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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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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.

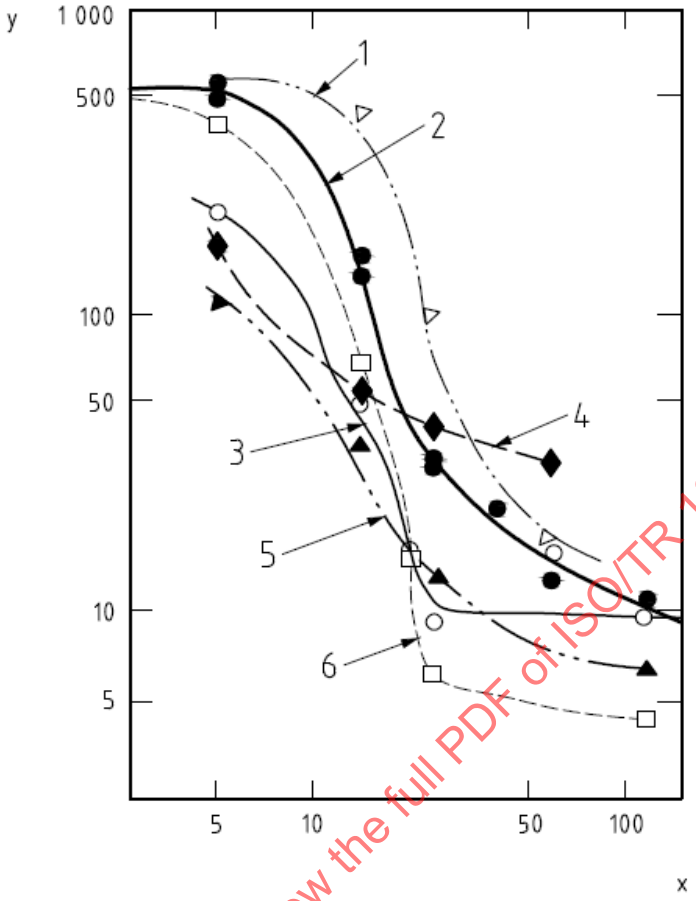
The mass of the sample is assessed before predip, after predip and after immersion in test solution. Immersion of the sample for 20 min. Note that care should be taken such that the solution temperature does not at any time exceed 92 °C or the sulfur dioxide dissolved in the solution will be boiled off.

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].

4 Results

4.1 Masking of cut surfaces

In Annex A is shown the report of the Working Group (Qualanod) on the replacement for the CPA test for sealing quality. In the conclusions of this report are given three possible candidates to replace the CPA test: the AASA test; the SA test; a phosphoric acid test (similar to CPA test but without the chromic acid).

The SA and phosphoric acid tests suffer the disadvantage that those acids attack bare aluminium. Because of this a means of protecting the cut edges of test coupons would have to be developed.

Initial trials were made where masking of the cut surfaces were made using nail polish. The nail polish was applied on cut surfaces after the initial weighing and removed using acetone (masked surfaces) followed by ethanol (full sample) before the second weighing. The preliminary results show that this could be a possible method to use. It is important however that the cut surfaces are smooth enough to facilitate the removal of the nail polish after performed test. More tests are needed however. For reasons described in 4.2 below the work with developing a masking method was not completed.

4.2 Bare aluminium and dissolution in the dissolution tests

When investigating the mass loss of a bare aluminium substrate under test conditions in the different acid dissolution tests the mass loss turned out to be very low, see Table 2, within the region of the accuracy of the measurement (the result from the CPA test is even negative). The total mass loss on a sample where the cut surface (bare aluminium surface) corresponds to 2 %, 5 % and 10 % of the total sample surface respectively was estimated to be less then 0,3 mg/dm^2. This is very low and we concluded that a masking method was not needed in cases where the bare aluminium surface is less than 5 % (the same criteria as for the AASA test).

Table 2 — Measured mass loss on a bare aluminium substrate

Dissolution test	Sample area (dm^2)	Mass loss (mg/dm^2)	Calculated mass losses for different percentages of bare aluminium (mg/dm^2)		
			2%	5%	10%
CPA	1,1	-2,3	-	-	-
AASA	1,1	2,5	0,05	0,12	0,25
SA	1,1	1,3	0,03	0,06	0,13

4.3 Hot sealing

4.3.1 Mass loss

In Table 3 the recommended working conditions in production and the sealing solution conditions during test are shown. Note that the test conditions on purpose go outside the recommended working conditions.

Figures 2 to 6 shows the mass loss on samples sealed with hot sealing (at pH 5,8 and at 97 °C if nothing else is stated). Figure 3 shows the mass loss response in the CPA test when compared with the mass loss in the sulfuric acid test; note different y-axes. Note the difference in response to the lowered sealing temperature (90 °C, 2 min/µm). Figure 4 shows the mass loss response in the CPA test when compared with the mass loss in the AASA test; note different y-axes. The response is similar even though the absolute value of the mass loss is lower for the AASA test. However, the AASA test generates mass losses with a larger variation for similar sealed samples (for example, compare the two sealed for 1 min/µm). In Figures 5 to 6 are shown also the data presented by Manhart and Cochran[9] as well as measured mass losses from samples from a production plant.

The mass loss in the AASA test is very flat in the relevant sealing time interval, such that it would be difficult to separate a good sealing from a bad, see Figures 5 to 6. The test results are easily within the maximum permitted mass loss 20 mg/dm^2 in spite of the poor sealing conditions. This is valid also for the CPA test, i.e. the test results are easily within the maximum permitted mass loss 30 mg/dm^2. The most significant difference in the mass loss with sealing time is seen for the SA test. Also included is the average mass loss of two samples from a production plant, which were measured about one week after production.

Table 3 — Recommended working and test conditions

Type of sealing	Product name	Manufacturer	Concentration (g/l)	Working conditions			Test conditions		
				°C	pH	min/µm	°C	pH	min/µm
Hot	Almeco Seal SLX	Henkel	2	97	5,8	3	90/97	5,2/5,8	1/2/3

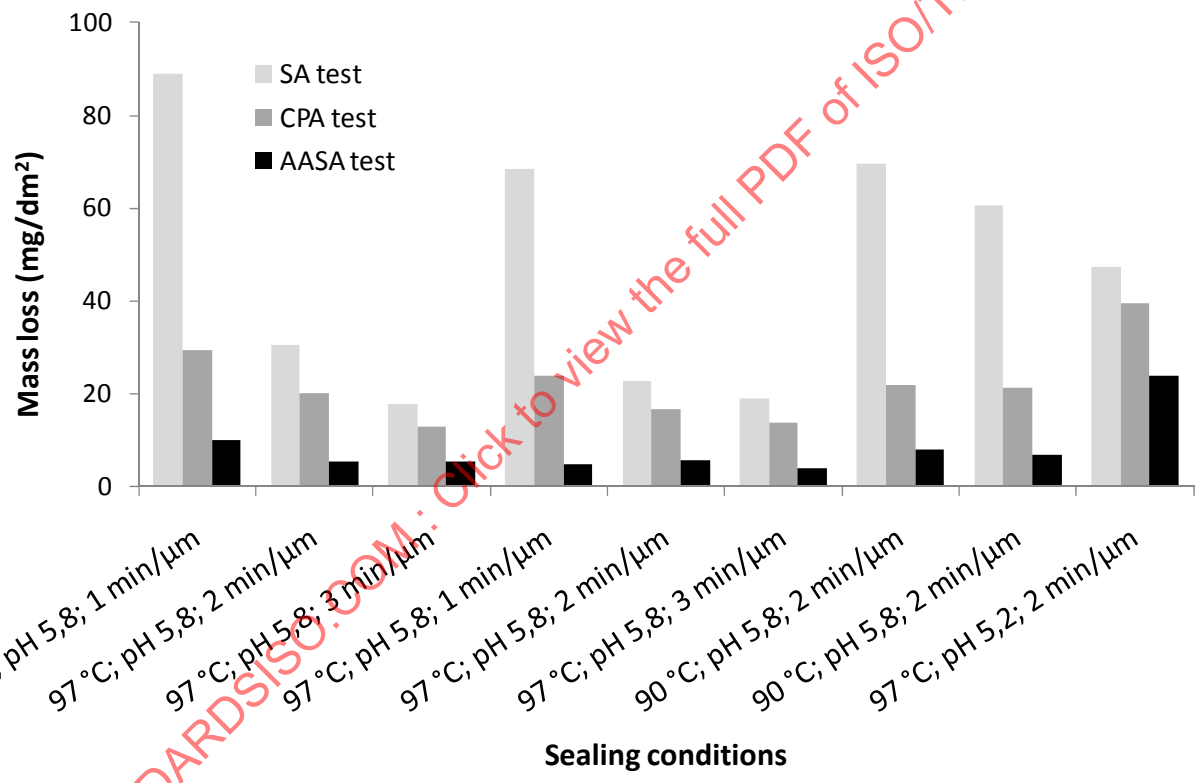


Figure 2 — Mass loss for 20 µm thick oxides sealed with hot sealing

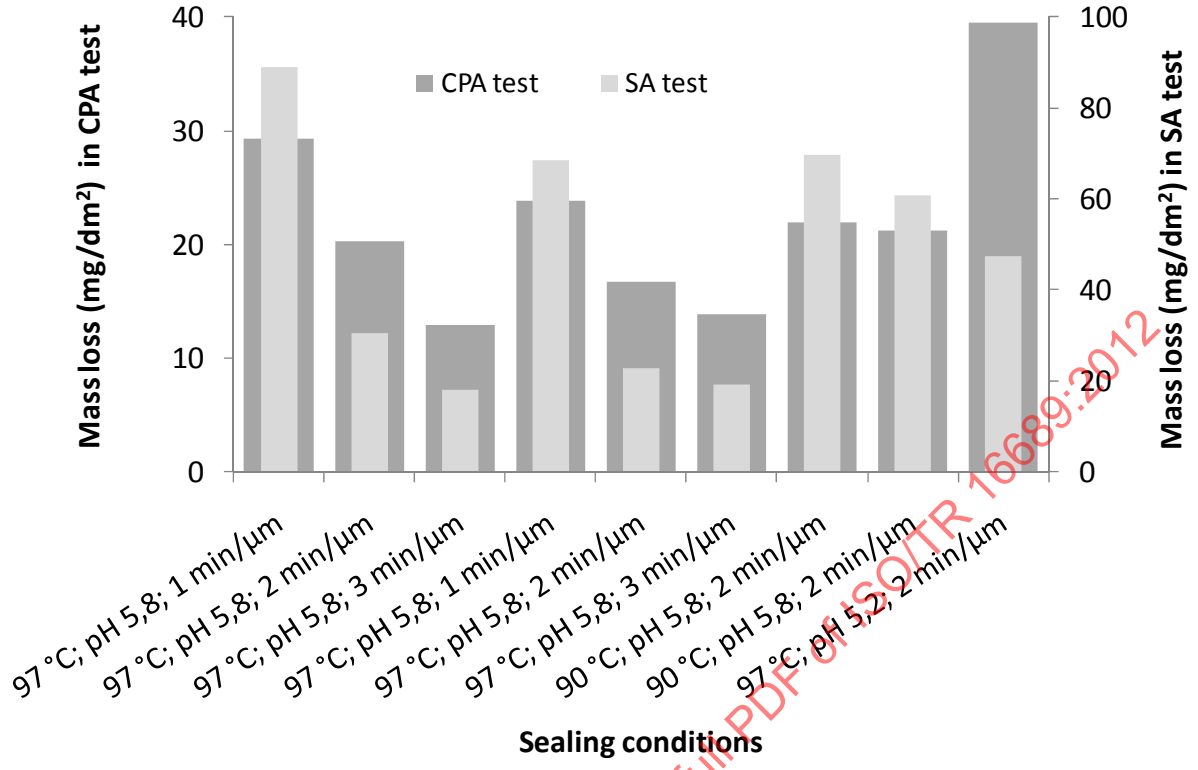


Figure 3 — Relative comparison of the mass loss for 20 µm thick oxides sealed with hot sealing using the CPA and SA tests

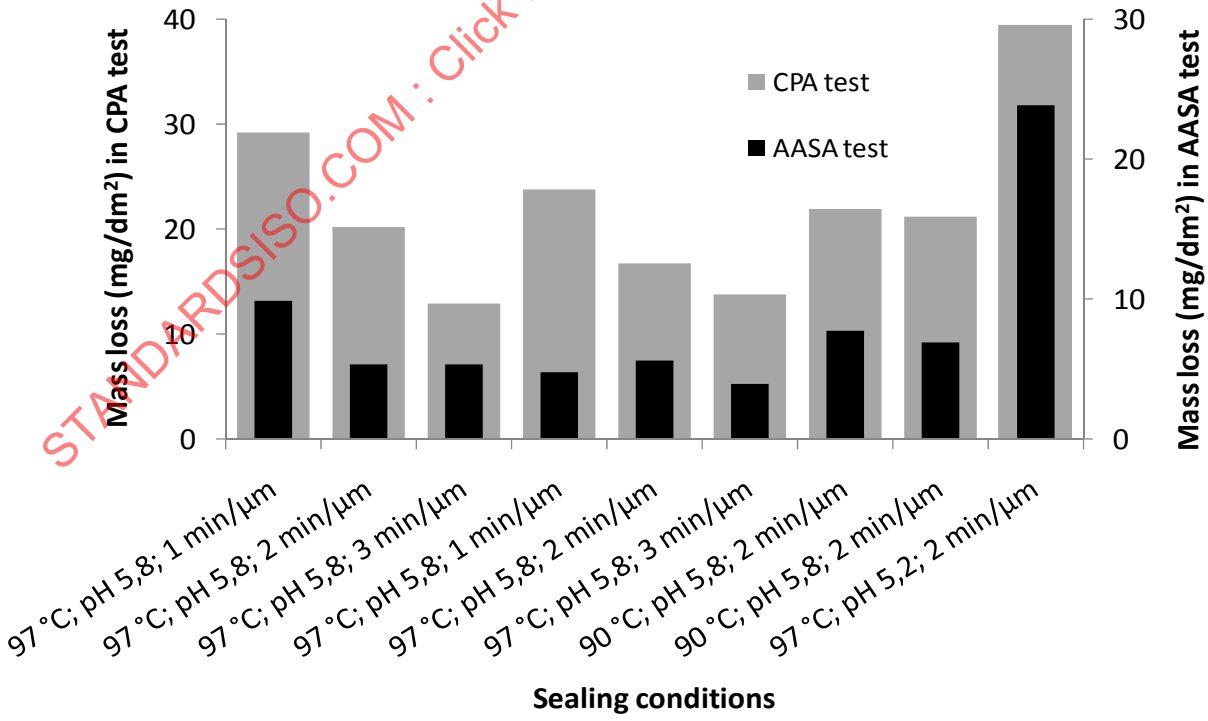


Figure 4 — Relative comparison of the mass loss for 20 µm thick oxides sealed with hot sealing using the CPA and AASA tests

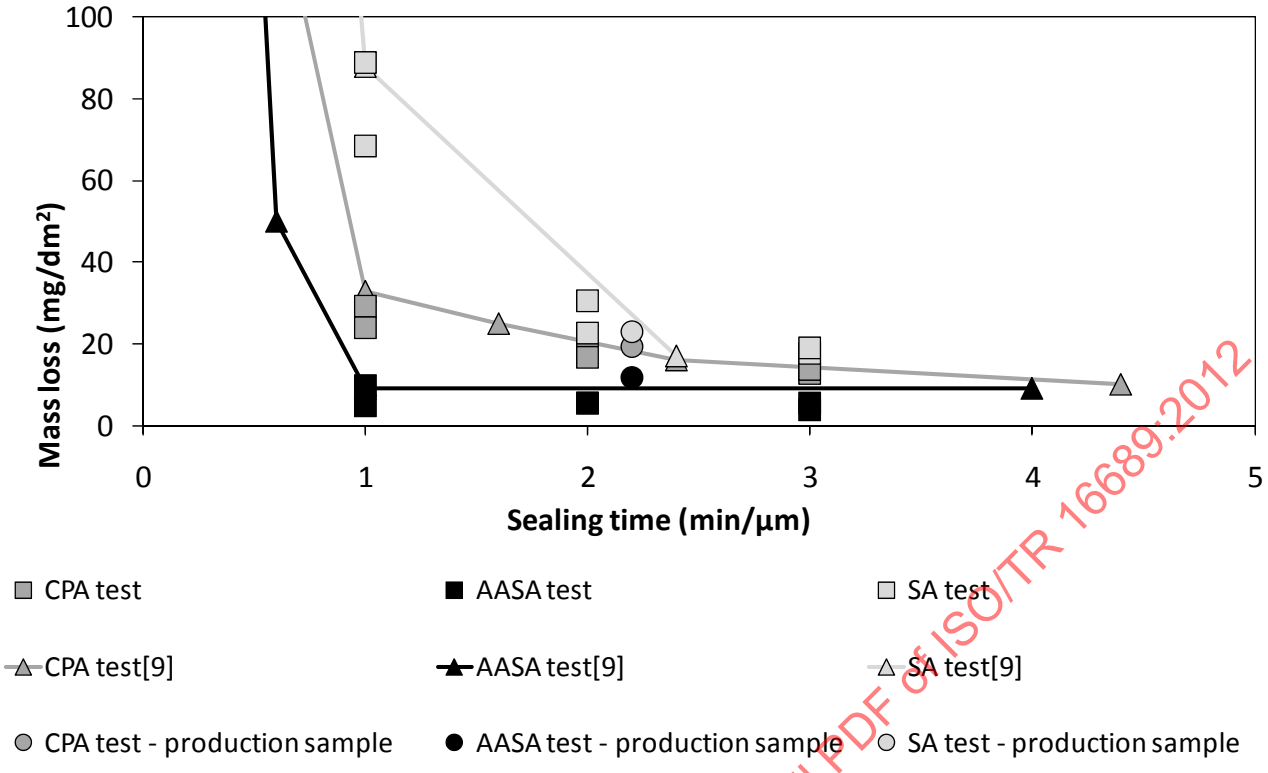


Figure 5 — Comparison of the mass loss for 20 µm thick oxides sealed with hot sealing

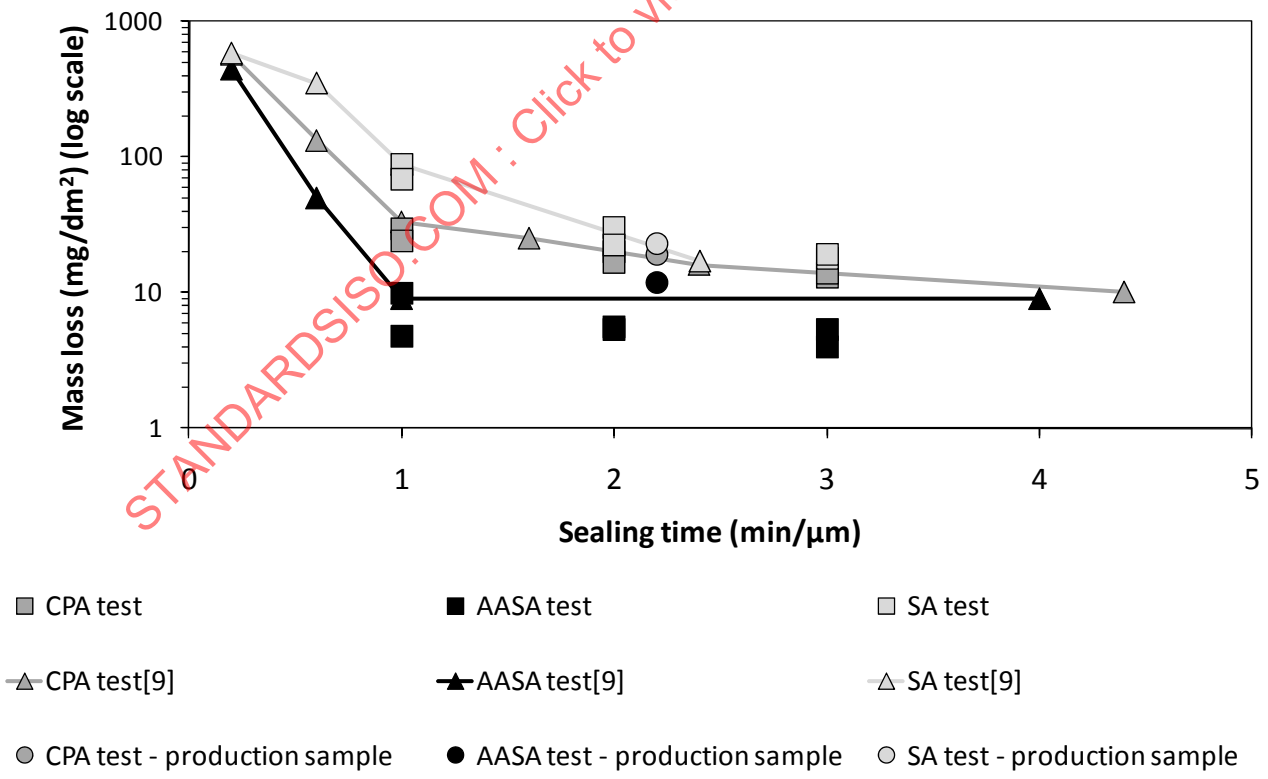


Figure 6 — Comparison of the mass loss for 20 µm thick oxides sealed with hot sealing (log scale)

4.3.2 Admittance

Figures 7 to 10 show the CPA test mass loss and the admittance as a function of sealing temperature of the hot sealing bath, oxide thickness 10 and 20 µm respectively and a sealing time of 2,5 min/µm. These data were taken from a previous investigation[18]. Approved value for the mass loss is 30 mg/dm^2. Approved admittance values for oxide thicknesses of 10 µm and 20 µm are approximately 40 µS and. 20 µS respectively.

Both the mass loss and the admittance respond well to an increased sealing bath temperature. The difference between the two methods (mass loss and admittance are that while the CPA test gives an approval already at a sealing temperature of 88 °C (10 µm oxide, see Figure 7) or 85 °C (20 µm oxide, Figure 9), the admittance gives an approval only at a sealing bath temperature of 97 °C (see Figure 8 and Figure 10).

A production sample sealed at 97 °C gave an admittance value of 16 µS.

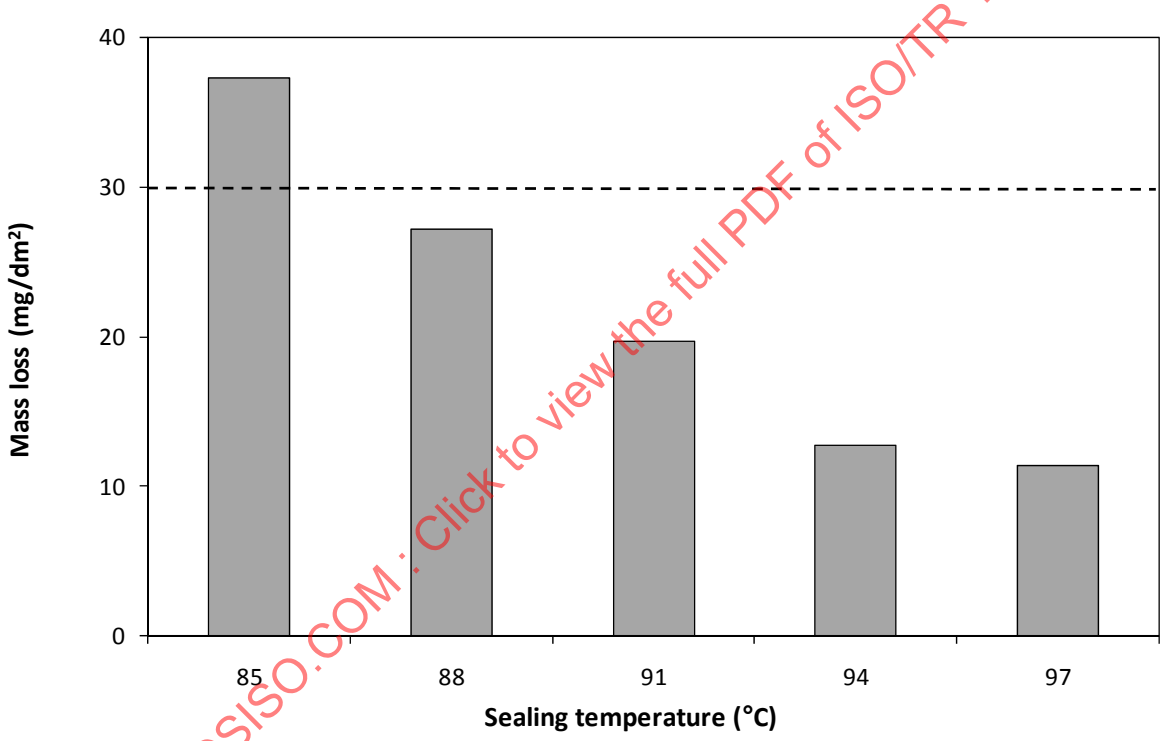


Figure 7 — CPA test mass loss of 10 µm thick oxides sealed with hot sealing at different temperatures

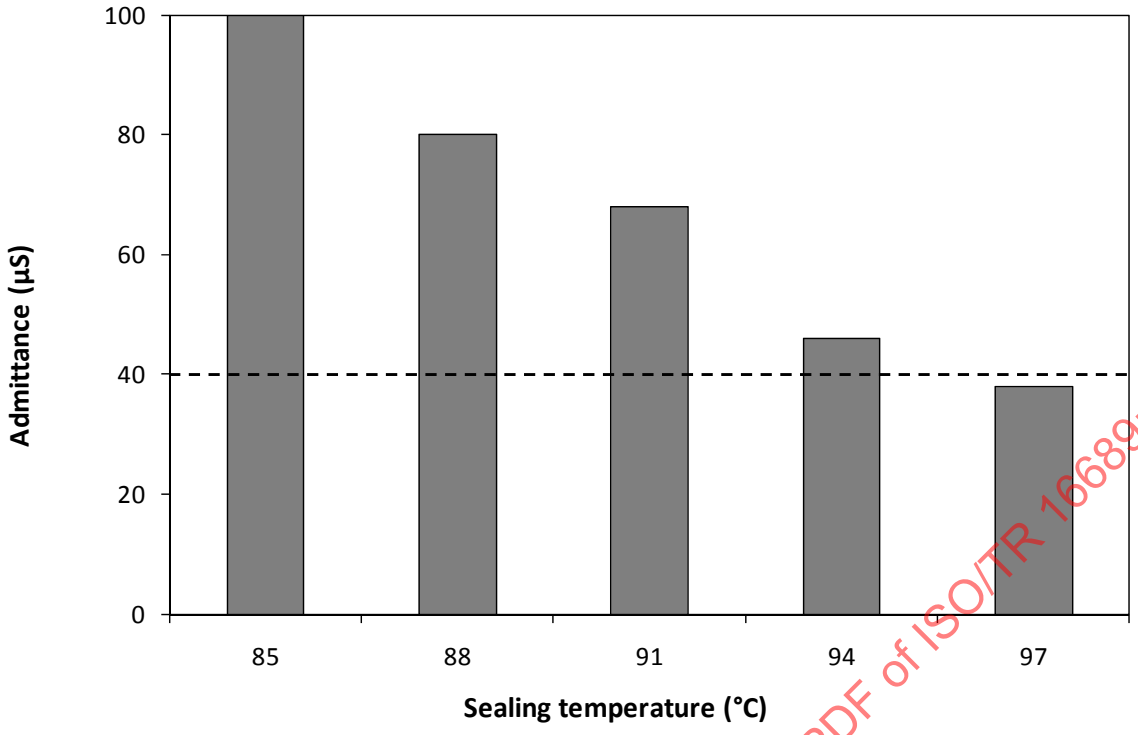


Figure 8 — Admittance of 10 µm thick coatings sealed with hot sealing at different temperatures

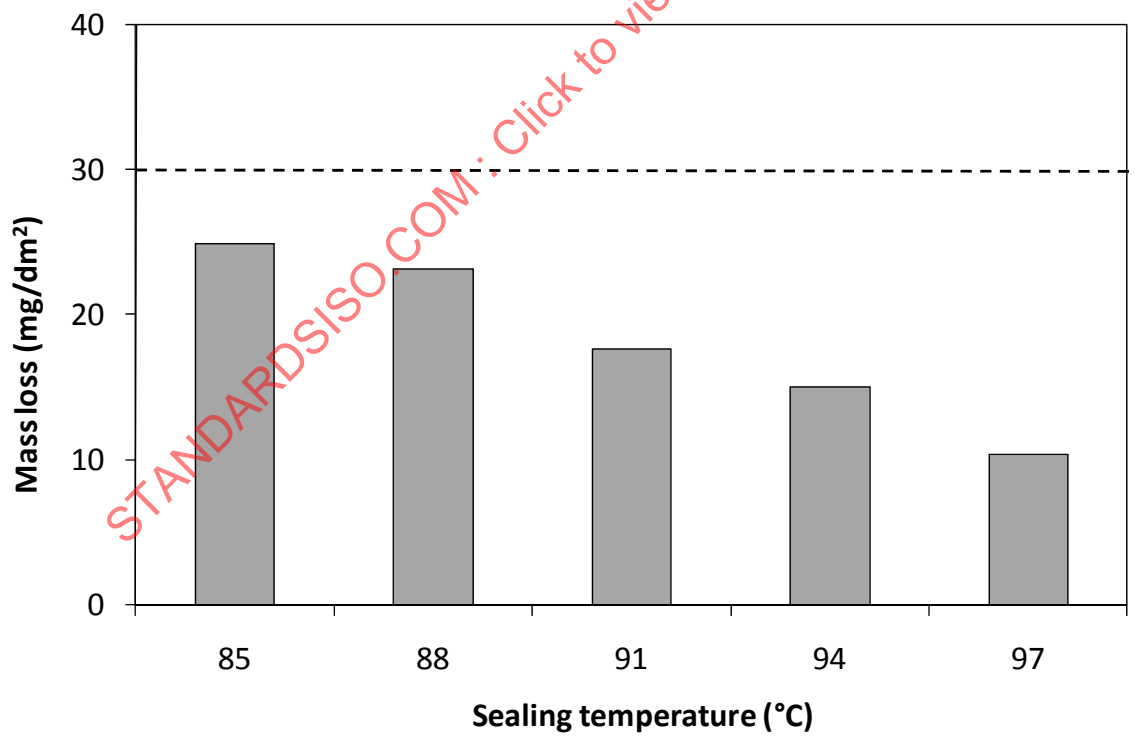


Figure 9 — CPA test mass loss of 20 µm thick oxides sealed with hot sealing at different temperatures

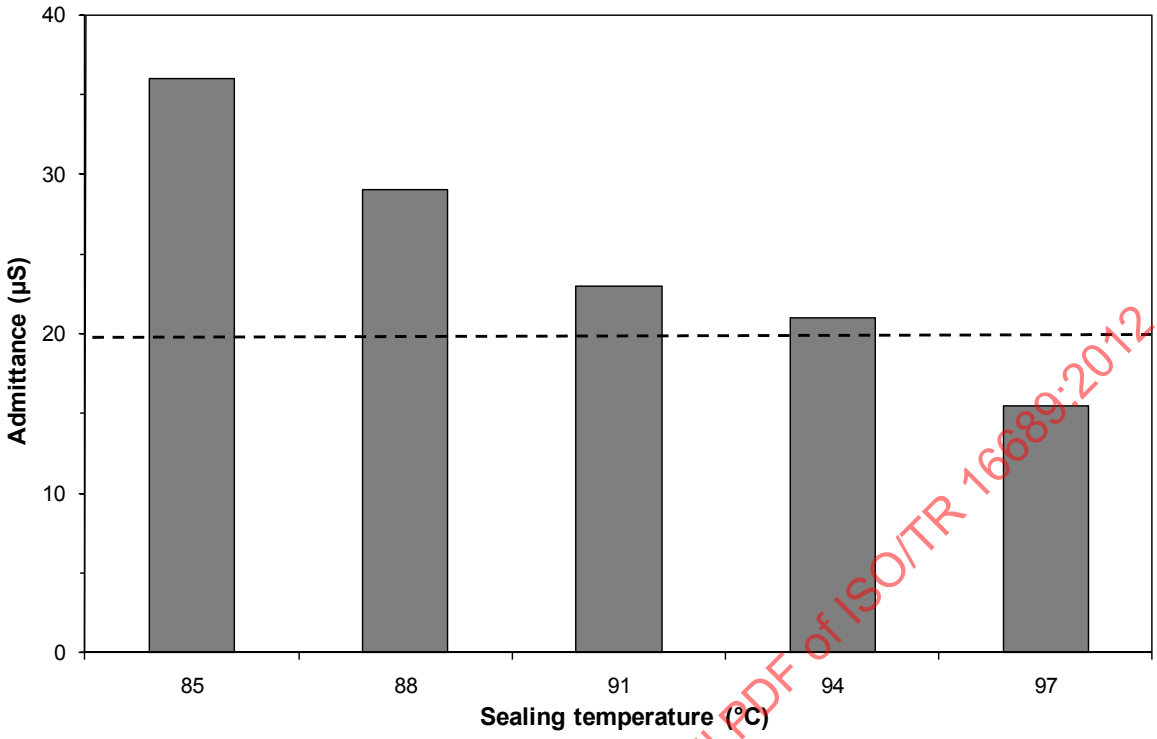


Figure 10 — Admittance of 20 µm thick coatings sealed with hot sealing at different temperatures

4.4 Cold sealing (two step)

4.4.1 Mass loss

In Table 4 the recommended working conditions in production and the sealing solution conditions during test are shown. Note that the test conditions on purpose go outside the recommended working conditions.

Table 4 — Recommended working and test conditions

Type of sealing	Product name	Manufacturer	Chemical	Working conditions			Test conditions		
				°C	pH	min/µm	°C	pH	min/µm
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									

Figures 11 to 15 shows the mass loss of the cold sealed samples. Figure 14 shows a relative comparison of the mass loss for the CPA and AASA tests (at a cold sealing pH of 6,0 if nothing else stated). The response to the different sealing times and different sealing solution parameters is very similar.

In Figure 15 a relative comparison of the mass loss for the CPA and SA tests is shown (at pH 6,0 if nothing else stated). The response for the sulfuric acid test is rather limited.

The test results are easily within the maximum permitted mass loss 30 mg/dm^2 (for the CPA test) and 20 mg/dm^2 (for the AASA test), in spite of the poor sealing conditions.

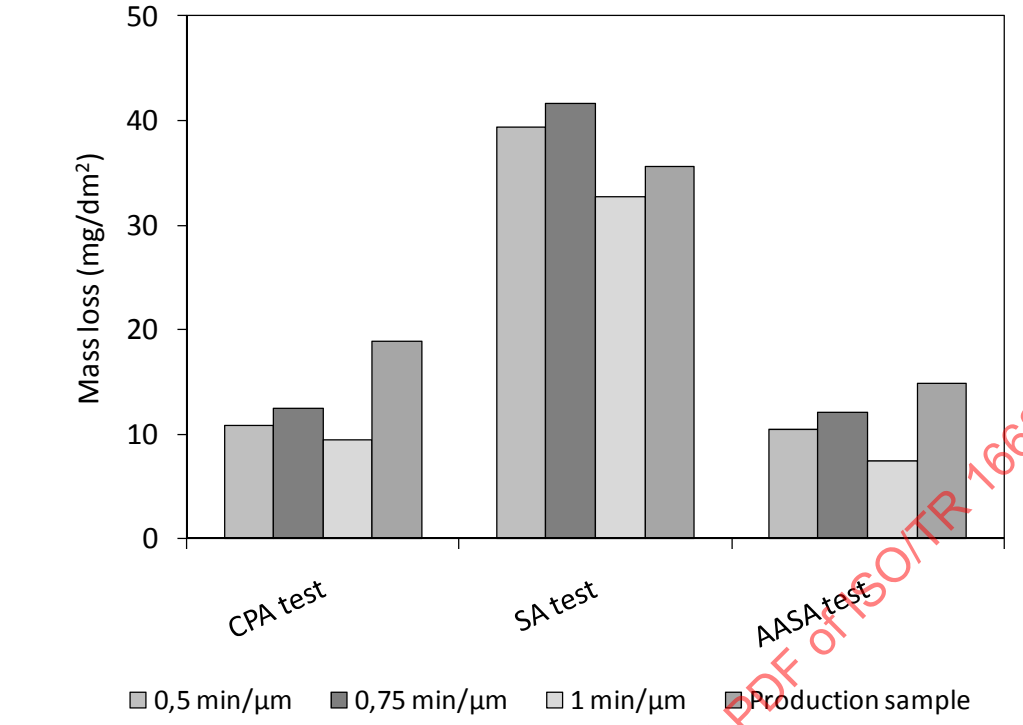


Figure 11 — Comparison of the mass loss for cold sealing at 30 °C and pH 6,0 with different times

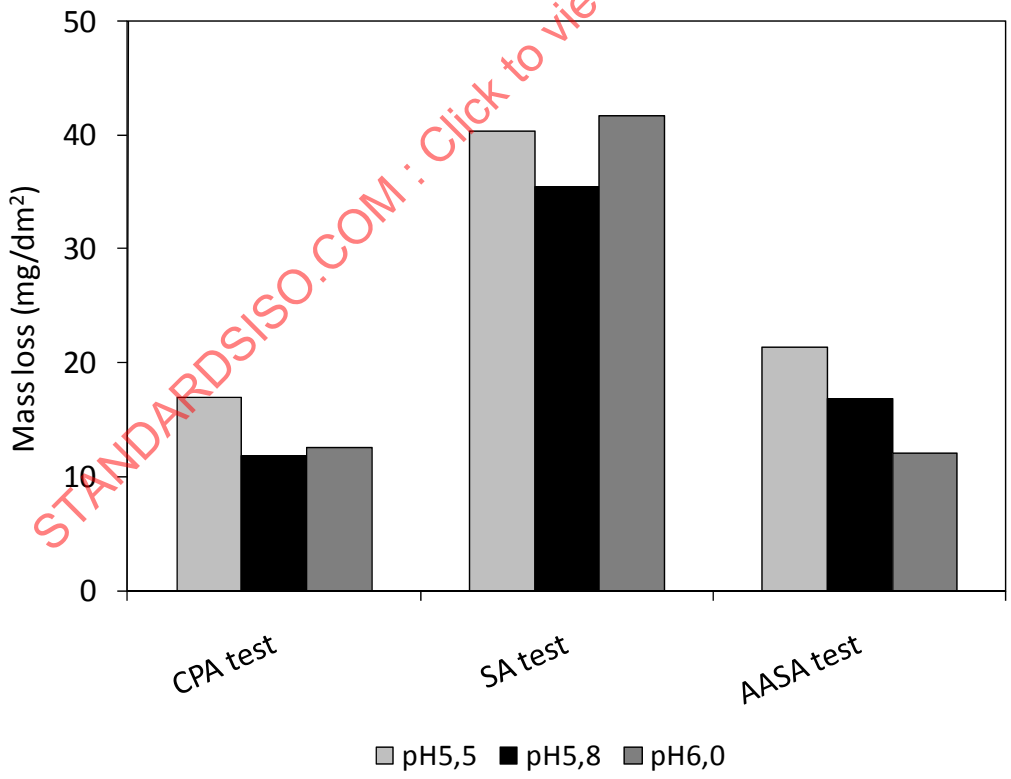


Figure 12 — Comparison of the mass loss for cold sealing at 30 °C and for 0,75 min/µm with different pH values

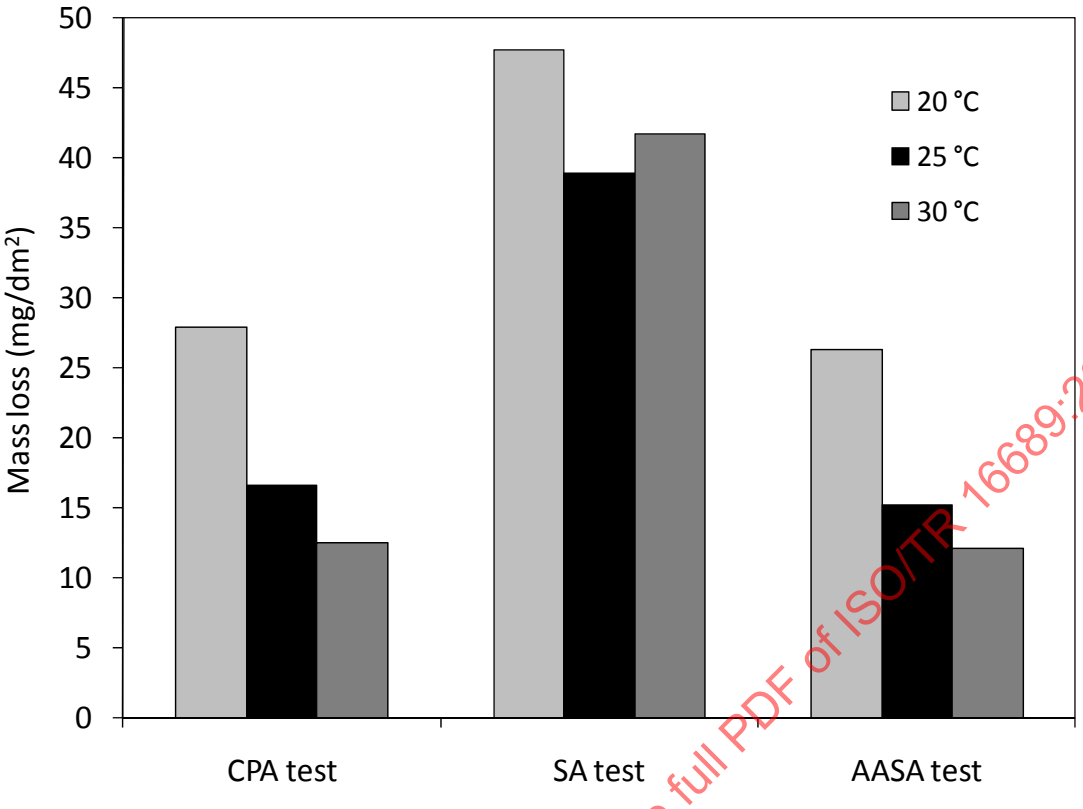


Figure 13 — Comparison of the mass loss for cold sealing at pH 6,0 and for 0,75 min/µm with different temperatures

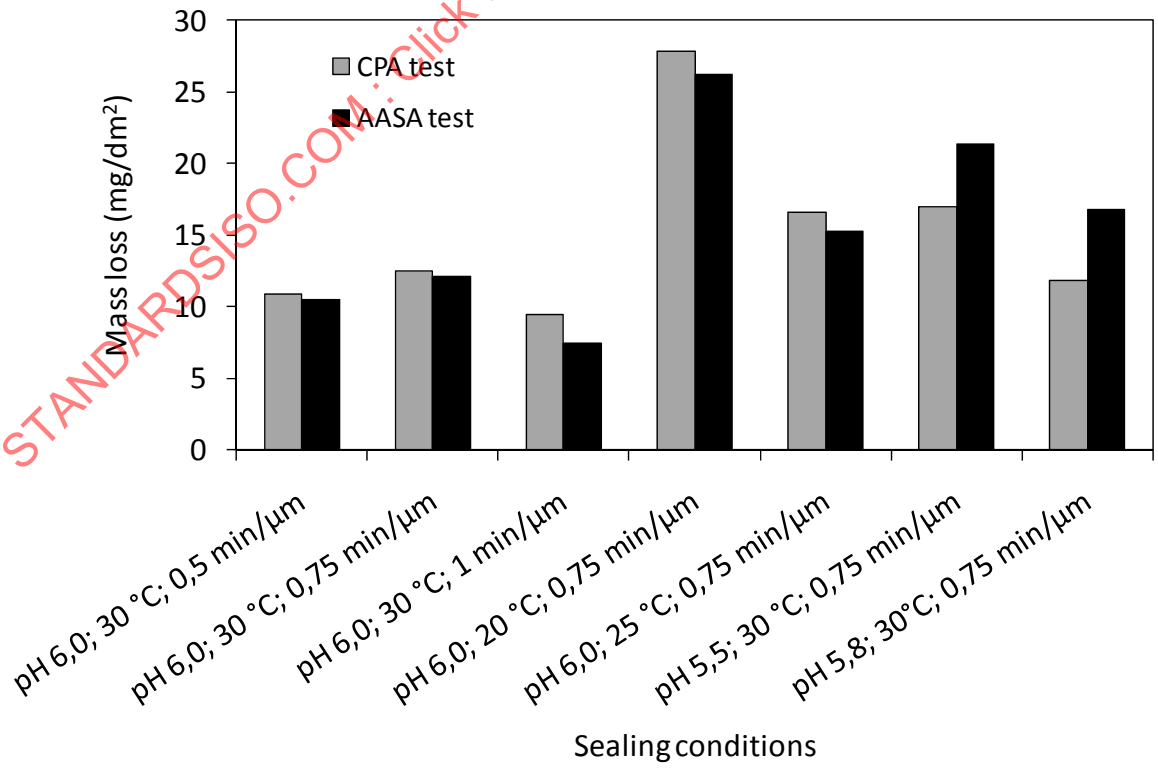


Figure 14 — Comparison of the mass loss for cold sealing under various conditions

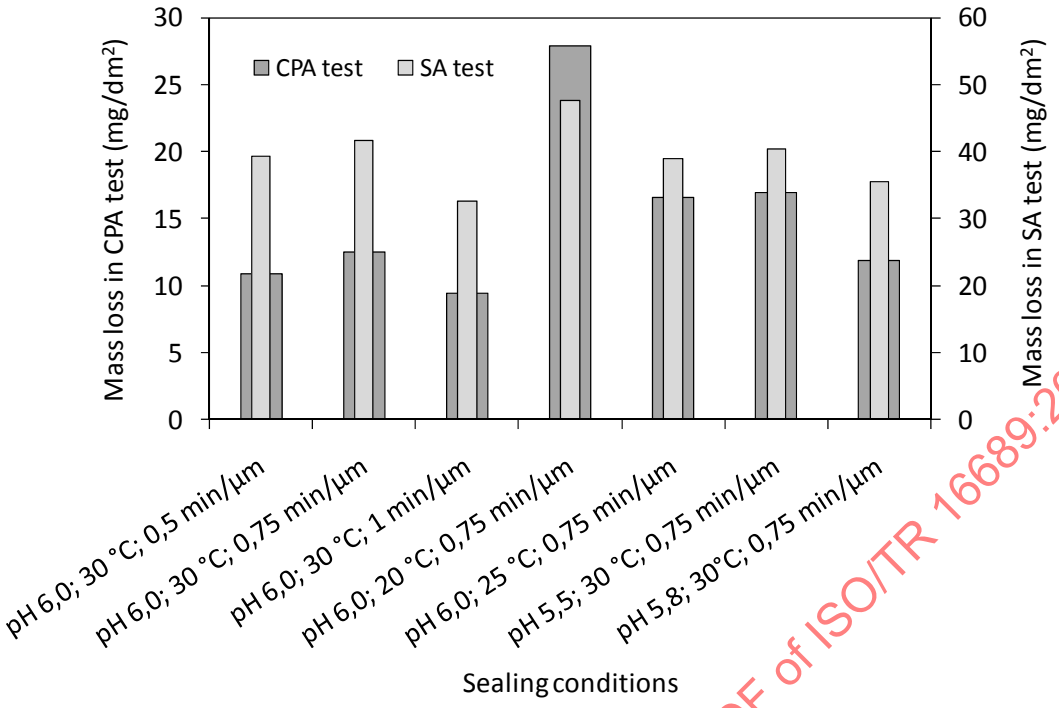


Figure 15 — Relative comparison of the mass loss for the CPA test and the sulfuric acid test

4.4.2 Admittance and dye spot

Table 5 shows the admittance and the dye spot test result of the nickel-based cold-sealed samples. Since the cold sealing solution was freshly made up, it turned out that the pH was very sensitive to the sealing process such that the pH increased after a limited amount of sealed material (a few square decimetres per litre solution). In the second series the pH was kept under strict control.

The admittance limit value for 20 µm oxides is 20 µS. The admittance and dye spot tests on the production sample were carried out 2 weeks after production. The coating thickness was 26 µm so the admittance limit value was 15,4 µS.

The admittance is strongly depending on the time that has elapsed since the sealing (compare one day and one week after sealing).

Table 5 — Admittance and dye spot result on the nickel-based cold-sealed (dual step) samples

	Temperature (°C)	pH	Sealing time (min/µm)	Admittance (µS)		Dye spot test rating after 1 day
				after 1 day	after 1 week	
1st series	30	6,0	0,5	22	11	1
	30	6,0	0,75	30	13	1
	30	6,0	1	18	10	0–1
	20	6,0	0,75	16,5	8,8	1
	25	6,0	0,75	20	10,2	0–1
	30	5,5	0,75	21	14,5	1
	30	5,8	0,75	22	11,5	1
2nd series	30	6,0	0,5	17	9,5	1
	30	6,0	0,75	16	10	1
	30	6,0	1	18	11	1
Production sample	30	6,0	1	-	8	0

4.5 Nickel-based medium temperature sealing

4.5.1 Mass loss

In Table 6 the recommended working conditions in production and the sealing solution conditions during test are shown. The recommended sealing times are 7, 11 and 15 min for coatings 10, 20 and 30 µm thick respectively. Note that the test conditions (sealing time) on purpose go outside the recommended working conditions.

Table 6 — 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
Midtemp	Houghto-seal A620	Houghton Chemicals	Nickel acetate	74–85	5,5–6,1	0,5–0,7	80	5,8	0,25–2

In Figures 16 to 19, the mass losses in the three tests are shown. Note that the mass loss trend differs significantly for the three tests. The recommended sealing times for 20 µm and 30 µm thick coatings are 0,55 min/µm and 0,5 min/µm respectively.

The tests were also run on a sample taken from production where a sealing time of 0,3 min/µm was used. The oxide thicknesses were higher on the samples from production being 30 µm as compared to 20 µm on the samples anodized at the pilot line at Sapa Technology.

The data in Figure 17 indicate that the CPA test acceptance criterion is achieved by a sealing time greater than 0,6 min/µm.

Concerning Figure 18, the coating thickness after the test indicated that almost all the coating was removed in the test. A mass loss of 500 mg/dm^2 for a removal of a 20 µm coating corresponds to a coating density of 2,5 g/cm^3.

Note that Figure 19 records a mass gain (negative mass loss) in the AASA test.

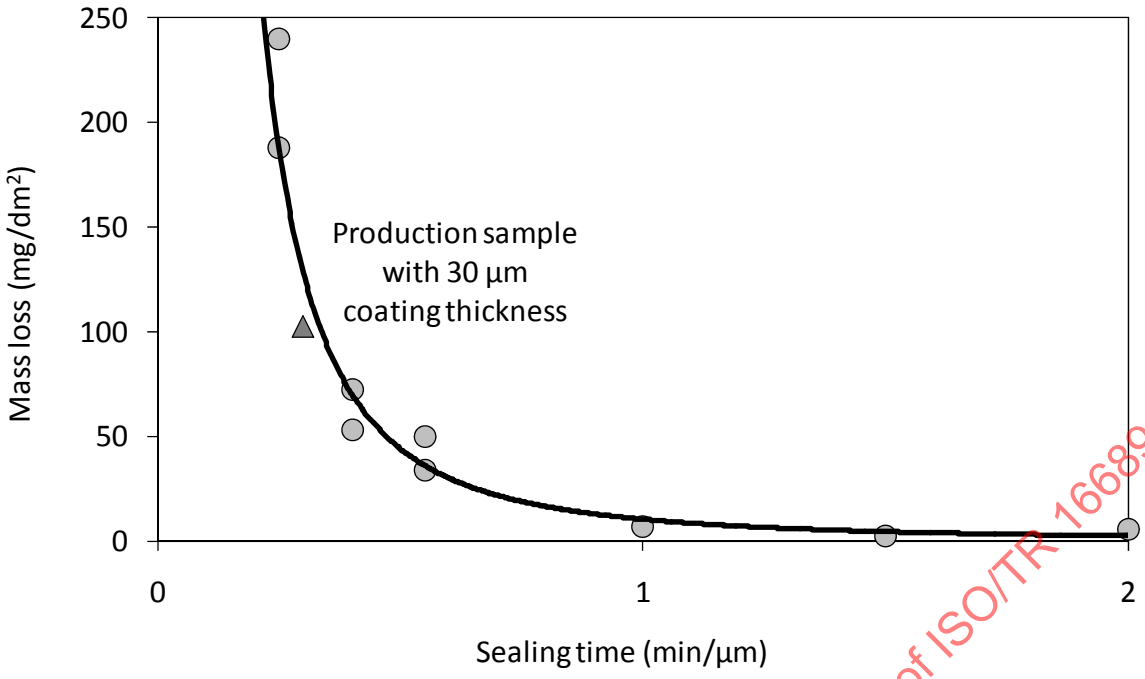


Figure 16 — Mass loss in the CPA test for samples with 20 µm thick coatings sealed using the nickel-based midtemp seal

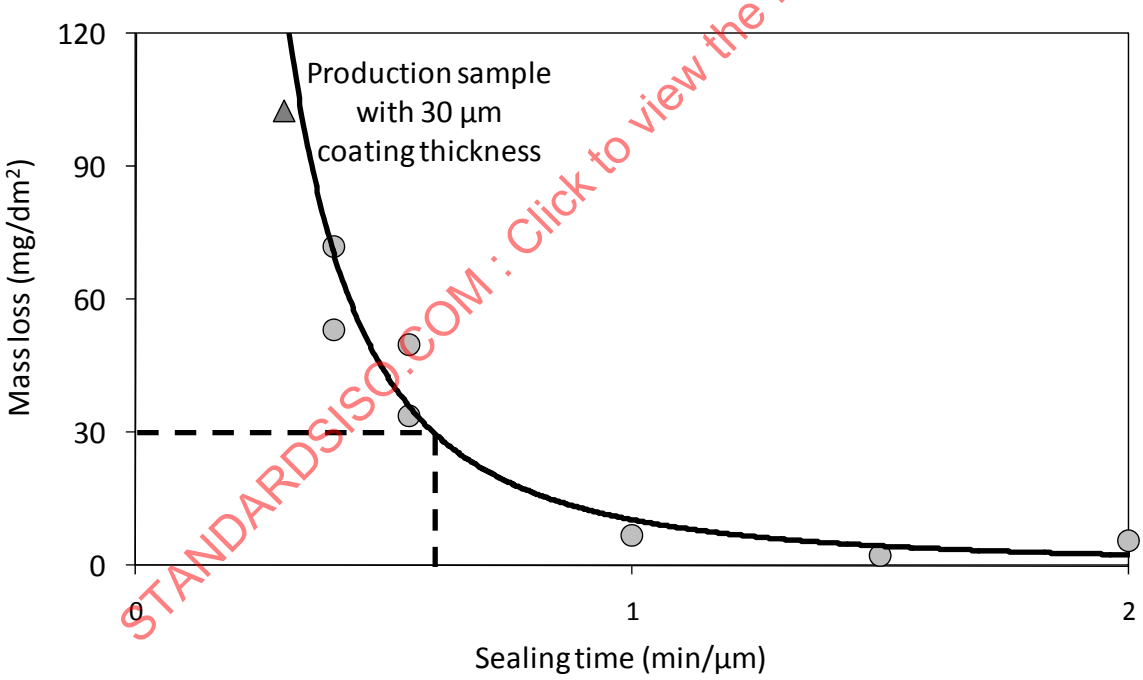


Figure 17 — Mass loss in the CPA test for samples with 20 µm thick coatings sealed using the nickel-based midtemp seal

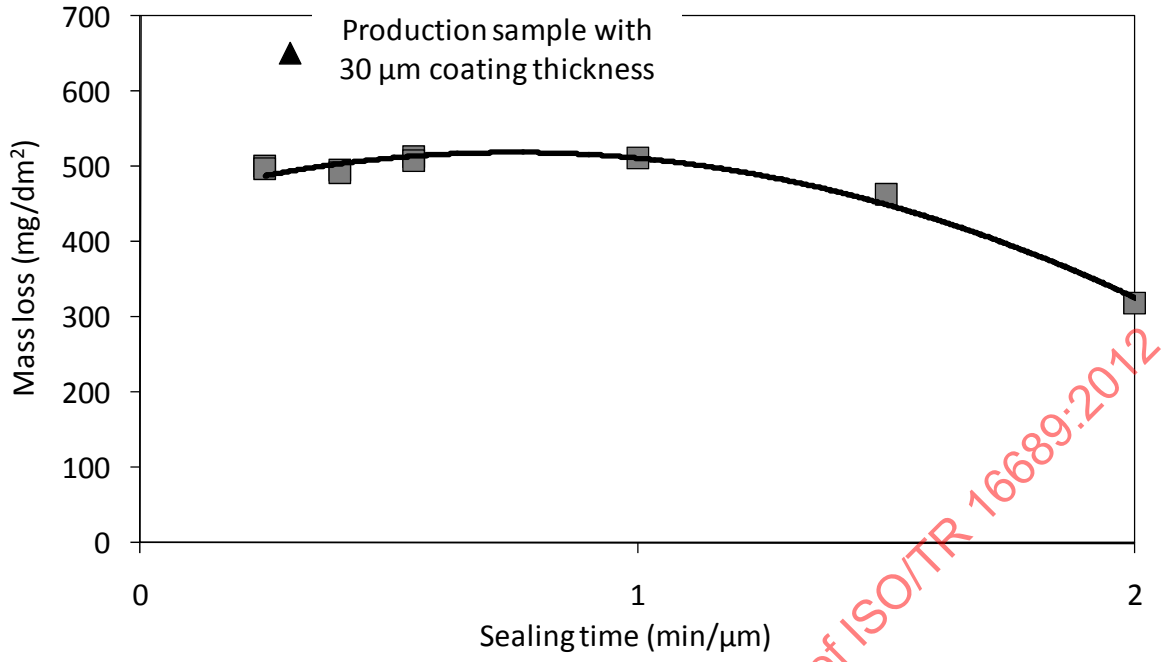


Figure 18 — Mass loss in the SA test for samples with 20 µm thick coatings sealed using the nickel-based midtemp seal.

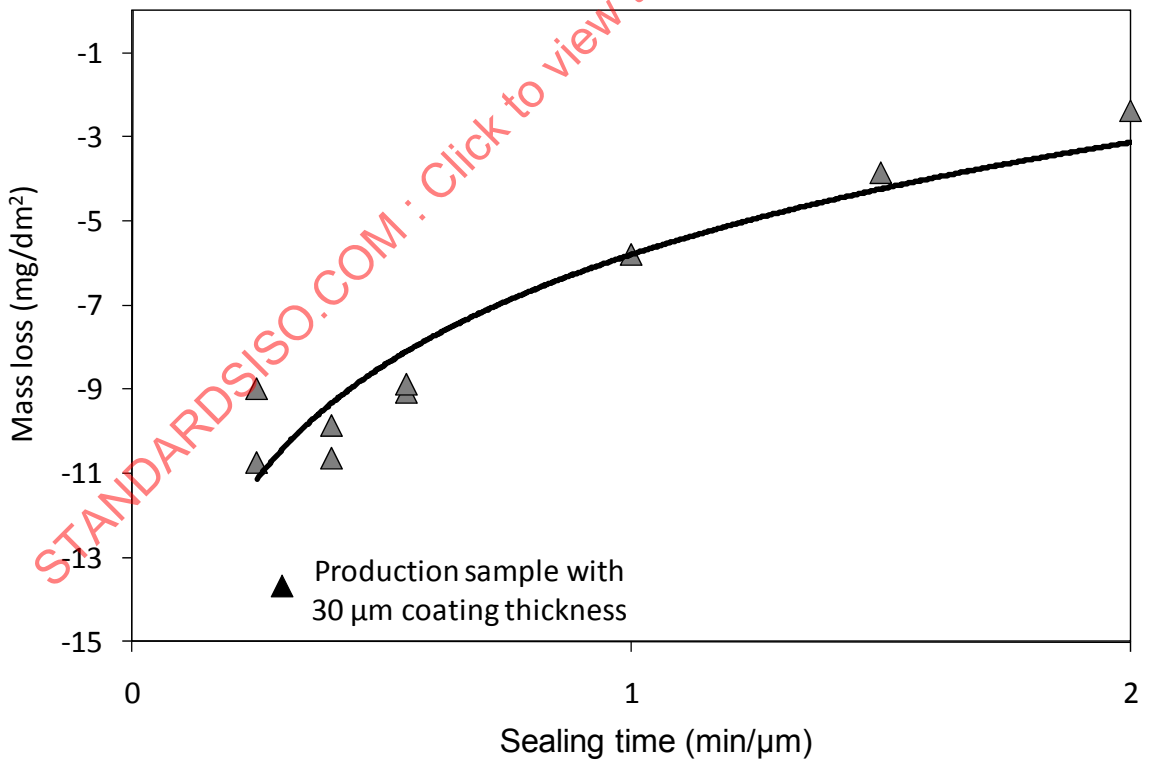


Figure 19 — Mass loss in the AASA test for samples with 20 µm thick coatings sealed using the nickel-based midtemp seal.

4.5.2 Admittance and dye spot

In Table 7 the admittance and the dye spot test result of the nickel-based midtemp sealed samples are shown. The coating thickness was 30 µm. The sample sealed for 0,3 min/µm was a production sample with a coating thickness of 20 µm; the admittance and dye spot tests were carried out 2 weeks after production. The recommended sealing times for 20 µm and 30 µm thick coatings are 0,55 min/µm and 0,5 min/µm respectively and the admittance limit values for coatings of 20 µm and 30 µm coatings are 20 µS and 14 µS respectively.

In Figures 20 to 21, the CPA test mass loss and corresponding admittance of nickel-based midtemp sealed samples with increasing sealing time are shown, here at an coating thickness of 10 µm and a recommended sealing time of 0,7 min/µm. The mass loss and admittance acceptance limits are 30 mg/dm^2 and 40 µS respectively. These data were taken from a previous investigation[18].

In order to be able to use the admittance test straight off the production line (or one day after production) the acceptance level needs to be significantly increased.

Table 7 — Admittance and dye spot result on the nickel-based midtemp sealed samples

Sealing time (min/µm)	Admittance (µS)		Dye spot test rating after 1 day
	after 1 day	after 1 week	
0,25	150	80	0
0,4	125	48	0
0,55	90	35	0
1	60	26	0
1,5	46	20	0
2	32	19	0
0,3	-	40	0

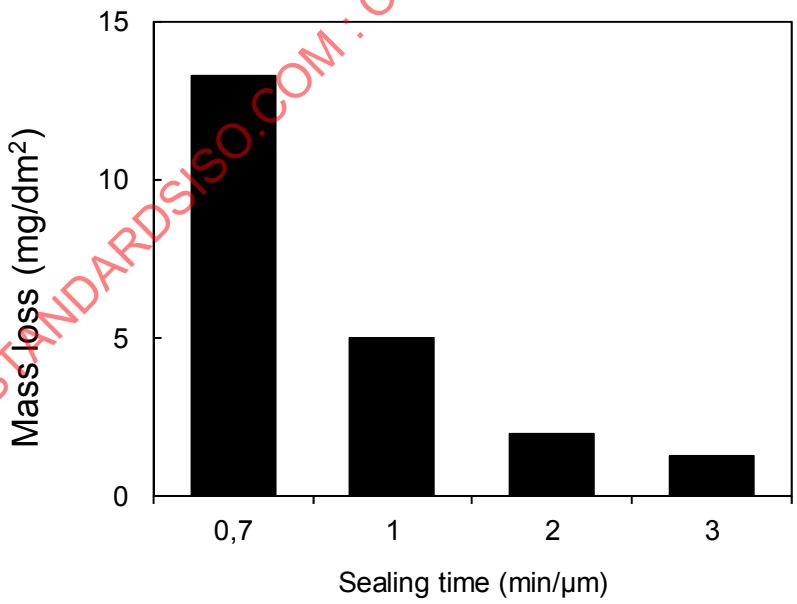


Figure 20 — CPA test mass loss of 10 µm thick coatings sealed with nickel-based midtemp sealing for different sealing times[18]

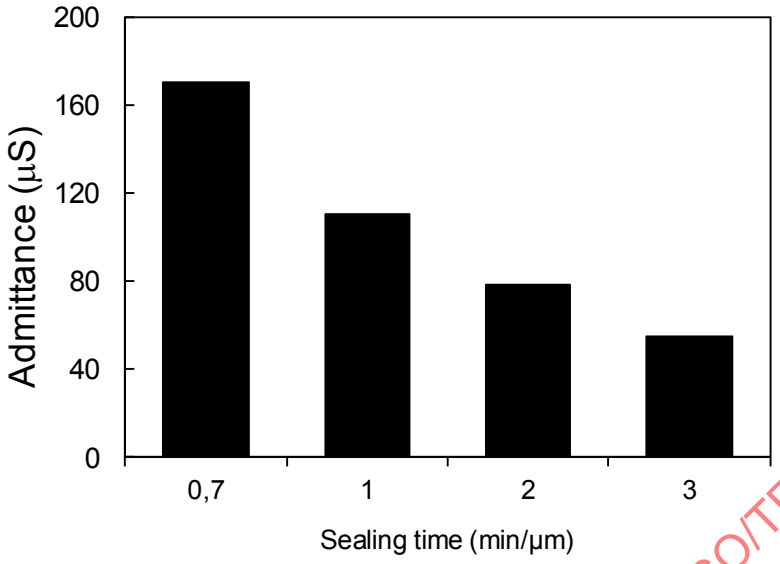


Figure 21 — Admittance of 10 µm thick coatings sealed with nickel-based midtemp sealing for different sealing time[18]

4.6 Nickel-free medium temperature sealing

4.6.1 Mass loss

In Table 8 the recommended working conditions in production and the sealing solution conditions during test are shown. Note that the test conditions (sealing time) on purpose go outside the recommended working conditions.

Table 8 — 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
Midtemp	Alfiseal 969	Alufinish	Mono- and dihexadecyl disulfonic diphenyloxide, disodium salt	86–90	5,8–6,1	3	88	6,0	1/2/3

In Figures 22 to 24, the mass losses in the three tests are shown. The recommended sealing time for the 20 µm thick coatings is 3 min/µm. The mass loss limit acceptance for the CPA test is 30 mg/dm^2. The changes in mass during the tests for production samples with coating thickness 30 µm were measured about four weeks after production. The averages of two samples for each test were –4,2 mg/dm^2, –42,6 mg/dm^2 and +0,9 mg/dm^2 for the CPA, SA and AASA tests respectively. Note the mass gain for the AASA test.

The CPA test and the SA test show a significant difference in the mass loss depending on the sealing time, see Figures 22 to 23. The CPA test though is very flat in the critical min/µm-interval (estimated to be 2 to 3 min/µm), making it difficult to distinguish between a good and a bad sealing. For the SA test the level of acceptance needs to be significantly higher for the nickel-free midtemp seal (as compared to hot seal and nickel-based cold seal).

In the AASA test there is a mass gain instead of a mass loss, see Figure 24. That test is therefore not a suitable replacement for the CPA test for the nickel-free midtemp seal.

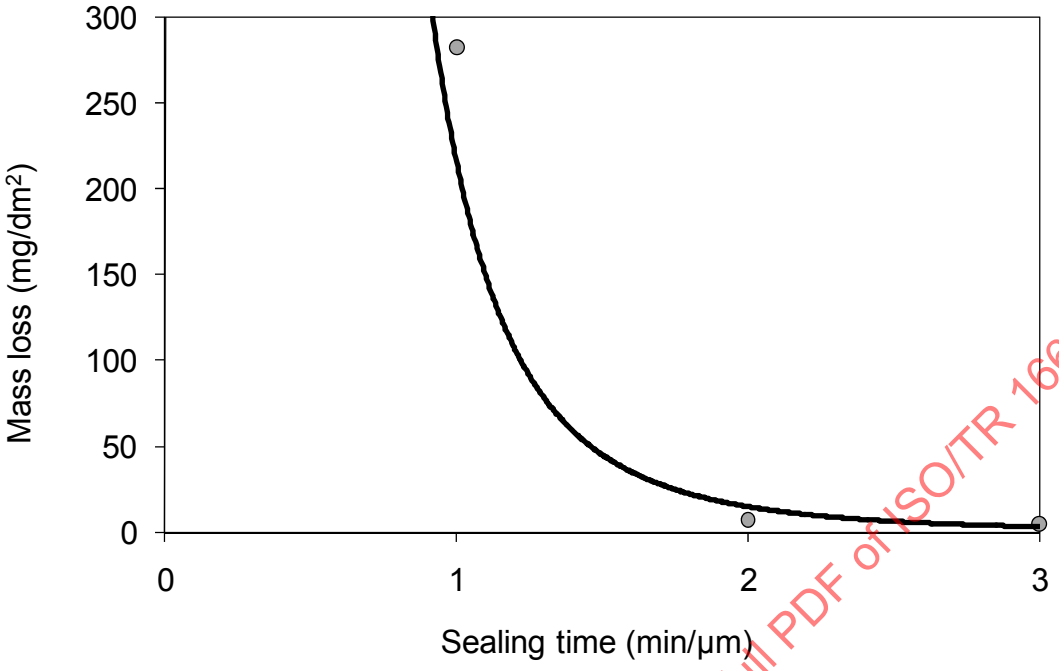


Figure 22 — CPA test mass loss of 20 µm thick coatings sealed with nickel-free midtemp sealing for different sealing times

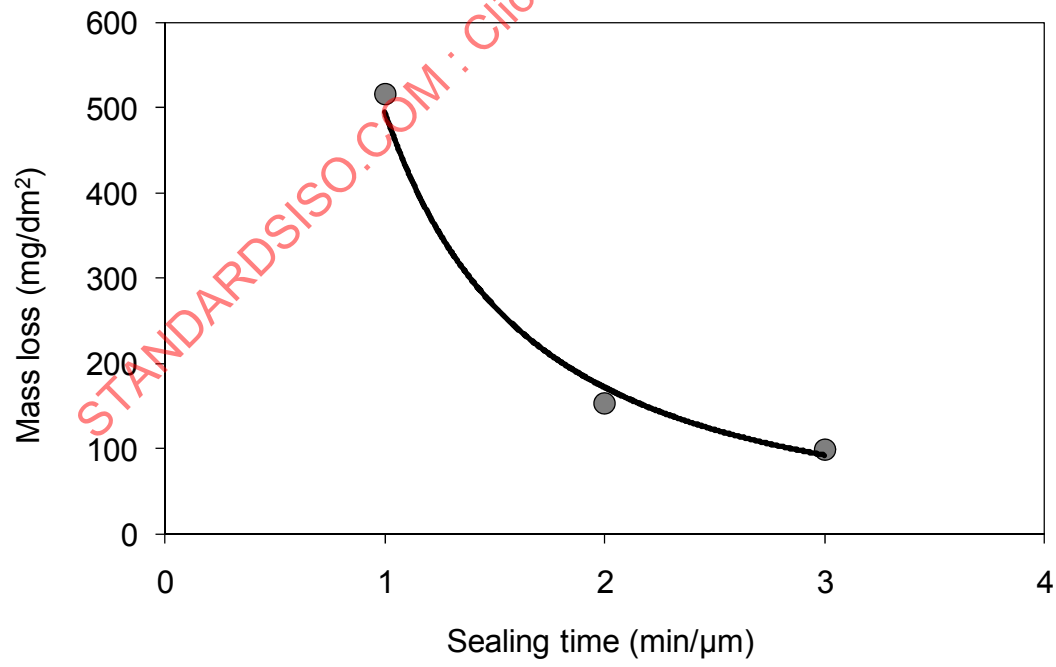


Figure 23 — SA test mass loss of 20 µm thick coatings sealed with nickel-free midtemp sealing for different sealing times

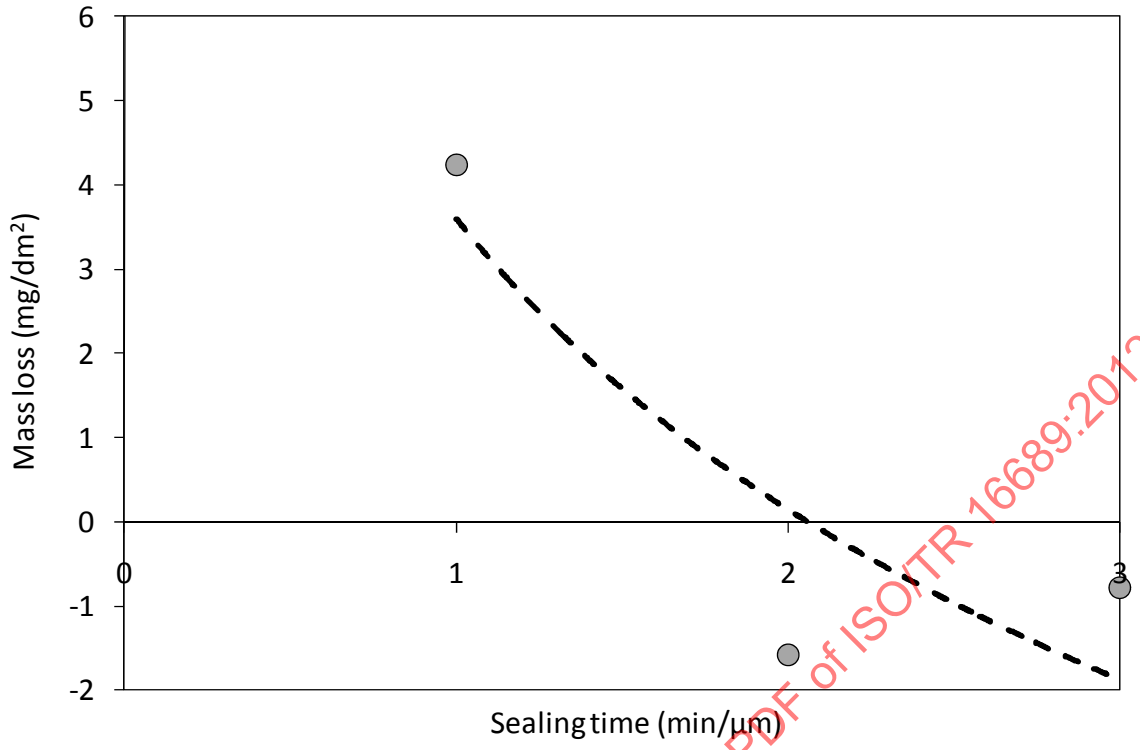


Figure 24 — AASA test mass loss of 20 µm thick coatings sealed with nickel-free midtemp sealing for different sealing times

4.6.2 Admittance and dye spot

In Table 9 the admittance and the dye spot test result of the nickel-free midtemp sealed samples are shown. The sample sealed for 3 min/µm was a production sample and the admittance and dye spot tests were carried out 4 weeks after production. The coating thickness was 20 µm so the admittance limit value was 20 µS.

In Figure 25 is shown the admittance of a 10 µm coatings as a function of time after anodizing (at recommended sealing time 3 min/µm), data taken from a previous investigation[18]. The admittance limit value for the coatings of 10 µm thickness is 40 µS. In order to be able to use the admittance test straight off the production line (or one day after production) the acceptance level needs to be increased however.

Table 9 — Admittance and dye spot result on the nickel-free midtemp sealed samples

Sealing time (min/µm)	Admittance (µS)		Dye spot test rating after 1 day
	after 1 day	after 1 week	
1	70	40	0
2	37	24	0
3	27	19	0
3	-	15	0

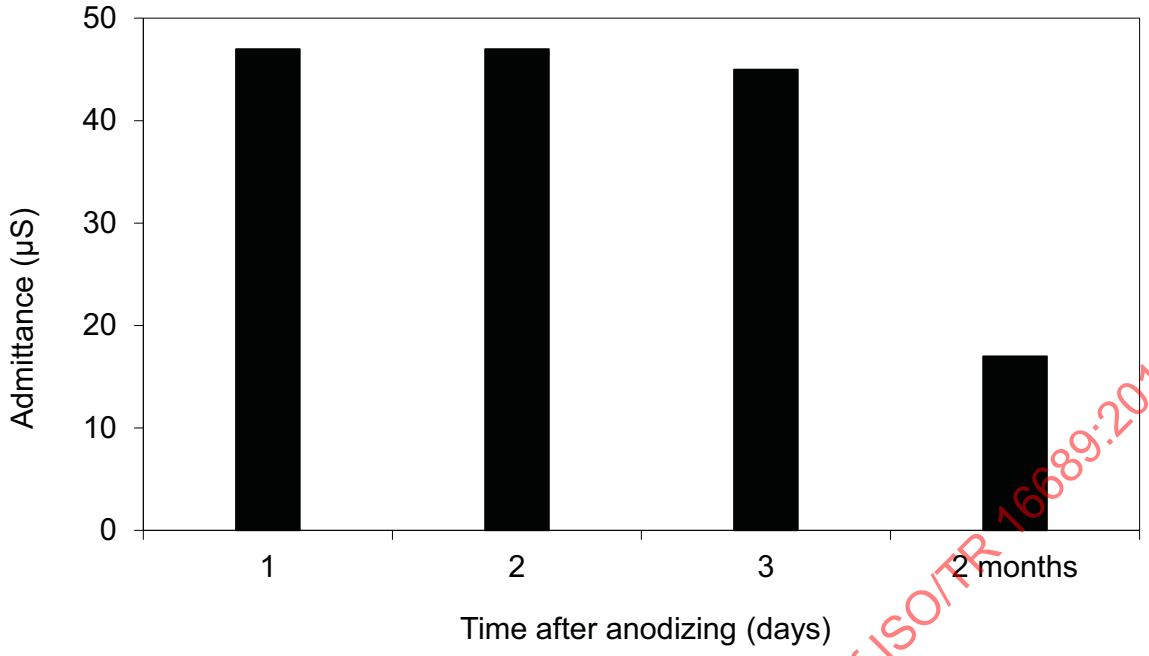


Figure 25 — Admittance of 10 µm thick coatings measured at various times after sealing with nickel-free midtemp sealing for 3 min/µm[18]

5 Discussion

A summary of the response to the different acid dissolution tests for different sealing methods is given in Table 10. This indicates that the AASA test could be an alternative to the CPA test for the nickel-based cold seal but not for any of the other sealing solutions. The SA test could be an alternative for the hot seal and the nickel-free midtemp seal but not for nickel-based midtemp seal.

The admittance test is in general good in distinguishing between a bad and a good sealing for all sealing methods used (hot, dual step cold, nickel-based midtemp, nickel-free midtemp). However, the acceptance level needs to be adjusted for the two midtemp sealing methods (nickel-based and nickel-free). One disadvantageous with the admittance test is that it is time sensitive, decreasing with time after sealing.