The automotive industry has the potential of increasing the use of electroless nickel for wear and corrosion protection. Many automotive parts are currently plated with electroless nickel for wear properties. A slip yoke (part of the front end) and a differential assembly, using an electroless nickel-plated central pin, are in full production in the U.S.

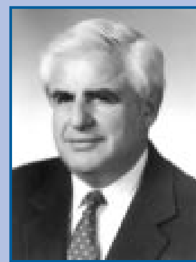
Electroless Plating: The Past is Prologue

The 37th William Blum Lecture

(Edited version of presentation at SUR/FIN® '96, Cleveland, OH)

By Dr. Juan Hajdu

In this presentation, the future developments of the main electroless processes, electroless nickel and copper plating, are considered by reviewing the major end uses. Also, special references are made to other electroless processes that may become important in the future.



I was especially grateful for the opportunity of delivering the William Blum Lecture in Cleveland, a vibrant city where I lived in the late sixties, and where I had the privilege of meeting and learning from high-caliber scientists who worked at the Case Institute of Technology and at the supply houses located here. Especially, I would like to recall the memory of Arthur DuRose, who worked for Harshaw in Cleveland and made major contributions to the art of electroplating and who received the AES Scientific award in 1969. Art DuRose, better than anyone, understood the value of creative cooperation between researchers working at learned institutions, the users and practitioners of applied electroplating, and those of us who make all this possible by supplying the needed materials and technologies to the industry. For this reason, in his Blum Lecture, Art traced the history of the supply houses contributing to the progress of plating.* I hope you will be able to take the opportunity to review Art DuRose's talk. I used his presentation as a background to my own, recalling how the triangle of academia, industry and supplier has worked over the years to the mutual benefit of all.

—Dr. Juan B. Hajdu

* Arthur H. DuRose, Plating, **57**, 793 (Aug. 1970).

The evolution of electroless plating during the last 30 years has been remarkable. We can claim rightfully that the digital revolution of our times was achieved through the continuous refinement of electroless plating techniques used for printed circuits and hard disk memory devices. Still, we have reached today a point where alternative technologies are threatening to replace electroless plating in several applications, and therefore we must explore the future evolution of the electroless plating industry. In other words, we must answer the question: Are we looking at the prologue of an era of growth or will this technology suffer stagnation and an eventual decline? We will try to answer this question by reviewing the major applications for electroless plating, and probing how these uses may evolve in the near future.

There are several ways to define electroless plating. Using the broadest definition, electroless plating is the technology of depositing metals from solutions without the use of an external source of electric current. The electrons for the reduction are provided internally, either by a chemical redox reaction (as in the autocatalytic processes), or by an exchange reaction with the substrate, as in immersion plating.

Advantages of Electroless Plating

The advantages of electroless plating are well known, especially when compared with electroplating—uniformity of coverage (even in recessed areas), the possibility of metallizing non-conductors, and the ability to plate selectively differentiates electroless plating from electroplating. Electroless processes are used mainly for functional coatings of metals and non-conductors in major industries, such as in the fabrication of electronic circuits and interconnections, magnetic memory disks and electromagnetic interference shielding. Electroless technologies yield alloy deposits with unique mechanical characteristics for wear and corrosion protection in automotive and aerospace applications, as well as for the protection of equipment used in chemical manufacturing, and in oil and gas production. An extended review of electroless processes can be found in *Electroless Plating: Fundamentals and Applications*.[1]

The two most important industrial electroless processes are copper and nickel plating. These processes are defined as "autocatalytic," because deposition occurs only in the presence of a catalyst; the copper or nickel surfaces are catalytic and allow the formation of relatively thick deposits. Industrial electroless processes for nickel use either a hypophosphite ion as the reducer, or aminoboranes or borohydride. Both processes deposit alloys of nickel, containing either phosphorus (1-12 wt percent P) or boron (0.5-5 wt percent B).

Copper is mainly deposited from plating solutions using

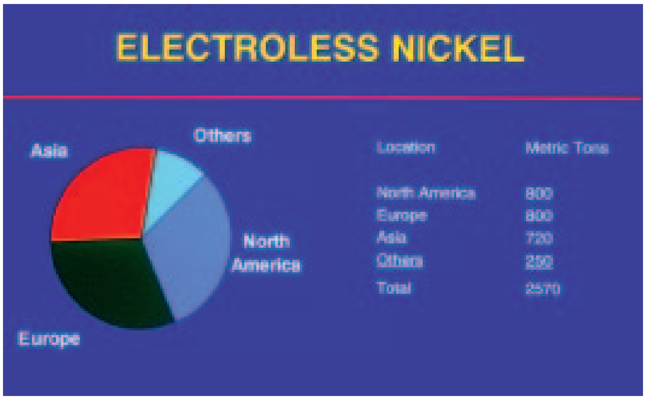


Fig. 1—Metric tons of nickel deposited by electroless process, 1993.

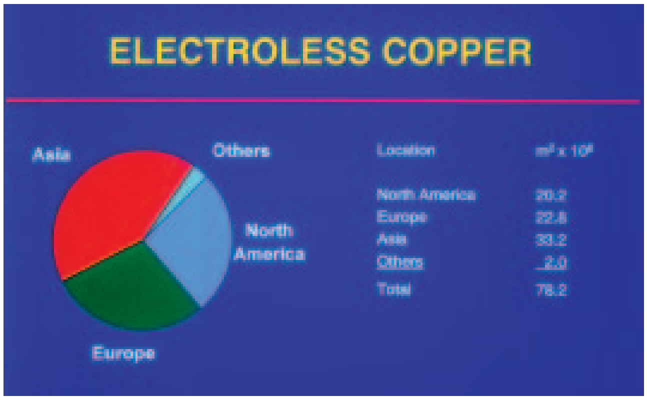


Fig. 2—Area metallized by electroless copper deposition, 1993.

formaldehyde as a reducer. Gold is deposited by immersion, but autocatalytic processes are of increasing interest. Other metals, such as palladium, tin, and cobalt are deposited for special applications, primarily in electronics fabrication.

An estimate of the electroless nickel and copper markets, based on 1993 statistics, can be observed in Figs. 1 and 2. Nickel is reported as tons deposited, while copper is given as area metallized. The reason for this method of reporting is based on the different modes of application. Electroless nickel is used mostly for relatively thick deposits (5 _m or more) in its most important functions as a wear-resistant coating and in memory disk fabrication. Electroless copper is mostly used for metallizing printed wiring boards, and its value is related to the surface area metallized. It is very difficult to establish the final value of the products fabricated via electroless plating, but most of these articles (such as printed wiring boards, hard disk drives, etc.) have a very high value added.

Aging Leads to the Search for Alternatives

While the electroless plating processes currently in use can be considered proven and reliable, alternative technologies have challenged their position in the market place. The main incentive for the search for alternatives derives from a common characteristic of plating solutions—aging (i.e., losing their performance properties with time). This is caused by solution contamination from the by-products of the redox reactions, ligands from the metal salts used for replenishment, and contaminants carried in by the parts processed that accumulate in the bath. Figure 3 shows this self-contamination process. It is based on memory disk processing, one of the most important commercial uses for electroless plating.

Aging limits the useful life of the bath. This creates problems, both economic and social. There are issues created by the need to dispose of the spent solutions properly. From the performance standpoint, the aging of the plating solutions affects deposit properties. There is a need to monitor and continually adjust the composition of the bath to preserve the quality of the deposits. Alternative technologies that are more robust, as well as environmentally friendlier, have challenged electroless plating in many of its present applications. These changes can be observed mainly in electronic manufacturing, such as printed wiring board fabrication, where the "direct plating process" has replaced electroless copper on many production lines.

Electroless Nickel

Electroless nickel provides wear and corrosion protection for a large variety of process equipment used in oil, gas and mineral production. Other applications include chemical, plastic and food processing equipment. The automotive industry also has the potential of increasing the use of electroless nickel for wear and corrosion protection. Many automotive parts are currently plated with electroless nickel for wear properties. A slip yoke (part of the front end) and a differential assembly, using an electroless nickel-plated central pin, (see Fig. 4) are in full production in the U.S. Electroless nickel is used to extend the life of fuel lines, brake and engine parts, transmission components, and in automotive electronics. The advantages of electroless nickel in protecting fuel lines against the corrosion of alternative fuels is well documented.[2] While the basic applications are well established, new specific uses are constantly being found, and new types

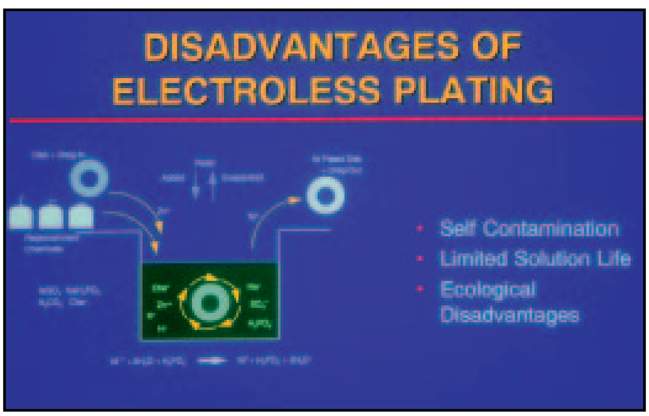


Fig. 3—Disadvantages of electroless plating.

Fig. 4—Slip yoke using an electroless nickel-plated central pin.

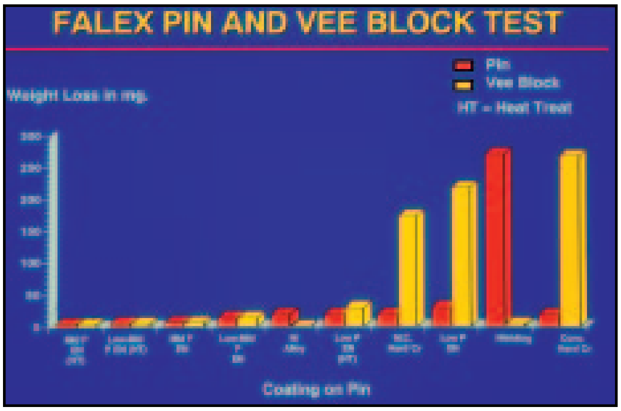


Fig. 5—Wear comparisons of electroless nickel finishes.

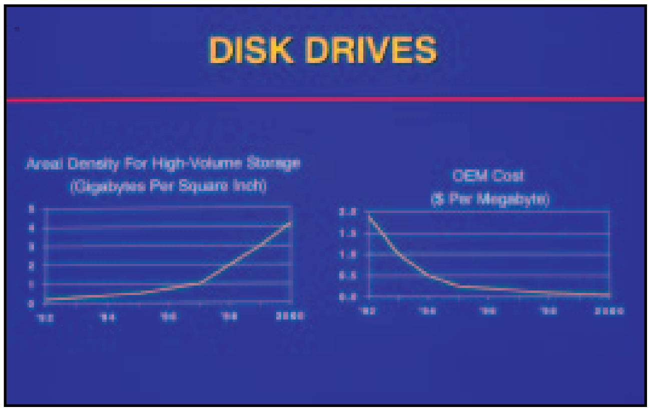


Fig. 6—Recording density vs. OEM cost projected over eight years.

of electroless nickel coatings are being developed.

Electroless nickel deposits, in general, have very good wear properties, especially under lubricated conditions, as shown in Fig. 5, which reports the results of Falex tests of various finishes. These results were obtained according to ASTM D2714-68 and show how electroless nickel coatings, as a group, can outperform alternative finishes.

There is renewed interest in coatings with exceptional hardness, wear and impact properties for automotive and other mechanical applications.[3] High-performance coatings include alloys of cobalt and tungsten, composites with fluoropolymers and EN deposits with as-plated hardness on the order of 800 Vickers. These coatings have potential for replacing hard chromium in many applications.

Largest Use of Electroless Nickel: Fabrication of Al Memory Disks

The largest use of electroless nickel, both in volume and value, is in fabrication of aluminum memory disks, where it has the very important function of protecting the aluminum substrate and providing a non-magnetic polishable base for the thin film magnetic medium. During recent years, several alternative recording technologies and alternative substrates to replace the aluminum disks were proposed. Still, the position of the electroless nickel-plated aluminum disk as the most cost efficient recording technology to be used in memory storage appears to be secure today and in the immediate future. An estimate of the annual growth of the market for aluminum memory disks is

- 1996 288 million disks
- 1997 354 million disks
- 1998 435 million disks

This preeminent position of aluminum hard disks was gained by means of continual improvements in recording technology, increased product quality and cost reduction. While hard disk drives have been around for many years, recording densities have increased consistently. Improvements in head technology allow for increases in recording densities and consequent reductions in device costs (see Fig. 6). Higher recording densities have created the need for continual quality improvements in the electroless nickel process, both in plating solution formulations and pre-treatment procedures.

Plating defects are a significant cause of rejects. These defects are of two types—pores and nodules. Many of these problems are caused by the mechanism of electroless nickel initiation and growth; pores are caused by lack of initiation (Fig. 7), while nodules can be formed by local galvanic acceleration. High-density recording will require improved flatness, reduced waviness, and the elimination of nodules by improved aluminum surface preparation techniques.

Another area for improvement is related to the magnetization of the disks during sputtering of the thin film medium. While nickel-phosphorus with a content in excess of 10 wt percent P is non-magnetic as deposited, it will become magnetic when heated over 300 °C.[4] As higher coercivities are required for higher recording density, magnetization is becoming an important question, especially as disks become thinner and therefore absorb less heat during sputtering. Modified bath formulations can delay the magnetization process,[5] but continual evolutionary improvements will retain electroless nickel as the preferred coating for aluminum memory disks.

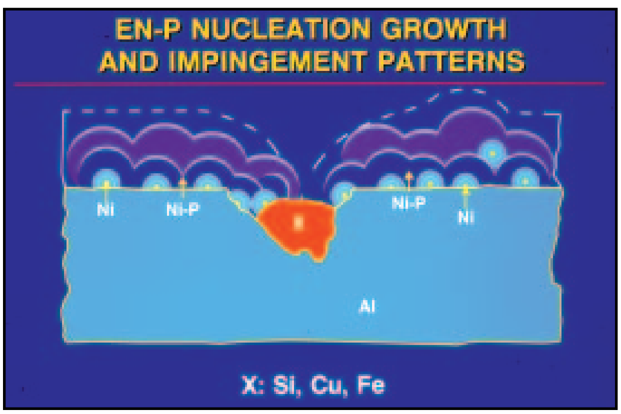


Fig. 7—Pore formation.

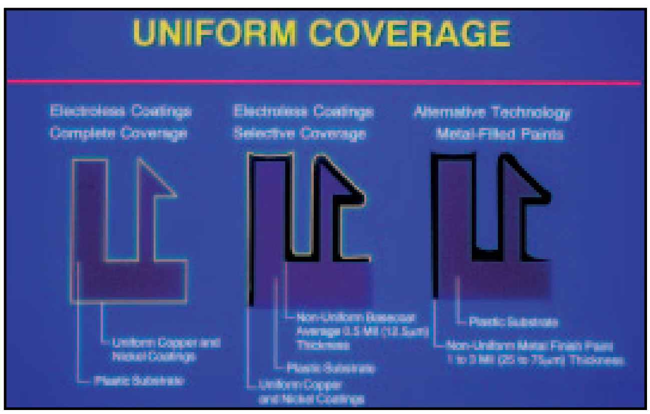


Fig. 8—Coverage for various modes of EMI shielding.

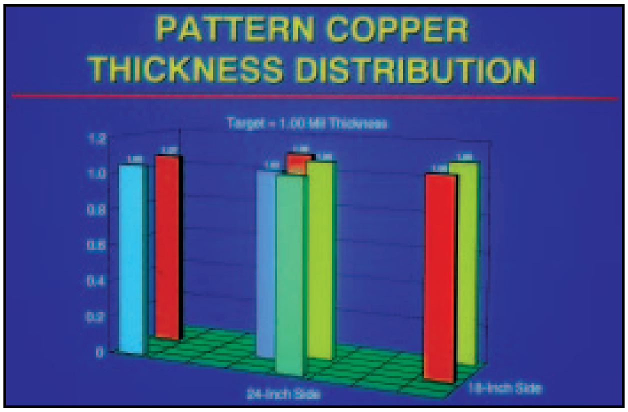


Fig. 9—Thickness variations of electroplated copper resulting from variations in current density.

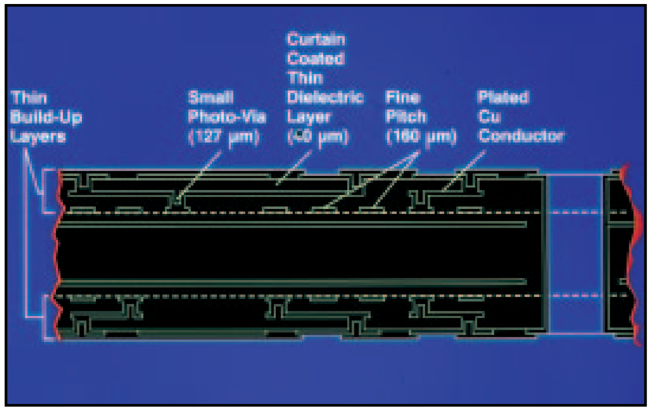


Fig. 10—Device fabricated by surface laminar process.

Electroless Copper/Electroless Nickel For EMI Shielding

A relatively new field that combines electroless copper and nickel plating is the shielding of plastic enclosures from electromagnetic interference (EMI). Electroless copper, followed by electroless nickel, is an established process for metallizing plastic enclosures to protect computers and telecommunications devices. The copper provides the shielding and the nickel protects the copper surface. There are two approaches for electroless shielding, using single-sided or double-sided metallization. Double-sided shielding uses the standard plating-on-plastic techniques, while for single-sided shielding, a catalytic basecoat is first applied (Fig. 8). Although double-sided shielding is electrically more effective, single-sided shielding has the advantage of allowing the use of colored molded enclosures that don't require a final finish with paint. Most electroless shielding is single-sided.

There are numerous alternative approaches to shielding that don't require wet processing.[6] The competition to plated shielding comes mostly from conductive metal-filled paints that are applied to the inside of plastic enclosures. Painted shielding has the advantage of requiring fewer processing steps than electroless plating and avoids the output of liquid waste as well. Still, because uniformity of the conductive layer is a major consideration for effective shielding, electroless plating can provide better attenuation and higher reliability than painted shielding.[7] For reasons similar to the case of printed circuits, electroless plating will be focused on the high-performance applications.

Electroless Copper & the PWB Industry

Electroless copper plating has been intimately connected with the printed wiring board (PWB) industry. This application represents an important economic value. This market is not growing, and may be slowly declining as a result of alternative metallization processes.

There are two main approaches to PWB fabrication. The subtractive process uses copper-clad laminates that are drilled, etched and then metallized, first with electroless copper, then by electroplated copper. The additive process deposits a full thickness of copper by electroless plating. Most printed wiring boards produced today use the subtractive method.

During the last five years, new processes have been introduced to replace the electroless plating step, using adsorbed conductive particles or conductive polymers, followed by direct electroplating of copper. These processes are commonly known in the industry as "direct metallization" processes and are quite different in their approach of forming a conductive layer on the surface of the laminate. The direct metallization systems that use conductive particles adsorb either particles of carbon or graphite, or use colloidal metals, such as palladium. The processes based on conductive polymers apply either pyrrol or thiophene compounds to the surface, which subsequently is polymerized to form a conductive layer.

Today, all three types of "direct metallization" processes are successfully used for wiring board fabrication and a comparative review of the different systems can be found in the literature.[8] Comparing these systems with electroless copper metallization, a common advantage can be found in the reduced amount of liquid waste generated, the absence of environmentally harmful chemicals (such as formaldehyde), and the potential for adapting the systems to the conveyorized handling of the circuit boards ("horizontal processing"). Electroless plating is a relatively slow operation that does not lend itself to conveyor-based equipment. Horizontal processing allows for important productivity gains over conventional vertical processing in tanks.

In view of these changes in technology, the future of electroless copper plating in printed wiring board fabrication can be questioned. Based on present trends, it is possible to predict that most of the standard commercial-type boards will be manufactured using a "direct metallization" process. Still, there are several types of circuits that will require continued use of electroless copper. Subtractive processes based on electroplated copper are inherently non-uniform because of current density variations, as can be seen in Fig. 9. Additive processing, using full thickness of electroless copper, yields

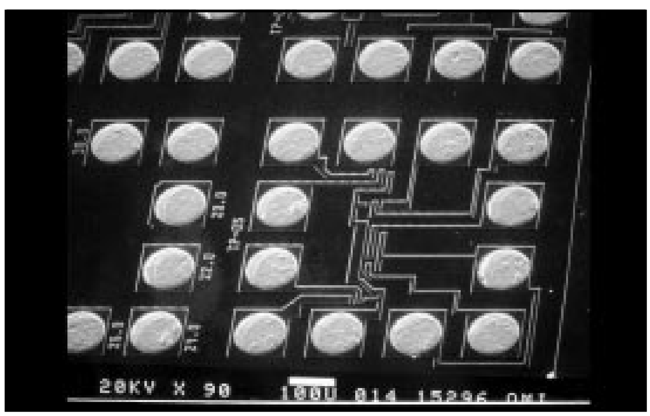


Fig. 11—Electroless nickel bumps coated with immersion gold.

uniform and planar circuits. Planarity is an important factor for higher yields in assembling the components on the circuit boards, while uniformity in the circuits adds value to the electrical properties by reducing impedance variations. For high-technology boards with fine line/space requirements, a higher number of multilayers, and blind vias, additive techniques are an attractive option. At present, several large board manufacturing facilities in Japan are using additive technologies to produce their boards.[9]

New technologies that are being used for high-density board production are the sequential techniques that build the boards up, using alternating layers of metallization and dielectrics. One of these sequential processes is the Surface Laminar Circuit, developed by IBM in Japan.[10,11] This technology uses photo via holes instead of drilled holes for connection, and photo-imageable resists as dielectric layers, as shown in Fig. 10. This new technique appears to be heading toward a broad range of applications, especially for direct chip attachment. Given the fine conductor layers and small holes generated in this process, the use of electroless copper is required for initial metallization. At this point it is safe to conclude that, for the manufacture of high-technology circuits, electroless plating will remain as the process of choice, compensating to a degree for the loss of markets caused by "direct metallization."

Electroless nickel, followed by gold, is another electroless process increasingly used in PWB fabrication. Especially for advanced assembly technologies (chip-on-board), it replaces tin-lead solder with quality and environmental advantages.

A potentially promising area for electroless copper plating is fabrication of semiconductors on silicon and gallium arsenide wafers. Current fabrication of semiconductors is based on aluminum connections deposited by vacuum processing. Copper metallization replacing aluminum is being actively investigated and both electroplating and electroless plating have been proposed. Semiconductor circuitry formed by electroless deposition is an interesting alternative, given the uniformity and planarity demands in wafer fabrication.[12] In addition, interconnections to the outside world for packaged semiconductors could offer an important use for electroless nickel and gold. Electroless nickel "bumps" coated with immersion gold can be formed on aluminum circuits replacing the tin-lead solder bumps used in the "flip-chip" packaging of semiconductors[13] (Fig. 11).

We can expect that additional applications for electroless plating will be found in the near future for electronic manufacturing. To make these processes successful, better electroless technologies will be needed, improving the selectivity and consistency of the deposits, as well as developing the automated processing equipment needed for wafer plating. The main challenge for the new applications will be in meeting the quality requirements of the deposits, as well as in assuring consistency of the processes. The environmental questions that the spent electroless solutions cause are also an important factor that the industry must consider when competing with alternative processes.

The Triangle of Academia, Industry & Suppliers Is Foundation for Bright Future

The future of electroless plating looks bright and rewarding. We see that new technologies are being developed for high performance needs, using alloys, composites and special "hard" electroless nickel coatings. Also, important advances in our technology will occur to satisfy the new requirements of the electronic industry. These advances will come from the triangle of academia, industry and suppliers. These changes will raise the currently used electroless technologies to new levels of quality and performance, and we may state with certainty that what has been done in the past is only the prologue to future growth.

References

1. *Electroless Plating*, G.O. Mallory and J. Hajdu, Eds., AESF, Orlando, FL, 1990.
2. L. Wing and G. Evans, *Proc. SAE International Congress* (March 1993).
3. A. Vaskelis, *Galvanotechnik*, **87**, 412 (1996).
4. J. Hajdu et al., *Proc. Electrochem. Soc.*, **PV 90-8**, 685 (1990).
5. G. Kline et al., *Proc. Electrochem. Soc.*, **PV 93-26**, 224 (1993).
6. B.G. Mottahed and S. Manoochehri, *Polym. Plast. Technol. Engng.*, **34**(3), 271 (1995).
7. W. Immel and J. Hajdu, *Metalloberfläche*, **47**(4), 180 (1993).
8. L. Flögel, *Galvanotechnik*, **86**, 657 (1995).
9. H. Akehoshi et al., *IEEE Trans. on Components, Packaging and Mfg. Technol., Part A*, **18**(1), 127 (March 1995).
10. Y. Tsukada and S. Tsuchida, *SMI Proceedings* (Sept. 1992).
11. T. Murakami, U.S. patent 5,092,032 (1992).
12. C. Mak, *MRS Bulletin*, 55 (Aug. 1994).
13. H. Homma et al., *J. Electrochem Soc.*, **141**(7), 1791 (1994).

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Dr. Juan B. Hajdu was the recipient of the 1995 Scientific Achievement Award. For more than 30 years, he has been affiliated with Enthone-OMI Inc., 350 Frontage Rd., West Haven, CT 06516. He obtained his PhD in 1956 at the University of Buenos Aires, Argentina, and is inventor or co-inventor on some 20 U.S. and international patents in the fields of electroless plating, PCB manufacturing, plating on plastics, RFI shielding, and electroplating. He is co-editor of Electroless Plating: Fundamentals and Applications, published by AESF in 1990. For more information on Dr. Hajdu and the Scientific Achievement Award, see p. 15.