Over the years, the hot air solder leveling (HASL) process has been established as a primary surface finish for circuit boards. It still remains the most solderable, and arguably the most durable, surface finish. Recent developments in PCB manufacturing have highlighted some problems with these finishes, creating an urgent need for solderable, durable, and inexpensive alternative surface finishes that would be environmentally friendly and would yield a planar surface. A number of these finishes have been tested and new ones are introduced in trade literature from time to time.

This article will concentrate on the evaluation of some of these alternative finishes, employing the sequential electrochemical reduction analysis (SERA) technique. This technique is used to study the solderability of HASL surfaces and as a process control tool in PCB manufacturing. We will explore its applicability to the study and control of alternative surface finishes.

Solder has been used for a long time as the preferred coating to protect the solderability of circuit boards and components, and HASL has become a favorite process for the application of solder to PCBs. In general, it has been a reliable coating process for retaining the solderability of printed circuits; however, it is far from being a trouble-free process.

For years, the industry has been searching for a viable method to evaluate the solderability of solder finishes. Tench et al. has evaluated the use of electroanalytical techniques for this purpose, and proposed the technique known as SERA for the evaluation of tin and solder finishes.1,2

The SERA technique involves isolation of a surface pad or a plated through-hole using a rubber gasket with an accurately defined area. Then the hole, or covered surface pad, is filled with borate electrolyte, and a small, but accurately defined, current is applied between the tested surface and the auxiliary electrode placed within the cell above the board. The electrode potential of the tested surface is then measured as a function of time against a reference electrode, which is placed in the electrolyte’s storage vessel. (Figure 1)

The recorded potential-time curve consists of a series of plateaus with characteristic shapes depending on the type and quality of the surface. For example, Figure 2 shows one such curve obtained for a tin-lead surface. It shows the presence of oxidized Cu/Sn intermetallic compounds, SnO and SnO₂ on the surface of the solder coating. The final plateau on the curve indicates hydrogen evolution due to reduction of the electrolyte, thus providing the highest cathodic value achievable with the given electrolyte. Other species that need to be reduced at a more cathodic potential cannot be detected in the above manner.

A number of publications1-5 have described the use of SERA for evaluation of surface species and solderability of solder finishes on printed circuits, as well as for process control during the various stages of the PCB manufacturing process. The objective of this article is to concentrate on the evaluation of alternate finishes, currently being proposed to replace HASL and electroplated tin-lead coatings.

Despite its wide-spread usage, the HASL coating is not trouble-free or universally applicable. Presently, when circuit board features are being miniaturized and environmental pressures are mounting, the search continues for the best candidate to replace the HASL process. Features, advantages, disadvantages, and costs of alternative coatings are being considered.

In spite of the many papers presented and published highlighting or evaluating various alternative coatings, no single coating has been
established as a single viable process to replace HASL. All seem to have some advantages as well as disadvantages. The SERA technique can be used as a tool for monitoring quality and consistency of alternative coatings. In addition, it is our feeling that all of these coatings will be used to a certain extent, and more will emerge in the near future as “the only viable process.”

SOLDER COATINGS
SERA is presently used for evaluating the solderability of solder finishes, as well as a process control tool during its preparation. It became clear from the initial work at Rockwell that an increase in the tin oxide reduction potential of the solder surface can be correlated with an increase in the PCB defect rate during the assembly process. Tench and others have shown that as the potential of the reduction process shifts to more cathodic (negative) values, the defect rate increases for a given flux. This provides a basis for evaluation of surfaces, fluxes, and soldering conditions during PCB manufacturing, as well as prior to assembly. Since higher cathodic potential means that the reduction of the oxide becomes more difficult,flux requirements can be selected prior to the assembly, based on the quality of the solder surface. This means that the higher the amount of SnO₂ on the solder surface, the more aggressive the flux condition must be to assure proper soldering.

In addition to the value of the reduction potential, other SERA curve features are being evaluated as potential process control indicators. These features include: presence and amount of the intermetallic compounds on the surface, open circuit potential, and hydrogen evolution potential. All of these parameters have been observed to vary during comparison of “good” v. “bad” boards. Currently, only the presence of intermetallic compounds has been clearly correlated with solderability problems. When a significant amount of intermetallic compounds are detected on the board’s surface, solderability issues arise. Figure 3 shows one such “bad” board with the presence of intermetallic compounds.

HASL ALTERNATIVES
A number of finishes have emerged as potential alternatives to HASL. They include thin and thick OSPs, immersion silver, immersion tin, and immersion gold over nickel. As these finishes are examined, we will discuss how the SERA method can be used as a tool for process control, and for surface evaluation of alternative coatings.

ORGANIC SOLDERABILITY PRESERVATIVES
Unlike the HASL process, where soldering is done by melting the existing solder coating, soldering with OSPs requires the removal of the OSP coating with heat and acid (flux). This must be done so that the attachment can take place on the copper surface under the OSP coating. Hence, OSPs must keep the Cu surface solderable prior and during the soldering process.

During storage, unprotected Cu surfaces are oxidized, leading to the formation of Cu₂O, and later, to a mixture of Cu₂O and CuO. If the copper surface has not been protected from oxidation, it might indicate the presence of three SERA detectible species. The nature of these species and reduction voltages are given in Table 1.

Coating copper surfaces with OSP protects the surface by formation of a complex between the OSP (imidazole, benzotriazole or substituted benzimidazole) and the copper surface. Figure 4 shows SERA curves of protected and unprotected Cu surfaces after one year of natural storage at ambient conditions. Clearly, the imidazole-protected surface prevented further oxidation of copper. This observation can be used as a basis for detection of OSP on the surface. Figure 5 shows SERA curves for surfaces with and without thin OSP coating after a short heating cycle. The protected surface is clearly distinguishable. Such a procedure is currently used by some PCB manufacturers to detect problems with thin OSP coatings soon after the manufacturing process. Since thick OSPs shift the reduction potential of the Cu-OSP complex, depending on their thickness, their presence is easily detected even without application of the heat. Thus, SERA offers a
simple method for detecting the presence of OSPs on the PCB surface. Also, variations in the curve can be used as a useful process control indicator.

Moreover, thin OSPs (25-100Å) are generally near-monolayer coatings, and their application is quite uniform across the surface. However, the coating thickness is too thin to be measured electrochemically. On the other hand, thick OSPs (500-6,000Å) generally vary in thickness depending on the type of OSP, the control of the chemical composition of the applied solution, and the type and quality of the application process. By using different electrolytes, SERA curves can be used to measure the thicknesses of thick OSP coatings. As an OSP thickness increases, the amount of the reducible material increases, and the time required to “drill” through the OSP coating is then correlated to the thickness of the OSP. Because SERA can be used on very small surfaces (1.6 mm diameter or less), it can be used to measure the thickness distribution of OSPs directly on the PCB, thus becoming a very powerful process control tool. Measurements of the relative distribution of the OSP on the surface allows one to improve and control the process itself. A number of papers describing SERA testing of OSPs have been published.6-8

The ideal goal is to correlate SERA measurements of OSP coatings to their solderability. Work performed at NPL9 revealed that SERA curves, obtained with yet another electrolyte, showed an increase in copper oxide formation and a decrease in OSP thickness, as the boards undergo consecutive simulated reflow cycles.

The NPL study involves a number of U.K.-based PCB shops, using different types of OSP coatings. Another, more thorough study has been focused on a single OSP coating with different thicknesses and different storage conditions.10 During this work, the results of SERA measurements were correlated to the results of wave soldering, which was performed by the counting of filled holes in specially prepared solderability test vehicles. It was found that the SERA technique can be used for monitoring boards coated with a “proprietary” OSP coating.

Summarizing the work with OSPs, the SERA method can be used as a process control tool to evaluate the presence, quality and thickness of the OSPs, as well as to show some correlations to solderability after simulated reflow cycles.

**IMMERSION SILVER**

Silver is considered to be a “precious” metal, but its chemical properties distinguish it from other precious metals such as gold and palladium.

The silver surface is quite reactive, and atmospheric corrosion of the silver surfaces occurs almost immediately upon contact with air. Corrosion, as expected, proceeds even faster in the production environment than in clean air. Presence of free sulphur or sulphur compounds in the environment causes rapid formation of the silver sulfide (Ag₂S). Higher humidity increases the rate of silver corrosion in the presence of sulphur compounds.11, 12

The main components of tarnish films on the silver surface are silver oxide (Ag₂O), silver sulfide (Ag₂S), silver sulphate (Ag₂SO₄) and silver chloride (AgCl). The presence of sulphur compounds on the surface causes solderability problems.11, 12

Since the immersion silver coating is relatively thin (0.1 µm) and sensitive to tarnishing, the surface of silver must be protected to maintain its solderability characteristics. The corrosion of silver can be inhibited by placement of thin organic or inorganic films on the
Commercially available immersion silver coatings are coupled with thin organic films which are supposed to provide the required protection from tarnishing; however, this compound is fragile, especially at elevated temperatures and under humid conditions. The solder wettability of fresh silver coatings is good, but degrades rapidly with the formation of a tarnish film. Therefore, it follows that the presence of a protective film on the surface of silver is extremely important for the protection of silver from tarnishing. Also of importance is a sufficient thickness of the silver layer itself. The presence of proper analytical techniques to monitor conditions and thicknesses of protective layers, tarnishing layers, and the thickness of silver itself is of utmost importance.

When a constant current is applied to a silver surface (SERA test), the resulting potential-time curve reveals a number of plateaus that correspond to the sequential reduction of compounds in the tarnishing film. SERA curves obtained from silver surfaces are similar in shape to those obtained from copper surfaces.

Fundamental work has recently been performed to identify and quantify the species of tarnishing films. It was found that components of tarnishing film reveal the following reduction potentials: \( \text{Ag}_2\text{O} +0.28 \text{ V}, \text{AgCl} +0.12 \text{ V}, \text{Ag}_2\text{S} -0.62 \text{ V} \) and \( \text{Ag}_2\text{SO}_4 -0.92 \text{ V} \).

Since SERA has detected the presence of both organic inhibitor and tarnish film, SERA can consequently be used as a process control tool for immersion silver coating. In addition, using an anodic current, the silver coating can be stripped coulometrically. This allows for an accurate (but destructive) measurement of the thickness of the silver coating.

**IMMERSION TIN**

Immersion tin is another of the emerging alternative coatings that can be evaluated using the SERA technique. For this process about a 1-µm-(40µ inches)-thick immersion tin layer is placed on top of a copper substrate. Some of the coatings might contain organic or inorganic materials that act as diffusion barriers between copper and tin, or protect the tin surface from excessive oxidation.

We have studied several immersion tin processes. Figure 7 shows SERA curves for a thin tin coating (0.26 µm, 10µ inch), before and after heat treatment (reflow). As can be seen from the curves, before the treatment, only SnO is visible on the surface. This does not pose any solderability problems. After the heat treatment, only oxidized Cu-Sn intermetallics are present on the surface. This indicates that all of the tin has diffused into the copper substrate. Hence, this surface would present serious solderability problems.

The above observation was confirmed by the destructive oxidation of the surface. Before the heat treatment, tin is clearly present on the surface, followed by a thicker layer of Cu5Sn6 intermetallic, and a very thin layer of Cu3Sn intermetallic. After heat treatment, no pure tin can be observed on the surface, the Cu5Sn6 intermetallic layer is slightly thinner, while the thickness of the Cu3Sn material has increased.

The presence of SnO2 and oxidized intermetallic compounds can be correlated to solderability problems on tin coatings. Thus, SERA can be used for QA process control of this coating. The destructive oxidation of the coating can be used for precise thickness determination of the tin coating, as well as for determining intermetallic thicknesses. The solderability of heated immersion tin was shown to diminish as the thickness of the Cu3Sn layer increased.

**ELECTROLESS PALLADIUM**

The promise of electroless palladium coating lies in its capability to be applied directly over copper. Previously published results showed that between 6 to 9 microinches (0.15 to 0.23 µm) thick palladium coating are needed to completely cover a copper surface. Even thicker coatings are required to prevent copper migration through the palladium layer during heating. Thus, the presence of copper on the surface or in the pores of a palladium coating is easily detected, and it can be used for evaluation of electroless palladium coatings on a copper substrate.

**IMMERSION GOLD**

The last coating to be discussed is immersion gold over a nickel barrier. This coating is being tested extensively as a promising alternative coating that can yield solderable and wirebondable surfaces. Some preliminary results have been presented in an earlier paper.

One possible cause for solderability problems on immersion gold coatings is the porosity of the gold, which allows oxidation of the exposed nickel barrier through the gold layer pores. As shown in Figure 8, the reduction of nickel oxides takes place at potentials more negative...
(cathodic) than hydrogen evolution on the gold surface. This makes it impossible to detect the reduction of nickel oxides in the presence of an exposed gold surface.

Tench1 has described a technique similar to SERA, named potentiometric evaluation of substrate oxidation (PESO). The PESO technique uses an acidic electrolyte such as NH4Cl (pH=4.0), and the corrosion potential of the gold surface is measured as a function of time. The presence of plateaus can be related to the presence (and thicknesses) of the nickel oxides, and the corrosion potential can be related to the porosity of the gold surface.

A second solderability problem arises due to the presence of organic materials on the gold surface. These materials can come from various sources, such as solder mask, oils, or contaminated ovens. Their presence on the surface of gold can be observed by a shift in the rest potential of the gold surface in the borate buffer (pH=8.4) electrolyte. Both the potential shift, as well as the signal “noise” disappear when the surface is cleaned with a strong acid and the solderability is restored.

The combination of SERA and PESO techniques can be used to evaluate immersion gold coating surfaces for organic contamination, porosity, presence of oxidized nickel in the pores of the gold, and presence of copper oxides on the gold surface.

These can lead to a loss of both solderability and wirebondability for this alternative coating. Further tests on this surface are being conducted.

CONCLUSION
In conclusion, it has been shown that the SERA technique can be a powerful tool for evaluating the surfaces of alternative coatings. More work needs to be done and additional studies are being performed which will be reported in the near future. Despite the work that still remains, SERA has already been established as a valuable process control tool for PCB manufacturing.

-Published in PC FAB Magazine, May 1999

Peter Bratin is vice president Michael Pavlov is product manager, and Gene Chalyt is product manager with ECI Technology, East Rutherford, NJ.
REFERENCES


