

# Standard Guide for Electroforming with Nickel and Copper<sup>1</sup>

This standard is issued under the fixed designation B832; 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  $(\varepsilon)$  indicates an editorial change since the last revision or reapproval.

# 1. Scope

- 1.1 This guide covers electroforming practice and describes the processing of mandrels, the design of electroformed articles, and the use of copper and nickel electroplating solutions for electroforming.
- 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.

#### 2. Referenced Documents

- 2.1 ASTM Standards:<sup>2</sup>
- B183 Practice for Preparation of Low-Carbon Steel for Electroplating
- B242 Guide for Preparation of High-Carbon Steel for Electroplating
- B252 Guide for Preparation of Zinc Alloy Die Castings for Electroplating and Conversion Coatings
- B253 Guide for Preparation of Aluminum Alloys for Electroplating
- B254 Practice for Preparation of and Electroplating on Stainless Steel
- **B281** Practice for Preparation of Copper and Copper-Base Alloys for Electroplating and Conversion Coatings
- B311 Test Method for Density of Powder Metallurgy (PM)
  Materials Containing Less Than Two Percent Porosity
- B343 Practice for Preparation of Nickel for Electroplating with Nickel
- **B374** Terminology Relating to Electroplating
- B489 Practice for Bend Test for Ductility of Electrodeposited and Autocatalytically Deposited Metal Coatings on Metals

- B490 Practice for Micrometer Bend Test for Ductility of Electrodeposits
- **B558** Practice for Preparation of Nickel Alloys for Electroplating
- B571 Practice for Qualitative Adhesion Testing of Metallic Coatings
- B578 Test Method for Microhardness of Electroplated Coatings
- B636 Test Method for Measurement of Internal Stress of Plated Metallic Coatings with the Spiral Contractometer B659 Guide for Measuring Thickness of Metallic and Inor-
- ganic Coatings

  P840 Specification for the Treatments of Iron or Steel for
- B849 Specification for Pre-Treatments of Iron or Steel for Reducing Risk of Hydrogen Embrittlement
- E8 Test Methods for Tension Testing of Metallic Materials E384 Test Method for Knoop and Vickers Hardness of Materials

# 3. Summary of Electroforming Practice

- 3.1 Electroforming is defined (see Terminology B374) as the production or reproduction of articles by electrodeposition upon a mandrel or mold that is subsequently separated from the deposit.
- 3.2 The basic fabrication steps are as follows: a suitable mandrel is fabricated and prepared for electroplating; the mandrel is placed in an appropriate electroplating solution and metal is deposited upon the mandrel by electrolysis; when the required thickness of metal has been applied, the metal-covered mandrel is removed from the solution; and the mandrel is separated from the electrodeposited metal. The electroform is a separate, free-standing entity composed entirely of electrodeposited metal. Electroforming is concerned with the fabrication of articles of various kinds.

#### 4. Significance and Use

4.1 The specialized use of the electroplating process for electroforming results in the manufacture of tools and products that are unique and often impossible to make economically by traditional methods of fabrication. Current applications of nickel electroforming include: textile printing screens; components of rocket thrust chambers, nozzles, and motor cases; molds and dies for making automotive arm-rests and instrument panels; stampers for making phonograph records, videodiscs, and audio compact discs; mesh products for making

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<sup>&</sup>lt;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.

porous battery electrodes, filters, and razor screens; and optical parts, bellows, and radar wave guides (1-3).<sup>3</sup>

- 4.2 Copper is extensively used for electroforming thin foil for the printed circuit industry. Copper foil is formed continuously by electrodeposition onto rotating drums. Copper is often used as a backing material for electroformed nickel shells and in other applications where its high thermal and electrical conductivities are required. Other metals including gold are electroformed on a smaller scale.
- 4.3 Electroforming is used whenever the difficulty and cost of producing the object by mechanical means is unusually high; unusual mechanical and physical properties are required in the finished piece; extremely close dimensional tolerances must be held on internal dimensions and on surfaces of irregular contour; very fine reproduction of detail and complex combinations of surface finish are required; and the part cannot be made by other available methods.

# 5. Processing of Mandrels for Electroforming

- 5.1 General Considerations:
- 5.1.1 Mandrels may be classified as conductors or nonconductors of electricity, and each of these may be permanent, semipermanent, or expendable (Table 1).

**TABLE 1 Types of Mandrel Materials** 

| 77522 1 Types of manarer materials |   |  |  |
|------------------------------------|---|--|--|
| Types                              | Typical Materials   |  |  |
| Conductors                         |   |  |  |
| Expendable                         | Low-melting point alloys; for example, bismuth-free 92 % tin and 8 % zinc Aluminum alloys                                 |  |  |
| Permanent                          | Zinc alloys Nickel Austenitic Stainless Invar, Kovar Copper and brass Nickel-plated steel Nickel/chromium-plated aluminum |  |  |
| None                               | conductors  |  |  |
| Expendable                         | Wax<br>Glass  |  |  |
| Permanent (or Semi-Permanent)      | Rigid and collapsible plastic; for example, epoxy resins and polyvinyl chloride Wood                                      |  |  |

- 5.1.2 Whether or not a mandrel is a conductor will determine the procedures required to prepare it for electroforming. Conductive mandrels are usually pure metals or alloys of metals and are prepared by standard procedures but may require an additional thin parting film to facilitate separation of the electroform from the mandrel (unless the mandrel is removed by melting or chemical dissolution).
- 5.1.3 Whether or not a permanent or expendable mandrel should be used is largely dependent on the particular article that is to be electroformed. If no reentrant shapes or angles are involved, it is possible to use permanent, rigid mandrels that

can be separated from the finished electroform mechanically and reused. If reentrant angles and shapes are involved, it is necessary to use mandrel materials that can be removed by melting or by chemical dissolution, or materials that are collapsible, such as polyvinyl chloride and other plastics. In some cases, multiple piece mandrels are used that can be removed even with reentrant features.

5.1.4 Many solid materials can be used to fabricate mandrels for electroforming, but the following generalizations may help in selecting a suitable material: permanent mandrels are preferred for accuracy and for large production runs; expendable mandrels must be used whenever the part is so designed that a permanent mandrel cannot be withdrawn; and it is important that the mandrel retain its dimensional stability in warm plating baths. Wax and most plastics expand when exposed to electroplating solutions operated at elevated temperatures. In such cases, it may be necessary to use acid copper, nickel sulfamate, and other electroplating solutions that function at room temperature.

# 5.2 Mandrel Design:

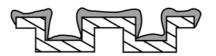
- 5.2.1 The electroforming operation can often be simplified by design changes that do not impair the functioning of the piece. Some of the design considerations are summarized in 5.2.2, 5.2.3, 5.2.4, 5.2.5, and 5.2.6. Examples of mandrel shapes that may present problems during electroforming are illustrated in Fig. 1.
- 5.2.2 Exterior (convex) angles should be provided with as generous a radius as possible to avoid excessive build up and treeing of the deposit during electroforming. Interior (concave) angles on the mandrel should be provided with a fillet radius of at least 0.05 cm per 5 cm (0.02 in. per 2 in.) of length of a side of the angle.
- 5.2.3 Whenever possible, permanent mandrels should be tapered at least 0.08 mm per m (0.001 in. per ft) to facilitate removal from the mandrel. (Where this is not permissible, the mandrel may be made of a material with a high or low coefficient of thermal expansion so that separation can be effected by heating or cooling).
- 5.2.4 A fine surface finish on the mandrel, achieved by lapping or by electropolishing, will generally facilitate separation of mandrel and electroform. A finish of 0.05  $\mu$ m (2  $\mu$ in.) rms is frequently specified.
- 5.2.5 Flat bottom grooves, sharp angle indentations, blind holes, fins, v-shaped projections, v-bottom grooves, deep scoops, slots, concave recesses, and rings and ribs can cause problems with metal distribution during electroforming unless inside and outside angles and corners are rounded.
- 5.2.6 An engineering drawing of the mandrel, the electroformed article, and auxiliary equipment or fixture for separating the electroform from the mandrel should be prepared. The drawing of the mandrel should provide for electrical connections to be made in nonfunctional areas of the electroform. It should provide reference points for and mechanical means of holding if finish machining is necessary before removal of the mandrel.

## 5.3 Mandrel Fabrication:

5.3.1 The method of fabrication of the mandrel will depend on the type selected, the material chosen, and the object to be

<sup>&</sup>lt;sup>3</sup> The boldface numbers in parentheses refer to the list of references at the end of this standard.

# FLAT BOTTOM GROOVES OR SHARP ANGLE INDENTATIONS



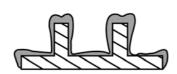
INSIDE AND OUTSIDE ANGLES SHOULD BE ROUNDED GENEROUSLY.

#### **BLIND HOLES**



BLIND HOLES ARE USUALLY EXEMPTED FROM MINIMUM THICKNESS REQUIREMENTS

#### **FINS**



FINS INCREASE THE ELECTROFORMING TIME AND COSTS FOR A SPECIFIED MINIMUM THICKNESS.

## **V SHAPED PROTRUSIONS**



BUILD UP ON JUT WILL ROB CORNERS OF THEIR SHARE OF THE DEPOSIT. CROWN THE BASE AND ROUND OFF ALL CORNERS

# **V BOTTOM GROOVES**



DEEP V-SHAPED GROOVES CANNOT BE ELECTROFORMED SATISFACTORY AND SHOULD BE AVOIDED. SHALLOW, ROUNDED GROOVES ARE BETTER.

#### **DEEP SCOOPS**



DEEP SCOOPS INCREASE ELECTRO-FORMING TIME AND COSTS FOR A SPECIFIED MINIMUM THICKNESS.

Note 1—Examples of deposit distribution on contours that require special consideration are shown in an exaggerated fashion. The designer should confer with the electroformer before designing an electroform having any of these contours. An experienced electroformer can minimize some of the exaggeration shown.

FIG. 1 Examples of Deposit Distribution on Electroforms

electroformed. Mandrels may be manufactured by casting, machining, electroforming, and other techniques. Permanent mandrels can be made by any of the conventional patternmaking processes.

- 5.4 Preparing Non-Conducting Mandrels:
- 5.4.1 Nonconducting mandrels must be made impervious to water and other processing solutions and then rendered conductive. Porous materials, for example, leather and plastic, may be impregnated with wax, shellac, lacquer, or a synthetic resin formulation. It is often preferable to use thin films of lacquer to seal porous, nonmetallic mandrels.
- 5.4.2 Nonconducting materials may be rendered conductive by applying a chemically reduced film of silver, copper, or nickel to the surface. In general, these processes are carried out by spraying the reagent containing the metal ions of choice simultaneously with a specific reducing agent onto the surface of the mandrel using a double-nozzle spray gun. The chemicals react at the surface; the metal is reduced and is deposited on the mandrel surface. Chemical reduction processes are preferred because dimensional accuracy is not affected, the film has little adhesion, and parting is not difficult. If necessary, a silver film can be stripped from a nickel electroform with either nitric acid, warm sulfuric acid, or a cyanide solution.
- 5.4.3 Other ways of making non-conducting materials conductive include: using finely divided metal powders dispersed in binders ("bronzing"), applying finely divided graphite to wax, and to natural or synthetic rubbers that have an affinity for graphite, and applying graphite with a binder.
- 5.4.4 Vapor deposition of silver and other metals is preferred for nonconducting mandrels used in the semiconductor industry, the optical disc industry, and the manufacture of holograms. In these cases the mandrel must be made of a material that does not outgas in the vacuum chamber. Glass is the preferred substrate for making masters and stampers for optical read-out discs of all kinds.
  - 5.5 Preparing Metallic Mandrels:
- 5.5.1 Standard procedures should be used whenever adherent electrodeposits are applied to metallic mandrels prior to and in preparation for electroforming. See Practices B183, B242, B254, B281, and B558, for example.
- 5.5.2 With most metallic mandrels an additional chemical treatment that forms a parting film on the surface is required to separate the electroform from the mandrel. After removing all traces of grease and oil by means of solvents, various metallic mandrels are given different treatments for this purpose (see 5.5.3, 5.5.4, 5.5.5, 5.5.6, and 5.5.7).

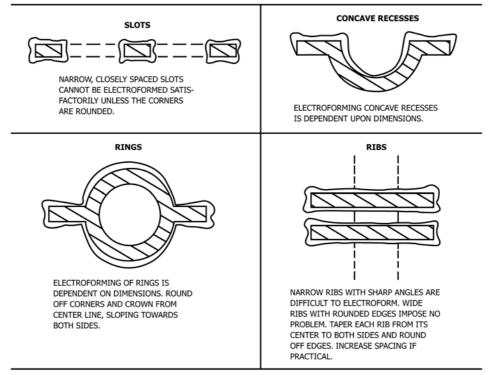


FIG. 1 (continued)

- 5.5.3 Stainless steel, nickel, and nickel- or chromium-plated steel are cleaned using standard procedures, rinsed, and passivated by immersion in a 2 % solution of sodium dichromate for 30 to 60 s at room temperature. The mandrel must then be rinsed to remove all traces of the dichromate solution.
- 5.5.4 Copper and brass mandrels that have been nickel and/or chromium-plated may be treated as described in 5.5.3. If not electroplated, the surface can be made passive by immersion in a solution containing 8 g/L sodium sulfide.
- 5.5.5 Aluminum alloys may require special treatments even when they are used as expendable mandrels to be separated by chemical dissolution. If the deposits are highly stressed, it may be necessary to use the zincate or stannate treatments included in Guide B253 to achieve a degree of adhesion that will prevent lifting of the deposit from the mandrel. When low-stressed deposits (near zero) are being produced, treatment of the aluminum by degreasing, cathodic alkaline cleaning, and immersion in a 50 % solution of nitric acid may be sufficient.
- 5.5.6 Zinc and its alloys may require no other preparation than conventional cleaning if used for expendable mandrels and are to be parted by chemical dissolution. In the case of nickel electroforming, it is necessary to electroplate the zinc alloy with copper and treat it accordingly to prevent attack of the mandrel. See Practice B252.
- 5.5.7 The low-melting point alloys included in Table 1 employed to make expendable mandrels that can be melted away have a tendency to leave a residue of tin on the surface of the electroform. The mandrel can be plated with copper prior to electroforming to prevent this.

# 6. Nickel and Copper Electroforming Solutions

- 6.1 The choice of metal selected for the electroform will depend on the mechanical and physical properties required in the finished article as related to function. The two metals selected most frequently are nickel and copper. The operation and control of nickel and copper electroforming solutions are described in this section.
- 6.2 The nickel electroplating solutions commonly used for electroforming are Watts and nickel sulfamate with and without addition agents. The advantages of nickel electroforming from sulfamate solutions are the low internal stress of the deposits and the high rates of deposition that are possible. The important copper electroforming solutions are copper sulfate and copper fluoborate. The formulations of nickel electroforming solutions, typical operating conditions, and typical mechanical properties of the deposits are given in Table 2. Similar information for copper electroforming is given in Table 3.
- 6.3 Watts Solutions—The Watts bath contains nickel sulfate, nickel chloride, and boric acid and yields nickel deposits that are matte in appearance and that are tensively stressed. The solution is relatively inexpensive and is successfully used for electroforming. Nickel sulfate is the main source of nickel ions. Nickel chloride increases solution conductivity and has a beneficial effect on the uniformity of metal distribution at the cathode. Boric acid acts as a buffer to control pH at the cathode-solution interface. Antipitting agents (wetting agents) are essential for avoiding pitting due to the clinging of air and

TABLE 2 Nickel Electroforming Solutions and Typical Properties of the Deposits

|  | Electrolyte Composition, g/L |                     |  |  |
|--|------------------------------|---------------------|--|--|
|  | Watts Nickel                 | Nickel Sulfamate    |  |  |
| NiSO <sub>4</sub> ⋅6H <sub>2</sub> O                                 | 225 to 300                   |                     |  |  |
| Ni(SO <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub> ·4H <sub>2</sub> O |                              | 315 to 450          |  |  |
| NiCl <sub>2</sub> ·6H <sub>2</sub> O                                 | 37 to 53                     | 0 to 22             |  |  |
| H <sub>3</sub> BO <sub>3</sub>                                       | 30 to 45                     | 30 to 45            |  |  |
|  | Operating Conditions         |                     |  |  |
| Temperature, °C  | 44 to 66                     | 32 to 60            |  |  |
| Agitation  | Air or mechanical            | Air or mechanical   |  |  |
| Cathode Current<br>Density, A/dm <sup>2</sup>                        | 3 to 11                      | 0.5 to 32           |  |  |
| Anodes   | nickel                       | nickel <sup>A</sup> |  |  |
| pH   | 3.0 to 4.2                   | 3.5 to 4.5          |  |  |
| Mechanical Properties  |                              |                     |  |  |
| Tensile Strength, MPa  | 345 to 485                   | 415 to 620          |  |  |
| Elongation, %  | 15 to 25                     | 10 to 25            |  |  |
| Vickers Hardness, 100 g<br>load                                      | 130 to 200                   | 170 to 230          |  |  |
| Internal Stress, MPa   | 125 to 185 (tensile)         | 0 to 55 (tensile)   |  |  |

A See 6.4 and 8.3.5

hydrogen bubbles. With care, the internal stress of the electroformed nickel can be controlled by means of organic addition agents. See 8.3.

6.4 Nickel Sulfamate Solutions-A formulation for nickel sulfamate solutions is included in Table 2. These are analogous to Watts solutions in which the nickel sulfate is replaced with nickel sulfamate. The internal stress is lower than in the Watts solution, as indicated by the information on mechanical properties in Table 2. The zero stress level may be obtained by maintaining the solution in a high state of purity and by eliminating the nickel chloride. To minimize hydrolysis of nickel sulfamate and the formation of sulfate and ammonium ions, these solutions may be operated above pH 3.5 and below 50°C. To ensure efficient dissolution of nickel anodes in the absence of chlorides, it is essential to use sulfur-activated nickel anode materials. A stable tensile stress can be maintained in nickel sulfamate solutions by including nickel chloride in the formulation, by using an adequate anode area (1.5 to 2 times the area of the cathode), and by using a fully-active nickel anode material to maintain the potential on the anode basket as low as possible, thus avoiding oxidation of the sulfamate anion (see 8.3.5). Under these conditions the stress level normally is about 35 MPa (5000 psi) tensile for a well-worked solution.

6.5 Copper Electroforming Solutions—Copper sulfate solutions are used more often than copper fluoborate solutions. The internal stress of copper deposits is generally lower than that of electrodeposited nickel. One of the features of the fluoborate solution is the ability to electrodeposit copper at high current densities.

# 7. Properties of Electrodeposited Nickel and Copper

7.1 The mechanical properties—tensile strength, elongation, hardness, and internal stress—are influenced by the operational variables including temperature, pH, and current

density, and by solution composition (4). The qualitative effects of these variables on the mechanical properties of nickel and copper electrodeposits are summarized in Table 4, Table 5, Table 6, and Table 7. Relatively small amounts of metallic impurities in solution can also affect mechanical properties. The properties are interrelated, and steps taken to increase the hardness of the deposit usually increase its strength and lower its ductility. The refinement of crystal structure, for example by the use of organic addition agents, is accompanied by increased hardness and tensile strength and reduced ductility. Typical properties of deposits from various additive-free baths are included in Table 2 and Table 3. See Refs. 5-7.

7.2 The mechanical properties, especially the percent elongation or ductility, may be affected by the thickness of the electrodeposited metal used in determining the properties. For example, the ductility of nickel increases with increasing thickness up to about 250  $\mu$ m after which it becomes relatively constant (8). Mechanical testing should be done at the thickness of interest even though it may be more convenient to test thick deposits.

# 8. Control of Electroforming Processes

8.1 Successful electroforming requires careful control of the purity of the electrolyte and of the operating variables, such as pH, current density, temperature, and agitation. The common problems encountered in electroforming include controlling metal distribution, internal stress, roughness, and nodule formation. Addition agents may help overcome some of these problems, but their concentrations must be closely controlled.

# 8.2 Metal Distribution:

8.2.1 The variation of the thickness of the metal deposited at various points on the surface of a mandrel is related to current distribution. Recessed areas will receive less current; areas that project from the surface will receive higher current. The current density and the rate of metal deposition will be lower in recessed areas than at areas which project from the surface. The result is that metal distribution will be nonuniform in many cases. The deposit will be relatively thin in recessed areas and relatively thick on projections.

8.2.2 Metal distribution is improved by proper racking and by the use of thieves, shields, and/or conforming or auxiliary anodes. The use of these processing aids makes it possible to control metal distribution and obtain relatively uniform deposits

# 8.3 Internal Stress:

8.3.1 The control of internal stress is extremely important in electroforming because of the deliberately low adhesion between the electroform and the mandrel. Internal stress refers to forces created within an electrodeposit as a result of the electrocrystallization process and/or the codeposition of impurities such as hydrogen, sulfur, and other elements. The forces are either tensile (contractile) or compressive (expansive) in nature; rarely are electrodeposits free of some degree of internal stress. Internal stress may be measured in accordance with Test Method B636.

8.3.2 Excessive tensile or compressive stress can cause the following problems: distortion of the electroform when it is

#### **TABLE 3 Copper Electroforming Solutions**

|  |  |                  | 9  |  |  |
|--|--|------------------|--|--|--|
|  |  |                  | Electrolyte Composition,   | g/L  |  |
|  | Copper Sulfate<br>CuSO <sub>4</sub> ·5H <sub>2</sub> O<br>H <sub>2</sub> SO <sub>4</sub> | 210–214<br>52–75 | Copper Fluoborate<br>Cu(BF <sub>4</sub> ) <sub>2</sub><br>HBF <sub>4</sub> |  | 225–450<br>sufficient to maintain pH<br>at 0.2–1.5 |
|  |  |                  | Operating Conditions   |  |  |
| Temperature Agitation Cathode current density  | 21–32°C<br>air or mechanical<br>1–10 A/dm²   |                  |  | 21–54°C<br>air or mechanical<br>8–44 A/dm <sup>2</sup> |  |
| Anodes   | wrought phosphorize  | ed copper        |  | copper   |  |
|  |  |                  | Mechanical Properties  |  |  |
| Tensile strength, MPa<br>Elongation,%<br>Hardness (Vickers<br>hardness, 100–g<br>load) | 205–380<br>15–25<br>45–70  |                  |  | 140–345<br>5–25<br>40–80                               |  |
| Internal Stress, MPa   | 0-10 tensile   |                  |  | 0-105 tensile  |  |

#### TABLE 4 Variables that Affect Mechanical Properties of the Deposit—Acid Copper Sulfate Solution

| Property         | Operational   | Solution Composition  |
|------------------|---|---|
| Tensile Strength | Decreases slightly with increasing solution temperature.          | Relatively independent of changes in copper sulfate concentration within the range suggested.                     |
|                  | Increases significantly with increase in cathode current density. | Relatively independent of changes in sulfuric acid concentration within the range suggested.                      |
| Elongation       | Decreases with increasing solution temperature.                   | High acid concentration, particularly with low copper sulfate concentration, tends to reduce elongation slightly. |
|                  | Increases slightly with increasing cathode current density.       |   |
| Hardness         | Decreases slightly with increasing solution temperature.          | Relatively independent of copper sulfate concentration.   |
|                  | Relatively independent of change in cathode current density.      | Increases slightly with increasing acid concentration.  |
| Internal Stress  | Increases with increasing solution temperature.                   | Relatively independent of copper sulfate concentration.   |
|                  | Increases with increasing carhode current density.                | Decreases very slightly with increasing acid concentration.   |

# TABLE 5 Variables that Affect Mechanical Properties of the Deposit—Copper Fluoborate Solution

| Property         | Operational  | Solution Composition                                      |
|------------------|--|---|
| Tensile Strength | Increases with icreasing solution temperature.     | Increases with icreasing copper fluoborate concentration. |
|                  | Increases with increasing cathode current density. | Relatively unaffected by fluoborate acid concentration.   |
| Elongation       | Increases with increasing solution temperature.    | Increases with icreasing copper fluoborate concentration. |
|                  | Increases with increasing cathode current density. | Relatively unaffected by fluoborate acid concentration.   |
| Hardness         | Decrease with increasing solution temperature.     | Decreases with icreasing copper fluoborate concentration. |
|                  | Increases with increasing cathode current density. | Unaffected by fluoborate acid concentration.              |

separated from the mandrel; difficulty of separating the electroform from the mandrel; curling, peeling, or separation of the electroform prematurely from the mandrel; and buckling and blistering of the deposit.

- 8.3.3 Internal stress is influenced by the nature and composition of the electroplating solution. Typical values of internal stress for electroforming solutions are given in Table 8.
- 8.3.4 Typical stress reducers for nickel electroforming are saccharin, para-toluene sulfonamide, meta-benzene disulfonate, and 1-3-6 sodium naphthalene trisulfonate. All of these organic stress-reducing agents introduce sulfur into nickel deposits, and this limits the temperature at which the electroform can be used in service. Nickel electrodeposits with small amounts of sulfur may become embrittled when heated to temperatures above 200°C. The exact temperature of embrittlement depends on the sulfur content, the time at the elevated temperature, and other factors. Control of internal stress by means of organic addition agents requires an optimum level of

the additive, regular replenishment as it is consumed, and frequent (or continuous) carbon treatment to control the concentration of decomposition products that form as a result of reduction of the additive at the cathode.

- 8.3.5 Anodic oxidation of sulfamate anions, a phenomenon that was first detected in nickel sulfamate solutions, forms species which diffuse to the cathode where they are reduced. This results in incorporation of sulfur that acts to lower internal stress and brighten the deposit. This occurs, for example, at insoluble primary or auxiliary anodes, or at nickel anodes that are operating at high potentials. This is avoided by employing active nickel anode materials in titanium baskets.
- 8.3.6 The use of levelling agents, such as 2 butyne 1:4 diol, for nickel electroforming can improve metal distribution on the mandrel by suppressing the growth of nodules and by preventing the formation of a plane of weakness when electroforming into a corner. In general, levelling agents increase internal

#### TABLE 6 Variables that Affect Mechanical Properties of the Deposit—Watts Solution

| Property         | Operational  | Solution Composition                                 |
|------------------|--|--|
| Tensile Strength | Relatively independent of plating solution temperature within range suggested.   | Increases with increasing nickel content.            |
|                  | Relatively independent of changes in cathode current density.  | Increases with increasing chloride content.          |
|                  | Relatively independent of pH variation within range suggested.   |  |
| Elongation       | Increases with temperature to 55°C followed by slight decrease at higher temperature.  | Decreases with increasing nickel content.            |
|                  | Relatively independent of pH variation within range suggested.   |  |
| Hardness         | Decreases with temperature rise to 55°C but increases with higher temperature.   | Increases with increasing nickel content.            |
|                  | Decreases significantly with increasing cathode current density to 5.4 A/dm <sup>2</sup> . At higher current densities the hardness increases with increasing current density. | Increases with increasing chloride content.          |
| Internal Stress  | Relatively independent of plating solution temperature.  | Increases slightly with increasing nickel content.   |
|                  | Decreases slightly, then increases with increasing cathode current density.  | Increases markedly with increasing chloride content. |
|                  | Relatively independent of pH variation within range suggested.   |  |

#### TABLE 7 Variables that Affect Mechanical Properties of the Deposit—Nickel Sulfamate Solution

| Property         | Operational   | Solution Composition  |
|------------------|---|---|
| Tensile Strength | Decreases with increasing temperature to 49°C, then increases slowly with further temperature increase.   | Decreases slightly with increasing nickel content.                  |
|                  | Increases with increasing pH.   |   |
|                  | Decreases with increasing current density.  |   |
| Elongation       | Decreases as the temperature varies in either direction from 43°C.  | Increases slightly with increasing nickel content.                  |
|                  | Decreases with increasing pH.   | Increases slightly with increasing chloride content.                |
|                  | Increases moderately with increasing current density.   |   |
| Hardness         | Increases with increasing temperature within operating range suggested.   | Decreases slightly with increasing concentration of nickel ion.     |
|                  | Increases with increasing solution pH.  | Decreases slightly with increasing chloride content.                |
|                  | Reaches a min at about 13 A/dm <sup>2</sup> .   |   |
| Internal Stress  | Decreases with increasing solution temperature.   | Depends on nickel metal content in the solution (see effect of pH). |
|                  | Reaches a min at pH 4.0–4.2 with a nickel metal concentration of 76.5 g/L. Reaches a minimum at 3.0–3.2 with a nickel metal concentration of 107 g/L. | Increases significantly with increasing chloride content.           |
|                  | Increases with increasing current density.  |   |

TABLE 8 Typical Values of Internal Stress for Electroforming Solutions

| Electroforming Solution                    | Internal Stress, MPa <sup>A</sup> |
|--|-----------------------------------|
| Watts nickel                               | 110–210                           |
| Nickel sulfamate, no chloride              | 0–55                              |
| Nickel sulfamate, with chloride (0-10 g/L) | 20-70                             |
| Copper sulfate                             | 0–14                              |
| Copper fluoborate                          | 0–20                              |

A Positive values are tensile.

stress in the tensile direction. Although the breakdown products formed by organic addition agents generally increase internal stress, continuous filtration through carbon removes only the breakdown products in the case of butyne diol, and the stress can be closely controlled with this additive.

# 8.4 Roughness:

8.4.1 Any condition which would tend to cause roughness in decorative plating will have a much more serious effect on electroforming operations. Nodules, nuggets, and trees will form. These become high current density areas, and the larger they get, the faster they grow, and the more they rob surrounding areas of deposit. As a consequence, the filtration rates used in electroforming are very high in an effort to prevent roughness; the rates may amount to passing the entire solution through a filter several times an hour.

8.4.2 The sources of roughness include airborne dirt, anode particles, crystallized salts that fall into the electroplating solution, and particles which precipitate from hard water constituents. Good housekeeping can eliminate most sources of roughness.

# 8.5 Treeing:

8.5.1 Treeing at edges and corners may be troublesome and is minimized by the use of shields. Certain addition agents, such as the levelling agents discussed in 8.3.6, suppress the treeing tendency. Another approach applicable in many cases is to extend the mandrel beyond the dimensions actually desired so that the treeing occurs on a part of the electroform that can be machined away. If nickel electroforming is interrupted to remove trees and nodules by machining, the machined nickel surface must be activated to insure good nickel-to-nickel adhesion. Methods of preparing nickel surfaces for deposition with nickel have been standardized (see Practice B343).

#### 8.6 Other Control Techniques:

8.6.1 Agitation of every kind, singly or in combination, should be employed whenever possible to control burning and pitting at high current density sites. Solution agitation, either air or mechanical, may induce roughness, however, unless the solution is kept clean by using a high filtration rate. Cathode rotation, when applicable, is an effective means of solution agitation.

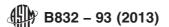
# 9. Post-Electroforming Operations

- 9.1 The operations that are performed after electroforming is completed are: machining and final finishing of the electroform, parting or separation from the mandrel, and backing the electroform.
  - 9.2 Machining and Finishing:
- 9.2.1 Necessary machining or other mechanical finishing operations are usually performed before the electroform is separated from the mandrel to avoid deformation. The machining and grinding of electrodeposited nickel may be difficult. Directions for machining and grinding of nickel and other electrodeposits have been published (9).
  - 9.3 Parting:
- 9.3.1 Electroforms are removed from permanent mandrels mechanically by the use of one or a combination of several of the following techniques:
  - 9.3.1.1 *Impact*, by a sudden pull or hammer blow.
- 9.3.1.2 *Gradual Force*, applied by a hydraulic ram to push, or a jack-screw or wheel-puller to pull the pieces apart.
- 9.3.1.3 *Cooling*, for example with a mixture of dry ice and naphtha. This works best if the mandrel has a lower coefficient of expansion than the electrodeposit. On withdrawal from the cold bath, the electroform will expand faster than the mandrel, permitting separation.
- 9.3.1.4 *Heating*, with a torch or hot water or oil bath, either to melt or soften a parting compound or to take advantage of a difference in coefficients of expansion between mandrel and electroform.
- 9.3.1.5 *Prying*, with a sharp tool may be used with care to separate relatively flat pieces, such as phonograph record stampers or engraving plates.
- 9.3.2 Expendable mandrels are melted or dissolved out as follows:
  - 9.3.2.1 Zinc alloys are dissolved with hydrochloric acid.
- 9.3.2.2 Aluminum alloys are dissolved in strong, hot sodium hydroxide solutions.
- 9.3.2.3 Low-melting alloys are melted and shaken out. The alloy may be collected and used over. If "tinning" occurs, a nickel electroform may be cleaned with strong nitric acid.
- 9.3.2.4 Thermoplastics may be softened by heat so that the bulk of the mandrel may be withdrawn, after which the electroform is cleaned with a suitable solvent. An alternative is to dissolve the entire mandrel with a solvent.
- 9.3.3 The separation of mandrel and electroform should be considered at an early stage since the separation can be simplified by certain design changes. A fine surface finish facilitates parting. Gripping devices may be incorporated on the mandrel, and a knock-off block may be provided so force can be applied for separating the mandrel and the electroform. A taper can be specified when feasible.
  - 9.4 Backing the Electroform:
- 9.4.1 It is often necessary to back the electroform with some other material, which is then finished to specified dimensions to fit into a bolster or onto a printing press. This is true, for example, in the case of molds, dies, printing plates, and tools in general.

9.4.2 The most important backing methods include the following: casting with low-melting temperature alloys, spraying with various materials, electroplating with other metals, use of thermosetting resins, and spark-eroded steel back-ups and electrochemical machining techniques that sink conforming cavities in the back-up material.

# 10. Product Requirements and Test Procedures

- 10.1 No single statement of requirements can be written that applies to all electroformed articles. Each electroform is unique and has its own particular set of functional requirements. The following should be considered in developing detailed requirements and test procedures.
- 10.2 The electrodeposited metal or alloy should be specified including any known detrimental effects of impurities. Chemical composition can be determined by common analytical procedures.
- 10.3 The density of electroformed materials is often an indication of its porosity compared to wrought materials of the same composition. Values of density for metals are listed in many handbooks. The density may be measured by the method described in Test Method B311 and should be at least 99 % of the value of the wrought material.
- 10.4 The mechanical properties, tensile strength, yield strength, and elongation should be specified if applicable. Special test specimens prepared before, during, and after electroforming may be tested by standard uniaxial tension testing, in accordance with Test Methods E8, to certify properties. Other test methods are included in Section 2 and may be applicable. For example, qualitative methods for measuring ductility (elongation) are given in Practices B489 and B490. In critical cases electroformed prototypes should be tested. The mechanical properties should be determined at the specified thickness even though it might be more convenient to measure thinner electrodeposits.
- 10.5 Hardness may be specified in certain applications and can be measured by the test methods given in Test Methods B578 and E384.
- 10.6 Thickness is often an important dimension of the electroform. It should be specified and measured using standard inspection tools of appropriate accuracy. Guide B659 is a guide to coating thickness measuring methods.
- 10.7 The appearance of the electroform, including surface finish, should be specified. The initial layers of electrodeposited metal will generally reproduce the finish on the mandrel with great fidelity and hence, the appearance and finish on the mandrel must also be specified. The appearance and finish of the surface farthest from the mandrel (the back of the electroform) may be important in some applications and should be specified when appropriate. Roughness on the back of the electroform may be controlled by the use of leveling agents, but in other cases the methods discussed in 8.4 may be applied. Cracks, pits, voids, and inclusions are often detrimental and must be controlled by visual inspection, fluoroscopic testing, dye penetrant inspection, and other techniques.



- 10.8 Adhesion may be specified in those cases where the electroform is comprised of two or more layers of electrodeposited metals. Test methods for determining adhesion qualitatively are given in Test Methods B571.
- 10.9 Electrical conductivity should be specified when it is a requirement.
- 10.10 Requirements for high- or low-temperature performance should be known and specified. The properties of electrodeposited metals are influenced by variations in temperature (7, 8).

# 11. Keywords

11.1 copper; copper electroforming; electroforming; electroplating; mandrels; nickel; nickel electroforming

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