Tech Talk

Fine Lines in High Yield (Part CLII)

Immersion & Electroless Metallization Processes

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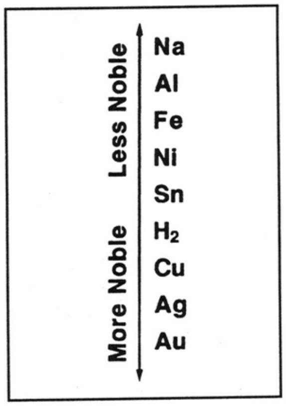
The term "electroless", as in e.g. electroless nickel process, is a curious one and has led to considerable confusion. In its literal meaning, it labels processes that proceed without applying an external electrical potential to drive the reaction. Thus, the English language defines "electroless" processes by what they are *not,* namely electroplating processes driven by an external potential. But this label does not tell us what *is* driving the electroless process, or processes. This is where the confusion sets in. There are two types of plating processes in use in electronics which are not driven by an external potential. One type uses a chemical reducing agent to convert metal ions to plated, zero-valence metal, the other type, so called immersion processes, is a chemical displacement of one metal by another, driven by the difference in electrochemical potential, or electromotive force (EMF) of the two metals. Only the former, chemically driven process is typically referred to as "electroless process". People in non-English speaking countries are better off and less confused, because they name e.g. electroless copper by what it is, "chemical copper", not by what it is *not.* So, we have "chemisch Kupfer" in Germany, "cuivre chimique" in France, and "cobre químico" in Spain. These languages have their own terms for "immersion" processes which distinguish them clearly from electroless processes (e.g. Sudgold for immersion gold in German). Confusion sneaks in when "Sudgold" is sometimes translated as immersion and sometimes as electroless gold. More confusion abounds when the industry convention for naming immersion and electroless processes is not adhered to which is often the case. When you go to the Transene Company's website (www.transene.com) you find a product labeled "Electroless Silver" which is then further characterized as an electroless immersion process, driven by "an electroless displacement of base metals by silver, brought about by a difference in the EMF potentials."

Aware of such confusion, the IPC's Plating subcommittee that just finished IPC-4554 "Specification for Immersion Tin Plating for Printed Circuit Boards", found it necessary to explain the difference between electroless and immersion processes in the Appendix of the document:

One might get the impression that a widely used immersion process, the immersion tin process, should not work at all, given the position of tin relative to copper in the Electromotive Series (see Fig. 1). Copper is the more noble metal and it should displace tin, not the other way around. To understand this reaction we have to familiarize ourselves with the so called Nernst Equation (Fig. 2), named after the German Physicist Walther Nernst. The Nernst Equation shows that the actual potential E of a metal may be different from the standard potential E_0 listed in the EMF series. E also depends on the logarithm of the ratio of the activity of the oxidant over the activity of the reductant of the redox pair. Fig. 2 shows only Cu^{+1}, assuming the concentration, or more accurately the activity, of Cu^0 is 1. R is the gas constant, T the absolute temperature, F is the Faraday Constant, and n the number of electrons that transfer. Note also that this modifying term will show a minus sign if the oxidant/reductant ratio is reversed).



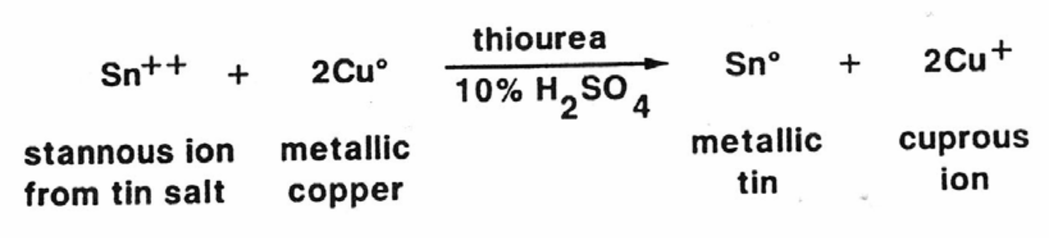
$$E = Eo + \frac{RT}{nF} \cdot \mathrm{Ln}\ a_{Cu^+}$$

Fig. 1: EMF-Series (qualitative & abbreviated) *Fig. 2: Nernst Equation (for Cu^{+1}/Cu^0)*

Depending on the concentration of the Cu^{+1} ions and the concentration of the tin (Sn^{++}) ions, the actual position of E for the two metals on the EMF could be significantly different from their E_0 positions. Thus, a complexing agent such as thiourea (see Fig. 3) which selectively complexes copper ions stronger than tin ions can reverse the effective E of both metals and thermodynamically favor the deposition of metallic tin (see Fig. 4).

$$2\ Cu^+ + 8\ SC(NH_2)_2 \longrightarrow 2\ Cu\left[SC(NH_2)_2\right]^+_4$$

Fig. 3: Complexation of Cuprous Ions with Thiourea



$$\underset{\text{stannous ion from tin salt}}{Sn^{++}} + \underset{\text{metallic copper}}{2Cu^\circ} \xrightarrow[10\%\ H_2SO_4]{\text{thiourea}} \underset{\text{metallic tin}}{Sn^\circ} + \underset{\text{cuprous ion}}{2Cu^+}$$

Fig. 4: Immersion Tin- Basic Chemical Reaction

Despite the popularity of immersion tin, one has to keep in mind that thiourea does not have a clean bill of health, especially in Europe, and that engineering and environmental controls need to be in place to assure safe handling. Thiourea can be converted to innocuous species by oxidative degradation.