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AESF Heritage: The 2002 Hydrogen Embrittlement Seminar: 3. Hydrogen Management – Averting a Crisis

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ABSTRACT

In cleaning and plating hardened ferrous and other substrates sensitive to embrittlement, careful attention must be given to post-plate hydrogen embrittlement (HE) relief thermal treatments. Because customers can't easily check the residual hydrogen level in the parts plated, they rely on the plater for assurances that sound hydrogen management practices have been instituted. Operators need awareness of the complexity of HE. This paper gives tips for HE management, such as: following a detailed cleaning and plating procedure; maintaining and calibrating oven equipment / controls; keeping quality records that are available for review; and performing periodic embrittlement tests.

Hydrogen gas causes pitting and streaking in our electrodeposits and builds up under a foam blanket in our electrocleaners until some careless operator sparks an ear-shattering explosion. Creating hydrogen, or any gas for that matter, diverts expensive power from its intended mission of depositing a metallic coating. It's a real nuisance to platers and we'd be best off to avoid it altogether. In Scouting, leaders have been known to remark, Scouting would be great if it wasn't for the boys. Restated for the plating – hydrogen scenario, one might be tempted to remark plating would be great if it weren't for the hydrogen. These are surrealistic statements; just like we can't take the boys out of boy scouting, as long as we're using aqueous based electrolytes - that is those based on di-hydrogen oxide or H_2O - we're stuck with hydrogen in one form or another. Since the part is negatively charged to attract the positively charged metal ions, it also attracts positively charged hydrogen ions. We can't eradicate hydrogen from our processes, but we can take precautions to manage the deleterious effects of hydrogen.

While a nuisance to platers, hydrogen can be catastrophic to the function of many components manufactured from hardened ferrous materials and other substrates sensitive to the disastrous embrittling effects of hydrogen. While this paper is restricted to hydrogen embrittlement in ferrous metals, other materials including alloys of nickel, titanium and aluminum are susceptible to the degrading effects of hydrogen. Even electroless copper has been shown to be weakened by increased hydrogen content.

When hydrogen gas diffuses into an HE sensitive material, even at low part-per-million levels, over time, the hydrogen can continue to diffuse along grain boundaries. As the smallest atom in the periodic table, it diffuses readily even at room temperature. It accumulates until the stress of the added volume of gas initiates a crack in the material. Further diffusion results in greater crack propagation resulting in potentially catastrophic failure: a helicopter falling out of the sky, a bridge collapsing, a failed prosthetic device, a brake pedal that is no longer connected. Any of these is a crisis in the making.

Unless you're an opportunistic lawyer, we're all interested in averting a crisis. Besides endangering lives, in the litigious society that we now live in, a crisis leads to lawsuits or at least damages far exceeding the value of plating services rendered. A plater's embrittlement records and documentation can become court records to redirect the suit happy finger pointers. If the records aren't available or complete, an unsuspecting plater can bear the brunt of liability whether or not embrittlement was positively identified as the root cause. Because there are so many uncertainties with the subject, it makes for an easy scapegoat. Records and documentation alone are only one facet of sound hydrogen management. Equally important are design and contract review, process control, calibration and training to mention but a few. Hydrogen management must be well integrated within a sound quality management system.

Few platers have any design authority. We must deal with the cards dealt us, but hydrogen management can and should start at the design stage. Dini suggests a multi-pronged approach to prevention of hydrogen embrittlement that includes elimination of residual stress in the part before processing. Residual tensile stress from grinding or cold working, for example, can render a part more sensitive to the embrittling effect of hydrogen. A stress relief bake prior to processing, as specified by many specifications, or as Dini suggests, electropolishing or shot peening will reduce absorption of hydrogen. In addition to calling for pre-plate stress reducing treatments, the design must permit the plater to easily ascertain the material type and hardness or tensile strength. In lieu of this, the onus falls on the buyer or purchasing agent issuing the purchase order. The plater arguing that "if embrittlement was a concern they should have called for a bake on their PO" doesn't hold up in court when the specification states "unless otherwise specified all ferrous parts shall be baked following plating." Plating firms need to be proactive in determining material hardness prior processing to clearly establish not only whether or not parts get baked after plating, but also whether or not they require a pre-plate stress relief bake. A clear, unambiguous drawing callout, something the designer certainly has authority over, is the first step in hydrogen management.

The specifications cited by the designer should also be consistent. The embrittlement language in AMS specs is quite different from MIL specs. For example, there are several AMS specs that make no reference to embrittlement testing. For electroless nickel, the MIL spec requires baking on parts HRC 40 or greater while many corporate standards cite HRC 36 as the minimum hardness where baking should begin. ASTM lowers this threshold of concern to HRC 31. Even within a particular organization, specifications can lead to confusion. For instance, take SAE's AMS specifications electroless nickel, namely 2404 and 2405. The former requires that the purchaser of the plating service cite the material's hardness or tensile strength in the ordering document. AMS 2405 contains no such language. It seems like no big deal, but led to an audit finding at Anoplate within the last month. Some specs are contradictory or at least confusing. For instance, a proprietary cyanide strip for copper from steel doesn't have to be embrittlement baked after stripping but if made up with generic NBS and cyanide, the exact proprietary formulation sold, the Boeing specification insists that it be baked for embrittlement relief.

Lastly, where on earth did ASTM Committee on Metallic and Inorganic Coatings dream up their specification for post plate embrittlement relief? It cites sixteen different baking cycles; however, this is nothing but a compendium of baking cycles from dozens of different sources. Which is the right one? Several factors must be carefully weighed when choosing a bake cycle. It is virtually impossible for the plating house to be able to choose. Paragraph 4.4 of ASTM B 850, Standard Guide for Post-Coating Treatments of Steel for Reducing Risk of Hydrogen Embrittlement, clearly drives this point home.

The electroplater, supplier or processor is not normally in possession of the necessary information, such as design considerations, operating stresses, etc., that must be considered when selecting the correct embrittlement relief treatment. It is in the purchaser's interest that his or her part designer, manufacturing engineer, or other technically qualified individual specify the treatment class on the part drawing or purchase order.

While the plater can plead ignorance when it comes to applied stress in final use of a component, he has knowledge of the plating process that may make parts more or less prone to failure due to hydrogen. For instance, chromium plating is a very inefficient process as evidenced by the amount of gassing that occurs. Due to the amount of hydrogen produced, the plater should be more concerned with baking following this process than one more efficient such as acid copper or cyanide silver, for example. Even when we're using an efficient bath, operating outside a specific current density window, for example, can result in greater hydrogen evolution. This is where the suppliers can assist. They must offer more than instructions on making up and operating the bath. They have to include maximizing cathode efficiency, tips on maintaining the desirable internal deposit stress and optimum crystalline structure.

One might ask is crystalline structure of the deposit critical in dealing with hydrogen embrittlement? When asked why manganese phosphate can be embrittlement relieved at room temperature Joe Menke, Materials Engineer with US Army's Rock Island Arsenal, pointed to the coatings crystalline deposit with 2 to 3% porosity. He challenged me to do a ferroxyl porosity test on a phosphate coating; it will always fail. In his argument he continued to cite the columnar deposit of low-embrittlement cadmium as opposed to brightened cadmium deposits which are laminar in structure. A columnar structure more easily permits hydrogen embrittlement relief and is why the military standard for cadmium plating forbids brighteners in the cadmium bath when plating hardened steel components.

A plater's Sales & Quoting department is often first to have contact with a buyer regarding a particular application. It is imperative that the ancillary requirements of the application – *e.g.*, special cleaning or baking – are identified during this interaction. Any specifications called out by the customer on the Request for Quote (RFQ) should be available for review since many processing requirements are contained in these documents. Furthermore, the plater should have some means to ensure that the most recent revision of the specification is be used as embrittlement requirements are often upgraded or otherwise revised. At a minimum, Sales & Quoting personnel must understand the properties of the to-be-plated material as well as the effects the required surface treatments will have on those properties, including the materials susceptibility to hydrogen embrittlement.

Once the RFQ has been accepted and the parts arrive at the facility for plating, a second round of contract review should be initiated. Contract review reconciles any discrepancy between customer's requirements (as delineated by the PO and including any drawings and / or specification cited therein) and the process and testing capabilities of the plating house. The callout is reviewed to determine whether (a) it can be done; and (b) how to best get it done given the intricacies of the shop and the specification requirements. This is also the time to clear up any vagueness and clarify expectations. For instance, if we've quoted a
particular part "this price assumes no baking required" and the customer sends in the job without citing the RFQ while still calling out a specification that calls for a bake, this is a good time to clarify expectations. Unlike plating that doesn't stick and can be stripped and redone, once a part is embrittled there is no recovery.

Many specifications including the aerospace industry's AMS and MIL specs include a section entitled "Ordering Documents." These typically contain language that requires the purchaser of such plating services to include the material type and hardness or ultimate tensile strength. Doing so ensures that the plating house knows whether or not to post plate bake the parts or not. Too often it's left up to the plater to guess. Since many of these specifications state unless otherwise specified bake, plating firms must be proactive in determining whether or not parts require baking. This means either someone in Planning must call the customer or another approach is to clearly state in quoting "PRICE PRESUMES NO BAKING" unless there is sufficient information to ascertain differently.

Buyers must create purchasing documents that clearly delineate the specific material and either hardness or ultimate tensile strength so that the plating house can make an informed decision as to whether or not the parts require embrittlement relief. There are certainly cases where the application is non-critical and where economics suggest the baking can be waived. However, this is the buyer's prerogative and should never be left up to the plating house. Once again, as alluded to in the ASTM guide on post-plate embrittlement relief, few plating shops have the resident metallurgist or staff engineer capable of rendering such a judgement, even when presented with all the application information.

Platers have to be aware of the catastrophic effects of hydrogen embrittlement and what can happen if they're lax in their duty to follow the prescribed procedures. Awareness is the most critical issue. A sharp plater may query why one EN job is baked for 4 hours while another is baked 24 hours. Don't try to rationalize or apply theory; two rules for responding to these types of inquiries: (1) reinforce awareness: "it's good that you are aware of potentially damaging hydrogen embrittlement " and (2) ordering document compliance: "we strictly comply with the specifications referenced by the PO or drawing." More than once I've been overheard telling operators "we can only get in trouble for not following the specification."

There are three parameters for any embrittlement bake that need to be controlled and recorded: the dwell time between parts coming out of the plating tank and the time the parts are at the minimum specified baking temperature, the temperature range for baking, and minimum duration for baking. A plating firm must be religious in how they control and record this information. Auditors have a passion for reviewing embrittlement records. Besides the oven chart itself, the individual router for the job should include exact time the parts were removed from the plating tank. Often this must be expanded to include serial numbers so the exact process for each individual part can be traced. If the firm has more than one oven, the records should include some sort of oven designation or description.

One of the most overlooked areas in regard to embrittlement relief are the ovens themselves. Like any other piece equipment used for processing, they fall into the category of Inspection, Measuring and Test Equipment. As such, they require periodic calibration and maintenance to ensure they are suitable and accurate for use. Calibration goes well beyond a simple thermocouple probe check. Semi-annual, 9-point (or more) uniformity surveys should be performed to ensure that that the temperature displayed and oven controls are representative for all regions of the oven, also defined as the "working zone." The how to of instrumentation, sensors and controls of thermal processing equipment, including system accuracy checks and uniformity surveys, is covered in many consensus and corporate specifications, but most often cited is AMS 2750 entitled Pyrometry. Even with a calibrated, state-of-the-art oven, some common sense must still be used. A recent article, "Are You Really Baking Out the Hydrogen Embrittlement" from *American Fastener Journal* retold one fastener manufacturer's trouble with a plating shop over baking. The author cited examples of how different size hardware takes varying lengths of time to come up to temperature in a given oven. Also, how ovens and bulk loads can have hot and cold regions so that parts in the center of a mass don't get baked as long as those on the outside of the load. The author concludes that for high volume platers doing tons of parts per shift, a continuous belt furnace provides more assurances than batch ovens.

Another important link in hydrogen management is monthly embrittlement testing. We've already agreed that hydrogen is a given in plating therefore we must periodically check how capable our process is at removal of the hydrogen. In some cases, this test is performed by a general testing lab, however, this is a specialized test and many labs catering their services to the metal finishing industry have gathered a wealth of history in this field. If all you're getting is a report with a pass/fail edict, you're paying too much. Anoplate testing house specializes in just embrittlement testing. Whenever there is a failure, we'll receive a checklist of possible areas to explore for process variation that can lead to test failure. Also, when you're having the test performed, make sure that it is indeed indicative of the requirement. For instance, how does one test for the 120-hour room temperature embrittlement relief cited in MIL-DTL-16232? Until we were recently corrected, we would process the bars, hold them for the mandated 5-day relief cycle and then ship them to our outside testing firm. They would commence the testing in a couple of days but what were we actually testing? Clearly we weren't testing the 120-hour requirement rather something greater depending on how quickly we shipped the bars and how quickly our test lab loaded the specimens. It takes a little more logistics and coordination, but today we're testing the 120-hour requirement.

To lay the blame for hydrogen on just electroplating is shortsighted. In Chapter 2, Hydrogen Embrittlement, of Dini's *Electrodeposition*, he lists eight potential sources of hydrogen as:

- Acid Type Corrosion
- Electrochemical Cleaning
- Pickling
- Electroplating
- Containment Vessels for Hydrogen
- Dampness in Molds During Casting
- Humidity in Furnaces During Heat Treating
- Remnants of Drawing Lubricants

Electroplating is only one source of eight named. A mechanical plater used to spout at every ASTM committee meeting that all electroplating specifications should suggest the use of mechanical plating over electroplating on hardened parts. While mechanical plating itself doesn't involve liberation of hydrogen, just as in electroplating, they must clean and descale parts prior to plating. Cleaning, whether anodic, cathodic, or soak, can emit hydrogen and certainly acid dipping, with or without an inhibitor can. Just replacing all electroplating with mechanical plating where hydrogen embrittlement is concerned is oversimplifying the problem. Perhaps the instigator had some ulterior motive (you think!).

Another panacea often cited are inhibitors, those magic elixirs added to mineral acids that retard hydrogen pickup. While Willan's study on inhibitor use did demonstrate their ability to act in this regard, the fact of the matter is that platers are wary of inhibitors. Typically these create a tenacious organic film on the surface of the part that requires additional cleaning and immersion in an uninhibited acid prior to plating. This lengthens the process and requires additional floor space. If this film isn't sufficiently removed, the adhesion of the plating is compromised. The merits of using inhibited acid are often outweighed by the fear of producing substandard plating quality. Furthermore, ASTM B 850's Note 3 states that use of inhibitors in acid pickling may not minimize hydrogen embrittlement.

Even when the evidence points to hydrogen embrittlement, manufacturers often differ in their response. In 1996 GE Aircraft Engine's Manufacturing & Quality Technology Department Best Practice 96-013 described cracked components following black oxide processing. They attributed the failures to the acid used to pretreat the 200 ksi tensile strength steel prior to black oxide. GE offered several "recommended best practices" but continues to specify black oxide on some of their aircraft engine components. On the other hand, during a crash investigation, Sikorsky identified caustic embrittlement as the mode of failure on steel parts that were black oxide treated. Their response was to ban the use of all black oxide, a coating we had been putting on various roller bearings for them and other aerospace manufacturers for decades.

In closing, a fastener manufacturer from Canada has demonstrated that if they closely control the entire manufacturing process from the steel mill through final chromating of the electroplated fastener, hydrogen embrittlement is of no concern even if the parts aren't baked. They've come to the realization that the entire manufacturing process results in cumulative contributions to internal stress which plating is often the tipping point. They'd come to ASTM to argue that they shouldn't be subjected to excessive bakes. However, baking provides added assurance since going without is certainly anything but best commercial practice.

As a recent Rockwell conference on electroplated tin and its propensity for whiskering was concluding, their plating engineer asked those platers in attendance "how many of you want to fly on plane with avionics and collision avoidance systems with tin plating?" Not surprisingly, no one raised their hand. Similarly, how many want to be in planes or highway bridges with electroplated fasteners from a process the manufacturer assures you keeps the hydrogen out? I'd want to know what their hydrogen management entails; since we can't remove hydrogen from plating, we have to better manage it.

References

- ASTM B 850-98. *Standard Guide for Post-Coating Treatments for Steel for Reducing Risk of Hydrogen Embrittlement*. ASTM International, W. Conshohocken, PA 19428.
- I.M. Bernstein and A.W. Thompson, *Hydrogen In Metals*, ASM International, Metals Park, OH, 1974.
- P.B. Csikos, "Are You Really Baking Out Hydrogen Embrittlement?" *American Fastener Journal*, November/December 2001; 64-65.
- Jack Dini, *Electrodeposition: The Material Science of Coating and Substrates*, Noyes Publications: Park Ridge, NJ, 1993.
- Joseph Menke, Personal interview. 31 Oct 2001.
- W. Craig Willan, *FINAL REPORT*: *The Effects of Acid Cleaning on Hydrogen Embrittlement*. Work Order 099-9905. Omega Research: Hurst, TX. 28 Aug.1999.
- W. Craig Willan, *HYDROGEN EMBRITTLEMENT*: *A Guide for the Metal Finisher*, Omega Research: Hurst, TX, 1991.