# Shop Talk

## Finishers' Think Tank Revisited—VII

By John Laurilliard, CEF Compiled by Dr. James H. Lindsay, AESF Fellow

### Mold in copper bath

**Q:** After several months of inactivity, we recently reactivated our bright acid copper plating bath, and the deposits were brittle and striated. Before plating, we removed what appeared to be mold from the surface of the bath. Is there a relationship between the mold and the poor results? How can we contend with the effects of the mold if indeed it is the cause?

A: It is not uncommon for mold to form on aqueous solutions that contain organic compounds. The mold is the result of bacteria feeding and breeding on the brighteners and other organic compounds. The effects of the mold and other organic materials can be eliminated either by a high-temperature treatment with potassium permanganate at 120 g/100 L (1 lb./ 100 gal), or preferably by a batch carbon treatment using 240 g/ 100 L (2 lb./ 100 gal). Other solutions that commonly suffer from bacterial activity are acid gold baths formulated with weak organic acids and organic dye baths for anodized finishes.

### Internal nickel plating

**Q:** We have a small, low-volume, specialty captive shop. Much of our work involves salvaging mismachined parts by heavily plating holes 6 to 50 mm (<sup>1</sup>/<sub>4</sub> to 2 in.) in diameter to bring them into the proper dimensional range. Presently, we take the old nickel anodes from our plating tank and use them as internal anodes because nobody can supply us with anodes the size and length we need. What other materials can we use for internal nickel plating?

A: It is a common practice to use old, dissolved, swordshaped remnants of nickel anodes for internal plating. However, these remnants are a poor choice because they vary greatly in size, shape and length. This geometric non-uniformity can cause serious variations in plating distribution. If you want to stick with nickel, you can use high-purity nickel rods such as the K-nickel type, which probably can be supplied in the diameter you need.

For the holes larger in diameter, it may be worth your while to fabricate a small-diameter titanium anode basket just large enough to accept a single column of SD nickel buttons. Platinized titanium anodes also can be used, but they have a limited lifespan. Pure platinum wire can be employed for a very small inside diameter (ID). It has long life, but is very expensive.

Graphite rods work very well, cheap and readily available, but are also fragile. The nickel and graphite anodes must be bagged because of loose particles that form during use. The anode bags should be cleaned and the loose particles removed from the anode frequently enough to prevent an accumulation that may affect anode polarization and, ultimately, distribution of plating thickness. Precise centering of the internal anode is most important for uniform thickness.

When plating heavy deposits, the ammeter in the anode circuit should be checked often and adjusted to maintain the current density. Several adjustments may be needed before a steady current can be maintained. If the current steadily drops off, even after several adjustments, it indicates severe anode polarization from too high an anode current density. This sometimes can be minimized by slowly pumping plating solution either into the ID being plated or directly into the anode bag. This practice will maintain the chemistry of the plating solution in the immediate vicinity of the anode surface.

When using inert anodes such as the graphite or platinum variety, solution replenishment is vital to maintain the nickel concentration and prevent a rapid drop in pH.

In summary, a great deal of attention must be paid to details when using internal anodes, compared with tank anodes, which generally receive little or no attention.

### Laminated deposits

Q: Parts that I had nickel plated for a customer have been rejected for a thickness under the minimum. The parts were returned to us, stripped, replated with a sufficient thickness and sent back to the customer. Some parts were again rejected, but this time for blistering and peeling. The latter was due to a laminated deposit. My customer has threatened to remove my company from his qualified vendors list because he claims that I added nickel plate to the rejected parts rather than stripping them down to the basis metal and starting from scratch. I told them that the parts were stripped and that, during the replate cycle, some parts may have experienced broken electrical contact, in which case the nickel would have become passive and a poorly adherent laminate would have formed when electrical contact was remade. My question is: Is there some way to distinguish between a laminated nickel deposit that results from interrupted current as opposed to one that results from adding nickel on top of a previously plated nickel deposit?

**A:** There are two techniques that may provide differentiation between the two types of laminates. However, neither is simple nor easy and some testing may be required to assure the accuracy of the technique.

The first involves microscopic examination of a mounted metallographic specimen. A small section,  $13 \times 13 \text{ mm}$  ( $\frac{1}{2} \times \frac{1}{2}$  in.) is cut out of the part, preferably in a high-current-density area, where the nickel deposit will be the thickest. This small section is then overplated with

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25 to 50  $\mu$ m (0.001 to 0.002 in.) of copper to preserve the edges and the flatness of the specimen. After mounting in Bakelite<sup>®</sup>, the section is rough ground on a wet belt sander using 80 to 120-grit silicon carbide. The specimen is then sanded using progressively finer grits of 240, 320, 400 and 600 silicon carbide abrasive paper. Afterwards, the specimen is given a rough polish with diamond abrasive (2 to 5  $\mu$ m) and then a final polish with 9.1  $\mu$ m  $\gamma$ -alumina. When all grinding and polishing is finished, the specimen is very lightly etched by swabbing with a 1:1 mixture of glacial acetic acid and nitric acid.

The microstructure of the laminated nickel is examined at 500X. If the laminate is due to broken electrical contact, the microstructure should be the same for both layers. If the laminate is due to two separate deposits plated at different times and probably under different conditions of bath composition, temperature and current density, there should be a difference in the microstructure.

In addition to metallurgical examination of the laminate structures, the nickel layers can be chemically analyzed by an electron microprobe technique. If the laminate is due to faulty electrical contact, the metallic impurities should be comparable in both layers; but if it is due to two separate layers plated at different times, the metallic contaminants plated out in each layer probably will be of different concentration because the chemistry of the plating solution and the impurities will vary with time.

The above suggestions are not within the capability of the average job shop and should be contracted to a service lab, instead. Moreover, a laboratory should be selected that has considerable metallographic experience, especially with electrodeposited coatings. A more careful approach is required when polishing and etching a plated coating than is involved when examining a steel structure, for instance.

In addition to inspecting the rejected parts in question, you should prepare two standard structures: one a laminated deposit created by making and breaking electrical contact, and the second made by plating two separate deposits several days apart. These standards will give you the confidence that the two types of laminates can be distinguished.

#### "Ti-Cad" plating

*This final topic clearly relates to a different time when cadmium, chromates and cyanides were in common use and well-respected – Tech. Ed.* 

**Q:** I am an active member of the AES and would appreciate any information yon have on plating cadmium-titanium alloy.

**A:** I am forwarding several articles on cadmium-titanium-alloy plating, a unique process used mainly by the aircraft industry to minimize hydrogen embrittlement for cadmium plating of high-strength steels.

"Ti-Cad" plating, as it is commonly referred to in the industry, basically calls for a standard cadmium cyanide solution with the organic brighteners left out and a sparsely soluble titanium compound plus hydrogen peroxide added instead. When properly operated, the deposit should contain from 0.1 to 0.5% titanium.

The bath composition is:

- Cadmium metal, 21 to 24 g/L (2.8 to 3.2 oz/gal)
- Total sodium cyanide, 105 to 128 g/L (14 to 17 oz/gal)
- Sodium hydroxide, 11 to 15 g/L (1.5 to 2.0 oz/gal)
- Titanium, 40 to 80 ppm
- Sodium carbonate, 38 g/L (5 oz/gal) maximum
- NaCN to cadmium ratio, 4:1
- Maximum iron impurity, 100 ppm and
- Temperature, 16 to 27°C (60 to 80°F).

The sequence of process steps is as follows:

- 1. Degrease.
- 2. Dry blast using 80 to 180-grit aluminum or silicon oxide.
- 3. Rinse in cold water for a maximum of 1 min.
- Cadmium plate in the above solution. Make electrical contact prior to inmersing parts in the bath. Use an initial strike at 4.3 to

5.4 A/dm<sup>2</sup> (40 to 50 A/ft<sup>2</sup>) for 15 sec, then reduce the current to 1.6 to 3.2 A/dm<sup>2</sup> (15 to 30 A/ft<sup>2</sup>) until the required thickness has been deposited.

- 5. Rinse in hot water and air dry.
- 6. Within 4 hr after plating, bake parts at  $191 \pm 14^{\circ}C (375 \pm 25^{\circ}F)$  for a minimum of 12 hr.
- 7. For parts requiring a type-II chromate conversion coating, immerse for 15 to 30 sec in the chromate solution. Rinse thoroughly in cold water, then in warm water, and dry.

To achieve the benefit of low hydrogen embrittlement, the process must be operated and controlled in strict accordance with recommended procedure and practice. This is not a process for a shop not accustomed to close and frequent solution controls and analyses.

The solution must be made up in a new tank or one that has been purged of previously absorbed impurities or potential contaminants. The tank, filter and all other surfaces that come in contact with the solution must be of 300-series stainless steel, titanium, PVC, polyethylene or polypropylene. The solution must be filtered continuously, and the filter must be of the type that permits the introduction of the titanium compound onto the filter pads, where it can slowly dissolve in the presence of hydrogen peroxide. The bath also may be continuously carbon-filtered to remove any organic contaminants.

Filter aid must be of the diatomaceous-earth type. Cellulosetype filter aids must not be used because the high caustic content of the solution dissolves some of the organic cellulose components, which act as a brightener and grain refiner, making the bath ineffective in its ability to prevent hydrogen embrittlement.

Solid cadmium anodes are preferred. Cadmium ball anodes can be used, but only with stainless steel or titanium anode baskets. Every effort must be made to prevent metallic impurities, especially iron, from accumulating in the bath. Steel parts that fall off of racks must be removed from the bottom of the tank. Deionized or distilled water should be used for makeup, replenishment and to replace evaporative losses.

The covering power of the solution generally is very poor; thus, the requirement of the initial strike. The strike time and current density must not be exceeded, or, again, the property of low hydrogen embrittlement will be impaired. Covering power is improved if parts are first dry blasted with the coarser 80-grit abrasive instead of the 180-grit.

A properly plated deposit will be smooth, dull gray or frosty white. A bright or shiny deposit indicates a malfunctioning that may produce embrittled parts. (For additional details, consult AMS 2419 and MIL-STD-1500.)

The cadmium-titanium cycle originally was developed in Japan in the early 1960s as a bright-deposit process. Superior corrosion resistance was its main claim, and the low-embrittlement properties were not discovered until the process was offered for trial to a large U.S. manufacturer of aircraft. A zinc-titanium process also was developed at the same time as the cadmium system, but has not been commercialized.

By not using titanium as an alloying agent more frequently, the plating industry is missing a great opportunity to improve the corrosion resistance of cadmium and zinc, two of the most common and useful finishing metals. If the standard cadmium plating process could be made more corrosion resistant, then less cadmium would corrode and enter the environment. Thinner cadmium deposits might also suffice in place of the heavy deposits used today. These aspects deserve investigation.

Tech Editor's Note: The edited preceding article is based on material compiled and contributed by John Laurilliard, CEF, as part of the "Finishers' Think Tank" series, which began its long run in this journal 25 years ago. It dealt with everyday production plating problems, many of which are still encountered in the opening years of the 21<sup>st</sup> century. As we have often said, much has changed ... but not that much. The reader may benefit both from the information here and the historical perspective as well. For many, it is fascinating to see the analysis required to troubleshoot problems that might be second nature today. In some cases here, words were altered for context.