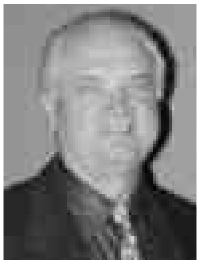
Advice & Counsel



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Bright Nickel Problems

Dear Advice & Counsel,
My company periodically experiences a number of plating problems in our barrel nickel plating operation. The major problems are appearance issues such as pitting and dark deposits, but periodically we also suffer brittle deposits and adhesion troubles. We need help.

Signed,
Odeon Niquel

Dear Mr. Niquel,

Based on a visit to your shop, the following is a summary of what I think is going on:

Barrel Copper-Nickel On Zinc Die Castings

This line utilizes the following processing steps:

a. Hot alkaline soak clean
b. Rinse
c. Acid pickle
d. Rinse
e. Caustic rinse
f. Cyanide copper plate
g. Drag-out rinse
h. Rinse
i. Rinse
j. Acid pickle
k. Rinse
l. Nickel plate
m. Rinse
n. Rinse

Major complaints on this line are parts exhibit discolored nickel deposits and nickel over nickel peeling.

Comments/Recommendations

Discoloration in the nickel deposit is typically traced to metallic impurities. Important impurities related to discoloration of nickel include copper, lead, zinc and tin. Of these, copper and zinc are obviously the most likely contaminants to be present in the plating solution in this line.

Copper is especially harmful to bright nickel, because concentrations at and around 5 ppm can cause poor adhesion when current is interrupted (such as occurs in barrel plating). Copper at lower concentrations can also cause dark deposits at low current density areas (as would be found near the center of a barrel load).

Zinc is well known to cause shiny black streaks in bright nickel deposits under normal current density conditions, and a dull dark deposit at low current densities. The effect of zinc may appear at concentrations as low as 20 ppm, but more often occurs when the concentration approaches 100 ppm.

Dirty rinse tanks indicate problems.

The use of a single rinse after acid pickling (step k in the sequence shown here) subjects the nickel plating solution to a continuous stream of zinc and copper contamination, which will cause the plating problems often experienced on this line.

We noted that all the rinses on this line are air agitated, but that the agitation was inoperable because of poor maintenance. Further, each rinse had water coming in at the top and going out at the top. When a rinse is not properly agitated and rinsewater comes in at very low flow and goes out the top, chemical stratification can occur, resulting in the next barrel load being ineffectively rinsed and cross contaminating all process tanks following such a rinse.

Also, we noted that each rinse on this line has large mounds of solid residue at the bottom, indicating a poorly functional rinse and confirming contamination problems.

We recommend replacing the air agitation with recirculating pump agitation (with eductors is preferred, if they can be fitted into the rinse tank). We would also like a 20 percent increase in water flow, if this is possible without affecting wastewater treatment efficiency.

We recommend that the barrels of work be rinsed in the rinses **after** nickel plating, in addition to the rinse that is used before nickel plating, to improve rinsing efficiency. Because the rinses after nickel plating are not recycled back to the plating tank, this will better protect the nickel from introduction of copper and zinc from the acid.

Copper and zinc will still be introduced continuously by the mere act of plating onto zinc parts that have a copper plate, because the nickel solution will dissolve some zinc from blind holes and other surfaces not covered by copper. For this reason, it is very important to operate the low current density dummying cell on a continuous basis. The cell we spotted had several deficiencies, including insufficient cathode surface area and purification at too high of a current density.

The following guidance, originally provided by Louis Gianelos in an article in *P&SF* way back in 1977, is still valid today:

Electrolytic Purification

In some cases, notably in plating zinc-base die castings, the solution is continuously contaminated with metallic impurities such as copper and zinc. When such contamination is troublesome, continuous electrolysis can be used to purify the solution without interrupting the plating operation. This method takes advantage of the fact that at very low current densities some metallic impurities—notably copper, zinc, lead and cadmium—plate out at a faster rate than at higher current densities. The procedure requires a small auxiliary tank suitably lined and equipped with a series of anode and cathode surfaces. It should be operated at a cathode current density of about 2–5 A/ft^2. A suitable arrangement of a pump and weir to maintain constant circulation of the plating solution from and to the plating tank should be provided. The auxiliary tank requires 0.1 $in.^2$ of dummy cathode for each 400L (1 ft^2/100 gal) of plating tank volume. Since agitation accelerates the removal of impurities, the auxiliary tank should circulate 1/4 to 1/3 or more of the total volume of solution per hour of operation. The nickel-plated dummy cathodes should be corrugated to provide current density variation and placed to have a maximum distance of 7.62 cm (3 in.) between the anode and cathode surface. The ultimate design of the auxiliary tank should provide a minimum flow rate of 1.8 m/min (6 ft/min) past the cathodes.

The nickel solution should be monitored for copper and zinc content, and these metals should be kept below 3 ppm for copper and preferably below 20 ppm for zinc (although a higher level for zinc may be viable with the concurrence of your additive supplier).

The barrels are continuously inundated with processing solution from barrels that pass over those sitting in tanks. As a result, large amounts of solids build up on the superstructure. These solids will contain copper, cleaner salts, and corrosion products. None of this material is compatible with the nickel plating solution. If a large chunk of solids falls into the solution periodically, serious plating quality problems will occur. Also, the chemical splashes are washing the anode hooks in the plating tank, causing corrosion of the copper bus and isolation of some anode baskets (which creates poor current distribution and anode polarization that can destabilize the chemical make-up of the solution). We recommend a rigorous program to reduce this problem:

a. The superstructure needs to be cleaned frequently to eliminate the residue.
b. The dwell time over a process before a barrel is moved over should be increased, if at all possible.
c. Anode hooks subjected to chemical splash need to be protected by installation of splash guards.

The barrel door clamps are located in such a manner that they pass too close to the anode baskets in the copper plating tank, producing a bi-polar condition that causes copper deposition on one end of the clamp, and clamp dissolution at the other end (contaminating the plating solution). This can be fixed by coating the clamps with plastisol or moving the anode baskets away from the clamps (closer to the tank wall).

There are large air gaps between processing tanks that should be covered with drip trays to prevent chemical loss to the floor and reduce waste generation.

Barrel Copper-Nickel on Steel

Problems experienced with this line are discoloration of plated parts and adhesion problems that appear to be nickel peeling off nickel. The nickel plating solution on this line is batch carbon-treated twice per year, yet periodically brittle deposits are obtained.

This plating line utilizes the following processing steps:

a. Parts are cleaned/washed off-line
b. Acid pickle
c. Cyanide copper plate
d. Drag-out rinse
e. Rinse
f. Rinse
g. Nickel plate
h. Rinse
i. Rinse
j. Rinse

Comments/Recommendations

This plating line has many of the same problems that were mentioned for the zinc die casting line (copper, zinc contamination, poor rinsing, poor rinse agitation, splashing from over-head traveling barrels).

There is an additional major flaw in the processing of parts on this line. There is no acid dip between the cyanide copper plate and the bright nickel plate. It is not reasonable to assume that the alkaline film that is present on the parts after copper plating will be rinsed off in the rinses after copper plating. Even if these rinses were highly effective (which is far from the case), the surface of the plated copper will carry an alkaline film that contains copper ions along with the other ingredients in a cyanide copper plating solution. This is then carried into the nickel, causing copper contamination of the nickel and introducing other contamination as well (tartrates, carbonates, organics).

An acid dip (plus rinsing) needs to be utilized between the cyanide copper and the nickel-plating processes.

The processing sequence should be:

a. Parts are cleaned/rinsed, off line
b. Acid pickle
c. Rinse
d. Rinse
e. Cyanide copper plate
f. Drag-out rinse
g. Rinse
h. Rinse
i. Acid pickle
j. Rinse
k. Rinse
l. Nickel plate
m. Rinse
n. Rinse
o. Rinse

Continuous carbon filtration appears to be adequate on this line, as 20 lb. of granular carbon are used for 1,800 gal of plating solution, which matches up with a rule of thumb 8 oz/50 gal of solution (that would calculate to 18 lb for 1,800 gal). The carbon is replaced weekly.

We suspect that the periodic bouts of brittleness are related to the high drag-in rate of organics caused by the absence of an acid dip and subsequent rinsing between the copper and nickel plating processes.

While the cyanide copper plating process provides additional cleaning and some corrosion resistance benefit, the company can consider a change to a process that deposits only nickel directly over the steel. Replacing the cyanide copper with an electrocleaning process can provide the added cleaning. The major benefits obtained from such a change would be:

a. Elimination of the source of copper contamination that plagues this line, resulting in lower reject levels and higher productivity

b. Reduction in operating costs, because cyanide waste is reduced
c. Increased safety/health by elimination of a cyanide source

Elimination of the cyanide copper plating process would require an increase in nickel plating thickness to maintain the corrosion resistance of the steel parts that are plated on this line. An investigation should be conducted into how much additional nickel is required. At first, a straight substitution of copper for nickel should be tried. If too much nickel is required to compensate for the loss of the copper (dimensions are affected too much), a duplex nickel plate consisting of semi-bright nickel followed by bright nickel has the ability to provide excellent corrosion protection over steel without a copper underplate.

Pitting in Nickel Plating

I did not see any pitting problems during my visit. The following is a summary of conditions that can cause pitting based upon my experience and that reported by others in the industry:

1. pH too low
2. Inadequate agitation
3. Too high current density
4. Low wetting agent content (maintain surface tension below 35 dynes/cm)
5. Organic contamination
6. Iron contamination
7. Copper contamination
8. Poor surface condition (burrs, surface porosity)

Because this line plates nickel over steel, the likely suspects are iron contamination, copper contamination, organic contamination, and (after looking at the parts) poor surface condition. Copper contamination can be treated by low current density electrolysis. Iron contamination can be treated through the addition of an iron complexer (commercially available), organic contamination is typically handled by carbon treatment procedure(s). Poor surface conditions are normally cured by improving part manufacturing/handling methods. P&SF

From the Mail Box

Dear Advice & Counsel
Enjoyed reading your column on "What Causes Macro-Cracks in Chromium Deposits" in *Plating & Surface Finishing*, December 2002.

Our Company, Godfrey & Wing, Inc. impregnates castings under MIL-STD-276A to solve porosity problems in cast metals. However, we also process a significant number of parts that are chrome plated in order to "seal" the chrome and eliminate or reduce the negative effects of micro or macro cracks in chromium. Many aviation applications detail the process specification as a solution to this problem.

Tom Shantz, Sales Engineer
Godfrey & Wing, Inc.
19800 Miles Road
Cleveland, OH 44128

Dear Tom
Thanks for the info. Impregnation is exactly what our client used to solve the problem of cracked chromium. I'll keep your company in my files.

Frank