INTERNATIONAL STANDARD

ISO 2177

Third edition
2003-03-15

Metallic coatings — Measurement of coating thickness — Coulometric method by anodic dissolution

Revêtements métalliques — Mesurage de l'épaisseur — Méthode coulométrique par dissolution anodique

Reference number
ISO 2177:2003(E)

PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

© ISO 2003

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Copyright International Organization for Standardization
Provided by IHS under license with ISO
No reproduction or networking permitted without license from IHS

Not for Resale

Contents

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 2177 was prepared by Technical Committee ISO/TC 107, *Metallic and other inorganic coatings*, Subcommittee SC 2, *Test methods*.

This third edition cancels and replaces the second edition (ISO 2177:1985), which has been technically revised.

INTERNATIONAL STANDARD **ISO 2177:2003(E)**

Metallic coatings — Measurement of coating thickness — Coulometric method by anodic dissolution

1 Scope

This International Standard describes a coulometric method, by anodic dissolution, for measuring the thickness of metallic coatings. It is only applicable to conductive coatings.

Typical combinations of coatings and substrates that can be tested by this method are given in Table 1. Other combinations may be tested with electrolytes in current use (see Annex A), or new electrolytes may be developed for them but, in both cases, it is necessary to verify the suitability of the complete system.

This International Standard is also applicable to multi-layer systems, e.g Cu-Ni-Cr (see also 8.5).

It may be used to measure the thickness of coatings applied by various means, if due account is taken of special features such as the presence of an alloy layer. In some cases, the presence and thickness of diffusion layers can also be measured. It can also be used to measure the thickness of coatings on cylindrical specimens and wires (see 8.7).

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 2064:1996, *Metallic and other inorganic coatings — Definitions and conventions concerning the measurement of thickness*

ISO 2080, *Surface treatment, metallic and other inorganic coatings — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 2064 and ISO 2080 as well as the following apply.

3.1
measuring area

area of the significant surface over which a single measurement is made

NOTE The measuring area for this method is the area enclosed by the sealing ring of the cell.

4 Principle

A well-defined area of the coating is subjected to anodic dissolution using a suitable electrolyte. The virtually complete dissolution of the coating is detected by a change in cell voltage. The coating thickness is calculated from the quantity of electricity used, in coulombs, which in turn may be calculated from:

a) the time interval between the start and the end of the test, if it is conducted at constant current density;

b) the integrated quantity of electricity used in dissolving the coatings.

5 Instrumentation

5.1 Suitable instruments can be constructed from readily available components but proprietary instruments are usually used (see Annex B).

5.2 Proprietary direct-reading instruments are available for use with electrolytes recommended by the manufacturer. Other instruments record the quantity of electricity, in coulombs, used in dissolving the coating from the measuring area (see 3.1), usually in arbitrary units, from which the thickness is calculated using factors or tables.

With direct reading instruments, the calculation of thickness from current density is made electronically.

5.3 The performance of the instrument shall be checked using specimens of known coating thickness. If the instrument readings agree to within ± 5 % of the known thicknesses of the specimens, the instrument may be used without further adjustment; otherwise, the cause of the discrepancy shall be removed. However, proprietary instruments shall always be calibrated in accordance with the manufacturer's instructions.

Suitable specimens of known coating thickness shall consist of the same type of coating and substrate as the specimen to be measured, and they shall have an accuracy of 5 % or better. In measuring alloy coatings, the use of correct specimens is of particular importance.

6 Electrolyte

The electrolyte shall have a known, adequate shelf-life and shall be such that:

a) there is no reaction with the coating metal in the absence of an impressed flow of current;

b) the coating dissolves anodically at an efficiency as close to 100 % as possible;

c) a detectable change in electrode potential occurs as the coating is penetrated and an increasing area of substrate is exposed;

d) the test area exposed in the test cell is completely wetted.

The electrolyte shall be chosen with reference to the coating and substrate materials, the current density and electrolyte circulation within the test cell.

NOTE Typical electrolytes that have been found satisfactory for use with one type of test apparatus for testing various electrodeposited coatings on specific substrates are described in Annex A.

For proprietary instruments, the electrolytes shall normally be chosen on the recommendations of the manufacturer.

Table 1 — Typical combinations of coatings and substrates that can be tested by the coulometric method

Coating	Substrate (underlying material)							
	Al [a]	**Cu and Cu alloys**	**Ni**	**Ni-Co-Fe alloys**	**Ag**	**Steel**	**Zn**	**Non-metals**
Cd	×	×	×	—	—	×	—	×
Cr	×	×	×	—	—	×	—	×
Cu	×	Only on brass and copper-beryllium	×	—	—	×	×	×
Au	×	×	×	×	×	×	—	—
Pb	×	×	×	×	×	×		×
Ni	×	×	—	×	—	×	—	×
Ni, autocatalytic [b]	×	×	×	×	—	×	—	×
Ag	×	×	×	—	—	×	—	×
Sn	×	×	×	—	—	×	—	×
Sn-Ni alloys	—	×	—	—	—	×	—	×
Sn-Pb alloys [c]	×	×	×	×	—	×	—	×
Zn	×	×	×	—	—	×	—	×

[a] The detection of the change in the cell voltage may be difficult with some aluminium alloys.

[b] The coulometric method can only be used if the phosphorus or boron contents of these coatings are within certain limits.

[c] The method is sensitive to alloy composition.

NOTE See Clause 5 for instrumentation.

7 Factors affecting the measuring accuracy

7.1 Coating thickness

Generally, the accuracy is lower than optimum for coating thicknesses greater than 50 µm and less than 0,2 µm, unless special equipment is used.

With coatings thicker than 50 µm, there may be an appreciable amount of bevelling or undercutting as the anodic dissolution proceeds. The amount of bevelling is largely dependent on the method employed for stirring the electrolyte. Undercutting may be eliminated, or reduced, by increasing the rate of dissolution, i.e. by increasing the current density used in the test.

7.2 Current variation

For instrumentation using the constant-current and time-measuring technique, current variation causes errors. For instruments using a current-time integrator, too large a change in current may change the anode current efficiency and interfere with the end-point thus causing an error.

7.3 Area variation

The accuracy of the thickness measurement will be no better than the accuracy to which the measuring area is known. Area variations due to gasket wear, gasket pressure, etc., may lead to measurement errors. Much greater accuracy can be obtained if the electrolytic cells are so designed that sealing rings consistently give well defined measuring areas. In some cases it may be advantageous to measure the area after it has been de-plated and compensate accordingly.

NOTE Error due to variations of the measuring area may, in some instances, be minimized by modifying the instrument calibration using coating thickness calibration standards. Such standards should create similar test conditions to those during actual tests, particularly if testing curved surfaces.

7.4 Agitation (if required)

Inadequate agitation and over-agitation can cause a false end-point.

7.5 Alloy layer between coating and substrate

The measurement of coating thickness by the coulometric method assumes implicitly that a sharply defined interface exists between the coating and the substrate. If an alloy layer exists between the coating and the substrate as, for example, in the case of coatings applied by hot dipping, the coulometric end-point can occur at some point within the alloy later, thus giving falsely high values for the thickness of the unalloyed coatings. See B.1.2.

NOTE It is possible to use a potential recording chart recorder to detect the potential step where the alloy commences and also when the pure substrate is reached by the dissolution process.

7.6 Purity of coatings

Materials that co-deposit with a coating metal (including alloying metals) can change the effective electrochemical equivalent of the coating metal, the anode current efficiency, and the coating density.

7.7 Condition of test surface

Oil, grease, paint, corrosion products, polishing ingredients, conversion coatings, passivity of nickel coatings, etc., can interfere with the test.

7.8 Density of coating material

Because the coulometric method measures intrinsically mass per unit area, variations in density from the normal density of the coating metal will cause corresponding variations in linear thickness measurements. Normal variations of the composition of an alloy result in small, but significant changes in alloy density and its electrochemical equivalent.

7.9 Cleanliness of the cell

Deposition of metal can take place on the cathode in some electrolytes. This deposit can alter the cell voltages or block the cell aperture. It is, therefore, essential to keep the cathode clean.

7.10 Cleanliness of electrical connections

In the case of instruments other than the constant current type, if the electrical connections are not clean, the current/potential relationship will be disturbed and false end-points obtained.

7.11 Calibration standards (if used)

Measurements made using calibration standards are subject to the additional error of the standards. If the thickness of alloy coatings is being determined, it is usually necessary to use coating standards and to test them using the same procedure.

NOTE The coating of the standards might not be similar to that being tested, e.g. zinc produced by an acid and by an alkali electroplating bath.

7.12 Non-uniform dissolution

If the rate of dissolution is not uniform over the measuring area, a premature end-point can be obtained, and yield falsely low results. Hence, the surface shall be examined after the test to verify that most of the coating has dissolved. On some substrates however, a visible, but insignificant, portion of the coating may remain.

The presence of other material in the coating, the roughness of the coating surface and interface and the presence of porosity in the coating can cause fluctuation of the cell voltage. Such fluctuations can prematurely affect the end-point.

8 Procedure

8.1 General

If commercial equipment is used, follow the manufacturer's instructions with respect to the operating procedure for measurement, the electrolytes and, if necessary, calibration (see 5.3). Appropriate attention shall be given to the factors listed in Clause 7.

NOTE If using instruments that require a pre-set voltage, it should be noted that the actual value is dependent on the particular metallic coating, current density, electrolyte concentration and temperature and circuit resistance, e.g. lead-out connections. For these reasons, it is considered advisable to first perform an evaluation test.

8.2 Preparation of test surface

The test surface (see 7.7) shall be cleaned immediately prior to beginning the test.

NOTE It may be necessary to activate the test surface by mechanical or chemical means, but care should then be taken to avoid removal of metal.

8.3 Cell application

Press the electrolytic cell, fitted with its flexible sealing ring, on to the coating so that a known area is exposed to the test electrolyte. If the cell body is metallic, e.g. stainless steel, it normally forms the cell cathode; if not, insert a suitable cathode (incorporated in some instruments as part of the electrolyte agitation mechanism).

8.4 Electrolysis

The electrolyte in contact with the surface being de-plated shall be continually replenished using the most efficient agitation possible. The agitation shall commence prior to the beginning of the test.

NOTE While simple stirring can be adequate for large areas, it is of little use for areas of 3 mm^2 or less; hence pulse or pumped agitation should be used. Ultrasonic agitation is also a possibility.

Make the connections, and operate the agitator as appropriate. Continue electrolysis until dissolution of the coating is complete, as indicated by a change in the anode potential or cell voltage, or by the operation of the automatic cut-out.

8.5 Undercoats

When one or more undercoats are to be measured, after measuring the top coating ensure that the top coat has first been completely removed from the whole of the measuring area. Remove the electrolyte from the cell using a suitable suction device, and thoroughly rinse out the cell with distilled or de-mineralized water.

Do not disturb the cell at any time during these operations. Abandon the test if the slightest displacement has occurred.

Reset the instrument controls for the next coating, introduce the appropriate electrolyte and continue the test as before.

8.6 Examination after test

After completion of the test(s), remove the electrolyte from the cell, rinse out with water, lift off the cell and examine the specimen to ensure that the removal of the coating is complete over the area enclosed by the seal (see 7.12).

8.7 Coatings on cylindrical specimens

If the surface area is too small to use the normal cell with a flexible gasket, replace the cell by an electrolyte container and an appropriate holding device, using an agitator if necessary. This device shall be adjustable and shall be pre-set to allow a known length of specimen to be immersed. For direct reading instruments, especially those with alternative cell sizes, calculate the length of the specimen to be immersed so that the same known surface area is presented to the cathode as for a test cell.

NOTE 1 In the majority of applications, the same electrolyte can be used, but, in order to obtain the optimum instrument sensitivity and accuracy, the operating conditions might have to be modified, e.g., the cut-off voltage and deplating current.

NOTE 2 An exact de-plating area is necessary for accuracy and the main source of error is due to the meniscus and current field at the electrolyte surface. In the case of large diameter cylinders, e.g., wires, the immersed cylinder end should be shielded from the current and electrolyte. The area of any exposed end should not exceed 2 % of the whole area.

9 Expression of results

The coating thickness, d, in micrometres, is given by the equation:

$$d = 100k \times \frac{QE}{A\rho} \quad (1)$$

where

k is the current efficiency of the dissolution process (equal to 100 in the case of 100 % efficiency);

Q is the quantity of electricity, in coulombs, passed in dissolving the coating; if an integrating meter is not used, calculate Q from equation (2);

E is the electrochemical equivalent, in grams per coulomb, of the coating metal for the conditions of the test;

A is the area, in square centimetres, from which the coating is dissolved, i.e. the measuring area;

ρ is the density, in grams per cubic centimetre, of the coating.

$$Q = It \quad (2)$$

where

I is the current, in amperes;

t is the test duration, in seconds.

The coating thickness, d, may also be calculated from the following equation:

$$d = XQ \tag{3}$$

where X is a constant for a given metal coating, electolyte and cell.

NOTE 1 The value of X can either be calculated theoretically from the area of the test specimen exposed by the sealing ring, the efficiency of anodic dissolution (usually 100 %) and the electrochemical equivalent and density of the coating metal, or be determined experimentally by measuring a coating of known thickness.

NOTE 2 With most commercial instruments, the thickness is either read directly from the instrument or the instrument reading is converted to thickness by applying a factor appropriate to the measuring area exposed by the cell and the coating metal.

10 Measurement uncertainty

The test equipment and the procedure shall be such that the coating thickness can be measured to within 10 % of its true thickness.

11 Test report

The test report shall include the following information:

a) reference to this document, i.e. ISO 2177;

b) identity of the test specimen;

c) area, in square centimetres, over which the measurements were made;

d) location of the reference area;

e) location(s) on the coated item at which the tests were carried out;

f) identity of the electrolyte used;

g) results of the test, indicating:

    1) measured thickness, in micrometres, at each area at which the tests were carried out

    2) number of measurements averaged for each reported measurement;

h) name of the operator and testing laboratory;

i) date of test;

j) any deviation from the method specified;

k) any factor that may have influenced the result;

l) identity of the instrument used.

Annex A
(informative)

Typical electrolytes

A.1 General

Although it is possible to use higher current densities with some proprietary electrolytes (and possibly with some of the electrolytes listed in this annex), the following electrolytes (see A.2 to A.18) were formulated to give substantially 100 % anodic efficiency with current densities ranging from 100 mA/cm^2 to 400 mA/cm^2. However, a few electrolytes were found only to be suitable when used towards the lower or upper ends of this current density range and these electrolytes are marked with an asterisk (*).

These electrolytes dissolve the metallic coatings at substantially 100 % anodic efficiency. Therefore, the thickness, d, in micrometres, can be calculated with satisfactory accuracy from the equation

$$d = 10\ 000 \times \frac{QE}{A\rho} \qquad \text{(A.1)}$$

or from instrument factors calculated from this expression. See Clause 9 for definitions of the symbols.

NOTE 1 Both direct calculation and use of calibration standards have inherent errors that should be considered; e.g., an error in the diameter of the test cell of 3 % will give 9 % error in measurement.

The solutions given in A.2 to A.5 should preferably be made up from reagents of recognized analytical grade and using distilled or demineralized water. Small variations in concentration of the solutions will not affect the accuracy of the results, but may affect the voltage settings if automatic cut-out mechanism, based on a pre-set voltage, is used. All the electrolytes, except A.10, have shelf-lives in excess of 6 months.

It is essential that the instrument manufacturer's advice or instructions be followed regarding whether any of these electrolytes may be used with their instruments or whether it is necessary to use proprietary electrolytes for any particular coating/substrate combination. A summary of the applicability of the electrolytes described in A.2 to A.18 is given in Table A.1.

NOTE 2 Some instrument manufacturers provide proprietary solutions of other than the compositions given below.

Table A.1 — Applicability of electrolytes

Coating	Substrate (basis material)					
	Al	Cu and Cu alloys (such as brass)	Ni	Steel	Zn	Non-metals
Cd	—	A.2	—	A.2	—	A.2
Cr	A.3 and A.5	A.4	A.3 and A.5	A.3	—	A.3 and A.5
Cu	A.6 and A.7	—	A.7	A.6	A.8	A.6, A.7 and A.8
Au	A.18	A.18	A.18	A.18	—	A.18
Pb	—	A.9	A.9	A.9	—	A.9
Ni	A.10	A.11	—	A.10	—	A.10 and A.11
Ag	—	A.12	A.12	—	—	A.12
Sn	A.14	A.13	A.13	A.13	—	A.13 and A.14
Sn-Ni alloys	—	A.17	—	A.16	—	A.16 and A.17
Zn	—	A.15	—	A.15	—	A.15

A.2 Electrolyte for cadmium coatings on steel, copper or brass

Prepare a solution containing 30 g of potassium chloride (KCl) and 30 g of ammonium chloride (NH_4Cl) per litre.

This electrolyte requires a critical pre-set voltage.

A.3 *Electrolyte for chromium coatings on steel, nickel or aluminium

Dilute 95 ml of orthophosphoric acid $c(H_3PO_4) = 1{,}75$ g/ml, to 1 000 ml with water and add 25 g of chromium(VI) oxide (CrO_3).

WARNING — Orthophosphoric acid causes burns; avoid contact with eyes and skin. Chromium(VI) oxide can cause fire on contact with combustible material and causes severe burns; avoid inhaling dust and prevent contact with eyes and skin.

This solution is only suitable for use at a current density of about 100 mA/cm^2 and for coatings up to 5 µm thick, when the results for thicknesses of chromium that are obtained with this electrolyteare within ± 10 % of the actual thicknesses.

NOTE Anodic dissolution of chromium in this electrolyte and in electrolytes A.4 and A.5 produces hexavalent chromium ions Cr(VI); the electrochemical equivalent for Cr(VI) should therefore be used when calculating the thickness.

A.4 *Electrolyte for chromium coatings on copper or brass

Prepare a solution containing 100 g of sodium carbonate (Na_2CO_3) per litre.

This electrolyte is only suitable for use at a current density of about 100 mA/cm^2, and for coatings up to 5 µm thick.

A.5 *Electrolyte for chromium coatings on nickel or aluminium

Dilute 64 ml of orthophosphoric acid $c(H_3PO_4) = 1{,}75$ g/ml, to 1 000 ml with water.

WARNING — See A.3.

This electrolyte is best used at a current density of about 100 mA/cm^2 and is, therefore, particularly useful on thin or decorative chromium coatings. (See also the note to A.3.)

A.6 Electrolyte for copper coatings on steel or aluminium

Dissolve 800 g of ammonium nitrate (NH_4NO_3) in water, dilute to 1 000 ml and add 10 ml of ammonia solution $c(NH_3) = 0{,}88$ g/ml.

WARNING — Ammonium nitrate can cause fire on contact with combustible material. Keep out of contact of all combustible material. Ammonia causes burns and is irritating to eyes, respiratory system and skin; avoid breathing the vapour and prevent contact with eyes and skin.

This electrolyte gives thickness results that are about 1 % to 2 % lower than the correct value.

A.7 Electrolyte for copper coatings on nickel or aluminium

Dissolve 100 g of potassium sulfate (K_2SO_4) in water, dilute to 1 000 ml and then add 20 ml of orthophosphoric acid $c(H_3PO_4)$ = 1,75 g/ml.

WARNING — See A.3.

A.8 Electrolyte for copper coatings on zinc or zinc die-cast alloys

Use pure hexafluorosilicic acid (H_2SiF_6), of concentration not lower than approximately mass fraction 30 %.

WARNING — Hexafluorosilicic acid causes burns and is toxic by inhalation, in contact with skin and if swallowed; avoid inhaling vapour and prevent contact with eyes and skin.

This solution dissolves copper coatings with 100 % efficiency at quite low voltages, with practically no anodic attack on the zinc substrate exposed at the end of the test. There is, however, a tendency to leave slight traces of copper, as spots, on the zinc, in the test area, but, although noticeable, they are normally too small to significantly affect the accuracy of the results.

It is important to note that:

a) a pure grade of hexafluorosilicic acid is essential, substantially free from impurities such as chlorides and sulfates which would allow anodic attack on the zinc substrate when it is exposed at the end of the test;

b) the acid should not have too high a water content, which would lead to an effect similar to that described in a).

NOTE If the water content of the available acid is too great, its deleterious effect can sometimes be overcome by dissolving a little magnesium hexafluorosilicate in the acid.

A.9 Electrolyte for lead coatings on steel, copper or nickel (with or without tin undercoats)

Prepare a solution containing 200 g of sodium acetate (CH_3COONa) and 200 g of ammonium acetate (CH_3COONH_4) per litre.

This electrolyte tends to give slightly lower than 100 % efficiency, but will probably give results that are not more than about 5 % higher than the correct value.

A.10 Electrolyte for nickel coatings on steel or aluminium

Dissolve 800 g of ammonium nitrate (NH_4NO_3) (see the warning given in A.6) in water, dilute to 1 000 ml and add 50 ml of a 76 g/l thio-urea [$CS(NH_2)_2$] solution.

This mixed solution has rather a short shelf-life and should thus be made up not more than 5 d before use, preferably from stock solutions of 800 g/l ammonium nitrate solution and 76 g/l thio-urea solution, which have shelf-lives of at least 6 months.

NOTE The efficiency of this electrolyte is reduced by passivity of nickel coatings. It will not dissolve nickel with 100 % efficiency if its surface is passive. Nickel surfaces can also become passive by the anodic action of phosphoric acid electrolyte used to remove chromium top coats before measuring the thickness of the nickel coating.

The cell voltage during the test can serve as a guide to this behaviour. If testing at about 400 mA/cm^2, the cell voltage for dissolving nickel with 100 % efficiency is normally less than 2,4 V, and a cell voltage of 2,5 V or more usually indicates either that the nickel is dissolving at much less than 100 % efficiency, usually accompanied by electropolishing of the nickel, or that oxygen is being evolved without any dissolution of the nickel.

If necessary, the nickel can be activated before the test by introducing a little dilute hydrochloric acid [$1\ \text{mol/l} \leqslant c(\text{HCl}) \leqslant 2\ \text{mol/l}$]1) solution into the cell, removing it after about 30 s to 1 min and rising well before introducing the ammonium nitrate/thio-urea electrolyte to test for nickel thickness.

A.11 *Electrolyte for nickel coatings on copper, brass or other copper alloys or on stainless steel

Dilute 100 ml of hydrochloric acid $c(\text{HCl})$ = 1,18 g/ml, to 1 000 ml with water.

WARNING — Hydrochloric acid causes burns and is irritating to the respiratory system: avoid breathing the vapour and prevent contact with eyes and skin.

This electrolyte is only satisfactory for nickel coatings on copper or copper alloys when used at current densities of about 400 mA/cm^2, but not when used at about 100 mA/cm^2.

NOTE Electrolytes A.10 and A.11 are also suitable for testing the thickness of cobalt, cobalt-nickel or nickel-iron alloy coatings. The electrochemical equivalents of cobalt and iron are very close to that of nickel, thus no significant error occurs when the thicknesses of alloys of these metals are calculated as though they were only nickel.

A.12 Electrolyte for silver coatings on copper, copper alloys or nickel

Prepare a 100 g/l potassium fluoride (KF) solution.

WARNING — Potassium fluoride is toxic by inhalation, in contact with skin and if swallowed: avoid inhalation of dust and prevent contact with eyes and skin.

This electrolyte is satisfactory for dull silver coatings or bright silver coatings incorporating sulfur-containing brighteners, but is not as satisfactory for bright silver alloy coatings containing small percentages of antimony or bismuth.

NOTE When testing silver coatings with electrolyte A.12, there is a tendency for the silver to be deposited as metal on the inside of stainless steel cells. However, the deposit is in the form of a uniform coating that does not block the aperture, but it can lower the cell voltage needed for dissolution of the silver coatings. It is therefore desirable to dissolve away the silver deposit from stainless steel cell bodies with nitric acid after each determination.

A.13 Electrolyte for tin coatings on steel, copper alloys or nickel

Dilute 170 ml of hydrochloric acid $c(\text{HCl})$ = 1,18 g/ml, to 1 000 ml with water.

WARNING — See A.11.

This solution dissolves tin coatings at very low cell voltages at which there is no anodic attack on the substrates when they are exposed at the end of the test. There is, however, a tendency for the tin to be deposited out of this solution during the test as a spongy deposit on the cathode, e.g. on a stainless steel cell body, and this deposit can block the cell aperture after a while and thus prematurely stop the test when testing very thick tin coatings or a number of thinner ones. The aperture of the cell should therefore be cleaned of these growths at fairly frequent intervals.

NOTE The electrolyte is believed to have 100 % efficiency.

A.14 *Electrolyte for tin coatings on aluminium

Dilute 50 ml of sulfuric acid $c(\text{H}_2\text{SO}_4)$ = 1,84 g/ml, with water to 1 000 ml by carefully adding the acid, in small portions, to the water, and dissolve 5 g of potassium fluoride (KF) in this solution.

---

1) Previously expressed as “1 N to 2 N”.

WARNING — See A.12. Sulfuric acid causes severe burns: prevent contact with skin and eyes and do not add water to sulfuric acid.

A.15 Electrolyte for zinc coatings on steel, copper or brass

Prepare a 100 g/l potassium chloride (KCl) solution.

This electrolyte requires a fairly critical pre-set voltage, but not quite as critical as that for testing cadmium coatings (A.2).

A.16 *Electrolyte for tin-nickel alloys on steel

Mix 100 ml of orthophosphoric acid solution $c(H_3PO_4)$ = 1,75 g/ml, with 50 ml of hydrochloric acid $c(HCl)$ = 1,18 g/ml, and 50 ml of a solution of oxalic acid dihydrate ($C_2H_2O_4{\cdot}2H_2O$) saturated at room temperature.

WARNING — See A.3 and A.11. Oxalic acid is harmful in contact with skin or if swallowed: avoid contact with eyes and skin.

This electrolyte is formulated for use at a current density of about 100 mA/cm^2 and at this current density the tin in the alloy is found to dissolve as Sn(II) ions. The correct electochemical equivalent for a 65/35 Sn/Ni alloy, with tin the divalent form, i.e. 0,505 mg/C, should be used for calculating the thickness. For greater accuracy the factor should be adjusted for the actual composition of the alloy (see 7.8).

A.17 *Electrolyte for tin-nickel alloys on copper or brass

Prepare a solution containing 12 g of nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$), 13 g of anhydrous Sn(IV) chloride ($SnCl_4$), 200 ml of water, 40 ml of hydrochloric acid $c(HCl)$ = 1,18 g/ml, and 50 ml of orthophosphoric acid solution $c(H_3PO_4)$ = 1,75 g/ml.

WARNING — See A.3 and A.11. Nickel chloride has a harmful dust and is irritating to skin and eyes: avoid breathing dust and avoid contact with eyes and skin. Sn(IV) chloride causes burns and is irritating to the respiratory system: avoid contact with eyes and skin and do not inadvertently allow it to come into contact with water.

This electrolyte is formulated for use at a current density of about 400 mA/cm^2 and at this current density the tin in the alloy is found to dissolve as Sn(IV) ions. The correct electrochemical equivalent for a 65/35 Sn/Ni alloy, with tin in the quadrivalent form, i.e. 0,306 mg/C, should be used for calculating the thickness. For greater accuracy the factor should be adjusted for the actual composition of the alloy (see 7.8).

A.18 *Electrolyte for gold coatings on aluminium, copper alloys, nickel, silver and steel

Prepare a 100 g/l potassium cyanide solution.

WARNING — Potassium cyanide emits lethal hydrocyanic acid gas in the presence of acids; the potassium cyanide itself is very toxic by inhalation, in contact with skin and if swallowed: avoid inhalation of dust and prevent contact with eyes and skin.

This electrolyte is satisfactory for dull gold coatings or bright gold coatings, but the results are sensitive to alloy composition and density.

Annex B
(informative)

Types of instrument

B.1 General

The instrument may operate on either of two principles:

a) measurement of the time of anodic dissolution at constant cell current;

b) measurement of the quantity of electricity consumed during the test by current-time integration.

With a), the current passed through the test cell should be controlled at a constant value, a timer then being used to measure the time interval between the start and the end-point of the test.

With b), an integrating meter is used to measure the quantity of electricity passed, in which case accurate knowledge of the magnitude of the current and separate measurement of the time interval is unnecessary. The results may be displayed as single time units, as the product of current and time (quantity of electricity) units or, more frequently with recent designs of apparatus, directly as thicknesses.

The end-point can be determined by observing the marked change in cell voltage on a suitable voltmeter, or a cut-out can be used to terminate the test automatically. In the latter case, the cut-out is set to operate at a predetermined value of either the cell voltage or the rate of change of cell voltage.

In the case of hot-dipped coatings, or other coatings where diffusion layer may have developed between the coatings and the basis metal, this predetermined value can be either that at which the main coating has been removed to expose the diffusion layer or that at which the diffusion layer has been removed to expose completely the basis metal.

By using a potential recording chart recorder, the changes of potential can be permanently recorded as the dissolution reaches and passes through the different materials. This is particularly useful in measuring the thickness of diffusion layers and also the thickness of different layers of the same material, e.g. duplex nickel ("Chrysler Step Test").

Other non-mandatory, but advantageous, features of coulometric instruments can include digital results display, electronic timing and switching for greater accuracy of end-point determination, and the capability of accepting different test cell sizes or use different current densities. The test cell sealing ring should be capable of being interchanged rapidly.

Many modern instruments display results as direct thickness measurements and might incorporate initial automatic setting of the cut-out at the start of each test to terminate the test at the correct end-point.

B.2 Electrolytic test cell

The electrolytic test cell consists of a container, usually cylindrical, applied under constant pressure to the article under test through an intermediate non-conductive and elastic seal made, e.g., of rubber or plastic material. The cell itself, if it is made of metal, e.g. stainless steel, can serve as the cathode, in which case the seal will also serve as insulation between the cathode and anode.

If the cell is of insulating material, a separate cathode is used and immersed in the electrolyte before the test commences.

The surface area enclosed by the seal should be well defined and small enough to permit its application to a curved surface. Smaller cells may be required for measuring the thickness of coatings on intricately shaped substrates, but these pose problems connected with the definition and measurement of the area of the seal. With any cell, the accuracy of the method is largely controlled by the accuracy of measurement of the area over which the thickness measurement is made. Inaccuracies can occur if the seal defining the test area is applied to a curved surface. A further inaccuracy can also arise from wear or distortion of the end of seal. This can be assessed visually by examination of the periphery of the circle of stripped coating.

For substantially flat surfaces, a typical de-plated area is 0,2 cm^2, but curved surfaces can be measured with cells of the sizes indicated in Table B.1, depending on the diameters of the de-plated area.

Table B.1 — Cell sizes for measurements on curved surfaces

Diameter of de-plated area cm	**De-plated area** cm^2	**Minimum diameter of curved surfaces** cm
0,32	0,080	3,00
0,22	0,038	1,00
0,15	0,018	0,40
0,10	0,008	0,15
0,05	0,002	0,15

ICS 25.220.40
Price based on 14 pages