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# International Standard



# 4539

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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

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## Electrodeposited chromium coatings — Electrolytic corrosion testing (EC test)

*Revêtements électrolytiques de chrome — Essai de corrosion électrolytique (Essai EC)*

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**Descriptors** : metal coatings, electrodeposited coatings, chromium coatings, tests, corrosion tests, test equipment.

## Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 4539 was developed by Technical Committee ISO/TC 107, *Metallic and other non-organic coatings*, and was circulated to the member bodies in September 1978.

It has been approved by the member bodies of the following countries :

Bulgaria	Italy	South Africa, Rep. of
Czechoslovakia	Japan	Spain
France	Korea, Rep. of	Sweden
Germany, F.R.	Libyan Arab Jamahiriya	Switzerland
Hungary	Mexico	USA
India	New Zealand	USSR
Ireland	Poland	
Israel	Romania	

The member body of the following country expressed disapproval of the document on technical grounds :

United Kingdom

# Electrodeposited chromium coatings — Electrolytic corrosion testing (EC test)

## 1 Scope and field of application

**1.1** This International Standard specifies a rapid and accurate method for evaluating the corrosion resistance characteristics of copper-nickel-chromium and nickel-chromium electrodeposits on steel or zinc-base die castings designed for outdoor service. It does not prescribe exposure periods to be used for a specific product, nor the interpretation to be given to the results.

**1.2** The suitability of this test and correlation of results with outdoor service experience should be determined before it is specified for coating systems or materials other than those described in 1.1.

**1.3** Test conditions are provided<sup>[1]</sup> to electrolytically dissolve the underlying coatings of nickel through discontinuities in the chromium overlay (whilst not attacking the chromium) at such a rate that electrolysis for 2 min produces about the same extent of corrosion as does 1 year of service<sup>[2] [3]</sup>. The same acceleration of corrosion in the EC test over the rate in outdoor service is maintained on specimens where the exposed nickel area increases rapidly (such as on those with high discontinuity density) by changing from constant potential control to constant current control when a predetermined current density is attained on the specimen surface.

## 2 Reagents

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

### 2.1 Electrolytes

**2.1.1 Electrolyte A**, for use when testing either zinc or steel basis metal specimens where corrosion sites are to be identified in a separate indicator solution.

Bath composition per litre :

Sodium nitrate (NaNO <sub>3</sub> )	10,0 g
Sodium chloride (NaCl)	1,3 g
Nitric acid (HNO <sub>3</sub> ), concentrated ( $\rho = 1,42$ g/ml)	5,0 ml
Water (distilled)	to make 1 litre

Bath life : 900 C/l.

**2.1.2 Electrolyte B**, for use when testing steel basis metal specimens where corrosion sites are to be identified in the electrolyte. (See clause 6.)

Bath composition per litre :

Sodium nitrate (NaNO <sub>3</sub> )	10,0 g
Sodium chloride (NaCl)	1,0 g
Nitric acid (HNO <sub>3</sub> ), concentrated ( $\rho = 1,4$ g/ml)	5,0 ml
1,10-Phenanthroline hydrochloride	1,0 g
Water (distilled)	to make 1 litre

Bath life : 200 C/l or until the colour of the solution masks the colour originating at a corrosion site.

### 2.2 Indicator solutions

**2.2.1 Solution C**, used to identify corrosion sites on zinc basis metal specimens after electrolysis.

Bath composition per litre :

Acetic acid (CH <sub>3</sub> COOH), glacial	2 ml
Quinoline (C <sub>9</sub> H <sub>7</sub> N)	8 ml
Water (distilled)	to make 1 litre

Bath life : until the turbidity of the solution masks the cloudy streamer which originates at a corrosion site.

**2.2.2 Solution D**, used to identify corrosion sites on steel basis metal specimens after electrolysis.

Bath composition per litre :

Acetic acid (CH <sub>3</sub> COOH), glacial	2 ml
Potassium thiocyanate (KCNS)	3 g
Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> ), 30 % (m/m)	3 ml
Water (distilled)	to make 1 litre

Bath life : until the colour of the solution masks the colour originating at a corrosion site.

### 3 Apparatus (see figure 1 and the annex)

**3.1 Potentiostat**, capable of regulating an anode potential within  $\pm 0,002$  V, having a minimum capability of  $3,3 \text{ mA/cm}^2$  ( $33 \text{ A/m}^2$ ) of surface being tested.

**3.2 Electrolytic cell**, of suitable size to contain sufficient electrolyte to cover the specimen (anode), the cathode and the reference electrode. If used both for electrolysis and for indication of corrosion of electroplated steel specimens with an electrolyte containing an indicator suitable for steel (see 2.1.2), the cell should have flat transparent sides and bottom with provision for uniformly illuminating the bottom.

**3.3 Indicator solution tank**, having flat transparent sides and bottom with provision for uniformly illuminating the bottom when steel basis metal specimens are tested and for illuminating the sides and blacking out the bottom when zinc basis metal specimens are tested.

**3.4 Cathode of insoluble metal**, such as platinized tantalum of sufficient area to permit an adequate anode current density.

**3.5 Saturated calomel electrode (SCE)**, with a leak rate of about  $8 \times 10^{-4} \text{ mm}^3/\text{s}$  ( $3 \text{ mm}^3/\text{h}$ ), for use as a reference electrode.

**3.6 Glass Luggin capillary**,<sup>[4]</sup> with a tip diameter of about 1 mm inside diameter and 2 mm outside diameter, sealed onto a glass tube having an inner diameter sufficiently large to allow introduction of the SCE (see 3.5).

**3.7 Electric timer**, for reading total current-on time to 0,1 min (6 s).

**3.8 C-clamp**, with a hardened, pointed bolt to ensure positive electrical connection to the specimen.

**3.9 Masking materials**, (paint or tape), for applying to surfaces which will be immersed in the electrolyte, but which are not to be tested (such as cut edges and reverse side of specimen).

### 4 Operating conditions

**4.1** Maximum current density of specimen :  $3,3 \text{ mA/cm}^2$ .

**4.2** Specimen potential with respect to the SCE :  $+ 0,3 \text{ V}$ .

NOTE — Lower as necessary to maintain current density of specimen. (See also note after 5.8.)

**4.3** Current cycle : 1 min on, and approximately 2 min off.

NOTE — Where less precise measurements are adequate, the cycle may be 2 min on, and approximately 2 min off.

### 5 Procedure

**5.1** Select a portion of the specimen to be tested. If necessary, cut the specimen to isolate the desired portion.

**5.2** Cover the reverse side, edges, and the portion of the front surface otherwise exposed to the electrolyte-air interface with an insulating paint or tape.

**5.3** Determine the surface area to be tested, and calculate the maximum value of the current, based on  $3,3 \text{ mA/cm}^2$ .

**5.4** Clean the test area by lightly scrubbing with magnesium oxide (MgO) slurry on a wad of cotton, until the surface is free of water breaks.

**5.5** Rinse thoroughly in clean running water.

**5.6** Place the specimen in the electrolytic cell (see figure 1) with the C-clamp attached. Fill the cell to the required height with electrolyte A (see 2.1.1). Locate the tip of the calomel electrode within 2 mm of the test specimen. Make the necessary connections. Adjust the potentiostat controls so that the specimen (anode) potential is  $+ 0,3 \text{ V}$ , with respect to the SCE (see 4.2).

**5.7** Start electrolysis and the timer simultaneously. Record the current (see figure 2).

**5.8** Continue electrolysis for  $60 \pm 2 \text{ s}$  (see 4.3).

NOTE — The current density at the start of the electrolysis is dependent upon the original area of nickel exposed through pores or cracks in the chromium layer. The relative amount of chromium discontinuity density can be immediately determined by comparing the initial current density of the specimen with that known for good specimens, although significant unpredictable errors with low values of discontinuity can be expected because the chromium surface also conducts a small ( $0,001 \text{ mA/cm}^2$ ), current when there is an anode potential of  $+ 0,3 \text{ V}$  with respect to the SCE. If at any time the current density on the specimen tends to exceed  $3,3 \text{ mA/cm}^2$ , the applied potential should be reduced so as to maintain this value. If a specimen is subjected to an anodic current density sufficiently high to oxidize chromium anodically to  $\text{Cr}^{6+}$  ion (evidenced by its characteristic orange colour), the test is invalidated, and the specimen and electrolyte should be discarded.

**5.9** Stop electrolysis and the timer.

**5.10** Remove the specimen, and flush it with clean running water.

**5.11** Transfer zinc basis metal specimens to indicator solution C (see 2.2.1), and steel basis metal specimens to indicator solution D (see 2.2.2).

**5.12** Observe the surface for red streamers in the case of steel basis metal, or white precipitate streamers in the case of zinc basis metal exuding in either case from one or more corrosion sites. This indicates penetration of the coating and corrosion of the basis metal.

NOTE — If a permanent visual record of the condition of a specimen is

desired, basis metal corrosion sites can be redeveloped in any accepted accelerated corrosion test such as the CASS test<sup>[5]</sup>, by a 1 to 4 h exposure.

**5.13** Remove the specimen, rinse in clean running water, and reimmerse in electrolyte A (see 2.1.1).

**5.14** Repeat steps 5.6 to 5.13 until the desired time of electrolysis has elapsed.

NOTE — The amount of electrolysis required is determined by the amount of simulated service desired; thus an electrolysis time of 2 min is equivalent to approximately a 1 year exposure in Detroit, Michigan, USA. The extent of any corrosion may be determined by either of the following approaches :

- a) Density, radii, and penetration of pits in the nickel deposits may be measured easily with an interference microscope after stripping the chromium.
- b) Complete penetration to the metal substrate can be signalled by the appropriate indicator solution (see 2.2.1 or 2.2.2).

**5.15** Stop electrolysis and the timer, and record the total current-on time.

## 6 Alternative procedure for steel basis specimens only

NOTE — The periodic operation of moving specimens from the electrolysis cell to the indicator solution may be eliminated by using electrolyte B (see 2.1.2) which incorporates an indicator. Although this electrolyte is more costly and has a shorter life than electrolyte A, it is frequently preferred, especially where small specimens are to be tested.

**6.1** Repeat the steps 5.1 to 5.9.

**6.2** Stir the electrolyte briefly, and keep the specimen in the electrolyte for 2 min.

**6.3** Observe the surface of the specimen for red streamers, indicating basis metal corrosion.

**6.4** Repeat steps 5.8, 5.9, 6.2 and 6.3 until the required time of electrolysis has elapsed (see note after 5.14).

**6.5** Stop electrolysis and timer, and record total current-on time.

## 7 Test report

The test report should contain the following information :

**7.1** The type and identification of the product tested.

**7.2** A reference to this International Standard.

**7.3** Result of the test.

**7.4** Whether clause 5 or 6 procedure used.

**7.5** Any deviation, agreed or otherwise, from the procedure described.

**7.6** Date of the test.

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## Annex

### Notes on apparatus

#### A.1 Potentiostat (constant potential controller)

The potentiostat selected for EC testing should be capable of maintaining the applied potential within  $\pm 2$  mV. It should have an "operate" and "stand-by" circuit to facilitate current interruption electrolysis without risk of current surge damage to the instrument. It also should have a multi-range milliammeter to allow maximum current limitations of the test to be controlled.

#### A.2 Reference electrode

The reference electrode should be a saturated calomel, half-cell fibre-tip type. This low leakage type is recommended to reduce the diffusion of  $\text{Hg}^+$  ions into the EC electrolyte.

#### A.3 Test cell

The size and shape of the electroplated specimen will determine the dimensions of the electrolytic cell. It should be constructed of, or lined with, non-conductive material. For tests requiring observations during electrolysis (indicator method), a transparent material is recommended.

#### A.4 Cell illuminator (optional)

Adequate lighting facilitates the observation of deposit penetrations (indicator method) during and/or after electrolysis. A satisfactory means of providing desired illumination is achieved by setting the cell over a uniformly illuminated translucent panel. Fluorescent lamps can be used to minimize local heating.

#### A.5 Agitation

A simple, chemically and electrically inert stirring rod or paddle is adequate.

#### A.6 Timing device

Though some tests have been conducted with a stopwatch and other laboratory timers, a resettable electric time meter is preferred. It should be connected in the main power circuit of the potentiostat with a common switch activating both instruments.

#### A.7 Microscope

An interference microscope can be made by attaching an interference objective to an ordinary upright microscope. The microscope should also be equipped with a calibrated fine focus knob and an eyepiece with a calibrated (bifilar) graticule. The light source can be a tungsten lamp with provision for intensity adjustments.

#### A.8 Masking tape or paint

Insulating tape or paint can be used to isolate the test area and to insulate conductive, non-significant areas from the electrochemical reaction of the test. Chemically resistant tape is recommended. Masking lacquers used in electroplating operations may also be satisfactory.

#### A.9 Wires and clips

All lead wires should be insulated and of adequate size to accommodate the current drawn by the anode. Copper wire (1,6 mm diameter) is satisfactory up to the maximum current limit of the potentiostat (15A). Clips and contacts should be of the positive screw type to ensure low resistance connections.

#### A.10 Cathode

Platinum-coated expanded tantalum or titanium sheet, with a 1 : 1 anode/cathode size ratio, is recommended. A variety of mesh sizes is available.