Sealing of Electrolytically Formed Porous Films Of Aluminum by Nickel Fluoride Process

By Majid R. Kalantary, D. R. Gabe and D.H. Ross

Since the early 1980s, nickel fluoride cold sealing of anodized aluminum, on the basis of energy saving processes, has been marketed in industry. Currently, it is possible to substitute cold sealing as an alternative to conventional hydrothermal sealing, almost without any drawbacks, while enabling reduced treatment time, reduced cost of operation and, most important, energy conservation. The most important criteria associated with cold sealing are covered, with attempts to present the findings as an independent view of the process.

A large proportion of wrought aluminum and aluminum alloys is anodized in sulfuric, chromic or phosphoric acids to yield a film consisting of a thin barrier layer and an outer porous layer. Other solutions, such as sodium tartrate, borate or boric acid, yield barrier-layer-only films for electronic applications; the film produced is much less than one µm in thickness. For architectural applications, the film thickness is required to be more than 20 µm to give adequate protection when it is exposed outdoors for as long as 25-50 years.’ To grow such a film thickness, anodizing is usually carried out in sulfuric acid electrolyte. The porous oxide film produced is absorptive in nature. Although the porous film can be colored by a variety of methods such as electrocoloring, application of dyes, or integral coloring for decorative applications, but this porous film can also be a site for corrosion if not sealed. For this reason, sealing after anodizing is essential to prevent staining of the film and increased corrosion.

There are many methods for sealing anodized aluminum. The most common is conventional hydrothermal sealing.[2] This involves immersion of fresh anodic film in boiling water, containing anti-smut additives, with sealing carried out typically at the rate of 2 to 5 min/µm of film thickness. Although this is simple, because of the long sealing time, it becomes uneconomical and uses substantial energy.

In the last ten years, alternative sealing has been introduced in the European market, based on nickel fluoride solutions that can be operated at room temperature and that require only a short sealing time.[3] The finishes produced by this method can show substantial energy savings, but fail to satisfy the standard tests immediately after sealing. Depending on the type of test carried out, aging of up to 30 days is required for cold-sealed film to pass the test originally designed for conventional hydrothermal sealing. Such a problem can be overcome, however, by a short post-treatment in hot water. This combination can be effective and can produce a sealed film comparable to conventional hydrothermal sealing and still reduce cost and conserve energy.

In this paper, the authors discuss and establish the following parameters for sulfuric-acid-anodized films:

1. Methods of seal quality assessment in relation to cold sealing.
2. Process constituents and parameters.
3. Atmospheric hydration (aging) of nickel fluoride cold sealing films.
4. Effect of post-treatment.

Method of Seal Quality Assessment

Assessment of seal quality is achieved by means of laboratory tests designed particularly for conventionally hydrothermal-sealed anodized aluminum. For assessing the seal quality of cold-sealed films (where appropriate) the following tests were carried out according to the British/ISO standards, as shown in Table 1.

Table 1

Seal Quality Tests	Acceptance Limit
Phosphoric acid/chromic acid (BS 6161 Part 3-IS0 3210:1983)	</= 30-40 mg/dm^2
Nitric acid pre dip dissolution (BS 6161 Part 4-IS0 2932:1981)	</= 10 mg/dm^2
Acetic acid/sodium acetate (BS 6161 Part 4-IS0 2932:1981)	</= 20 mg/dm^2
Acidified sodium sulfite (BS 6161 Part 4-IS0 2932:1981)	</= 20 mg/dm^2
Dye spot (absorption) test (BS 6161 Part 5-IS0 2143:1981)	0-2
Admittance test (BS 6161 Part 6-IS0 2931:1983)	</= 20 µS for 20 µm film thickness

Process Constituents and Parameters

Cold Sealing Main Solution Ions Concentration

The nickel and fluoride ion concentrations in the sealing solution are the prime constituents which help the plugging of the pores of anodic film. Low concentration does not seal the film adequately or efficiently; high concentration causes deterioration of the film. The published literature advocates a seal solution having free fluoride content of 0.5 to 1.2 g/L and nickel ion content of 1 to 2 g/L.[3-6]

The authors’ experience with cold sealing solutions is that excess fluoride will cause a rapid reaction in the pores of anodic film by increasing the pH level so that it causes some dissolution of the film. Although direct measurement is difficult, it is possible to check by analyzing the nickel fluoride bath for aluminum after treatment of anodized film. Excess fluoride content causes the rapid precipitation of nickel at the top surface of the film, preventing efficient entry of nickel in the pores, resulting in pore plugging at the outer surface of the film and the remaining pores remaining unsealed.[7]

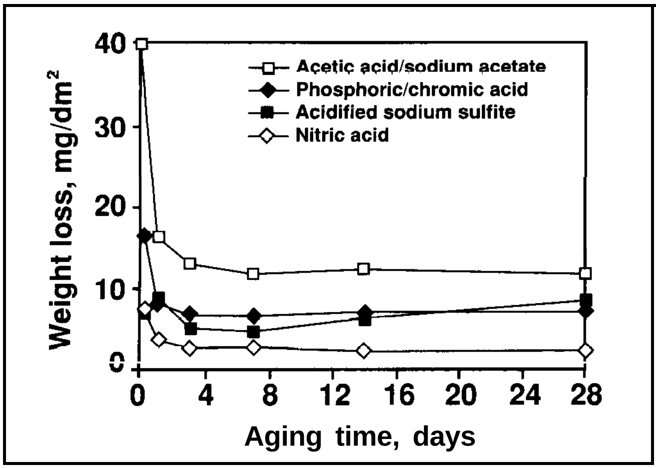

Fig. 5—Effect of aging on sea/ quality of nickel-fluoride cold-sealed films, determined by acid dissolution tests.[9]

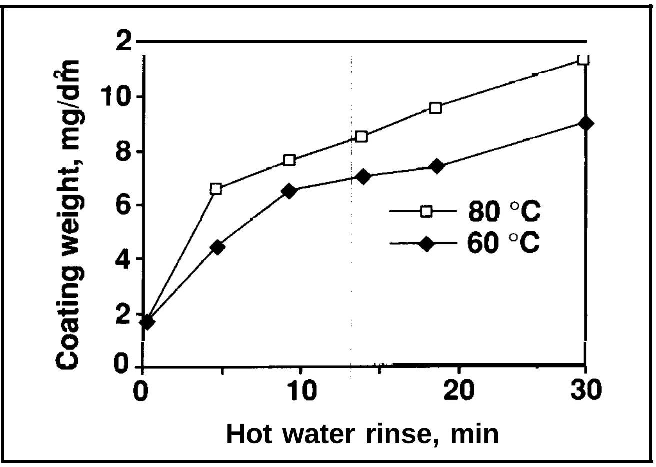

Fig. 6—Weight gain of cold-sealed films with hot-water rinse post-treatment vs. time.

The admittance test is a measure of the electrical properties of the film and indicates the degree and depth of pore closure. The admittance results on cold-sealed films indicate that the finished product requires an aging period of 14 to 28 days (depending on the temperature and humidity of the environment) to pass this test. Such aging behavior is explained by the mechanism of cold sealing[7-9] that takes place in a two-step hydration process: (a) the cold-seal materials (suggested to be a mixture of aluminum hydroxy-fluoride/nickel hydroxy-fluoride)[10] in the pores of the anodic films physically adsorb water molecules from the atmosphere, resulting in swelling and progressive pore blocking, indicated by an increase in weight with time;[9] (b) the aging process proceeds by gradual transformation of physically absorbed water molecules into a chemi-absorbed form;[11,12] accordingly, material in and adjacent to the pores at this stage becomes more crystalline. The hydration proceeds over a period of 14 to 28 days. After this time, the pores are virtually totally blocked and characterized by low conductivity of the film, as shown by admittance test results.

From the above findings, it can be said that the standard accelerated corrosion test (CASS test- BS 1615 Appendix J or ISO 3770), which simulates the outdoor performance of the coating, will not show that the cold-sealed film passes the test immediately after sealing. Anodized products are not usually installed immediately after sealing, however; therefore, they often have sufficient time to age (preferably at least 14 days) before installation. Experience with cold-sealed films shows that the product requires at least 24 hr to stabilize enough not to alter color if water is splashed on it or if it comes in contact with dyes.' To avoid this, it is now common practice to rinse cold-sealed films in water at a temperature of 60 “C for a short time. This allows rapid drying and partial hydration at the same time. The product treated by the latter method is also believed to be adequately sealed and can be exposed immediately to the outdoor environment, just as with hydrothermal sealing.

The question of accelerated corrosion testing (CASS test) is further complicated by the conditions of the test. The test runs at 50 “C at high humidity. These are conditions which may be expected to accelerate the aging process on a cold-sealed film. Accordingly, erratic test results may be expected if testing is carried out before the film has had a chance to stabilize.

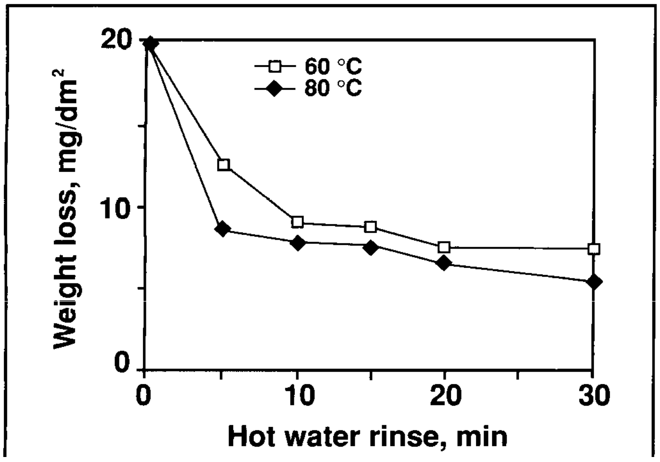

Fig. 7—Effect of not- water rinse post-treatment on seal quallty, determined by phosphoric/chromic acid dissolution test.[8]

Effect of Post-Treatment

The effect of post-treatment on nickel-fluoride cold-sealed films was studied. Most of the cold-sealed finishes were post-treated at 60 and 80 “C. One set of samples, however, was post-treated by boiling in deionized water at the rate of 0.5 min/µm.

Post- Treatment Hydration

The rapid hydration resulting from post-treatment of cold-sealed films is shown as a weight gain (Fig. 6). The gravimetric measurement shows that the weight increased rapidly for samples treated at 60 and 80 °C for 5 to 30 min of post-treatment. The weight increased with an increase in post-treatment time and temperature. Although there is no direct correlation between weight gain and seal quality test results, as can be seen below, the results generally imply a better seal quality with an increase in post-treatment time and temperature immediately after treatment.

Seal quality assessment of post-treated cold-sealed finishes

The effect of time and temperature of post-treatment on the results of seal quality determined by phosphoric acid/chromic acid dissolution tests show (Fig. 7) that the higher the temperature or longer the time of post-treatment, the better the seal quality. The admittance test, which measures the depth and degree of pore closure, generally shows some improvement in value after post-treatment at 60 and 80 °C for 5 to 30 min (Table 3). In general, the longer the post-treatment time and temperature, the lower the initial admittance value. None of the samples, however, could satisfy the admittance test immediately after post-treatment and further room temperature aging was required for samples to pass the test. it is interesting to see (Table 3) that the cold-sealed film post-treated at **60 "C passed tests** in a shorter aging time than those post-treated at 80 "C. The reason for this is that partially sealed samples enable the film to hydrate more rapidly than those sealed almost completely.[8,9]

The Qualanod Specification also suggests an alternative post-treatment in which cold-sealed films are treated in 5 to 10 g/L solution of nickel sulfate ($NiSO^4$- $7H_20$), operated at 60 "C for 0.8 to 1.2 min/μm.[3]The specification fails, however, to report whether this would in fact pass the admittance test. The authors have serious doubts that it would. Perhaps for this reason, the specification suggests that the more relevant tests are dye absorption and phosphoric acid/chromic acid dissolution.[3]An alternative post-treatment, which could allow cold-sealed finishes to pass all the seal quality tests, involves the process termed as "dual sealing." This involves the usual cold-sealing under optimized conditions, followed by a very short post-treatment (equal to or less than 0.5 min/μm) in boiling deionized water, The total time required for sealing is less than half that of conventional hydrothermal sealing and the seal quality of dual-sealed films is much better than the former procedure (see Table 3).

Mura has studied the effect of fluoride contamination in the range of O to 100 ppm in the following post-treatment solutions .13

1. Buffered distilled hot water at the rate of 3 min/μm.
2. 10 g/L $NiSO_4$bath at boiling point for 0.3 min/μm.
3. Hot sealing in the $NiSO_4$bath for 2.5 min/μm.

Mura has shown, using phosphoric acid/chromic acid dissolution tests, that the weight loss was lowest for samples sealed in bath 2 and, in the case of baths 1 and 3, the long sealing duration adversely affected the seal quality performance. Although the results are interesting, it must be mentioned that the beneficial effects of cold sealing would be outweighed if a long post-treatment was used. The question also arises that, if hot water sealing (bath 1) is to be used as a post-treatment for a short time (0.3 min/μm), would it produce a film less resistant to fluoride contamination than its counterpart, hot nickel sulfate post-treatment (bath 2)?. Also, assuming that the fluoride contamination occurs as a result of fluoride drag-out from the , pores of cold-sealed film during post-treatment, would the time required for this to happen be long enough if the film sealed at 0.3 rein/pm? If this were to happen, the authors would naturally recommend the addition of nickel sulfate in hot water.

Findings

From the results, it can be concluded that the future of cold sealing depends on better awareness of the process parameters that are crucial for successful sealing, on the way it is marketed, and more evidence of its application in aluminum finishing.

The application of dual sealing maybe necessary in a cold marine environment such as North Europe, but it is less relevant in most of Europe. The authors suggest that the degree of sealing should be established between the anodizer and the customer, in which the degree of sealing is suited to the environment to which the finished product is to be exposed. This can reduce the cost, save energy and increase efficiency.

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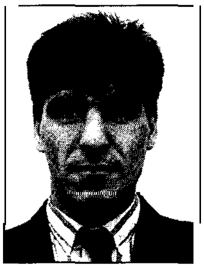
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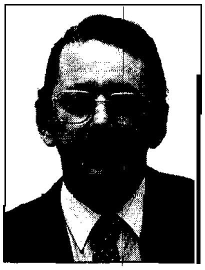
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