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**AESF Heritage: The 2002 Hydrogen Embrittlement Seminar:
2. Practical Prevention of Hydrogen Embrittlement on a Plating Line**

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ABSTRACT

This paper will discuss the sources of hydrogen embrittlement (HE) on a plating line and propose ways to minimize and prevent the occurrence of HE during the pretreatment and plating cycles.

Hydrogen embrittlement (HE) has been defined as the loss of ductility of a metal due to the presence of adsorbed hydrogen in the metal's crystal structure. There are two generally recognized types of HE, internal HE and environmental HE. The former occurs when hydrogen enters a molten metal and becomes supersaturated with hydrogen after solidification. The latter occurs when a solid metal adsorbs atomic hydrogen. It is the environmental HE that is of concern to the plater.¹

Metals susceptible to HE are typically high-strength steels having a Rockwell hardness value of Rc 40 and above. These steels can be embrittled by a very small amount of hydrogen, as little as a few parts per million. The hydrogen can result from pickling, electroplating and aqueous corrosion. All of these processes are electrochemical in nature and involve the discharge of atomic hydrogen, H, at the metal's surface. The atomic hydrogen then migrates into the metal.²

The sources that produce or liberate hydrogen at the steel's surface on a plating line include cathodic electrocleaning, acid dips and the electrodeposition of metals from plating solutions. When an electrical current is applied to an electrolyte such as water in an electrolytic cell, the water molecules dissociate into hydrogen gas and oxygen gas. Hydrogen gas is liberated at the cathode and oxygen gas at the anode.³ The result of the chemical reaction of steel with an acid is the dissolving of the base metal into the solution as ferrous ions and the liberation of hydrogen gas at the surface of the steel.⁴ Both sources of hydrogen gas production, whether it is from an electrolytic reaction or from the chemical reaction of steel with acids, involve the production of atomic hydrogen as an intermediate step leading to HE.

It is important to know the history of the steel to be plated since it is possible for it to come to the plating line in an embrittled state from prior operations such as pickling or stripping in acidic solutions. If a part has been pickled to remove rust or scale prior to reaching the plating line, HE can be present if the part has not been effectively HE-relieved by proper baking. A typical procedure for the removal of hydrogen from steel is to bake for 3 hours at 190°C. It should be noted that depending upon the type of steel, a bake time of up to 24 hours might be necessary for proper relief from HE. It has been shown that the use of acid inhibitors in pickling solutions can reduce the amount of HE generated during pickling. Also, pickling for shorter times and at lower temperatures reduces the amount of HE produced. The optimum situation for prevention of HE is to use steel that is free of rust and heat treat scale so that aggressive pickling is not required.⁵ Mechanical cleaning processes such as blasting, brushing or tumbling are alternatives to acid pickling. These methods for rust and scale removal do not produce hydrogen at the surface of the steel.

Once the steel arrives at the plating line, the first process step is typically an immersion in an alkaline soak cleaner to remove oils, grease and other soils. Since this step does not involve the use of current, there is no evolution of hydrogen at the surface of the steel. Electrocleaning is normally the next process step. Steel is usually electrocleaned anodically and oxygen is evolved at the surface during this process step. It has been reported that cathodic electrocleaning creates HE in susceptible steels. The use of higher temperatures in the electrocleaning solution, higher electrolyte concentrations and higher current densities create more HE during cathodic electrocleaning.⁶ A simple precaution for the plater to take to prevent accidental HE during the

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electrocleaning step is to trace the connections from the rectifier to the electrocleaner tank to ensure that the parts to be cleaned are truly anodic. This is especially important when starting up a new plating line, when a new rectifier has been added, or when the bussing has been taken apart for maintenance. The use of a technique called periodic reverse electrocleaning has been employed in the plating industry for descaling and derusting on the plating line. This is a process of alternating the polarity of the parts during the residence time in the electrocleaner. The cathodic portion of this cycle will introduce hydrogen into susceptible steels. If possible, the parts should be removed from the electrocleaning tank during the anodic portion of the cycle. This will minimize any HE created by the cathodic portion of the cycle.

After appropriate rinsing, the parts are transferred to the acid dip tank. As mentioned above, the chemical reaction of a metal with an acid results in the dissolution of the metal into the acid solution and the liberation of hydrogen at the metal surface, thus providing a source for hydrogen adsorption into the metal. Hydrochloric acid is most commonly used in the acid dip on a plating line. Sulfuric acid is also used, but to a lesser extent. It has been reported that hydrochloric acid produces less HE than sulfuric acid and the use of inhibitors in the acid also reduces the amount of HE induced.⁷ The use of acid salts, either alone or in combination with lesser amounts of acid, can provide good metal activation while reducing the amount of hydrogen generated compared to the use of just the raw acid. When dissolved in water, the acid salts create a relatively mild acidic solution that does not have the acidity of the acids normally used. Utilizing shorter dwell times, weaker acids supplemented with acid salts, acid salts alone, lower temperatures, and acid inhibitors can reduce the tendency for HE to occur during the acid dip process step.

After proper cleaning and acid activation, the steel is ready for plating. Some of the metals commonly plated onto steel include copper, zinc, zinc alloys, cadmium, tin, nickel and chromium. To prevent or minimize HE, the plater needs to understand the tendency for these plating solutions to liberate hydrogen at the cathodic surface of the steel during plating. This is a function of the plating solution's cathode efficiency. Under normal conditions, a plating solution that exhibits 100% cathode efficiency uses all of the current applied to the part to deposit metal and does not liberate hydrogen. On the other hand, a plating solution that is 50% cathode efficient uses 50% of the current applied to deposit metal at the cathode and the other 50% to produce hydrogen at the cathode surface. Obviously, plating from solutions with less than 100% cathode efficiency can lead to HE occurring during the plating process step. A general statement can be made that to prevent or minimize HE during plating, the plater should utilize those solutions that exhibit the highest possible cathode efficiencies. For any given plating solution, the chemistry and plating conditions should be optimized to attain the highest possible cathode efficiency. It is possible to liberate hydrogen at the cathode even when using plating solutions that are 100% cathode efficient. This is done by exceeding the limiting current density or "burn point" for the part that is being plated.⁸ The "burn point" is that point at which normal metal deposition ceases and the evolution of hydrogen begins. Table 1 shows various plating solutions and their cathode efficiencies.⁹

Table 1 – Plating solutions and their cathode efficiencies.⁹

Plating Solution	Cathode Efficiency (%)
Cyanide cadmium	90-95
Cadmium fluoborate	100
Acid copper sulfate	95-100
Copper fluoborate	95-100
Copper pyrophosphate	95-100
Acid zinc sulfate	95-100
Cyanide zinc	65-95
Alkaline non-cyanide zinc	65-95
Acid chloride zinc	95-100
Cyanide copper strike	30-50
Cyanide copper plate	100
Hard Chromium (Conventional sulfate catalyst)	13-18
Hard Chromium (Sulfate & Fluoride catalyst)	16-24
Nickel sulfamate	95-100
Watt's nickel	95-100
Nickel fluoborate	95-100

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Many studies have been performed to determine the amount of HE produced in susceptible steels from various plating solutions and how to reduce or eliminate the effects. The following are some selected observations from those studies.

Thompson reported that plating from cyanide solutions of zinc, cadmium and copper can lead to HE.¹⁰ It has been reported that the cyanide used in plating solutions acts to poison or slow down the recombination reaction of the atomic hydrogen, H, generated at the cathode surface. This allows the atomic hydrogen to migrate into the steel instead of forming hydrogen gas, H₂.¹¹ More HE is formed than would be generated from an alkaline non-cyanide plating process containing the same metal.

There are alternatives to cyanide zinc such as acid zinc and alkaline non-cyanide zinc systems. The acid zinc electrolyte is approximately 95% cathode efficient and minimizes the amount of atomic hydrogen formed. While having higher cathode efficiencies than those of the cyanide zinc and alkaline non-cyanide zinc systems, the throwing power of the acid zinc process is not as good as that of a cyanide or alkaline non-cyanide zinc process. The thickness distribution of the deposits from the cyanide and alkaline non-cyanide zinc electrolytes is much more uniform than that from an acid zinc electrolyte. An alternative to the cyanide cadmium electrolyte is the cadmium fluoroborate electrolyte. It also exhibits poor metal distribution.

Willan noted that when plating from cyanide cadmium plating solutions, there is more of a tendency for HE to occur when there are high levels of brightener. He also states that highly brightened deposits from zinc and nickel plating solutions make the HE relief bake step more difficult.¹² Wanhill and De Rijk reported that a dull deposit from a cyanide cadmium solution facilitates removal of hydrogen by baking. Dull deposits tend to be more porous than brighter deposits and allow the hydrogen entrapped in the steel to be removed more easily.¹³

Parthasaradhy reported that during hard chromium plating, a "strike" procedure leads to higher hydrogen intake by the steel as compared to plating without a "strike". Striking is the process of using higher current densities than normal for a short period of time to enhance coverage on the part. After striking, the current density is lowered to within the normal range for the buildup of the chromium deposit.¹⁴

An activation technique that is sometimes used prior to hard chromium plating is a "hydrogen wash" step. It is known that at the beginning of hard chromium plating a part, when the voltage and current are ramped up slowly, there is a point at which hydrogen gas is generated at the surface of the steel prior to the deposition of chromium. Some platers use this as an activation procedure and purposely allow the part to remain in this condition. This "hydrogen wash" step should be avoided to minimize HE.

After plating, steel that is susceptible to HE should be placed in the bake oven as soon as possible. It is reported that many specifications call for a maximum delay prior to baking of 4 hours and some call for entry into the oven as soon as 15 minutes after plating.¹⁵

1. When plating steel that is susceptible to HE, the following suggestions can be made to the plater to minimize and/or eliminate hydrogen embrittlement:
2. Bake the part prior to plating if it has been pickled or stripped in an acidic stripping solution.
3. Electroclean parts anodically.
4. Minimize the exposure to acids and/or use inhibitors in the acids.
5. Select the most cathode-efficient plating process possible.
6. Optimize the chemistry and plating conditions to obtain the highest possible cathode efficiency.
7. Minimize the use of brighteners.
8. After plating, the parts should be put into the HE relief oven as quickly as possible.

References

1. J.R. Davis, ed., *Metals Handbook Desk Edition*, 2nd Ed., ASM International, Materials Park, OH, 1998; p. 33.
2. J.R. Davis, ed., *Corrosion Understanding the Basics*, ASM International, Materials Park, OH, 2000, p.182.
3. John C. Bailor Jr., ed., *General Chemistry*, Raytheon Education Co., Boston, MA, 1968, p. 92.
4. *General Chemistry*, *ibid*, p.102.
5. *Corrosion Understanding the Basics*, *ibid*, p. 183.

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6. N.V. Parthasaradhy, *Plating*, **61**, 58, (1974).
7. T. Lyman, ed., *Materials Handbook*, 8th Ed. Vol. 1, ASM International, Metals Park, OH, 1961, p. 10.
8. Dr. C. J. Raub, *Plating and Surface Finishing*, **80**, 32, (1993).
9. L. Durney, ed., *Electroplating Engineering Handbook*, 4th Edition, Van Nostrand Reinhold Company, New York, NY, (1984), p. 235.
10. A.W. Thompson, *Plating and Surface Finishing*, **65**, 36, (1978).
11. S. Venkatesan and S.K. Rangarajan, *Metal Finishing*, **69**, 55, (1971).
12. C. Willan, *First International Technology Transfer Conference, Hydrogen Embrittlement of Fasteners*, p. 1, 1995.
13. R.J.H. Wandhill and P. DeRijk, *Metal Finishing*, **73**, 32, (1975).
14. N.V. Parthasaradhy, *Metal Finishing*, **72**, 52, (1974).
15. F. Altmayer, *Plating and Surface Finishing*, **78**, 9, (1991).