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Anodizing of aluminium and its alloys — Experimental research on possible alternative sealing quality test methods to replace the phosphoric acid/chromic acid immersion test — Evaluation of correlations

Anodisation de l'aluminium et ses alliages — Recherche expérimentale sur les méthodes alternatives possibles d'essai de qualité de colmatage pour remplacer l'essai d'immersion dans l'acide phosphochromique — Évaluation des corrélations

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Contents

Page

Foreword

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ISO/TR 16689 was prepared by Technical Committee ISO/TC 79, *Light metals and their alloys*, Subcommittee SC 2, *Organic and anodic oxidation coatings on aluminium*.

Introduction

The chromic/phosphoric acid solution (CPA) test is the main test used internationally to assess the quality of sealing of anodic oxidation coatings on aluminium. The method is described in ISO 3210[1], ASTM B680[2], EN 12373-6[3] and EN 12373-7[4]. ISO 7599[5] and EN 12373-1[6] designate it to be the referee test, as do the voluntary standards of Qualanod[7] and the AAMA (American Architectural Manufacturers' Association)[8].

The CPA test was originally proposed by two workers at Alcoa, J. H. Manhart and W. C. Cochran, in the early 1970s[9]. They compared it for hot-water sealing with various simple laboratory tests including other acid dissolution tests, some of which were in regular use at that time and were described in ISO 2932[10]. Since the adoption of the CPA test, practical experience has revealed that low-coating mass loss is an indication of good sealing quality and of the ability of the coating to resist staining and blooming in many types of service.

There is mounting concern in Europe over the use of this test because the test solution contains hexavalent chromium [Cr(VI)] which is a human carcinogen via inhalation. Chromic acid was included, 2010-12-15, in The European Chemicals Agency candidate list of substances of very high concern for authorization. Special authorization will have to be obtained for the use of such substances in every application.

In 2007 Qualanod initiated a study to identify potential alternative tests. It was decided to restrict this to acid dissolution tests because it was expected that they would behave in a manner most similar to the CPA test. A list of criteria was drawn up for alternative tests to be assessed against. These criteria included ones that would favour easy-to-use immersion tests. The technical literature was reviewed and a shortlist of tests produced.

The next stage was to carry out experimental work to determine whether the alternative tests were comparable to the CPA test for a range of sealing methods. Sapa Technology offered to undertake this project. Sapa found that neither of the acid immersion tests evaluated were suitable alternatives to the CPA test. This was because they responded very differently depending on the sealing method. It is believed that the response of any immersion test is dependent on the solution composition. Sapa also found that the admittance test was good at distinguishing sealing quality for all the sealing methods. However, admittance is a property of the whole of the anodized coating whereas the CPA test is surface-specific, providing a prediction of the likelihood of surface degradation during service.

This Technical Report contains an edited version of Sapa Technology technical report D09-0179[11].

It is believed that future investigations should focus on finding a test method that will enable the prediction of superficial, cosmetic degradation during exposure to the weather. This would not include the ability of an anodized coating to protect the aluminium from pitting corrosion, which can already be assessed using a salt spray test. Rather, it would assess the susceptibility to weathering effects such as staining, blooming, chalking, resmutting and iridescence.

Anodizing of aluminium and its alloys — Experimental research on possible alternative sealing quality test methods to replace the phosphoric acid/chromic acid immersion test — Evaluation of correlations

1 Scope

This Technical Report contains data from an evaluation of candidates to replace the chromic/phosphoric acid solution (CPA) test for the quality of sealing of anodic oxidation coatings on aluminium.

Following a review by Qualanod (see Working Group report in Annex A), it was agreed with Sapa Technology that the candidate tests for evaluation would be as follows:

— acetic acid/sodium acetate solution (AASA) test as described in ISO 2932[10], a method used in the 1970s;

— sulfuric acid solution (SA) test as described by Manhart and Cochran[9].

The evaluation consists of a comparison of the candidates with the CPA (EN 12373-6[3]), dye absorption (EN 12373-4[12]) and admittance tests (EN 12373-5[13]) using four different sealing methods:

— hot-water sealing;

— cold sealing;

— medium-temperature (midtemp) sealing using a nickel-containing solution;

— midtemp sealing using a nickel-free solution.

An immersion test based on the CPA test, but without the inclusion of chromic acid, was excluded due to the similarity with the SA test. The scope of the work to develop a new phosphoric acid method was considered too comprehensive for this project.

In general, the sealed coating (pores filled by hydration) loses mass and thickness linearly with dissolution time. Different sealing methods (or sealing conditions of time, temperature, pH, composition of sealing solution) result in different pore-filling material with differences in resistance to acid dissolution. When considering replacing the CPA test with an alternative acid dissolution test, there are some criteria for a new test. If possible, the response to the test should be similar for different sealing methods, i.e. it should be possible to use the same standard even if the sealing method is different. There should be a significant difference in the mass loss for a good and a bad sealing.

2 Literature research

2.1 General

A comprehensive survey of the methods of testing the sealing quality of anodic coatings was given by Manhart and Cochran[9] and by Kape[14] in the 1970s. A more recent survey was made in 1987 by Wernick and al.[15] where the main acid dissolution tests are:

— acidified sulfite test (Kape test);

— AASA test;

— CPA test.

These tests are explained below, see 2.2 to 2.4.

In Figure 1 is shown the correlation of several acid dissolution tests with sealing time for sulfuric acid coatings published by Manhart and Cochran[9]. Note that the curves generally exhibit the same shape with a difference in the absolute value of the mass loss. The thickness of the anodic oxide is about 25 µm (estimated from given anodizing conditions).

2.2 Acidified sulfite test (Kape test)

The test solution is a mixture of sodium sulfite, acetic acid and sulfuric acid at 90 °C to 92 °C and pH 2,5 such that sulfur dioxide is evolved but mainly retained in solution. Test solution: 1 000 ml deionized water to which have been added glacial acetic acid (20 ml/l to 40 ml/l) to give a pH of 3,6 to 3,8 followed by 5 N sulfuric acid (10 ml/l to 15vml/l) to give a pH of 2,5 at room temperature. A predip is made 10 min in 50 % by volume nitric acid at room temperature.

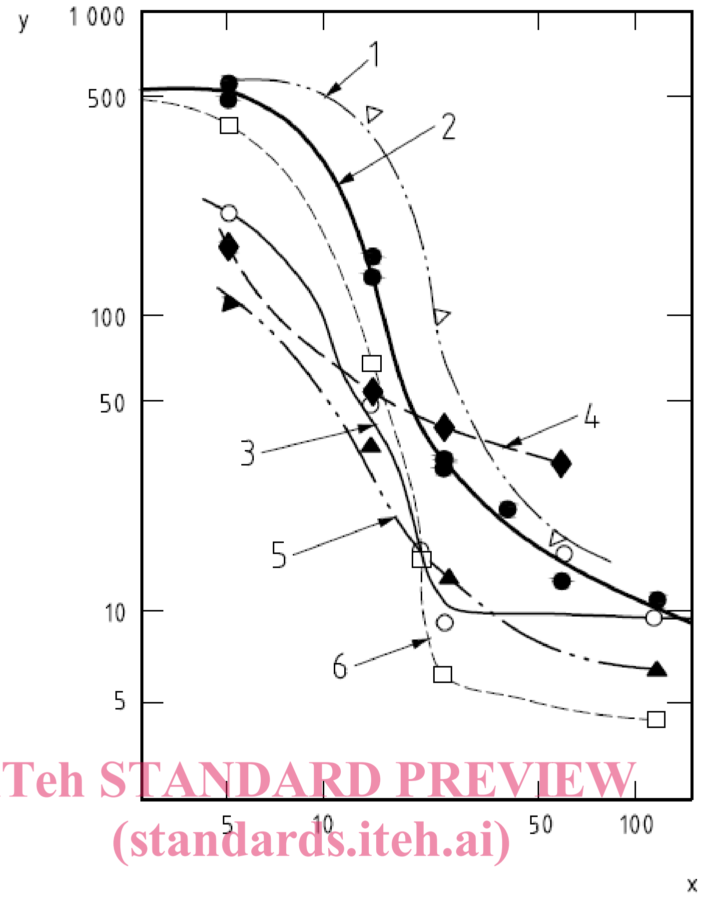
The mass of the sample is assessed before predip, after predip and after immersion in test solution. Immersion of the sample for 20 min. Note that care should be taken such that the solution temperature does not at any time exceed 92 °C or the sulfur dioxide dissolved in the solution will be boiled off.

For a coating of good quality the loss of mass between the first and second weighing is negligible (a significant difference indicates an excessively porous coating). Assessment of total mass loss is made using the mass loss between the second and third weighings. A maximum mass loss 20 mg/dm^2 is permitted[15] (not specified in the standard). The test is described in the standard ISO 2932[10] which was withdrawn in 1991.

2.3 Acetic acid/sodium acetate solution test

This sealing quality test was made according to standard ISO 2932[10]. The method was used in the 1970s but the standard was withdrawn in 1991 being replaced with the CPA test.

The test solution is a mixture of 100 ml/l acetic (glacial) acid, 0,5 g/l sodium acetate in deionized water at pH 2,3 to 2,5. Renewed solution after each test is recommended. Not more that 3 dm^2 surface area of immersed sample per litre of solution. Non-anodized areas are not taken into account when calculating the surface area since the solution only slightly attacks bare metal (not more than 0,05 mg/cm^2), unless the bare areas exceeds 5 % of the total surface area of the sample. During immersion, 15 min, the solution is maintained at boiling point. A maximum mass loss of 20 mg/dm^2 is permitted[15]. Furneaux and Wood pointed out that this test might be less suitable for other sealing methods than conventional hot sealing (e.g. nickel-based cold sealing)[16].



Key

y mass loss, expressed in mg/dm^2 (log scale)
x sealing time, expressed in minutes (log scale)
1 15 % H_2SO_4
2 2 % CrO_3–5 % H_3PO_4
3 acetic acid
4 6 % citric acid
5 acidified Na_2SO_3
6 20 % HNO_3

NOTE This figure is reproduced with permission from the National Association for Surface Finishing, 1155 15th St., NW, Suite 500, Washington, DC 20005 USA.

Figure 1 — Correlation of several acid dissolution tests with sealing time for sulfuric acid coatings[9]

2.4 Chromic/phosphoric acid solution test

This test was originally proposed by Manhart and Cochran in 1971[9] and was then adopted as the general referee mass loss test previously described by ISOv3210[1]. The sealing quality is evaluated with a mass loss test today according to EN 12373-6[3]. The mass loss test is destructive and frequently used as a complement to the dye spot test (EN 12373-4[12]). The better the sealing, the lower the mass loss in this test. The specifications on the mass loss vary depending on the application, even though for normal applications a mass loss of less then 30 mg/dm^2 is needed for approval according to Qualanod[7].

The test solution is a mixture of 2 % by mass chromic acid and 5 % by mass phosphoric acid, operated at 37,8 °C for 15 min [the same solution is used at higher temperature for determination of oxide density (EN 12373-2[17])].

Note the drying procedures associated with the weighing. Prior to weighing the sample is:

— degreased for 30 s in a suitable organic solvent (e.g. ethanol);

— left to dry 5 min in ambient atmosphere;

— placed in a drying oven pre-heated to 60 °C for 15 min;

— left to cool for 30 min over silica gel in a closed desiccator.

When this test is performed in a production line however the drying procedures are probably always simplified (i.e. no drying in oven and no cooling down in desiccator). This sealing test is sometimes combined with a 10 min predip in an aqueous solution containing (470 ± 15) g/l nitric acid (EN 12373-7[4]), specified according to Qualanod[7].

The test solution should not be used for more than 10 dm^2 surface area of immersed sample per litre of solution. The result is similar as with Kape and AASA tests but with greater mass losses (sulfuric acid anodized coatings)[14]. Some of the mentioned advantages[9] with the CPA test are the stability, convenient operating temperature, no attack of uncoated metal, a convenient test period and no unpleasant odour. Thickness loss and mass loss occur at the same rate.

2.5 Sulfuric acid solution test

This method is described by Manhart and Cochran[9]. The test solution contains sulfuric acid in deionized water at 48,9 °C. The immersion time is 20 min. It is written that bare metal surfaces should be protected since the test solution also dissolves the aluminium and that the test might need a nitric acid predip.

3 Materials and experimental

3.1 Anodizing

Anodizing trials were made in an in-house anodizing pilot plant at Sapa Technology in Finspång, Sweden. The process sequence was: degreasing, alkaline etching, desmutter, anodizing, sealing. Profile samples for anodizing were of alloy EN AW 6063 and temper T6. The anodized area was 1 dm^2 (100 mm x 50 mm x 3 mm). An electrolyte with 185 g/l sulfuric acid at 20 °C was used anodizing at a current density of 1,5 A/dm^2 and, if nothing else is stated, with a target thickness of (20 ± 1) µm which requires 42 min anodizing.

3.2 Sealing

Details about the sealing additives used and conditions used during tests are shown in Table 1. Cold sealing was always made in combination with a hot sealing (i.e. dual step sealing) being 10 min. Note that the test conditions on purpose go outside the recommended working conditions.

Table 1 — List of tested sealing additives with recommended working conditions and test conditions

Type of sealing	Product name	Manufacturer	Chemical	Working conditions			Test conditions		
				°C	pH	min/µm	°C	pH	min/µm
Hot	Almeco Seal SLX	Henkel	Anti-smut	97	5,8	3	90/97	5,2/5,8	1/2/3
Midtemp	Houghto seal A620	Houghton Chemicals	Nickel acetate	74–85	5,5–6,1	0,55	80	5.8	0,25/0,4/ 0,55/1/ 1,5/2
	Alfiseal 969	Alufinish	Mono- and dihexadecyl disulfonic diphenyloxide, disodium salt	86–90	5,8–6,1	3	88	6,0	1/2/3
Cold	PS41	Metachem	Nickel fluoride	28–32	5,8–6,4 (6,3)	0,8–1,2	20/25/ 30	5,5/5,8/ 6,0	0,5/0,75/ 1
NOTE The cold sealing step was followed by 10 min hot sealing at 96 °C.									

3.3 Measurements of sealing quality

3.3.1 Acid dissolution tests

These are mass loss tests that assess the resistance to dissolution by acid solutions.

3.3.1.1 CPA test

The sealing quality was evaluated with a mass loss test according to EN 12373-6:1998[3]. A mass loss of less than 30 mg/dm^2 is needed for approval according to Qualanod[7].

The test solution is a mixture of 2 % by mass chromic acid and 5 % by mass phosphoric acid, operated at 37,8 °C [the same solution is used at higher temperature for determination of oxide density (EN 12373-2[17])]. Note the drying procedures associated with the weighing. Prior to weighing the sample is:

— degreased for 30 s in a suitable organic solvent (e.g. ethanol);

— left to dry 5 min ambient atmosphere;

— placed in a drying oven pre-heated to 60 °C for 15 min;

— left to cool for 30 min over silica gel in a closed desiccator.

When this test is performed in a production line however the drying procedures are probably always simplified (i.e. no drying in oven and no cooling down in desiccator).

This sealing test is sometimes combined with a 10 min predip in an aqueous solution containing (470 ± 15) g/l nitric acid (EN 12373-7[4]), specified according to Qualanod[7].

The test solution should not be used for more than 10 dm^2 surface area of immersed sample per litre of solution. The mass loss of a bare aluminium substrate under test conditions was evaluated in 4.2.

3.3.1.2 AASA test

The test solution is a mixture of 100 ml acetic (glacial) acid, 0,5 g sodium acetate in deionized water (total volume 1 000 ml) pH 2,3 to pH 2,5. During immersion, 15 min, the solution is maintained at boiling point. After the test the sample is rinsed in deionized water, dried and reweighed. A maximum mass loss of 20 mg/dm^2 is permitted[15].

Renewed solution after each test is recommended. Not more that 3 dm^2 surface area of immersed sample per litre of solution. Not anodized areas are not taken into account when calculating the surface area since the solution only slightly attacks bare metal (not more than 0,05 mg/cm^2 (5 mg/dm^2) according to the standard) unless the bare areas exceed 5 % of the total surface area of the sample. The mass loss of a bare aluminium substrate under test conditions was evaluated in 4.2.

3.3.1.3 SA test

The test solution described contains 15 % sulfuric in deionized water at 48,9 °C[1]. For simplicity the temperature of the test solution in the trials made in this project was kept at 50 °C. The immersion time is 20 min[9].

It is written that bare metal surfaces should be protected since the test solution also dissolves the aluminium and that the test might need a nitric acid predip[9]. The mass loss of a bare aluminium substrate under test conditions in the sulfuric acid test was evaluated in 4.2.

3.3.2 Admittance test

The sealing quality was also evaluated using the admittance test according to EN 12373-5[13]. The instrument used for the admittance measurements was an Anotest YD from Fischer (ring diameter 13 mm). Measurements were performed (if nothing else is mentioned) approximately 24 h after sealing and (according to the standard) the measuring probe was left in the electrolyte 2 min before reading the result. Approved value for an oxide thickness of 20 µm is approximately 20 µS. Values above this value are not approved.

Unlike the dye spot test and the mass loss test the admittance measurement takes into account the total oxide film thickness such that it is sensitive to the sealing of the pores (pore filling) in the bulk.

Note that, depending on sealing additive used, different results might be achieved (i.e. the sealing additive might influence the results obtained). The use of admittance measurements where cold (nickel fluoride) sealings have been used is not recommended according to Qualanod[7]. The presence of heavy metals (like nickel) in the oxide might increase the conductivity and therefore the admittance of the oxide. Nevertheless, in the datasheets for Alfiseal 985 (nickel fluoride cold sealing from Alufinish) impedance is however mentioned as one method to control the sealing quality (earliest 15 h after sealing).

The test is simple, fast (2 min) and in principle non-destructive (contact to the base metal is made with a screw preferably in one end of the profile).

Some admittance measurements were taken from a previous work reported in D07-0223[18].

3.3.3 Dye spot test

The samples were evaluated with a dye spot test according to EN 12373-4. Rating 0 to 2 is accepted and 3 to 5 not accepted according to Qualanod (rating 0 is good quality; rating 5 is poor sealing quality)[7].

