



Designation: B 656 – 91

Standard Guide for Autocatalytic (Electroless) Nickel-Phosphorus Deposition on Metals for Engineering Use¹

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1. Scope

1.1 This guide gives information about the deposition of autocatalytic nickel for engineering uses (**Note 1**). It is not intended to be a standardized procedure, but rather a guide for obtaining smooth, adherent, and uniform coatings of a nickel-phosphorus alloy from acid-plating solutions (**Note 2**).

NOTE 1—Autocatalytic nickel is also known as electroless or chemical nickel.

NOTE 2—Nickel-boron alloys are not covered in this document.

1.2 Autocatalytic nickel deposits covered in this guide are alloys of nickel and phosphorus produced by autocatalytic chemical reduction with hypophosphite. Because the nickel deposit is a catalyst for the reaction, the process is self-sustaining.

1.3 The chemical and physical properties of the deposit vary with the pretreatment of the substrate, plating bath chemistry, phosphorus content, and subsequent heat treatment. For more details on such properties, see *ASTM STP 265 (1,2,3,4,7)*.² Also, refer to **Fig. X1.1**, **Fig. X1.2**, and **Fig. X1.3** in **Appendix X1**.

1.4 This guide covers the metal preparation and deposition process. The testing of autocatalytic nickel-phosphorus deposits is covered in Specification B 733B 733.

1.5 *This standard does not purport to address all of the safety problems 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.* See **8.11** and **8.13** for specific safety precautionary statements.

2. Referenced Documents

2.1 ASTM Standards:

¹ This guide is under the jurisdiction of ASTM Committee B-8 on Metallic and Inorganic Coatings and is the direct responsibility of Subcommittee B08.08 on Engineering Coatings.

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² The boldface numbers in parentheses refer to the list of references at the end of this standard.

A 275/A275M Test Method for Magnetic Particle Examination of Steel Forgings³

B 177 Guide for Chromium Electroplating on Steel for Engineering Use⁴

B 183 Practice for Preparation of Low-Carbon Steel for Electroplating⁴

B 242 Practice for Preparation of High-Carbon Steel for Electroplating⁴

B 252 Practice for Preparation of Zinc Alloy Die Castings for Electroplating and Conversion Coatings⁴

B 253 Practice for Preparation of Aluminum Alloys for Electroplating⁴

B 254 Practice for Preparation of and Electroplating on Stainless Steel⁴

B 281 Practice for Preparation of Copper and Copper-Base Alloys for Electroplating and Conversion Coatings⁴

B 322 Practice for Cleaning Metals Prior to Electroplating⁴

B 374 Terminology Relating to Electroplating⁴

B 480 Guide for Preparation of Magnesium and Magnesium Alloys for Electroplating⁴

B 481 Practice for Preparation of Titanium and Titanium Alloys for Electroplating⁴

B 678 Test Method for Solderability of Metallic-Coated Products⁴

B 733 Specification for Autocatalytic Nickel-Phosphorus Coatings on Metals⁴

E 165 Test Method for Liquid Penetrant Examination⁵

F 519 Method for Mechanical Hydrogen Embrittlement Testing of Plating Processes and Aircraft Maintenance Chemicals⁶

2.2 Military Specifications:

MIL-S-13165 Shot Peening of Metal Parts⁷

MIL-C-26074 Coating, Electroless Nickel, Requirements for⁷

³ Annual Book of ASTM Standards, Vol 01.05.

⁴ Annual Book of ASTM Standards, Vol 02.05.

⁵ Annual Book of ASTM Standards, Vol 03.03.

⁶ Annual Book of ASTM Standards, Vol 15.03.

⁷ Available from Standardization Documents Order Desk, Bldg. 4 Section D, 700 Robbins Ave., Philadelphia, PA 19111-5094, Attn: NPODS.

MIL-R-81841 Rotary Flap Peening of Metal Parts⁷
2.3 Aerospace Materials Specifications (AMS):
 AMS-2404 Electroless Nickel Plating⁸
 AMS-2405 Electroless Nickel Plating, Low Phosphorus⁸

3. Significance and Use

3.1 This guide provides procedures for the inspection and preparation of the substrate and control of the plating process. This guide is recommended to the manufacturer, the purchaser, and the user of autocatalytic nickel.

3.2 Autocatalytic nickel-phosphorus coatings are used to improve the performance of the metal article by providing corrosion resistance, wear resistance, solderability, or certain magnetic properties.

4. General Considerations

4.1 Autocatalytic nickel will deposit uniformly on clean wetted surfaces. The deposit may be applied to most metals. The as-plated coating is a hard nickel phosphorus alloy of uniform thickness. The structure of alloys containing more than 8 % phosphorus is predominantly amorphous as defined by X-ray diffraction.

4.2 Aluminum, beryllium, cobalt, copper, iron, nickel, titanium and their alloys can be plated directly. Other basis materials can be plated by special processes (see 5.3).

4.3 Articles that have blind holes, crevices, porosity, burrs, or have surfaces that have been burned or carbonized, require special pretreatment and plating procedures for optimum deposit performance.

4.4 The required thickness of autocatalytic nickel coatings can vary from as little as 1.0 μm to over 150 μm . The selected thickness will depend upon the application and service conditions to which the finished part is exposed, as well as the surface condition of the basis metal. Rough surfaces require thicker deposits for minimum porosity and maximum corrosion resistance. The following are typical examples:

For soldering	1 to 7.5 μm
For preventing the rusting of steel in air	5 to 15 μm
For mild wear conditions	5 to 25 μm
For moderate corrosion wear	13 to 30 μm
For severe wear	30 to 75 μm
For severe corrosion	50 to 125 μm
For salvage	as required

The thickness of autocatalytic nickel coatings formed with good solution agitation and part movement is quite uniform. Thickness of less than 25 μm can be controlled to close tolerances by controlling the operating parameters that influence the deposition rate. Small diameter holes are an exception and the thickness of the deposit therein may vary.

4.5 Autocatalytic nickel-phosphorus coated products may be soldered, brazed, or welded. Inert gas welding methods are necessary for optimum joint strength.

4.6 The basis metal composition and general surface condition must be taken into account when selecting a pretreatment procedure.

4.7 After several metal turnovers the plating solution contains considerable amounts of by-product salts and the deposits become more stressed and porous.

5. Metal Preparation

5.1 Practices for the preparation of basis metals for electroplating have been published by ASTM. Generally, with some degree of variation, these practices are also applicable to the preparation for autocatalytic nickel deposition. Particularly useful is Practice B 322B 322. The practices and guide listed below have sections that, when properly modified, are helpful: B 177B 177, B 183B 183, B 252B 252, B 253B 253, B 254B 254, B 281B 281, B 322B 322, B 480B 480 and B 481B 481

5.2 To ensure that an adherent corrosion resistant, essentially pore-free deposit is produced, the metal surface must be clean and uniform. Surface defects such as pores, pits, inclusions, scale, crevices, burns, corrosion products, and oxides will reduce the deposit integrity (see Test Methods A 275A 275/A275M/A 275M and E 165E 165). Surface contaminants that must be removed are: handling soils, environmental matter, drawing oils or compounds, polishing abrasives and binders, rust preventatives, or protective coatings. Mechanical and chemical treatments must be used to properly prepare the substrate. Because each basis metal alloy reacts uniquely, different pretreatments and various cleaning procedures must be used to produce a clean surface.

5.3 On parts made from zinc, lead, cadmium, tin, bismuth, arsenic, antimony, and alloys containing high proportions of these metals (such as lead solders), apply a copper or nickel strike to prevent these metals from contaminating the bath. Copper, brass, or bronze parts may be plated directly with galvanic initiation. Magnesium parts require special pretreatment and plating solution (see Guide B 480B 480).

5.4 Surface Conditions:

5.4.1 **Hardness**—In hardened and high-strength steels, internal stress may cause cracking during and after cleaning and deposition. Articles made of severely cold-worked steel or steels with tensile strength greater than 1050 MPa are to be stress-relieved according to Table 1 before cleaning.

NOTE 3—Surface-hardened parts can be stress-relieved at 130–150°C for not less than 5 h. If required, the heat treatment shall not reduce the surface hardness. Shorter times at higher temperatures may be used if the resulting loss of surface hardness of the substrate is acceptable. Stress-relieving heat treatment is not normally required for nonferrous parts.

NOTE 4—Parts higher than 1050 MPa in tensile strength, which have been acid stripped for recoating, should be baked for embrittlement relief before processing in accordance with Table 1.

5.4.2 Autocatalytic nickel coatings will not fill in surface scratches, pits, tool marks, etc. The smoothness of the surface

TABLE 1 Heat Treatment for Stress Relief Before Plating and Hydrogen Embrittlement Relief After Plating

Maximum Specified Tensile Strength (MPa)	Hours at 190 \pm 15°C
1000 and below	none
1051 to 1450	2
1451 to 1800	18
1800 to up	23

⁸ Available from the Society of Automotive Engineers (SAE), 400 Commonwealth Drive, Warrendale, PA 15096.

to be plated, therefore, must be equal to the surface finish required of the finished product. Avoid mechanical operations that produce grinding checks or glazing. Welding spatter and flux residues must be removed by mechanical means prior to cleaning.

5.5 Surface Preparation:

5.5.1 *Precleaning*—The metal surface must be degreased or soak-cleaned, or both, when grease, oil, and buffing compounds are present. For this purpose use vapor degreasing, organic solvents, emulsion or spray cleaners. Whenever practical, supplement the degreasing by anodic or periodic reverse electrolytic alkaline cleaning. To remove heavy scale, sodium hydride or some other molten salt bath may be used (5).

5.5.2 *Abrasive Cleaning*—Oxide and scale may be removed by mechanical means, using abrasives such as fine emery on a cloth or wheel, pumice slurry, or greaseless buffing compounds. Grit blasting, wet blasting, or vapor honing are recommended on rough castings, corroded and other nonuniform surfaces. Small parts can often be cleaned by barrel finishing with a mild abrasive.

5.5.2.1 Follow abrasive cleaning with a suitable cleaning procedure (for example, electrolytic alkaline cleaning) to remove all traces of the abrasives, which can reduce deposit adhesion and corrosion performance. Abrasive material shall be free of metal particles and dirt to avoid contamination of the surface.

5.5.3 *Peening*—Peen high-strength steels to induce compressive stress within the substrate to minimize the loss of fatigue strength and of stress-corrosion resistance (see MIL-S-13165 and MIL-R-81841).

5.5.4 *Masking*—If required, apply masking after vapor degreasing and mechanical cleaning. Test the masking compound and tape used for suitability (see 8.1).

5.5.5 *Racking*—Position racked or wired parts so as to minimize trapping of hydrogen gas in cavities and holes and to allow free circulation of solution over all surfaces to obtain uniform coating thickness. Significant surfaces shall not show rack or wire marks. The location of rack or wire marks shall be agreed upon between the purchaser and the producer.

5.5.6 *Alkaline Cleaning*—Final removal of dirt, abrasive scale, grease, and oil is best performed by anodic alkaline cleaning. Then, if this is impractical because of the size or shape of the part, clean and immerse in a hot alkaline-soak cleaner or mechanically clean. Proprietary cleaners are commonly used that should be operated in accordance with the directions furnished by the manufacturer. Periodic reverse cleaning is recommended for parts with smutty or scaly surfaces, or when pickling cannot be used; the final cleaning cycle must be anodic.

5.5.7 *Acid Pickle*—To obtain optimum deposit adhesion, remove all traces of oxide from the surface by acid treatment. Generally, 50 % by volume hydrochloric acid is satisfactory; however, with high-carbon steels, it may produce smut, which must be removed (see 5.5.8 and A1.2). Sulfuric acid can also be used; adjust the acid concentration and immersion time to minimize attack on the basis metal. Uniform gassing is generally an indication of adequate surface preparation. The addition of wetting agents or inhibitors is not recommended.

5.5.8 *Smut Removal*—When the hydrochloric acid treatment of steel results in the production of smut, it must be removed. Heavy smut can be removed by anodic treatment in a caustic solution (see A1.2 and Practice B 242B 242).

5.5.9 Anodic-Acid Etching:

5.5.9.1 An anodic-acid etch with a subsequent rinse as the final step in the preparation of high-carbon steel alloys is recommended in securing adhesion; it is not suitable where deep recesses are present. Without such an anodic treatment, poor adhesion may occur. The anodic-acid-treatment is capable of removing a small amount of smut or oxides formed by a preceding treatment. If more substantial amounts of smut must be removed, use the procedure described in A1.3.

5.5.9.2 A 250 to 1000 g/L sulfuric acid (94 to 96 %) solution used at not more than 30 °C is effective for anodic etching of high-carbon steel. The addition of 125 g/L of sodium sulfate is of benefit for most steel grades. The part is given an anodic treatment in the acid for a time usually not exceeding 1 min at a current density of 10 to 16 A/dm² (see A1.3).

5.5.9.3 High acid content, high current density, and low temperature (with reference to the ranges specified) will minimize the attack on the basis metal and produce a smoother surface.

NOTE 5—To obtain maximum coating adhesion it may be necessary to etch highly finished metal surfaces.

5.5.10 *Stainless Steel*—Stainless steels and other high-alloy substrates may require a nickel strike prior to autocatalytic nickel plating to obtain maximum adhesion (see A1.4).

5.5.11 *Aluminum*—The pretreatments of aluminum alloys can vary widely and depend significantly on the alloy composition and the plating bath formulation. Zincating is frequently used after deoxidizing and desmutting of the aluminum surface (see Practice B 253B 253).

5.5.12 Titanium and titanium alloys are subject to stress corrosion cracking after processing. Pretreatment solutions including rinses should not contain methanol, halogenated hydrocarbons, or more than 50 ppm chlorides, all which may cause subsequent halide stress corrosion cracking when the parts are heated to 260°C or higher (see Practice B 481B 481).

5.5.13 *Oxidation*—To prevent oxidation of the surface make the time interval between the final pretreatment cleaning operation and the plating process as short as possible.

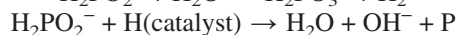
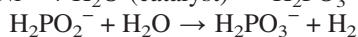
5.5.14 *Rinsing*—Thorough rinsing is required between cleaners, activators, and plating solutions to prevent contamination of the solutions by drag-in. Agitate rinses and provide spray or counterflow cascading, or both, to conserve the use of water. Deionized water is recommended for the final rinse.

NOTE 6—The appearance of water breaks following a rinse indicates incomplete removal of soil and insufficient cleaning. Inspect for water breaks after pickling and after the final rinse or acid dip because the presence of alkali may mask the presence of organic surface contaminants. Final rinsing with deionized water is recommended. If a water break occurs, repeat the pretreatment process. There is no completely reliable test to determine if the surface of a part has been properly prepared other than the subsequent performance of the coating under conditions of service.

6. The Plating Process and Its Operation

6.1 This guide covers only the catalytic reduction of nickel and phosphorus from aqueous solutions using hypophosphite as the reducing agent. Typical formulations are shown in [Table 2](#).

6.2 In the hypophosphite bath three simultaneous reactions take place:



6.3 The functions of nickel sulfate and sodium hypophosphite are to provide the nickel ions and the metal-reducing agent. The plating solution also contains organic acids which are buffers, complexing agents, and sometimes deposition rate accelerators.

6.4 Stabilizers are critical additives that control the catalytic nickel deposition and prevent spontaneous decomposition of the solution.

6.5 The control and maintenance of nickel and hypophosphite ion concentration, stabilizers and complexing agents, as well as solution pH and temperature are imperative for successful operation of the plating process. The accumulation of phosphite ions as a by-product of the reaction limits the life of the solution due to the precipitation of slightly soluble nickel phosphite.

6.6 The replenishing solutions are highly concentrated to minimize dilution of the plating solution. Adding liquid replenishment chemicals slowly will prevent the precipitation of nickel compounds. These will produce roughness on shelf areas even when operating with constant filtration and good solution agitation. To avoid coating patterns and bare spots, additions should not be made near articles plating in the solution.

6.7 Deposition Rate:

6.7.1 The deposition rate depends on the temperature, the pH, and the solution composition. Some plating solutions operating at peak efficiency will deposit 25 $\mu\text{m}/\text{h}$. A deposition rate of 10 to 20 $\mu\text{m}/\text{h}$ is common.

6.7.2 Since the bath composition changes during use, a consistent rate of deposition depends on keeping the ingredients at optimum concentrations. Good bath control therefore, is imperative. When using proprietary processes, follow the supplier's recommendations for solution analysis and maintenance.

TABLE 2 Published Formulations

NOTE 1—Optimum molar ratio of nickel to hypophosphite is 0.3 to 0.4.

Component	Formulation		
	No. 1	No. 2	No. 3
Nickel sulfate monohydrate, g/L	20	30	30
Sodium hypophosphite hexahydrate, g/L	23	10	36
Sodium citrate, g/L	10
Sodium hydroxyacetate, g/L	...	50	30
Lactic acid, g/L	30
Stabilizer, ppm ^A	1–2	1–2	2–3
pH	4.5–5	4–6	5
Temperature, °C	95	90	85

^A Some stabilizers used are: thiourea; selenic acid; sulfides of lead, antimony, arsenic or bismuth; and molybdic acid.

6.7.3 A uniform plating temperature throughout the tank and close control of the temperature are important to maintain a consistent plating rate and alloy composition.

6.7.4 Maintain the pH in the recommended operating range for the specific bath formulation. With a decrease in pH, the deposition rate decreases rapidly, while the phosphorus content of the deposit increases.

6.8 *Several Factors Must be Considered in Equipment Design:*

6.8.1 Tanks can be fabricated from molded polyethylene, stress-relieved natural polypropylene, Type 304 or, preferably Type 316 stainless steel. Direct heating with polytetrafluoroethylene (PTFE) steam coils, derated Type 304 or preferably Type 316 stainless steel electric immersion heaters, Type 316 SS plate coils, or indirect heating in jacketed tanks or Type 316 SS heat exchangers can be used. Avoid concentrated high heat which can cause decomposition of the solution.

6.8.2 Continuous agitation using air, mechanical, or solution circulation is recommended.

6.8.3 Protect the plating solution from foreign materials, such as dirt, rust, oil (such as from hoists), and dust from buffing operations.

6.8.4 Depending on the bath chemistry, there is a ratio between tank volume and surface area that will produce optimum plating efficiency. A typical ratio is 85 to 170 cm^2 of metal surface per litre of solution (50 to 100 $\text{in.}^2/\text{gal}$).

6.8.5 Continuous filtration of ten turnovers per hour is recommended. Frequent batch filtration may also be used. Bag or cartridge filters that remove particles 3 μm and larger are recommended.

6.9 Many proprietary autocatalytic nickel plating solutions are available or one of the published formulations may be considered if they meet the coating requirements (see [Table 2](#)).

7. Deposit Composition

7.1 The deposit can contain from 1 to 13 mass % phosphorus, the balance being nickel and trace elements, as shown in [Table 3](#).

7.2 Typical Composition.

7.2.1 For certain specific applications, control of trace elements within the deposit may be required. Close communications between engineering, quality control, and purchasing will reduce potential problems.

7.3 The phosphorus content of the deposit is dependent on the pH of the solution, the type and concentration of complexing agents, the nickel and hypophosphite concentrations, the temperature, and the age of the solution. By controlling these, and especially the pH to within ± 0.1 , the phosphorus content of the deposit will not vary more than $\pm 1\%$. In general,

TABLE 3 Chemical Composition of the Deposit

Element	Minimum, %	Maximum, %	Typical, %
Nickel	87	99	88 to 95
Phosphorus	1	13	5 to 12
Trace Elements:			
Al, Bi, C, Cd, Cr, Cu, Fe, H, Mn, Mo, Ni, Nb, Pb, S, Sb, Se, Si, Sn, V, Zn	0.01	2	0.1