



Designation: F326 – 23

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

This standard is issued under the fixed designation F326; 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.

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

1.3 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statement, see Section 8.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

D1193 Specification for Reagent Water

F519 Test Method for Mechanical Hydrogen Embrittlement Evaluation of Plating/Coating Processes and Service Environments

<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.

Current edition approved Jan. 1, 2023. Published February 2023. Originally approved in 1978. Last previous edition approved in 2017 as F326 – 17. DOI: 10.1520/F0326-23.

<sup>2</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.

## 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  $I_E$  or  $I_e$  = 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  $\lambda$  = 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

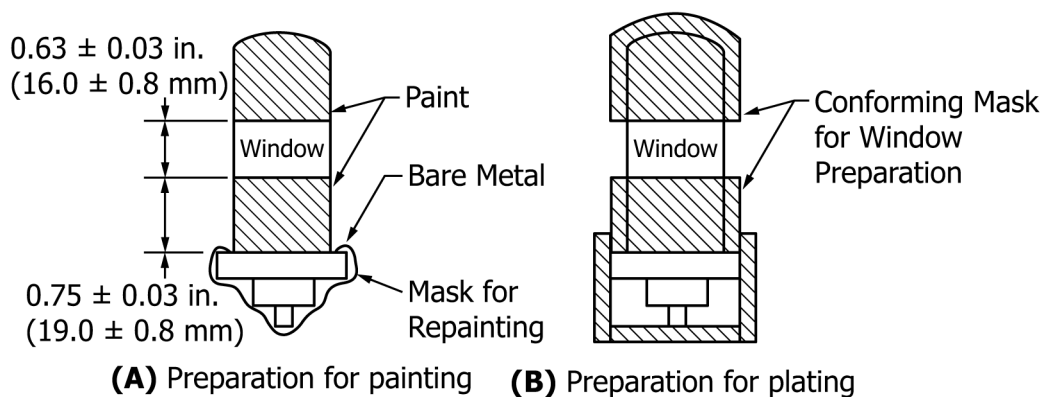


FIG. 1 Probe Configuration

the calibration data of the probe, a number related to the porosity of the electroplated metal relative to hydrogen is obtained.

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 F519. For this method,  $HP$  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  $HP$  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.

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 in.  $\pm$  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>3</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>3</sup> *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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 °C to 27 °C (65 °F to 80 °F).

7.1.6 Water, Distilled or Deionized, minimum electrical resistivity 50 000 Ω·cm (for example, Specification D1193).

7.2 Materials:

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

7.2.2 Anodes (Plating), cadmium rods, A-A-51126 6.4 mm to 12.7 mm (0.25 in. 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 mm to 19 mm, thickness small enough to seal.

7.2.4 Glass 1-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 A/dm<sup>2</sup> ± 0.2 A/dm<sup>2</sup> (10 A/ft<sup>2</sup> ± 2 A/ft<sup>2</sup>)—Use nominal dimensions of Fig. 1(A) for current calculations.

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

11.3 Probe Current, I<sub>E</sub>, 6 mA ± 0.2 mA.

11.4 Electronic Probe Bakeout, Cathode current, 80 mA to 103 mA.

11.5 Probe I<sub>H</sub>: 1 I<sub>H</sub> unit = 10<sup>-7</sup> A

Linearity, ±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 Bakeout cathode current should reach 86.5 mA ± 16.5 mA. If the Bakeout cathode current does not maintain this current, the probe may not be used.

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 s ± 1 s after removal from the bakeout unit, turn the probe on.

12.2.1.3 Observe the peak value of I<sub>H</sub>. 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<sub>H</sub> 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<sub>H</sub> = 0.5 or less with 5 min, bake out again. If three successive bakeouts do not reduce I<sub>H</sub> 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<sub>E</sub>. Probe I<sub>E</sub> should read 6.0 mA ± 0.2 mA. If I<sub>E</sub> 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.

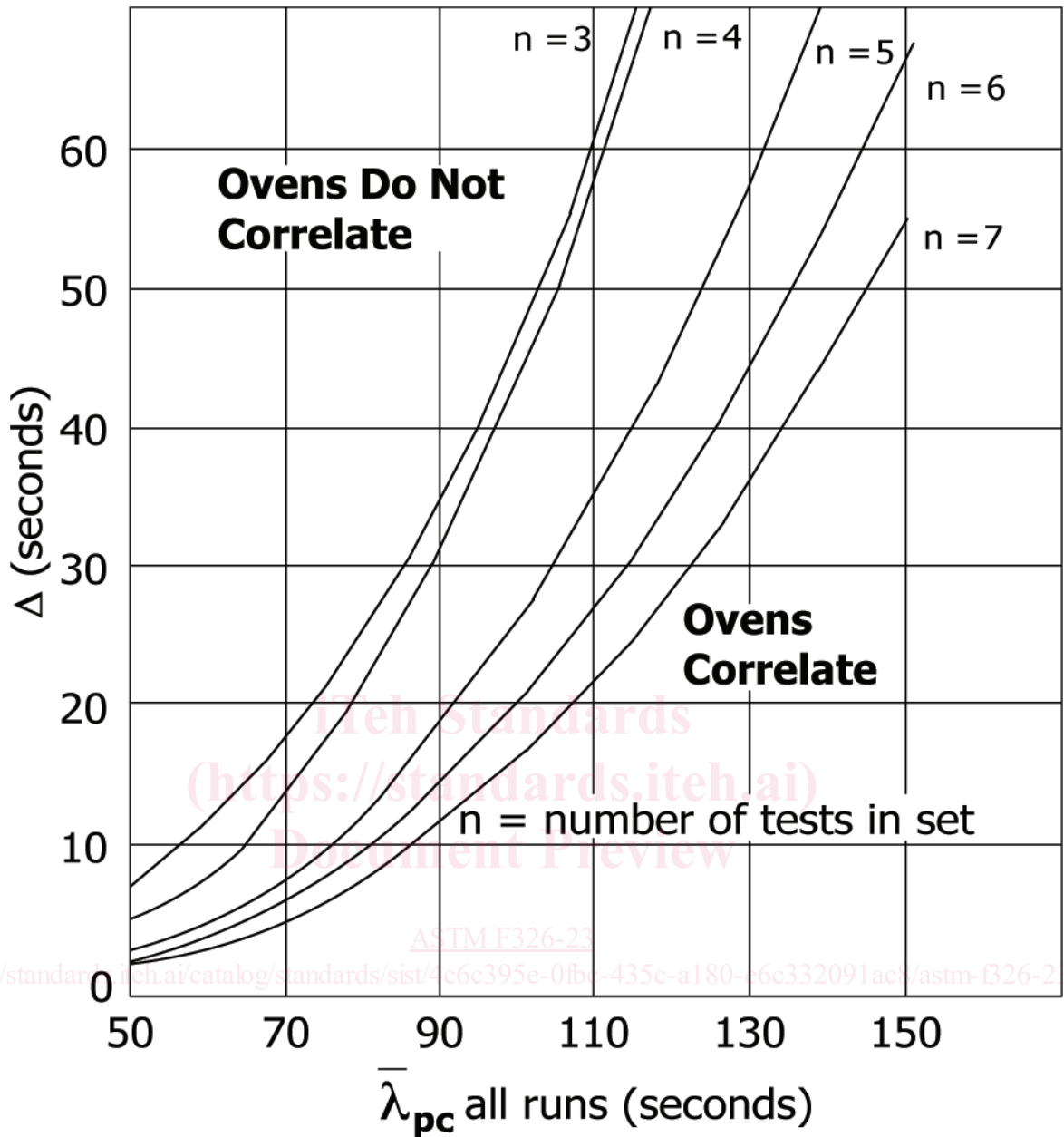


FIG. 2 Oven-Correlation Limit

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 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  $4.32 \text{ A/dm}^2$  ( $40 \text{ A/ft}^2$ ), 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 mL  $\pm$  50 mL (28.6 fl oz  $\pm$  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  $\pm 1^\circ\text{C}$  ( $\pm 2^\circ\text{F}$ ). The temperature must be 18  $^\circ\text{C}$  to 27  $^\circ\text{C}$  (65  $^\circ\text{F}$  to 80  $^\circ\text{F}$ ).

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 to the cathode side of the rectifier and the calibration anodes to the anode side of the rectifier.

12.4.4 With plating current off, immerse the probe into the calibration solution equidistant from the anode rods with the probe pointing down and support so that the upper window edge is 3 mm to 6 mm ( $\frac{1}{8}$  in. to  $\frac{1}{4}$  in.) below the surface of the solution. The probe must be immersed within 10 min of blasting for the run to be valid.

12.4.5 Within 30 s of the probe immersion, cathodically charge the probe at the calibration setting, 1.08 A/dm<sup>2</sup> (10 A/ft<sup>2</sup>), for 180 s  $\pm$  2 s (3 min  $\pm$  2 s). Inspect the window surface during charging to ensure absence of bubbles, fingerprints, and visible contamination.

12.4.6 At the end of the charging period, break the plating circuit.

12.4.7 Remove the probe from the solution within 15 s of the end of the charging period and support so that the probe is pointing down.

12.4.8 Thoroughly wash with water (7.1.6) all probe surfaces wetted by the solution. Do not allow the runoff to drain into the calibration solution. Set the instrument to read  $I_H$  and turn the probe power on.

12.4.9 Thoroughly dry all probe surfaces with air or with acetone (7.1.2), using a firm stream from polyethylene wash bottle, for about 10 s. Do not allow the runoff to drain into the calibration solution.

12.4.10 Allow the probe to dry; do not allow the runoff to drain into the calibration solution. Remove the excess acetone from between the screw-cap and window or from the dome of the probe by wiping with a folded tissue paper. Do *not* touch the probe window with tissue paper. The probe must be completely dry before continuing.

12.4.11 Assure that  $I_E$  is 6.0 mA  $\pm$  0.2 mA and start the recorder. Remove the plug from the oven 80 s  $\pm$  10 s from the

time the probe is on. Insert the probe into the oven 10 s from removing the plug. The oven light should cycle ON/illuminate. Note the oven used in records. Hold the probe holder firmly in the oven.

12.4.12 Observe  $I_H$ . Note and record the maximum value as  $HP$  and  $I_Y$  if available. On adjustable units, adjust  $I_E$ , as required, to 6.0 mA  $\pm$  0.2 mA before  $HP$ , do not adjust  $I_E$  after  $HP$ . Do not change the range after observing  $HP$  as the reading may vary from scale to scale as a result of zero shift.

12.4.13 Continue observing  $I_H$ . Mark the chart when  $I_H$  equals  $HP/2$  (50 %  $HP$ ). Record displayed  $\lambda$  if available.

12.4.14 Remove the probe from the oven, reinsert the oven plug, and allow the probe to cool. Recommend baking out probe within an hour to increase probe life expectancy. Calibrated probes may be stored in a manner that precludes contamination and rusting, but must be baked out before the next run (12.1.2, 12.1.3, and 12.1.4).

12.4.15 See 13.3 for interpretation of calibration.

12.4.16 Reprocess as in 12.1, 12.2, and 12.3 and proceed as in 12.5.

#### 12.5 Low-Hydrogen Embrittlement Plating of Probe:

12.5.1 Pour 850 mL  $\pm$  50 mL (28.6 fl oz  $\pm$  0.17 fl oz) of plating solution (Section 9) into a clean dry 1 L beaker and insert four cadmium anodes (7.2.2) equally spaced and rigidly mounted to fit snugly inside the beaker. Anodes must be immersed in the solution at least 10 min before the plating to remove oxide film.

12.5.2 Record the solution temperature to within  $\pm 1^\circ\text{C}$  ( $\pm 2^\circ\text{F}$ ). The temperature must be 18  $^\circ\text{C}$  to 27  $^\circ\text{C}$  (65  $^\circ\text{F}$  to 80  $^\circ\text{F}$ ).

12.5.3 With probe off, set instruments with nonautomatic range selector to 100. Insert the prepared probe into the socket assembly and screw on the cap. Electrically connect the probe window by means of the socket assembly to the cathode side of the rectifier and the cadmium anodes to the anode side of the rectifier. Alternate between the ovens on consecutive tests. Use a probe calibrated in the same oven to be used for the plating run.

12.5.4 With the plating current off, immerse the probe into the plating solution equidistant from the anode rods with the probe pointing down and support so that the upper window edge is 3 mm to 6 mm ( $\frac{1}{8}$  in. to  $\frac{1}{4}$  in.) below surface of the solution. The probe must be immersed within 10 min of blasting for the run to be valid.

12.5.5 Within 30 s of probe immersion, plate the probe at the minimum applicable plating current density setting for a time to achieve maximum plating thickness allowed by the plating specification. Do not stir or agitate solution while plating, since this will increase  $\lambda$  values for contaminated solutions.

NOTE 3—For standard procedure, tests will require no stirring. However, when the procuring agency has authorized stirring, it can be used for process control tests.

12.5.5.1 Inspect the window surface during plating to ensure the absence of fingerprints and visible contamination.

12.5.5.2 The probe assembly may occasionally be tapped gently to dislodge adherent gas bubbles from the window surfaces.