Finishers' Think Tank Revisited—V

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Oops! HCl in chromium tank

Q: Hydrochloric acid, instead of sulfuric acid, was accidentally added to my chromium plating tank. My chromium work is totally unacceptable. How can I remove or inactivate the effects of the chloride?

A: Chloride may be introduced into chromium plating solutions by accident, as in your case, from the previous nickel plating solution, or with tap water added to make up evaporative losses. Excessive chloride content may be reduced by high-current density electrolysis at a high temperature such as 70°C (158°F). Use a small cathode area.

Silver oxide has been suggested to precipitate chloride from a chromium-plating solution. Approximately 0.22 g/L (0.03 oz/gal) of silver oxide for each g/L of chloride to be precipitated is required. Silver oxide is insoluble in water but may be dissolved in a portion of the plating bath and added to the tank.

Destroying concentrated cyanide

Q: In our shop, we use a 90 g/L (12 oz/gal) heavy-duty alkaline cleaner for cleaning and desmutting steel after pickling. We had always been plagued with yellowish-brown stains on the work, resulting from carryover of dissolved iron salts from the pickle bath. On the advice of our local plating supplier, we eliminated the staining by adding and maintaining 30 to 45 g/L (4 to 6 oz/gal) of sodium cyanide in the cleaner. I am satisfied with the results, but now I have the problem of getting rid of 4,540 L (1,200 gal) of spent cyanide cleaning solution every six weeks. I can't dilute it. How can I destroy the cyanide, cheaply, to the point that I can just dump it down the drain?

A: One of the most uncomplicated techniques used to destroy concentrated cyanide solutions is simply to heat to as high a temperature as possible until the cyanide decomposes. A 120 g/L (16 oz/gal) cleaner will boil at approximately 104°C (220°F). If maintained at this temperature for a sufficient length of time, the cyanide will eventually be reduced to a low concentration. However, if caustic soda is added to a concentration of 720 g/L (6 lb/gal), the boiling point can be raised to about 145°C (293°F) and the time required can be reduced greatly. Aeration enhances the reaction.

Although this method is simple, it would cost $1,100 to take 4,540 L (1,200 gal) of solution and add caustic soda to a concentration of 720 g/L (6 lb/gal) (1,200 gal × 6 lb/gal × $0.15/lb = $1.080). Alternatively, the 4,540 L (1200 gal) of cleaner could be boiled down to approximately 760 L (200 gal), where the boiling point would be in the range of 145°C (293°F). This approach would cost approximately $50 for energy just to evaporate 3,785 L (1,000 gal) of water. One gallon of oil at $0.75 (or $1.22 in August 2005) is required to evaporate 57 L (15 gal) of water. The practice of boiling at 145°C (293°F) will reduce the 30 g/L (4 oz/gal) sodium cyanide concentration to 0.75 g/L (0.1 oz/gal) in about 36 hr. The standard method for cyanide destruction is, of course, high-pH chlorination, which converts cyanide to cyanate. It would cost $144 to chlorinate this solution with sodium hypochlorite (0.25 lb NaCN/gal × 1,200 gal × 1.2 gal NaOCl / lb NaCN × $0.40/gal NaOCl = $144).

You might combine the boil-down technique with chlorination. First, boil the solution down to 760 L (200 gal), and continue boiling until the cyanide has been reduced to 0.75 g/L (0.1 oz/gal). Allow the solution to cool to room temperature and add 7.5 L (2 gal) of sodium hypochlorite to destroy the last bit of cyanide. At that point, the solution can be slowly diluted while being discharged with your other waste, unless your effluent-discharge requirements prohibit this.

You might also consult the August 1980 issue of *P&SF*, p. 56, for an article entitled "Cyanide Waste Treatment Technology: The Old, the New, and the Practical." This article reviews many of the known techniques and methods for the waste treatment of cyanide and cyanide-containing wastes.

Corrosion of stainless coils

Q: I am using a room temperature nitric/hydrofluoric acid mixture for pickling titanium. The etching reaction is vigorous and the temperature of the etching solution tends to increase. If the temperature gets too high, etching becomes preferential and deep pitting results. I have installed a welded, 300-series stainless-steel cooling coil to keep the temperature from rising. Initially, I tried PVC and Teflon cooling coils but the heat transfer was not good enough. The stainless-steel coils are custom-made for us by a neighboring fabricator. My problem is that while the stainless pipe seems to resist attack from the acid, the area of the weld corrodes rapidly and perforates. Do you have any ideas on why my coils are failing? Is the welder using

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the wrong welding rods? What other recommendations on materials do you have?

A: Your coils are preferentially corroding in the welded area because of "sensitization" of the stainless during welding. Sensitization is the harmful precipitation of complex chromium carbides along grain boundaries within the temperature range of 400 to 900°C (752 to 1,652°F), with temperatures near 650°C (1,200°F) most damaging. Grain-boundary precipitation greatly reduces the corrosion resistance of 300-series stainless steel. The trouble shows up with preferential and rapid corrosion of the metal at these grain boundaries when the sensitized metal is exposed to a corroding medium such as nitric acid, which selectively passivates the unsensitized portion of the stainless steel while attacking the sensitized area.

Several methods are available for combating sensitization:

1. After welding, reheat the coil above the sensitizing range to allow the chromium carbide to dissociate and redissolve into the matrix of the grain. The annealing temperature for different alloys increases as the carbon content increases. Experience indicates that annealing in the range of 1,050 to 1,100°C (1,900 to 2,000°F) will always cause the boundary carbides to dissolve. Rapid cooling, as by quenching, will prevent their reforming.
2. Use a grade of stainless with a low carbon content - less than 0.03%. However, even these grades will sensitize if held at temperature for extended times in the sensitizing range.
3. The most satisfactory and popular method is to use a stabilized grade of stainless such as type 347 containing niobium or type 321 containing titanium. The niobium and the titanium have a greater affinity for carbon than chromium. They expropriate any available carbon, leaving the chromium free for its operation of passivation.

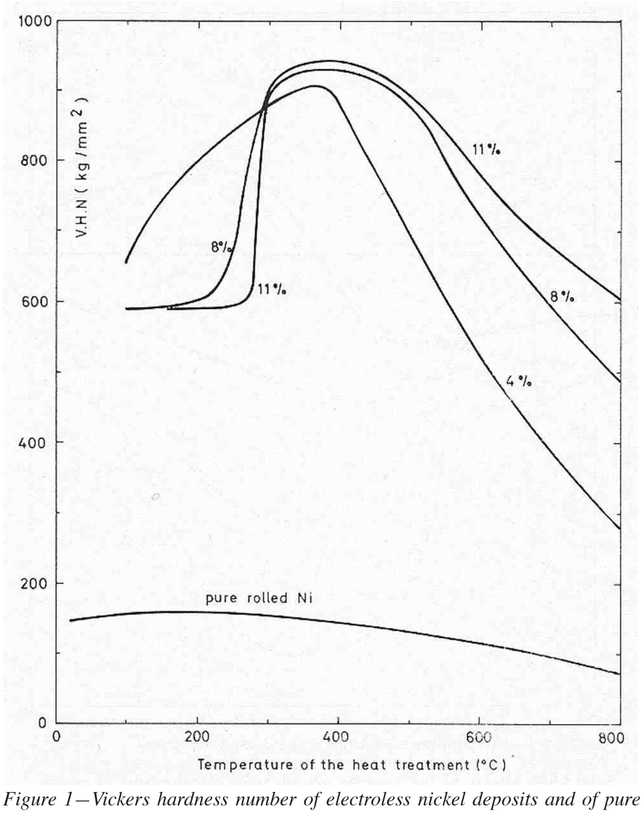

Figure 1—Vickers hardness number of electroless nickel deposits and of pure nickel as a function of heat treatment temperature for different phosphorus contents.

A few other suggestions are in order:

- Assemble your coil by cutting threads and using fittings. This eliminates the welding problem.
- Use tubing rather than pipe and bend a coil to eliminate the welding or the threading and fittings.

Lastly, let me suggest the use of another material with much lower corrosion rates in nitric/hydrofluoric acid than 300-series stainless steel. One such alloy is Inconel 690, which was developed specifically for use in nitric/hydrofluoric acid mixtures. Corrosion rates are stated at 0.15 to 0.25 mm/yr (6 to 10 mil/yr), much lower than standard 300-series stainless.

Electroless nickel plating

We are in need of information regarding electroless nickel plating. We manufacture small, precision slide mechanisms made of aluminum, steel or brass (note the enclosed samples). Our problem is one of wear. The present electroless nickel plating is done by an outside job shop but does not fully satisfy all of our customers who use our parts in assemblies where high force and vibration prevail. I have conducted a limited search of the available literature and find some confusion and contradictions. These are the questions I have:

Q: How does the phosphorus content of the plating bath effect heating time and temperature with respect to hardness?

A: The phosphorus content of the bath in the form of hypophosphite ion has little influence on the time or temperature of heat treatment used to increase the hardness of electroless nickel deposits. The phosphorus content of the deposit is independent of the hypophosphite concentration. The pH of the plating bath is the controlling factor affecting the phosphorus content of the deposit. In general, the higher the pH, the lower the phosphorus content. At pH 8.5, the phosphorus content of the deposit may be as low as 5.5%, whereas deposits produced at pH 3.0 can be as high as 15.6%. Sodium phosphite, the oxidation product of sodium hypophosphite, increases in concentration in direct proportion to the amount of hypophosphite consumed in the plating bath. However, the phosphorus content of the deposit is not influenced by the amount present in the bath, even at concentrations as high as 200 g/L (26.7 oz/gal). In general, the temperature of heat treatment is the dominant factor in determining the hardness of the deposit. Maximum hardness is obtained at about 400°C (752°F) within 15 to 20 min of heating. The hardness of the as-plated deposit is about 600 kg/mm^2. It increases as the temperature increases, reaching 950 kg/mm^2 at 400°C (752°F). At higher temperatures the hardness decreases, the decrease being more rapid for deposits with lower phosphorus content, as shown in Fig. 1.

Q: Is there any heat treatment that would be effective at lower temperatures, say 150 to 200°C (302 to 392°F)? Our aluminum-alloy parts would be affected by high temperature, therefore heat treating must be performed at 200°C (392°F) or lower.

A: At a phosphorus content above 9%, there is little increase in hardness until a temperature of 300°C (572°F) is reached. At a phosphorus content below 9%, a lower heat-treating temperature does produce an increase in hardness. As the phosphorus content decreases below 9%, hardness can be increased at temperatures below 300°C (572°F). The effect of low-temperature heat treatment is most effective at 3 to 4% phosphorus. At this low level of phosphorus, heating to 125°C (257°F) produces a noticeable increase in hardness, as shown in Fig. 2.

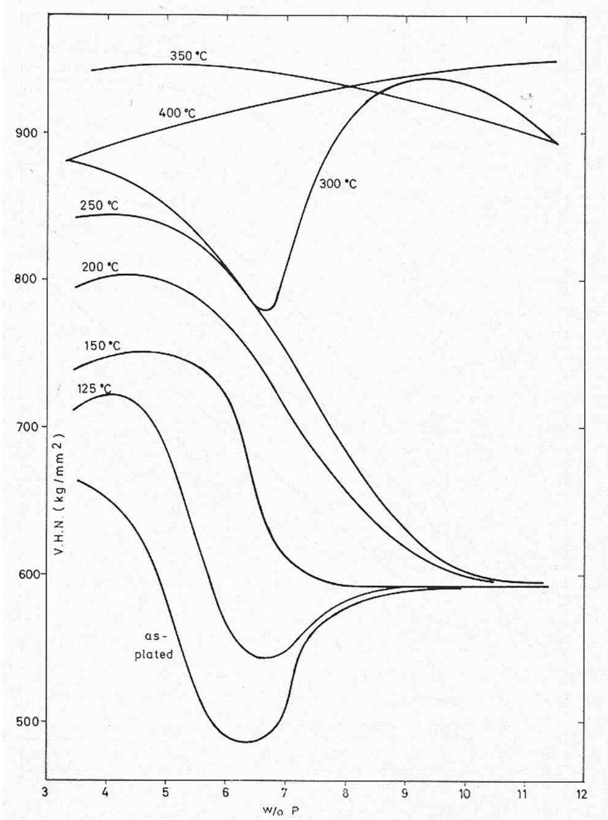

Figure 2—Vickers hardness number of electroless nickel deposits as a function of phosphorus content for heat treatment ranging from 100 to 400°C (212 to 752°F).

Q: Is hardness of the plate an indicator of wear resistance, all other things being equal?

A: Yes, as hardness increases, wear resistance increases. Maximum wear resistance can be expected from high phosphorus deposits (11%) heat treated in the range of 400 to 600°C (752 to 1,112°F). For low-phosphorus deposits of 4%, wear resistance is increased slightly with heat treatment up to 400°C (752°F), but, above 400°C, wear resistance falls off rapidly. Deposits containing 4% phosphorus wear out between 10 and 100 times more rapidly than those containing 8 to 12% phosphorus. On non-heat-treated deposits, minimum wear resistance occurs with deposits of 6 to 7% phosphorus.

Q: Is the thickness of the plate an indicator of wear resistance, all other things being equal?

A: Some research indicates that thin, 7.5-μm (0.0003-in.) electroless nickel coatings are more wear resistant than thick, 17.5-μm (0.0007-in.) coatings. Deposits hardened 1 hr at 400°C (752°F) are more wear resistant.

Q: Must heat treating be done in a controlled atmosphere? If so, please specify.

A: A reducing atmosphere such as hydrogen must be used to prevent surface oxidation when the coating is exposed to temperatures above 290°C (554°F).

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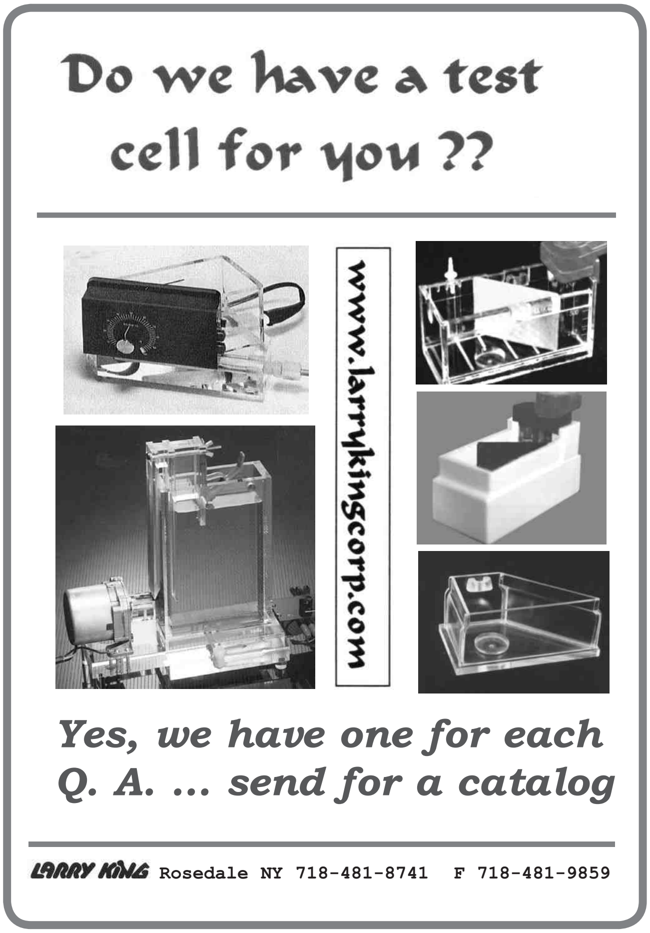

Carbon Treatment

The following procedure should be used to eliminate contamination caused by oils, greases, buffing compounds and other organic impurities:

1. Transfer solution to a clean and suitably-lined storage tank.
2. Adjust pH of solution to 3.0–3.5.
3. Adjust temp of solution to 65–75°C (150–170°F).
4. Add 4.8 to 9.6 g/L (4–8 lb/100 gal) of activated carbon. 4.8–6.0 g/L of carbon are usually sufficient, but in cases of badly contaminated solution, 9.6 g/L or even more may be necessary. Two separate carbon treatments using 4.8 g/L (4 1b/100 gal) are better than one treatment using 9.6 g/L (8 lb/100 gal), but two filtrations are involved.
5. While temp is maintained, carbon should be stirred in carefully for at least 2 hr. Allow solution to settle for an hr or more. Clean plating tank and anode bags; replace worn out bags and anodes.
6. Filter back into cleaned plating tank using pre-coated filter. Draw solution from near the top to avoid picking up loose quantities of carbon sludge which could restrict the flow or even stop-up the filter.
7. It is advisable to maintain an even rate of flow by adding about 1.2 g/L (1 lb/100 gal) of “filter aid.” This should be added slowly in the storage tank near the suction hose as the level of the solution is reduced.
8. Adjust solution level and pH to optimum plating range. The pH can be raised by circulating solution through a filter unit which has been packed with nickel carbonate and “filter aid.” The pH can be lowered by adding diluted sulfuric acid.
9. Adjust and add addition agent(s) as required.
10. Resume plating operations.

High pH Treatment With Nickel Carbonate

If high pH is required for the removal of metallic impurities, the following procedure should be followed:

1. Transfer solution to a clean and suitably-lined storage tank.
2. Adjust temp to between 65-75°C (150-170°F).

Prepare slurry of nickel carbonate and water, on a basis of 1 kg of dry nickel carbonate to one Liter of water with 7 ml of the anti-pitter used in the nickel bath (8 lbs of dry nickel carbonate to one gal of water with 1/4 oz anti-pitter). Stir this mixture, preferably with a mechanical stirrer, until completely dispersed. Do not add dry nickel carbonate directly to the solution in the storage tank. Always use a slurry.

4. Slowly add the nickel carbonate slurry to the heated solution in the storage tank, stirring constantly. The amount of nickel carbonate added will vary with the original pH of the solution, but 6 g/L (5 lb/100 gal) of dry nickel carbonate to plating solution is usually sufficient.
5. While temp is maintained, solution should be stirred for about one hr or more. Then check pH of a filtered sample of solution and adjust again with nickel carbonate slurry until pH is at least 5.2.

Allow solution to settle for at least eight hr, preferably overnight. Clean plating tank and anode bags; replace worn out bags and anodes.

7. Filter back into the cleaned plating tank, using pre-coated filter. Draw solution from near top to avoid flow restriction or filter stop-up.
8. It is advisable to maintain an even rate of flow by adding about 1.2 g/L (1 lb/100 gal) of “filter aid” to plating solution. This should be added slowly to the storage tank near the suction hose as the level of the solution is lowered.
9. Reduce pH to operating range with diluted sulfuric acid.
10. Adjust temp and addition agent(s). Resume plating.

Combination Treatment with Carbon and Nickel Carbonate

Treatments involving both activated carbon and nickel carbonate are ideally performed separately and in the order given. Lacking sufficient time to perform both treatments, a satisfactory compromise can be used when the solution is first treated with activated carbon followed by nickel carbonate. The following procedure should be used: Perform Steps 1 through 5 under “Carbon Treatment”. Instead of allowing the solution to settle under Step 5 above, perform Steps 3 through 10 as directed under “High pH Treatment.” **P&SF**

Shop Talk

Continued from page 8

Q: Is flaking of the plate due to dirty substrate surfaces or improper cleaning?

A: Looking at the parts under 20X magnification reveals some chipping and peeling on the edges, corners and linear-shaped bare areas on the spline. I think the problem is not so much cleanliness but abrasion of the zincate pretreatment prior to commencement of deposition of the nickel. Adhesion of the nickel to aluminum can be increased by a 1-hr bake at 150°C (302°F).

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 21^{st} century. As we have often said, much has changed … but not that much. The material is not meant to be an update, but rather what was done before. 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. **P&SF**