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Standard Test Method for Gross Defects and Mechanical Damage in Metallic Coatings by the Phosphomolybdic Acid (PMA) Method[1]

This standard is issued under the fixed designation B877; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test standard covers equipment and methods for using phosphomolybdic acid (PMA) to detect gross defects and mechanical damage including wear through in metallic coatings of gold, silver, or palladium. These metals comprise the topmost metallic layers over substrates of nickel, copper, or copper alloys.

1.2 Recent reviews of porosity testing, which include those for gross defects, and testing methods can be found in the literature.[2,3] 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 and gross defects test standards are Test Methods B735, B741, B798, B799, B809, and B866, Specifications B488, B679,and B689.

1.3 The values stated in SI units are the preferred units. Those in parentheses are for information only.

1.4 *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:*[4]

B374 Terminology Relating to Electroplating
B488 Specification for Electrodeposited Coatings of Gold for Engineering Uses
B542 Terminology Relating to Electrical Contacts and Their Use
B679 Specification for Electrodeposited Coatings of Palladium for Engineering Use
B689 Specification for Electroplated Engineering Nickel Coatings
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B741 Test Method for Porosity In Gold Coatings On Metal Substrates By Paper Electrography (Withdrawn 2005)[5]
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”)
B866 Test Method for Gross Defects and Mechanical Damage in Metallic Coatings by Polysulfide Immersion

3. Terminology

3.1 *Definitions*—Many terms in this test method are defined in Terminology B374 or B542

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *base metal, n*—any metal other than gold, silver, platinum, palladium, iridium, or rhodium. Typical base metals used as underplates or substrates are copper, nickel, tin, lead, and their alloys.

3.2.2 *defect indications, n*—colored droplets resulting from the reaction between the PMA reagent and the underlying metal.

3.2.3 *gross defects, n*—those breaks in the coating that expose relatively large areas of underlying metal to the environment. Gross defects include those produced by mechanical damage and wear, as well as as-plated large pores with diameters an order of magnitude greater than intrinsic porosity and networks of microcracks.

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[1] 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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[2] Clarke, M., “Porosity and Porosity Tests,” *Properties of Electrodeposits*, ed. by Sand, Leidheiser, and Ogburn, The Electrochemical Society, 1975, p. 122.

[3] Krumbein, S. J., “Porosity Testing of Contact Platings,” Trans. Connectors and Interconnection Technology Symposium, Philadelphia, PA, October 1987, p. 47.

[4] 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.

[5] The last approved version of this historical standard is referenced on www.astm.org.

NOTE 1—Large pores and microcrack networks indicate serious deviations from acceptable coating practice (dirty substrates and contaminated or out-of-balance plating baths).

3.2.4 *intrinsic porosity, n*—the normal porosity that is present, to some degree, in all commercial thin electrodeposits (precious metal coatings for engineering purposes) that will generally follow an inverse relationship with thickness.

NOTE 2—Intrinsic porosity is due to small deviations from ideal plating and surface preparation conditions. Scanning electron microscope (SEM) studies have shown the diameter of such pores at the plating surface is 1 to 2 µm so only small areas of underlying metal are exposed to the environment.

3.2.5 *measurement area, n*—that portion or portions of the surface that is 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.

3.2.6 *metallic coatings, n*—include electrodeposits, claddings, or other metallic layers applied to the substrate. The coating can comprise a single metallic layer or a combination of metallic layers (gold over palladium).

3.2.7 *porosity (general), n*—the presence of any hole, crack, or other defect that exposes the underlying metal to the environment.

3.2.8 *underplate, n*—a metallic coating layer between the substrate and the topmost metallic coating. The thickness of an underplate is usually greater than 1 µm, in contrast to a strike or flash, which is usually thinner.

3.2.9 *wear through, n*—the exposure of underplate or substrate as a direct result of wear. Wear through is an observable phenomenon.

3.2.10 *wear track, n*—a mark that indicates the path along which physical contact has been made during a sliding process (the mating and unmating of an electrical contact).

4. Summary of Test Method

4.1 This test method involves the use of a solution of phosphomolybdic acid (PMA), which is a solid complex of molybdenum trioxide, Mo_2O_3, and phosphoric acid, H_3PO_4. In this state, molybdenum is very reactive with many free metals and may be used to detect exposed underplates and substrate metals. The part is exposed briefly to fumes of hydrochloric acid to remove oxides in the defect region. A small drop of the aqueous PMA solution is applied to the spot in question using an applicator. If it contacts base metals from exposed underplate or substrate, the Mo_2O_3 will immediately be reduced to lower oxides, forming the intensely colored, molybdenum blue complex (heteropoly blue).[6]

4.2 This test may not be suitable for some precious metal alloy coatings that contain significant concentrations of nonprecious metals (base metals) like nickel or copper. (See .)

4.3 The reagents in this test also react with tin, lead, and tin-lead solder.

5. Significance and Use

5.1 The primary purpose of the PMA 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 PMA test can serve to indicate the existence of such damage.

5.3 This test is used to detect underplate and substrate metal exposed through normal wear during relative motions (mating of electrical contacts) or through mechanical damage. As such, it is a sensitive pass/fail test and, if properly performed, will rapidly detect wear through to base metals or scratches that enter the base metal layers.

5.4 This test is relatively insensitive to small pores. It is not designed to be a general porosity test and shall not be used as such. The detection of pores will depend upon their sizes and the length of time that the reagent remains a liquid.

5.5 This test cannot distinguish degrees of wear through or whether the wear through is to nickel or copper. Once base metal is exposed, the colored molybdenum complex is formed. While relatively small area defects (compared to the area of the droplet) may be seen at the bottom of the drop as tiny colored regions immediately after applying the PMA, any larger areas of exposed base metal will cause the entire droplet to turn dark instantly.

5.6 The PMA test also detects mechanical damage that exposes underplate and substrate metal. Such damage may occur in any postplating operation or even at the end of the plating operation. It can often occur in assembly operations where plated parts are assembled into larger units by mechanical equipment.

5.7 The PMA test identifies the locations of exposed base metal. The extent and location of these exposed areas may or may not be detrimental to performance. The PMA test is not recommended for predictions of product performance, nor is it intended to simulate field failure mechanisms. For such contact performance evaluations, an environmental test known to simulate actual failure mechanisms should be used.

5.8 The PMA test is primarily intended for the evaluation of individual samples rather than large sample lots, since evaluations are normally carried out one at a time under the microscope (see Section 10).

5.9 This test is destructive. Any parts exposed to the PMA test shall not be placed in service.

6. Apparatus

6.1 In addition to the normal equipment (beakers, weighing balances, funnels, etc.) that are a part of every chemical laboratory.

6.2 *Microscope, Optical, Stereo, 10 to 30×* —It is preferred that one eyepiece contain a graduated reticle for measuring the

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[6] Van Wazer, J. P., *Phosphorous and Its Compounds*, Interscience Publishers, New York, 1961.

defect location. The reticle shall be calibrated for the magnification at which the microscope is to be used, preferably 10×.[7]

6.3 Light source (illuminator) for microscope, incandescent.

6.4 Glass volumetric flask, 10 mL.

6.5 Glass bottle of a stable shape and with glass stopper. The bottle opening shall be 2.5 cm (1 in) minimum. An example is a 50-mL low-form weighing bottle or a flask-shaped weighing bottle.

6.6 *Applicators* (see 9.2)—Platinum wire, 32 AWG, or disposable glass micropipets, 1 or 0.5 µL size.

7. Reagents and Materials

7.1 *Phosphomolybdic Acid (PMA)*—Crystalline, ACS certified grade.

7.2 *Concentrated Hydrochloric Acid*— ACS analytical reagent (AR) grade or better.

8. Specific Safety and Health Precautions

8.1 All the normal precautions shall be observed in handling the materials required for this test. This shall include, but is not 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. Preparations

9.1 Preparation of solutions:

9.1.1 Two types of PMA solutions can be used with this method.

9.1.1.1 *Method A,* the preferred method, uses a dilute 8 % solution of PMA in water.

9.1.1.2 *Method B,* uses a saturated solution of PMA in water.

NOTE 3—The dilute solution is preferred because it works well with silver, gold, and palladium coatings, while the saturated solution reacts with silver to give false indications. In addition, the saturated solution has a tendency to dry up quickly on the test surface before proper evaluations can be made.

9.1.2 Dilute (8 %) PMA solution (for Method A):

9.1.2.1 Place a small, clean, and dry glass funnel in the neck of a clean, dry 10 mL volumetric flask.

9.1.2.2 Tare out the weight of the funnel and flask on a balance.

9.1.2.3 Weigh 0.8 (±0.1) g PMA into the flask, using a plastic or glass spatula.

9.1.2.4 Rinse the funnel with distilled or deionized water to drain any adhering PMA into the flask.

9.1.2.5 Dilute to mark with deionized water.

9.1.2.6 Place stopper in flask and mix thoroughly. Cloudy solution will clear after standing 10 to 15 min.

9.1.2.7 Pour clear solution into a clean glass bottle and seal with glass stopper. Label bottle with PMA concentration and date of preparation.

9.1.2.8 Store bottle in refrigerator. Solution may be used for one week.

9.1.3 Saturated PMA solution (for Method B):

9.1.3.1 Prepare solution in accordance with 9.1.2.1 – 9.1.2.6, except use approximately 5 g of PMA instead of 0.8 g. (Filter out sediment, if necessary.)

9.1.3.2 Mix thoroughly for at least 10 min.

NOTE 4—There shall be a small excess of PMA, seen as a sediment in the bottom of the flask. This indicates saturation.

9.1.3.3 Pour into a clean bottle and label bottle with contents and preparation date.

9.1.3.4 Solution may be used for one week. Store in refrigerator when not in use.

9.1.4 Hydrochloric acid (for both methods):

9.1.4.1 Fill the special glass bottle (see 6.4) to approximately halfway from the top.

9.1.4.2 Label glass bottle with contents.

9.1.4.3 Keep stoppered and under a fume hood when not in use.

9.2 Preparation of applicators:

9.2.1 The applicator shall not react with the PMA solution. Examples are as follows:

9.2.1.1 *Platinum*—Make a small loop using a 32 AWG platinum wire and an appropriate size mandrel (such as a needle). Leave a small gap to facilitate release of the PMA droplet (see Fig. 1). Attach loop to a wooden or plastic handle.

9.2.1.2 Platinum inoculating loops with handles may be purchased. Cut the loop with a knife to create a small gap (Fig. 1), which will facilitate the release of the PMA droplet.

9.2.1.3 Glass capillary micropipets in the 1-µL size or smaller.

9.2.2 If a platinum loop is used as the applicator, the loop diameter shall preferably be 1 mm and shall not exceed 2 mm. The loop diameter is kept small for the following reasons:

9.2.2.1 The small dimensions of many examination areas.

9.2.2.2 The ability of the loop to release a rounded droplet instead of a thin sheet of solution, which dries too fast.

9.2.2.3 Difficulty in controlling flow and observing reactions in large drops.

9.3 Preparation of test samples:

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

9.3.2 Prior to being cleaned, the samples shall be prepared so the measurement area is accessible and can be placed in a

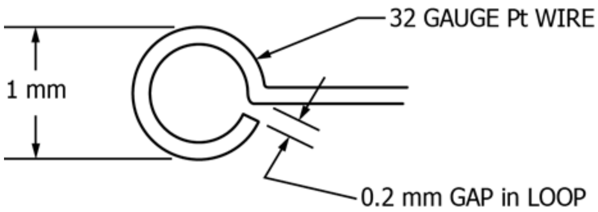

FIG. 1 Sketch of Platinum Wire Loop

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[7] Magnification standards suitable for calibrating optical microscopes may be purchased from U.S. National Institute of Standards and Technology, Office of Standard Reference Materials.

basically horizontal plane. This allows for easy viewing through the microscope and prevents the PMA solution from running off during application.

9.3.3 Masking:

9.3.3.1 The PMA solution will react with any exposed base metal such as nickel, copper, tin, lead, or solder. If the examination area is within a millimetre of exposed or thinly plated substrate metal, masking may be necessary.

9.3.3.2 If masking is necessary, clean per 9.3.4. Carefully paint the nonmeasurement areas with stop-off lacquer under a microscope using a fine artist's brush. Allow the samples to dry thoroughly.

9.3.4 Cleaning the Test Samples:

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

9.3.4.2 Thoroughly clean the particle-free samples with solvents or solutions that do not contain CFC's, chlorinated hydrocarbons, or other known ozone-destroying compounds. The procedure outlined in Note 5 has been found to give satisfactory results for coatings with mild to moderate surface contamination.

NOTE 5—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 that contains a hot (65 to 85°C) 2 % aqueous solution of a mildly alkaline (pH 7.5 to 10) detergent; (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 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; and (7) Do not touch measurement area of the samples with bare fingers after cleaning.

9.3.4.3 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. Test Procedure

10.1 Allow the appropriate PMA solution (see 9.1.1) to come to room temperature (approximately 10 min).

10.2 In the meantime, calibrate the microscope reticle at a convenient magnification in the 10 to 20× range using a stage micrometre or other device. Do not change magnification after calibration.

10.3 Fill a 10-mL beaker with deionized water and another 10-mL beaker with PMA solution.

10.4 Check PMA solution by applying a drop to a piece of copper. It should turn blue instantly. Alternately, test a deeply scratched or unplated section of sample. Nickel shall be exposed to acid fumes before testing.

NOTE 6—On silver finishes, the dilute solution will very slowly turn light green to blue/green. Before testing silver parts, run a PMA test on silver foil that has been cleaned and exposed to acid fumes. Note the color of the droplet in accordance with 10.8.

10.5 For samples with nickel underplates, hold sample inside top of bottle containing the hydrochloric acid in a working fume hood. Expose the measurement area to the HCl fumes for 3 to 5 s.

NOTE 7—If multiple samples are exposed at the same time, they should all be tested within 10 min of the acid fume exposure using a timer.

10.6 Place sample under microscope so that the measurement area is in a horizontal plane. If necessary, use a fixture or press into modeling clay to hold sample in place.

10.7 Use the applicator to apply a rounded droplet to the measurement area. For areas larger than the loop diameter, apply more drops to different parts of the measurement areas as needed. It is preferable not to have the drops run together.

NOTE 8—If a loop is used, clean any dried PMA or blue PMA solution from the loop using deionized water and tissue before continuing. Apply droplets to visible burnish marks and any other suspected defect areas. Make note if these fall outside the measurement areas.

10.8 Observe each droplet. Note any color changes within the following time limits: (1) 20 s for a loop diameter less than 0.6 mm; (2) 30 s for micropipets or for a loop diameter of 0.6 to 1.5 mm; and (3) 40 s for a loop diameter greater than 1.5 mm.

11. Examination and Evaluation

11.1 When base metals or alloys are attacked by PMA, Mo(VI) oxide is reduced to lower oxides forming intensely colored molybdenum blue. Watch the droplet for 20 to 40 s after its application, as specified in 10.8. Note all color changes. When multiple drops are applied, note location of any color changes. For example, the starting point of a burnish mark may be gouged, turning the droplet dark blue instantly, while a shallower burnish mark may not give any significant color change.

11.1.1 Unplated areas and worn spots will show up immediately upon application of the droplet as a color change from yellow to dark blue.

NOTE 9—The entire droplet will turn blue. This test does not pinpoint the exact location of the defect(s) within the droplet.

11.1.2 Smaller defects and cracks will tend to turn the droplet blue more slowly, but still within the time periods specified in 10.8.

11.1.3 Large pores may show up as minute blue spots within the droplet. The droplet may gradually change to green (small amounts of blue color in a yellow drop).

11.1.4 Thinly plated areas or areas with very small pores may not be seen immediately as blue spots, but the droplet may gradually change color from yellow to green.

NOTE 10—Observations 11.1.3 and 11.1.4 may or may not be significant, depending upon the reason for the test.

11.1.5 When the droplet is applied, distinct spots may turn blue instantly and then disappear; or they remain blue without turning the whole droplet blue. This appears to be due to a salt or metal flake on the surface of the examination area. To check into this, (1) Use the edge of the applicator to rub the spot gently. A flake will either break up or come loose and float around the droplet. The small particles may disappear by being dissolved by the phosphoric acid present in the PMA solution; (2) Rinse the sample thoroughly with deionized water, drying with methanol and then air. Expose the examination area to acid fumes and retest in accordance with 10.5 – 10.8. Flakes should be gone. Wear through or defects will show up normally if actually present.

12. Precision and Bias

12.1 *Precision*—This test method is essentially a pass/fail test to detect or identify large breaks in the plating primarily due to nonuniform coverage and mechanical damage, as well as after wear testing. Deliberately damaged platings will be used to determine the precision of this test method.

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

13. Keywords

13.1 electrodeposits; gross defects; mechanical damage; metallic coatings; porosity; testing for defects; wear through

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