

Finishers' Think Tank Revisited—VI

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Q: Is there a faster way of raising the pH of a nickel solution than using nickel carbonate?

A: Freshly precipitated nickel hydroxide, rather than nickel carbonate, may be used to raise the pH of a nickel solution. Nickel sulfate is dissolved in water and sufficient sodium hydroxide (50% solution) is added to precipitate the nickel as a hydroxide. The nickel hydroxide precipitate is thoroughly washed free of sodium hydroxide by repeatedly stirring, settling, decanting and adding fresh water to the nickel hydroxide.

As you may realize, using nickel carbonate is the standard means of raising pH and, all things considered, may still be the best if you do it properly. When operating a nickel solution, the nickel carbonate should be slurried and picked up in the nickel filter, where it will be neutralized slowly as nickel solution is pumped through the filter. Under no circumstances should sodium hydroxide or ammonium hydroxide be used for pH adjustment. Many bright nickel solutions have a low tolerance for sodium ion and the ammonium ion will cause brittle deposits.

Normally, the pH of a nickel solution should always be increasing. If your pH is continuously decreasing, you probably have a problem with passive anodes.

Electropolishing Titanium

Q: In connection with one of our R&D activities, we are seeking information on electropolishing titanium components to a very high finish. The components are rings machined from pure titanium to about 20 mm (0.79 in.) in diameter and with a wall thickness of 4 mm (0.16 in.). Mops of felt cloth and chamois leather are used for initial polishing, and final polishing is performed electrolytically. The main requirement is the elimination of surface imperfections to achieve a mirror-like smoothness. Brightness is desirable but only of secondary importance. Final dimensions are of no significance. Could you furnish us with electropolishing details concerning solution composition, voltage, current density, temperature, agitation, cathode material and the like?

A: There are several solutions listed in the literature for electropolishing titanium and titanium alloys. The following conditions are claimed to be suitable for commercial

electropolishing.¹ Bath composition is not critical and the electropolished finish is good.

Chromic acid (CrO ₃)	400 g/L (53 oz/gal)
Hydrofluoric acid (48 wt%)	100 mL/L (13 oz/gal)
Current density	22 to 54 A/dm ² (200 to 500 A/ft ²)
Temperature	16 to 21°C (61 to 70°F)
Voltage	3 to 7 V

The following process is operable on a small scale, but is less desirable than the above.^{1,2} The substitution of methanol for water inhibits chemical attack. However, too much methanol (*i.e.*, too dilute a solution) whitens the surface and ruins the polish.

Phosphoric acid (90 wt%)	45 to 85 vol%
Hydrofluoric acid (50 wt%)	10 to 18 vol%
Methanol	5 to 40 vol%
Current density	54 to 108 A/dm ² (500 to 1000 A/ft ²)
Voltage	8 to 17 V

A solution for producing a jewelry finish on titanium requires rapid agitation and is stable for about one week.³ It is comprised of the following:

Ethyl alcohol	180 mL
n-Butyl alcohol	20 mL
Aluminum chloride (AlCl ₃)	12 g
Zinc chloride (ZnCl ₂)	56 g
Current density	15.5 A/dm ² (144 A/ft ²)
Temperature	23 to 30°C (73 to 86°F)
Voltage	30 to 60 V
Cathode	Stainless steel
Time	1 to 6 min

Another solution,⁴ developed initially as an anodic etch for titanium, can be used for electropolishing under the proper operating conditions:

Hydrofluoric acid (50 wt%)	100 g
Ethylene glycol	833 g
Temperature	20 to 40°C (68 to 104°F)
Current density	8 to 11 A/dm ² (75 to 100 A/ft ²)
Cathode	Graphite, copper, nickel

This solution reportedly produces a very smooth finish, as low as 2.5 μ -in. (RMS). Remove the part from the solution with the current on, as rapidly as possible to prevent local attack. The current density must be in excess of 5.4 A/dm² (50 A/ft²).

Based on an original article from the "Finishers' Think Tank" series [*Plating & Surface Finishing*, 67, 10 (December 1980) and 68, 16 (January 1981)]

An alternative to electropolishing titanium is chemical polishing. A standard solution is as follows:

Nitric acid (70 wt%)	40 vol%
Hydrofluoric acid (50 wt%)	4 vol%
Water	56 vol%
Temperature	30 to 35°C (85 to 95°F)

Rapid agitation is required to prevent solution depletion at the surface. Small parts may be processed in a rotating barrel. Solution cooling is required to prevent excessive reaction rates. Removal rates will decrease as nitrogen dioxide builds up in the bath.

References

1. Sakae, Tajima, Takemi & Mori, *Products Finishing*, **19**, 26 (October 1954).
2. J. F. Jumer, *Metal Finishing*, **56**, 67 (October 1958).
3. "Method of Applying a Jewelry Finish on Titanium," *Light Metal Age*, **22**, 5-6, 15 (1964).
4. W. Coiner, M. Feinleib & J. Reding, *J. Electrochem. Soc.*, **100**, 485 (November 1953).

Stripping rhodium

Q: Our job shop quoted on a rhodium plating job, but when the work came in, I found that it had already been plated by another outfit and rejected for blisters and pits. I've got to strip it before I replate it, but everything I've tried doesn't touch it. The rhodium thickness is 2.5 μm (0.001 in.) over a 2.5- μm (0.001 in.) nickel strike on a steel basis metal. What can I do to get the rhodium off?

A: You really have a problem! Rhodium is extremely difficult to strip from defectively plated parts without some attack of the basis metal. This is because rhodium is inert to practically every common chemical reagent that has been tried.

While the metal itself cannot be attacked, the recommended method of stripping, especially with thin deposits, is to take advantage of the porosity of the coating and dissolve the underlying strike deposit, most commonly nickel or silver. Dissolving the strike from under the topcoat allows it to flake off so that the part and the rhodium can be reclaimed.

Rhodium with a silver strike may be stripped by making the part anodic in either a chloride or hydrochloric acid solution. A sodium cyanide solution also may be effective for stripping the silver. For rhodium with a nickel strike, an anodic treatment is recommended in a solution of 60 vol% sulfuric acid at 30 to 40°C (86 to 104°F) and 7V. It also has been reported that rhodium is soluble in molten sodium bisulfate or molten sodium chloride.

The above anodic methods even at their best leave a lot to be desired. If the strike strips off and exposes the basis metal before all the rhodium has flaked off, there is a possibility that some attack of the substrate will occur. On precision parts requiring close tolerance, you may end up with expensive scrap.

Another approach, although slower and more costly, but one which will not pit the basis metal, is to use abrasive blasting with a fine 220-grit aluminum oxide or with glass beads. Keep the pressure low, approximately 10 to 15 psi, with the nozzle about 12 in. from the workpiece to prevent localized abrasion. With glass beads, a higher pressure may be used. Wet blasting would provide a more gentle removal with a smoother surface. The nickel or silver strike will minimize the abrasion on the basis metal. Once the rhodium is removed, any strike may be stripped by conventional means. Removal of rhodium by mechanical means also may be accomplished by buffing or polishing through to the basis metal.

This type of problem is a perfect example of why it is so important to pay attention to details so that plating is done right the first

time. Once plated there's no going back to do it over without a lot of heartache and grief.

Replace galvanizing

Q: I am looking to replace zinc galvanizing for parts supplied to the automotive industry. I need good corrosion resistance, equal to or better than that provided by galvanizing, and preferably a finish that is as cheap or cheaper.

A: One proprietary process* may be what you're looking for. The coating consists of heat-bonded chromated zinc platelets with a thickness of 5.0 to 7.5 μm (0.0002 to 0.0003 in). As applied, the coating looks very much like zinc plate, but in fact it's not a plated finish at all.

For small parts, the process comprises dipping in an aqueous zinc-flake dispersion, spinning to remove the excess coating, and heating to 200°C (392°F) to set the finish. The parts are cooled to room temperature. A second coat of the product is then applied to cover bare contact or nesting marks caused by parts touching one another. After spinning, the parts are given a final cure at 300°C (572°F). The coating thickness is controlled by the viscosity and by rpm of the spinner.

As with most coating processes, cleanliness of the basis metal is all important. The preferred cleaning method is either alkaline cleaning or vapor degreasing followed by - and this is the important step - vibratory cleaning or dry honing with aluminum oxide or glass beads.

Some advantages of the coating are:

1. It offers excellent corrosion resistance, more than 500 hr of salt spray without red rust.
2. It does not induce hydrogen embrittlement.
3. It provides outstanding galvanic compatibility.
4. It is pollution-free.
5. It is a good base for painting.
6. It is electrically conductive.

Black oxide

Q: Enclosed are some rejected thermo-hold down buttons that have been processed through our chemical black oxide solution. From time to time, these parts come out with a brown color rather than the jet black that we are accustomed to. Is there anything we can do to adjust the process to get black parts?

A: Your problem is not your process, but the basis metal that your supplier is sending you. The surface chemistry is different than the interior composition. I took one of your parts, blasted one side with aluminum oxide, ran it through my black oxide solution, and it also came out brown, except for the area that was blasted. This indicates surface contamination from some previous metallurgical or manufacturing operation. You can either resort to blasting or some other chemical surface treatment such as mild pickling to remove this surface layer before blackening.

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. 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.

* Dacromet 320, Metal Coatings International, Chardon, OH.