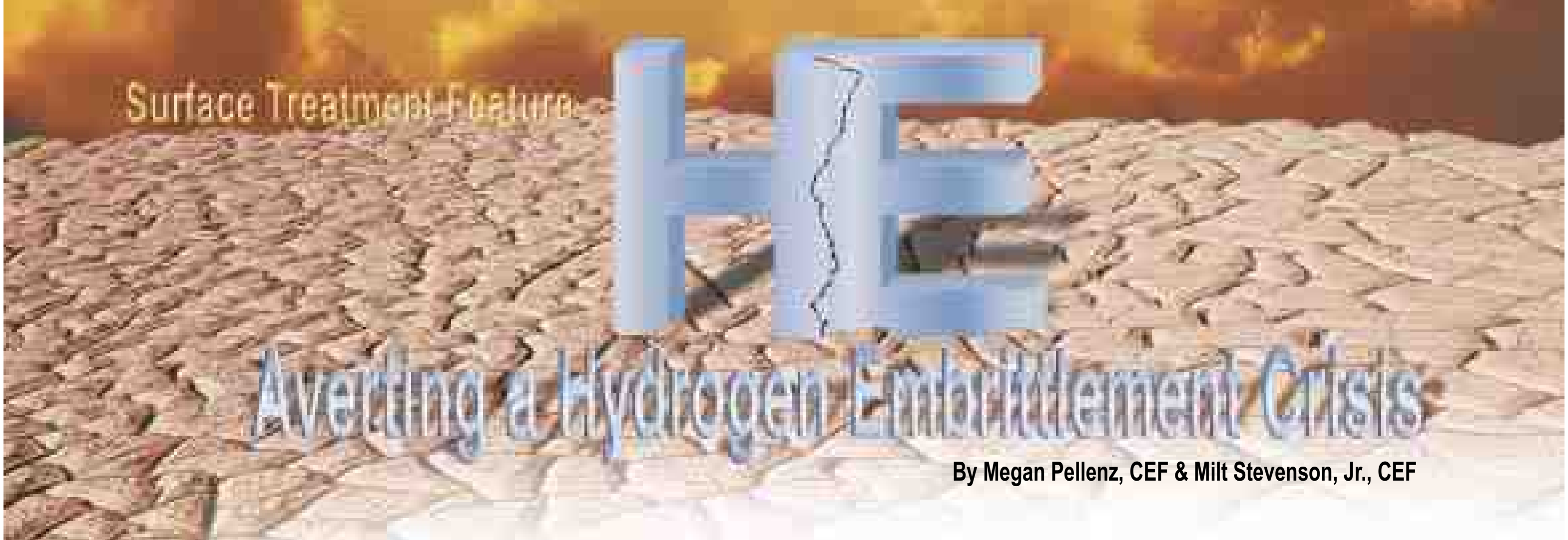

Averting a Hydrogen Embrittlement Crisis

By Megan Pellenz, CEF & Milt Stevenson, Jr., CEF

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 feature, an edited version of a paper presented at AESF Week 2002, 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;**
- **Performing periodic embrittlement tests.**

A Familiar Problem

Hydrogen gas causes pitting and streaking in electrodeposits, and builds up under a foam blanket in electrocleaners. Add a careless operator, and an ear-shattering explosion is sparked. 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 would be best to avoid altogether. As long as we're using aqueous-based electrolytes—those based on di-hydrogen oxide or H_2O—we're stuck with hydrogen in one form or another. Because 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 our discussion here is restricted to hydrogen embrittlement in ferrous metals, other materials—including alloys of nickel, titanium and aluminum—are susceptible to the degrading affects 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 parts-per-million levels) the hydrogen can continue over time 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.

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 a few. Hydrogen management must be well integrated within a sound quality management system.

Start with the Design

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 called for 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 identify 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 argument 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 to processing to clearly establish whether or not parts get baked after plating, and also whether or not they require a pre-plate stress-relief bake. A clear drawing call-out—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. There are several AMS specs, for example, 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. SAE's AMS specifications for electroless nickel—2404 and 2405—are examples. The former (2404) 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 may seem like no big deal, but it recently led to an audit finding at one company. Some specs are contradictory, or at least confusing. A proprietary cyanide strip for copper from steel, for example, 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.

Another example is the ASTM Committee on Metallic and Inorganic Coatings specification for post-plate embrittlement relief. It cites 16 different baking cycles. However, this is nothing but a compendium of baking cycles from dozens of different sources. Which one 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."

Work with Suppliers

While the plater can plead ignorance when it comes to applied stress in the final use of a component, he has knowledge of the plating process that may make parts more or less prone to failure caused by hydrogen. Chromium plating, for instance, is a very inefficient process, as evidenced by the amount of gassing that occurs. Because of the amount of hydrogen produced, the plater should be more concerned with baking following this process than more efficient processes, such as acid copper or cyanide silver. Even when using an efficient bath, operating outside a specific current density window 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.

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 the U.S. Army's Rock Island Arsenal, pointed to the coating's crystalline deposit with 2 to 3 percent porosity. He issued a challenge to do a ferroxyl porosity test on a phosphate coating. It will always fail. In his argument, he cited the columnar deposit of low-embrittlement cadmium, as opposed to a brightened cadmium deposit, which is laminar in structure. A columnar structure more easily permits hydrogen embrittlement relief. That is why the military standard for cadmium plating forbids brighteners in the cad bath when plating hardened steel components.

A plater's sales and 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, because 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 to be used, as embrittlement requirements are often upgraded or revised. At a minimum, sales and 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.

Avoiding Discrepancies

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 the 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 shop. The call-out 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 as "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, have 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. Too often, it's left up to the plater to guess. Because many of these specifications state "*unless otherwise specified, bake*," plating firms must be proactive in determining whether or not parts require baking. This means someone in planning must call the customer. 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 about whether or not the parts require embrittlement relief. There are cases where the application is non-critical, and where economics suggest the baking can be waived. This is the buyer's prerogative, however, 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 judgment, even when presented with all the application information.

Be Aware of the Effects

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.

A sharp plater may question why one EN job is baked for four hours while another is baked 24 hours. Don't try to rationalize or apply theory. Two rules for responding to these types of inquiries are:

1. Reinforce awareness: "It's good that you are aware of potentially damaging hydrogen embrittlement."
2. Ordering document compliance: "We strictly comply with the specifications referenced by the PO or drawing." You can only get in trouble by not following the specification.

Control & Record

There are three parameters for any embrittlement bake that need to be controlled and recorded:

1. The dwell time between parts coming out of the plating tank and the time the parts are at the minimum specified baking temperature.
2. The temperature range for baking.
3. The minimum duration for baking.

A plating shop must be religious in how it controls and records this information. Auditors have a passion for reviewing embrittlement records. Besides the oven chart itself, the individual router for the job should include the 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 shop has more than one oven, the records should include some sort of oven designation or description.

One of the most overlooked areas regarding embrittlement relief is the oven itself. Like any other piece of equipment used in processing, an oven falls into the category of "Inspection, Measuring and Test Equipment." As such, ovens require periodic calibration and maintenance to ensure that they are suitable and accurate for use. Calibration goes well beyond a simple thermocouple probe check. Semiannual, nine-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—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 the one cited most is AMS 2750, entitled "Pyrometry." Even with a calibrated state-of-the-art oven, some common sense must still be used. A recent article in *American Fastener Journal* told of one fastener manufacturer's trouble with a plating shop over baking. The author cited examples of how different-sized hardware takes varying lengths of time to come up to temperature in a given oven. It told 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 article concludes that a continuous belt furnace provides more assurances than batch ovens for high-volume platers processing tons of parts per shift.

Test Regularly

Another important link in hydrogen management is monthly embrittlement testing. We've already established that hydrogen is a given in plating; therefore, we must periodically check on how capable our process is at removal of the hydrogen. In some cases, this test is performed by a general testing lab. This is a specialized test, however, and many labs servicing 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's testing house specializes in just embrittlement testing. Whenever there is a failure, we'll review 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-hr room-temperature embrittlement relief cited in MIL-DTL-16232? At one time, we would process the bars, hold them for the mandated five-day relief cycle, and then ship them to our outside testing firm. The firm would begin the testing in a couple of days. But what were we actually testing? Clearly, we weren't testing the 120-hr requirement, but 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 we're now testing the 120-hr requirement.

To lay the blame for hydrogen on just electroplating is short-sighted. 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, parts must be cleaned and descaled prior to plating. Cleaning, whether anodic, cathodic, or soak, can emit hydrogen (as can acid dipping), with or without an inhibitor. Just replacing all electroplating with mechanical plating where hydrogen embrittlement is concerned is over-simplifying the problem.

Inhibitors

Other panaceas 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 floorspace. 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. Failures were attributed 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 its 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.

Management is the Key

A fastener manufacturer from Canada has demonstrated that if the entire manufacturing process is closley controlled, 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 realize that the entire manufacturing process results in cumulative contributions to internal stress, and plating is often the tipping point. They have gone to ASTM to argue they shouldn't be subjected to excessive bakes. However, baking provides added assurance, because going without is certainly anything but best commercial practice.

At a recent Rockwell conference on electroplated tin and its propensity for whiskering, a plating engineer asked those in attendance: "How many of you want to fly on a plane with avionics and collision avoidance systems with tin plating?" Not surprisingly, no one raised his hand.

Similarly, how many want to be in planes or on highway bridges with electroplated fasteners from a process the manufacturer assures keeps the hydrogen out? I'd want to know what their hydrogen management entails. Because we can't remove hydrogen from plating—we have to manage it better. ***P&SF***

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