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Metallic and other inorganic coatings — Chromate conversion coatings on zinc, cadmium, aluminium-zinc alloys and zinc-aluminium alloys — Test methods

Revêtements métalliques et autres revêtements inorganiques — Couches de conversion au chromate sur zinc, cadmium et alliages d'aluminium-zinc et de zinc-aluminium — Méthodes d'essai

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ISO 3613:2010(E)

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Foreword

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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 3613 was prepared by Technical Committee ISO/TC 107, *Metallic and other inorganic coatings.*

This third edition cancels and replaces the second edition (ISO 3613:2000), which has been technically revised.

Introduction

This International Standard specifies methods for the qualitative determination of the presence of chromate conversion coatings as well as the total chromium content of chromate conversion coatings.

The application of very thin, colourless, practically invisible chromate conversion coatings is frequently called "passivation", while the application of thicker, coloured chromate conversion coatings is called "chromating". The term "passivation" is not correct, does not comply with the ISO 2080 designation and is therefore deprecated.

INTERNATIONAL STANDARD **ISO 3613:2010(E)**

Metallic and other inorganic coatings — Chromate conversion coatings on zinc, cadmium, aluminium-zinc alloys and zinc-aluminium alloys — Test methods

WARNING — This International Standard calls for the use of substances and/or procedures that may be injurious to health if adequate safety measures are not taken. This International Standard does not address any health hazards, safety or environmental matters associated with its use. It is the responsibility of the user of this International Standard to establish appropriate health, safety and environmentally acceptable practices and take suitable actions for any national and international regulations. Compliance with this International Standard does not in itself confer immunity from legal obligations.

1 Scope

This International Standard specifies methods for the determination of

- the presence of colourless chromate conversion coatings,
- the presence of hexavalent chromium in colourless and coloured coatings on zinc or cadmium or aluminium-zinc (mass fraction of aluminium: 55 %, within a range of 54 % to 56 % mass fraction) and zinc-aluminium (mass fraction of aluminium: 5 %) alloys,
- the total chromium content per unit area on zinc and cadmium,
- the mass per unit area of both colourless and coloured coatings,
- the satisfactory adhesion of chromate conversion coatings, and
- the quality of chromate coatings.

These methods are applicable

- to colourless and coloured chromate conversion coatings containing trivalent and hexavalent chromium in varying proportions and produced by either chemical or electrochemical processes, and
- only to chromate coatings that are free from any supplementary coatings, such as oil, water or solvent-based polymers or wax.

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 3892, *Conversion coatings on metallic materials — Determination of coating mass per unit area — Gravimetric methods*

ISO 4520, *Chromate conversion coatings on electroplated zinc and cadmium coatings*

IEC 60068-2-30, *Environmental testing — Part 2-30: Tests — Test Db: Damp heat, cyclic (12 h + 12 h cycle)*

3 Reagents

Use only reagents of recognized analytical grade and distilled water or water of equivalent purity, unless otherwise specified, for analysis.

3.1 Test solution A (see 5.2).

Dissolve 1 g of diphenylcarbazide in a mixture of 20 ml of acetone, 60 ml of glacial acetic acid and 40 ml of distilled water contained in a beaker. Add 15 ml of concentrated hydrochloric acid ($\rho = 1{,}18$ g/cm^3), stir and add slowly 30 ml of sodium hypochlorite solution (10 % to 15 % available chlorine). Add 5 ml of hydrogen peroxide (30 % volume fraction) slowly with continuous stirring. Leave the solution in the open beaker for 24 h in a fume cupboard, to allow excess chlorine to escape, before use.

The solution does not deteriorate with age and can be kept in a bottle with a loosely fitted stopper. However, there may be losses due to evaporation and the concentration may alter so it is discarded after 6 months.

3.2 Test solution B (see 5.3).

Dissolve 50 g of lead acetate trihydrate $[(CH_3COO)_2Pb{\cdot}3H_2O]$ in 1 l of distilled water or water of equivalent purity. Ensure that the pH of the solution is between 5,5 and 6,8 as prepared. If the pH of the solution is outside this range, discard the solution and obtain a new supply of lead acetate.

Any white precipitate formed during the initial preparation of the solution may be dissolved by small additions of glacial acetic acid, provided that the pH is not reduced to a value below 5,5. Discard the stock solution if the white precipitate does not disappear.

3.3 Test solution C (see 5.5)

3.3.1 Test solution C 1

Dissolve 0,4 g of diphenylcarbazide in a mixture of 20 ml of acetone and 20 ml of ethanol (96 %). After dissolution, add 20 ml of 75 % orthophosphoric acid solution and 20 ml of distilled water. Prepare this solution not more than 8 h prior to use.

3.3.2 Test solution C 2

Add 700 ml of orthophosphoric acid, of specific gravity 1,7, to 250 ml of distilled water or water of equivalent purity and make up to 1 000 ml.

Dissolve 1,0 g of 1,5-diphenylcarbazide in 100 ml of acetone, adding one drop of glacial acetic acid to help dissolution. Keep the solution in a dark glass bottle in the refrigerator. The solution shall be discarded after 4 weeks.

For the Cr(VI) standard solution, dissolve 0,113 g of $K_2Cr_2O_7$ in distilled water or water of equivalent purity and make up to the mark in a 1 000 ml volumetric flask. Measure 2,5 ml of this solution into a second 1 000 ml volumetric flask and make up to the mark. 1 ml of this standard solution contains 0,1 µg of Cr(VI). The solution shall be discarded after 9 months.

For the preparation of comparison solution, add 1 ml of phosphoric acid and 1 ml of diphenylcarbazide solution to 50 ml of standard Cr(VI) solution, and mix thoroughly. Allow the solution to stand for 10 min for the colour reaction to be completed.

3.4 Test solution D (see 5.6 and 5.7).

Dissolve 0,50 g of diphenylcarbazide in 50 ml of acetone. Dilute slowly, while stirring, with 50 ml of water (rapid mixing can result in precipitation of diphenylcarbazide).

For maximum stability, store the solution under refrigeration in an amber-coloured glass bottle.

3.5 Sulfuric acid, diluted 1 + 3.

Slowly add 1 volume of concentrated sulfuric acid ($\rho = 1{,}84\ \text{g/cm}^3$) to 3 volumes of water.

3.6 Ammonium persulfate [$(NH_4)_2S_2O_8$].

3.7 Sodium hydroxide (NaOH), 240 g/l solution.

3.8 Silver nitrate ($AgNO_3$), 17 g/l solution.

3.9 Potassium dichromate ($K_2Cr_2O_7$), standard solution.

Dilute 2 ml of standard volumetric potassium dichromate solution (4,9 g/l) to 1 000 ml.

3.10 Phosphate buffer solution.

Dissolve 55 g of sodium dihydrogen orthophosphate monohydrate ($NaH_2PO_4 \cdot H_2O$) in 100 ml of water.

4 Apparatus

Use normal laboratory apparatus and the following.

Clean all glassware thoroughly. It is recommended that cleaning be done by boiling the glassware with nitric acid (HNO_3) of 30 % mass fraction and then rinsing thoroughly with distilled water or water of equivalent purity.

4.1 Photoelectric absorptiometer (colorimeter), with a filter having a mean transmission of 520 nm. The absorptiometer shall be used with an absorption cell having an optical path length of 10 mm.

4.2 Spectrophotometer, with wavelength set at 540 nm. The spectrophotometer shall be used with an absorption cell having an optical path length of 10 mm.

4.3 Analytical balance, capable of weighing to the nearest 0,1 mg.

5 Test methods

5.1 General

The test surface, prior to the following tests, shall be free of all contaminants, finger prints and other extraneous stains. If the surface is coated with a thin oil film, this shall be removed prior to the test by degreasing using a suitable solvent at room temperature (not exceeding 35 °C). If it is necessary to store samples, they shall be stored at temperatures not exceeding 40 °C and at a relative humidity below 70 %. For test purposes, the samples shall not be subjected to forced drying at temperatures in excess of 35 °C. Treatment in alkaline solutions shall not be performed as chromate conversion coatings are broken down by alkalis. Spot tests are not always a precise means of determining the presence of chromate coatings.

The test methods for

a) the presence of a colourless chromate coating on zinc, cadmium and aluminium-zinc alloys,

b) the presence of hexavalent chromium in both coloured and colourless chromate coatings,

c) the determination of hexavalent chromium content, and

d) the determination of total chromium content are given in 5.2 to 5.7.

The tests shall be carried out within the following time limits:

- a minimum of 24 h after the application of the chromate conversion coating for all tests (5.2 to 5.10);
- a maximum of 3 d for tests specified in 5.2 to 5.5;
- a maximum of 30 d for the tests specified in 5.6 and 5.7.

The test methods for

- the determination of mass per unit area of chromate conversion coatings,
- adhesion by abrasion, and
- the evaluation of the quality of chromate layer

are given in 5.8, 5.9 and 5.10, respectively.

5.2 Test for the presence of a colourless chromate coating on zinc

Apply 1 drop of test solution A (3.1) to the chromated zinc surface. The formation of a red or red-violet colour in the drop shall be deemed to indicate the presence of chromate film.

5.3 Test for the presence of a colourless chromate coating on zinc and cadmium

Place 1 drop of test solution B (3.2) on the surface to be tested.

In the case of a zinc substrate, observe the appearance of the spot for 3 min. The formation of a dark or black stain, at least 1 min after the application of the test solution, shall be deemed to indicate the presence of a colourless chromate conversion coating.

Black stain formation after more than 3 min can be indicative of the presence of supplementary coatings, such as wax or oil.

In the case of a cadmium substrate, observe the appearance of the spot for 1 min. The formation of a dark or black stain at least 5 s after the application of the test solution shall be deemed to indicate the presence of a colourless chromate conversion coating.

Black stain formation after more than 1 min can be indicative of the presence of supplementary coatings, such as wax or oil.

For comparison purposes, test an untreated surface similarly. Untreated zinc and cadmium surfaces, or the surfaces that have been treated for the chromate conversion coating but do not have a continuous coating, will react with the lead acetate solution to form a black stain on the untreated or bare zinc and cadmium surfaces almost immediately, within 2 s to 5 s, after the application of the test solution.

No significance is to be placed upon any differences in the reaction time to black-spot formation between 1 min and 3 min on a zinc substrate, or between 5 s and 60 s on a cadmium substrate, with a colourless chromate conversion treatment. Factors such as substrate surface texture (roughness), chromate film thickness variations (due to processing conditions), variations in the ambient temperature of the test, and precise pH control of the lead acetate solution have an influence on the reaction time and therefore preclude any rating based upon times beyond those already stated. Similarly, the test cannot be used to compare the corrosion protection of chromate conversion coatings made from various types of chromate treatment solutions.

Because of the sensitivity of the method, the test is considered to be a quality control tool for the processor. Items with damaged chromate layers should not be tested by this method.

Chromate conversion coatings exposed to temperatures above 60 °C will have considerably reduced resistance to corrosion in the accelerated test method (see 5.10), and will show a black stain in less than 60 s on zinc, and less than 5 s on cadmium.

5.4 Test for the presence of a colourless chromate coating on and zinc-aluminium (mass fraction of aluminium: 5 %) alloys

Expose the test specimen for 24 h to an accelerated damp heat test, in accordance with IEC 60068-2-30.

The formation of a dark grey to black stain over the main part of the area shall be deemed to indicate the absence of chromate conversion coating.

NOTE This test does not have any significant effect on the surface appearance if a chromate conversion coating is present.

5.5 Test for the presence of hexavalent chromium in both colourless and coloured chromate coatings

Carry out the following test methods for the presence of hexavalent chromium.

5.5.1 Test method employing test solution C 1

Place 1 drop to 5 drops of test solution C 1 (3.3.1) on the surface to be tested. If hexavalent chromium is present, a red to violet colour will appear within a few minutes. Ignore any colour that appears much later, for example on drying. For comparison purposes, test an untreated surface similarly.

NOTE The treatment will not have any significant effect on the surface appearance.

5.5.2 Test method employing alternative test solution C 2 (destructive)

In this test method the Cr(VI) content of a coated part is extracted by boiling in water. The extracted solution is examined according to the colour reaction with 1,5-diphenylcarbazide. Cr(VI) oxidizes 1,5-diphenylcarbazide to 1,5-diphenylcarbazone, which forms a red-violet coloured complex with the developed Cr(III).

Cut a test piece measuring about 50 mm × 50 mm from the coated item and remove any sealing, such as paint or wax, etc., by scraping the surface. The resulting abrasion shall also be analysed.

Immerse the sample in boiling distilled water, or water of equivalent purity, in a suitable vessel for 10 min and totally immerse the test specimen in it with anti-bumping granules. Remove the sample after 10 min and allow the beaker content to cool to ambient temperature. If necessary, filter the solution using, for example, a 0,45 µm filter and make up the solution to the mark (e.g. 50 ml) with water (see Clause 3) or reduce it to the mark by boiling. Add 1 ml of orthophosphoric acid (3.3.2) per 50 ml volume and 1 ml of diphenylcarbazide solution (3.3.2) and mix well. Allow the solution to stand for 10 min for the colour to be completed. Compare the colour of the solution obtained against the comparison solution (3.3.2).

5.5.3 Expression of results

The results are expressed as shown in Table 1.

Table 1 — Comparison of solutions

Observation	Cr(VI) concentration
The colour intensity of the sample solution (see 5.5.2) is lower than that of the comparison solution (3.3.2)	$< 0{,}1$ µg/cm^2
The colour intensity of the sample solution (see 5.5.2) is higher than that of the comparison solution (3.3.2)	$> 0{,}1$ µg/cm^2

If a clear visual estimation is not possible with the comparison solution, or if, before making the indicator addition, a disturbing self-colouring of the solution occurs, carry out a photometric measurement at a wavelength of 540 nm against the comparison solution.

5.6 Determination of hexavalent chromium content of coloured chromate coatings

5.6.1 Preparation of calibration graph

5.6.1.1 To a series of five 250 ml volumetric flasks, add respectively 0 ml (i.e. the compensation solution), 10 ml, 20 ml, 30 ml and 40 ml of standard potassium dichromate solution (3.9). Add to each flask 100 ml of water and 3 ml of dilute sulfuric acid (3.5). To one flask, add 3 ml of test solution D (3.4) and mix well. Exactly 2 min after the addition of test solution D, add 25 ml of phosphate buffer solution (3.10), dilute to the mark and mix. Repeat this procedure with the other four flasks.

5.6.1.2 Transfer a portion of each solution to an absorption cell and measure the absorbance in the absorptiometer (4.1) or spectrophotometer (4.2). Complete each reading within 25 min of adding test solution D (3.4) as the colour is not stable. Subtract the compensation solution (see 5.6.1.1) from each reading and plot the differences against micrograms of chromium per 250 ml.

5.6.2 Blank test

Carry out a blank test in accordance with 5.6.3 and record the result.

NOTE Prepare the test sample for the blank test as follows: pour 0 ml of standard potassium dichromate solution (3.9) in a flask, add the reagents, and test solution as described in 5.6.1.1.

5.6.3 Determination

5.6.3.1 Cut a test piece measuring about 50 mm × 100 mm from the coated item. Bring to the boil 50 ml of distilled water in a suitable vessel and totally immerse the test specimen in this. Leach for exactly 5 min while the water continues to boil, remove the specimen and rinse over the vessel. Cool the vessel and its contents to room temperature, add 3 ml of dilute sulfuric acid (3.5) and mix. Transfer the contents to a 250 ml volumetric flask. Rinse the vessel twice into the flask with 10 ml to 15 ml of distilled water, add 3 ml of test solution D (3.4) and mix. Exactly 2 min after the addition of test solution D, add 25 ml of phosphate buffer solution (3.10), dilute to the mark and mix.

5.6.3.2 Transfer a portion of the solution to an absorption cell and measure the absorbance in the absorptiometer (4.1) or spectrophotometer (4.2). Complete the reading within 25 min of adding test solution D (3.4) as the colour is not stable. Subtract the blank test reading (see 5.6.2) from the instrument reading and, using the calibration graph (see 5.6.1), convert the result into micrograms per 250 ml.

5.6.3.3 If the reading obtained falls within the portion of the calibration graph below 10 µg, repeat the determination using a larger test piece (1,5× to 2× the dimensions given in 5.6.3.1).

5.6.4 Expression of results

Determine the total surface area of coating on the test specimen, in square centimetres. Divide the hexavalent chromium content, obtained in accordance with 5.6.3, by the surface area of the coating. The hexavalent chromium content shall be expressed in micrograms per square centimetre.

5.7 Determination of total chromium content of coloured chromate coatings

5.7.1 Preparation of calibration graph

Prepare a calibration graph in accordance with 5.6.1.

5.7.2 Blank test

Carry out a blank test in accordance with 5.6.2.

5.7.3 Determination

5.7.3.1 Cut a test piece measuring about 50 mm × 100 mm from the coated item. Heat 25 ml of dilute sulfuric acid (3.5) to 40 °C to 50 °C and pour into a suitable vessel containing the test specimen. Swirl continuously so that all surfaces are exposed to the acid for 10 s to 15 s. Remove the test specimen, and rinse it over the vessel. Dilute to about 175 ml, add about 0,1 g of ammonium persulfate (3.6) and 3 ml of silver nitrate solution (3.8). Then add anti-bumping granules and boil for 30 min. Cool and adjust the pH to 1,5 to 1,8 using about 20 ml of sodium hydroxide solution (3.7). To measure the pH, transfer a drop to the pH paper; do not immerse the paper in the solution. Transfer to a 250 ml one-mark volumetric flask. Rinse the vessel twice into the flask with 10 ml to 15 ml of water, add 3 ml of test solution D (3.4) and mix. Exactly 2 min after the addition of test solution D, add 25 ml of phosphate buffer solution (3.10), dilute to the mark and mix.

WARNING — For health and safety reasons, sodium hydroxide shall not be added directly to sulfuric acid.

5.7.3.2 Transfer a portion of the solution to an absorption cell and measure the absorbance in the absorptiometer (4.1) or spectrophotometer (4.2). Complete the reading within 25 min of adding test solution D (3.4) as the colour is not stable. Subtract the blank test reading (see 5.7.2) from the instrument reading and, using the calibration graph (see 5.7.1), convert the result into micrograms per 250 ml.

5.7.4 Expression of results

Determine the total surface area of coating on the test specimen, in square centimetres. Divide the total chromium content obtained in accordance with 5.7.3 by the surface area of the coating. The total chromium content shall be expressed in micrograms per square centimetre.

5.8 Determination of mass per unit area of both colourless and coloured chromate coatings by gravimetric method

The mass per unit area shall be determined in accordance with ISO 3892. The mass per unit area shall be expressed in milligrams per square centimetre.

5.9 Test for adhesion by abrasion

Test the adhesion of the chromate by lightly rubbing the surface for about 10 strokes with white paper, such as a No. 40 Whatman filter paper[1] or a gritless, soft gum eraser. The adhesion of the coating shall be deemed satisfactory if no more than the faintest stain is visible on the paper and there is no sign of the underlying metal surface due to the removal of the coating.

NOTE This test method is not quantifiable.

5.10 Quality evaluation test of chromate layers on zinc and cadmium surfaces

Carry out the neutral salt spray (fog) test (see References [1] and [2]) to evaluate the quality of chromate layers on zinc and cadmium surfaces.

The time for formation of white corrosion products on chromated cadmium or zinc coatings shall be not less than the values given in ISO 4520.

The requirements of this method are primarily for quality acceptance and for the qualification programme. The duration and results of artificial atmospheric deterioration of coatings for quality control tests may bear little relationship to the service life of the coated article and, therefore, the results obtained are not to be regarded as a direct guide to the corrosion resistance of the tested coatings in all environments where these coatings may be used.

6 Test report

The test report shall contain the following information:

a) a reference to this International Standard (i.e. ISO 3613:2010);

b) detailed information concerning the test method, including the test solutions used;

c) the number of samples tested;

d) the results of the test, including the results of the individual determinations and their mean values;

e) any deviations from the procedures specified;

f) any discrepancy observed during the test;

g) the date of the test and that of the report.

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[1] No. 40 Whatman filter paper is an example of a suitable product available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

Bibliography

[1] ISO 9227, *Corrosion tests in artificial atmosphere — Salt spray tests*

[2] ASTM B117, *Standard Practice for Operating Salt Spray (Fog) Apparatus*

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