INTERNATIONAL STANDARD

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

Part 1: Determination of resistance to chemical corrosion by acids at room temperature

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

Partie 1: Détermination de la résistance à la corrosion chimique par les acides à température ambiante

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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 28706-1 was prepared by the European Committee for Standardization (CEN) (as EN 14483-1) 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 2722:1997 and ISO 8290:1998, 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 1: Determination of resistance to chemical corrosion by acids at room temperature

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 an acid at room temperature, and also specifies a method of classifying the results.

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

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

ISO 4788, *Laboratory glassware — Graduated measuring cylinders*

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

3 Principle

Part of the surface of a test specimen is exposed under defined conditions to attack by an acid solution. Resistance is assessed by methods based on the appearance and cleanability of the enamelled surface.

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 Degreasing solvent, such as ethanol, or water (4.1) containing a few drops of liquid detergent, suitable for cleaning the test apparatus and test specimens.

4.3 Titanium dioxide, pigment grade.

4.4 Citric acid monohydrate, ($C_6H_8O_7 \cdot H_2O$), crystalline.

4.5 Sulfuric acid, (H_2SO_4), analytical grade, $c(H_2SO_4)$ = 0,5 mol/l.

5 Materials and apparatus

5.1 Graduated measuring cylinder, capacity 100 ml, conforming to the requirements of ISO 4788.

5.2 One-mark volumetric flask, capacity 100 ml, conforming to the requirements of ISO 1042.

5.3 Pipette, of a suitable size (see 7.1).

5.4 Towel, of white cotton or linen.

5.5 Filter paper, free from fluoride, thickness less than 0,18 mm, approximately 30 mm in diameter (only to be used for testing of curved surfaces).

5.6 Filter paper, free from fluoride, thickness greater than 0,38 mm, approximately 25 mm in diameter (only to be used for testing of curved surfaces).

5.7 Filter paper, free from fluoride.

5.8 Pencil, HB hardness or equivalent.

5.9 Caps (e.g. curved glasses), made of polyethylene or other suitable flexible material, or glass, having an external diameter approximately 30 mm.

6 Test specimens

The test specimens shall be commercial items, parts thereof, or test pieces especially prepared in accordance with the appropriate standard for that base material.

The production of test specimens for testing vitreous and porcelain enamels for steel sheet, cast iron and aluminium is specified in ISO 28764.

Each test specimen shall be cleaned with the degreasing solvent (4.2), then rinsed with hot water until the water spreads evenly on the surface, and then finally dried by dabbing (not rubbing) with a clean towel (5.4).

7 Procedure

7.1 Attack by the test solution

Using the pipette (5.3), place a few drops of the attacking medium (see 9.1, 10.1 and 11.1), on each specimen and keep it at a temperature of 23 °C ± 3 °C during the whole period of the test, ensuring that there is a continuous treatment area, the diameter of which shall be less than that of the cap (5.9). Cover the treatment area immediately with the cap.

In the case of curved surfaces, place a thin filter paper (5.5) on the area to be treated. On top of this put the thicker filter paper (5.6). Apply a few drops of the attacking medium (see 9.1, 10.1, 11.1) to the top filter paper (5.6) until both filters are saturated. Cover the filter papers to prevent evaporation, for example with a cap (5.9), and keep the specimen at a temperature of 23 °C ± 3 °C.

After the predefined test time, remove the cap (5.9) and filter papers (5.5 and 5.6), wash the test specimen with either water (4.1) or tap water, and then dry it by dabbing (not rubbing) with filter paper (5.7).

When using tap water, ensure that a residual film is not allowed to form, otherwise the classification may be affected.

7.2 Determination

7.2.1 General

Examine each test specimen within 2 h of completion of the attack by the test solution. For the evaluation, consider only that part of the surface which has been exposed to the attacking medium as a treatment area.

Base the evaluation on the examinations described in 7.2.2, 7.2.3 and 7.2.4, which are in accordance with the scheme and classification given in Figure 1 and Table 1.

7.2.2 Visual examination

View, using normal or corrected vision, the different areas at varying angles at a distance of 250 mm from the test specimen, without the aid of a magnifying glass, in order to ascertain whether the treated area differs from the non-treated area (e.g. whether the brightness or the colour has changed or whether some spots have appeared). Carry out the examination either in daylight, avoiding direct sunlight, or in artificial light, provided the latter is uniform and sufficiently intense. Judge the test specimen to have failed the visual examination if the treated area differs in any respect from the non-treated area.

7.2.3 Rubbing test (dry)

Draw, using a pencil (5.8), a number of approximately parallel lines across both the treated and the non-treated areas. For black and dark coloured enamels, rub titanium dioxide (4.3) on to the two areas instead of using a pencil. Then rub the test specimen with a dry towel (5.4). Judge the test specimen to have failed the dry rubbing test if the markings on the treated area are more difficult to remove than those on the non-treated area.

7.2.4 Rubbing test (moist)

Draw, using a pencil (5.8), a number of approximately parallel lines across both the treated and the non-treated areas. For black and dark coloured enamels, rub titanium dioxide (4.3) on to the two areas instead of using a pencil. Then rub the test specimen with a towel (5.4) which has been moistened with water (4.1) and thoroughly wrung out (do not use soap or detergent). Judge the test specimen to have failed the moist rubbing test if the markings on the treated area are more difficult to remove than those on the non-treated area.

8 Classification of results

Dependent on the results of the determinations which have been performed in accordance with 7.2, classify the vitreous or porcelain enamel as shown in Table 1.