Finishers' Think Tank Revisited—III

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Cadmium thickness estimate

Q: Do you have any suggestions for a "quick and dirty" shop method for estimating cadmium plate thickness? I don't want to put laboratory instruments in the shop where they will surely be dropped on the floor or doused with plating solutions.

A: A very simple dip test can be used to estimate cadmium thickness on small parts. Set up two 150-mL glass beakers. Fill one with a solution of 25 g/L of chromic acid and 35 mL/L of concentrated nitric acid, and the other with 5 vol% hydrochloric acid. Place the cadmium-plated part into the chromic acid solution. Remove, rinse in water and immerse in the hydrochloric acid solution to remove the brown film. Repeat this sequence until steel appears (or a bright layer in the case of brass). Each dip is equivalent to 1.3 μm (0.00005 in.). The time per dip depends on the temperature of the chromic acid solution. At 16°C (60°F) it is 14.8 sec. At 21°C (70°F), it is 14.0 sec. At 27°C (80°F), it is 12.9 sec.

Do not agitate the part in the chromic acid. Remove it from the hydrochloric acid as soon as the brown film sloughs off. Rinse thoroughly after each solution and use a stopwatch for accurate timing. It would also be advisable to correlate dip-test thicknesses with those derived from your usual instrumental methods and make the necessary corrections.

Chromating zinc

Q: I am having a problem chromating zinc after a 23-hr, 190°C (375°F) post-plate embrittlement-relief bake. The chromate is not uniform and has a dark dull greenish-gray finish, rather than a bright, iridescent, greenish-yellow one. Both the cyanide zinc bath and the chromate solution are analytically controlled and are always in chemical balance. I don't have this problem with cadmium.

A: There may be more than one cause of your problem. Baking plated parts for extended periods will form an invisible oxide and tend to make them non-reactive to the chromate solution, if not removed. The non-uniformity of the chromate indicates improper surface preparation. Zinc-plated parts that have been baked should be immersion cleaned in a mildly alkaline, proprietary metal cleaner for zinc, not in highly caustic steel cleaners, which etch the zinc plate.

After cleaning, and just prior to chromating, the zinc-plated parts should be activated by a short immersion (5 to 10 sec) in a 1/4 to 1% sulfuric acid solution. It is important that the zinc plate be clean and bright after the activation step. Any dulling or smutting will result in dull and off-color chromate coatings. The activator must be kept free of metallic contamination other than zinc. At the first sign of dullness or smut, the activator should be discarded. The cost of a new activator is minimal when compared to the cost of reworking or replating poor-quality chromate.

It is important that the chromating solution be used solely for zinc. Cadmium- and zinc-plated parts should never be chromated in the same solution. This will affect the color and appearance. Lastly (or more correctly, firstly) the zinc-plated parts should be bright and uniform as they come from the plating tank. The plating solution must also be free of both metallic contamination and an excess of metallic brighteners. Codeposited metals deleteriously affect the color and formation of a proper chromate coating.

Arc burning

Q: What can I do to eliminate arcing of parts during barrel plating?

A: Arcing can result in a problem of appearance because of surface disfigurements or impaired physical properties of the basis metal. The latter is a very serious and insidious condition. Heat-treated steel parts that become arc-burned during plating will contain a small spot of untempered martensite. This spot is a potential site from which premature fatigue failure may originate. Too high a current with too small a contact surface is the cause of arcing or arc burning during barrel plating.

A standard 36 × 76 cm (14 × 30 in) hexagonal barrel with a typical flexible dangler will draw approximately 400 A at 12V. Dangler contacts have a tendency to ride on top of the load rather than in the load. The contact area is very small. The number of small pieces in actual contact with each dangler knob may be as few as a hundred. Since the total contact area can be as small as 0.4 cm^2 (0.06 in^2), the current flow per cross-sectional area of contact surface could be 51,800 A/dm^2 (480,000 A/ft^2). The high current, coupled with both the relatively high resistance of steel and the point-contact resistance between the dangler and the steel part, makes arcing inevitable.

To answer your question, increase the contact area by the use of imbedded button contacts or strip contacts running along the ribs of the barrel. But this is expensive.

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The easiest thing to do is to replace the knob contact end of the dangler with a hexagonally-shaped plate. The plates are made of 0.48-cm (3/16-in) 300-series stainless steel. For a 36 × 76 cm (14 × 30 in) barrel, the plate should be approximately 23 cm (9 in) wide. The center of the plate is attached to the end of the flexible dangler by a threaded bushing that allows the plate to rotate, preventing twisting and binding of the dangler cable. The size of the plate is large enough to keep a substantial portion buried in the load at all times, providing sufficient contact surface to eliminate arcing and arc burns.

Commercial thickness

Q: What would you consider a good thickness to give a customer when he specifies "commercial thickness"?

A: "Commercial thickness" is a term mostly used in the job-shop plating business and means different things to different people. The customer, who wants the cheapest plating job, doesn't feel the need to meet ASTM or government specifications for items sold to the general public. By specifying "commercial plate," the cost of plating should be much cheaper. To one plater "commercial plate" means approximately 3.81 μm (0.00015 in). To another it might mean 1.27 to 2.54 cm (0.00005 to 0.0001 in). The latter plater is going to quote a cheaper price and will probably get the order. By not agreeing on a specific minimum thickness the customer is actually doing himself a disservice. He thinks he is getting something slightly less than government specification, when actually he could be getting 1/2 or 1/4 of that thickness. It has been my impression that some customers only want enough plating on the part to make it look saleable before it peels, discolors or rusts.

I would think that most job shops issue quotes with definite thickness call-out and not some indeterminate terminology such as "commercial plate." Every plater should make it his business to educate manufacturers of the significance, necessity and value of including a thickness specification when asking for plating quotations.

Eliminate spotting

Q: I am plating small cast-iron colonial escutcheon plates with 8 μm (0.0003 in) of brass, but am having considerable problems with spotting after drying. Do you have a remedy for this condition?

A: Spotting, or spotting-out, is the result of retention of cleaning, pickling or plating chemicals in microscopic pores in the basis metal. These pores may not be present in the original basis metal but may be caused by attack of the cleaning or pickling solutions on segregated impurities in the basis metal. The spotting-out is the result of the action of high humidity with the hygroscopic occluded compounds in the pores of the metal.

The best remedy is to use a basis metal with less porosity. Aside from that, thorough drying, followed by a low-temperature bake and subsequent lacquering, may help.

Surface burnishing by mild, dry tumbling sometimes eliminates spotting, but one method reported to be 100% effective is to treat parts anodically in a 0.5% solution of hydrochloric acid at 1.1 A/dm^2 (10.0 A/ft^2).

Nitride resist

Q: Several weeks ago we copper plated a job for selective nitriding. The job was sent out for a 72-hr treatment. When the copper was stripped and the stopped-off area examined, it was found that the nitride had penetrated the copper and formed hard spots in the basis metal. The customer says our copper deposit was of poor quality, or else it wouldn't have leaked through. Should I put on a thicker copper deposit? The customer originally specified 25 μm (0.001 in) of copper.

A: Copper is a poor choice as a nitride stop-off. If your customer specified copper he is in error and should be so informed. Even if you doubled the copper thickness to 50 μm (0.002 in.), it probably wouldn't help.

A tin plate of 5 μm (0.0002 in.) is a good nitride resist, but, because of its low melting point, has a tendency to flow if the deposit is too thick. Bronze plate is a better choice and is recommended. The alloy deposited should be 88% copper and 12% tin. The thickness should be approximately 13 μm (0.0005 in.) but a thicker deposit might be advisable to insure sufficient thickness in recessed areas.

One other suggestion: Try a 2.5-μm (0.0001-in.) tin flash over a good, sound copper deposit, 25 μm (0.001 in.) thick. This technique has been tried and proven in the past.

Phosphate etching

Q: Recently, a job that we phosphated was rejected because of etching of the basis metal. The basis metal is AISI 8740, heat treated to HRC-40. The phosphating was done to an automotive-company specification. I have made up a new solution and I still get etching. Do you think the problem is caused by the heat treater? The parts do not have much heat-treat scale, just a slight temper discoloration.

A: You did not indicate what type of surface preparation you used prior to the manganese-phosphate treatment. Surface preparation is extremely important prior to any type of phosphate treatment. The severe alkaline cleaning or acid pickling often used on heat-treated steel should be avoided. Abrasive blasting is the best method of surface treatment for the formation of sound phosphate coatings. If your parts do not readily lend themselves to abrasive blasting, available proprietary cleaners will promote good phosphate coatings.

If an extremely fine manganese-phosphate crystalline structure is required, immersion in a special grain-refining solution is necessary. However, it must be specific for manganese. The standard refiners based on a titanium formulation, often used for zinc-phosphating processes, are not effective.

The primary reason for experiencing etching during manganese phosphating is the imbalance between the total acid and free acid. A ratio of total acid to free acid should be maintained above 6.5 to 1. A low level of free acid must be maintained. The free acid tends to rise, because of hydrolysis, to a point at which excessive etching of the work occurs. Etching of the basis metal due to high free acid is generally accompanied by incomplete, black, smutty coatings which do not produce the characteristic white streak when lightly scratched with a fingernail.

High free acid may be caused by:

1. Prolonged idle periods when the bath is at operating temperature but no work is processed
2. Excessive evaporation without water additions
3. Overheating the solution (*i.e.*, boiling)
4. Processing small work loads in a relatively large-volume tank.

If the free acid increases above the correct range it can be reduced, but the method depends on the concentration of iron and total acid. If the iron concentration is below the recommended range of 0.2 to 0.4% and the free acid is above the specified maximum, the free acid may be reduced by processing large quantities of clean steel wool, steel grit or pickled scrap steel. When visible gassing subsides, remove, repickle and reimmerse in the solution. Repeat this cycle until the free acid is reduced sufficiently or until the iron concentration reaches a maximum.

If the iron content is at the upper limit, add 4 oz of manganese carbonate per 100 gal of solution for every point that the free acid must be reduced (one point equals 1 mL of 0.1N NaOH titrated

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chromium systems (HC) all had substrate corrosion early into all of the different corrosion tests. These systems, which are not micro-discontinuous, are not permitted for exterior decorative automotive applications. They have also been removed as acceptable options for SC 3 and SC 4 in the 2003 edition of ASTM B 456.

Trivalent chromium deposits (micro-porous as plated, TC) and hexavalent chromium deposits (with micro-porosity generated through an additional step, MP) performed almost identically in substrate protection and after corrosion appearance throughout all the tests. Except for the faintly darker color and slightly more surface pitting of the trivalent chromium deposits, both micro-porous systems were equivalent. The difference in color would be less today because of the changes made in the trivalent chromium electroplating technology over the 26 years of this study. Also, recent service experience has shown that this slight increase in surface pitting would most likely have been almost eliminated if a thin, noble nickel deposit was deposited between the bright nickel and the chromium, as required in North American automotive specifications today.

The value of Duplex nickel (semi-bright and bright nickels) versus single nickel (bright nickel) plating systems, both with a total nickel of 25 μm (0.001 in.), was dramatically demonstrated in this study. The single nickel systems developed substrate corrosion during the first year of exposure to all of the outdoor sites. They developed an extensive amount of corrosion after five years. There was a slight improvement when micro-discontinuous chromium, trivalent (TC) and hexavalent (MP and MC), was used. Some of the Duplex nickel systems developed one or two small substrate corrosion sites early in the testing but all micro-discontinuous systems, trivalent and hexavalent, were about equal in performance even at the end of the long-term outdoor tests.

Conclusion

This study demonstrated that SC 4 and possible SC 3 plating systems most likely would last for 10 years without substrate corrosion on decorative exterior automobile parts. The deposits lasted over 10 years when uniformly plated over good quality substrates and micro-discontinuous chromium was utilized. Also, all trivalent chromium deposits performed at least as well as micro-porous hexavalent chromium deposits. This was observed even when plating systems thinner than SC 3 were used. Both trivalent and micro-porous hexavalent chromium deposits performed much better than standard hexavalent chromium deposits without micro-porosity.

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per 10-mL sample). Place the weighed manganese carbonate into a bucket, add water, stir to make a slurry and pour evenly over the solution surface. Never add to the solution any oxidizing agents such as hydrogen peroxide, potassium permanganate or compressed air to oxidize ferrous iron. When ferrous iron oxidizes to ferric and precipitates as iron-phosphate sludge, free phosphoric acid is formed, reducing the ratio of total to free acid. Severe etching and lower-quality coatings are obtained with an increased consumption of phosphating materials.

An indication that the free acid is too high is the continued gassing during phosphating. In a balanced solution, gassing will normally subside within 8 to 12 min, especially if a grain refiner precedes the phosphating and the ratio of total to free acid is 6.0 to 1 or above.

The secret to consistent, good-quality phosphate coatings, whether manganese or zinc, and trouble-free operation is frequent and regular chemical analysis and additions to maintain solution chemistry and balance. Once the solution is heated, adjusted and ready to operate, process the work continuously without delays between loads. When work is finished reduce the temperature immediately. Do not idle at operating temperature. An excellent source of practical operational information of the phosphating process can be found in MIL-HDBK-205.

Technical Editor's Note: *The edited preceding article is based on material compiled and contributed by John Laurilliard, 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.*