Designation: B764 – 04 (Reapproved 2014)

Standard Test Method for Simultaneous Thickness and Electrode Potential Determination of Individual Layers in Multilayer Nickel Deposit (STEP Test)[1]

This standard is issued under the fixed designation B764; 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 method closely estimates the thickness of individual layers of a multilayer nickel electrodeposit and the potential differences between the individual layers while being anodically stripped at constant current density.[2,3]

1.2 This test method does not cover deposit systems other than multilayer electroplated nickel deposits.

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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[4]

B456 Specification for Electrodeposited Coatings of Copper Plus Nickel Plus Chromium and Nickel Plus Chromium
B504 Test Method for Measurement of Thickness of Metallic Coatings by the Coulometric Method
D1193 Specification for Reagent Water

3. Summary of Test Method

3.1 This procedure is a modification of the well-known coulometric method of thickness testing (Test Method B504). It is also known as the anodic dissolution or electrochemical stripping method.

3.2 Coulometric thickness testing instruments are based on the anodic dissolution (stripping) of the deposit at constant current, while the time is measured to determine thickness. As commonly practiced, the method employs a small cell that is filled with an appropriate electrolyte, and the test specimen serves as the bottom of the cell. To the bottom of the cell is attached a rubber or plastic gasket whose opening defines the measuring (stripping, anodic) area. If a metallic cell is used, the rubber gasket also electrically insulates the test specimen from the cell. With the specimen as the anode and the cell or agitator tube as the cathode, a constant direct current is passed through the cell until the nickel layer is dissolved. A sudden change in voltage between the electrodes occurs when a different metallic layer starts to dissolve.

3.3 Each different metal or species of the same metal requires a given voltage to keep the current constant while being stripped. As one nickel layer is dissolved away and the next layer becomes exposed, there will be a voltage change (assuming a constant current and difference in the electrochemical characteristics of the two nickel layers). The elapsed time at which this voltage change occurs (relative to the start of the test or previous voltage change) is a measure of the deposit thickness.

3.4 At the same time, the amplitude of the voltage change can be observed. That is, the ease (or difficulty) with which one layer can be dissolved or stripped with reference to another layer can be compared. The lower the voltage needed the more active the metal or the greater the tendency to corrode preferentially to a more noble metal adjacent to it.

3.5 Where the metallic layers are of such a similar nature that change of the stripping voltage is small, there can be problems in detecting this change if the voltage between the deplating cell (cathode) and the sample (anode) is measured. As the sample is dissolved anodically, cathodic processes are occurring on the deplating cell (cathode) surface that can also give rise to voltage changes, due to alterations of the cathode surface, thus obscuring the anode voltage change. This difficulty can be avoided by measuring the potential of the dissolving anodic sample with respect to an unpolarized third electrode (reference) placed in the cell. By recording this

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[1] This 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] For discussion of this test, see Harbulak, E. P., "Simultaneous Thickness and Electrochemical Potential Determination of Individual Layers in Multilayer Nickel Deposits," *Plating and Surface Finishing*, Vol 67, No. 2, February 1980, pp. 49–54.

[3] U.S. Patent 4,310,389. Assignee: The Chrysler Corp., Highland Park, MI 48203.

[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.

potential any difference in electrochemical activity between layers is more readily detected. The equipment may be calibrated against standards with known STEP values.

3.6 The thickness of any specific nickel layer may be calculated from the quantity of electricity used (current multiplied by time), area dissolved, electrochemical equivalent of nickel, anode efficiency, and density of the nickel layer.

3.7 Commercial instruments using this principle are available. They are usually a combination coulometric and STEP instrument. Reference standards are available to calibrate the instrument. The STEP Test, as is the Coulometric Test, is rapid and destructive to the coating.

4. Significance and Use

4.1 The ability of a multilayer nickel deposit to enhance corrosion resistance is a function of the difference in the electrode potentials of the nickel layers (as measured individually at a fixed current density in a given electrolyte versus a reference electrode) and the thicknesses of the layers. The potential differences must be sufficient to cause the bright nickel or top layer to corrode preferentially and sacrificially with respect to the semi-bright nickel layer beneath it.

4.2 This test procedure allows the measurement of these potential differences directly on an electroplated part rather than on separate foil specimens in such a way that time determines the thickness of each layer, while the potential difference between nickel layers is an indication of the corrosion resistance of the total nickel deposit.

4.3 The interpretation and evaluation of the results of this test should be by agreement between the purchaser and the manufacturer.

NOTE 1—This test may be used as a quality assurance test of the multilayer nickel coatings applied in production. It should be understood that due to many factors that influence the progress of corrosion during actual use of the part, the performance of different multilayer nickel deposits in the test cannot be taken as an absolute indicator of the relative corrosion resistance of these deposits in service.

5. Apparatus

5.1 *Composition of the Electrolyte*[5]:

Nickel Chloride ($NiCl_2 \cdot 6H_2O$)	300g/L
Sodium Chloride (NaCl)	50g/L
Boric Acid (H_3BO_3)	25g/L
pH	3.0[A]

[A] The pH may be adjusted with diluted hydrochloric acid or sodium hydroxide, as required, and is more critical than the composition of the electrolyte.

Prepared in Purified Water—Type IV or better as specified in Specification D1193.

5.2 *Constant Current Source*—This should supply a constant current that can be varied between 0 and 50 mA (typical 25 to 35 mA). A current of 30 mA corresponds to a stripping rate of 7.8 µm/min at 100 % current efficiency when used with a gasket providing 0.08 cm^2 stripping area. (This is achieved with the solution stated in 5.1.) Most commercial coulometric thickness testers can be used as the current source.

5.3 *Electrolyte Agitation Source*—All commercial coulometric thickness testers incorporate a means to agitate the solution. It is possible to purchase these types of units separately, if so desired, to be used externally in conjunction with other power supplies.

5.4 *Recorder*—Any time-based recorder with an input impedance of at least 1.0 MΩ and capable of running at approximately 0.5 mm/s (3 cm/min) can be used.

5.5 *Deplating Cell*—The cell may be similar in construction to commercially available coulometric deplating cells. It is usually a cup-shaped cell of either 316 stainless steel, copper-nickel alloy, or plastic that engages a round rubber or plastic gasket to the work piece or sample. The opening through the cell and gasket allows contact of the electrolyte to the test specimen and defines the stripping area.

NOTE 2—A coulometric deplating cell could be constructed of plastic using a cylindrical stainless steel or copper-nickel alloy sheet cathode located in the larger upper area of the cup. The advantages of such a cell are the prevention of whisker growth and the choking off of the small bore opening, and the ease of cathode removal for cleaning or replacement.

5.6 *Reference Electrode*—Either silver or platinum wire of approximately 1.5 mm in diameter can be used. Silver is probably the better choice due to its ability to form a silver-silver chloride electrode when used in a chloride containing electrolyte. The tip of the reference electrode should extend so that the distance between the tip of the electrode and the bottom of the agitator tube is approximately 5 mm.

NOTE 3—It is necessary to condition the silver electrode before using in order to form the silver-silver chloride surface. This is easily done by anodically treating approximately a 75-mm length of wire in 1 *N* hydrochloric acid solution for 10 to 15 s using 35-mA anodic current. This will form a gray film on the wire, which should always be present. Once the gray film is formed, it is not necessary to repeat the conditioning treatment unless the film has been removed. It may be advisable, however, to recondition the electrode after a prolonged period of inactivity or when the electrode has been allowed to remain dry for an extended period of time. Drying off the electrode should be avoided by immersion in either the hydrochloric acid conditioning solution, the step test solution, or distilled water when not in use.

NOTE 4—A ceramic junction reference electrode that does not require conditioning is available commercially.

5.7 *Millivolt Meter (optional)*—When using a sensitive and well-calibrated recorder, a millivolt meter is not necessary. If one is desired, however, any sensitive, high-input impedance meter can be used. A standard pH meter with a millivolt setting would be satisfactory. The meter should have a range from 0 to 2000 mV. If a millivolt meter is used which has low-output impedance facilities, it can be used in parallel to drive the recorder and will serve as a buffer amplifier. Most laboratory pH meters have such output terminals.

6. Procedure

6.1 Set up equipment as recommended by the manufacturer. If necessary, turn on the recorder and the millivolt meter and allow them to warm up.

6.2 If chromium is present on the nickel surface, remove it with concentrated hydrochloric acid. Make sure the nickel surface is clean. Rinse well and dry off the surface.

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[5] Electrolyte can be obtained commercially that meets the requirements of this test.

NOTE 5—Chromium can be removed by using the coulometric deplating cell as is done on many commercial coulometric testers. If this is done, secure the cell and gasket to the test piece as in 6.3 and 6.4 but do not insert the electrode assembly. Fill the cell with a common test stripping solution for chromium (Test Method B504) and hook up only the cell and test piece to the power supply. Apply the current until all the chromium has been removed. A dense blanket of bubbles on the surface of the sample indicates that all the chromium is removed. Remove the stripping solution from the cell without moving or disturbing the seal of the gasket to the test surface. Wash the cell three times with purified water (Type IV or better as specified in Specification D1193) and once with the step test solution. Proceed to 6.5.

6.3 Position the test specimen in a secure horizontal position so that the chromium-stripped nickel surface is directly beneath the cell gasket.

6.4 Lower the coulometric deplating cell assembly; secure by sealing the gasket to the nickel surface. A flat test area of approximately 10 mm in diameter is desirable but not required. The criterion is that there be no leakage of the electrolyte. If leakage does occur, discontinue test and start a new one.

6.5 Fill the coulometric deplating cell to the appropriate level with the step test solution making sure that no air is trapped within the solution.

6.6 Lower the reference electrode assembly into the coulometric deplating cell, if necessary. The positioning of the reference electrode should be such that the distance from the end of the electrode to the test specimen is reproducible to within 1 mm and be held constant throughout the test.

NOTE 6—The insertion depth of the electrolyte agitation tube which includes the reference electrode is important and should always be the same. The *difference* of potential rather than the absolute potential is the important measurement.

6.7 Check all electrical connections. Make sure all connections are secure and that no corrosion exists at the contact points and that all contact points are secure.

6.8 Start the recorder (turn on milliampere meter, if used). The recorder must be calibrated in order to determine the thickness of the nickel layers. This may be accomplished by using commercially available thickness standards or by applying Faraday's Law. The latter requires information about the current, corroding area, electrochemical equivalent of nickel, density of nickel, efficiency, and the time base of the recorder (see 6.11).

6.9 Turn on the constant current source and agitator, which in turn will start the deplating reaction. Continue recording until the surface underlying the nickel is reached. This end point can be recognized graphically by a sudden change in voltage. If the basis metal is zinc, iron, or steel, the voltage will decrease; if it is copper or brass, the voltage will increase.

6.10 Stop the test by turning off the agitator, constant current source, recorder, and milliampere meter. Remove the electrode assembly, if necessary, and empty the cell of the stripping solution. Wash the cell three times with purified water (Type IV or better as specified in Specification D1193) before continuing to the next test.

6.11 This test is based on a measured current-time relationship necessary to remove a given amount of nickel from a specific area.

Example: if the constant current source produces 30 mA, the recorder time base is 30 mm/min, and the deplating area is 0.08 cm^2, it would take 19.2 s to deplate 2.5 µm of nickel. The chart would travel 9.6 mm. A general equation that may be used is as follows:

$$\frac{(SL)\ (A)\ (I)}{(0.303)\ S} = T \tag{1}$$

where:

SL = chart scan length, mm,
S = chart speed, mm/min,
I = cell current, mA,
A = deplating area, cm,
T = nickel thickness, µm, and
0.303 = constant calculated from the electrochemical equivalent and density of nickel.

NOTE 7—Commercial units are available that will modify and may simplify the above procedure.

7. Factors Affecting the Accuracy of the Method

7.1 *Excessive Metal Build-Up in Coulometric Deplating Cell*—Excessive buildup of deposited nickel or the formation of "whiskers" on the inside of the coulometric deplating cell (cathode), especially near the gasket hole, can cause erratic results and produce "noisy" curves. When buildup is observed, remove it completely according to the manufacturer's instructions or as follows:

7.1.1 If a metallic cell is used as a cathode:

7.1.1.1 Ream with a round, fine file. (A drill or reamer may be used.)

7.1.1.2 Soak for 15 to 20 s in a solution of four parts concentrated sulfuric acid and one part concentrated nitric acid. If 316 stainless steel is used for the cell, it may be soaked in concentrated nitric acid until all nickel is dissolved.

7.1.1.3 Rinse in water (Type IV or better as specified in Specification D1193) and dry.

7.1.1.4 Repeat 7.1.1.1 to 7.1.1.3 as many times as necessary to remove all metallic buildup. This cleaning process should be done after every ten tests or more frequently, if necessary.

NOTE 8—It has been found that giving the coulometric deplating cell (cathode) a nickel strike prior to using will help prevent erratic buildup or treeing around the gasket hole and cleaning will not be required as often.

7.1.2 If a metallic agitator tube is used as a cathode:

7.1.2.1 Place a stainless steel or nickel plate under the gasket, lower the cell, and rinse it with DI water.

7.1.2.2 Fill the cell with 2 to 2.5 M H_2SO_4, reverse the polarity of the current and strip the nickel from agitator tube. A cleaning current of about 55 mA for about 45 s should suffice. If the nickel is not completely removed, drain the cell, refill it with H_2SO_4, and repeat the cleaning.

7.1.2.3 Wash the cell thoroughly with water.

7.1.2.4 If the tube still looks coated, remove the coating by rubbing the agitation tube with a soft rubber eraser, followed by washing with water.

7.2 *Reference Electrode Preparation*—If the electrode has not been used for a day or has been allowed to dry for a period of time, one or two conditioning runs will have to be made prior to running a meaningful test. (See Note 2.)

7.3 *Cleanliness of Test Surface*—Make sure the surface area to be tested is free of water breaks, foreign material, etc. Nickel surfaces that have been exposed to air for some time may have become passive. Abrade lightly prior to testing to remove any oxide films present. (Abrading mildly with an eraser usually suffices: if not, clean with dilute sulfuric acid.)

7.4 *Anode Area Variation*—Use only enough pressure on the gasket to seal it to the test area without solution leaks. Excess pressure can distort the gasket and change the anode area affecting the thickness results. If test results vary significantly, examine the resulting deplated area with a magnifying glass to determine if the area has varied in size. Small variations in the anodic area can give large variations in test results. The area defined by the gasket can vary significantly between gaskets. When a different gasket is used, recalibrate the instrumentation.

7.5 *Electrical Noise*—To obtain good, smooth curves, eliminate all electrical noise caused by extraneous voltage fluctuations. Using a buffer amplifier with the shortest leads possible to the cell to drive the recorder may be required to obtain usable results. Shielding the leads to the test cell will also help. If the curves are extremely noisy (erratic), make at least two curves on the same area to determine if the results are meaningful and consistent. It may be necessary to insert an electrical filter in the line source ahead of the constant current supply.

7.6 *Insertion Depth of Agitation Tube*—If the agitation tube contains the reference electrode, insert the tube in the cell to the same depth each time (see 6.6), but not so deep as to“ shield” or interfere with the area being stripped.

7.7 *Incomplete Dissolution of the Nickel*—Even though an apparent end point is observed, the nickel may not be completely dissolved. There may be small islands of nickel left, or the periphery of the depleted area may be irregular or uneven. This may be associated with a tilt of the cell relative to the coating surface. Examine the test area with a magnifying lens after each test to insure that all the nickel has been dissolved from the test area. If nickel is present, rerun the test until the test area does not contain any nickel.

8. Interpretation of Results

8.1 The data obtained from this test will be shown on the recorded graph, which plots the thickness (stripping time) of nickel on the *X*-axis versus the millivolt (potential) of the nickel layers on the *Y*-axis. The thicknesses of the individual layers (or time differential) is measured between the steps or breaks in the curve along the x-axis while the electrode potential difference is determined by the change in amplitude of the curve on the *Y*-axis. It is desirable that at least two tests, within 6 to 8 mm of each other, be made on each test area and the results averaged.

8.2 *Interpretation of Curve*—Referring to Fig. 1, it can be seen that there are steps or breaks (changing potential) or steps in the curve when moving left to right (increasing thickness).

NOTE 9—The values given in Fig. 1 are included only to simplify the discussion for the Interpretation of Results. The actual values obtained during testing will depend on the nature of the equipment, experimental technique, the specific characteristics of the electroplating processes used to produce the multilayer coatings and other details. It is emphasized that the curve in Fig. 1 is an idealization of an actual result. Although the potential differences are reproducible, the values of the individual potentials may shift depending on the experimental results.

8.2.1 *Microdiscontinuous Nickel*—The first break or step, A to C, in the solid curve is small and occurs at a nickel thickness of approximately 3 µm in Fig. 1. The deposit represented by this curve, from 0 to 3 µm, is a nickel strike which might be used to induce microdiscontinuity in the chromium deposited over this strike, see Note 10. In Fig. 1, the difference in activity between this nickel strike deposit, B (750 mV), and the bright nickel deposit, C (730 mV), is 20 mV. This makes the deposit less active (cathodic) than the bright nickel deposit.

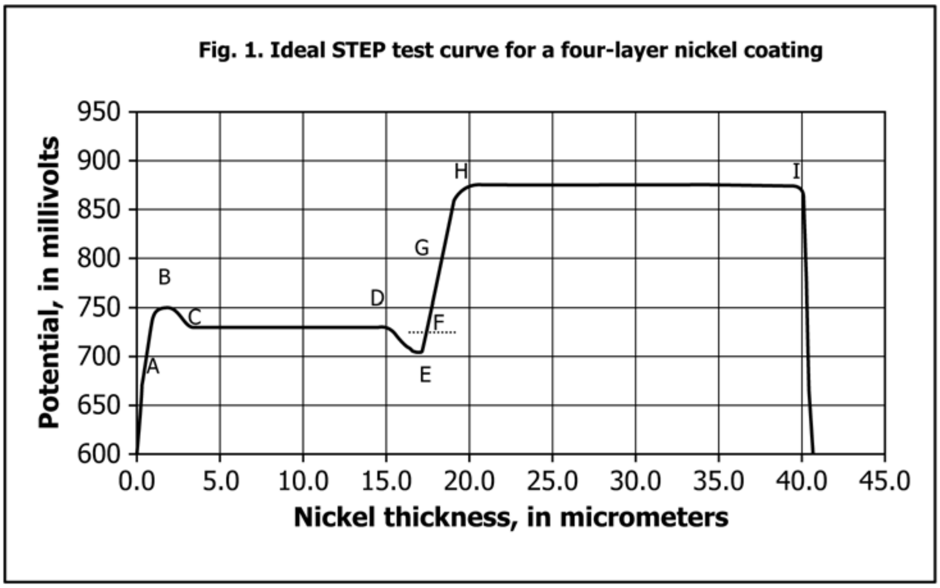

FIG. 1 T-Shaped Reference Electrode Assembly

NOTE 10—This nickel deposit is referred to as microdiscontinuous nickel when it contains inert particles (particle nickel) to produce micro-porous chromium or when it is microcracked (stressed nickel deposit) to produce microcracked chromium. When the nickel strike deposit is not used to produce discontinuities in the chromium, it can be referred to as "noble nickel" if its electrode potential (millivolt activity) is more noble (less active) than the adjacent bright nickel deposit.

8.2.2 *Bright Nickel*—After the first section of the curve ending at about 3 µm, the curve in Fig. 1 experiences another break or step at the 15 µm thickness mark in the figure, point D. This represents at least 12 µm of bright nickel (see 8.2.4) with a potential of 730 mV.

8.2.3 *High Potential Nickel Strike*—The line D to F in Fig. 1 between 15 µm and 18 µm represents the shape of the curve of a high potential nickel strike that in this case is 3 µm thick. For it to be classified as a high potential strike, it must have an electrode potential more active than the adjacent bright nickel deposit. In this example, the 705 mV (E) high potential nickel strike is 25 mV more active than the 730 mV bright nickel deposit (D).

8.2.4 *Semi-bright Nickel*—In Fig. 1, a large potential change occurs, F to H. This slope is the result of the cell transitioning from dissolving the last of the higher activity bright nickel and starting to dissolve the lower activity semi-bright nickel deposits. In Fig. 1, the semi-bright nickel has an electrode potential that is 145 mV less active (cathodic) than the bright nickel deposit. This is the STEP value for this multi-layered nickel coating. Determining the thickness of the bright and semi-bright nickel deposits, as in Fig. 1, normally involves making an estimate. Since the distance along the x-axis between points F and H is when the cell is transiting between the bright and the semi-bright nickel deposits, assigning half of the thickness to both deposits is usually an acceptable procedure. This thickness is usually very small compared to the thickness between C and D for the bright and H and I for the semi-bright nickels. Alternative procedures are presented in 8.2.6 and 8.4.

NOTE 11—The step in the curve is never a straight perpendicular line. As the bright nickel is dissolved, the plotted potential is associated only with the bright nickel until the semi-bright nickel is exposed and starts to dissolve. At this point, the measured potential increases and continues to increase until only semi-bright nickel is exposed except for bright nickel on the walls of the pit formed by dissolution of the nickel. From this point on the recorded potential is due primarily to the semi-bright nickel.

NOTE 12—Most corrosion studies have demonstrated that for the best corrosion results, if a nickel strike is used between the chromium deposit and the bright nickel, it should have an electrochemical electrode potential equal to, or preferably more noble (less active) than the bright nickel deposit. The semi-bright nickel deposit should also be more noble (less active) than the bright nickel deposit (see Specification B456).

8.2.5 *Substrate*—The line after at about 40 µm in Fig. 1 represents the direction the curve will take if a steel substrate is under the semi-bright nickel deposit. The curve would turn up if a copper substrate was used.

8.2.6 *Thickness and STEP Measurements*—Since the rise of the actual STEP curve is normally not a nearly straight line as depicted in Fig. 1, it is best to read the thickness at the midpoint on the rising portion of the curve (see Fig. 2 and 8.4) if it is difficult to assign a millivolt reading due to the shape of the curve, see 8.4 and Notes 13 and 14.

8.3 When a STEP value is referenced, such as in a standard, it refers to the electrode potential in millivolts between the bright nickel and the semi-bright nickel deposits. In Fig. 1, the STEP is 145 mV. When additional STEP values are presented, they must include the deposit being referenced and its relative activity to the deposit in which it is paired. In Fig. 1, the STEP for the high potential nickel strike is 25 mV more active than the bright nickel deposit.

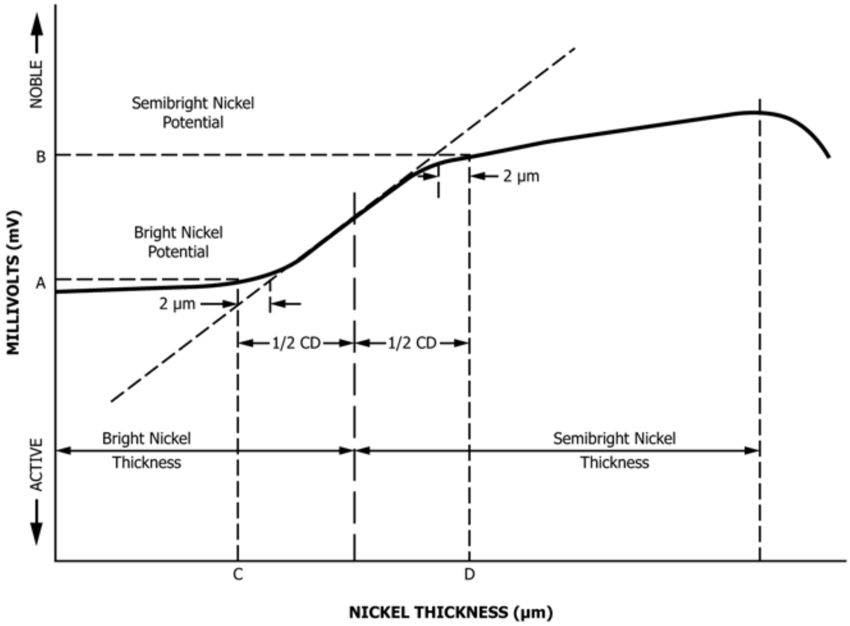

FIG. 2 Midpoint Nickel Thickness Curve

8.4 In some instances, the obtained curves may show irregularities such as drift (deviation from a straight line) in the plot for the semi-bright nickel, the bright nickel deposit, or both. The drift may be more noticeable with thick multilayer deposits. The curve also may exhibit a greater than normal drift or elongation of the step (rising portion of the plot). In order to minimize error in interpreting this type of curve, the millivolt reading for the bright nickel is taken 2 µm before the rise of the curve, point A on Fig. 2 (the point at which the semi-bright nickel is first exposed in the cell), and the mV reading for the semi-bright nickel is taken 2 µm after the rise of the curve, point B on Fig. 2 (the point at which the potential reading is due predominantly to the exposure of only the semi-bright nickel). Where the multilayer nickel contains a thin layer of a high potential deposit, the potential of the bright nickel will be taken at a point 2 µm before the dip in the curve attributed to the high potential layer. Use of an indicating (digital display) meter is helpful if the chart is periodically annotated (every 15 to 30 s) with the display reading.

NOTE 13—Due to the much thinner "microdiscontinuous nickel" and "high potential nickel" strikes, compared to the bright and semi-bright nickel deposits, an estimate of their potentials and thickness is sometimes all that is obtainable.

NOTE 14—Another method is to determine the point of inflection of the curve, which is the point of maximum slope. If it is not evident to the eye, the use of a straight edge can be helpful. The straight edge is lined up with the step portion of the curve as shown in Fig. 2. The segment of the plot with the maximum slope should be of finite length, line C-D in Fig. 2, and the midpoint of the segment can be taken.

9. Precision and Bias

9.1 In the case of multilayer nickel coatings, the measurement uncertainty or precision of the method has been studied on electroplated panels. Results based on measurements made in three laboratories showed that the thickness of semi-bright and bright nickel layers can be determined with a standard deviation of ±1.65 µm with a variance of 9.2 %. The potential difference between semi-bright and bright nickel can be measured with a standard deviation of ±3.7 mV with a variance of 2.6 %.

NOTE 15—The relatively high variance in the thickness measurements, 9.2 %, was due to actual variation in coating thickness at various points on the panel. This was confirmed by measuring thickness by the microscopical method at points close or adjacent to the spots used in the STEP tests. The results were in close agreement, that is, the variation in local thickness displayed in the STEP test measurements was also observed in the microscopical measurements. Also, the electrode potential results from tests made at different current-density locations on a single sample can vary greatly due to the different characteristics of nickel electroplated at different current densities.

9.2 Measurements made on primary standard reference materials[6] that certify the thickness, thickness uniformity, and the potential difference between the semi-bright and bright nickel layer showed that thickness could be measured with a standard deviation of ±0.5 µm with a variance of 2.1 %. The potential difference was measured with a standard deviation of ±0.82 mV with a variance of 0.7 %.

9.3 3 Determination of the bias or accuracy of the method has not been studied in detail. Note 12 suggests, however, that the STEP test provides as accurate a determination of the local nickel thickness as does the microscopical method.

10. Keywords

10.1 potential; STEP; thickness

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[6] Primary Standard Reference Material (SRM) Number 2350 for calibrating this method is available from the National Bureau of Standards, Office of Standard Reference Materials, Gaithersburg, MD 20899.