Some Production Plating Problems & How They Were Solved—Part 9

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1. Chromate conversion coating on zinc die castings: Premature corrosion breakdown of barrel-finished die castings.

The customer was using a steel grit barrel finishing machine to remove flash and produce an overall even appearance on zinc die-cast parts. It was found that these allowed an excellent appearing chromate conversion film to be produced. However, when subjected to salt spray, the parts showed heavy white corrosion in less than 24 hr. The company specification called for no white corrosion after 72 hr.

In working with zinc die castings which had been barrel finished with the steel grit, it was found that steel particles had become embedded in the zinc die casting and that it was impractical to try to remove these by chemical means. Trials with chemical pre-treatments before chromating showed that if a 2% phosphoric acid pickle was substituted for the 2% sulfuric acid pickle prior to chromating, a satisfactory-appearing chromate film was obtained, which passed the 72 hr of salt spray with no white corrosion.

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2. Grit blasting: Avoiding harmful effects of embedded grit.

Wet and dry abrasive grit blasting are widely used in the industry to remove such surface contaminants as oxides, solid materials and oils. Various grits are used, such as pumice, aluminum oxide, carborundum and sand, and these grits come in sizes ranging from very fine flour to 60-mesh.

In grit blasting sliding electrical contacts, a very fine aluminum oxide was used to clean the surface before other treatments, and subsequent plating. Some of these contacts were made of copper alloy; some were gold alloys. Some were plated and some were simply machined surfaces which were polished by blasting. When subjected to electrical tests, these parts showed a high “noise” level. In some cases, this noise level was higher than before blasting. Even parts which were subsequently plated showed an excessive noise level. The electrical noise was caused by the contact bouncing or vibrating as it passes over the surface, and is very undesirable when a signal is being transmitted.

It is not so well known that a small amount of the grit becomes embedded in the surface of soft metals such as copper, aluminum and gold when they are cleaned by blasting. In some applications, this embedded material does not have a harmful effect, but in others, it does. For example, when aluminum which has been polished is subsequently anodized, streaking results in the anodic coating. For this reason, the aluminum is often bright dipped before anodizing in order to remove the contaminated surface layer.

For slip rings, grit blasting was preferred to other methods of cleaning because of its simplicity, effectiveness and convenience. Various materials and sizes of grits were evaluated but these efforts did not eliminate the high noise level problem.

The problem was finally solved by using a grit of a water-soluble substance, such as sodium bicarbonate. This was suspended in a saturated solution of the same salt, and used for blasting parts in the same equipment that was used for wet blasting. This process eliminated the possibility of leaving non-conducting particles on the surface since the salt was completely and easily dissolved from the piece. Also, the solubility of the salts seemed to produce a smoother finish, since the corners of the undissolved crystals which do the cleaning are rounded by the solution. This was effective in removing the soil and the resulting surface was very smooth with a very low noise level.

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3. Cleaning aluminum before anodizing

The cleaning cycle for our overhead crane anodizing process consisted of a silicated non-etch aluminum cleaner, rinse, deoxidize, rinse, caustic etch and rinse. Since this was a job shop operation, we encountered many different types of soils, oxides and markings on the aluminum being processed.

Quite often, cleaning in the silicated non-etch cleaner is incomplete in the allotted time and this results in a non-uniform etch in the caustic solution. Subsequently, this etch pattern shows up in the aluminum after the anodizing.

The tank operators found that if the parts were dipped into the deoxidizer solution first and then put through the above cycle a uniform caustic etch was obtained every time. This extra predip could be done without interfering

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Based on an original article from the “Plating Topics” series [*Plating*, **54**, 78 (January 1967)]

with the production schedule. However, this procedure contaminated the deoxidizer and required more handling.

The problem was solved by substituting a non-silicated, non-etch aluminum cleaner for the silicated aluminum cleaner. This cleaner was able to clean satisfactorily all the work in the allotted time and thus allow the caustic to produce an even etch.

There is no need to tolerate a poor cleaning situation. In this instance, the cleaner company studied the problem and came up with a cleaner which did a better job in our facility.

4. Gold plating: Colorimetric determination of cobalt in acid solutions

An acid gold plating bath we are using contains cobalt as a simple (not a complex) ion, and deposits an alloy containing about 99% gold and 1% cobalt. The hardness of the deposit, ranging from 200 to 240 KHN, as well as the brightness, depend to a large extent on the cobalt content. The bath temperature, pH and current density are also factors but these are usually controlled within a narrow range.

The cobalt content of the plating bath may be determined spectrographically but the equipment is expensive and not readily available [in 1967]. Titrimetric methods for the determination of cobalt in concentrations of a few tenths of a g/L are not practical.

The following colorimetric procedure for determining cobalt was developed by the writer to provide “in-house” analytical control of our acid gold bath. A determination takes thirty min and has an accuracy of about 10%. If the cobalt is present as a complex ion, the sample must be boiled with sulfuric acid until it fumes to destroy the complex, before following the procedure given below:

Reagents:

A. Potassium thiocyanate, crystal, AR: 215 g
Distilled Water: 100 mL

B. Reagent A (above): 40 vol%
Isopropanol, 99%: 40 vol%
Distilled Water: 20.0 vol%

C. Standard cobalt solution (0.5 g/L Co)
Cobalt Sulfate•$7H_2O$, AR: 2.337 g
Distilled Water to make 1000 mL

Note: Solution A is stable for several months if kept in amber glass. Solution B should be prepared on same day as used. Solution C is stable indefinitely.

Procedure:

1. Pipette exactly 20 mL of gold/cobalt plating solution into a clean, dry 250 mL beaker. Add 40 mL distilled water and 1 level teaspoon of activated carbon to the beaker.

2. Using a glass stirring rod, stir the contents intermittently for 5 min. This carbon purification removes the yellowish discoloration which interferes with the bluish color of the cobalt complex.

3. Filter the solution through Whatman #1 filter paper into a clean, dry 250 mL beaker. Save the filtrate for tests.

4. Set up a color comparator cell with 2 tubes:
   a. Tube No. 1: Calibration line at 20 mL volume
   b. Tube No. 2: 1 mL divisions to 20 mL volume
   Both tubes identical in ID.

5. Pipette 1 mL of standard cobalt solution C into Tube No. 1. Dilute to the 20 mL mark with reagent B. With Tube No. 1 stoppered, invert the tube three times to mix and develop the typical blue color.

6. Pipette 1 mL of filtrate (from Step No. 3) into Tube No. 2, add 2 to 3 mL of reagent B and invert three times. Compare the color intensity of both tubes. Continue dilution of Tube No. 2 with reagent B (1 mL increments) until the blue color of Tube No. 2 is identical to that of Tube No. 1.

7. Record the final volume of Tube No. 2.

Note: If the final volume of Tube No. 2 exceeds 20 mL, repeat from Step No. 6 using a 2 mL sample of filtrate (Step No. 3).

Calculation of cobalt, g/L:

1. When using a 1 mL sample of filtrate: mL (Tube No. 2) X 0.075 = g/L Co

2. When using a 2 mL sample of filtrate: mL (Tube No. 2) X 0.0375 = g/L Co

For better accuracy, the above procedure can be used with colorimeters or spectrophotometers.

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5. Decorative chromium: Skipping

Our trouble started after we had converted our Watts bright nickel to a high chloride bright nickel. The solution was operated in a semi-automatic plating machine and a large variety of shapes and sizes were plated. The trouble was skipping or mischroming, *i.e.*, a large percentage of the bright nickel plated parts would not accept a chromium plate.

In attempting to solve the problem, we thoroughly checked the nickel plating solution with particular reference to inorganic and organic contaminants as well as the possibility of excess nickel brightener. These were well within operating limits. The chromium bath was also completely checked and found to be OK.

We also checked the operating conditions of the nickel and chromium solutions as well as the equipment. The rectifier on the chromium tank was checked for possible single phasing. Everything here also looked OK.

Finally, our attention turned to the change which had been made in the heating coil. The lead coil which had been used with the Watts bath was replaced by a Karbate heater for the high chloride solution. Since the Karbate heater was much thicker than the lead coil, several anodes had to be removed at the end of the nickel plating area.

It was reasoned that the low current density plating on the final nickel surface dummied out impurities and this surface was not receptive to a chromium plate. When this fact was brought out, a way was found to place nickel anodes back into this area and subsequently the problem disappeared.

The moral of this story is evident. When necessary changes in equipment are made, the full impact of these changes must be thoroughly considered. [This is a perfect example of a systems approach to problem-solving.]

6. Color anodizing of aluminum: Consistent results with black dye

In order to obtain consistently good black anodized coatings, the many factors in the anodizing and dyeing processes must be carefully controlled. In this story, I shall describe our processing sequence and discuss some of the troubles we have encountered in our shop, what the causes of these troubles were and the remedial actions which were taken.

The parts are cleaned, deoxidized and "desmutted" for 10 min in a solution containing equal volumes of nitric acid, sulfuric acid and water. They are then anodized in a 15% sulfuric acid bath at 21 to 27°C (70 to 80°F) and sealed. Wrought products are anodized at 15 A/ft^2 (1.6 A/dm^2) for approximately 45 min. Castings are anodized about 1 hr at 12 to 14V.

The black dye must have good light fastness. Finished parts must have a rating of 5 to 10 on the Munsell Neutral Gray scale as used in AATCC Method 16B-1964T (see ASTM Standards, Part 24). Any of the black dyes listed in Specification MIL-A-S625B section 6.8 meet this requirement. These dyes must be used at the specified pH in order to get maximum color absorption.

What follows is a discussion of some of the troubles we have encountered:

1. *Smutty deposit on wrought products.*
   - Anodizing bath temperature too high, at about 27°C (80°F) for copper alloys or 27 to 32°C (80 to 90°F) for other alloys.
   - Anodize time greater than about 55 min.
   - Smutty deposits can also be reduced to a minimum by the use of surfactants in the sealing treatment.

2. *White spots on castings.*
   - This is caused by acid bleed-out which destroys the dye. It can be minimized by soaking the parts in dilute ammonia or sodium bicarbonate solution after anodizing and before dyeing, and by longer rinsing in agitated, cold running water. Impregnating the casting with plastic before anodizing also minimizes this condition.

3, *Off-shade (purple) black.*
   - The cause may lie either in the anodizing or in the dyeing conditions. A thin anodized coating caused by too low a current density or too low a bath temperature will result in insufficient dye absorption. The dye bath may be too weak, be at a pH above that recommended or be operated above the recommended temperature, resulting in partial sealing of the anodized coating.
   - Off-shade (purple) black color on certain heat treated alloys such as 6061 may be caused by insufficient removal of the heavy oxide. This may be remedied by longer time in the deoxidizer or by a caustic etch.
   - Insufficient dye pickup may occur on high silicon castings. This may be rectified by a final treatment before anodizing in a bath containing 5 vol% nitric acid and 1 vol% HF until the part gasses for 10 to 20 sec.

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***Technical Editor's Note**: The edited preceding article [Plating, **54**, 78 (January 1967)] is based on material compiled and contributed by Dr. Samuel Heiman, as part of the Plating Topics series that ran in this journal. It dealt with everyday production plating problems, many of which are still encountered in the opening years of the 21st century. 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.*