Some Production Plating Problems & How They Were Solved—Part 23

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There is an old saying to the effect that "When one hears hoof beats, one should expect to see horses more frequently than zebras." This saying applies emphatically to the solving of production problems. In collecting a list of production plating problems from the technical service records of a plating supply house, it is easy to classify the causes into either "horses" or "zebras" with the horses far outnumbering the zebras. However, as with our contemporary news reporting media, zebras make the more interesting copy. Although the following cases contain more zebras, be cautioned that the obvious causes of trouble are the most frequently encountered. It certainly bears repeating that when problems occur in a process that has been successfully operated, some variable has changed out of range, and a systematic comparison with the operating variables obtained when the system was operating successfully will usually pinpoint the problem. Needless to say, this comparison is only possible if the acceptable ranges of these variables are known, and for this reason, a good basic guide for trouble shooting is, "Be just as busy when things are running smoothly, collecting data and observing, so that, when things go wrong, you have a basis for comparison."

Copper Roughness

Roughness has been a common problem in cyanide copper plating. It can be caused by a number of factors. Some cases are cited below:

Case No. 1

A plater was experiencing sporadic roughness which he had traced to the copper plating section of his copper-nickel-chromium process on zinc die castings. The roughness would appear suddenly and disappear almost as fast, usually by the time a serviceman arrived. The plater would begin to make additions and changes when the roughness appeared, such as adding cyanide, lowering currents, changing filters, adjusting temperatures and saying prayers, though not necessarily always in the same order, and eventually the roughness would disappear. There was a strong temptation to credit the last change with the solution to the problem, but the plater became suspicious when the "last change" varied through the whole spectrum.

This was equally frustrating for the serviceman, who arrived after the roughness had subsided for the first few calls and who had only rough chromium-plated castings to look at, feel, nod and act sympathetic. Analysis of the solution would show no possible clue and filtration of a gallon sample through a filter paper showed no evidence of insolubles.

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The cyanide copper solution was air-agitated, well-filtered and contained in a lined tank. The anodes were bagged and in sufficient quantity. All the work was pretreated in the standard manner. Plating racks were in good shape with no signs of nodular build-up or deterioration. The air intake for the air agitation system was piped from the outside through the roof and was equipped with a filter. The blower itself was located at the tank side.

The source of the problem was finally found in dismantling the air blower for other reasons. When the intake pipe was disconnected from the blower, some small pieces of scale dropped out. The intake pipe was black iron and, though the outside of the pipe had been well protected with periodic painting, the inside was heavily corroded. The black iron pipe was replaced with plastic pipe and the sporadic roughness disappeared. It was concluded that scale would become detached from the pipe and become ground into small particles before being blown into the solution.

Case No. 2

Jake (a fictitious name to protect the guilty) was running a department plating zinc die castings with copper-nickel-chromium in an automatic machine. Cyanide copper, in Jake's experience, was always rough and this was one of the facts of life. Quoting the printable portion, Jake said, "Roughness in cyanide copper is unavoidable. For 20 years, I've been fighting roughness and it can't be corrected or I would have fixed it by now."

The plating cycle was normal for zinc and the physical set-up didn't appear to be any different from others doing similar work. In fact, Jake had put additional filtering capacity onto the copper tank during one of his earlier campaigns to reduce the roughness.

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After some prolonged visits by a serviceman, it was determined that there was a varying degree of roughness - severe, tapering off to very little. The severe stage was not regular with the clock, but would usually start rough and sometimes go through a second peak later in the day. Despite Jake's claims though, it wasn't constant roughness, but more sporadic in nature. The problem then developed into tracing the reasons for the sporadic nature and finding some correlation with other occurrences during the shift.

Several tests and observations were made:

1. Roughness was definitely traced to the copper plating tank by: (a) turning parts over after the strike showed roughness only on the top as it left the copper plating tank and (b) buffing some copper-plated parts and replating in the copper produced parts just as rough as the normal production.
2. Roughness was caused by particles in the copper solution. These were not often discernible in samples taken from the solution. Chemical analysis showed that the composition was not unusual and an inspection of the analyst's records showed exceptionally little variation, with very frequent analysis.
3. The filtration procedure was checked. The lines going to the filters were rubber hoses, with inlets at one end of the tank and outlets at the other. The filters were shut down at the end of the day. (Jake had once lost a copper solution when an outlet hose slipped out of the tank at night.) This was supposed to give any suspended dirt or particles a chance to settle, and, with the filter inlet at the bottom of the tank, and permit picking this up more quickly when the filters were started the next day. Jake was fully aware that the filters required careful attention and had thoroughly impressed the filter man (who had several years of experience) of their importance. The filter man came to work two hours early in order to repack the filters and get them on stream while he adjusted tank levels and temperatures. He was thorough to the point of checking a sample of the filter effluent for clarity.

The reasons for the sporadic nature of the roughness were eventually found and were examples of stressing one point to the exclusion of others. First, when the filter man checked the effluent of the filters, he would raise the outlet hose to fill the sample bottle. This disturbed the particles that had settled overnight, as well as washing out several anode bags in the vicinity. The effluent stirred the tank to the extent that the advantage of letting the particles settle overnight was lost in a few seconds of pumping.

This would only account for part of the sporadic nature, and it took further work to determine that the analyst was sampling the solution from one of the filter hoses, though not a regular sampling procedure. The solution was sampled once a day though not always at the same time. The analyst was too well aware that the sample had to be representative, and he had been in trouble before by dipping his sample from the top of the solution shortly after a water addition had been made. Since that time, he had long adopted the procedure of checking with the man on the machine to see if water had been added recently. If not, he dipped his sample. If it had, he would pull up the filter hose for his sample, giving the anodes another unwanted washing and the tank another stirring).

As fate would have it, changing the habits of the filter man and the analyst did not eliminate all of the roughness, but it minimized its sporadic nature. This simplified the subsequent trouble shooting to the point where other changes were noticeable and bit by bit, the sources of the particles could be identified and corrective steps taken. The filter lines inside the tank were changed to pipe and permanently mounted. The inlet going to the filter was changed to a spider arrangement on the tank bottom to permit more thorough pickup, and the outlet was piped into a weir box to minimize the velocity.

Jake, if he were alive today, would be saying "If you are too careful you can get rough copper."

Dull Copper

Case No. 3

An owner of a plating shop called to ask for help in correcting his copper bath. The shop had a small automatic plating copper-nickel-chromium for zinc die castings. The work would be fairly bright for a few hours, but would soon begin to blister and produce dull areas. His plating "consultant" had him set up to add peroxide when the blistering occurred. When the plater did this, the blistering and dullness would disappear, but in the meantime he would lose several racks to scrap. The work was plated only for appearance and had no special thickness specifications to meet. The plater wanted to be able to correct the dullness and blistering by some other means or be able to predict when to add the peroxide before any rejects occurred.

Chemical analysis of the bath showed normal limits. The solution contained Rochelle salts and a supplier's metallic brightening agents. Hull cell tests run in the normal manner gave bright deposits with no indication of dullness or blistering.

The first suspect in blistering from a cyanide copper bath is chromium, and in this case it proved true, again. A second Hull cell test was run by delaying the electrical contact for one minute after immersion of the test panel. No deposit was obtained after applying the current for one minute. This simple test is very sensitive to the amount of hexavalent chromium in a cyanide solution and will easily detect less than 5 ppm.

In the tank, which had a power supply with current interruption, the work had the delayed contact necessary to passivate the copper surface from the copper strike. Work entering the strike had electrical contact before immersion and was not affected by the chromium present there. The strike was sound and quite bright. Thus, as the chromium-contaminated copper solution was being worked, the normal reducing action of the cyanide and the excess hydrogen generated at the passive surface would begin to reduce the hexavalent chromium to lower oxidation states. When it reached a sufficiently low level, the copper would begin to deposit, though non-adherent and with dull blotches. At this time, the plater would add peroxide and re-oxidize the chromium so that no deposition would occur. The copper deposit exiting from the copper tank was mistaken for plate but actually it was only the copper strike deposit. If the strike had not been so bright, the plater would have caught this sooner. A thickness specification would also have shown the problem.

The problem was corrected by discontinuing the peroxide additions and the "consultant" services, and adding a proprietary chromium reducing agent.

Carbonate Build-up in Cyanide Copper

Case No. 4

A plater had moved the plating department to a new location and expanded his facilities. Solutions were transferred and increased in volume with new salts. Carbonates were determined along with the other components after the solution had been adjusted in the new location. The carbonates had leveled off in his old operation at about 75 to 90 g/L (10 to 12 oz/gal) without any special treatments. At the new installation, an analysis, after only a few weeks, showed carbonates increasing at an alarming rate. When these reached 150 g/L (20 oz/gal), the plater wanted to know what to do and the reason for the increase.

The new solution was air-agitated; but so was the old one. Drag-out rates should have been of the same order because the parts were the same, only more of them. The anode area was sufficient and equivalent to about the same anode current density used in the old set-up.

Anode efficiencies were determined with samples of the solutions (with adjustments for the increased carbonates) and nothing unusual was found. Observations of the new system showed that the problem could be traced to the position of the air intake for the air agitation system. In the relocation process, the air blower was placed on an aisle and the intake was pulling the exhaust from internal combustion engines nearby.

After piping the fresh air intake from outside to the blower, the carbonates stopped increasing and began to drop slowly until leveling off at about 90 to 105 g/L (12 to 14 oz/gal). There were other possible contributors to this problem, such as operating with partially plugged anode bags, or improper bags and poor solution circulation. However, the presence of several times the normal amount of carbon dioxide in the air, and the efficient absorption of this by the alkaline copper bath, with the large quantities of air blown through the solution, combined to produce the rapid increase in carbonates.

Case No. 5

A new plating machine was installed to copper-nickel-chromium plate a rather complex zinc die casting. The copper cyanide solution was made up new. Periodic analysis showed an alarming increase in carbonates after only three months.

The copper solution was air-agitated and had the maximum anode area that the tank could physically hold. The anodes were bagged with an open weave cotton bag. The anode current density, calculated on total anode area, was about 0.54 A/dm^2 (5 A/ft^2). Chemically, the bath was normal though the concentrations were kept to high limits. Anode corrosion aids were being used and maintained at normal concentrations.

Anode efficiency curves on samples of the solution were normal. Figures showed a very low consumption of cyanide. Observation of the operation showed that owing to the complexity of the part, auxiliary nickel anodes were attached to the rack for aid in nickel and chromium plating. The auxiliary anode circuit was also being used at operating voltages (2V) in the copper plating tank. Thus, nickel anodes and not the copper tank anodes were carrying a significant portion of the current.

The operator had been reluctant to shut off the auxiliary power because the auxiliaries would then function as intermediate electrodes and the side nearest the tank anodes would act as a cathode and copper would deposit on the nickel auxiliaries. This would later dissolve in the nickel tank and contaminate the nickel solution. The operator was also reluctant to reduce the auxiliary current in the copper tank because of the fear that the part would be receiving too low a current and be more prone to low current density problems in the copper.

The rate of carbonate buildup was reduced and the total decreased and leveled off at a more reasonable level by reducing the voltage on the auxiliary circuit to a very low level, just barely enough to prevent copper deposition. The side of the auxiliary facing the tank anodes was eventually coated with rack coating and it was possible to shut off the auxiliary current in the copper tank.

Reduced Corrosion Resistance

Case No.6

A manufacturer of engine components was using a sulfamate nickel plating process. The part is exposed to high temperatures in use and has to meet a specification which includes a minimum resistance to salt spray after heating for a specified time and temperature. The manufacturer was having difficulty in meeting this specification consistently and asked for assistance.

The sulfamate nickel was being used in several tanks of various sizes to accommodate different parts and all the solutions were periodically analyzed and held within close limits. Stress analysis of the deposits were also routinely performed. All the tanks used the same type of rolled carbon nickel anodes from one source.

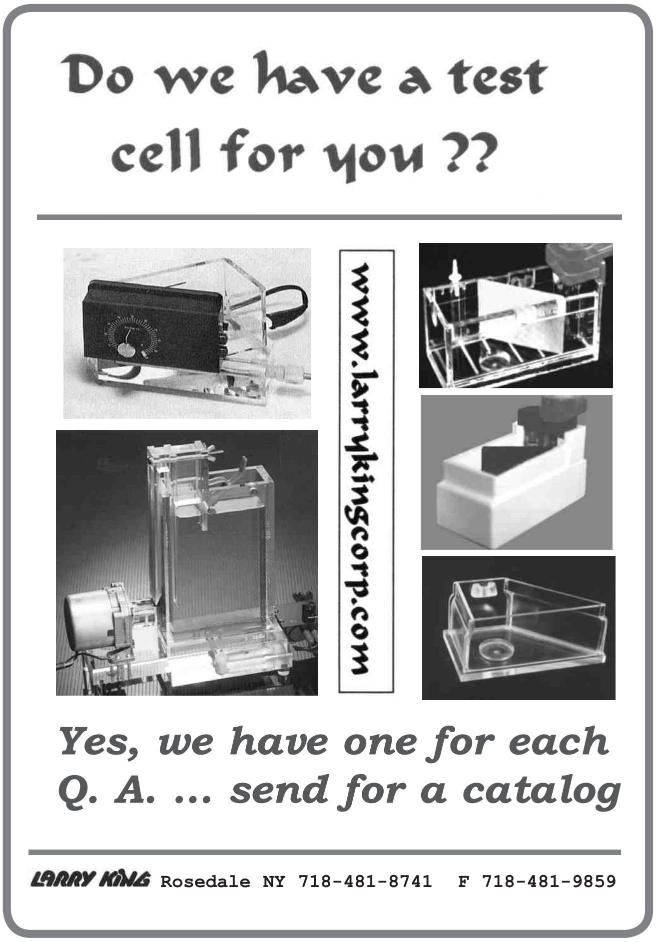
Chloride content of the solution was kept within specified limits. The operating conditions were kept standard for the different tanks. No visible difference could be noted from the deposits, and yet some would fail the salt spray test.

In tracing this problem, the following points were determined:

1. Sample parts passed the salt spray tests consistently if they weren't subjected to the heat treatment.
2. Some tanks produced more consistent results than others and regularly passed the heat-corrosion tests. These were identified.
3. Although the analysis and contaminant levels were comparable, the stress tests gave lower values for the more troublesome baths.

These three facts pointed to the source of the problem. Operation of sulfamate nickel with anodes of less than maximum activity with low chloride (or bromide) content in the solution will form small amounts of unstable sulfur compounds. These, if allowed to accumulate, will codeposit with the nickel. As this increases in amount, several changes can take place. The first indication is a lowered resistance to high temperatures. Further increases will produce, in order:

1. Lower stresses, eventually compressive.
2. Decrease in pH of the solution.
3. Increase in hardness and changes in other physical properties of the deposit.
4. Decrease in nickel concentration of the solution.



The accumulation of the unstable sulfur compounds had reached the first stage and was entering the second. The varying tank sizes were not using currents proportional to their size. Some larger tanks were used for plating relatively small areas on larger parts and some small tanks using more current per gallon of solution.

The problems were found but the solution was easier said than done with nickel shortages. The use of sulfur-depolarized nickel corrects the problem, but this plant had to delay making this change. In the meantime, increasing the chloride and modifying the tank loading practices to use maximum solution volumes for the currents used aided in the reduction of rejects. Purifying procedures were developed to treat the solutions to reduce the objectionable sulfur compounds.

Case No.7

A job shop was to nickel plate steel castings that had been extensively machined. The application called for about 75 μm (3 mil) of nickel, primarily for corrosion protection. The production was to be low and an air-agitated sulfamate nickel solution was to be used. In attempting to plate the first samples, the parts showed a few small pinpoints of rust forming after plating before the parts were dried from the rinsing.

Parts were cross-sectioned through the pinpoints of rust and examined under a microscope. Before sectioning, the parts were cyanide copper plated over the nickel to aid in the inspection. The cross section showed some surprising results. The pit in the nickel was due to a pit in the steel casting and, though the nickel failed to deposit inside this pit, the cyanide copper topcoat did. This is contrary to normal; the acid nickels have reportedly better microthrowing power than cyanide copper. Reasoning from this fact, then the logical difference between the two might be the cleaning power. To test this, other parts were cleaned more thoroughly, and though the pinpoints were reduced, some were still present. The improvement was significant, though, so a very stringent cleaning and rinsing cycle was tested. This included soaking for extended times in cleaners (one hr) for the test cycle, adding wetting agents to rinses just prior to rinsing the part, adding wetting agents to the acid pickle and following rinses, and increasing the wetting in the nickel solution. No pinpoints of rust appeared and the part was cross-sectioned through a pit in the steel which had been located before plating. The cross section showed the pit to be plated with substantial thickness of nickel.

With the problem identified, the pretreatment cycle was modified to clean out the pits and the problem disappeared. The casting through its many machining operations had been soaked in many oils at different machining stages and these had been absorbed in the tiny crevices of the porous (pit) areas. These oils were difficult to clean out and the nickel would not plate through them. The cyanide copper did and provided the best clue to correction.

The edited preceding article [Plating, ***56****, 546 (May 1969)] is based on material compiled and contributed by Dr. John D. Horner, as part of the Plating Topics series, originated by Dr. Samuel Heiman, that ran in this journal. It dealt with everyday production plating problems in the late 1960s, many of which are still encountered in the opening years of the 21st century. Much has changed ... but not that much. Although many cyanide processes are no longer with us, cyanide copper remains very important today. 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.*