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Reminiscences of Early Electroless Plating

by
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Editor's Note: The development of autocatalytic deposition was one of the most important developments in the history of surface finishing. Here, the "Father of Electroless Plating" recalls why and how it came about.

These reminiscences of electroless plating go back about 40 years. I am depending on my memory for these details, as the records that I kept on the subject were discarded when I retired from the National Bureau of Standards (NBS) about 13 years ago. Therefore, these reminiscences may not be entirely correct.

Electroless plating was a spinoff of the war effort. At the risk of boring the reader, I shall recount the events that led to the development of the process. During World War II the NBS cooperated with the Geophysical Institute, a part of the Smithsonian Institution, on the improvement of firearms. It was located within walking distance of the campus of NBS, which at that time was also situated in Washington, DC, in the northwest portion.

The Geophysical Institute, which normally was engaged only in basic research, had a contract with the NDRC to improve the life of the 50-caliber machine-gun barrel. Under the condition of rapid fire, the barrel became red-hot and the lands of the rifling were simply flattened or washed out altogether, so that accuracy was greatly impaired. Obviously, a metal with better hot hardness than steel was required. Various alloys were tried, among them a commercial alloy, "Stellite," which contains cobalt, chromium and tungsten. It performed better than steel.

To simplify the testing of the machine gun, rifled liners were used. These were tubes about 12 inches long with an internal diameter of 0.5 inch and wall thickness of about 0.25 inch. The liner, which could be formed from various kinds of alloys, was inserted into the breech end of the gun and the latter fired until failure occurred.

At this time, Grace E. Riddell and I were investigating the electrodeposition of nickel-tungsten and cobalt-tungsten alloys, and it was logical for us to apply these coatings to the liners. We attempted to electrodeposit a coating on the interior of the liner, using an ammoniacal citrate nickel-tungsten plating bath with an insoluble anode. The deposit always was highly stressed and cracked, and this was attributed to the oxidation of the organic components of the bath, as was evident both from the coloration of the bath and the peculiar odors emanating therefrom.

To prevent oxidation at the anode, Grace and I introduced various reducing agents to the bath, and these were generally ineffective. One reducing agent that we tried was sodium hypophosphite. The results of this experiment were very confusing. Although there had been considerable gassing during the electrolysis, the cathode current efficiency was about 130 percent. Furthermore, although an inside anode only was employed, the outside of the liner was also plated. It took a little while to understand that chemical deposition had occurred along with normal electrodeposition. Thus, autocatalytic plating was born.

Patent problems

Two papers on the process were published about a year later in the *Journal of the Research of the National Bureau of Standards* (Vol. 37, July 1946, and Vol. 39, Nov. 1947) and two patents were granted in 1950 - three years after the date of our applications (U.S. 2,532,283 and 2,532,284).

The patenting of the electroless plating process proved to be difficult, because it turned out that there was prior knowledge - going back about 30 years - to the effect that sodium hypophosphite would reduce nickel and cobalt salts to a black metallic powder. High concentrations of hypophosphite were used generally in strongly alkaline solutions. The powders were advocated for reducing organic compounds. We learned of all this in our subsequent literature search.

The patent examiner claimed that since the same compounds were used in the powder process and in our plating process, the latter had no novelty. I argued that a spontaneous chemical reaction that produced a black powder was not the same as a controlled autocatalytic process that produced a smooth, coherent metal coating. We finally invited the examiner to witness a demonstration at our laboratory. Two one-liter beakers of solution were prepared, one according to the literature citation and the other for electroless nickel plating. Both beakers of solution were placed on the steam bath in the hood to heat up. There were several anxious minutes, during which nothing happened. Then we noticed that the competing solution began to darken slightly, and this sight was a great relief. A few minutes later the spontaneous decomposition set in and the competing solution foamed out of the beaker and all over the water bath in a dramatic display of activity. The electroless plating solution, by contrast, continued to be well behaved. It gassed slightly and produced a satisfactory nickel deposit on the steel strip that had been immersed in it. This was one time we did not mind leaving a mess in the hood. The patent examiner was impressed, and we had no further trouble in obtaining a patent, except that we had to translate the simple, clear language of our applications into some kind of archaic English.

We needed a name for the new process. Dr. William Blum, NBS section chief, coined the word "Electroless" to indicate that the process was similar to electroplating in that a metal coating was produced but that it was dissimilar because no electric current was involved.

The patents that Grace and I received were "public patents," which meant that anyone could use them without payment of a royalty. However, a user was legally required to obtain a license, which was given free. I don't think that anyone would have been prosecuted if he had failed to obtain a license. The licensing, however, was an advantage to us, as it indicated the degree of interest in the process.

For about a decade or more I kept track of the number of licenses that were issued and also of the numerous improvement patents that were based on our process. I was a little envious that others seemed to be obtaining patents with the greatest facility, contrasting with our hard-fought bout with the patent office. At the time that I ceased keeping these records, which was about two decades ago, over 100 licenses had been issued and over 200 publications, including technical papers and patents, had appeared.

An "Orphan" process

After the initial development of electroless plating, we continued research on the process in a somewhat subdued manner, as the process was some kind of an orphan; that is to say, it never had the formal status of an approved project. Normally at NBS, after a research project was approved it was given a definite allocation of money and a project number against which expenditures could be charged. Although this was not the case with electroless plating, it cannot be said that the research was carried on _sub rosa_, because Dr. Blum was well aware of all the activities in the Electroplating Section, but he was very lenient with respect to moderate digressions, as long as the approved projects were not neglected.

The support for projects at NBS came partly from direct allocations by the Congress and partly from funds transferred to NBS by other government agencies for specific projects. The Electroplating Section in particular received the largest part of its funding from various outside government agencies. During the war years, Dr. Blum was very successful in attracting financial support from the military agencies. Thus, it would seem that these military departments supported the early electroless plating developments without being aware of it.

So electroless plating remained an orphan and never received a direct government grant. In later years I did submit proposals for further research to a government agency, but they were not accepted. I admit that I was a trifle annoyed when a private organization obtained a contract from the government for research on some phase of electroless plating, whereas I had been unsuccessful. During the 1950s I had a guest worker, Dr. Clara H. de Minjer, who did further research on electroless plating. But in this case the funding came from the American Association of University Women, which sponsored her research.

Strangely enough, I had strong financial support from various government agencies for my academic research work, which had no obvious practical applications.

Commercial interests

In the early days of electroless plating, Dr. Blum thought that the process would have little commercial use. I was a trifle more optimistic but did not consider that its use would be widespread because of the cost of sodium hypophosphite. But we did have some faith in even limited utility of the process and approached the Oldbury Electrochemical Company with a view toward interesting it in the production of less-expensive sodium hypophosphite. At that time the compound cost about 72 cents per pound.

Also in those early days electroless plating was somewhat of a headache to me because the mail I received on the subject was far from flattering. Usually, someone would write that he had tried the process, and complained that he had problems. Apparently, it was my responsibility to write to him giving my analysis of the situation and a recommendation for solving his problem.

During the first decade after the initial development of electroless plating, several companies made use of the process. These were mentioned in a survey that I made ("Electroless Plating Comes of Age," *Metal Finishing*, Nov/Dec 1954). Of these companies, the American Transportation Company was most interested and did a considerable amount of research on the process. They obtained a number of patents and called their improved process "Kanigen," which stood for catalytic nickel generation. The company was interested in selling licenses for their patents, for which I had heard they charged $10,000. I do not know how many licenses they sold but I was told not many. In order to interest others in their patents, the company by innuendo implied that our original process was impracticable and that only the Kanigen process was satisfactory. We were somewhat nettled by this attitude but kept our quiet.

The American Transportation Company also set up a custom plating plant for electroless plating. For their own use, the company had an unusual application. The company supplied tank cars for shipping concentrated caustic solutions. To keep iron from contaminating the solution they conceived the idea of coating the inside of an entire tank car with electroless nickel. I understand that this was accomplished successfully but I have no information on the number of tank cars plated or how well they held up in service.

One result of General American Transportation's involvement in electroless plating was that the company became interested in having me join the organization to do further research on the process, and I was invited to Chicago to see their extensive facilities. However, in talking to their research supervisor, I learned that the research project the company had in mind was the development of an electroless plating process for chromium. I told the supervisor that I thought this was not possible. This unreasonable expectation was partly the reason I decided to stay with the NBS.

Surprised at developments

The publication of "Studies on Electroless Nickel Plating" by my guest worker, Dr. de Minjer, in 1957 (*Plating*, Vol. 44, p. 1297) marked the end of my active interest in electroless plating, although I continued to have a cursory interest in new developments. Dr. de Minjer, after her research was finished at NBS, returned to her former position as research worker in the Philips Research Laboratory in Eindhoven, Holland. She kept an active interest in electroless plating and applied it to some of the company's products. She has been retired from the company for a number of years.

Since Grace Riddell and I never had any commercial connections with electroless plating - we did not even receive the traditional dollar for a government patent - I am not the one who can discuss either the present or the future trends of the process. However, I can say that I have been surprised at the proliferation of new developments in a field that to me had seemed finished. There have been not only improvements in the operation and stability of the solutions, but also extensions of electroless processes to other reducing agents, and, most interesting of all, to other metals.

About the author

Dr. Abner Brenner was Chief of the Electrodeposition Section of the National Bureau of Standards (now the National Institute of Science and Technology). Dr. Brenner was born August 5, 1908, in Kansas City, Missouri. He studied at the universities of Missouri, Wisconsin and Maryland. He received a doctorate from the University of Maryland. In 1930, he joined the staff of the National Bureau of Standards, from which he retired in 1971.

After leaving government service, Dr. Brenner set up a one-man laboratory where he continued his research on the electrochemistry of nonaqueous systems. Among other projects, he developed a protective coating for acrylic paintings. He was the author of more than 100 papers and the recipient of more than 30 patents, the last of which he received at the age of 90. His two-volume *Electrodeposition of Alloys* is, in itself, a major contribution to the field. Published in 1963, it is still frequently referred to by electrochemists.

Dr. Brenner was the recipient of no fewer than 15 awards from the leading scientific societies in his field: the Electrochemical Society, the Institute of Metal Finishing and the AESF. In honor of his many contributions, on August 5, 1998, in honor of Abner Brenner's 90th birthday, an endowment fund was set up to establish the former "best papers published in Plating & Surface Finishing" as the "Abner Brenner Best Paper Awards." The Brenner Awards were first presented at AESF SUR/FIN 1999.

In 1961, Dr. Brenner was the fourth recipient of the AESF's highest honor, the William Blum Scientific Achievement Award. He was also the first recipient (1974) of the Electrochemical Society's Award in Electrochemical Engineering and Technology.

Although many of his colleagues thought of him as an inventor and discoverer, he thought of himself as a "basic scientist; more specifically, as an explorative researcher - a person interested in investigating new phenomena." He was not bound by accepted doctrine or theory but kept his mind open to the careful observation of his own creative experiments.

Dr. Brenner's influence was much more than intellectual in nature. His influence extended into the industrial and commercial world as others capitalized on his discoveries. Following his invention of a coating thickness gauge, many of these gauges came into extensive industrial use. Two additional well-known and useful instruments invented by Brenner were the spiral contractometer and the eddy-current thickness gauge. Of greater significance was his discovery of electroless nickel. This process was quickly taken over by electroplaters, and there is now an entire industry dependent upon it.

Respected not only by the members of the electrochemistry community, Dr. Brenner was especially respected by his colleagues. Working with him was not only fruitful, but also a great pleasure. He was at all times helpful and thoughtful-leading, not directing, his colleagues to think through the various problems of the particular research being explored. This was done with wisdom and good humor. His generosity in helping his associates was unbounded.

After a long and fruitful life, Dr. Brenner died on August 13, 1999, just one week after his 91st birthday.

Editor's Note: This biography was part of a tribute published in *Plating & Surface Finishing* on the occasion of Dr. Brenner's passing. It was based on a memoriam prepared by Dr. Fielding Ogburn for *The Electrochemical Society Interface*.