Finishers' Think Tank Revisited—IV

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

Hull cell test

Q: From time to time I develop darkness in low-currentdensity areas during bright nickel plating. When I check the bath with a Hull cell, the panel looks perfect - no dullness at the low-current end and uniform brightness up to the high-current density end of the panel. I am running a standard 3A, 3-min panel. Why do I see the dark areas on my parts and not on the Hull cell panel?

A: One of your problems may be the length of time that you are running your Hull cell. A 3-min panel may not be long enough for the symptoms to manifest themselves. The Hull cell panel should plate for approximately the same length of time that it takes for the problem to develop in the plating tank. If the work is plated for 25 min, you should run your Hull cell for approximately the same length of time. Also, if you are using air agitation in your production tank, use air agitation in the Hull cell. In order for your Hull cell panel to give the most information, it must be plated under and experience the same set of conditions as your production parts.

Rinsing blind holes

Q: What recommendations do you have for drying small, gold-plated, finned tubing with deep blind holes? My problem is bleed-out, or weeping, from the blind hole. Final rinsing involves several cold rinses, a hot rinse and a final rinse in methyl alcohol to displace or dissolve the remaining water.

A: The standard method for rinsing parts with narrow blind holes is to use a rinse cycle, alternating back and forth between hot and cold water. This is effective if the holes are not too deep or narrow. Holes are very difficult to rinse if the diameter is so small that capillary action prevents the free drainage of water. The addition of a small amount of wetting agent to reduce surface tension is helpful. A practice that is more effective, but only for manual operations, is to use regular cold-water rinsing and then centrifuge in a spin drier without heat. Spin for a minute or so, shake the basket to reorient the parts and then spin again. Rinse the parts again in cold water, then hot and spin dry. You might consider the use of a Freon (solvent) drying system, which works on the displacement principle. The high density and low surface tension of Freon TF solvent and a hydrophobic surfactant enhance water separation. The solvent is used in the familiar two- or three-sump vapor degreaser and can effectively remove water from metal or plastic parts or assemblies. [Of course in 2005, there is a different take on Freon. – JHL}

Rough nickel plate

Q: I have a serious problem of roughness in my bright nickel plating bath. The nickel solution is a standard Watts formulation with air agitation and continuous filtration. The roughness isn't too bad on Monday but becomes progressively worse toward the end of the week. I've replaced the anode bags with close-weave double bags, but that doesn't help. Enclosed is a lamp base showing a typical case of roughness. Do you have any idea what can be causing it?

A: From the looks of the lamp base you have what is commonly referred to as "shelf roughness," the result of fine particulate matter settling on the upper horizontal surfaces of parts during plating. The identification and elimination of the source of these particles is the crux of the problem.

First, determine if the preplate cycle, the cleaning acid activation or the copper strike is contributing to the problem. One way to do this is to place several parts on a rack, leaving room to add pieces after each process step. Start the rack through the plating cycle. Add a part that has been cleaned manually or on another trouble-free line, after the cleaning step. After acid activation, add another part, again previously cleaned and activated elsewhere. After the copper strike, if used, add another part prepared as above but eliminate the copper plate on this part. Continue this scheme for any neutralizers, activators or predips in the plating cycle. If the source of roughness is in any of the preplate steps, all parts placed on the rack previous to that step will be rough. Those placed on after will not be rough.

Another technique to determine which step is causing the roughness consists of using a gloved finger to wipe a different part on the rack after each process step. If any of the preplate steps are causing roughness, evidence of the wiping will be seen after the nickel plate.

If you eliminate the preplate cycle as the cause, concentrate on the nickel tank. Double check and confirm that the nickel-plating step is the cause. Take a part, cleaned and activated in the lab or some other nonsuspect facility, and plate it in the nickel tank without using the preplate steps.

Based on an original article from the "Finishers' Think Tank" series [*Plating & Surface Finishing*, **67**, 12 (August 1980) and **67**, 16 (September 1980)]

If roughness occurs, the nickel is definitely the cause. With this verification there are several areas that must be investigated to zero in on the cause. Make sure you are not putting dirt into the nickel tank with the air blower. Rig up a clean plastic pipe directly from the blower or a take-off valve. Run it into a 55-gal drum of clean water and operate for several hours. Filter a 1-L sample of the aerated water and examine the filter paper under 30X magnification for evidence of particles.

Filter a sample of the nickel solution, wash away the nickel solution with a small quantity of distilled water and examine for particles. Also, filter a sample taken directly from the discharge hose of the filter. If particles are found, the filter should be inspected for ruptured diaphragms. If particles are found from any of the above filtering tests try to ascertain their nature. Are they magnetic? If so, they are either nickel or iron. Analyze to determine which they are. If they are nickel, look to the anodes. Even though new anode bags are being used, anodic particles could still be getting out. Keep the solution level a few inches below the top of the anode bag to prevent solution from sloshing in and out of the anode basket. Slowly remove an anode or anode basket, collect the drainage in a beaker, filter and examine for particles. Small nickel particles also can be generated by high-current-density burning on unoccupied rack contacts. Analyze the bath, including impurities such as aluminum, iron, calcium and magnesium.

A low or very high concentration of boric acid can cause roughness. High pH can cause iron hydroxide to precipitate out. A high concentration of copper can also cause roughness. Low chloride can cause irregular anode corrosion with resultant detached anode particles. Calcium, accumulated from additions of hard tap water to replace evaporation losses, can precipitate out as calcium sulfate. Calcium sulfate has an inverse solubility. As temperature increases, solubility decreases. This is a common cause of roughness, but it's often overlooked because of neglect in keeping track of impurity buildup in the nickel solution. Prevent buildup of this type of impurity by using distilled or deionized water to replace evaporation losses. If calcium sulfate is the problem, a portion can be removed by increasing the temperature of the solution to 77°C (170°F) and filtering. Fluoride also may be used to precipitate calcium, but should not be used if titanium anode baskets are employed.

Check whether the steel parts are magnetic. This could attract small particles of iron or nickel, but the roughness pattern would not be confined to the upper horizontal surfaces. Don't forget the air quality in the shop as a source of contamination leading to roughness. Is dirt settling out of the air from some nearby buffing or grinding operation, or maybe entering the shop through open windows from a neighboring plant?

When you think you've located the problem and decide on a course of action, consult with your vendor of bright nickel plating chemicals before proceeding, especially if it involves the bath chemistry or changing materials that come in contact with the plating solution.

Cadmium, Chromate and Rust

Q: Is it all right to use a rust-preventive oil on cadmium-plated and chromated parts? I am working with steel parts that are selectively plated in only one area. During the humid months of May to October, the unplated areas develop a light film of rust and the parts are rejected.

A: A rust-preventative oil similar to those that meet specification MIL-C-16173, "Corrosion Preventive Compound, Solvent Cutback, Cold-Application," Grade 3, should prevent rusting without damaging the chromate conversion film. However, one note of caution: The chromate film should be allowed to age 24 hr to dry and harden before the rust preventative is applied.

Buffing copper

Q: I expect to be copper-nlckel-chromium plating large quantities of hollow tubular-steel furniture fittings. To get the quality the customer requires, I must buff the copper. Because manual buffing is such an expensive operation, I want to do everything I can to reduce time and effort yet achieve a good-quality finish. Which cyanide copper bath formulation produces the most buffable deposit?

A. Let me first say that I know of no studies or data on the buffability of copper from different plating formulations. If you talk to manufacturers and suppliers of polishing and buffing supplies, they will say you must adapt your techniques and practices to match the material being worked on. This is understandable advice. It is a great credit to the buffing and polishing industry that they have developed over the years a variety of abrasive compounds and buffing wheels of various types, shapes, density and materials and techniques to deal with just about any material or shape imaginable.

When you talk to the plating suppliers for recommendations about copper buffability, they invariably suggest proprietary bright acid copper rather than cyanide copper. To anyone who has buffed both types of copper the choice is obvious.

The fact that your parts are steel and hollow necessitates a cyanide copper solution. To use acid copper on hollow steel parts would result in loosely adherent immersion copper deposits on the interior surfaces. There would be a rapid buildup of iron in the bath causing increased electrical resistance and lowered copper sulfate solubility. More serious would be the roughness caused by the dislodged immersion copper deposits from the interior surfaces of the parts.

Some platers use an immersion nickel process to coat interior surfaces and avoid these dislodged copper deposits. The bath consists of 60 g/L (8 oz/gal) of nickel chloride and 40 g/L (5.5 oz/gal) of boric acid at 70°C (160°F). If the recessed areas are not too deep, a nickel strike consisting of 120 g/L (16 oz/gal) of nickel chloride and 50 mL/L (6 oz/gal) of hydrochloric acid can be used. Another approach may be to use a plug, a stopper or some other stopoff technique to prevent contact of the acid copper with the interior surfaces.

For buffing, the acid copper deposit is much better than the cyanide copper and every effort should be made to overcome the immersion copper problem. Cyanide copper often is harder than the acid copper deposit and therefore is more difficult to buff. Cyanide copper also has a tendency to become rougher as deposit thickness increases, requiring a polishing operation before final buffing. Cyanide copper has poor microthrowing power and does not have the capability to level and fill in scratches, grooves or pores in the basis metal. Bright acid copper is outstanding in this respect. Surface roughness from polishing basis metal can be improved greatly with bright acid copper. Surface roughness can be reduced from 17 to 22 μ -in. to 2.0 to 3.5 μ -in. with a 13- μ m (0.0005-in.) deposit and down to 0.5 to 1.5 μ -in. with a 25- μ m (0.001-in.) deposit.

With the above cited advantages, it is easy to see that costs for polishing and buffing both the basis metal and the copper deposit may be greatly reduced and possibly eliminated. If you must use a cyanide copper deposit, then a bath formulation and operating conditions that produce the softest deposit should be tried.

Although no data on buffability are available, there is much information the effects of bath composition and operating conditions on physical and mechanical properties of copper plated from various solutions such as sulfate, fluoborate, pyrophosphate and cyanide. Much of this data can be found in AES Research Project

140-year-old Plating Shop in Providence Still Provides Valuable Finishing Services

A 140-year-old metal finishing job shop is a rarity in the U.S. R.E. Sturdy Company, Providence, RI, has a rich history in the plating industry, and the shop has remained in the same family for most of its history, according to Dorothy Perkins-McCauley, secretary of the company and a descendent of the early owners who built the business into a successful plating shop.

History

The original shop was established as the J.E. Sturdy Company in 1868 by Joseph E. Sturdy, said Perkins-McCauley. Sturdy was a pioneer in depositing precious metal using a porous earthen jar with zinc plates and a chemical solution to generate electricity. "The firm's name was changed to R.E. Sturdy Company in 1885 when Rolphe E. Sturdy succeeded his father as owner," Perkins-McCauley said.

The shop was run successfully by Rolphe Sturdy until he died in March of 1910. His wife, Sara Baxter Sturdy, became owner, but sold the shop for \$10 to Charles Hastings of Hehoboth, MA, in 1915.

Hastings changed the company name to the Charles B. Hastings Company, but died shortly after the acquisition. Following the death of Hastings, the shop was acquired by Frank Fairbrother, who sold it in 1916 to Levi J. Perkins and Richard S. Rosa for \$10, the same amount that Hastings had paid.

In December of 1916, Perkins and Rosa formed a partnership under the former name of R.E. Sturdy Company. "The partnership dissolved within a year," said Perkins-McCauley, "with Rosa dropping out, leaving Levi Perkins the sole proprietor for an investment of \$5."

Originally from Clinton, Iowa, Levi Perkins moved to Providence in 1904 to work for the R.E. Sturdy Company at 190 Eddy Street. In the 1920s, he moved the company to 67 Clifford Street.

In 1923, Levi Perkins served as president of the Providence-Attleboro Branch of the American Electroplaters Society.



Fourth generation Perkins family members still run R.E. Sturdy Company that was founded in 1858. From left: Thomas Perkins, treasurer; Dorothy Perkins-McCauley, secretary; Lloyd Perkins, president; and Robert Perkins, vice president.

During these early years, the majority of the work performed by the company was for jewelry.

When Levi Perkins died, his wife, Johanna, took over the business, with the help of William Perkins, their only child. Johanna ran the business until her death in 1940, when William Perkins became owner. Following World War II, two sons of William Perkins came to work for the company.

In 1951, R.E. Sturdy Company was incorporated and moved to 171 Pine Street, according to Perkins-McCauley. It was about this time that William Perkins retired and turned the business over to his two sons—William and Thomas. At that time, the company specialized in plating buckles, jewelry findings, and silverware.

William, the oldest brother, left the business in the early 1960s, leaving Thomas Perkins owner. In 1965, Thomas purchased a building at 271 Plain Street. During the next few years, his three sons—Lloyd, Robert and Tom, Jr.—came to work for the company.

Many of the hotels and restaurants in the area changed from using silverware to

stainless steel, which reduced the amount of business that the job shop was doing. To make up for the reduction, the company began to plate more military insignias (buckles, medals and buttons).

The three Perkins brothers saw a need to expand the business, so they bought a shop in Leominster, MA, called Electrochem from Harold Narcus. Electrochem was providing barrel plating on plastics. In 1982, the brothers moved Electrochem from Leominster to the Providence location.

In the next few years, barrel plating on plastics became the largest portion of the company's business. Because of that, and increasing compliance regulations, the business was forced to move to a larger building at 928 Eddy Street. In 1987–88, R.E. Sturdy Company operated from two locations. During this time, Dorothy, the daughter of Thomas Perkins, came to work for the company.

Even before he fully retired, Thomas Perkins turned ownership and control of the business over to his children, creating the fourth generation of Perkins to operate R.E. Sturdy Company. Today, the business is managed by Lloyd Perkins, president;

Shop Talk

Continued from page 7

Constituent	All-potassium	Proprietary bright
CuCN	40 g/L (5.4 oz/gal)	75 g/L (10 oz/gal)
KCN (free)	8.0 g/L (1.1 oz/gal)	22.5 g/L (3.0 oz/gal)
K,CO,	40 g/L (5.4 oz/gal)	
Rochelle salt	45 g/L (6.0 oz/gal)	
KOH		22.5 g/L (3.0 oz/gal)
Brightener		Selenium-type
Temperature	60°C (140°F)	80°C (176°F)
Current density	2.0 A/dm ² (20 A/ft ²)	4.0-6.0 A/dm2 (40-60 A/ft

21, "Physical and Mechanical Properties of Electrodeposited Copper." The soft deposits from cyanide baths were produced from formulations shown in the accompanying table.

In summary, I think it would be cheaper to mask or strike with nickel and use the bright acid copper, with inherent advantages of brightness, leveling, buffability, superior micro-throwing power and ease of operation and control.

Cyanide analysis

Q: The cost of reagent-grade silver nitrate is approximately \$250/lb. At that rate, 1 gal of 0.1 normal (N) silver nitrate solution costs \$35. Is there a method for cyanide analysis other than titrating with silver nitrate?

A: A potential substitute for silver nitrate for the analysis of cyanide in plating solutions is nickel sulfate (NiSO₄·7H₂O). A 0.1N solution of nickel sulfate (14.05 g/L NiSO₄·7H₂O or 2.935 g/L of Ni metal) is prepared and used in the same fashion as silver nitrate.

Procedure:

- 1. Pipette a 10-mL sample of cyanide plating solution into a 250-mL Erlenmeyer flask.
- 2. Add 100 mL of distilled water.
- 3. Titrate with 0.1N nickel sulfate solution until permanent turbidity appears.

Calculation

mL of 0.1N NiSO₄ × 0.131 = oz/gal NaCN mL of 0.1N NiSO₄ × 0.173 = oz/gal KCN

During the titration, nickel combines with cyanide to form insoluble nickel cyanide:

 $Ni^{+2} + 2CN^{-} = Ni(CN)_{2}$

The nickel cyanide instantly redissolves as long as an excess of cyanide exists: $Ni(CN)_2 + 2CN^- = Ni(CN)_4^{-2}$ When all excess cyanide has been combined to form the tetra-cyanonickelate. any further addition of nickel again forms insoluble nickel cyanide and the solution becomes permanently turbid:

$$Ni(CN)_{4}^{-2} + Ni = 2Ni(CN)_{4} \downarrow$$

The nickel reagent should be standardized against a known concentration of sodium or potassium cyanide (previously standardized against 0.1N silver nitrate) or against 0.1M EDTA.

Another approach to analyzing cyanide is to add nickel sulfate in excess of that required to precipitate the cyanide as nickel cyanide, and titrating the excess nickel with 0.1M EDTA using Murexide indicator. First, take a quantity of standard 0.1 M nickel sulfate solution, which will leave an excess of nickel after reacting with the cyanide in the sample. Add 3 mL of ammonium hydroxide for each 100 mL of nickel solution and titrate with 0.1M EDTA using Murexide indicator.

Next, take a volume of 0.1M nickel used in the above titration, add the ammonium hydroxide, then the cyanide sample to be analyzed. Titrate this mixture with the EDTA solution as above. From a difference in the volumes of EDTA used in the two titrations, the quantity of cyanide in the sample is calculated. A difference of 0.1 mL of 0.1M EDTA corresponds to 19.6 mg of NaCN or 26.4 mg of KCN.

Technical 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 21st 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.

Robert Perkins, vice president; Thomas Perkins, treasurer; and Dorothy Perkins-McCauley, secretary.

Still Providing Finishing Services

R.E. Sturdy Company is still located in a 23,000 ft2 facility at 928 Eddy Street. The shop still specializes in barrel plating on plastics, but also performs rack and barrel plating on metal substrates. The company primarily serves the jewelry, garment, military insignia, advertising specialities, religious and household goods industries. The shop also performs polishing, sandblasting, lacquering, oxidizing, stress relieving and packaging.

Perkins-McCauley can recall a number of unique items finished by R.E. Sturdy over the years. "Among this items was Los Angeles Police Badge #714, which was featured on 'Dragnet,' the television show," she said. "Also, we plated the horseshoes that Secretariat wore while winning the triple crown, and we put different colors of gold on the Hiccock Award the year Pete Rose won it."

The company has been pro-active in the community in recent years. Tom Perkins served two years as president of Rhode Island Contract Electroplaters, an organization with the mission of educating elected government officials about the impact of legislation and regulations on the surface finishing industry in the area. He was also appointed by the Governor of Rhode Island to serve on the Narragansett Bay Commission, the local sewer commission.

But, there is also a sad note for this historic plating shop. Environmental compliance issues have had an enormous impact on the company. In recent years, the company has been forced to invest in wastewater treatment and air emissions equipment. This has prevented investments in modern finishing technology to increase production and quality. "It's probably the number one reason we are unable to compete in the global market," said Perkins-McCauley, "and the reason we expect to be forced to close within the next decade." *P&sf*