"Measles Outbreak"

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Dear Advice & Counsel,

I am a plating shop manager at a captive facility that specializes in the production of aerospace components. We have a very small shop that only plates cadmium and zinc-nickel on hardened steel parts. As more production changes from the cadmium finish to zinc-nickel, we have run into a problem that has us totally confused.

We operate an alkaline zinc nickel plating process that delivers a 95% zinc deposit. The additive package is purchased from a commercial supplier. The plating tanks and rectifiers are less than one year old and are in very good condition. We analyze the solutions daily, and they are typically well within recommended concentrations. The brighteners are evaluated using Hull Cell tests, and we make adjustments based upon visual examination of panels plated before and after additions of various proprietary additives.

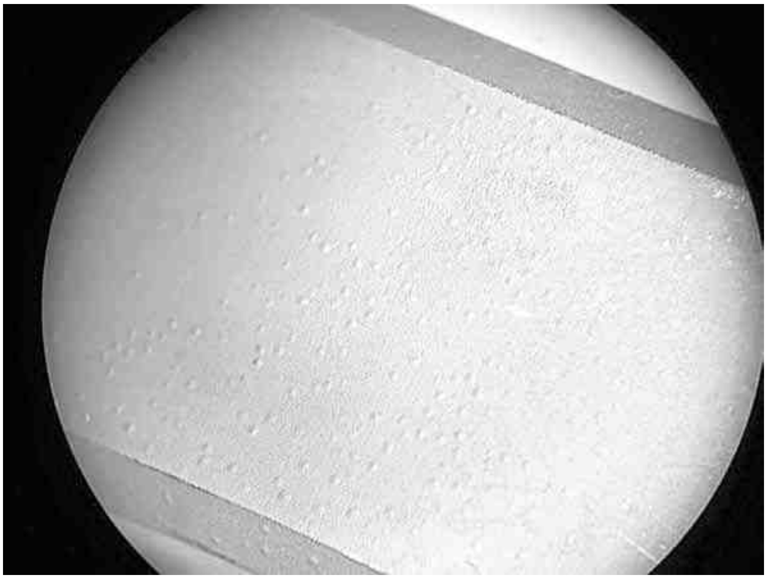
Most all of our parts require hydrogen embrittlement relief baking after plating. Some parts are baked at 375°F (190°C), others require a lower temperature (275°F; 135°C). Our plating thickness is generally around 0.0005" (12.7 μm). A new solution functions very well and we seem to have no problems.

After several weeks of production, parts show very small blisters only after baking (See photo.). These usually show up within the first 60 minutes of baking. The blisters are uniformly dispersed and do not appear to be related to current density or part geometry, but they do seem to be far more prevalent over ground or blast surfaces versus machined surfaces.

If we change to a new solution, using the same steps for part preparation, the problem goes away, but returns after several more weeks of operation. We are convinced that something is going on with our plating solution, but we don't know what. We have checked the plating solutions for impurities and we did find as high as 3.5 ppm lead on one of our three plating solutions, but we experience blistering even when the lead content is at "not detected" levels.

Please investigate this problem for us.

Signed,
Stymie



Dear Stymie,

Our first discussion needs to cover the general issue of hydrogen effects and steel. Any plating process that is less than 100% cathode current efficient is going to generate some hydrogen gas along with the deposit. High strength steels will absorb hydrogen ions during the first burst of applied current for plating. As plating builds up, the deposit acts as a barrier to further absorption of hydrogen. As a result, the hydrogen concentration profile consists of a "bump" in hydrogen concentration that tails off to "zero" concentration as we go deeper into the steel. The more stressed the steel is from operations such as blasting and grinding, the higher the tendency for absorption of hydrogen. Some blast and ground finished parts need to be baked ***before*** plating to limit the hydrogen take-up during plating. Also, past experience has shown better results when thin deposits are applied, and then baked, and then the balance of the specified deposit is plated over the initial one. The hydrogen has an easier time diffusing through a thin deposit than one that is 0.0005" (12.7 μm) thick. A final bake is then used as insurance.

Studies have shown that we need to get rid of this "bump" in hydrogen concentration near the surface of the steel, and we do this by heating the part at a temperature high enough and for a time long enough to cause the hydrogen to diffuse out of the steel into the atmosphere. The bake also causes some of the hydrogen to diffuse into the steel and "spread out." The result is that no spot within the steel has a hydrogen concentration high enough to initiate a crack, which would cause failure of the part when statically loaded.

In your case, we investigated several parts and found that the blisters were located between the basis metal and the initial plated deposit. We also found that some parts had far more plating than specified (three times too much). Further, the solution you are using has an additive package that includes brightener(s) and other organics. We therefore concluded that the blistering was caused by hydrogen gas which could not readily diffuse through the deposit during the baking because the deposit was not porous enough. Instead, the hydrogen gas expanded and "pushed" up on the deposit, creating the blisters.

We dug a bit deeper into your process and found that organic additives were being added under less than optimum conditions. Normally, the additives are added based upon ampere-hours of operation, while you were adding them based upon visual interpretation of Hull Cell panels. We suspect that this visual method resulted in the addition of large amounts of additives. After a few weeks of operation with this visual control, the organic content of your solutions would reach a level where the deposit was too "dense" to allow for hydrogen diffusion.

Additionally, we found that the zinc-nickel plating process was operated with no control over anode-cathode ratio and little control over plating current density (Parts were racked without regard to total surface area.). Further research and a few calls to some friends in the NASF community revealed some interesting information:

Boeing has a patent pending on a low hydrogen embrittlement zinc-nickel plating process (L.M. Tran, M.P. Schriever & J.H. Jones, U.S. Appl. #20060254923, application published 11-06-2006). In the text of this patent, Boeing teaches the following:

"The plating solution is substantially free of brightening agents, which retard hydrogen bake-out, ... or at least inhibit release of hydrogen from the article."

"It is most preferred that the coating consist of about 90% weight zinc and about 10% nickel. Here, corrosion resistance is maximized and hydrogen embrittlement is minimized."

"Best results occurred at 45 ASF, giving a good coating distribution, good resistance to corrosion and good resistance to hydrogen embrittlement. Specimens at 36 ASF and 68 ASF also showed good results in all categories, but the specimen at 68 ASF showed slight corrosion."

German Patent DE 19834353A1 (02-03-2000) teaches the following:

"Electrolysis of alkaline zinc-nickel baths containing poly(alkyleneimines) produces amine breakdown at the anode into nitriles and cyanides if the anode is exposed to the plating bath."

Taskem Inc. has a patented method of avoiding this problem by encasing the anode in a membrane cell [R.E. Frischauf & W.E. Eckles, U.S. Patent 6,755,960 (06-29-2004)].

Based on the above, I recommend the following:

1. The anode cathode ratio should be controlled by measuring the surface area of the parts and making sure the ratio is less than 2:1, preferably 1.5:1
2. Consider baking the parts before plating and consider baking twice - first after applying a thin (0.0001"; 2.5 μm) deposit then applying the majority of the deposit.
3. The current density needs to be more carefully controlled.
4. Additives should be added based on ampere-hours.
5. Keep the brightener concentration as close to zero as possible (be careful not to infringe upon the Boeing patent).
6. Consider increasing the nickel content to near 10%.

Note: Our thanks to Becky Zinni-Kettering of Taskem Inc., for her help with this problem.

In Memoriam

Richard (Dick) Russell, 78, of Duluth, Georgia, died October 15, 2007. A memorial service was held on October 19 at Peachtree Corners Baptist Church in Norcross, Georgia. Mr. Russell, a native of Detroit, Michigan and a graduate of the University of Detroit, was a veteran of the U.S. Army, and the owner/operator of Dixie Industrial Finishing, Tucker, Georgia, for 40 years. He was a member of the First Baptist Church of Atlanta, Berkeley Hills Country Club and a past Board Member of the NAMF. He is survived by his wife Margaret Russell of Duluth, Georgia; son, Robert Russell of Lawrenceville, Georgia; two daughter and sons-in-law, Patti and David Henderson.of Norcross, Georgia and Terri and Dave Boyce of Alpharetta, Georgia; two sisters and brother-in-law, Doris Weyant of Hudson, Florida and Elaine and Roger Zatkoff of Bloomfield Hills, Michigan; and four grandchildren, Kyle Henderson, Kasey Henderson, Caleb Boyce and Lauren Boyce.

Test Your Plating I.Q. #436

By Dr. James H. Lindsay

Preparation for electroplating

1. Rank the following soil types in the order of their ease of removal (easiest first): (a) buffing compounds, (b) light mineral oils, (c) silicones, (d) general metalworking lubricants, (e) mold release compounds

2. The first step in a plating preparation cycle is precleaning. What is its primary purpose?

3. The last step in a plating preparation cycle is a pickling, or acid dip. This step is essential to two major attributes in the final part. What are they?

4. Ultrasonic cleaning involves frequencies above the audible range, generally from ___ to ___ kHz; nominally ___ kHz. What is its primary mechanism in cleaning?

5. Name some precleaning processes (up to five major ones).

Answers on page 51.