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Standard Practice for Preparation of Plastics Materials for Electroplating¹

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1. Scope

- 1.1 This practice is a guide to the surface preparation of plastic materials for decorative and functional electroplating, where the sequence of chemical treatments may include: cleaning, conditioning, etching, neutralizing, catalyzing, accelerating, and autocatalytic metal deposition. Surface preparation also includes electrodeposition of metallic strike coatings immediately after autocatalytic metal deposition. These treatments result in the deposition of thin conductive metal films on the surface of molded-plastic materials, and are described in this practice.
- 1.2 Once molded-plastics materials have been made conductive, they may be electroplated with a metal or combination of metals in conventional electroplating solutions. The electroplating solutions and their use are beyond the scope of this practice.
- 1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.
- 1.4 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use. (See Section 4.)
- 1.5 This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

- 2.1 ASTM Standards:²
- B532 Specification for Appearance of Electroplated Plastic Surfaces
- B533 Test Method for Peel Strength of Metal Electroplated Plastics
- B553 Test Method for Thermal Cycling of Electroplated Plastics (Withdrawn 1991)³
- B604 Specification for Decorative Electroplated Coatings of Copper Plus Nickel Plus Chromium on Plastics

3. Significance and Use

3.1 A variety of metals can be electrodeposited on plastics for decorative or engineering purposes. The most widely used coating consists of three layers—copper plus nickel plus chromium—for decorative applications. However, brass, silver, tin, lead, cadmium, zinc, gold, other metals, and combinations of these are used for special purposes. The key to producing electroplated plastics of high quality lies in the care taken in preparing plastics for electroplating. The information contained in this practice is useful in controlling processes for the preparation of plastics for electroplating.

4. Hazards

- 4.1 Some chemical solutions are exothermic upon mixing or in use, thereby requiring cooling and proper containment to prevent injury to personnel.
- 4.2 For details on the proper operation and safety precautions to be followed by vapor degreasing, see ASTM STP 310.⁴

5. General Considerations

5.1 Nature of Plastics Suitable for Electroplating:

¹ This practice is under the jurisdiction of ASTM Committee B08 on Metallic and Inorganic Coatings and is the direct responsibility of Subcommittee B08.02 on Pre Treatment.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ The last approved version of this historical standard is referenced on

 ⁴ Handbook of Vapor Degreasing, ASTM STP 310A, ASTM, 1976.

- 5.1.1 Plastics suitable for electroplating may be a combination of one or more polymers so formulated as to allow selective etching of one or more constituents. The most commonly electroplated material, acrylonitrile-butadienestyrene (ABS), is a terpolymer. During etching, soft butadiene rubber particles dispersed in the acrylonitrile-styrene matrix are selectively attacked. The microscopic pockets formed by the etching process provide sites for the physical interlocking of the plastic substrate and subsequently applied metallic coatings. The resultant mechanical bonding is instrumental in achieving metal to plastic adhesion.
 - 5.2 Plastics Suitable for Electroplating:
- 5.2.1 The plastics materials commonly used for injection molded articles to be electroplated are:
 - 5.2.1.1 Acrylonitrile-butadiene-styrene (ABS),
 - 5.2.1.2 Polypropylene,
 - 5.2.1.3 Polysulfone,
 - 5.2.1.4 Modified Polyphenylene Oxide,
 - 5.2.1.5 Polycarbonate,
 - 5.2.1.6 Polyester, and
 - 5.2.1.7 Nylon.
- 5.2.2 The preparation of these materials for electroplating generally involves the basic steps described in this practice, but substantial variations may be necessary to achieve optimum results with plastics other than ABS.

5.3 Molding Considerations:

- 5.3.1 The chemical nature of plastics combined with the nature of the injection molding process produces plastic parts that are somewhat heterogeneous in composition and structure. During the molding of ABS, for example, the shape, size, and distribution of butadiene rubber particles may vary considerably within a part and may affect the uniformity of subsequent surface etching treatments. As a result, under- and over-etching of the surface may occur, either of which can interfere with the adhesion of metal coatings. The use of a properly formulated etchant combined with an organic conditioner may overcome problems of nonuniform etching.
- 5.3.2 Although it may be possible to overcome problems of nonuniform etching by suitable chemical treatments, control of the injection molding process is critical if plastic parts are to be electroplated successfully. It is essential that the resin be thoroughly dried before molding. The temperature of the mold and all heating zones, the pressure, the total cycle time, and the fill time must be controlled and monitored. Devices exist for controlling all molding parameters precisely.
- 5.3.3 The visible defects that may arise in the molding process are described in Specification B532. Molded parts that are obviously defective should not be processed without the approval of the purchaser.
- 5.3.4 Mold release agents interfere with the adhesion of metallic coatings on plastic substrates and should not be used.

5.4 Process Selection:

5.4.1 Due to the complexity and proprietary nature of commercially available processes for preparing plastics for electroplating, a complete process should be selected for a specific type of plastic, and operated according to the specific instructions of the supplier of the process.

- 5.5 Handling of Molded Plastic Parts:
- 5.5.1 Molded-plastic parts must be kept clean and carefully handled. It is a common practice to use cotton gloves in removing parts from the mold and for all subsequent handling.
- 5.5.2 The trimming of plastic parts and the removal of flash and runners should be done with care to avoid introducing surface defects. These and other mechanical finishing operations should be completed before beginning the chemical treatment of parts for electroplating. Runners are sometimes left intact to facilitate racking for electroplating at a later stage.

5.6 Racking:⁵

- 5.6.1 Molded-plastic parts can be prepared for electroplating in barrels, trays, or baskets and then transferred to racks designed specifically for electroplating, or they can be processed on racks that are used in both the preparation and electroplating cycles. Which method of racking to use may be dictated by the size of the parts, by efficiency, and other considerations. The first is the bulk method; the second is called "through-racking."
- 5.6.2 Bulk Method—Small parts are often processed in polypropylene baskets or plastic-coated steel baskets. Somewhat larger parts can be processed in layered baskets made of stainless steel (UNS Types S30400 or S31600), titanium, or plastic-coated mild steel. Parts are placed as closely as possible compatible with the need to provide for complete solution wetting and drainage.
 - 5.6.3 Through-Racking:
- 5.6.3.1 The design of racks to be used in both preparation and electroplating processes is dictated by the requirements of electroplating and the corrosive nature of the solutions.
- 5.6.3.2 Rack splines and hooks are generally made of copper or copper alloys. Rack cross bars are made of copper or copper alloys if they are to conduct current from the splines to the contacts, but may be made of steel if their function is solely to strengthen and make the rack rigid. Rack contacts are usually stainless steel, although titanium has also been used. If spring action is necessary, phosphor bronze may be used as the contact member with a short stainless steel piece for the tip.
- 5.6.3.3 The entire rack is sandblasted, primed, and coated with plastisol before use, except for the stainless steel contacts. During the preparation process, the rack coating may become coated with metal, but this does not usually occur because hexavalent chromium is absorbed in the plastisol and prevents autocatalytic metal deposition from occurring.
- 5.6.3.4 Control of immersion times in neutralizing, catalyzing, and accelerating steps is critical to prevent metal deposition on the rack coating.
- 5.6.3.5 Parts are positioned on racks to optimize the thickness and appearance of electrodeposited coatings, and to minimize solution dragout.
- 5.6.3.6 It may be necessary to use current thieves, shields, or auxiliary anodes to obtain uniform metal distribution. The number of contacts is greater for plastic parts than for comparable metal parts. For example, if the total area being

⁵ Standards and Guidelines—Electroplated Plastics, American Society of Electroplated Plastics, Washington, DC, Second Edition, 1979.

electroplated in less than 0.02 m², one contact point is usually sufficient; if the area is 0.25 to 0.60 m², 16 contact points are recommended.

5.6.3.7 Metal deposited autocatalytically or electrolytically must be chemically removed from contacts after each cycle. This is usually accomplished by using nitric acid-containing solutions, or proprietary rack strippers.

6. Preparation of Plastic Substrates⁶

6.1 Alkaline Cleaning:

- 6.1.1 Cleaning in alkaline solutions is optional. If the parts are carefully handled and kept clean after molding, alkaline cleaning can usually be avoided.
- 6.1.2 Fingerprints, grease, and other shop soil should be removed by soaking plastic-molded parts in mild alkaline solutions that are commercially available. A suitable solution may contain 25 g/L of sodium carbonate and 25 g/L of trisodium phosphate operated at 55 to 65 °C. Parts are immersed in the solution for 2 to 5 min (see Note 1).

Note 1—Thorough rinsing after alkaline cleaning and after each of the following processing steps is essential. Multiple water rinses are recommended.

6.2 Conditioning:

- 6.2.1 Conditioning is an optional step that precedes the etching step. Conditioning can eliminate adhesion problems associated with inadequate etching. The conditioner may be a solution of chromic and sulfuric acids, or it may contain an organic solvent. Proprietary solutions are available and should be operated according to supplier's directions.
- 6.2.2 Chromic/Sulfuric Acid Type—This type of conditioner may contain 30 g/L of chromic acid and 300 mL/L of sulfuric acid (93 mass %; density 1.83 g/mL) dissolved in water and is maintained at a temperature of $60 \,^{\circ}\text{C} \pm 3 \,^{\circ}\text{C}$. Parts are immersed in the solution for 1 to 2 min. Because of the relatively large amount of sulfuric acid in the solution, the acrylonitrile-styrene matrix, as well as the butadiene phase, are attacked.
- 6.2.3 Organic Solvent Type—This type of conditioner is a solution of an organic solvent in deionized water. The organic solvent may be acetone or other ketone; for example, 2,4-pentadione is sometimes used. The solution may contain 100 to 125 mL/L of the appropriate organic solvent and is maintained at a temperature of 40 to 45 °C. Treatment is by immersion of the plastic parts for 2.0 to 2.5 min (see Note 2 and Note 3).

Note 2—Solutions containing volatile organic solvents require adequate ventilation and must not contact metals. These materials chelate ionic metal contaminants. Annealed polypropylene tanks are therefore used to hold this type of solution.

Note 3—Multiple hot water rinses are required after using the organic solvent-type conditioner. Because organic solvents soften and swell the plastic surface, time of immersion and of transfer to rinse tanks may affect the appearance of the final product, and should be controlled.

6.3 Etching:

- 6.3.1 Etchants are strong oxidizing solutions that microroughen and chemically alter the surface of molded plastic parts. The etching step is the most important step in achieving serviceable adhesion of metals to plastics. Commercially used etchants are either chromic acid types, chromic/sulfuric acid types, or chromic-sulfuric-phosphoric acid types.
- 6.3.2 Chromic Acid Type—Concentrated etchants usually contain greater than 850 g/L of chromic acid and as much as 1200 g/L. The temperature of the solution is maintained at 50 \pm 3 °C and treatment is by immersion for 8 to 10 min. Concentrated solutions of chromic acid tend to oxidize butadiene rubber particles in the case of ABS, selectively.
- 6.3.3 Chromic/Sulfuric Acid Type—This type of etchant may contain 250 to 350 g/L of chromic acid and 200 to 250 mL/L of sulfuric acid (93 mass %, density 1.83 mL/L) dissolved in water. Immersion times of 5 to 10 min at a solution temperature of 65 \pm 5 °C are commonly used. Several proprietary baths are available.
- 6.3.4 Chromic-Sulfuric-Phosphoric Acid Type¹⁰—This type of etchant solution normally consists of 3 % by mass chromic acid, 56 % by mass sulfuric acid (density 1.83 g/mL), 10.5 % by mass phosphoric acid (density 1.87 g/mL), and the balance water. An immersion time of about 3 min at 74 to 77 °C is commonly used.

6.4 Neutralizing (Sensitizing):

- 6.4.1 After thorough rinsing, all residual chromic acid must be chemically removed from the surface of the molded-plastic parts. Neutralizers are used and are typically mild acid or alkaline solutions containing complexing or reducing agents. In the case of ABS, it is common to use a solution containing a mixture of an acidsalt and a reducing agent, such as sodium bisulfite, to eliminate all traces of chromic acid. Typical processing conditions are 1 to 2 min immersion at 40 °C.
- (6.4.2) Neutralizers may also contain ionic surfactants to increase the adsorption of catalyst. The use of surfactants, however, can lead to activation of the rack coating and subsequent metal deposition on the rack. Surfactants should therefore be used with caution. Ionic surfactants are not normally used in processing ABS (see Note 4).

Note 4—Some plastics, for example, polyphenylene oxide, may require treatment in dilute solutions of ethylenediamine after neutralization to insure adequate adsorption of the catalyst.

6.5 Catalyzing (Activating):

- 6.5.1 Small amounts of palladium are chemically deposited on the surface at this stage of processing. Palladium functions as a catalyst for autocatalytic deposition of copper or nickel to follow. Palladium is deposited either by the older, two-step procedure or by the more reliable one-step procedure.
- 6.5.2 Two-Step Procedure—The molded-plastic parts are first immersed in a solution of stannous chloride, 6 to 10 g/L, operated at pH 1.8 to 2.4 (pH adjusted with hydrochloric acid), and at 20 to 25 °C for 1 to 3 min. The parts are then rinsed

⁶ Adcock, J. L., "Electroplating Plastics—an AES Illustrated Lecture," American Electroplaters' Society, Inc., Winter Park, FL, 1978.

⁷ The use of 2,4-pentadione is patented.

 $^{^8}$ The use of concentrations greater than 900 g/L has been patented. See U.S. Patent Numbers: 3,668,130; 3,708,430.

⁹ See U.S. Patent Numbers: 3,142,582; 3,370,974; 3,515,649.

¹⁰ This is commercially used for polysulfone printed circuit boards, but may be used with ABS and polypropylene plastics.

thoroughly to remove excess hydrochloric acid and transferred to a solution containing 0.1 to 1.0 g/L of palladium chloride dissolved in water at a pH of 1.6 to 2.0 adjusted with sulfuric acid. The palladious ions adsorbed on the surface react with stannous ions to form palladium metal and stannic chloride in the interstices of the etched plastic components. After thorough rinsing, the parts can be coated with nickel or copper by autocatalytic deposition.

6.5.3 One-Step Procedure—The molded-plastic parts are immersed in a solution of colloidal stannous chloride and palladium chloride containing excess hydrochloric acid. The stannous chloride concentration is 120 to 140 g/L, the palladium metal concentration is 0.05 to 0.15 g/L, and the hydrochloric acid concentration is approximately 3.0 N (see Note 5). The solution is maintained at 20 to 30 °C and the parts are immersed in the solution for 1 to 3 min. Rinsing in water leads to the formation of metallic palladium nuclei on the surface surrounded by stannic hydroxide. The stannic hydroxide is removed in the acceleration step prior to autocatalytic deposition.

Note 5—These solutions are proprietary and considerably more difficult to prepare than implied in this section.¹¹

6.6 Acceleration:

6.6.1 Stannous hydroxide is removed by treatment in a dilute solution of hydrochloric acid, or a solution of an acid salt. Fluoride or fluorinated compounds are often added to increase the effectiveness of the acceleration process. In most cases, a solution containing 1.0 N hydrochloric acid maintained at a temperature of 50 °C, agitated with air, in which parts are immersed for 30 to 60 s adequately removes excess stannous chloride and stannic/stannous hydroxide remaining on the surface after the one-step palladium activation procedure.

6.7 Autocatalytic Deposition:

6.7.1 Solutions for the autocatalytic deposition of either copper or nickel are used to render plastic parts conductive. The solutions contain a metal salt, a reducing agent, a complexant, a stabilizer, and buffers to control pH. The palladium on the surface of the plastic parts acts as a catalyst to initiate deposition after which the autocatalytic reduction of the metal occurs. A uniform metal film about 0.25 to 0.5-µm thick is deposited (see Note 6).

6.7.2 Autocatalytic Nickel—The commercially available processes for autocatalytic nickel deposition on plastics commonly use sodium hypophosphite as the reducing agent. The solutions are operated at 30 to 35 °C, at pH 10 to 11, and produce a nickel deposit with 2 to 6 % phosphorous. Parts are kept immersed in the solution for 5 to 10 min to achieve the desired thickness of metal. Although there may be considerable variation in bath formulations, autocatalytic nickel solutions may contain nickel sulfate, sodium citrate, ammonium chloride, ammonium hydroxide, sodium hypophosphite, and sodium hydroxide. Stabilizers are used to prevent spontaneous decomposition of the solution and to control the deposition rate.

6.7.3 Autocatalytic Copper—The commercially available processes for autocatalytic deposition of copper on plastics use formaldehyde as the reducing agent. Room temperature processes are used, as well as high temperature ones. Each produce deposits of pure copper. Parts are immersed in the solution for 5 to 10 min.

Note 6—Autocatalytic nickel or copper is used commercially in the preparation of plastics, and either may give acceptable results. The use of autocatalytic copper, however, may improve the performance of electroplated plastics in wet corrosive environments. Parts that are inadequately etched or that are made from grades of plastics that are difficult to etch are less likely to fail in severe corrosive environments when autocatalytic copper is used. 12,13,14

6.8 *Electrodeposited Strikes:*

6.8.1 Additional thicknesses of either copper or nickel are applied by low-current density electrodeposition from suitable strike baths. Metal thickness is increased to 2.5 to $4.0~\mu m$ to facilitate electrodeposition of decorative or functional coatings by conventional means.

6.8.2 Typical copper and nickel strike solutions are given in Table 1.

TABLE 1 Typical Strike Solution Compositions

Strike Solution	Composition
Copper Strike:	
Pyrophosphate Type:5768	
Copper (Cu)	24–37 g/L
Pyrophosphate (P ₂ O ₇ ⁻⁴)	185—250 g/L
Nitrate (NO ₃ ⁻¹)	5–10 g/L
Ammonia (NH ₃)	1–4 g/L
рН	8.4–8.8 g/L
Temperature	50–55 °C
Voltage, d-c	2-3 V
Current density	250-400 A/m ²
Acid Copper Sulfate Type:	
Copper sulfate (CuSO ₄ ·5H ₂ O)	210-225 g/L
Sulfuric acid (H ₂ SO ₄)	45–60 g/L
Temperature (room)	18–22 °C
Voltage, d-c	2.5–3.0 V
Current density	250-400 A/m ²
Nickel Strike:	
Watts Type:	
Nickel sulfate (NiSO ₄ ·6H ₂ O)	300-340 g/L
Nickel chloride (NiCl ₂ ·6H ₂ O)	30–60 g/L
Boric acid (H ₃ BO ₃)	30–40 g/L
pН	3–4 g/L
Temperature	60–65 °C
Voltage, d-c	2.5–3.0 V
Current density	250-600 A/m ²
Sulfamate Type:	300–350 g/L
Nickel sulfamate ^A	30–45 g/L
Boric acid (H ₃ BO ₃)	3.0–4.5 g/L
рН	45°–55°C
Temperature	250-600 A/m ²
Current density	

^A Usually available as a liquid concentrate.

¹¹ See U.S. Patent Numbers: 3,011,920; 3,874,882; 3,904,792; 3,672,923; 3,672,938; 3,682,671; 3,960,573; 3,961,109.

¹² Di Bari, G. A., "Performance of Decorative Copper-Nickel-Chromium Coatings on Plastics—Final Report of Corrosion Programs Conducted by ASEP and ASTM," copies of the report may be requested by writing to ASTM Headquarters.

¹³ Wedel, R. G., "Characteristics of Corrosion-Associated Blisters on Plated Plastics," *Plating and Surface Finishing*, January 1975.

¹⁴ Wedel, R. G., "A Mechanism for Corrosion-Associated Blisters on Plated Plastics," *Plating and Surface Finishing*, March 1975.