The Evolution of a Process: Fifty Years of Electroless Nickel

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Electroless nickel plating is a relatively new technological process. The first laboratory experiments were done in 1944 by A. Brenner and G. Riddell[1] during World War II. Public announcements were made a few years later. This work had been done without knowledge of the earlier observations by Roux in 1916[2] and by Wurtz[3] in 1845. The early work was not successful due to poor quality reagents and other factors. Thus, Brenner and Riddel are credited as the discoverers of this technology, as they developed the first workable baths and began scientific investigations of the process.

This is not a very long history for a technology. Most of the details of its evolution are still readily available for study. These data show that the field has undergone a very rapid initial expansion in scientific understanding coupled with a wide range of practical uses. Further technological development has continued at a slower pace, but usage has been rapidly increasing both in terms of number of applications and total usage. The field has not yet become static or mined out.

Looking at the background of the process, it is obvious that electroless plating is not a unique field by itself, but is only one of a series of closely related surface-coating techniques. They can be conveniently divided into gas-phase and liquid-phase processes. The gas-phase types can be easily subdivided into many other categories, such as thermal- and electron-beam evaporation, plasma spray or reactive sputtering. There are some basic technical differences in the way these are divided. Liquid-phase processes are based on reactant reduction by an internal electron flow. Gas-phase processes usually use some form of thermal energy input rather than electron flow. (Some forms of ion plating using a charged substrate are exceptions.) In this view, electroplating and electroless plating are conceptually closely related.

Despite the difference in techniques among the basic categories, the same types of coatings can be obtained from each process, whether it be nickel, nickel-phosphorus or other alloys; for example, a nickel-phosphorus coating can be made by thermal decomposition of nickel carbonyl and a phosphine,[4] electrolysis of a nickel solution containing hypophosphite,[5] or by electroless deposition.[5-8] These coatings may be the same by bulk chemical analysis, but important differences can be found. The most important practical differences may include:

Deposition rate
Practical maximum thickness deposited
Stress of deposit
Adhesion to surface
Corrosion resistance
Crystal structure
Homogeneity of coating thickness
Ability to coat particular substrates
Technical utility
Reproducibility
Cost of deposit
Process hazard
Process toxicity
Waste products
Alloy homogeneity

Electroless deposition can be conveniently divided into three general areas, deposition on metals, on bulk dielectrics, and on particulate dielectrics as shown in Table I. These three areas in the table mainly correspond to the basic types of electroless nickel baths now available. This is one basis for commercial product differentiation. Intensive research has led not only to special electroless nickel baths for each substrate, but to special pretreatments, which allow the same electroless bath to be used on many substrates.

Metals are easily coated with electroless deposits using a hot bath. The pretreatments needed for plating on such metals as stainless steel, aluminum, zinc or copper are vastly different but can allow use of one electroless formulation on a wide range of substrates; for example, aluminum must be deoxidized and preferably zincated before electroless nickel plating, while zinc must be copper-plated instead.[5-8] For nonconductors, room temperature baths are usually used. Nonconductors need coating with catalyst to initiate plating and usually special etchants and other pretreatments are necessary for optimum adhesion and coverage.[9]

A third area is plating on particulate dielectrics.[10] This is a much newer field, and baths that are much more stable are needed. Two separate subfields are involved.

One subfield consists of codeposition of electroless nickel with another particulate material onto the surface of a part. The coating is a two-phase system that incorporates a continuous

Table I. Substrates for Electroless Nickel Coating

Metals
Stainless steels
High strength steels
Mild steels
Aluminum
Zinc
Copper
Exotic metals and alloys
Bulk Dielectrics
Plastics
Ceramics
Glass
Fabrics
Intermetallics
Natural products
Fibers
Silicon
Particulate Dielectrics
Glass spheres
Diamonds
Abrasives
Plastics

electroless nickel phase that acts as a binder to hold the particulates. Teflon deposits obtained via codeposition have superior lubricity and anti-galling properties.[11] Aluminum nitride, chromium carbide[12] and silicon carbide[13] electroless nickel composites have very good wear resistance. For grinding wheels, a diamond composite with electroless nickel yields better properties for grinding wheels;[5] the addition of 6% graphite reduces the friction and rate of wear.[14]

The other subfield consists of coating only the particles, whether dielectric or metallic, to yield discrete particles coated with the electroless metal deposit. Glass microballoons coated with electroless nickel for laser fusion targets, and electroless nickel-coated diamonds for sintered grinding wheels are typical examples.

A wide range of substrates can now be commercially plated using these methods. Although a nickel-phosphorus alloy is deposited in each case, particular needs have necessitated the development of specialized baths. There are hot baths for metals and some nonconductors, room-temperature baths for heat-sensitive materials, highly stabilized baths for plating on fine particles, and even spray solutions for very rapid deposition on glass for architectural uses.

The other emphasis of product differentiation focuses not on the substrate but on the bath itself. Table II shows the types of baths available. The authors estimate that over 200 formulations are available worldwide. Many times that number have been published, exist in the patent literature, or were simply abandoned.[5,15]

The options available are all the more remarkable, because 50 years ago, only one basic type of bath (the "Brenner" bath) was used on mild steel.

Wurtz's discovery, around 1845, was that nickel salts and hypophosphite react to give a black powder—a discovery of little use to surface finishing.[3] Roux and Breteau,[2,16] during a period around 1915, both found that a nickel-phosphorus film could be formed. Roux received a patent for plating aluminum, but nothing further was done.[2] Brenner independently discovered the process in 1944 and pursued and publicized its early development for commercial use.[1]

Table II. Electroless Nickel-Phosphorus Bath Types

Slow or fast rate
Dull or bright
Low or high phosphorus
Regenerable or single use
Hot or room temperature
High or low stability

Commercial interest began around 1950. A vigorous research program continued for many years at GAT and at many other labs.[5] At this time, much of the basic science of the process was understood and most of the commercially important discoveries were made. Much work was done on heat treatments, corrosion resistance, regeneration of baths and stabilizers. The discovery and development phase largely ended with the issuance of GAT patents on plating of particulates[17] and with the development of room-temperature baths for plating on plastics.[18]

The period since the mid-1960s has been devoted to consolidation and refinement of the basic processes and to development of new applications for electroless-nickel coatings. Much technical information has been developed, especially in the areas of mechanisms, stability, corrosion testing, and EMI/RFI shielding.[19]

Many specialized applications have been proposed, but not all have been or will be commercially successful (Table III). All of these ideas have been proven in laboratory use. Most have shown sufficient promise to warrant writing a patent and some are commercially successful now.

Table III. Electroless Nickel Applications

Magnetic alloys
Architectural glass coatings
Improving amalgam adhesion for dental fillings
Consolidation of sand layers during oil well drilling
Coating glass microspheres for fusion energy
Initial surface layer on printed circuit boards
Alloys for gold replacement
Diamond plating for grinding wheels
Composite coatings for abrasion resistance
Composite coatings with plastics (Teflon) for lubricity
Precoat on iron for porcelain coating
Brazing alloy on aluminum
Coating of stainless steel power for fusibility
Coating of plastic and zinc molds
Replacement of hard chromium
Use as a nitriding mask
Solar panels
EMI/RFI shielding

What does the future hold in store for electroless nickel plating? There is a real need for more fundamental work on the whole process of electroless plating. Much of the available data were obtained many years ago. Often the baths now in use are completely different, especially in terms of bath purity and deposit composition, stabilizers and brighteners.

It is safe to predict that most of the new developments will be in the application field; however, new pretreatments will be developed, especially for nonconductors. New alloy combinations will be invented, possibly including leveling electroless nickels or colored coatings. A recent development is a method for blackening an electroless nickel for possible solar applications. Hypophosphite may face competition by some as-yet-uninvented organonitrogen, organophosphorus, or organoboron reducing agent.

And is it even necessary to mention economics? Cost-cutting processes will be important, but only if they cut total costs. Even then, the customer may be unappreciative; for example, one customer had a new zinc process installed and ran it at a higher current density allowing substantially higher throughput on his line. The customer then complained that the process was using up zinc anodes too quickly!

Environmental regulations will also influence the future. Users must become increasingly conscious of the total costs of chemical processing. It is no longer possible to consider only the purchase price of solutions. Treatment costs, and the effects of the chemicals on internal waste stream processing, effluent quality, and final environmental effects must also be considered. Perhaps new solutions will be developed to more safely plate plastics; or perhaps new plastics or plastic-filler combinations will be developed that can be etched without chromic acid.

Permanganate etchants, ozone-based etchants, and plasma etching are all in use; for example, in electroless nickel, most baths for plating on plastics contain ammonia. Several states now have very stringent limits on ammonia discharges, giving rise to the development and availability of new ammonia-free baths, which will start a new learning cycle as they become more widely used.

In addition, hot carbonate-buffered baths are also being developed for metal plating. They have a number of advantages over the ammonia buffered baths: they do not fume, so there are no health or corrosion problems (ammonia additions must be made frequently and the inevitable fumes are irritating); and carbonate baths hold the proper pH range much better because the components are not volatile (additions are infrequent and consist of liquid caustic or carbonate solutions).

In some cases, burn-off is less with the carbonate bath. Deposition rates are similar to ammonia baths, so no line-cycle changes are needed. The same racks, rack coatings, and tanks may be used. Waste treatment is much simpler, since no ammonia is present to redissolve precipitated metals or violate effluent limits. Also, plating aluminum with carbonate-buffered baths results in better adhesion and reduced blistering.

There are a few cautions to observe with the carbonate-based plating on plastic baths. The most dramatic is that the bath color is green, not blue. This will actually help operators realize that the bath is now different and should be treated differently. Good water quality is essential for bath makeup, and preferable for the rinse before plating. Continuous 10–25 micron filtration is recommended during plating.

In other applications, faster electroless nickels may be introduced to replace the "strike" deposits, or to function as the sole finish on plastics. This might entail the combined improvements of better plastics; lower temperature, fast-rate, electroless nickels; and brighter nickel deposits. Perhaps electroless nickel deposited on superconducting fibers would lead to new applications. Electroless plating from organic solvents is also under development.[15] Electroless coatings are being used increasingly for EMI/RFI shielding and for electrostatic discharge elimination. Processing laboratories may disclose completely new applications or may show that some properties are greatly enhanced when plating is done in a microgravity field. New alloys will be developed for special uses, and still other applications may be developed to take advantage of the amorphous structure of electroless deposits to help solve intergranular corrosion problems.

CONCLUSION

The fifty-year-old electroless nickel-plating field is far from being static. New discoveries and applications will continue to expand the frontiers of electroless plating. MF

References

1. Brenner, A., "A History of the Electroless Plating Process," Symposium on Electroless Nickel Plating, ASTM Special Technical Publication No. 265; 1959
2. Roux, F.A., U.S. Patent 1,207,218; 1916
3. Wurtz, A., *Comptes Rendus, 21:149; 1845*
4. Krutenat, R.C., "Metallic Coatings," *A Concise Encyclopedia of Chemical Technology*, pp. 749–751; Wiley, New York; 1985
5. Gavrilov, G.G., *Chemical (Electroless) Nickel Plating*, Portcullis Press Ltd., Radhill, England; 1979
6. Mallory, G., and J. Hajdu (Eds.), *Electroless Plating*, AESF 1990
7. Paunovic, M., and I. Ohno (Eds.), "Electroless Deposition of Metals and Alloys," *Electrochemical Society Proceedings*, Vol 82-12; 1988
8. Krulik, G.A., "Electroless Plating," *Encyclopedia of Chemical Technology*, 3rd Ed., pp. 738–750, Wiley, New York; 1979
9. Krulik, G.A., "Electroless Plating of Plastics," *Journal of Chemical Education*, 55(6):361–365; 1978
10. Henry, J., "Electroless (Autocatalytic, Chemical) Plating," *Metal Finishing*, 90(1A):353–366; 1991
11. Tulsi, S.S., "Electroless Nickel: PTFE Composite Coatings," *Transactions of the Institute of Metal Finishing* 61(4):147; 1983
12. Dennis, J.K., et al., "Electroless Composite Coating," *Transactions of the Institute of Metal Finishing*, 59(4):118; 1981
13. Hubbell, F.N., "Chemically Deposited Composites," *Plating and Surface Finishing*, 65(12):58; 1978
14. Izzard, M., and J. K. Dennis, "Deposition and Properties of Electroless Nickel/Graphite Coatings," *Transactions of the Institute of Metal Finishing* 65(3):85; 1987
15. Domino, F.A., (Ed.) *Plating of Plastics: Recent Developments*, Noyes Data Corp., Park Ridge, N.J.; 1979
16. Duffy, J.F., (Ed.) *Electroless and Other Non- Electrolytic Plating Techniques: Recent Developments*, Noyes Data Corp., Park Ridge, N.J.; 1980
17. Parker, K., U.S. Patent 3,562,000; 1971
18. Muller, G., and D. Baudrand, *Plating ABS Plastics*, Robert Draper Ltd., Molesey, Surrey, England; 1967
19. Krulik, G.A., "Corrosion Resistance of Electroless Deposits for Electromagnetic Interference Shielding," *Plating and Surface Finishing*, 12:56–58; 1984