



Designation: F 326 – 96 (Reapproved 2001)<sup>e1</sup>

## Standard Test Method for Electronic Measurement for Hydrogen Embrittlement From Cadmium-Electroplating Processes<sup>1</sup>

This standard is issued under the fixed designation F 326; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>e1</sup> NOTE—Editorial corrections were made throughout the standard and in Fig. 3 in May 2001.

### 1. Scope

1.1 This test method covers an electronic hydrogen detection instrument procedure for measurement of plating permeability to hydrogen. This method measures a variable related to hydrogen absorbed by steel during plating and to the hydrogen permeability of the plate during post plate baking. A specific application of this method is controlling cadmium-plating processes in which the plate porosity relative to hydrogen is critical, such as cadmium on high-strength steel.

1.2 *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.* For specific hazard statement, see Section 8.

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

### 2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water<sup>2</sup>

F 519 Test Method for Mechanical Hydrogen Embrittlement Evaluation of Plating Processes and Service Environments<sup>3</sup>

### 3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *hydrogen pressure peak*—the maximum hydrogen pressure value (see  $I_H$ ) obtained when the probe is heated following calibration, plating, or fluid testing.

3.2 *Symbols:*

3.2.1  $HP$  = calibration hydrogen pressure peak.

3.2.2  $HP_p$  = plating hydrogen pressure peak.

3.2.3  $I_E$  = probe cathode emission current.

3.2.4  $I_H$  = probe hydrogen pressure.

3.2.5  $I_\gamma$  = integral of  $I_H$  curve from probe on to  $HP$ .

3.2.6  $\lambda$  = time in seconds for hydrogen pressure peak to drop to half its value.

3.2.7  $\lambda_c$  = lambda obtained from a calibration run.

3.2.8  $\lambda_p$  = lambda obtained from a plating run.

3.2.9  $\lambda_{pc}$  = normalized test lambda, obtained as follows:

$$\lambda_{pc} = \lambda_p (40/\lambda) \quad (1)$$

3.2.10  $\bar{\lambda}_{pc}$  = arithmetic average of normalized lambdas for a set of tests.

3.2.11 *range* = difference between maximum  $\lambda_{pc}$  and minimum  $\lambda_{pc}$  for a given set of tests.

3.2.12 *run* = calibration or plating of a probe.

3.2.13 *test* = single evaluation of a plating solution for hydrogen embrittlement determination; run using a previously calibrated probe.

3.2.14 *set of tests*—all consecutive tests on a plating solution for a given operator-instrument-day evaluation.

3.2.15 *window*—test surface of a probe described in Fig. 1(A).

### 4. Summary of Test Method

4.1 This method uses a metal-shelled vacuum probe as an ion gage to evaluate electrodeposited cadmium characteristics relative to hydrogen permeation. After calibration, a section of the probe shell is electroplated at the lowest current density encountered in the cadmium electroplating process. During the subsequent baking of the probe at a closely controlled temperature, the probe ion current, proportional to hydrogen pressure, is recorded as a function of time. From these data and the calibration data of the probe, a number related to the porosity of the electroplated metal relative to hydrogen is obtained.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee F07 on Aerospace and Aircraft and is the direct responsibility of Subcommittee F07.04 on Hydrogen Embrittlement.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 15.03.

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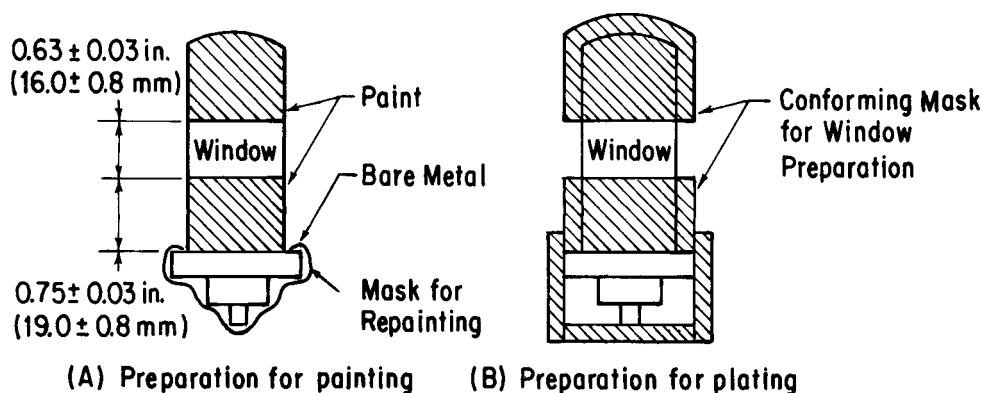


FIG. 1 Probe Configuration

4.2 During the initial part of the bakeout, hydrogen continues to diffuse through the metal shell of the probe and the ion current increases. Within a short time, however, a maximum current is observed and then falls off as hydrogen is driven out of the system.

4.3 Observations of the ion current-time curve indicate that the slope of the curve has an empirical relationship with failure data on stress rupture specimens such as those in Test Method F 519. For this method,  $I_\gamma$  and  $\lambda$  variables (see Section 3) must be empirically correlated with results from the stress rupture specimens. This gives a quick means of measuring ease of baking hydrogen out of cadmium-electroplated parts.

4.4 Before an electroplating test, calibration is accomplished by electrolyzing the probe in a standard solution and baking it to determine  $I_\gamma$  and  $\lambda$  of the unplated steel shell of the probe.

## 5. Significance and Use

5.1 Hydrogen is evolved during metal electrodeposition in aqueous baths. Some of this hydrogen enters parts during plating. If the absorbed hydrogen is at a level presenting embrittlement hazards to high-strength steel, it is removed by baking parts after plating to expel this hydrogen. However, the lack of plate porosity itself may block hydrogen egress. Thus, it becomes important to know both the relative amount of hydrogen absorbed and the plate porosity.

5.2 This test provides a quantitative control number for cadmium plate porosity that can be used to control a cadmium plating process and the status of cadmium-plated hardware. It can also be used for plating process troubleshooting and research and development to determine the effects on plate porosity by process variables, contaminants, and materials. When used to control a critical process, control numbers for plate porosity must be determined by correlation with stress rupture specimens or other acceptable standards.

5.3 There is no prime standard for plate porosity. For this reason, two ovens must be used, with tests alternated between ovens. Data from the ovens are compared to ensure no equipment change has occurred.

## 6. Apparatus

6.1 *Hydrogen Detection Instrument*—A system consisting of a control unit, two special ovens, auxiliary heater, recorder, test probes, and associated equipment.<sup>4</sup>

6.2 *Oven*—The oven warms the probe to increase the hydrogen diffusion rate into the probe. Oven parameters are selected by apparatus manufacturer to provide a standard reading for all hydrogen detection instruments.

6.3 *Oven Stopper*—Stopper covering the oven opening. Remove 10 s before inserting the probe.

6.4 *Window*—The window is the unpainted, bare steel portion of the probe,  $0.63 \pm 0.03$  in. in height, that is plated in the solution under test. The window is shown in Fig. 1.

6.5 *Abrasive Blast*—Abrasive blast window area in the same way, using the same media, as used for the parts. Probe should be rotated while being blasted to provide uniform surface.

6.6 *Electronic Bakeout Unit*—This heats the probe electrically to remove hydrogen absorbed into the probe after testing. May be part of hydrogen detection instrument.

## 7. Reagents and Materials

### 7.1 Reagents:

7.1.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.<sup>5</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

<sup>4</sup> A list of manufacturers of equipment and probes capable of performing these tests is available from ASTM Headquarters.

<sup>5</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

7.1.2 Acetone (C<sub>3</sub>H<sub>6</sub>O), technical.

7.1.3 Anode Cleaning Solution—Concentrated nitric acid (HNO<sub>3</sub>), reagent grade.

7.1.4 Cadmium Stripping Solution—Ammonium Nitrate (125 g/L)—Dissolve 125 g of ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>, technical) in water and dilute to 1 L. Use at room temperature.

7.1.5 Calibration Solution—Sodium Cyanide (50 g/L) Plus Sodium Hydroxide (50 g/L)—Dissolve 50 g of sodium hydroxide (NaOH) in water. Add 50 g of sodium cyanide (NaCN) and dissolve. Dilute to 1 L. Use at 18 to 27°C (65 to 80°F).

7.1.6 Water, Distilled or Deionized, minimum electrical resistivity 50 000 Ω·cm (for example, Specification D 1193).

7.2 Materials:

7.2.1 Anodes (Calibration), solid-carbon arc rods, 5.1- to 12.7-mm (0.20- to 0.50-in.) diameter.

7.2.2 Anodes (Plating), cadmium rods, A-A-51126 6.4 to 12.7 mm (0.25 to 0.50 in.) thick, round or square.

7.2.3 Polytetrafluoroethylene (PTFE) Tape—The tape should be appropriate for use in solution, width about 12 to 19 mm, thickness small enough to seal.

7.2.4 Glass I-L Beaker.

## 8. Hazards

8.1 Sodium cyanide, cyanide, cadmium, nitric acid, and acetone can be health hazards. Use adequate face, hands, and respiratory protection commensurate with standards established by American Conference of Government and Industrial Hygiene for these chemicals.

## 9. Sampling

9.1 Stir plating bath to ensure homogeneity. The plating bath sample must be representative of the bath. Obtain the sample from beneath the surface of the bath, not by skimming the surface. Chemical constituents must be within normal operating range.

## 10. Preparation of Apparatus

10.1 Plug in instrument and allow sufficient time for warmup.

10.2 Turn on the oven and allow 4 h for warmup.

10.3 Leave the instrument on continuously.

10.4 Clean contaminated anodes in cleaning solution, (7.1.3) until heavy gassing is observed. (**Warning**—See Section 8.)

## 11. Calibration of Apparatus

11.1 Calibration Position,  $1.08 \pm 0.2 \text{ A/dm}^2$  ( $10 \pm 2 \text{ A/ft}^2$ )—Use nominal dimensions of Fig. 1(A) for current calculations.

11.2 Plating Position,  $\pm 2\%$  of Current—Set plating current density at the minimum value allowed by the plating specification.

11.3 Probe Current,  $I_e$ ,  $6 \pm 0.2 \text{ mA}$ .

11.4 Electronic Probe Bakeout,  $100 \pm 10 \text{ mA}$ .

11.5 Probe  $I_H$ : 1  $I_H$  unit =  $10^{-7} \text{ A}$

Linearity,  $\pm 2\%$  full scale within each range, 1 to 10 000

11.6 Ovens—Ovens are calibrated by the manufacturers against standard ovens that in turn were calibrated with

notched tension specimen data. Oven stability is checked by comparing ovens against each other in duplicate tests.

11.7 Correlation of Ovens—To correlate ovens, determine  $\bar{\lambda}_{pc}$  for all tests of a set (except tests discarded in accordance with 13.4.4). From  $\bar{\lambda}_{pc}$  and the number of tests, determine  $\Delta$  from Fig. 2. Separate data and compute  $\bar{\lambda}_{pc}$  for each oven. Let  $\bar{\lambda}_{pc}(A)$  be the higher value and  $\bar{\lambda}_{pc}(B)$  the lower value. Where  $\bar{\lambda}_{pc}(A) - \bar{\lambda}_{pc}(B)$  is less than  $\Delta$ , the ovens are comparable. Where  $\bar{\lambda}_{pc}(A) - \bar{\lambda}_{pc}(B)$  is greater than  $\Delta$ , the ovens are not comparable.

## 12. Procedure

12.1 Bakeout of Probe:

12.1.1 Strip cadmium-plated probes in stripping solution (7.1.4) and rinse in 50°C (122°F) water for 2 min before bakeout.

12.1.2 Insert a probe into the socket of an electronic bakeout unit.

12.1.3 Within 30 s, the heater should stabilize or be adjusted to  $86.5 \pm 16.5 \text{ mA}$ . If the heater does not register current, the probe is defective and must be discarded.

12.1.4 Bake out the probe for the time required to meet the limits in 12.2. Do not continuously bake out probes for longer than 2 h to preclude damaging paint.

12.2 Probe Checkout—Probes that are new, or have been calibrated or plated and stripped, need to be baked out to meet checkout requirements as follows:

12.2.1 Hot Probe:

12.2.1.1 Set the range to 10.

NOTE 1—Here and throughout the specification, range settings are for full-scale reading.

12.2.1.2 Remove the probe from the electronic bakeout unit; plug into the socket assembly and  $15 \pm 1 \text{ s}$  after removal from the bakeout unit, turn the probe on.

12.2.1.3 Observe the peak value of  $I_H$ . If less than 1, proceed with surface activation. If it is greater than 1.0, screw on the cap and insert probe into the oven.

12.2.1.4 If  $I_H$  is 0.5 or less within 5 min of inserting the probe into the oven, proceed to surface preparation. If the probe does not drop to  $I_H = 0.5$  or less with 5 min, bake out again. If three successive bakeouts do not reduce  $I_H$  to 0.5 or less within 5 min of insertion into the oven, discard the probe.

12.2.1.5 Set the instrument to read  $I_E$ . Probe  $I_E$  should read  $6.0 \pm 0.2 \text{ mA}$ . If  $I_E$  does not read or cannot be adjusted to this, the probe or the instrument is defective. Check the instrument with other probes to determine which is defective. Discard defective probes.

12.2.2 Cold Probe:

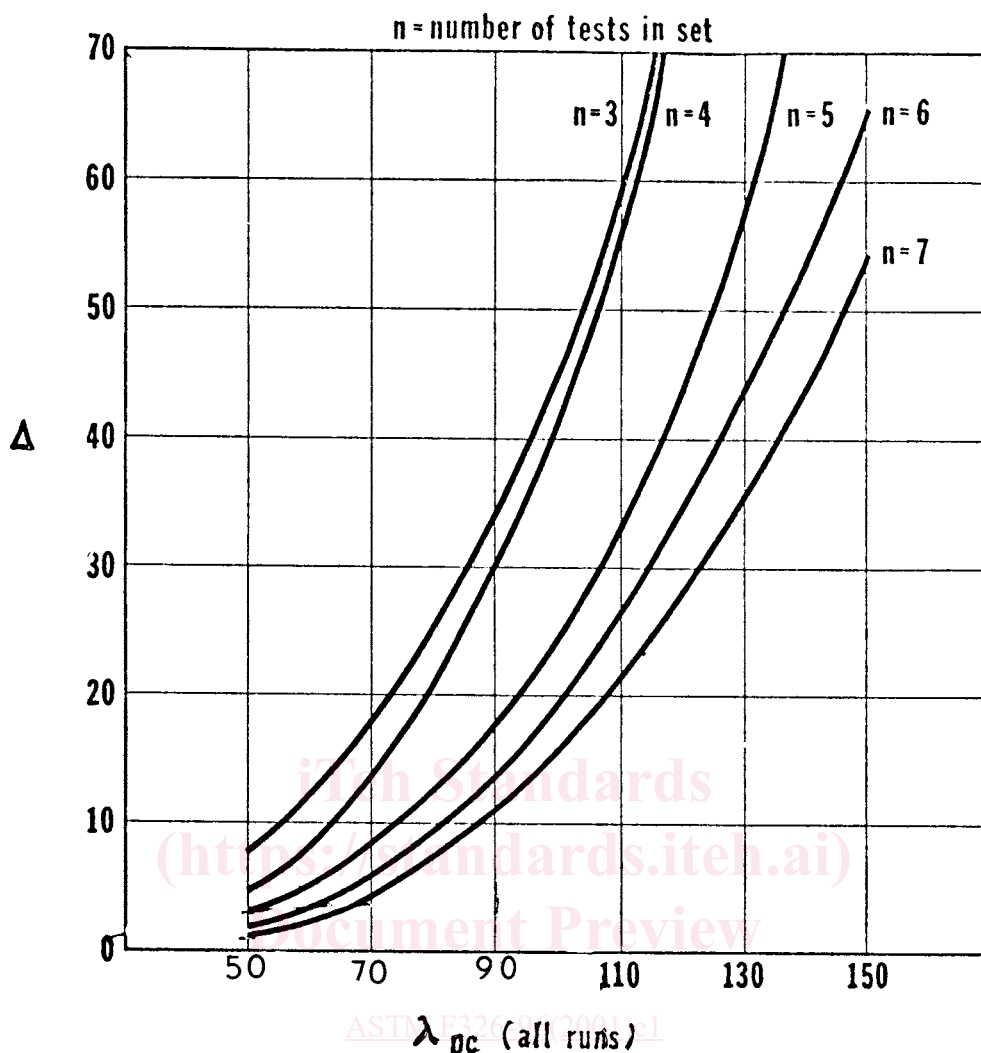
12.2.2.1 Set the range to 1.0.

12.2.2.2 Plug the probe into socket assembly and turn on.

12.2.2.3 Observe the peak value of  $I_H$ . If less than 0.2, proceed to surface preparation. If greater than 0.2, insert into the oven.

12.2.2.4 Proceed as in 12.2.1, 12.2.1.4, and 12.2.1.5.

12.3 Surface Preparation—Before the probe window preparation, check to ensure the window width and height above the probe base meet the requirements of Fig. 1(A). The probes



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 $\lambda_{pc}$  (all runs)

FIG. 2 Oven-Correlation Limit

having windows out of limits must be cleaned and repainted in accordance with the suppliers' instructions or discarded.

12.3.1 Mask the probe to meet the requirement of Fig. 1(B) using conforming masks, supplied with instruments or PTFE adhesive tape. Edges of masks must coincide with edges of window with no paint being visible. Protect the base of the probe. Remove abrasive dust from the rubber masks to avoid paint damage.

12.3.2 For processes using current densities under 4.32 A/dm<sup>2</sup> (40 A/ft<sup>2</sup>), use production equipment to blast production parts. For processes with higher current densities, use laboratory blast equipment. Dry abrasive blast the window area of the probe. Use material, size, air pressures, and distances representative of production blasting. Dry abrasive blast before calibration may be in a laboratory cabinet.

NOTE 2—Some production facilities may not be adaptable to blasting of probes. Special procedures will need to be approved by the procuring agency.

12.3.3 Remove conformal blasting masks, ensuring that the window area is not touched. Remove loose abrasive by blowing off with filtered compressed air or by using a tissue

paper, taking care not to scratch the paint. Fingerprints or visible contamination on the window invalidate the run.

12.3.4 Visually inspect the window area for cleanliness and uniformly textured surface representative of production parts. Repeat Steps 12.3.1-12.3.3 as required to provide acceptable cleanliness and texture.

12.3.5 Proceed to the calibration run or plating run as applicable; immerse the probe within 10 min after sandblasting.

12.4 Probe Calibration:

12.4.1 Pour 850 ± 50 mL (28.6 ± 0.17 fl oz) of calibration solution (7.1.5) into a clean, dry 1-L beaker and insert four carbon anodes, (7.2.1) equally spaced and rigidly mounted to fit snugly inside the beaker.

12.4.2 Record the solution temperature to within ±1°C (±2°F). The temperature must be 18 to 27°C (65 to 80°F).

12.4.3 Place range selector switch to 100 if instrument does not select range automatically. With  $I_H$  off, insert the prepared probe into the socket assembly and screw on the cap. Electrically connect the probe window by means of socket assembly