Shop Talk

Some Production Plating Problems & How They Were Solved—Part 11

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1. Color anodizing: Poor dye work due to the decomposition of dye solutions.

Dye solutions are mixtures of organic materials and as such are subject to decomposition. This can have a serious effect on the results obtained. Anodizers and platers generally handle stable inorganic chemicals and may not be aware of this property of their dye solutions.

The effect of decomposition of a dye solution is manifested in the following ways:

- 1. The color goes off.
- A gelatinous, stringy precipitate forms in the dye solution. This precipitate sticks to the work and results in staining.
- 3. The pH varies more than usual and is thus harder to maintain.
- 4. The dye solution develops a bad odor.

These troubles may happen to all colors but are more prone to occur with the orange, gold and blue dyes.

The amount of decomposition is temperature- and time-dependent. Thus, it occurs mostly during the summer months, when the temperature of the cooled-down dye baths is in the 21 to 32°C (70 to 90°F) range, and less often in the winter. It is also most likely to happen when these baths stand at room temperature for a period of time, such as on weekends, vacations or other times when the bath is not used.

Once the decomposition has started, the addition of fresh dye generally does not restore the color value to that of a fresh bath. Apparently the byproducts of the organic decomposition interfere with the absorption of color. This means, then, that the bath must be discarded and replaced. It has been demonstrated that in certain cases the decomposition is caused by microorganisms which feed upon and decompose the ingredients in the dyestuffs. Dyes are generally mixtures of the coloring material and additives or standardizing agents which contribute to a more uniform coloring strength. Efforts to build germicides into the dyes have not been successful.

The anodizer may minimize this condition by taking the following steps:

- 1. In making up a new dye solution, clean out the tank thoroughly to remove all of the old solution which may serve as a culture in the new bath.
- 2. After makeup, boil the new dye solution.
- Periodically raise the temperature of the dye solution to about 71°C (160°F).
- 4. Use stainless steel, fiberglass, or plastic tanks. Wooden tanks should not be used as they are impossible to clean thoroughly.

Frank P. Stiller, Sandoz, Inc., New York, NY

2. Gold plating: Low cathode efficiency

The trouble was that the efficiency of our neutral gold bath decreased from the normal 90% to about 45%. This not only slowed production but also made the plating rate calculations unreliable and, therefore, resulted in incorrect thicknesses of gold on the work.

The gold was plated over a nickel undercoat only on the tabs of the printed circuit boards. This was accomplished by applying a stop-off tape to prevent plating on unwanted areas. The tape was pressed down with a rubber roller to improve adhesion.

We suspected organic contamination since this could well account for the loss in efficiency, but the puzzle was where the organic contamination was coming from. It was essential to prove to management that the proprietary solution used was not the cause. The tendency is usually first to blame the plating bath, since it is certainly prone to troubles because of instability, breakdown products, contamination, etc. However, this proprietary bath was a purely inorganic system.

The first break in the problem came when we ran a spectrographic analysis of the plating solution. This revealed appreciable amounts of nickel and boron, which, of course, indicated the presence of boric acid. This proved that there was dragover of nickel plating solution into the gold tank. However, we reasoned that the trouble was not due to these inorganic constituents but to organic contamination from the stress reducer and wetting agent in the sulfamate nickel bath which was being used. A batch carbon treatment was indicated and this did indeed solve the problem.

The dragover of nickel solution occurred because the tape did not serve as a perfect stop-off. The top of the copper printed wire was indeed sealed, but not the space in the corner between the side of the copper and the plastic board. Once nickel solution penetrated this crevice, it was

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impossible to rinse it out. To prevent the problem from recurring, it was necessary to get a perfect seal so that no spaces for entrapment of solution could form. We found that we could do this by replacing worn rollers and by the application of appropriate pressure. The rollers now, you can be sure, are inspected at regular intervals.

3. Fused tin: Another cause of poor solderability

A manufacturer of electronic parts used fused tin for solderability. The trouble was that some of the parts could not be soldered. After a thorough evaluation of all the technical aspects of the problem, no explanation could be found. The baffling part was that the problem occurred at random and there was no correlation at all between the occurrence of the bad parts and any factor connected with the plating operation.

By this time, the front office had an unsympathetic, hard-nosed attitude and, lacking any concrete answer to this pressing problem, viewed any attempt at a scientific discussion of the subject as a snow job with a high fog factor.

Finally, during a cursory examination of some plated parts in storage, the answer was found. Coffee! The plated parts were stored in cardboard drums. Similar drums were used for trash. After coffee-break time, the paper cups containing residual amounts of coffee were tossed into the trash drum, but a certain percentage landed in the nearby storage drums! The coffee tarnished the tin and those parts could not be soldered. The writer now expects that this cause of poor solderability will find its way into textbooks and reviews of this important subject.

> Milton Weiner, Metal Finishing Consultant, Santa Fe Springs, CA.

4. Cadmium plating: Loss in bright plating range

On large cast iron or welded steel structural components which had been descaled by grit blasting, the deposit from the bright cadmium plating bath used had progressively lost brightness, although the constituents were maintained at the proper level for the proprietary brightener used.

Preliminary laboratory investigation indicated that the trouble might have been caused by an accumulation of nickel. After correcting this condition, the decay in bright range continued, although the yellowish off-color appearance of the plating was eliminated.

In the course of the investigation, it was discovered that the bath plated with a normal bright range if:

1. A moderate periodic reverse cycle was used.

2. A full wave, single phase rectifier was used as a current source.

Furthermore, treatment with activated carbon had no effect, and treatment for heavy metals was moderately effective.

It was also determined that an addition of 30 g/L (4 oz/gal) of sodium nitrate increased the operating bright range of the bath. As a result of this discovery, an addition of 30 g/L of sodium nitrate was made to the production bath and did result in improved performance for a time. However, the bright plating range continued to narrow. Analysis of the bath indicated an exceptionally high ferroferricyanide content. Spectrographic analysis of typical deposits indicated the possibility that the arsenic content was higher than in the deposits from other baths in use containing the same proprietary brightener, but not exhibiting the loss in bright range.

These findings suggested that the trouble might have its origin in the fine dust left on the large cast iron and welded steel parts, because it was the operating practice to grit blast the work, and while still rust free and comparatively clean, to place it directly in the cadmium bath. This procedure functioned quite well, although it was not a desirable method. It was decided to steam-gun clean the parts thoroughly before plating. After about six months of operation following the use of this cleaning procedure, the appearance of the deposit returned to normal as did the Hull cell bright plating range.

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5. Chromate conversion coating on zinc plate: Deterioration due to baking

It is well known that the corrosion resistance of chromate conversion coatings on zinc or cadmium is adversely affected by overheating. For this reason, the drying temperature for chromated work should be kept below about 71°C (160°F). Also, the heating of plated work for hydrogen embrittlement relief must be done before the application of the chromate coating. To quote Specification QQ-Z-325a, "all steel parts having a hardness of Rockwell C40 and higher shall be baked at $375 \pm 25^{\circ}$ F (191 \pm 14°C) for three hours after plating. Heat treatment shall be given prior to the application of supplementary coatings. Zinc surfaces passivated as a result of the baking operation shall be reactivated prior to receiving the supplementary chromate treatment."

However, we had a problem which was more complex. The chromate coating was applied to the zinc-plated part to serve as a paint base, but some areas had to be left unpainted. The phenolic paint required heat curing for one hr at 200°C (392°F), which resulted in salt spray failure of the unpainted areas within 4 hr. Twenty-four hour salt spray corrosion resistance was required. We therefore needed a method of restoring the corrosion resistance of this chromate coating which was almost completely destroyed by the heat. One way to solve this problem might be to strip the baked-on chromate coating on the finished painted part and to rechromate. However, we could not find a method which would do this without attacking the zinc.

We found that the protective value of the baked-on chromate coating could be restored to the required 24-hr specification by immersing the parts in either (1) the original chromate conversion solution or (2) a sodium dichromate solution similar to that used in sealing anodized aluminum (5% solution; pH = 6; temperature = 95° C (203°F).

If the parts become soiled in the baking operation, they should be cleaned and activated in a mild alkaline cleaner, prior to the above chromating dips.

6. Electroless palladium plating

This process has been used to deposit palladium on many metals and alloys, but it is not suitable for direct deposition of palladium on copper or its alloys, zinc or magnesium. The process is a true electroless process which employs hydrazine as a reducing agent to produce pure palladium deposits from an ammoniacal solution of a complex palladium compound.

The bath composition which has been found generally useful is:

- Dichlorodiammino palladium, $Pd(NH_2)_2Cl_2$ 15 g
- Disodium diammine tetra-acetic acid
 8 g
- Ammonium hydroxide (Conc.)
 515 mL
- Water to make 1 L

The solution should be allowed to stand overnight and then filtered through a retentive filter to remove any undissolved solids. Adjust temperature to 30°C (86°F) for plating and avoid over- heating.

The reducer solution used with this bath is made fresh daily. It is made by dissolving 1.3 g hydrazine sulfate in concentrated ammonium hydroxide and diluting to 100 mL with water. Theoretically, 12 mL of this 0.1M solution of N_2H_4 · H_2SO_4 reduces 1 g of palladium. Preferably, the reducer should be added periodically, a rate of 5 mL per 15 min of plating being appropriate for batch operation.

Pretreatments employed on the parts to be plated have been similar to those used for electroplating. In operation of the electroless palladium plating, it is essential to avoid contamination with copper, keep the bath clean and avoid overheating. The palladium bath can be rejuvenated repeatedly by the addition of the dichlorodiammino palladium.

Literature references to papers on this process by R. N. Rhoda are:

- 1. Plating & Surface Finishing, 50, 307 (1963).
- 2. J. Electrochem. Soc., 108, 707 (1961).
- 3. Trans. IMF, 36, 82 (1959).

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Technical Editor's note: The edited preceding article 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 in the mid-1960s, 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.