Plating & Surface Finishing Retrospective

Originally contributed by Ronald Kornosky Compiled by Dr. James H. Lindsay, AESF Fellow

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Silver on pewter

Q: Our small jobshop is having a problem silver plating pewter and brittania metal for refinishing purposes. The silver does not adhere. We are degreasing, rinsing, dipping in 10% fluoboric acid at 120°F (49°C), rinsing, activating with potassium cyanide, silver striking, silver plating and rinsing. The pewter often turns black after the dip in fluoboric acid. What are we doing wrong?

A: Pewter isn't usually electroplated because it is popular in its natural form of 65 to 85% tin and up to 35% lead. Some compositions also contain small amounts of antimony and/or copper. Brittania metal, generally composed of 92% tin, 5% antimony and 3% copper, resembles pewter to an extent but is electroplated by some shops.

If your parts have been polished, I suggest you use powdered pumice to remove residue and make sure that good chemical cleaning is provided as well. The use of fluoboric acid shouldn't hurt, but I believe something less than a 10% concentration at room temperature would be better than what you're using now. You might also add a copper strike, as does Gordon Laraman of Sheffield Plating Co., Casselberry, FL.

Mr. Laraman remarks: "We commonly plate brittania metals, but do not heat the fluoboric acid or use a silver strike. Instead, we clean the metal, use a very quick dip - no more than 1 min - in fluoboric acid, then use a copper cyanide strike before silver plating. The copper strike seems to be the best way of promoting adhesion. Alternatively, you could try dipping the metal in hot caustic soda before silver plating, but we still recommend the copper strike.

"We've never heard of anyone plating pewter." Mr. Laraman continues. "However, I suspect the copper strike also would be advantageous on that substrate as well."

Uncoated racks

Q: We exclusively rack plate using cyanide zinc solutions. In order to keep costs down, we were thinking of using steel uncoated racks. What are the pros and cons?

A: The good news is that these racks would be inexpensive to buy. End of good news. The other side of the coin

is that steel has only about 12% the current conductivity of copper. So unless your current flow is low or your rack diameter thick, heat may result from the current flow. Without the rack coating, the whole rack would be plated with zinc, robbing metal from the part and wasting valuable time. All things considered, the rack with a coating is the least expensive step in the long run.

Strange film on bolts

Q: I hope you can give me some answers on these bolts I'm sending. As far as I can tell, there is some type of protective coating on them. When cadmium plated, large blisters are the result. When cyanide zinc plated, there is little if any coverage. What's happening?

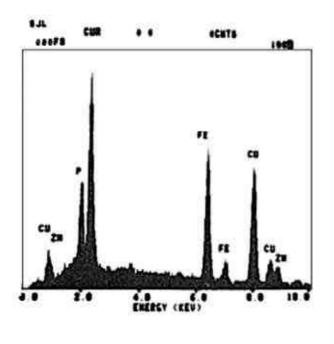
A: I checked the hardness of the bolts and it exceeded 40 on the Rockwell C scale. Therefore, some special considerations are involved in surface preparation. To find out exactly what the "film" is on the bolts, John Laurilliard of SPS Technolgies, Jenkintown, PA, did a little analysis. Here are his comments:

"The bolt was degreased and examined at 20X magnification. A crystalline surface coating similar to zinc phosphate was evident. The bolt surface was then subjected to electron-probe analysis using energy-dispersion-system techniques. This analysis revealed high concentrations of zinc, phosphorus, sulfur, iron and copper. The zinc, iron and phosphorus confirm the suspicion of the zinc phosphate coating. The sulfur may be due to organic sulfonate residuals from the original oil film. The presence of copper could be due to additives or accelerators in the phosphating bath.

"Regardless of composition and origin of the coating, the main problem is how to remove it so that the bolts can be successfully zinc or cadmium plated. The most effective method of removing scale, although not the cheapest, is blasting with 220- or 320-grit aluminum oxide. It's clean, efficient and does not cause hydrogen embrittlement. A good chemical method is alkaline permanganate descaling. Treat the scaled parts in 18 oz/gal (135 g/L) of caustic soda and 8 oz/gal (60 g/L) of potassium permanganate at boiling temperature (about 220°F; 104°C) for 5 to 10 min.







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Energy dispersion scan of film on bolt. (Courtesy of SPS Technologies, Jenkintown, PA.)

"The following is a typical procedure:

- 1. Vapor degrease.
- Immerse in a heavy-duty alkaline soak cleaner for 3 to 5 min at 180°F (80°C).
- 3. Cold water rinse.
- 4. Immerse in 30 to 50 vol% hydrochloric acid (20° Bé) for 2 min at room temperature.
- 5. Cold water rinse.
- 6. Immerse in permanganate solution for 5 to 10 min.
- 7. Cold water rinse.
- 8. Repeat Step 4.
- 9. Cold water rinse.
- 10. If scale is not completely removed, repeat Steps 6-10.

"Federal and military plating specifications prohibit the use of chemical descaling on parts with a hardness of RC40 and above, allowing only mechanical methods to prevent hydrogen embrittlement," Mr. Laurilliard points out. "The hardness of this bolt was determined to be RC41 (188,000 psi), which means that these bolts are definitely susceptible to hydrogen embrittlement due to plating.

"After plating, the parts must be baked for 3 hr at $375^{\circ}F(\pm 25^{\circ}F)$. I'm returning to you the descaled bolt and the original energy-dispersion scan."

Cast in color anodizing

Q: We have two integral-color anodizing tanks. On occasion, we have a problem in that the anodized film (dark bronze and black) has a blue cast. We are at a loss to the cause, having tried everything we can think of – initial break-in periods, tank cleaning, filtration, etc. We're using a proprietary coloring solution containing sulfophthalic acid. What are your thoughts?

A: It's difficult to say what's wrong without having a sample to inspect, but it sounds as though the aluminum alloy you're using may be off in terms of composition. I'd suggest keeping pieces of a good lot on hand at all times to check. This way, you'll always have a known standard to which you may refer when in trouble. Then you can determine whether the bath is at fault or not.

Gerry Kissin, a consultant specializing in anodizing and based in Spokane, WA, believes your problem centers either on metal composition or sealing practices. He says there are three potential problem areas with respect to the latter:

- 1. Low-temperature seals have been known to cause color casts. The temperature should be above 208°F (98°C).
- Organic contaminants could be accumulating in the sealing bath due to the decomposition of ion-exchange resins in the demineralizer or an oil film.
- 3. Your sealing time may be excessive. There is no need to seal longer than 1 min per micrometer of coating thickness.

Mr. Kissin poses the following questions: "Is the blue cast observable directly after anodizing *-i.e.*, before sealing? If so, it could be that the metal composition is off or that bath contamination is at fault. Was etching smut properly removed?"

Special aluminum project

Q: I am doing developmental work on improving the rapid generation of steam when applying water to a heated 350°F (176°C) aluminum surface. Primarily, I am interested in finishes applied to aluminum that would improve the steaming characteristics. Do you have any suggestions?

A: After talking with Charlie Grubbs, CEF, of Reynolds Metals, Richmond, VA, we assumed this would be done in a controlled environment - not in the salt air on the beach - and with deionized or distilled water. If this is so, then bare aluminum may be your best bet. A 5000-series alloy, which is high-purity aluminum alloyed with magnesium, should give the best corrosion resistance. The 6000 series (aluminum/magnesium silicide alloys) also may work for this application. Any treatment such as anodizing would probably result in the development of insulating properties.

Dan Schardein, affiliated with R&D at Reynolds, had these additional comments: "Obtaining intimate contact or wetting is essential for your work. In a study a few years ago, I found that water dropped on a horizontal plate wetted out completely up to about 320°F (160°C). Evaporation was nearly instantaneous between 260 and 320°F (127 and 160°C). I did not study the effect of finish, but I suspect a roughened or textured surface would produce more steam than a smooth one. I seriously doubt if any surface coating other than perhaps silver or copper would improve the heat-transfer characteristics. Anodic or conversion coatings would reduce the thermal conductivity across the interface. However, since bare aluminum would tend to corrode and build up an insulating layer of corrosion product, you might try a thin chromate conversion coating. This would not be an improvement over clean, bare aluminum, but may well provide a better surface over a long period of time."

Coatings on electroless nickel

Q: We have a problem getting paints and coatings (sometimes Teflon) to adhere to electroless nickel-phosphorus deposits. Are there optimum conditions and/or pretreatment cycles for this application?

A: First, you must make sure the surface is clean. Proper rinsing after plating, a final deionized water rinse, and drying are necessary. Because one of electroless nickel's properties is a low coefficient of friction, perhaps adhesion could be improved by mechanical means. Sand or grit blasting may be effective if used with care. Some nickel is removed as a result. A nitric acid etch of the surface would be hard to control and proper rinsing would have to be assured, so this is not recommended.

Konrad Parker, a specialist in electroless nickel plating headquartered in Park Ridge, IL, says paint adhesion on your electroless nickel might be increased by immersing the plated parts in 5% sodium hypochlorite (*e.g.*, Chlorox) or by lightly etching with 5 to 10% sodium bisulfate.

Copper/nickel on shackles

Q: I'd like to determine the best finish for steel shackles (the steel is a lead mixture). Right now, we're using a 0.0001-in.-thick (2.5- μ m-thick) cyanide copper strike with about 0.00030 in. (7.5 μ m) of bright nickel on top. Nickel alone seems to be a better way to go both economically and environmentally, but what will actually happen if the copper strike is eliminated? Also, what are some of the available tests for determining corrosion protection under normal atmospheric conditions?

A: A copper strike will influence part longevity, but the use of multiple nickel coatings with copper would seem apropos for this application. The combination of three types of nickel baths/deposits with or without a microporous or microcracked chromium gives quite a variety of properties. If the service atmosphere is high in SO_2 , copper can be quite an advantage.

Louis Gianelos of The Harshaw Chemical Co., Cleveland, OH also sees a need for the copper strike. "Leaded steels contain up to 5% lead as a homogenous dispersion. Therefore, there is always some lead exposed at the surface of the alloy. The cleaning cycle for this type of steel should include a 15 to 20 vol% fluoboric acid dip followed by adequate rinsing and a copper strike. Following additional rinsing and neutralization, the part can be plated with nickel.

"The use of a copper strike will not in itself contribute to improved corrosion protection. On the other hand, eliminating the copper strike could cause severe problems. The problems result from the nature of the alloy steel surface. The reason for using the fluoboric acid dip is to produce soluble lead salts. The use of muriatic and especially sulfuric acids can result in the formation of insoluble lead salts where lead is exposed on the surface. These salts will inhibit the deposition of nickel and produce porosity, pitting or lack of adhesion. Introducing the cleaned and acid-dipped part directly into the nickel solution will result in the formation of insoluble lead sulfate on the part surface due to the reaction of the lead with the sulfate in the nickel solution. Therefore, the copper strike is necessary to produce a sound coating on top of the leadbearing areas of the alloy surface."

Mr. Gianelos concludes, "Regarding your question about corrosion tests, ASTM documents on the subject include those on salt spray (B117-57T), CASS (B368-62T), Corrodkote (B380-61T), acetic acid salt spray (B287-62), cycle immersion (B192-44T) and constant immersion (B185-43). Several electrolytic tests also can be used. For example, steel parts can be made anodic in an electrolyte such as 10 g/L NaNO₃, 1.0 g/L NaCl, 5 mL/L concentrated HNO₃ and 1.0 g/L phenanthroline hydrochloride at a potential of 0.3 V maximum and a current density of 3 A/ft² (3.3 mA/cm²) "on" for 1 min and "off" for 2 min, with stirring. Each of these tests shows resistance to one type of corrosion, so you must make a careful selection.

Gold on stainless steel

Q: We're having problems activating watch bracelets in order to plate them with gold. The foreign supplier claims the material is 304 stainless steel, which we doubt. When we use 35% HCl for activation, it etches the polished areas of the substrate. We degrease in 1,1,1-trichloroethane for 1 min; ultrasonically clean in a detergent solution for 1 min; electroclean cathodically for 1 min; activate in an acid salt solution for 2 min, then with 35% HCl for 30 sec; gold strike; low-karat gold plate; 23-karat gold plate and blow dry at 200° F (93°C). We've tried a Wood's nickel strike in place of the gold strike but with the same results. Peeling occurs between the stainless steel and the first electrodeposited layer. Any suggestions?

A: A short, mild anodic electroclean should precede the Wood's nickel strike, usually at 100 to 200 A/ft² (10 to 20 A/dm²) for 2 min. Anodic treatment in sulfuric acid (70 wt%) at 100 A/ft² for 3 min also should provide good adhesion. Activation with cathodic HCl may work, but is not preferred.

As you suggest, there is the strong possibility that the material is not 304 stainless steel. John Norton of Engelhard, E. Newark, NJ, proposes two alternatives. First, you can make the part anodic in concentrated H_2SO_4 at 5 V for 5 to 10 sec and follow with a Wood's nickel strike or an acid chloride gold strike (1.8 g of Au as gold chloride plus 100 cm³ of HCl). Dilute to 1 liter and plate at room temperature at 4 to 5 V. The second option is to make the part cathodic in 20 vol% H_2SO_4 (5 V, 5 to 10 sec), and follow with Wood's nickel and acid gold strikes. "If the watch bracelets were a true stainless steel," comments Mr. Norton, "a Wood's strike would activate the surface."

Similarly, Hrant Shoushanian of Technic, Inc., Providence, RI, remarks, "I would have to agree that the material might be something other than 304 stainless steel." Mr. Shoushanian suggests trying a reduction in time (to 20 sec) in the cathodic cleaner, a 30-sec dwell time in the acid salt solution, and an increase in both plating time and current density in the gold strike. He says the gold strike you're using may be too thin to promote good adhesion on this particular substrate. *P&sf*

The edited preceding article is based on material compiled by Mr. Ronald Kornosky, then of Hager Hinge Co., in Montgomery, AL, as part of the Finishers Think Tank series, which began its long run in this journal 26 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.