Plating & Surface Finishing Retrospective

Originally conributed by Ronald Kornosky
Compilied by Dr. James H. Lindsay, AESF Fellow

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Pitting on anodic finish

Q: A client makes fire extinguishers for offshore use. Some parts are 6262T6 or 6262T9 and are anodized (clear or black). We want no evidence of corrosion upon 240 hours of neutral salt-spray testing. So far, however, pitting has occurred. With good quality control and a thick anodized film, is this goal realistic?

A: If a choice were always available, every anodizer would select the alloy you have to work with. Five-hundred hours of resistance to neutral salt spray should be no problem for this application. Perhaps the anodizing thickness is short of what it should be. This is easy to check by calculating the area, weighing the piece with an analytical balance and stripping the coating in a 30 to 40 g/L solution of 75% phosphoric acid and 20 to 25 g/L of chromic acid at 88°C (190°F) for 8 to 15 min or until no further weight loss is noted. The use of any caustic or alkali to strip the coating will attack or etch the basis metal.

Sealing of the film is also an important area to look at. The oxide is converted to a hydroxide (with a hot water seal) or other compound, depending on the seal employed. The pores on the film are then closed, making the coating harder, denser and rendering it incapable of absorbing more dye. One quick test would be to drop ink from a fountain pen onto the surface, let it sit for a minute or so, and then rinse it off with water but without scrubbing. Absorption of the ink should not occur.

The goal of 240 hr of salt-spray resistance is very realistic, so a thorough check of the process parameters should be performed. Gerry Kissin, a consultant in Spokane, WA, adds that, "I would expect an aluminum article made from 6262 alloy, anodized under proper conditions in 15% sulfuric acid to a thickness of 10 μm (0.0004 in.) or greater, and properly sealed to survive 1000 hr of neutral salt exposure without visible pitting.

"I would check all aspects of anodizing and sealing operations: bath concentration, temperature, current density, time, impurities, etc. Is adequate coating thickness and density being achieved? Is the aluminum-alloy composition within limits for 6262 alloy? Is direct current being used for anodizing? Look for a possible electrical short between the work and the sealing-tank wall. It might be causing galvanic corrosion of the work. Is the sealing bath contaminated with halide or phosphate ions or other harmful impurities? What other materials are used in the construction of the fire extinguisher? Could they be giving rise to galvanic corrosion of the aluminum components in the salt environment? Is the salt used in the test of the grade called for in ASTM specs and is the test being conducted properly? These are the most likely areas to check. If the answer isn't there, then a metallographic examination of the corrosion sites might give useful clues." says Mr. Kissin.

Discolored copper

Q: We are presently dipping our copper parts in cyanide to remove a discoloration. Is there an alternative?

A: A solution of 5% sulfuric acid with 16 g/L (2 oz/gal) of potassium dichromate should do it. However, this may leave a thin chromate film that can render the copper passive. So, if the part is to be plated, beware of a potential adhesion problem.

Control of pH / chromium

Q: In our small shop, we have had a problem with chromium leaking into the pH adjust water. The cyanides and the chromium rinses are kept separate and treated batch style. The pH adjust water is monitored regularly. I don't want to change the pH to 2.0, add sodium metabisulfite to reduce to trivalent chromium, and adjust the pH back to 8.5 to 9.0. Any suggestions?

A: It is possible to reduce the chromium from the hexavalent to the trivalent state on the alkaline side. Sodium hydrosulfite will do this in quantities of about 1.36 kg (3 lb.) per 454 g (1 lb.) of chromic acid. This will also simultaneously precipitate the chromium. The cost of this treatment will be about four times greater than if you used sulfur dioxide, but the process works without acid-resistant tanks and associated equipment and can be used with confidence when a problem comes up quickly.

Try chromate coating

Q: We process aluminum parts for use in a moderate environment. With an eye toward lowering costs, how can we protect them other than anodizing?

A: A simple chromate dip of the aluminum should be looked into. It provides a high degree of protection, even in a marine, humid environment, and can be dyed for identification purposes. The process still requires cleaning, deoxidizing and accompanying rinses, but the chromate bath needs no current. Coating weights from 3.2 to 11 mg/dm^2 (30 to 100 mg/ft^2) are possible with a yellow to brown coating. Much thinner deposits with less brilliant color also are achievable. The chromate film is also a good paint base. ASTM B-449-67 or MIL-C-5541A will provide you with further information.

Embrittlement of springs

Q: After installation of our zinc-plated screen-door hinges, many of them break. Our vendor claims a problem with the spring supplier, who subsequently passes it back to the plater. Who is right?

A: The first thing to do is check with the plater. The problem very likely is hydrogen embrittlement of the spring. Any hardened or high-strength material is subject to this phenomenon. Hydrogen gas actually is absorbed in the surface of the substrate and, unless allowed to escape, results in a high-stress area susceptible to breakage. The thinner the material, the more likely it is to fail. Usually, thick materials not subject to bending are no problem.

The hydrogen can evolve from a number of places. A sample lot of hinges should be heated at 148 to 190°C (370 to 375°F) for an hour to drive out any hydrogen picked up before plating. If this does not prevent breakage after plating, an excessive amount of hydrogen is being accumulated during the cleaning and electrodeposition cycles.

Acid dips, especially long ones, used to neutralize alkaline surface films also evolve hydrogen on the substrate. However, by imposing an anodic potential on the workpiece, you can prevent or at least reduce the amount of hydrogen intake during acid dipping. Replated work stripped by acid dipping is another potential problem area.

If the plating bath is a cyanide or alkaline non-cyanide type, the efficiency of the bath is less than 100%, and, as electroplating proceeds, hydrogen is evolved at the work surface and locked in. The usual procedure is to bake the parts as soon as possible after plating. Typically, a bake for 3 to 4 hr at 148 to 190°C (300 to 375°F) will drop the hydrogen content to a safe level. If a deposit thicker than 4 μm (0.0002 in.) is desired, plate to that thickness, bake the part, and then return it to the bath for further plating.

Acid zinc baths will minimize this problem and may solve it for you. These baths operate slightly on the acidic side and have almost 100% efficiency. Pulsating the current also has been reported as being effective for reducing hydrogen pickup during zinc or cadmium plating in cyanide baths.

Automation/ Computerization

Q: I am in the process of automating and computerizing the control and analysis of an eight-cell nickel sulfamate electroforming operation. What are your thoughts on the subject?

A: Control of the mechanical transfer of parts through any plating system can be handled by a number of equipment manufacturers ... once you have established what you want to do and how much automation you want to pay for! You must first plan a complete desired cycle. Chemical control for the metal ions involved can be effected utilizing polarographic analysis [*E.g.*, see, M.L. Rothstein, *Plating & Surface Finishing*, **68** (6), 78 (1981)]. This technique should pick up the nickel and any other metal - perhaps iron or copper - that might build up in the bath so that routine electrolytic purification can be employed. The use of automatic colorimetric analysis also appears to be gaining favor when very low concentrations of metal ions are involved.

The concentration of chloride and ammonia may be monitored using specific ion electrodes with some modification, since their main use is in trace analysis. Boric acid may be a problem and might have to be controlled either by using a metering pump or making additions based on another constituent lost only by dragout.

Hardness of the deposit, internal stress and impurity content are affected by current density, so this would be another variable to control through automation.

To the best of my knowledge, only portions of this type of an automated program are used by the average metal-finishing company, and I doubt if anyone does instant analysis of all constituents. The precious-metal platers, however, have made the best inroads so far toward computerized automation.

Penny identification

Q: How do I tell if a new penny is of the zinc-based copper-plated variety or of the old 95% copper / 5% zinc alloy?

A: Destructive testing would tell you immediately. Cut one in half. If the outside shell has a thickness of about 7.5 μm (0.0003 in.) of copper with a zinc interior, you have a new one.

Seriously though, because the electrodeposited copper is on the outside, the coin will act like copper to any chemical test. All the materials are non-magnetic, so you can forget about using a magnet. A simple non-destructive test is that for weight difference. Checking the specific gravity of copper and zinc, the new coin will be about 19% lighter in weight than the old one. Two coins from my pocket, 1979 and 1980 models, weighed 3.0382 and 3.1106 g, respectively (3.0744 average), differing in weight by 2.4%. Those same coins in copper-plated zinc would hit the scale at 2.4610 and 2.5196 g (average of 2.4903). This weight difference of about 0.58 g per coin can be determined on a simple laboratory balance.

Aluminum in nickel bath

Q: We felt that our nickel bath was contaminated with dissolved aluminum, so we pumped it into a holding tank. How should we treat it?

A: Aluminum is a harmful contaminant only in relatively large quantities. If the pH of the bath gets high (approximately 4.0 and above), the aluminum will be precipitated and may cause pitting and a rough deposit. A prescribed treatment would be to use nickel carbonate to raise the pH to 5.0 – at which point the hydroxide is formed - and filter the solution. However, aluminum hydroxide is jelly-like and tends to plug filter pores quickly. Proper care must be taken with respect to filter media.

Copper on polyimide

Q: I am looking for a process to deposit electroless copper on the surface of a 76-μm-thick (3-mil-thick) polyimide. Has anyone been successful in doing this?

A: At least one company I'm-aware of has plated this flexible plastic on a continuous machine for several years, and with good results. The process is proprietary, as we discussed by phone, and their application and product requirements may differ from yours. The finish is about 0.4 μm (1.5 μ-in.) of electroless copper and not of a decorative quality.

Further details are offered by Dr. Alan Poskanzer, Research Manager for Thiokol/Dynachem Corporation, Santa Ana, CA. Dr. Poskanzer's comments and suggestions are as follows:

"This polyimide, like most other dielectric materials, can be plated easily using an electroless copper process. The problem is not one of coverage. The problem is adhesion. This polyimide has such a smooth and chemically inert surface that the plated copper has practically no adhesion.

"In order to plate the polyimide with reasonable adhesion, the surface must be slightly roughened or etched. Sandblasting, though harsh and extreme, will leave a sufficiently roughened surface on which to plate. A chemical etching method is recommended, however. The most widely accepted method of pretreating the product for better plating adhesion is to immerse the substrate into a hot caustic soda solution and let it soak. The more concentrated the solution, the better. The hotter, the better and the longer, the better. A soak cleaner to remove oils and fingerprints prior to caustic immersion is a good idea. An example of a typical process cycle might be as follows,' says Poskanzer.

1. Soak in a hot alkaline cleaner at the recommended temperature and concentration with agitation for 5 min.
2. Rinse.
3. Immerse in 20% caustic soda at 65°C (150°F) for 10 to 15 min.
4. Rinse.
5. Plate with electroless copper.

Dr. Poskanzer adds that a typical electroless plating sequence would be:

1. Clean and condition at the recommended makeup and temperature for 5 min.
2. Rinse
3. Activate in pre-dip for 2 min.
4. Activate in palladium-tin for 3 min.
5. Rinse
6. Rinse again
7. Immerse in accelerator for 6 min.
8. Rinse
9. Rinse
10. Plate with a slow [0.025 μm/min (1.0 μ-in/min)] electroless copper bath.

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. **P&SF**