The Plater's Lament: Tell Me Why ...*

... impurities such as copper and nickel collect as a sludge on zinc anodes in an acid-zinc bath?

... my cleaner representative tells me my set-up is good, but I still encounter blistering on my die castings—particularly in recessed areas?

... I have a problem in meeting thickness specs on some of the racked parts in my manually operated unit?

... my rejects in plating aluminum parts are excessive?

By Dr. Donald A. Swalheim
Updated by Dr. James H. Lindsay, AESF Fellow

Solving problems is always challenging, but you might find the job more interesting if you have a basic understanding of the principles of electrochemistry to which the problems lamented above apply.

The electromotive series (EMF) may be considered as the bible of electrochemistry. To understand this arrangement of the metals, let's examine what happens when we immerse different metals in solutions of their salts (Fig. 1).

Zinc generates a potential or voltage when immersed in a solution of zinc sulfate. It dissolves and becomes negatively charged because electrons accumulate on the surface. Nickel also dissolves to a lesser extent and becomes negatively charged. A reverse reaction takes place with copper, however, instead of dissolving, copper ions are discharged and deposit on the copper. This requires removal of electrons from the copper and the copper becomes positively charged. If we measured the voltages on these metals, we would expect to find a negative charge on the zinc, a lower negative charge on the nickel and a positive charge on the copper. The order in which the metals are placed in the EMF series is based upon voltages (Fig. 2).

Our predictions based on behavior were correct. Zinc shows a voltage of -0.76, nickel a value of -0.23 volts, and copper a value of +0.34 volts. The voltages are measured using the hydrogen electrode as a reference. Hydrogen, the standard of reference, has a voltage of zero.

Now, what does all this mean to the plater? The EMF series explains why an active metal like zinc dissolves chemically and why the zinc content of baths will increase over a weekend when the bath is not in operation. Copper is less active chemically and precautions must be taken to prevent anodic polarization, a term which will be discussed later. Copper plates with greater ease, however, and in some cases will plate out in a non-adherent form, even though current is not applied.

Problems in plating zinc die castings are illustrated in Fig. 3. Zinc is a very active metal and will dissolve chemically to a small extent, even though no current is applied. We now have electrons on its surface. As a result, its behavior is similar to that of a rectifier. What happens to the electrons? Metals below hydrogen in the EMF plate

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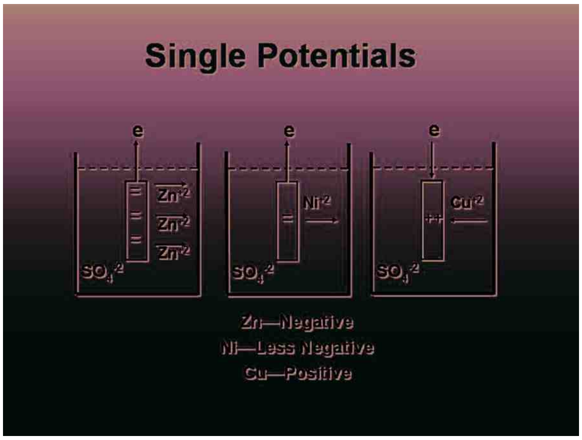
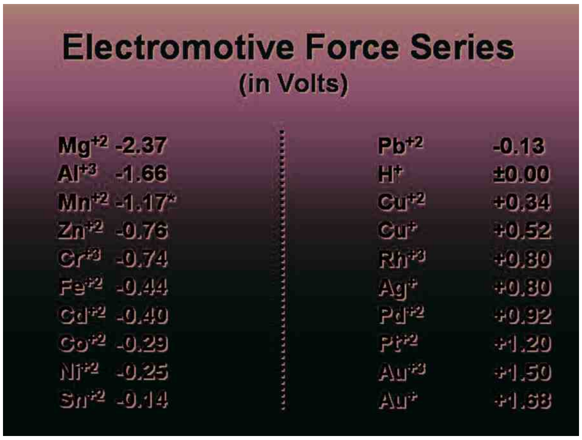
*Based on an original article from the "AES Update" series [*Plating*, **64**, 20 (March 1977)].



Single Potentials

Zn—Negative
Ni—Less Negative
Cu—Positive

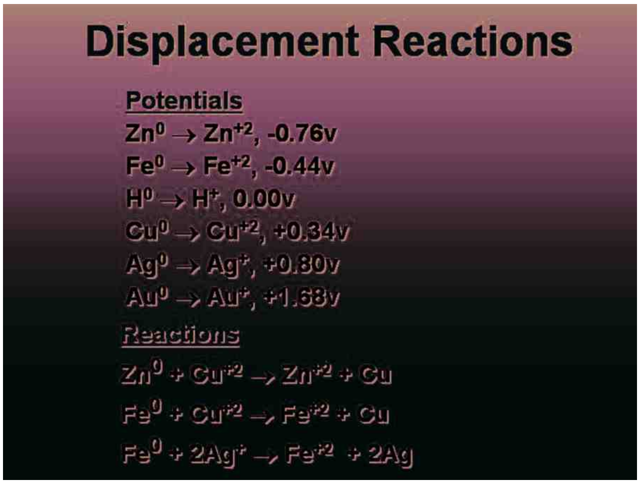
Fig. 1—Single potentials.



Electromotive Force Series
(in Volts)

Mg^{+2}	-2.37	Pb^{+2}	-0.13
Al^{+3}	-1.66	H^+	±0.00
Mn^{+2}	-1.17*	Cu^{+2}	+0.34
Zn^{+2}	-0.76	Cu^+	+0.52
Cr^{+3}	-0.74	Rh^{+3}	+0.80
Fe^{+2}	-0.44	Ag^+	+0.80
Cd^{+2}	-0.40	Pd^{+2}	+0.92
Co^{+2}	-0.29	Pt^{+2}	+1.20
Ni^{+2}	-0.25	Au^{+3}	+1.50
Sn^{+2}	-0.14	Au^+	+1.68

Fig. 2—Electromotive force series.



Displacement Reactions

Potentials

$Zn^0 \rightarrow Zn^{+2}$, -0.76v

$Fe^0 \rightarrow Fe^{+2}$, -0.44v

$H^0 \rightarrow H^+$, 0.00v

$Cu^0 \rightarrow Cu^{+2}$, +0.34v

$Ag^0 \rightarrow Ag^+$, +0.80v

$Au^0 \rightarrow Au^+$, +1.68v

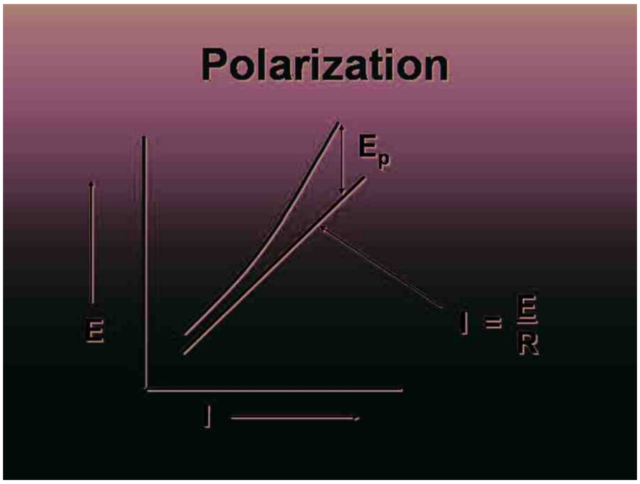
Reactions

$Zn^0 + Cu^{+2} \rightarrow Zn^{+2} + Cu$

$Fe^0 + Cu^{+2} \rightarrow Fe^{+2} + Cu$

$Fe^0 + 2Ag^+ \rightarrow Fe^{+2} + 2Ag$

Fig. 3—Displacement reactions.



Polarization

Fig. 4—Polarization.

out rather readily. As we might predict, the electrons neutralize the charges on the copper ions to form metallic copper. This is called immersion plating. Unfortunately, the copper is not adherent in this case and will cause serious problems.

Let's assume you are plating zinc die-castings with a copper cyanide strike, acid copper, nickel and chromium. If the thickness of the copper strike in the recess is not adequate, the recessed area will dissolve in the acid copper bath and the part will be blistered. As a general rule, any metal high in the EMF series will displace a metal lower in the series—especially if there is a significant difference in potential or voltage. Before discussing how we prevent immersion deposition in plating zinc die castings, we should mention a practical application of immersion deposition.

Immersion Deposition

Preparation of aluminum or its alloys for plating represents an excellent example. Aluminum is a very active metal with a negative potential of 1.67 volts. If we placed an aluminum part in an acid copper bath, it would dissolve and non-adherent copper would be deposited, even though current was applied as the part was immersed. In order to avoid this problem, we first apply a coating of zinc over the aluminum. Instead of using an acid-zinc bath, we immerse the part in an alkaline-zincate bath. The rate of immersion deposition of zinc is relatively slow and the deposit is adherent. Sometimes aluminum parts are given a double zincate treatment to insure complete coverage. Assuming the parts are cleaned properly and you have a problem in blistering of subsequent deposits, odds are that the parts are not protected adequately with zinc.

Preventing immersion deposition is a subject of great significance to platers. We use a different type of plating bath (cyanide copper) and avoid immersion deposition by tying up or complexing the copper. Basically, we have changed the electrode potential of copper. Instead of a positive voltage value, the complexed copper ion has a negative potential of -1.1 volts. This means that the copper plates out with greater difficulty. If we place a zinc die-casting or steel in this solution, nothing happens until we apply current. When current is applied, copper plates out in an adherent form. Dilute or strike solutions are normally used in order to obtain maximum adhesion. Having applied a suitable thickness from the strike bath, zinc die-castings, zincated aluminum or steel parts can then be plated with either acid copper or high efficiency cyanide copper, with no problem associated with immersion deposition.

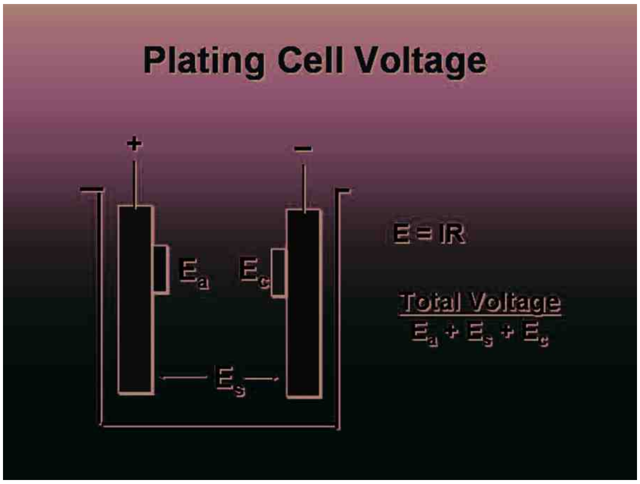
The electrode potentials of zinc and copper in a cyanide solution are very similar. Therefore, cyanide solutions are used to plate brass, an alloy of copper and zinc. You might conclude that control of potentials might be an ideal approach to controlling composition and color of brass deposits. It has been shown in unpublished results of research that other factors also influence composition of the deposited alloy and that this method of control offers no practical value.

Having discussed electrode potentials, let's direct our attention to deposition potentials. We previously stated that the single electrode potential of nickel was -0.23 volts and develops as a result of nickel dissolving to form nickel ions. In order to reverse the reaction and deposit nickel, we must apply a potential somewhat higher than 0.23 volts. This leads us to a new term called *polarization*. The subject is complex, but Fig. 4 can help define the term.

Polarization Simplified

Every plater knows that he can increase the current by increasing the voltage. It would be logical to express this relationship by drawing the lower line in Fig. 4. If we were only dealing with the electrical resistance of the plating bath, this relationship would hold true. However, the voltage or energy requirements are similar to the fuel requirements in flying an airplane. As the velocity of the head winds increase, it requires additional fuel to maintain a certain ground speed. Instead of a wind factor, we have resistance factors at the anode and the cathode. The additional voltage required to overcome these resistances is called *polarization*. In actual practice, the relationship is expressed more accurately by the upper line. It is important to note that the voltage required because of polarization (E_p) increases with the current or the current density.

The relationship between voltage and current (Fig. 5) would follow a straight line if we were only dealing with the resistance



Plating Cell Voltage

E = IR

Total Voltage

$E_a + E_s + E_c$

Fig. 5—Plating cell voltage.

of the plating bath. This voltage requirement appears as E_S. An additional voltage E_A is required to overcome polarization at the anode and an additional voltage E_C at the cathode.

First, let's consider polarization at the anode. As the metal dissolves anodically, we build up a high concentration of metal ions at the surface of the anode. This requires an additional voltage E_A to dissolve the metal. The situation is quite different at the cathode. As the metal plates on the part, we have a decrease in the metal ions in the cathode film. This requires an additional voltage E_C to deposit the metal. Under normal operating conditions, these polarization factors E_A and E_C do not cause problems to a plater. It simply means he has to apply a somewhat higher voltage to maintain the current as the current density increases.

Anode Problems

The situation is not always this simple, however. It is obvious at this point that the normal polarization at the anode and the cathode can be reduced with effective solution circulation. If the voltage required to obtain a given value of current rises abruptly and becomes abnormally high, abnormal anode polarization is indicated. This is primarily associated with malfunctioning of the anodes and can result in serious problems. The anodes are probably operating at too high a current density, which can result in several problems. In most cases, the anode will not corrode anodically at close to 100% efficiency because part of the current will be wasted in liberating oxygen. As a result, the metal content of the solution will drop and higher chemical additions will be required to maintain the solution.

The problem is even more serious in cyanide copper plating. Oxygen liberated at the anode surface may react with the copper to form an insulating film of copper oxide and current will eventually cease to flow. If the copper oxide becomes detached from the anode and physically contacts the part being plated, it is reduced to copper metal and becomes welded to the surface. This creates high current density points and produces serious particle roughness.

Failure to maintain good electrical contact between the bus bars and the anodes probably represents the greatest single factor in excessive or abnormal anode polarization. This can lead to variations in thickness of deposits, especially in manually-operated installations.

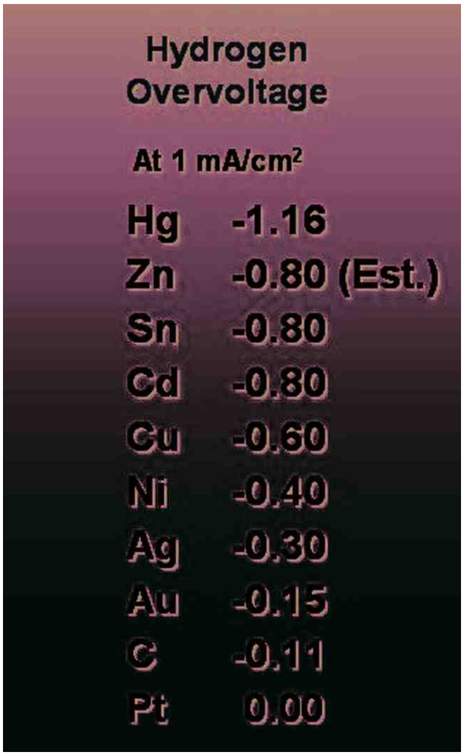
A relatively simple test can be conducted to establish if a significant number of anodes is not making contact with the bus bars. Apply an electrical clip to a Hull Cell panel and connect an ammeter (5-10 A range) in series using an insulated or covered copper wire. Immerse the Hull Cell panel near the parts on the rack and contact the cathode bus bar with the bare end of the copper wire. Record the current on the ammeter. Take readings at several positions throughout the length of the tank and repeat the operation on the parts facing the other anode bus bar. All readings should be approximately equal. If you find wide variations, check the anode contacts by cleaning the bus bar in the position where low values of current were obtained and repeat the current survey.

Hydrogen Overvoltage

Another type of polarization, hydrogen overvoltage, may occur at the cathode or surface of parts being plated. Primarily associated with zinc plating, it is simply the polarization involved in the evolution of hydrogen. In order to understand the term, we can consider hydrogen overvoltage as a two-step process. First, atomic hydrogen (H_{ADS}) is formed and the atoms then combine to form molecules of hydrogen. The hydrogen overvoltage on a platinum surface is zero, because the hydrogen atoms combine very rapidly to form hydrogen molecules.

The hydrogen overvoltage on zinc is -0.8 volts, however. In other words, it requires a potential higher than 0.8 volts to deposit hydrogen. You will also note that the single electrode potential of zinc is -0.76 volts. The voltages required to discharge hydrogen and deposit zinc from a sulfate solution are quite similar, so hydrogen tends to co-deposit with zinc.

Before discussing problems associated with hydrogen overvoltage, let's examine how the values vary with different metals (Fig. 6). These are only approximate values because a number of factors influence hydrogen overvoltage, such as smoothness of the surface, type of electrolyte, current density and temperature.



Hydrogen Overvoltage

At 1 mA/cm²

Hg	-1.16
Zn	-0.80 (Est.)
Sn	-0.80
Cd	-0.80
Cu	-0.60
Ni	-0.40
Ag	-0.30
Au	-0.15
C	-0.11
Pt	0.00

Fig. 6—*Hydrogen overvoltage on metals.*

One of the problems associated with hydrogen overvoltage is hydrogen embrittlement in plating high carbon steel. The problem is caused by the carbon. Although the value for hydrogen overvoltage on carbon is not given in Fig. 6, it is lower than the value on pure zinc. This is significant because hydrogen will tend to deposit in preference to zinc. The damage to the high carbon steel part is done before the hydrogen is released as a gas. The culprit is atomic hydrogen. It travels through the crystal lattice of the part and becomes absorbed in the metal, causing serious embrittlement. In some cases, thin gauge high carbon steel parts will even fracture during the plating operation because of the high stress. If the part becomes embrittled, the only remedy is to heat-treat the part at 190°C (375°F) for a period of up to 24 hours to drive out the hydrogen.

Most platers are fully aware of the problems in plating cast iron in which the problem is associated with another form of carbon—graphite. Hydrogen overvoltage on graphite is also low. Although steps can be taken to minimize exposure of graphite on the surface, one solution is to apply a copper strike. Copper will plate at a lower voltage and cover the graphite on the surface. You can then proceed to plate the part with zinc.

Problems in plating high carbon steel and cast iron parts have been minimized to some extent with the development of the bright acid zinc plating baths. Problems of hydrogen overvoltage are not as serious. **P&SF**

Technical Editor's note: *Dr. Donald A. Swalheim was the originator of the "AES Update" series that ran in this journal. His goal was to bring practical information to the metal finisher. Since this article was written, much has changed ... but not that much. The problems Dr. Swalheim outlined still plague us today. He drove home the point that an understanding of what is going on in the tank is paramount. The reader may benefit both from the information here and the historical perspective as well. In some cases here, words were altered for context.*