 if it was pre-sealed for only 30 min) at ambient temperature. After two weeks, all pre-sealed specimens had admittance values well below the established threshold (specifically, $16 \,\mu$ S). As can also be seen from Fig. 6, aging was much slower in the absence of pre-sealing.



Fig. 7—Changes in the admittance of the specimens pre-sealed in a $2\text{-cm}^3/L$ TEA solution at 50 °C for 30, 45 and 60 min as a function of the time of aging in a wet chamber at 50 °C.



Fig. 8—Variation of the impedance of specimens pre-sealed in a 2-cm³/L TEA solution at 50 °C for 60 min as a function of the time of aging at ambient temperature: (\bigcirc) immediately after sealing, and after 1 day (+), 2 days (x), 7 days (\square) and 14 days (\bigcirc) of aging.

On the other hand, the admittance for the specimens aged at 50 °C was close to the 20- μ S threshold within the first day of aging (see Fig. 7). Subsequently, the admittance seemingly leveled off at about 7 μ S if aging was continued.

Changes in sealing quality with aging can be monitored much more precisely with EIS than with standard control tests. Impedance diagrams, such as those of Fig. 8, which shows changes during aging at ambient temperature of specimens pre-sealed by immersion in a TEA solution at 50 °C for 60 min, allow derivation of various electrochemical parameters typical of the porous and barrier layers. Accordingly, Fig. 9 shows the variation of the resistance of the porous layer, R_p , at the different pre-sealing times, as a function of the time of aging in a highly moist atmosphere at ambient temperature. The higher the R_p , the greater the extent to which hydration reactions developed within pores and the more perfect the sealing.

As can be seen in Fig. 10, which compares changes in R_p as a function of the aging time at ambient temperature and 50 °C for specimens pre-sealed in a TEA solution at 50 °C for 30 min, sealing quality improved substantially as the aging

temperature was raised. As a result, if 100–200 k Ω cm² is taken to represent the minimum quality required by the standards,^{9,10} EIS can no doubt assess much higher quality levels than those established by the traditional tests and so clearly surpasses them as an evaluation tool.

Changes in the capacitance of the porous layer, C_{p} , which can also be derived from impedance diagrams, can be used to monitor sealing completeness. If there are unsealed anodic layers, C_n is not initially apparent because the porous layer does not act as an insulator, inasmuch as it is crossed by as many pores as cells it contains. Above a given degree of hydration, such as that provided by pre-sealing, pores are saturated and $C_{\rm p}$, which tends to decrease with increasing sealing quality (Fig. 11), can be determined. At the end of the process, $C_{\rm p}$ ranges from 10^{-9} to 10^{-8} F/cm² (*i.e.*, about 1000 times lower than the typical $C_{\rm b}$ values for layers about 1000 times thicker than the barrier layer). The invariability of $C_{\rm b}$ (Fig. 11), another parameter that can be derived from impedance diagrams, also testifies experimentally to the fact that barrier layers are not significantly affected by sealing.

Discussion

Figures 1 and 2 reveal that pre-sealing causes pores to be partially filled (about one-third of the overall volume at the shortest pre-sealing time). However, the high relative humidity imposed during the aging process virtually saturates the whole length of the pores within a week (Figs. 1 and 2). Consequently, the conversion of anhydrous alumina into hydrated alumina must produce the total pore blocking during aging.

The behavior of anodic layers pre-sealed in a TEA solution at 50 °C is similar to that of materials subjected to cold sealing. The latter do not meet quality standards immediately after sealing; rather, they require aging for as many as 30 days, depending on the type of test used.¹³ Specimens presealed in TEA do not fulfill the standard requirements immediately after immersion, either; however, they do so after aging at ambient temperature for two weeks (Figs. 3 and 6), or for only 24 hr if the aging temperature is raised to 50 °C (Figs. 4, 5 and 7).



Figure 9—Variation of the resistance of the porous layer of specimens presealed in a $2 - cm^3/L$ TEA solution at 50 °C for 30, 45 and 60 min with the time of aging in a wet chamber at ambient temperature.



Fig. 10—Variation of the resistance of the porous layer of specimens presealed in a 2- cm^3/L TEA solution at 50 °C for 30 min with temperature during aging in a wet chamber.

The accelerating (catalytic) effect of TEA traces, which penetrate into pores during pre-sealing, continues to be exerted during aging. This is apparent from Fig. 6, which compares changes in admittance of pre-sealed and unsealed specimens stored in a wet chamber.

The water absorption capacity is rapidly lost, especially if aging takes place at 50 °C; consequently, the dye spot test cannot detect changes in the layer beyond the first 24 hr (Fig. 4). Such a limited sensitivity also affects the acid dissolution (Fig. 5) and admittance tests (Figs. 6 and 7), where values rapidly level off. Hydration is far from complete by that time, however, and major transformations continue to take place within the pores, as reflected in the impedance diagrams obtained after aging for a variable time (Fig. 8) and in the variation of electrochemical parameters for the porous layer derived from such diagrams (Figs. 9–11).

Accordingly, R_p continues to increase indefinitely for weeks (Figs. 9, 10), months, years or even decades,^{11,14} so the last stage of sealing, probably the transformation of alumina trihydrate, which is usually formed below 70–80 °C, into a thermodynamically more stable variety, proceeds also indefinitely. In any case, EIS continues to provide valuable information well after routine sealing quality control tests become ineffective.

Conclusions

- 1. Adding TEA to the sealing bath accelerates or catalyzes hydration reactions within the pores of aluminum coatings. The effect continues to be exerted during aging and further improves sealing quality.
- 2. Pre-sealing for a short time in a TEA solution at 50 °C leads to results similar to those of cold sealing procedures. In both cases, standard quality requirements are not met immediately after sealing but are easily met after aging for a short period.
- 3. The time needed to meet standard quality requirements is less than two weeks at ambient temperature and only 24 hr if the aging temperature is raised to 50 °C.
- 4. The EIS technique allows changes in the porous layer during the aging process following sealing to be monitored with much higher precision than that afforded by classical standard quality control tests.



Fig. 11—Variation of the capacitance of the barrier and porous layers during aging at ambient temperature and at 50 °C, of anodic layers presealed by immersion in a 2-cm³/L TEA solution at 50 °C for 60 min.

Editor's note: Manuscript received, July 1997.

Acknowledgment

This work was financially supported by the Comisión Interministerial de Ciencia y Tecnología (CICYT) of the Spanish Ministry of Science and Education within the framework of Project MAT95-0060.

References

- 1. T.P. Hoar & G.C. Wood, *Electrochim. Acta*, **7**, 333 (1962).
- R. Lizarbe, *Teoría y Práctica de la Lucha Contra la Corrosión*, J.A. González (Coord.), 461-484, Ed CSIC Madrid, 1984; Ch. XVI.
- S. Wernick, R. Pinner & P. Sheasby, *The Surface Treat*ments of Aluminium and Its Alloys, 5th Ed., ASM International and Finishing Publications Ltd., Metals Park, OH, 1987; pp. 773-856.
- 4. A.W. Brace, *The Technology of Anodizing Aluminium*, Technicopy Ltd., Stonehouse, Glos. (England), 1979; pp. 1-19.
- J.A. González, E. Otero, A. Bautista & V. López, *Plat.* and Surf. Fin., 84, 59 (July 1997).
- 6. A. Bautista, V. López, E. Otero & J.A. González, *Plat. and Surf. Fin.*, to be published.
- 7. H. Birtel & W. Bunk, Aluminium, 44, 736 (1968).
- 8. R.C. Spooner, *Met. Finish.*, **66**(12), 44 (1968); **67**(1), 80 (1969).
- 9. R. Lizarbe & S. Feliu, *Rev. Metal, Madrid*, **8**, 85 (1972).
- R. Lizarbe, J.A. González, W. López & E. Otero, *Aluminium*, 68, 140 (1992).
- 11. R. Lizarbe, J.A. González, E. Otero and V. López, *Aluminium*, **69**, 548 (1993).
- 12. Anon., Standards ISO 2143 and 2931.
- 13. M.J. Kalantary, D.R. Gabe and D.H. Ross, *Plat. and Surf. Fin.*, **80**, 52 (Dec. 1993).
- 14. R. Lizarbe, V. López and J.A. González, *Pinturas y Acabados Industriales*, **35** (207), 70 (1993).
- E.F. Barkmann, Anodized Aluminium, ASTM STP NI 388, Philadelphia, PA 19103, 1965; pp. 85-120.

continued on page 78