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Vitreous and porcelain enamels — Determination of resistance to chemical corrosion —

Part 4:
Determination of resistance to chemical corrosion by alkaline liquids using a cylindrical vessel

Émaux vitrifiés — Détermination de la résistance à la corrosion chimique —

Partie 4: Détermination de la résistance à la corrosion chimique par des liquides alcalins dans un récipient cylindrique

Reference number
ISO 28706-4:2008(E)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 28706-4 was prepared by the European Committee for Standardization (CEN) (as EN 14483-4) and was adopted, under a special “fast-track procedure”, by Technical Committee ISO/TC 107, *Metallic and other inorganic coatings*, in parallel with its approval by the ISO member bodies.

It cancels and replaces ISO 2734:1997 and ISO 2745:1998, which have been technically revised.

ISO 28706 consists of the following parts, under the general title *Vitreous and porcelain enamels — Determination of resistance to chemical corrosion*:

- *Part 1: Determination of resistance to chemical corrosion by acids at room temperature*
- *Part 2: Determination of resistance to chemical corrosion by boiling acids, boiling neutral liquids and/or their vapours*
- *Part 3: Determination of resistance to chemical corrosion by alkaline liquids using a hexagonal vessel*
- *Part 4: Determination of resistance to chemical corrosion by alkaline liquids using a cylindrical vessel*
- *Part 5: Determination of resistance to chemical corrosion in closed systems*

Introduction

Corrosion of vitreous and porcelain enamels by aqueous solutions is a dissolution process. The main component of the enamel, SiO_2, forms a three-dimensional silica network. After hydrolysis, it decomposes and forms silicic acid or silicates. These are released into the attacking medium. Other components, mainly metal oxides, are hydrolysed as well and form the corresponding hydrated metal ions or hydroxides. All corrosion products are more or less soluble in the attacking medium. The whole process results in a loss in mass per unit area.

For some aqueous solutions, the attack on the enamel proceeds linearly during the corrosion time; for other aqueous solutions, the attack on the enamel proceeds in a logarithmic manner during the corrosion time. Only for the first series of solutions can a scientifically exact rate of loss in mass per unit area ($g/m^2 \cdot h$) be calculated as well as a corrosion rate (mm/year).

The most important parameters influencing aqueous corrosion of the enamel are the enamel quality, the temperature and the pH-value. Inhibition effects resulting from the limited solubility of silica can also contribute. The following list describes different types of enamel attack for different corrosion conditions:

a) In aqueous alkali solutions like 0,1 mol/l NaOH (see Clause 9 of ISO 28706-4:2008), the silica network of the enamel is considerably attacked at 80 °C. Silicates and most of the other hydrolysed components are soluble in the alkali. Attack proceeds linearly during regular test times. Therefore, test results are expressed in terms of a rate of loss in mass per unit area (mass loss per unit area and time) and a corrosion rate (millimetres per year).

b) At room temperature, in weak aqueous acids like citric acid (see Clause 9 of ISO 28706-1:2008) or also in stronger acids like sulfuric acid (see Clause 10 of ISO 28706-1:2008), there is only minor attack on the silica network of the enamel. Other constituents are leached to some extent from the surface. Highly resistant enamels will show no visual change after exposure. On less resistant enamels, some staining or surface roughening will occur.

c) In boiling aqueous acids (see ISO 28706-2), the silica network of the enamel is being attacked, and silica as well as the other enamel components are released into solution. However, the solubility of silica in acids is low. Soon, the attacking solutions will become saturated with dissolved silica and will then only leach the surface. The acid attack is inhibited and the rate of corrosion drops markedly.

   NOTE The glass test equipment also releases silica by acid attack and contributes to the inhibition of the corrosion.

   Inhibition is effectively prevented in vapour phase tests. The condensate formed on the test specimen is free of any dissolved enamel constituents.

   Examples of enamel corrosion proceeding in a logarithmic manner [see 1)] and linearly [see 2)] are:

   1) **Boiling citric acid (see Clause 10 of ISO 28706-2:2008) and boiling 30 % sulfuric acid (see Clause 11 of ISO 28706-2:2008)**

      Since only minute amounts of these acids are found in their vapours, the test is restricted to the liquid phase. The attack is influenced by inhibition effects, and corrosion depends on the time of exposure. Therefore, test results are expressed in terms of loss in mass per unit area; no rate of loss in mass per unit area is calculated.

   2) **Boiling 20 % hydrochloric acid (see Clause 12 of ISO 28706-2:2008)**

      Since this is an azeotropic boiling acid, its concentration in the liquid and the vapour phase are identical, and liquid phase testing need not be performed. Vigorous boiling supplies an uninhibited condensate, and the attack proceeds linearly with time of exposure. Therefore, test results are only expressed in terms of rate of loss in mass per unit area (mass loss per unit area and time) and the corrosion rate (millimetres per year).

d) At high temperatures, with tests in the liquid phase under autoclave conditions (see ISO 28706-5), aqueous acid attack is severe. To avoid inhibition, the test time is restricted to 24 h and the ratio of attacking acid to attacked enamel surface is chosen so that it is comparatively high (similar to that in a chemical reaction vessel). In addition, only low-silica water is used for the preparation of test solutions. Under these conditions, attack will proceed linearly with time of exposure. Therefore, test results with 20 % hydrochloric acid (see Clause 8 of ISO 28706-5:2008), artificial test solutions (see Clause 10 of ISO 28706-5:2008) or process fluids (see Clause 11 of ISO 28706-5:2008) are also expressed in terms of a rate of loss in mass per unit area (loss in mass per unit area and time).

e) In boiling water (see Clause 13 of ISO 28706-2:2008), the silica network is fairly stable. The enamel surface is leached and silica is dissolved only to a small extent. This type of attack is clearly represented by the vapour phase attack. In the liquid phase, some inhibition can be observed with highly resistant enamels. However, if the enamel being tested is weak, leached alkali from the enamel can raise pH-values to alkaline levels, thus increasing the attack by the liquid phase. Both liquid and vapour phase testing can give valuable information.

f) Since the attack may or may not be linear, the results are expressed only in terms of loss in mass per unit area, and the test time should be indicated.

g) For standard detergent solution (see Clause 9 of ISO 28706-3:2008), it will not be certain whether the linear part of the corrosion curve will be reached during testing for 24 h or 168 h. Calculation of the corrosion rate is therefore not included in the test report.

h) For other acids (see Clause 14 of ISO 28706-2:2008) and other alkaline solutions (see Clause 10 of ISO 28706-3:2008 and Clause 10 of ISO 28706-4:2008), it will also not be known if a linear corrosion rate will be reached during the test period. Calculation of the corrosion rate is therefore not included in the test reports of those parts of this International Standard.

For vitreous enamels fired at temperatures below 700 °C, the test parameters (media, temperatures and times) of this International Standard are not appropriate. For such enamels, for example aluminium enamels, other media, temperatures and/or times should be used. This can be done following the procedures described in the clauses for “Other test solutions” in Parts 1, 2, 3 and 4 of this International Standard.

Vitreous and porcelain enamels — Determination of resistance to chemical corrosion —

Part 4:
Determination of resistance to chemical corrosion by alkaline liquids using a cylindrical vessel

1 Scope

This part of ISO 28706 describes a test method for the determination of the resistance of vitreous and porcelain enamelled articles to attack by alkaline liquids at temperatures between 25 °C and 95 °C. The apparatus used is a cylindrical vessel in which only one enamelled specimen is tested.

NOTE 1 The test method was initially set up for determination of the resistance of vitreous and porcelain enamels to a hot sodium hydroxide solution. Within the scope of this part of ISO 28706, the resistance of other alkaline liquids can be tested.

NOTE 2 This part of ISO 28706, which uses a cylindrical vessel, is generally used for tests carried out on vitreous and porcelain enamel coatings for the chemical industry.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 48, *Rubber, vulcanized or thermoplastic — Determination of hardness (hardness between 10 IRHD and 100 IRHD)*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 28764, *Vitreous and porcelain enamels — Production of specimens for testing enamels on sheet steel, sheet aluminium and cast iron*

EN 10088-1, *Stainless steels — Part 1: List of stainless steels*

3 Principle

An enamelled specimen is exposed to attack by an alkaline liquid under specified conditions of temperature and time. The solution is not stirred during the test.

The loss in mass is determined and used to calculate the rate of loss in mass per unit area and, if necessary, the corrosion rate.

4 Reagents

During the determination, use only reagents of recognized analytical grade, unless otherwise specified.

4.1 Water, conforming to the requirements of grade 3 of ISO 3696, i.e. distilled water or water of equivalent purity.

4.2 Acetic acid solution, 50 ml/l, for cleaning the test specimens.

4.3 Degreasing solvent, such as ethanol (C_2H_5OH), or water containing a few drops of liquid detergent, suitable for cleaning and degreasing the test specimens.

4.4 Sodium hydroxide (NaOH).

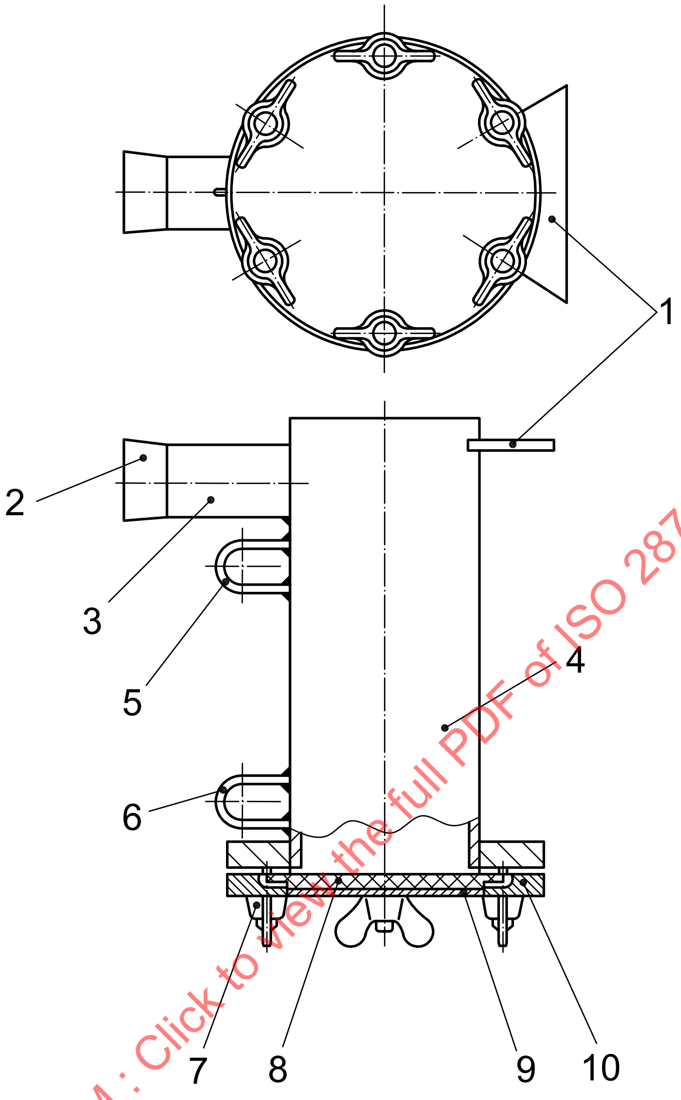
5 Apparatus and material

5.1 Test apparatus: cylindrical vessel

5.1.1 General

The assembled test apparatus is shown in Figure 1. It is composed of the cylinder with the following welded-on elements as shown in Figure 2:

- a plate on one end;
- a circular flange with six welded-on threaded bolts at the other end;
- a foot at the end remote from the circular flange;
- two lifting rings;
- a filling nozzle.



Key

1 foot
2 stopper
3 filling nozzle
4 cylinder
5 lifting ring
6 lifting ring
7 wing nut
8 test specimen
9 protective envelope
10 flange plate

Figure 1 — Test apparatus

The cylinder is sealed by the flange plate and a specimen which is enclosed in a protective envelope and put between the cylinder and the flange plate. The flange plate is fastened to the circular flange by means of six wing nuts. The filling nozzle is closed with a stopper.

The height of the foot depends on the outer diameter of the circular flange. It shall be placed in a way that the surface of the test specimen is totally covered by the liquid if the test apparatus is filled with 1 l of the test solution and placed on a plane surface.

Dimensions in millimetres

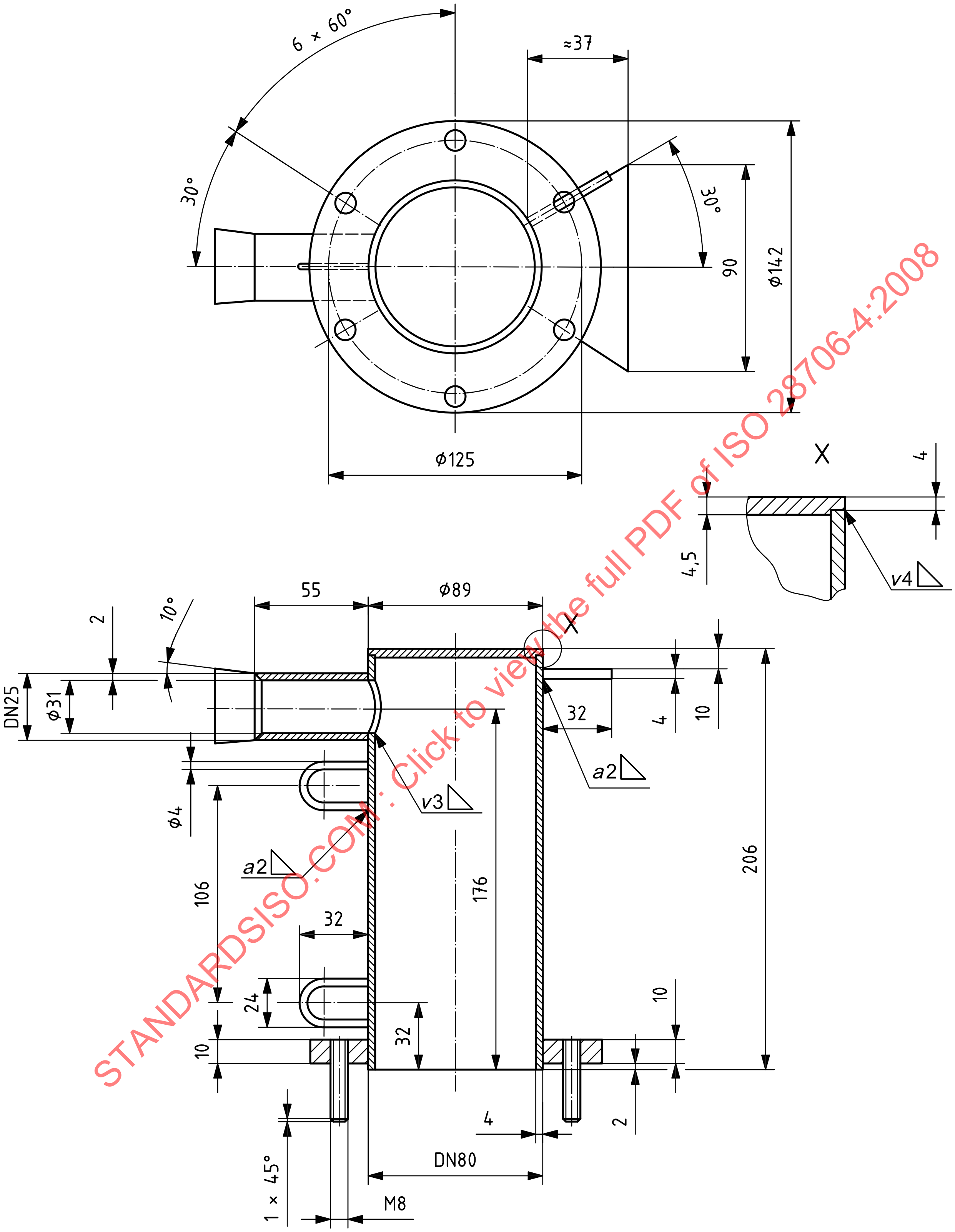


Figure 2 — Cylinder

5.1.2 Cylinder, with all surfaces consisting of bare metal and all edges deburred. All parts shall be made of the same stainless steel, for example 1.4571 stainless steel conforming to the requirements of EN 10088-1.

NOTE The main constituents of 1.4571 steel are 16,5 % to 18,5 % Cr, 10,5 % to 13,5 % Ni, 2 % to 2,5 % Mo, max. 0,08 % C and an addition of Ti.

5.1.3 Protective envelope, shown in Figure 3, made of synthetic rubber of hardness 70 RHD as determined in accordance with ISO 48. The material shall be resistant to alkaline solutions at 100 °C (e.g. chloroprene or ethylene-propylene).

The rubber and the circular dam usually have a thickness of 2 mm; other thicknesses can also be used, however.

Dimensions in millimetres

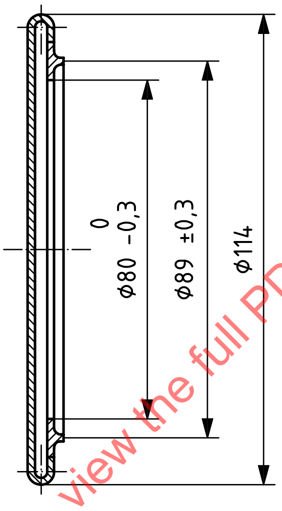


Figure 3 — Protective envelope

5.1.4 Flange plate, shown in Figure 4, with all surfaces consisting of bare metal and all edges deburred. It shall be made of stainless steel, for example 1.4571 stainless steel conforming to EN 10088-1.

Dimensions in millimetres

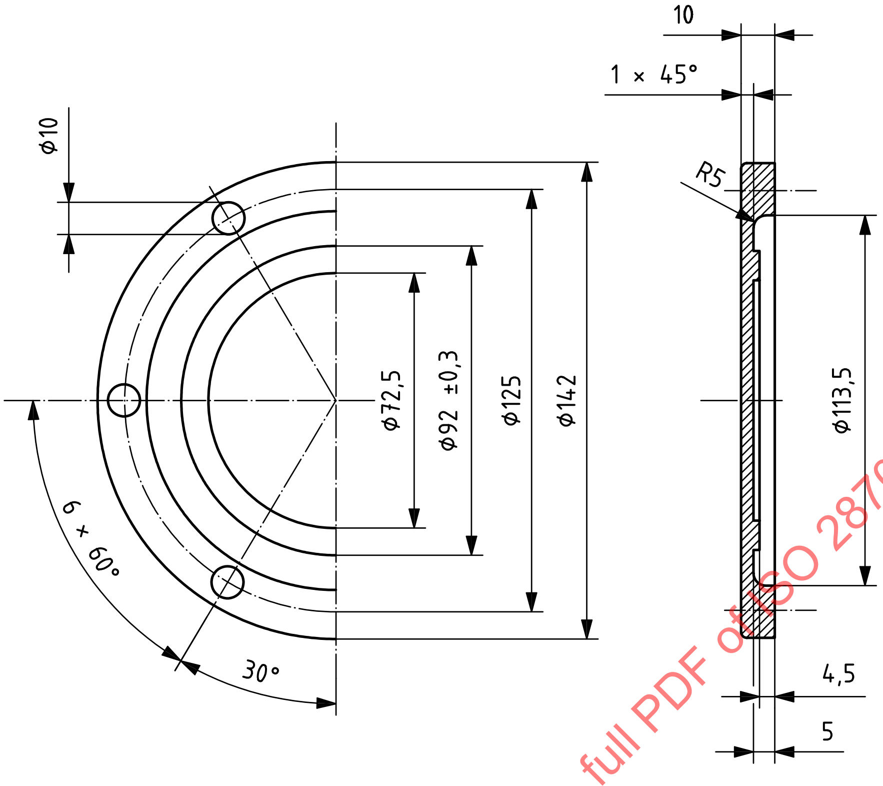


Figure 4 — Flange plate

5.1.5 Six wing nuts, with threads fitting the threaded bolts of the cylinder. They shall be made of stainless steel, for example 1.4571 stainless steel conforming to the requirements of EN 10088-1.

5.1.6 Stopper, shown in Figure 5, made of synthetic rubber of hardness 70 IRHD as determined in accordance with ISO 48. The material shall be resistant to alkaline solutions at 100 °C (e.g. chloroprene or ethylene-propylene).

Dimensions in millimetres

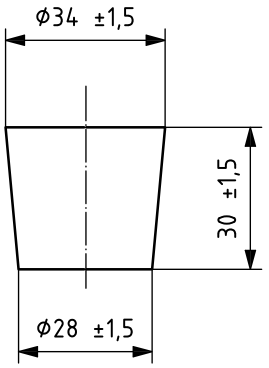


Figure 5 — Stopper

5.2 Thermostatically controlled water bath (containing demineralized or distilled water), incorporating a stirrer or other rotating device, for use with one or more pieces of test apparatus. It shall be capable of being sealed against losses by evaporation and shall allow temperatures up to 100 °C to be kept constant to 0,1 °C.

5.3 Thermometer, calibrated, graduated in 0,1 °C steps, for use with the thermostatically controlled water bath.

5.4 Drying oven, capable of maintaining temperatures of at least 130 °C.

5.5 Desiccator, with an internal diameter of at least 200 mm.

5.6 Polypropylene bottle, of 1 000 ml capacity, capable of being closed.

5.7 One-mark volumetric flask, of 1 000 ml capacity, conforming to the requirements of class A of ISO 1042.

5.8 Funnel, of maximum diameter 70 mm.

5.9 Balance, accurate to $0{,}2 \times 10^{-3}$ g.

5.10 Cotton wool.

6 Test specimens

Prepare the test specimens in accordance with ISO 28764.

Rinse the test specimens with water. If necessary, use a degreasing solvent (4.3). Then dry them for 2 h in the drying oven (5.4) at 110 °C ± 5 °C. Allow the specimens to stand for at least 2 h in the desiccator (see 5.5) and, finally, weigh each to the nearest $0{,}2 \times 10^{-3}$ g. Record the starting mass, m_S.

7 Procedure

Test at least two specimens. Carry out one determination for each test specimen.

Place a test specimen in the protective envelope (5.1.3) such that the face with the enamel coating faces the opening in the envelope.

Fix the test specimen in the test apparatus such that the side with the unprotected enamel coating faces the interior of the apparatus.

Screw down the wing nuts (5.1.5) evenly so that the test apparatus is watertight.

NOTE Damage to the enamel on weak or distorted test specimens in the apparatus can be avoided by placing a rubber ring between the protective envelope and the flange plate of the apparatus. 2 mm to 3 mm thick rubber rings made of heat-resistant rubber are suitable for this purpose (inside diameter 80 mm, outside diameter 100 mm, Shore hardness A/70/1 as determined in accordance with ISO 868).

Place the sealed test apparatus in the thermostatically controlled water bath (5.2), heated to the specified temperature (see Clauses 9 and 10), such that the filling nozzle projects out of the water bath by about 10 mm. Leave the test apparatus in this position for at least 10 min before filling it with the test solution.

The test apparatus can also be placed in the cold thermostatically controlled water bath and heated to the specified temperature.

Heat about 1 000 ml of the test solution (see Clauses 9 and 10) to the required temperature (see Clauses 9 and 10) in the polypropylene bottle (5.6) and then pour 1 000 ml of it through the funnel (5.8) into the test apparatus which is still in the thermostatically controlled water bath. Then seal the cylinder of the test apparatus with the stopper and cover the opening of the water bath.

With its bulb close to the test apparatus in the water bath at half the height of the test apparatus, use the thermometer (5.3) to check that the test temperature is maintained throughout the test. If two or more pieces of test apparatus are used, place the thermometer between them.

When the specified test period (see Clauses 9 and 10) has elapsed, remove the test apparatus from the bath using hooks, pour away the test solution and rinse the interior of the test apparatus with water (4.1).

Take the test specimen out of the protective envelope and wipe it three times with cotton wool (5.10) soaked in cold acetic acid solution (4.2), then rinse it with cold water (4.1).

Carefully remove any residues of the protective envelope from the test specimen, then dry the latter for 2 h in the drying oven (5.4) at 110 °C ± 5 °C.

After a further 2 h in the desiccator (5.5), weigh the test specimen to the nearest $0{,}2 \times 10^{-3}$ g and record the final mass, m_f.

Calculate the arithmetic mean value of three measurements of the diameter of areas exposed to attack. The individual values shall not differ from the mean value by more than ± 1 mm. Calculate the exposed area of attack, A, using this mean value of the diameter.

8 Expression of results

8.1 Total loss in mass per unit area

Calculate the total loss in mass per unit area for the total duration of the test, $\Delta\rho_\mathrm{A}$, expressed in g/m², using the equation:

$$\Delta\rho_\mathrm{A} = \frac{(m_\mathrm{s} - m_\mathrm{f})}{A} \tag{1}$$

where

m_s is the starting mass, in g;

m_f is the final mass, in g;

A is the area exposed to attack, in m².

In order to distinguish between the test results for different test periods, the number of test hours shall be stated as a subscript to the symbol; for example, for a test period of 24 h, $\Delta\rho_\mathrm{A24}$.

Results for test specimens which show defects such as pinholes down to the metal, chipped edges or edge corrosion shall be discarded and a corresponding number of new specimens shall be tested.

Express the result as the arithmetic mean of the individual values to the nearest 0,1 g/m². The individual values shall not differ from the mean value by more than 20 %.

8.2 Corrosion rate

For the sodium hydroxide test (see Clause 9), the corrosion of the enamel proceeds linearly with time. The corrosion rate, v, expressed as the rate of loss in mass per unit area, $\mathrm{g \cdot m^{-2} \cdot h^{-1}}$, is calculated from the equation:

$$v = \frac{\Delta\rho_\mathrm{A}}{t} \tag{2}$$

where t is the test time, in h.

Calculate the corrosion rate, w, in mm per year from the equation:

$$w = 3{,}504 v \tag{3}$$

NOTE In Equation (3), it is assumed that enamel is a homogeneous material (without gas bubbles) with a density of 2,5 g/cm³.