



# Standard Test Method for Gross Defects and Mechanical Damage in Metallic Coatings by Polysulfide Immersion<sup>1</sup>

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## 1. Scope

1.1 This test method covers equipment and methods for detecting gross defects and mechanical damage (including wear-through) in metallic coatings where the breaks in the coating penetrate down to a copper or copper alloy substrate.

1.2 This test method is suitable for coatings consisting of single or combined layers of any coating that does not significantly tarnish in an alkaline polysulfide solution. Examples are gold, nickel, tin, tin-lead, and palladium, or their alloys.

1.3 Recent reviews of porosity testing (which include those for gross defects) and testing methods can be found in literature.<sup>2,3</sup> An ASTM guide to the selection of porosity and gross defect tests for electrodeposits and related metallic coatings is available as Guide B765. Other related porosity test standards are Test Methods B735, B741, B798, B799, and B809.

1.4 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>4</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee B08 on Metallic and Inorganic Coatings and is the direct responsibility of Subcommittee B08.10 on Test Methods.

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<sup>2</sup> Clarke, M., "Porosity and Porosity Tests," in *Properties of Electrodeposits*, edited by Sard, Leidheiser, and Ogburn, The Electrochemical Society, 1975, p. 122.

<sup>3</sup> Krumbain, S. J., "Porosity Testing of Contact Platings," *Trans. Connectors and Interconnection Technology Symposium*, Philadelphia, PA, October 1987, p. 47.

<sup>4</sup> For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

- B246 Specification for Tinned Hard-Drawn and Medium-Hard-Drawn Copper Wire for Electrical Purposes
- B374 Terminology Relating to Electroplating
- B488 Specification for Electrodeposited Coatings of Gold for Engineering Uses
- B542 Terminology Relating to Electrical Contacts and Their Use
- B545 Specification for Electrodeposited Coatings of Tin
- B605 Specification for Electrodeposited Coatings of Tin-Nickel Alloy
- B679 Specification for Electrodeposited Coatings of Palladium for Engineering Use
- B689 Specification for Electroplated Engineering Nickel Coatings
- B733 Specification for Autocatalytic (Electroless) Nickel-Phosphorus Coatings on Metal
- B735 Test Method for Porosity in Gold Coatings on Metal Substrates by Nitric Acid Vapor
- B741 Test Method for Porosity In Gold Coatings On Metal Substrates By Paper Electrography (Withdrawn 2005)<sup>5</sup>
- B765 Guide for Selection of Porosity and Gross Defect Tests for Electrodeposits and Related Metallic Coatings
- B798 Test Method for Porosity in Gold or Palladium Coatings on Metal Substrates by Gel-Bulk Electrography
- B799 Test Method for Porosity in Gold and Palladium Coatings by Sulfurous Acid/Sulfur-Dioxide Vapor
- B809 Test Method for Porosity in Metallic Coatings by Humid Sulfur Vapor ("Flowers-of-Sulfur")

## 3. Terminology

3.1 *Definitions:* Many terms used in this test method are defined in Terminologies B374 or B542.

### 3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *defect indications*—black or dark colored products resulting from the reaction between the alkaline polysulfide reagent and exposed copper or copper alloy underlying metal.

3.2.2 *gross defects*—breaks in the coating that expose relatively large areas of underlying metal to the environment (compare with *intrinsic porosity* (3.2.3)). Gross defects include

<sup>5</sup> The last approved version of this historical standard is referenced on www.astm.org.

those produced by mechanical damage and wear, in addition to as-plated large pores (with diameters an order of magnitude greater than intrinsic porosity) and networks of microcracks.

NOTE 1—Such large pores and microcrack networks indicate serious deviations from acceptable coating practice (as, for example, dirty basis-metal substrates and contaminated or out-of-balance plating baths).

3.2.3 *intrinsic porosity*—the “normal” porosity that is present, to some degree, in all commercial thin platings (such as in precious-metal coatings for engineering purposes) and will generally follow an inverse relationship with thickness.

NOTE 2—Intrinsic porosity is due primarily to small deviations from ideal plating and surface preparation conditions. Scanning electron microscope (SEM) studies have shown that the diameter of such pores, at the plating surface, is of the order of micrometres, so that only small areas of underlying metal are exposed to the environment.

3.2.4 *measurement area*—the portion or portions of the surface examined for the presence of gross defects or mechanical damage (and wear-through). The measurement area shall be indicated on the drawings of the parts, or by the provision of suitably marked samples.

3.2.5 *metallic coatings*—platings, claddings, or other metallic coatings applied to the basis-metal substrate. The coating can comprise a single metallic layer or a combination of metallic layers.

3.2.6 *porosity (general)*—*in a coating*, the presence of any hole, crack, or other defect that exposes the underlying metal to the environment.

3.2.7 *underplate*—a metallic coating layer between the basis metal and the topmost metallic coating. The thickness of an underplating is usually greater than 1  $\mu\text{m}$ , in contrast to a strike or flash, which is usually thinner.

3.2.8 *wear-through*—the exposure of underplate or basis metal as a direct result of wear. Wear-through is an observable phenomenon.

3.2.9 *wear track*—a mark that indicates the path along which physical contact had been made during a sliding process (such as the mating and unmating of an electrical contact).

#### 4. Summary of Test Method

4.1 The test samples are immersed in an alkaline polysulfide solution at 74°C (165°F) for 60 s. After rinsing and drying, the samples are examined for dark or discolored areas which indicate exposure of copper or copper alloys to the solution through breaks in the coating.

#### 5. Significance and Use

5.1 The purpose of the alkaline polysulfide immersion test is to determine the presence of mechanical damage, wear-through, and other gross defects in the coating. Most metallic coatings are intended to be protective and the presence of gross defects indicates a serious reduction of such protection.

5.2 The protection afforded by well applied coatings may be diminished by improper handling following plating or as a result of wear or mechanical damage during testing or while in service. The alkaline polysulfide test serves to indicate if the damage has extended down to the copper or copper alloy basis metal since it will not detect exposed nickel underplate.

5.3 The alkaline polysulfide test has been specified in several ASTM specifications for tin-plated coatings, namely Specifications B246 and B545. This test could also be used to detect gross defects and mechanical damage in other metallic coatings, such as tin-nickel alloy (Specification B605), nickel (Specification B689), gold (Specification B488), palladium (Specification B679), and autocatalytic nickel-phosphorous coatings (Specification B733).

5.4 This test detects mechanical damage that exposes copper underplate and copper basis metal. Such damage may occur in any post-plating operation or even towards the end of the plating operation. It is most often seen to occur in product assembly operations.

5.5 If properly performed, this test will also detect wear-through, provided the wear-through reaches a copper or copper-alloy layer.

5.6 Many types of gross defects are too small to be seen, except at magnifications so high (as in SEM) that a realistic assessment of the measurement area cannot be easily made. Other defects, such as many types of wear-through, provide insufficient contrast with the coating surface. Gross defects tests (as with porosity tests) are, therefore, used to magnify the defect sites by producing visible reaction products in and around the defects.

5.7 The polysulfide solution will react with copper and copper alloys to produce a dark brown or black stain (the defect indications) at the site of the defect. Silver also turns black under the same conditions. The test solution will not react with nickel and is only useful when the presence or absence of copper exposure is a specific requirement.

5.8 The polysulfide immersion test is relatively insensitive to the presence of small pores. It shall not be used as a general porosity test. (Test Method B809 should be used instead.)

5.9 The extent and location of the gross defects or mechanical damage (revealed by this test) may or may not be detrimental to product performance or service life. Such determinations shall be made by the user of the test through practical experience or judgment.

5.10 The present test can be used on samples of various geometries, such as curved surfaces. It can also be used for selective area coating if allowance is made for tarnish creepage from bare copper alloy areas.

5.11 This test is destructive in that it reveals the presence of gross defects by contaminating the surface with reaction-product films. Any parts exposed to this test shall not be placed in service.

5.12 However, the defect indications on the sample surfaces that result from this test are stable; samples may be retained for reference purposes.

5.13 This test is neither recommended for predictions of product performance nor is it intended to simulate field failure mechanisms. For such product performance evaluations, an environmental test that is known to simulate actual failure mechanisms should be used.

## 6. Apparatus

6.1 In addition to the normal equipment (beakers, bottles, weighing balances, funnels, and so forth) that are part of every chemical laboratory, the following apparatus are required:

6.1.1 *Microscope*—Optical, stereo, 10 to 30×. It is preferred that one eyepiece contain a graduated reticle for measuring the diameter of tarnish spots. The reticle shall be calibrated for the magnification at which the microscope is to be used, preferably 10×.

6.1.2 *Hydrometer*, 1.120 to 1.190 specific gravity, 150–mm scale.

6.1.3 *Light Source (Illuminator) for Microscope*, incandescent, or circular fluorescent.

## 7. Reagents

7.1 *Sodium Hydroxide*, pellet, ACS certified grade or better.

7.2 *Sodium Sulfide*, 9-hydrate, ACS “Analytical Reagent” (AR) grade, or better.

7.3 *Sulfur*, precipitated, USP grade.

## 8. Hazards

8.1 All of the normal precautions shall be observed in handling the materials required for this test. This shall also include, but not be limited to, procuring and reviewing Material Safety Data Sheets that meet the minimum requirements of the OSHA Hazard Communication Standard for all chemicals used in cleaning and testing, and observing the recommendations given.

## 9. Preparation

9.1 *Preparation of Solutions:*

9.1.1 *Polysulfide Solution*—**Warning**—All work shall be done under an operating fume hood since the gases emitted and the polysulfide solution are toxic.

9.1.1.1 Make a saturated solution of sodium sulfide by dissolving 20 to 25 g of sodium sulfide in 100 mL of deionized or distilled water. Stir for 30 min at minimum. Make sure that undissolved crystals are present in the solution. If not present, continue adding increments of approximately 0.5–g sodium sulfide, with stirring, until the solution is saturated (excess solids present).

9.1.1.2 With stirring, slowly add 30 to 35 g of sulfur to the saturated sodium sulfide solution.

9.1.1.3 Cover the beaker. Stir for 60 min at minimum.

9.1.1.4 Allow solution to stand for 24 h without stirring.

9.1.1.5 Filter solution through qualitative grade filter paper into a 250-mL beaker.

9.1.1.6 Set aside about 10 mL of filtered solution in a small stoppered vial. Label the vial, “Concentrated Polysulfide Solution,” and date it.

9.1.1.7 Pour remaining solution into a 250-mL graduated cylinder or hydrometer cylinder. Adjust the specific gravity using a hydrometer to  $1.142 \pm 0.005$ , at 20 to 30°C, by adding a few millilitres of deionized water and stirring with a glass rod to mix thoroughly. Recheck specific gravity. Continue adding water and mixing until desired specific gravity is reached. If solution becomes too dilute (less than 1.142), add the concentrated polysulfide solution (see 9.1.1.6) as needed.

9.1.1.8 Store solution in a tightly capped 250-mL plastic bottle labeled, “Polysulfide Solution, sp gr 1.142,” and date it.

9.1.2 *Alkaline Polysulfide Reagent:*

9.1.2.1 Measure 75 mL of the polysulfide solution, sp gr 1.142 into a 600-mL beaker containing a teflon-coated stirring bar.

9.1.2.2 Weigh out 75 g of sodium hydroxide pellets into a plastic weighing dish.

9.1.2.3 Add the sodium hydroxide carefully to the polysulfide solution. Cover beaker. Stir to dissolve.

9.1.2.4 Add 375 mL of deionized water to the beaker, cover, and stir to mix.

9.1.2.5 Store solution in a tightly stoppered 500-mL plastic bottle labeled, “Alkaline Polysulfide Reagent,” and date it.

9.2 *Preparation of Test Samples:*

9.2.1 Handle samples as little as possible, even before cleaning, and only with tweezers, microscope-lens tissue, or clean soft cotton gloves.

9.2.2 Before being cleaned, the samples shall be prepared so that the measurement areas may be viewed easily through the microscope. If samples are part of assembled products, they may need to be disassembled to ensure proper access to these areas and to enable the part to be immersed in the alkaline polysulfide solution.

NOTE 3—Since the test is specific to the plated metallic portions of the product, the latter should be separated from plastic housings, etc., whenever possible, before cleaning. Also, nonmetallic materials, such as paper tags, string, tape, and so forth, shall be removed, but take care to maintain sample identity.

9.2.3 *Cleaning:*

9.2.3.1 Inspect the samples under 10× magnification for evidence of particulate matter. If present, such particles should be removed by “dusting” (that is, blowing them off the sample) with clean, oil-free air.

9.2.3.2 Thoroughly clean the particle-free samples with solvents or solutions that do not contain CFCs, chlorinated hydrocarbons, or other known ozone-destroying compounds. The procedure outlined in Note 4 has been found to give satisfactory results for coatings with mild to moderate surface contamination.

NOTE 4—*Suggested Cleaning Procedure:*

(1) Keep individual pieces separated if there is a possibility of damage to the measurement areas during the various cleaning steps.

(2) Clean samples for 5 min in an ultrasonic cleaner which contains a hot (65 to 85°C) 2 % aqueous solution of a mildly alkaline (pH 7.5 to 10) detergent (such as Micro or Sparkleen).

(3) After ultrasonic cleaning, rinse samples thoroughly under warm running tap water for at least 5 s.

(4) Rinse samples ultrasonically for 2 min in fresh deionized water to remove the last detergent residues.

(5) Immerse samples in fresh analytical reagent-grade methanol or isopropanol and ultrasonically “agitate” for at least 30 s to remove the water from the samples.

(6) Remove and dry samples until the alcohol has completely evaporated. If an air blast is used as an aid to drying, the air shall be oil free, clean, and dry.

(7) Do not touch measurement area of the samples with bare fingers after cleaning.

9.2.3.3 Reinspect samples (under 10× magnification) for particulate matter on the surface. If particulates are found,

repeat the cleaning step. Surface cleanliness is extremely important. Contaminants, such as plating salts and flakes of metal, may give erroneous indications of defects.

## 10. Procedure

10.1 **Warning**—All work shall be performed in a fume hood since the vapors are noxious and toxic.

10.2 Before each test, check the effectiveness of the alkaline polysulfide reagent (9.1.2.5) by dipping a clean copper or copper alloy (>95 % copper) wire or piece into the reagent at room temperature. If the copper does not blacken within 10 s, discard solution and make fresh alkaline polysulfide reagent.

NOTE 5—If bare copper pieces are not available, scratch a plated sample heavily through to the copper and test the reagent.

10.3 Place sufficient alkaline polysulfide reagent in a beaker so that the measurement area may be immersed. Cover beaker with a watch glass to prevent evaporation. Heat the solution, with gentle stirring, to  $74 \pm 3^\circ\text{C}$ .

10.4 Immerse the examination area by any convenient method in the hot reagent for 60 s. Agitate samples if stirring is insufficient to remove air bubbles.

10.5 Remove and gently rinse with warm running tap water and thoroughly dry with clean dry air.

10.6 Cool the reagent. Filter it back into the bottle for reuse. The reagent may be reused as long as it passes the copper wire test described in 10.2.

## 11. Examination and Evaluation

11.1 Using an incandescent or ring fluorescent lamp, examine the measurement areas at  $10\times$  magnification for the presence of dark brown or black stains or spots, which will usually not protrude from the surface. Because burnished gold can appear black under certain lighting conditions, be certain to rotate the sample to ensure that the black is not a result of the light being reflected out of the field of view.

NOTE 6—One limitation of this test is that copper exposed in a deep

recess, such as a crack or gouge, will not be detected unless the copper itself is easily visible under low magnification.

11.2 If the defect indications are to be counted, the following additional instructions are recommended.

11.2.1 A defect indication should be measured and counted when at least one half of the indication falls within the measurement area. Unless otherwise specified, products that initiate outside the measurement area but fall within it and are irregular in shape should not be counted. However, for small measurement areas or where the migrating indication covers a significant portion of this area, the presence of such products should be recorded.

11.2.2 Indication size shall be defined by the longest diameter of the product. Unless otherwise specified, products less than 0.05 mm (0.002 in.) in diameter shall not be counted. A graduated reticle in the microscope eyepiece is useful as an aid to counting and sizing.

NOTE 7—A useful sizing technique is to tabulate the defect indications in accordance with three size ranges. These are (approximately): (a) 0.12 mm diameter (0.005 in.) or less, (b) between 0.12 and 0.40 mm diameter (0.005 and 0.015 in.), and (c) greater than 0.40 mm diameter (0.015 in.).

11.2.3 The acceptable number, sizes, and locations of the defect indications shall be as specified on the appropriate drawing or specification, or as agreed upon by the producer and the user.

## 12. Precision and Bias

12.1 *Precision*—The precision of this test method will be investigated with samples containing deliberately damaged areas.

12.2 *Bias*—The procedure in this test method has no bias because the presence and size of the gross defects are defined only in terms of this test method.

## 13. Keywords

13.1 electrodeposits; gross defects; mechanical damage; metallic coatings; polysulfide immersion; porosity testing; wear-through

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