

Troubleshooting Decorative Electroplating Installations, Part 4: Plating of Non-conductors

by N.V. Mandich, CEF, AESF Fellow & D.W. Baudrand, CEF

The brief historical development and basic chemical steps for the metallizing of non-conductors in general, and plating on ABS plastics in particular, are offered. The main emphasis, however, is directed toward the presentation of a comprehensive troubleshooting guide, where the main technical problems typically encountered in a plating-on-plastic plant are detailed. The possible causes of plating defects and solutions of the problems are elaborated. For reasons of clarity, theoretical explanations presented are kept at the basic level, and technical language is used in the simplest form. In Parts 1-2, emphasis was given to troubleshooting of the sequences for preplating and electroplating the metals.¹ In Part 3, the background, causes, symptoms, and troubleshooting for pores, pits, stains, blistering, and "spotting-out" phenomena were analyzed from phenomenological and practical standpoints.² Troubleshooting of decorative and functional chromium electroplating baths is given elsewhere in detail.³

In their biblical teachings, the ancient alchemists recorded the deposition of metals on other metals. However, as time went on, newer metals and materials were found, and the need for finishing them in different effects or colors to suit the individual requirements soon presented a new field for search and activity. Particularly so was the case in which metals had to be deposited on insulating materials for new fields or industries. Such was the case, for instance, of electrotyping, where a wax impression of type matter is reproduced in metal so that it may be used as a printing medium itself. The museums of the larger cities have on exhibition examples of metallized wood and terracotta made by the Egyptians. This was done only for decorative purposes.

About the earliest recorded method for mold making is accredited to H. Jacobi⁴ who, in 1837, deposited metals on wax, and subsequently stripped (separated) them. About the same time, Alexander Parks⁵ was granted a patent for metallizing animals, insects, flowers and fruits by the application of a silver nitrate solution. The silver nitrate formed a part of many other processes, which varied simply in their methods of application. For example, a patent obtained by Noualheir and Provost⁶ in January 1857, described the metallization of a soft surface such as a human corpse by placing the body in a suitable attitude and spreading pulverized silver nitrate over it with a brush. It was then electroplated in a copper sulfate bath, thus producing a copper-plated mummy.

Electroless plating began almost as soon as modern electroplating.⁷ The first description by von Liebig⁸

in 1835 was the reduction of silver salts by reducing aldehydes. Despite its early start, progress in this field remained slow until World War II.

Modern electroless plating began in 1944, when Brenner and Riddell^{9,10} rediscovered that hypophosphite could cause nickel deposition. Their subsequent work led to the first patents on commercially usable electroless nickel (EINi) solutions. Although early solutions were very useful for coating metals, they could not be used on most plastics because their operating temperature was 90-100°C. The first electroless nickel solution capable of wide use on plastics was introduced in 1966¹⁰, as it could operate at room temperature and was extremely stable.

Electroless copper (EICu) solutions underwent a similar development during the same period.¹¹ The most commonly plated plastic, ABS, deforms at temperatures above 65°C. This prompted the use of low-temperatures EICu solutions, but these solutions were several orders of magnitude less stable than room temperature EINi solutions.

General interest in electroless plating grew as it was shown that uniformity of deposition was very high. This eliminated any high- and low-current-density complications, customized anodes and special plating fixtures needed with the use of electrolytic plating. The lack of a need for electrical continuity made electroless baths an ideal solution to the problem of plating on plastics and plating unconnected metal areas on printed circuit boards (PCB).

Rationale

Deposition Process

The typical plating-on-plastics process is presented in Table 1. (Note: For reasons of simplicity, necessary rinsing steps are omitted.) It consists of the following sequence:

- Etching
- Etch neutralization
- Catalyst application
- Catalyst activation
- Electroless plating

Most commercial applications, except RFI/EMI shielding, use the initial electroless deposit as a base for subsequent electrolytic plating. In decorative chromium applications, the initial copper or nickel layer is coated with successive layers of electrolytic copper, nickel, and chromium. The exact types and thicknesses of metal used are determined by the end use of the part, *e.g.*, automotive exterior, decorative, plumbing, and others.¹²

Chemistry

Successful preplating steps rely on the optimized interaction of intricate chemical solutions^{13,14} which clean, roughen and catalyze the surface before plating. These steps are critical for the formation of an adherent, continuous and conductive electroless deposit and for the best possible durability after final electrolytic plating.

Pre-etching

In some situations, a separate, pre-etch is needed to prepare the plastic or other platable non-conductor for better etching. For more uniform etching, a swelling step can be introduced.¹⁵

Etching

This crucial step is necessary to give the best possible adhesion of metal to plastic. For plating of ABS plastic substrates, solutions of strongly oxidizing chromic acid-sulfuric acid-water or chromic acid-water are operated near the point of mutual saturation. The etchant both physically roughens the surface and chemically modifies it to give a very hydrophilic surface. Metal adhesion takes place because of the combination of chemical bonding and mechanical interlocking to the roughened surface. ABS plastic is a polymer consisting of polybutadiene spheroids dispersed in a continuous phase of polystyrene-acrylonitrile (SAN). During the etching step, chromic acid attacks the polybutadiene at a much higher rate than the continuous SAN phase. The primary adhesion is from mechanical interlocking. It is important to create holes that have a smaller opening than the diameter inside the hole. Catalyst enters the hole allowing deposition to take place inside the hole and join with the deposit on the outer surface to form the mechanical interlock. Because the butadiene is spherical and more easily etched, ABS is an ideal plastic to plate successfully. Plating-grade ABS must be specified. This gives an excellent micro-roughened surface with superior metal-to-plastic bond strength. A typical etchant formulation consists of 20 vol% sulfuric acid, 420 g/L chromic acid, and 0.1-1.0% of a fluorocarbon wetting agent. The plastic is treated with this formulation for 6-10 min at 60-65°C. For plating of non-conductors other than ABS, pre-etch and/or etching steps are outlined in the Appendix.

Neutralizing

Residual hexavalent chromium must be removed from the etched surface of the part. Hexavalent chromium shortens the life of the catalyst, and trace amounts completely inhibit electroless nickel deposition. The neutralizer is usually a mildly acidic or basic reducing agent, but other types of neutralizers are available, specific to substrates that are difficult to plate. The neutralizer may also contain surfactants or other surface-active compounds that promote and increase catalyst absorption. Efficient absorption promoters are frequently needed for non-ABS plastics where interlocking is often marginal.

Catalysis

Covering the prepared plastic surface with a thin layer of highly conductive metal layer is accomplished by an acidic solution of the stabilized reaction product of stannous chloride and palladium chloride. The older, almost obsolete, two-step process consisted of separate hydrochloric acid solutions of tin (sensitizer) and palladium (activator)

chlorides. It is now rarely used except in special applications, because the racks can become readily catalyzed and accept plating. Adhesion to rack coatings is poor, resulting in flakes that can fall off into the electroless plating solution causing instability or spontaneous decomposition.

Catalyst absorption is typically on the order of 1-5 $\mu\text{g Pd/cm}^2$. Other precious metals (Au, Pt) can be used, but they are not as performance or cost-effective. The exact chemical nature of this catalyst has been a matter of extensive research.¹⁶⁻²⁵ It is generally agreed to be a stabilized colloid, codeposited on the plastic with excess tin.

Today, there is a trend toward using higher activity catalysts at lower concentrations and higher temperatures. Typically, one uses 40-150 ppm of palladium at a maximum of 60°C in the company of a 30- to 60-fold excess of stannous chloride. Different catalyst alternatives are occasionally used that contain alkaline and non-noble metal catalysts.²⁶

Acceleration

After the catalytic step, the plastic surface is covered with a thin, continuous layer of palladium, stannous and stannic hydrous oxides and oxychlorides. The acceleration or activation step is needed to remove excess tin from the catalyzed surface, which would otherwise inhibit electroless plating. It also exposes the active palladium sites and removes loose palladium, which can destabilize the electroless plating bath. Acceleration can be done by any acid or alkaline solution that solubilizes excess tin.

Electroless Plating

This step provides a continuous surface layer of metal, in either copper or nickel form. Some research has indicated that copper may be better for corrosion resistance.²⁷⁻³¹ Experimental evidence shows that lateral anodic dissolution of an initial electroless nickel deposit proceeds faster than electroless copper deposit regardless of subsequent electrodeposition applied.³²

While the electroless copper plating systems are similar to those used in printed circuit processing, electroless nickel processes are notably different from those used in metal electroplating and are not interchangeable. Room temperature nickel solutions are usually mildly alkaline and give a low and uniform deposition rate. At present, automotive and other heavy-duty applications use copper, whereas decorative and interior articles are often plated with nickel.

Radio frequency interference (also known as electromagnetic interference, or RFI/EMI) shielding applications use nickel-phosphorus for low shielding requirements or a copper layer coated with nickel or other metal for high shielding.³³⁻³⁶

Room temperature electroless nickel systems are easily controlled and replenished with indefinite bath lives.³⁷⁻⁴¹ Electroless copper solutions can approach these bath lives when carefully controlled. Because only thin metal layers are deposited, the actual usage of metal for plating can be comparable to the drag-out losses. On the other hand, drag-out can help bath stability by preventing buildup of the reaction byproducts.⁴²

A 0.15-0.50- μm -thick layer can be obtained within a plating time of 5 to 20 min. That thickness allows the parts to be further processed in the electroplating step, as though they were totally metallic. Plated parts, except those needing RFI/EMI shielding, are electroplated with sequential layers of copper, nickel, and chromium. Precautions must be taken to control the initial application of the current at the begin-

ning of the electroplating. Otherwise, the thin deposits may locally overheat and lose electrical continuity (*i.e.*, “burn off”). To avoid this, a nickel or copper strike is typically applied prior to applying the desired decorative or functional deposit. Electroless solutions are not generally used for the buildup of metal (due to the high cost relative to electroplating solutions),

but only to provide the sufficient surface conductivity of the plastic part.⁴³⁻⁴⁹

Types and thicknesses of deposits depend on the end use of the part. They range from 22-25 μm total Cu + Ni + Cr for mild service conditions to 25-45 μm for more severe conditions. The recommended minimum electroplated thicknesses for a bright chromium finish [ASTM B604-91 Reapproved 1997] are: bright acid copper, 15 μm , semibright nickel, 20 μm , bright nickel, 10 μm (30 μm total nickel thickness) and chromium 0.25 μm .

With all technical improvements that occurred in the last 50 years, it must be clear that preparation of plastics and non-conductors for electroplating will be always inherently more complex than it is for preparing a platable metal. This was recognized early on by the experienced practitioners.⁵⁰⁻⁵⁴

Troubleshooting

Determining the causes of plated plastic imperfections, flaws, and miscellaneous defects is far from simple or clear-cut. The main reason is that in most cases the defect is seen only on the finished product, *i.e.*, after plating is completed. Moreover, many plating defects look alike superficially and it requires considerable experience before accurate diagnosis can be implemented and the right cure can be administered.

On the whole, it is possible to distinguish between defects, which are related to the material itself, or those from the plating operation. The remedies for the first are, of course, to be sought in changes in the material or its manufacturing. Today, these defects account for the highest proportion of rejected parts by far. This subject will be further discussed and presented in the form of a comprehensive Troubleshooting Chart (Table 2) at the end of this article.

If both the manufacturing and the plating are done in the same plant, and this is always recommended, the management should leave the supervision of both processes to the same person; otherwise, the responsibility for defects will not be accepted by either department—a situation that is never in the interest of the company as a whole.

The manufacturer of molded plastic parts (molder) must have sufficient understanding of the electroplater's difficulties to support the electroplater in the search for causes of trouble, and he must be sufficiently self-critical to accept the need for changes in his own department where necessary.

It often happens that defects, which arise from faults in the material and/or in manufacturing, do not appear until the part has been treated in the preplating step and is ready for electroplating. When the plant is running at full capacity,

Table 1
Typical Plating-on-Plastics Processing Cycle

STEP	SOLUTION FUNCTION
Alkaline soak cleaning-optional	Removes shop oils, fingerprints, etc.
Pre-etchant	Promotes etching
Etchant	Promotes surface for adhesion
Neutralizer	Removes residual etchant
Conditioner (HCl 3-5% by vol.)	Conditions surface for catalyst (often no rinse)
Catalyst	Deposits tin-palladium layer
Accelerator	Activates catalyst
Electroless plating	For plated plastics, nickel or copper; for RFI/EMI, copper
Electrolytic plating	For plated plastics, copper, nickel or chromium
Rack stripping	Prevents plating on the plating racks and fixtures

such faults may be overlooked until plating rejects draw attention to them.

For example, stresses in the plastic may be visible after etching. Stresses are not properly etched, causing poor adhesion or blistering. Severe stresses have been known to crack the parts during etching. Stressed areas can be detected, *i.e.*, made visible by immersion in glacial acetic acid for 2-5 min. If stresses are found, molding techniques need to be improved. Heat treating mildly stressed parts sometimes helps anneal the parts. The best practice, however, is to make better molds. Some of the factors that influence stress are the number and location of gates, molding temperature, time, cooling time rate of fill and others.

To determine whether or not the cause of the defect lies in the plastic material itself, it is necessary to proceed systematically.⁵⁵ The first step should be to investigate a part that has been micro-roughened in the etching step and allowed to dry. A microscope may be required for this purpose. If no defect is established at this stage, the surface of the part should then be blackened with graphite to help make faults visible. If this does not reveal any defects, the metal deposit should be removed from the plated part. If the defect is actually in the plastic itself, it is certain to appear at this stage, otherwise it will lie somewhere in the preplating or electroplating steps. The virgin unfinished plastic parts can be examined only for gross defects such as cavities, sinks, flow-lines, and so forth, as their lack of specular surface reflectivity hides any finer faults.

If it is certain that the defect is related to the plastic material or the manufacturing (molding) process, more often than not, it is relatively easy to determine the remedy. Almost all plastics manufacturers have trained technical service engineers who are available to assist. Moreover, the instructions, which accompany the individual plastics materials normally, contain sufficient information on possible sources of defects for the fabricator to diagnose any troubles himself.

Inherently it is a good deal more intricate when the parts are not finished in the same plant where they are produced. In this case, it is vital for the electroplater to adopt an exact written specification for the quality of the parts supplied for plating, and it is essential that the outside manufacturer diligently follow this specification. There is no point at all in electroplating poor or badly molded material, as the finishing process can never hide the defects in the latter.

Conclusion

The troubleshooting approach and troubleshooting table are not intended to be a unique method of problem-solving, nor

are they a remedy for all problems that can occur in the present day treatment of plating on different kinds of platable plastic in a modern plant. It is only an effort to explain after many years of practical, production experience a troubleshooting method which is as applicable as any, and hopefully better than most. Other processes may call for a more or less different approach to the given problems, and hence their solutions. The main difference is in the surface conditioning-etching step. The procedures as outlined above, are presented as a remedial effort to a specific problem, of plating on ABS plastic. However, this troubleshooting scheme should not significantly vary for plating on different kinds of plastic and the employment of such a process.

The above problems are a synopsis of most of the normal plating difficulties, which may be encountered in a day-to-day plating-on-plastic operation. Proper attention to management, maintenance, and manpower will keep this operation as productive and profitable as it should be.

Appendix

Processing non-conductors other than ABS. Preparing other types of non-conductors for plating differs from that used for ABS in that the etching process is different for each plastic basis material.

Acrylic. Etch in a solution of 159 g/L sodium hydroxide and 150 mL/L ethyl alcohol for 5-15 min at 60-65°C. Rinse. Immerse in a solution containing 50 g/L sodium hydroxide and 50 mL/L ethyl alcohol. Rinse and proceed as for ABS.⁵⁹

Cyanate ester and other difficult-to-etch surfaces. Clean. Etch in sulfuric acid/chromic acid ABS etchant to provide a hydrophilic surface. Etch penetration is slight so that it is not suitable for plating. Immerse in a 2 vol% polyacrylic acid solution (molecular wt. = 250,000) for 30 sec. Drain and dry. Proceed as for ABS.

Polyethylene terephthalate glycol copolymer (PETG). Alkaline clean. Etch in a solution of 750 mL/L sulfuric acid and 30 gm/L chromic acid for five min at 72°C. Rinse. Alkaline treat in a solution of 240 g/L sodium hydroxide and 5 mL/L ethylene glycol for one min at 72°C. Rinse and proceed as for ABS.

Mineral-filled nylon. Nylon filled with inorganic fillers is etched in a 30 mL/L hydrochloric acid for three to eight min at room temperature. Rinse. A second etch is then done in 60-100 mL/L hydrochloric acid for one to two min at 25-35°C. Then process as for ABS.

It should be noted that if chromic acid is used as an etchant, a complex is formed with nylon, which is difficult to remove and causes problems with subsequent process steps. Sulfuric acid will cause the nylon to hydrolyze. Nylon takes up large quantities of water, and drying at 70-90°C is recommended after plating. Hydrochloric acid dissolves the amorphous layer on the surface and some of the crystalline layer, exposing the inorganic filler and forming the right type of roughening. However, the adhesion is not quite as good as that for ABS.⁵⁹

Polyacetal. Clean, then etch in 800 mL/L phosphoric acid (89%) solution for two to eight min at 75-85°C. Rinse, then etch in a solution of 150-200 g/L sodium hydroxide for four to eight min at 70-90°C. Proceed as for ABS.⁶⁰

Polyester. Clean the pre-etch in a solution of 550 g/L sulfuric acid and 200 g/L chromic acid for five min at 68°C. Rinse, then etch in 200 g/L sodium hydroxide solution for 20 min at 70°C. Rinse, then immerse in a solution of 50 mL/L hydrochloric acid for two min at room temperature.⁵⁹

Polyethylene terephthalate. Etch in a 200 g/L sodium hydroxide solution, containing 200 mL/L of a proprietary additive at 55-65°C for two to five min. Rinse, then etch in a 100 g/L sulfuric acid solution containing 200 g/L of a proprietary additive for two to five min at 35-45°C. Proceed as for ABS.⁵⁹

Polycarbonate. Pre-etch in a 60-80% solution of dimethyl formamide for five to ten min at 35-60°C. Rinse, then etch in a solution of 600 g/L sulfuric acid, 100 g/L phosphoric acid and 30 g/L chromic acid for 10-25 min at 70-75°C. Rinse, then immerse in a promoter. Proceed as for ABS.⁵⁵

References

1. N.V. Mandich, & W. Saas, *Plating & Surface Finishing*, **87**, 121 (June 2000); **87**, 63 (July 2000).
2. N.V. Mandich, *Plating & Surface Finishing*, **87**, 74 (December 2000).
3. N.V. Mandich, *Metal Finishing*, **97**, 100 (June 1999); **97**, 42 (July 1999); **97**, 42 (August 1999); **97**, 79 (September 1999); **97**, 30 (October 1999).
4. B.S. Jacobi, *Raboty po elektrokhemii*, (*Works on Electrochemistry*), Izdatelstvo AN SSSR, Moscow (1957).
5. A. Parks, in S. Wein, ed.: *Metallizing of Nonconductors*, Industrial Pub. Co, New York, NY (1945).
6. Nouhauer & Provost, *ibid*.
7. C. Singer & co-eds., "The Industrial Revolution" in *History of Technology*, Vol. 4, Oxford University Press, New York, NY (1958).
8. J. von Liebig, U.S. Patent 33,721 (1861).
9. A. Brenner & G. Riddell U.S. Patent 2,532,283 (1950).
10. A. Brenner, *Plating & Surface Finishing*, **71**, 24 (July 1984).
11. E.B. Saubestre, *Plating*, **59** 563 (1972).
12. ASEP, *Standards & Guidelines for Electroplated Plastics*, 3rd Ed., Prentice-Hall, Englewood Cliffs, NJ, (1984).
13. G.A. Krulik, *J. Chem. Ed.*, **55**, 361 (1978).
14. N.V. Mandich, *Plating & Surface Finishing*, **80**, 68 (November 1993).
15. N.V. Mandich, *Trans. IMF*, **72**, 41 (January 1994).
16. G.A. Krulik, *Platinum Met. Rev.*, **26**, 58 (1982).
17. N.V. Mandich & G.A. Krulik, *Plating & Surface Finishing*, **80**, 68 (December 1993).
18. E. Matijevic, A.M. Poskanzer & P. Zuman, *Plating & Surface Finishing*, **62**, 958 (October 1975).
19. G.A. Krulik, *J. Catal.*, **6**, 95 (May 1980).
20. N.V. Mandich, *Plating & Surface Finishing*, **78**, 50 (December 1991).
21. N.V. Mandich & G.A. Krulik, *Trans. IMF*, **70**, 111 (March 1992).
22. N.V. Mandich & G.A. Krulik, *Trans. IMF*, **70**, 117 (March 1992).
23. C.R. Shipley, U.S. Patent 3,001,920 (1963).
24. R.L. Cohen & K.W. West, *J. Electrochem. Soc.*, **120**, 502 (April 1973).
25. J. Horkans, *ibid*, **130**, 311 (February 1983).
26. N. Pearlstein, U.S. Patents 4,087,586; 4,132,832 (1972).
27. G.A. DiBari & R.L. Coombes, *Products Finishing*, **41**, 54 (April 1977).
28. R.G. Wedel, *Int. Met. Rev.*, **217**, 97 (1977).
29. G.O. Mallory, *Plating*, **61**, 1005 (1974).
30. R.G. Wedel, *Plating*, **62**, 40 (1975).
31. R.G. Wedel, *Plating*, **62**, 235 (1974).

32. R.R. Wiggle, V. Hospadaruk & D.R. Fitchmun, *J. Electrochem. Soc.*, **118**, 158 (January 1971).
33. J. Hajdu & G.A. Krulik, *Plating & Surface Finishing*, **70**, 42 (July 1983); G.A. Krulik, *ibid*, **71**, 56 (December 1984).
34. N.V. Mandich, *Plating & Surface Finishing*, **81**, 60 (September 1994).
35. N.V. Mandich & D. Tuomi, *Trans. IMF*, **72**, 72 (February 1994).
36. G.A. Krulik & N.V. Mandich, US Patents 5,212,138; 5,219,815 (1993).
37. G.A. Krulik, & N.V. Mandich, "Metallic Coatings," in: *Kirk-Othmer Encyclopedia of Chem. Technology*, Vol. 8, 4th ed., Wiley, New York, NY (1995); pp.258-291.
38. N.V. Mandich, & R. Tuszynski, "Metallizing of Plastics," in: *Engineered Materials Handbook*, ASM International, Materials Park, OH (1995); pp. 356-364.
39. J. McDermott, *Plating of Plastics with Metals, Chemical Technology, Review No.138*, (1979); J.I. Duffy, ed, *Electroless & Other Non-electrolytic Plating Techniques, Recent Developments, Chemical Technology Review No.171*, Noyes Data Corp, Park Ridge, NJ (1980).
40. G.G. Gawrilov, *Chemical (Electroless) Nickel-Plating*, Portcullis Press, Redhill, UK, (1979).
41. G.O. Mallory & J. Hajdu, eds., *Electroless Plating: Fundamentals & Applications*, AESF, Orlando, FL (1990).
42. J.K. Dennis & T.E. Such, *Nickel & Chromium Plating*, 3rd Ed., Woodland Pub. Co. Cambridge, UK (1993).
43. D.J. Coombes, *Plating & Surface Finishing*, **68**, 58 (July 1981).
44. S. Jahn & N.V. Shanmugam, *Metal Finishing*, **84**, 51 (March 1986).
45. W. Goldie, *Metallic Coating of Plastics* (two volumes), Electrochemical Publications Ltd., Middlesex, UK (1968).
46. L.J. Durney, ed, *Electroplating Engineering Handbook*, 4th ed., Van Nostrand-Reinhold Co., Inc., New York, NY (1984).
47. M. Paunovic & I. Ohno, *Proc ECS*, Vol.88-12, The Electrochemical Soc., Inc, Pennington, NJ, (1988).
48. W. Riedel, *Electroless Nickel-Plating*, ASTM International, Materials Park, OH (1991).
49. R. Weiner, ed., *Electroplating of Plastic*, Finishing Publications, Middlesex, UK (1977).
50. G. Muller & D.W. Baudrand, *Plating ABS Plastics*, Teddington, UK (1971).
51. H. Narcus, *Plating*, **55**, 816 (1968).
52. G.H. Carlson, *Products Finishing*, **44**, 70 (September 1980).
53. E. Pollard, *ibid*, **23**, 23 (May 1970).
54. C.C. Weekly, *Plating & Surface Finishing*, **53**, 107 (January 1966).
55. N.V. Mandich, *Proc. AESF SUR/FIN 1999*, Cincinnati, OH, AESF, Orlando, FL (1999).
56. N.V. Mandich, *Metal Finishing*, **97**, 42 (August 1999).
57. N.V. Mandich, *Plating & Surface Finishing*, **85**, 91 (December 1998).
58. M. Jamison, *Proc. ASEP 10th Annual Meeting*, San Diego, CA (1977).
59. Technical Bulletin, Okuno Co, Osaka, Japan.
60. S. Kawagishi, Okuno Co, Osaka, Japan, private communication.

About the Authors



Dr-Ing N.V. Mandich, CEF, AESF Fellow, is founder, president and research director of HBM Electrochemical Co., Lansing, IL. He holds a Dipl-Ing degree in chemical engineering from the University of Belgrade, Yugoslavia; a MSc. in theoretical chemistry from Roosevelt University, Chicago; and a PhD in applied electrochemical engineering from Aston University, England, under professor J.K.

Dennis. He is an AESF certified instructor and a member of the Hard Chromium and Pulse Electrodeposition Plating Committees of the AESF. He also belongs to the ECS, ISE, and the AAAS and is a Fellow of the IMF. He consults and lectures in the U.S. and abroad. He holds 12 U.S. patents and patent applications and has more than 100 technical and research papers either published or submitted.



Donald W. Baudrand, CEF, was founder and president of Electrochemical Laboratories, Los Angeles, vice president of R&D for Allied Kelite, Witco Corp., and VP and business manager for Allied-Kelite. He retired in 1994, and is now a consultant in electro- and electroless plating processes. He has numerous patents in electroless plating and microelectronics, and has written over 70 papers. He

contributed to the ASM Metal Handbook, the Electronic Materials and Processes Handbook, and Electroless Plating: Fundamentals and Applications. He has co-authored Plating of ABS Plastics, the AES 1960 Plating Handbook and others. He holds a BS in chemistry from Whittier College, with graduate studies in nuclear physics and chemical engineering at the University of California, Berkeley.

Table 2
Plating-on-Plastic Defects: Their Causes & Remedies

Symptom	Possible Cause	Remedy
Blistering after electroless deposition	<ol style="list-style-type: none"> 1. Poor etching 2. Greasy surface 3. Reducer in electroless solution is too concentrated 4. Electroless deposition is too fast 5. Entrapped moisture in the plastic substrate; or strains & stresses present 	<ol style="list-style-type: none"> a. Increase etching treatment time b. Increase temperature c. Agitate etching solution or work d. Use wetting agent in etching solution e. Analyze for CrO_3 & H_2SO_4. Adjust to correct concentration a. Renew etching solution b. Prolong cleaning time or raise temperature c. Provide operators with gloves <p>Dilute electroless plating solution & adjust other ingredients</p> <p>Lower the reducer's concentration, or reduce temperature</p> <p>Contact molder for remedial action</p>
Roughness	<ol style="list-style-type: none"> 1. Activator solution too old 2. Excessive time in activator 3. Overetching 4. Excessive H_2SO_4 in etch solution 5. Contamination of electroless solution 6. Deposition on plating racks 	<p>Replace solution</p> <p>Reduce treatment time</p> <p>Reduce etch time, and/or temperature</p> <p>Analyze and correct by dilution, followed by CrO_3 addition</p> <p>Filter solution and clean (strip) tank</p> <ol style="list-style-type: none"> a. Strip racks thoroughly b. Use stainless steel or titanium racks c. Reduce temperature in catalyst d. Reduce time in catalyst
Blistering after electroplating step	<ol style="list-style-type: none"> 1. Overheating at rack contact points, due to the poor electrical contact at these points or neighboring areas of the parts 	<p>Redesign the rack contacts</p>
No deposition	<ol style="list-style-type: none"> 1. Incorrect polymer 2. Low reducer in electroless bath 3. Low etch temperature 4. Insufficient activation 5. Insufficient acceleration 	<p>Check the grade and type of polymer for platability</p> <p>Analyze and correct</p> <p>Check thermostat and heaters</p> <p>Increase temperature in the activator, or decrease time in accelerator</p> <p>Increase acceleration time; analyze and correct concentration</p>
Slow electroless deposition	<ol style="list-style-type: none"> 1. Catalyzing and/or activating solution too dilute 2. Sensitizing and/or activating solution too cold 3. Electroless plating solution too dilute 4. Electroless deposit too cold 5. pH of electroless solution too low 	<p>Strengthen sensitizing and/or activating solution</p> <p>Warm-up sensitizing and/or activating solution</p> <p>Regenerate electroless solution per operating instructions</p> <p>Warm-up solution</p> <p>Adjust pH</p>
Conducting layer burns during electroplating	<ol style="list-style-type: none"> 1. Electroless deposit too thin 2. Current density too high 3. Contact points too small 4. Contact points worn by work movement 5. Bipolar effect; anodic dissolution 	<p>Prolong the plating time</p> <p>Reduce current density to 3-5 A/ft²</p> <p>Increase contact area or size of contacts</p> <p>Attach work better on racks</p> <p>Improve spacing of racked parts</p>
Poor adhesion to plastic	<ol style="list-style-type: none"> 1. Plastic surface contaminated with mold release compound 2. Etching time too short 3. Etching time too long 4. Etching solution too concentrated/too hot 5. All other conditions being satisfactory, molding characteristics such as stresses & strains are present in the molded parts 	<p>Do not use mold release compound</p> <p>Prolong etching time</p> <p>Reduce etching time</p> <p>Dilute etching solution or work at lower temperature</p> <ol style="list-style-type: none"> a. Contact molder b. Use full strength Watts nickel bath or use a Wood's or sulfamate nickel strike c. Use copper pyrophosphate bath before bright copper or nickel bath
Poor adhesion between electroless & electroplated Ni	<ol style="list-style-type: none"> 1. Electroless nickel has become passive 	<ol style="list-style-type: none"> a. Use live entry going into bright copper & nickel⁵⁶ or nickel activation.⁵⁷ b. Shorten transfer time from electroless nickel to first plating tank
Poor adhesion between electroless metal & plastic	<ol style="list-style-type: none"> 1. Etching solution out of balance 2. Stresses and strains in molded plastic part 3. High pH/low conc. in catalyst solution 4. Too long post-catalyst treatment 5. Electroless solution plates too fast 	<p>Analyze for Cr(VI), Cr(III) and total acidity</p> <p>Contact molder for remedial action, after checking for strains and stresses using glacial acetic test</p> <p>Analyze</p> <p>Lower treatment time</p> <p>Lower temp in electroless bath or concentration of metal reducer</p>

—Continued on next page

Table 2
Plating-on-Plastic Defects: Their Causes & Remedies (Continued)

Incomplete (skip) deposition, or complete absence of plating	1. Work contaminated with silicone	a. Avoid use of silicone mold release compounds b. Replace cleaner or increase its concentration
	2. Inadequate etching	Extend treatment time in etching bath and increase temperature
	3. Work racked too close	a. Improve the racking of the parts b. Increase contact area or size of contacts
	4. Neutralizer exhausted	a. Replace neutralizer b. Increase time
	5. pH or temperature of electroless solution too low	a. Adjust pH b. Warm-up electroless solution
	6. Excessive etch solution run-out from blind holes, recesses, etc.	Improve rinsing and agitation
	7. Low concentration of catalyst metal, and low temperature at low pH	a. Analyze and correct catalyst bath b. Adjust the temperature and pH
	8. Etch time & temperature too low for certain ABS plastics & highly stressed surfaces	Stressed surfaces and certain plastics may require highest obtainable temperatures and/or longer times
	9. Contaminated etch	Increase time in neutralizer
	10. Electroless deposit dissolving in acid copper solution	a. Strike electroless deposit in Woods nickel strike b. Strike in copper pyrophosphate before transferring to acid copper bath
No electroplated deposit	1. Bad racking	Improve racking, so that contact points are in med. to high CD areas
	2. Initial current density too high, causing "burnoff" of thin electroless deposit	Start electroplating step at low current density, ramping to full current
	3. Electroless deposit dissolving in acid copper solution	Strike deposit in Woods nickel strike or in copper pyrophosphate strike before transferring to acid copper bath
	4. Passive electroless nickel	Electroplate immediately, or activate in activating dip
Sandpaper effect	1. Electroless bath out of balance, precipitating solid particles.	Analyze and filter electroless bath
	2. Plastic surface over-etched	Lower etch time and temperature
	3. Dirty electroless solution	Filter bath
Stardusting	1. Controversial problem ⁵⁸	a. Eliminate SnCl ₂ sensitizer b. Use electroless copper instead of electroless nickel
	2. Buildup of TiO ₂ and/or SiO ₂ in the etchant ⁵⁵	a. Reduce surface tension in the etch solution b. Use hot save rinse after etch without agitation c. Use full spray rinses d. Guard against over-etching
Plating on plating racks	1. Poor rack maintenance	Strip racks regularly
	2. High pH and catalyst concentration	Lower the concentration of catalyst and/or pH
	3. High temperature in the catalyst solution	Lower the temperature of the catalyst solution
	4. High concentration and/ or time in the catalyst solution	Lower the concentration and the time in the catalyst solution
	5. Too long time in the post-catalyst (accelerator) solution	Lower the time in the accelerator solution
	6. Build-up of the catalytic metal or metallic dust in rack stripper solution	Replace the rack stripper solution
	7. Contaminated accelerator solution due to the build up of metal dust	Replace the accelerator solution
Voids or air pockets	1. Poor cleaning	Analyze or replace cleaner
	2. Insufficient agitation	Increase agitation
	3. Low total acidity in etch tank.	Analyze for total acidity in the etch solution
	4. Poor rinsing of etch solution; or inefficient conditioner solution	Improve rinsing or replace conditioner solution
Dull electroless plating	1. Electroless bath out of balance	Analyze and correct the bath
	2. Over-etching	Lower the temperature and/or time in the etch tank
High drag-in	1. Poorly engineered rinse tanks	Change rinse tank design to countercurrent flow and add spray rinses, especially after etch and catalyst tanks
Overall poor appearance of plated part	1. Sink marks, pits, splay marks, etc.	Contact molder