Shop Talk: Practical Information for Finishers

EMF Series: A Guide to Troubleshooting

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This is the eighth in a series of reviews looking back on the 25-year-old series, "AES Update," begun by the late Dr. Donald Swalheim, and continued by others. Often, material from decades ago remains relevant today, but is easily forgotten. The key to many plating problems may lie in an old issue of *Plating & Surface Finishing* that sits in a cardboard box in a basement, storage crib . . . or on the floor next to a neglected, leaky drum of nickel salts. The latter, of course, is double trouble.

This month, you might find the chosen article quite handy. The venerable electromotive force (EMF) series, has been around since time immemorial. Dr. Swalheim put together a terrific article, which put the EMF series to work, as a guide to troubleshooting. Usually, I add some of my own comments in brackets [ ], just to put things in perspective. This time, the material is so good that I would be remiss if I didn't let it speak for itself. Do not get overly excited because the word "cyanide" is sprinkled throughout the text. Instead, you can take the principles outlined here and extend them to other, more modern systems. So let's read Dr. Swalheim's words as he tells us that the "electromotive force series helps diagnose problems on the plating line."

"The electromotive force (EMF) series is familiar to most chemists, but many electroplaters do not fully appreciate its *practical* value as a guide to troubleshooting. We're going to discuss some of those practical applications right after we define in brief and simple terms what is meant by the EMF series. Let's take a specific example involving zinc.

"If a piece of zinc metal is placed in a solution of its salt, the following reaction takes place:

$$\mathbf{Zn\ Zn^{+2} + 2e}$$

"Zinc goes into solution and electrons accumulate on the surface of the metal. As a result, the zinc metal acquires a negative charge, otherwise known as a negative potential. It can be measured by constructing a cell in which the zinc is coupled to a "reference" electrode such as a calomel cell. The difference in potential is measured using a high-impedance voltmeter.

"Similarly, if we measure the potential of copper sulfate, we would find that the copper acquires a *positive* charge. Plainly, this means that the copper does not tend to go into solution; the reverse reaction actually occurs. Electrons from the copper neutralize the positive charges on the cupric ions and a small amount of copper is deposited, leaving the copper with a positive charge:

$$\mathbf{Cu^{+2} + 2e\ Cu}$$

"The standard potentials shown for several metals in the accompanying table will assist in the understanding of the following situations involving troubleshooting using the EMF series.

Activation, Porosity & Smut

"In this discussion, activation will be defined as treating a metal or alloy in acid to remove any surface oxide. In particular, we're going to focus on the activation of zinc diecastings.

"You will note from the EMF series that zinc has a high negative potential, which simply means that it is a very reactive metal. Specifically, zinc reacts with acid and liberates hydrogen. Zinc diecastings normally are activated in a dilute acidic solution containing about 0.5 percent by weight sulfuric acid. However, if the acid is much stronger or if the immersion time is too long, the surface of the diecasting will be roughened excessively. As a general rule, the diecasting should be withdrawn when hydrogen evolves visibly, usually after 15 to 30 sec of immersion.

"Another common problem when activating zinc diecastings or steel is smut formation due to copper contamination, particularly when copper or brass parts are processed in the same line. Again, the EMF series provides an explanation. Any metal in the series will displace another metal if it is significantly lower in the series. The explanation is relatively simple, as expressed by the following equations:

$$\mathbf{Zn\ Zn^{+2} + 2e}$$
$$\mathbf{Cu^{+2} + 2e\ Cu\ Metal}$$

"Zinc basically functions as a rectifier, generating electrons as it dissolves. The electrons react with copper ions in solution and loosely adherent copper metal deposits on the surface of the diecasting. The copper particles are usually dark in appearance, and similar results are obtained with steel parts. The steel or iron dissolves, generating electrons that neutralize the charges on the copper ions.

When to Strike

"Generally speaking, the purpose of a strike is to avoid immersion deposition or to activate the surface to achieve good adhesion.

"If you examine the EMF series, no nickel strike is required before plating steel with nickel because the potentials are relatively close together—iron is -0.44 volts (V) and nickel is -0.25 V. However, a gold strike is usually specified before plating over a nickel deposit. The need for this practice becomes obvious when you refer to the potential of nickel (-0.25 V) and the potential of gold (+1.68 V). The difference in potential, 1.93 V, and the driving force to deposit gold by immersion are very high.

"Now, let's take another example. Problems are frequently encountered in obtaining good adhesion on zinc diecastings plated in bright acid copper. It is obvious that a cyanide copper strike is required. The single-electrode potential of zinc in a cyanide bath is about -1.1 V, compared to -0.76 V for the potential in a zinc sulfate bath. However, the single electrode potential for copper in a cyanide bath is also about -1.1 V. Therefore, when a zinc diecasting is immersed in a cyanide copper bath, no immersion deposition will occur because of the similarity in potential.

"However, if the copper strike is too thin, it will be porous and deposition will occur in the pores when the parts are immersed in a highly acidic, bright, acid sulfate copper bath because of the large difference in potential between exposed zinc and copper (-0.76 vs. +0.34, or 1.1 V). Usually, zinc diecastings are given a strike of 5 to 7 min in cyanide copper prior to acid copper in order to avoid immersion deposition in recessed areas.

"Another case of immersion deposition leading to problems during nickel plating is copper contamination. As the steel part (-0.44 V) enters the nickel-plating tank, copper (+0.34 V) deposits by immersion. Frequently, the presence of copper on the steel surface cannot be detected by visual observation, but the problems of (1) lack of adhesion of the nickel and (2) haze in the nickel are quite common in the field.

Aluminum & Zincate

"You will note from the EMF series that aluminum is a very active metal with a high single-electrode potential of -1.67 V. The first step in plating on aluminum is to apply an immersion coating of zinc or tin. In either case, an alkaline solution containing sodium zincate [$Na_2Zn(OH)_4$] or sodium stannate [$Na_2Sn(OH)_6$] is employed. Reaction of the aluminum with the zincate solution is as follows:

$$2Al\ 2Al^{+3} + 6e$$
$$3Zn(OH)_4^{-2} + 6e\ 3Zn + 12OH^-$$

"The zinc forms a complex salt in the alkaline zincate solution and immersion deposition leads to the formation of an adherent deposit of zinc on the aluminum.

Electromotive Force Series

Electrode	*Potential, v*
$Al\ 8\ Al^{+3}$	**-1.67**
$Zn\ 8\ Zn^{+2}$	**-0.76**
$Fe\ 8\ Fe^{+2}$	**-0.44**
$Ni\ 8\ Ni^{+2}$	**-0.25**
$Pt / H_2\ 8\ H^+$	**0.00**
$Cu\ 8\ Cu^{+2}$	**+0.34**
$Ag\ 8\ Ag^{+1}$	**+0.80**
$Au\ 8\ Au^{+1}$	**+1.68**

Chromate Conversion

"The EMF series is also useful for diagnosing the problem of dark deposits on chromate conversion coatings. However, we must examine the EMF series from the standpoint of reactions of metals in acidic solutions. Any metal *above* hydrogen in the EMF series will react with an acid to form a salt and liberate hydrogen.

"Let's assume we're attempting to apply a clear chromate conversion coating over zinc deposited from a bath contaminated with copper. The zinc deposit contains a small amount of codeposited copper. When the parts are bright-dipped in dilute nitric acid prior to chromating, the deposit darkens rather than improving in appearance. In essence, the zinc dissolves, leaving finely divided copper on the surface because copper is below hydrogen in the EMF series. For the same reason, further darkening will usually occur during the chromating step. This problem can be avoided only by purifying the zinc plating bath to remove copper.

Hydrogen Embrittlement

"Hydrogen embrittlement is frequently encountered when plating high-carbon or carbonitrided steel with zinc. The culprit, of course, is the hydrogen that is codeposited with the zinc. The atomic hydrogen enters the grain boundaries of the steel and combines to form molecular hydrogen, which builds up tremendous pressure within the steel.

"If we examine the EMF series, we find that the single-electrode potential of hydrogen on platinum is zero. What this means, very simply, is that hydrogen is liberated on platinum at a very low applied voltage. In contrast, it requires a potential of about -0.80 V to deposit hydrogen on zinc. Because the single-electrode potential of zinc is of the same magnitude, hydrogen codeposits with zinc as the metal is plated.

"The situation with high-carbon steel or cast iron is somewhat different. The surface of the high-carbon steel contains carbon and the surface of the cast iron contains graphite. The deposition potential of hydrogen on carbon and graphite is low. In other words, hydrogen deposits in preference to zinc from a cyanide bath. Electrochemists prefer the term *overvoltage* when explaining the problem. They state that the overvoltage of hydrogen on cast iron is low; translated, this simply means that the deposition potential required to liberate hydrogen is low.

"The acid zinc bath is preferred for plating high-carbon steel and cast iron. The overvoltage of hydrogen is significantly higher and zinc plates in preference to hydrogen. The degree of hydrogen embrittlement is not as serious, but baking to relieve the hydrogen is required for critical applications because some hydrogen is codeposited with the zinc.

Sacrificial Protection

"The sacrificial protection of steel by zinc or aluminum can be explained electrochemically. These metals have high electrode potentials, which means they corrode preferentially to the steel and protect it. By codepositing small amounts of sulfur in the second layer of duplex nickel it becomes more anodic than the sulfur-free layer and corrodes preferentially, thereby protecting the first layer. Corrosion is frequently associated with formation of anodic and cathodic sites. For example, if a metal is stressed it becomes more anodic than the unstressed surface of the metal. This can lead to catastrophic failures in many cases.

"We have discussed but a few examples of the practical value of the EMF series as a troubleshooting tool. However, these cases illustrate the important role of the EMF series, something with which every electroplater should become familiar." ***P&SF***