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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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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 107, *Metallic and other inorganic coatings,* in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 262, *Metallic and other inorganic coatings, including for corrosion protection and corrosion testing of metals and alloys,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This fourth edition cancels and replaces the third edition (ISO 3613:2010), which has been technically revised. The main changes compared with the previous edition are as follows:

- Table 1 has been revised;
- analysis method described in 6.5 was aligned with the method described in IEC 62321-7-1;
- procedure for the preparation of test solution C 2 in 4.3.2 has been revised and a second standard solution has been added;
- limiting time has been amended in 6.1;
- procedure for testing with test solution C 2 has been revised in 6.5.2;
- description of the calibration of spectrophotometer has been added.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This document 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, as it does not conform to the ISO 2080 designation, and is therefore deprecated.

Chromate conversion coatings are based on a solution containing Cr(VI). Both the process solution and the coating contain hexavalent chromium. The term passivation is nowadays often used for Cr(VI)-free coatings replacing chromate conversion coatings. Products containing Cr(VI) are not allowed within EU and processes using Cr(VI) are strictly regulated.

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

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

1 Scope

This document 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
- chromate coatings that are free from any supplementary coatings, such as oil, water or solvent-based polymers or wax.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

4 Reagents

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

4.1 Test solution A (see 6.2).

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 (ρ = 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 can be losses due to evaporation and the concentration can alter so it is discarded after six months.

4.2 Test solution B (see 6.3).

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.

4.3 Test solution C (see 6.5).

4.3.1 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.

4.3.2 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 0,5 g of 1,5-diphenylcarbazide of analytical reagent grade in 50 ml of acetone of analytical reagent grade. Dilute slowly, while stirring, with 50 ml of distilled water or water of equivalent purity (rapid mixing can result in precipitation of diphenylcarbazide). Keep the solution in a dark glass bottle in the refrigerator. The solution shall be discarded after four weeks or earlier when the solution becomes discoloured.

For the Cr(VI) stock solution, dissolve 0,113 g of $K_2Cr_2O_7$ of analytical reagent grade (dried for 1 h at 100 °C before use) in distilled water or water of equivalent purity and make up to the mark in a 1 000 ml volumetric flask. The solution shall be discarded after nine months.

From this stock solution, prepare two Cr(VI) standard solutions.

For 0,10 µg/ml Cr(VI): 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 0,10 µg of Cr(VI).

For 0,13 µg/ml Cr(VI): Measure 3,3 ml of this solution into a third 1 000 ml volumetric flask and make up to the mark. 1 ml of this standard solution contains 0,13 µg of Cr(VI).

For the preparation of the comparison solution for 0,10 µg/cm^2 Cr(VI), add 1 ml of orthophosphoric acid and 1 ml of diphenylcarbazide solution to 50 ml of the standard Cr(VI) solution solution with 0,10 µg/ml Cr(VI) and mix thoroughly. Then add 2 ml of the diphenylcarbazide solution and mix. Allow the solution to stand for 10 min for the colour reaction to be completed.

For the preparation of the comparison solution for 0,13 µg/cm^2 Cr(VI), add 1 ml of orthophosphoric acid to 50 ml of the standard Cr(VI) solution with 0,13 µg/ml Cr(VI) and mix thoroughly. Then add 2 ml of the diphenylcarbazide solution and mix. Allow the solution to stand for 10 min for the colour reaction to be completed.

4.4 Test solution D (see 6.6 and 6.7).

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.

4.5 Sulfuric acid, diluted 1 + 3.

Slowly add one volume of concentrated sulfuric acid (ρ = 1,84 g/cm^3) to three volumes of water.

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

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

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

4.9 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.

4.10 Phosphate buffer solution.

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

5 Apparatus

Use normal laboratory apparatus and the following.

Glassware shall be of grade A. Pipettes shall be calibrated.

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. Adequate cleanliness should be demonstrated through the analysis of method blanks.

5.1 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.

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

5.3 Analytical balance, with an accuracy of 0,10 mg.

6 Test methods

6.1 General

The test surface, prior to the following tests, shall be free of all contaminants, fingerprints 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 the following are given in 6.2 to 6.7:

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;

d) the determination of total chromium content.

The test methods for the following are given in 6.8, 6.9 and 6.10, respectively:

e) the determination of mass per unit area of chromate conversion coatings;

f) adhesion by abrasion;

g) the evaluation of the quality of chromate layer.

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 almost all tests (6.2 to 6.4, 6.5.2 and 6.6 to 6.10);
- a minimum of 5 d after the application of the chromate conversion coating for the test specified in 6.5.3 to 6.5.5;
- a maximum of 3 d for the tests specified in 6.2 to 6.4 and 6.5.2;
- a maximum of 30 d for the tests specified in 6.6 and 6.7. It could be recommendable to apply this limit also to the test specified in 6.5.3 to 6.5.5.

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

Apply one drop of test solution A (4.1) 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 a chromate film.

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

Place one drop of test solution B (4.2) 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 process. 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 6.10). They will show a black stain in less than 60 s on zinc and less than 5 s on cadmium.

6.4 Test for the presence of a colourless chromate coating on 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 a chromate conversion coating.

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

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

6.5.1 General

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

6.5.2 Test method employing test solution C 1

Place one to five drops of test solution C 1 (4.3.1) 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, e.g. on drying. For comparison purposes, test an untreated surface similarly.

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

6.5.3 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).

The sample to be tested should have a surface area of (50 ± 5) cm^2. For fasteners or samples with a smaller surface area, use a suitable number of samples to obtain the total required surface area. In cases where obtaining a total surface area of (50 ± 5) cm^2 is not possible, a reduced total sample surface area may be used by reducing the water extraction volume, while maintaining the same surface area to extraction volume ratio (1 cm^2:1 ml). A minimum surface area of 25 cm^2 is recommended. Similarly, a higher sample surface area can be used by keeping the same ratio. The type of adjustment shall be recorded in the final report. Remove any sealing, such as paint or wax, etc., by scraping the surface. The resulting abrasion shall also be analysed.

Fill 50 ml of distilled water or water of equivalent purity with anti-bumping granules into a beaker with volume graduation, cover it with a watch glass and bring it to boiling temperature. Let the water boil for at least 10 min to deoxygenate it. Then totally immerse the sample into the boiling water and cover the beaker again with a watch glass. Extract the sample for (10 ± 0,5) min once boiling is resumed. If necessary, add water to ensure that the sample is totally submerged during the extraction. Remove the sample and allow the beaker content to cool to ambient temperature. The solution should be colourless and free of precipitate. Adjust the volume to 50 ml. If necessary, filter the solution through a 0,45 µm membrane filter into a dry beaker. Make up the solution to the mark with water (see Clause 4) or reduce it to the mark by boiling. Add 1 ml of orthophosphoric acid (4.3.2) per 50 ml volume and mix well. Pour 25 ml of the solution using a graduated cylinder into another dry beaker. Add 1 ml of diphenylcarbazide solution (4.3.2) and mix well. Allow the solution to stand for 10 min for the colour reaction to be completed. The remaining portion of the extract will serve as the blank.

If there is a colour interference (e.g. from a coating dye), a correction against the blank shall be performed. Transfer a portion of the sample solution to an absorption cell and measure the absorbance at 540 nm against the blank with the spectrophotometer (5.2). Make three measurements and take the average as the final absorbance of the sample. In some cases, depending on the type of spectrophotometer used, the correction for the blank has to be made manually in the collected data.

Measure the absorbance of the comparison solution for 0,10 µg/cm^2 Cr(VI) (4.3.2) three times as described above. Take the average of three measurements as the final absorbance of that comparison solution.

Measure the absorbance of the comparison solution for 0,13 µg/cm^2 Cr(VI) (4.3.2) three times as described above. Take the average of three measurements as the final absorbance of that comparison solution.

6.5.4 Expression of results

The results are expressed as shown in Table 1.

Table 1 — Comparison of solutions

Observation	Resulting Cr(VI) concentration in coating	Definition
The colour intensity of the sample solution (see 6.5.3) is lower than that of the comparison solution for 0,10 µg/cm^2 Cr(VI) (4.3.2).	<0,10 µg/cm^2	The sample is free from Cr(VI).
The colour intensity of the sample solution (see 6.5.3) is not lower than that of the comparison solution for 0,10 µg/cm^2 Cr(VI), but not higher than that of the comparison solution for 0,13 µg/cm^2 Cr(VI).	≥0,10 µg/cm^2 and ≤0,13 µg/cm^2	The result is inconclusive. Unavoidable coating variations can influence the determination. If additional samples are available, perform a total of three trials to increase the sampling surface area. Use the average of the three trials for the final determination.
The colour intensity of the sample solution (6.5.2) is higher than that of the comparison solution for 0,13 µg/cm^2 Cr(VI) (4.3.2).	>0,13 µg/cm^2	The sample contains Cr(VI).

In cases where the sample colour after the colorimetric reaction is significantly more intense than the colour of the comparison solution for 0,13 µg/cm^2 Cr(VI) (4.3.2) such that the result can be clearly determined as positive for Cr(VI), measurement with the spectrophotometer is not necessary. However, the report shall state that the result is significantly above 0,13 µg/cm^2 Cr(VI) based on visual observation and no colorimetric measurement was performed. A colorimetric measurement shall always be performed if the Cr(VI) is not clearly above 0,13 µg/cm^2.

6.5.5 Calibration of spectrophotometer

The spectrophotometer shall be calibrated using a blank and three standard solutions at a minimum. The standard solution concentrations shall bracket 0,10 µg/ml Cr(VI) and 0,13 µg/ml Cr(VI).

Zero the spectrophotometer with the 0,0 µg/ml blank standard and save this solution to re-zero the instrument before reading samples and standards.

Read the standard solutions. Construct a calibration curve and determine a line equation by plotting absorbance values against µg/ml of Cr(VI) for each standard including the 0,0 µg/ml standard. The calibration curve (linear fit with zero intercept) shall have a correlation coefficient ≥0,995 or a new curve shall be built.

Calibration curves can be used for up to one month from initial generation.

Colorimetric instruments designed specifically for hexavalent chromium detection at 540 nm can have a permanent calibration provided by the manufacturer and no further calibration is needed. Refer to the manufacturer's instructions to ensure that the instrument is functioning properly and its working range is appropriate for this analysis.

Regardless of the instrument type, a performance verification using the two comparison solutions (see 4.3.2) shall be carried out prior to sample measurements and at the end of each sample sequence to ensure the instrument is functioning properly.

In the event that either of the comparison solutions measured prior to sample measurements result in concentrations that differ from the expected values (0,10 µg/ml and 0,13 µg/ml) by more than 15 %, the calibration shall be re-measured.

In the event that either of the comparison solutions measured at the end of the instrumental sequence result in concentrations that differ from the expected values by more than 15 %, the calibration and all of the samples in the sequence shall be re-measured.

6.6 Determination of hexavalent chromium content of coloured chromate coatings

6.6.1 Preparation of calibration graph

6.6.1.1 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 (4.9). Add to each flask 100 ml of water and 3 ml of dilute sulfuric acid (4.5). To one flask, add 3 ml of test solution D (4.4) and mix well. Exactly 2 min after the addition of test solution D, add 25 ml of phosphate buffer solution (4.10), dilute to the mark and mix. Repeat this procedure with the other four flasks.

6.6.1.2 Transfer a portion of each solution to an absorption cell and measure the absorbance in the absorptiometer (5.1) or spectrophotometer (5.2). Complete each reading within 25 min of adding test solution D (4.4) as the colour is not stable. Subtract the compensation solution (see 6.6.1.1) from each reading and plot the differences against micrograms of chromium per 250 ml.

6.6.2 Blank test

Carry out a blank test in accordance with 6.6.3 and record the result.

Prepare the test sample for the blank test as follows: pour 0 ml of standard potassium dichromate solution (4.9) in a flask, and add the reagents and test solution as described in 6.6.1.1.

6.6.3 Determination

6.6.3.1 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 (4.5) 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 (4.4) and mix. Exactly 2 min after the addition of test solution D, add 25 ml of phosphate buffer solution (4.10), dilute to the mark and mix.

6.6.3.2 Transfer a portion of the solution to an absorption cell and measure the absorbance in the absorptiometer (5.1) or spectrophotometer (5.2). Complete the reading within 25 min of adding test solution D (4.4) as the colour is not stable. Subtract the blank test reading (see 6.6.2) from the instrument reading and, using the calibration graph (see 6.6.1), convert the result into micrograms per 250 ml.

6.6.3.3 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 times to 2 times the dimensions given in 6.6.3.1).

6.6.4 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 6.6.3, by the surface area of the coating. The hexavalent chromium content shall be expressed in micrograms per square centimetre.