New Application of the SERA Method - Assessment of the Protective Effectiveness of Organic Solderability Preservatives.

P. Bratin, M. Pavlov, G. Chalyt and R. Gluzman
ECI Technology, East Rutherford, NJ

New electrochemical method to assess the protective effectiveness of Organic Solderability Preservatives (OSP) will be presented. Main features of the method will be demonstrated. Experimental results obtained from bare copper PWBs coated with different types of OSP will be discussed. The influence of elevated temperatures on the protection effectiveness of OSP will be shown.

Introduction.

Organic coatings have been successfully used in the past for inhibition of copper corrosion. The most widely used coatings are azole related compounds such as imidazole and benzotriazole. In the recent years, there has been an ever increasing push in the electroplating industry to use these compounds as Solderability Preservatives (OSP), in place of Tin and Tin/Lead coatings. Unfortunately, most organic coatings can be affected by exposing them to elevated temperature and humid atmosphere. Under such conditions the OSPs loose the uniformity, and the copper oxide layer starts to grow on the surface of the protected specimen, causing solderability problems. Several methods have been used to study the behavior of the OSPs, including X-ray Photoelectron Spectroscopy (XPS or ESCA), Auger Electron Spectroscopy [1], Electrochemistry, and Spectroscopy. The X-ray and electrochemical methods provide atomic information about the surface region, as well as some details about oxidation states of the presented elements [2]. Azolate film thicknesses can be measured indirectly by UV/Vis Spectroscopy [3].

Recently an electrochemical method has been presented for assessment of the solderability of tin/lead finished surfaces [4]. This method involves sequential reduction of oxides (and other species) on a metal's surface. This non-destructive technique called Sequential Electrochemical Reduction Analysis (SERA™) has been successfully used for Sn and Sn/Pb surfaces and recently has been included in military specifications for through-holes.

The purpose of this paper is to introduce the new application of SERA method - assessment of the protection effectiveness of OSPs and to show the major capabilities of this new method.

Principles of SERA Method.

Chronopotentiometry has previously been applied to analysis of oxides on the metals surface [5]. Recently, this work has been extended to the assessment of solderability loss caused by formation of metal oxides[6]. The method involves sequential reduction of surface oxides, and provides a quantitative measure of the type and amount of each oxide present on the surface.

In the SERA method, the part to be analyzed is brought in contact with the deaerated electrolyte, chosen to facilitate reduction and to minimize the chemical dissolution of the oxides of interest. A constant cathodic current is then applied between the part and an inert counter electrode. The potential of the tested part is monitored as a function of time relative to the reference electrode. The applied current is chosen to avoid excessive polarization of the cathode and is typically very small ($< 100\ \mu A/cm^2$). The electrolyte contains boric acid and sodium tetraborate (pH=8.4).

SERA curve features.

Figure 1 shows the theoretical SERA curve, showing electrode potential as a function of time. When copper is covered with a film of mixed oxides, an underlayer of cuprous oxide and outer cupric oxide is present on the copper surface and the curve will show two plateaus, one for each oxide. For this ideal case, the cathode voltage initially decreases to a plateau corresponding to the reduction of the most easily reduced specie (cuprous oxide). As soon as the reduction of cuprous oxide is completed, the voltage again changes to the value required for the reduction of the cupric oxide. When both oxides are removed from the surface, the voltage will decrease one more time. The last plateau corresponds to an electrolysis of the water with the accompanying evolution of hydrogen.

Any other reducible species present at the surface will reduce at appropriate potentials, and curve will show additional plateaus.

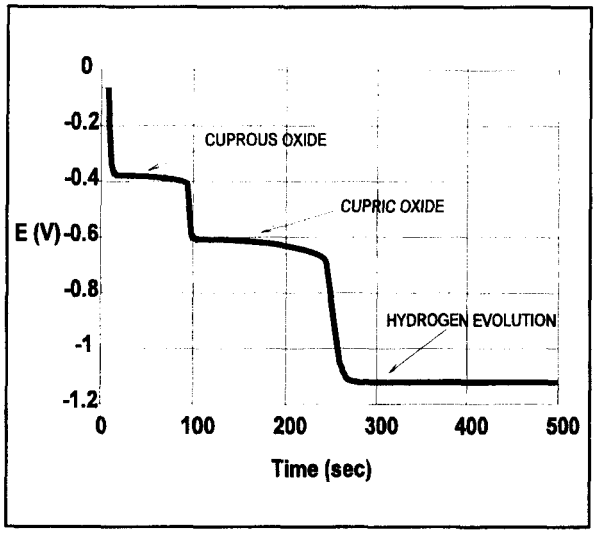

Figure 1. SERA curve for bare copper

Formation of the oxide film on copper.

Two stable oxides, Cu_2O and CuO, are formed on a copper surface which is in contact with moisture and oxygen. The cuprous oxide (Cu_2O) is formed first at any oxygen partial pressure and its thickness grows logarithmically until it reaches 65 to 90 Å. After an incubation period of 90 to 120 min a new component, CuO, appears in the film [5]. The oxide layer can be described as a dual film: the layer closer to the metal is a compact Cu_2O film, layer on the surface is CuO. It is very important to note that, the primary oxidation product is always Cu_2O. Ageing or heating of copper will increase the thickness of the CuO. The exact chemical nature of the species, whether they are oxides, hydrated oxides, or hydroxides, is beyond the scope of this article, and it depends on the conditions present during oxidation process.

Interaction of OSP with copper/copper oxide.

The mechanism by which azoles inhibit the oxidation of the copper has been extensively investigated [7-11]. All investigators, who studied the mechanism of corrosion inhibition of copper, agree that the interaction of azoles with the copper surface occurs according to the following equation:

$$2(AH)_{aq} + Cu_2O \rightleftharpoons 2Cu\,(A) + H_2O$$

It means that the presence of cuprous oxide on the

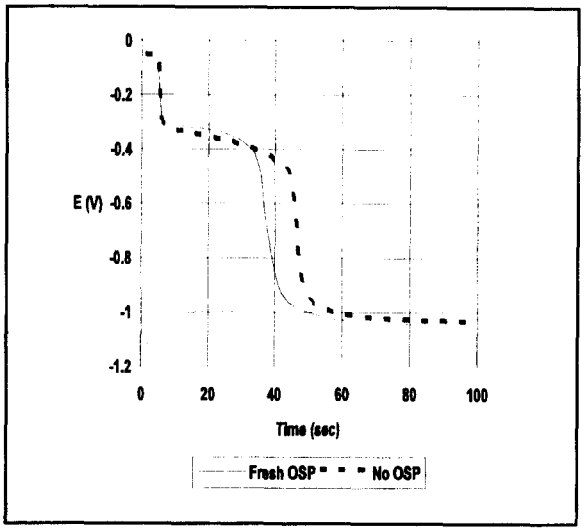

Figure 2. Comparison of SERA curves for protected and unprotected specimens.

copper surface is necessary for attachment of the organic molecules[12]. SERA curves obtained from samples coated with "thin" OSP layer confirm that the protective layer is attached to thin layer of Cu_2O. The reduction plateaus obtained from a fresh copper surface (without OSP) and copper surfaces protected with thin

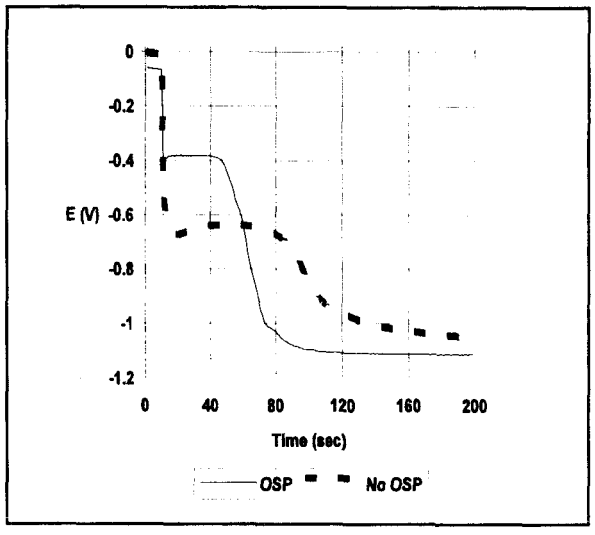

Figure 3. Comparison of SERA curves for one year old protected and unprotected specimens.

OSP layers were similar (Figure 2). If both, protected and unprotected surfaces were aged for extensive period of time a year for example, the reduction plateau obtained from unprotected copper has shifted to more negative potentials, presumably due to conversion of Cu_2O to CuO (Figure 3). Azole related compounds can

create protective layers with various thicknesses (20 - 5000 Å)[3]. The difference in the thicknesses could be related to the presence of benzoic ring and substitution of hydrogen atoms in the benzoic ring, as well as due to multi layer coatings, accomplished with help of codeposited copper.

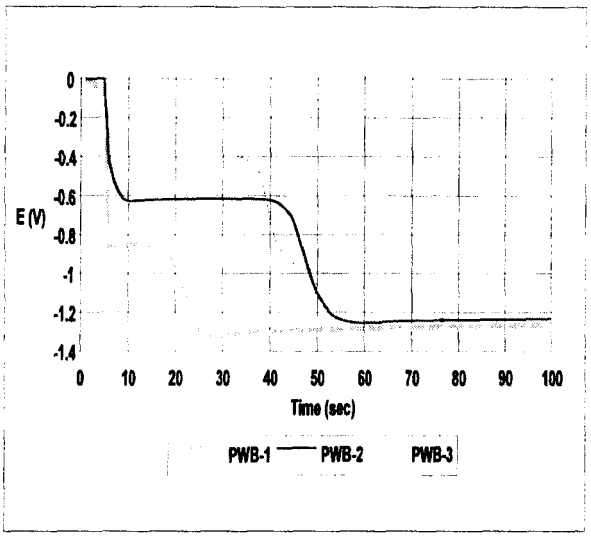

Figure 4. *Comparison of SERA curves for three different OSPs.*

Figure 4 compares SERA curves obtained from three PWBs freshly coated with different OSPs. It is clear from these curves, that the reduction voltage of the underlaying copper oxides probably depends on the thickness of the coating. From Figure 4, it is clear that the PWB-1 which is coated with the thickest proprietary OSP shows the most negative reduction voltage. Despite the thickness of a protective layer, all of these organic coatings protect copper surfaces from further oxidation. At regular conditions (room temperature and average humidity), it will take long time to brake down the protective layer. In order to evaluate the protective effectiveness of OSPs and speed up the oxidation process, thermal treatment of the coated specimens has been studied. The high temperature treatment also can be used to simulate the conditions of the soldering process and assess the influence of this temperature on the stability of the protective films.

Experimental.

Two different proprietary coatings have been selected for testing. The main difference of tested OSPs was the thickness of the protective film. The thickness of one OSP film was in range from approximately 20 - 50 Å, the second was in the range from 3000 to 5000 Å. For the sake of simplicity, we will call them as "thin" and "thick"coatings.

Both coatings were at about the same time placed on the copper specimens. All experiments were performed using QC-100 Solderability Tester *. The protective effectiveness of organic coatings was studied by exposing the coated specimens to elevated temperatures, performing SERA tests, and comparing their curves to once obtained with untreated control

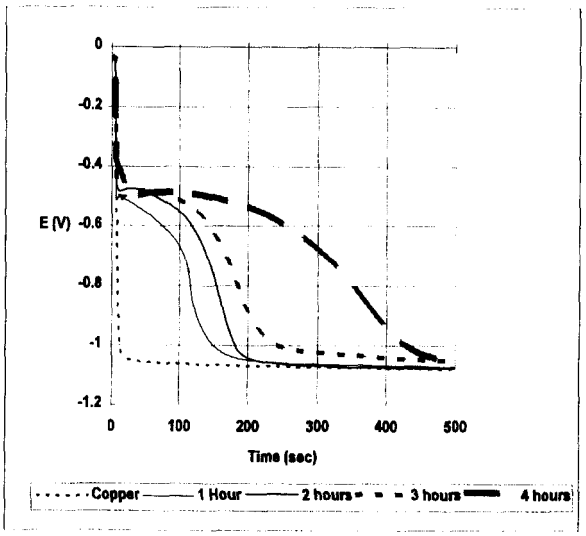

Figure 5. *Oxidation of copper at 100 " C.*

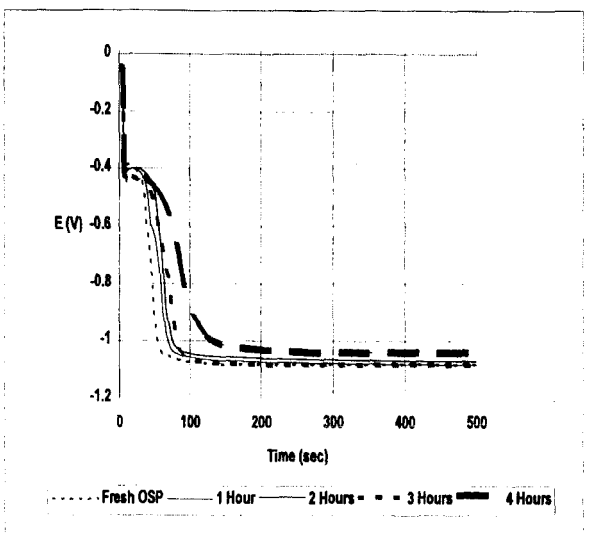

Figure 6. *Oxidation of copper protected with "thin" OSP.*

*QC-100 is a trade mark of ECI Technology

specimens. First thermal treatment was performed at 100°C in air atmosphere. Three specimens, two protected with different OSPs and one unprotected, were cut to four pieces and placed into the oven. One sample of each group was consequently withdrawn

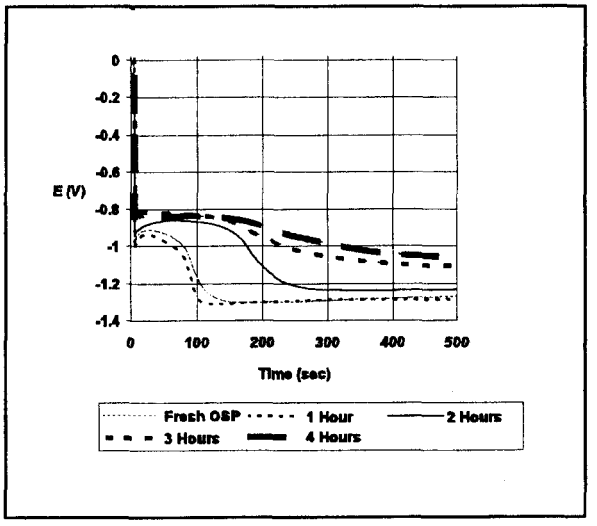

Figure 7. Oxidation of copper protected with "thick" OSP at 100 ° C.

from an oven every hour, and analyzed. Results obtained for an unprotected sample are presented in Figure 5. The expected growth of cuprous oxide layer can be observed. Figure 6 shows results obtained for copper protected with "thin" organic layer. No significant increasing of oxide thickness was detected, even after four hours of thermal treatment. It is important to note that final potential was virtually the same for unprotected copper, as well as for one protected with "thin" OSP. The final potential

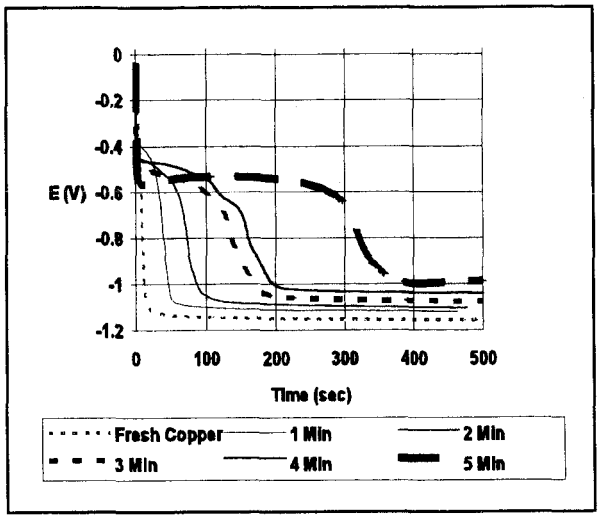

Figure 8. Oxidation of unprotected copper at 181 °C.

corresponds to the hydrogen evolution process and has stable value for each metal or alloy. Figure 7 shows the transformation in the shape of SERA curves obtained

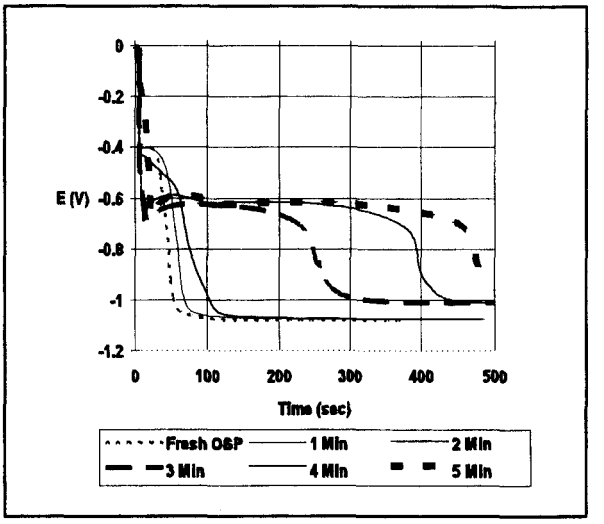

Figure 9. Oxidation of copper protected with thin OSP at 181 ° C.

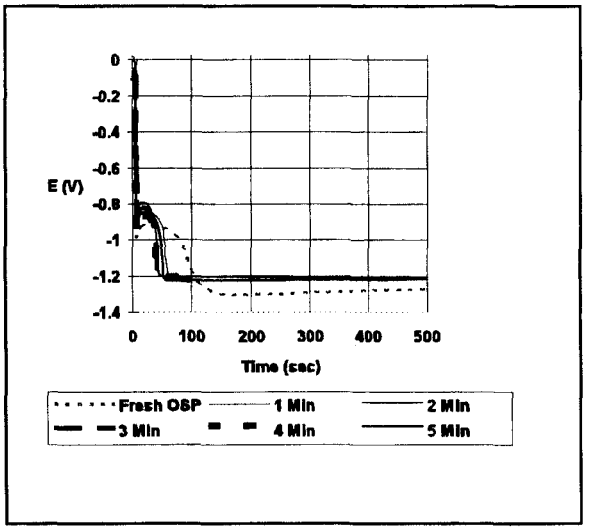

Figure 10. Oxidation of copper protected with "thick" OSP at 181 ° C.

from the sample protected with "thick" OSP. The changes are observed not only in thickness of oxide, but also in the value of the final potential, which can be explained by the deterioration or reorganization of the organic layer.

For second experiment, the temperature of 182±2°C (which is near the melting point of eutectic Sn/Pb alloy) was selected. Set of samples identical to ones prepared for first experiments was used. At times larger than 2 minutes, the "thin" protective layer has

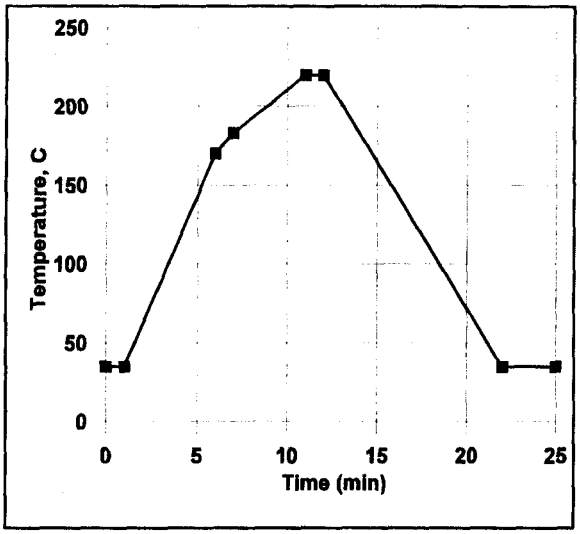

Figure 11. Temperature profile.

larger than 2 minutes, the "thin" protective layer has significantly deteriorated, and did not provide any protection. At the same time, the "thick" layer was

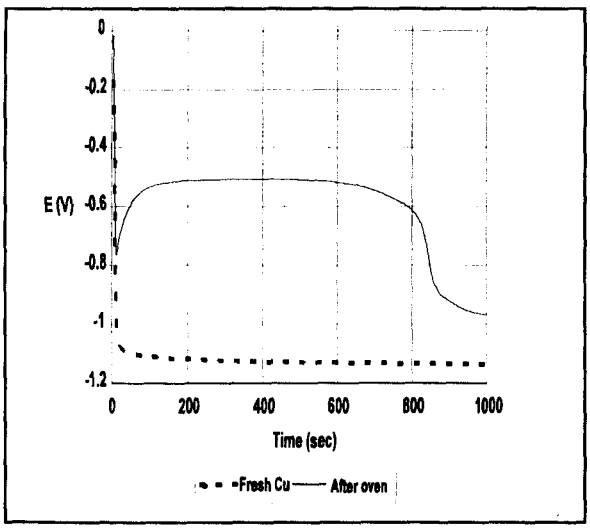

Figure 12. Dynamic oxidation of unprotected copper.

stable even after 10 minutes of this temperature treatment. The soldering process using a wave soldering machine is not performed at a single temperature, but includes preheating, soldering process and cool-down. To evaluate effect of such process, a dynamic temperature treatment was applied to the test samples. The temperature profile is shown in Figure 11. Again, the bare copper specimen was tested together with coated samples. In order to remove all oxides from the surface, the bare copper was cleaned with 10% HCl prior to the heating cycle. Results obtained for bare copper before and after the heating are shown in Figure 12. From this graph, it is clear that the copper surface was unimpededly oxidized in the air atmosphere. The thickness of surface oxide, if required, can be easily calculated [13]. As we pointed before, the SERA curves obtained from bare copper and freshly coated copper with "thin" OSP are similar. After dynamic temperature treatment, this similarity disappeared and SERA test detects the presence of the several reducible species (additional reduction plateaus) on the surface of the

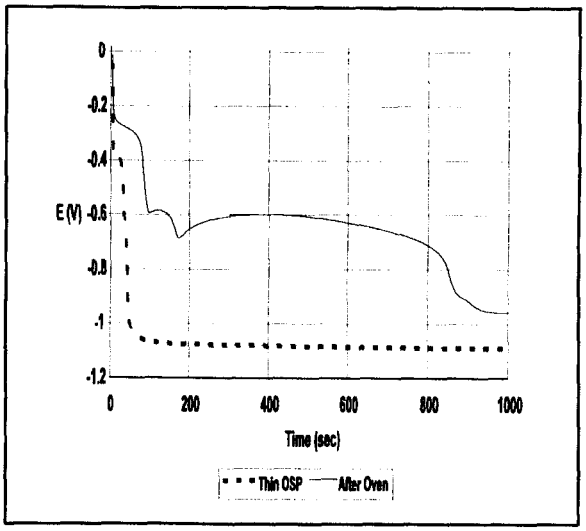

Figure 13. Dynamic oxidation of copper protected with "thin" OSP.

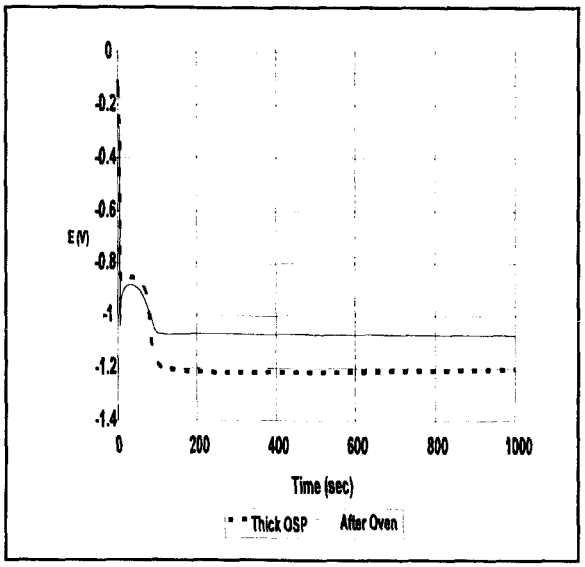

Figure 14. Dynamic oxidation of copper protected with "thick" OSP.

protected sample (Figure 13). The total thicknesses (reduction time) of these films were similar for both samples. Figure 14 shows the changes in the shape of SERA curves for "thick" OSP, before and after the dynamic heat treatment. The width of a reduction plateau after temperature treatment remained virtually unchanged. It means that the amount of oxide has not changed after temperature treatment. The initial drop

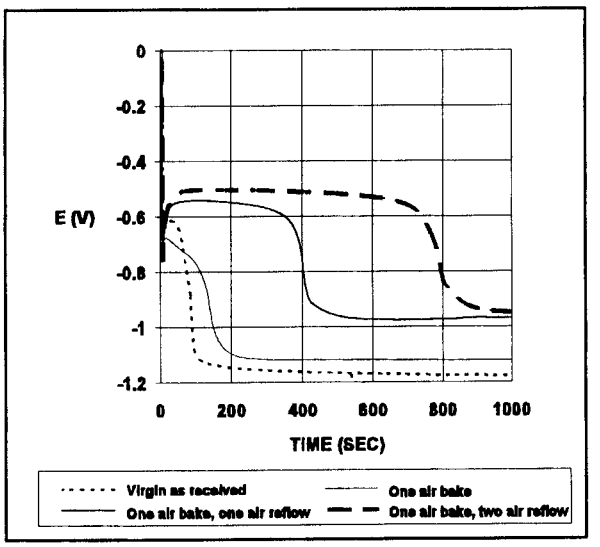

Figure 15. *Effect of thermal assembly process steps in air atmosphere.*

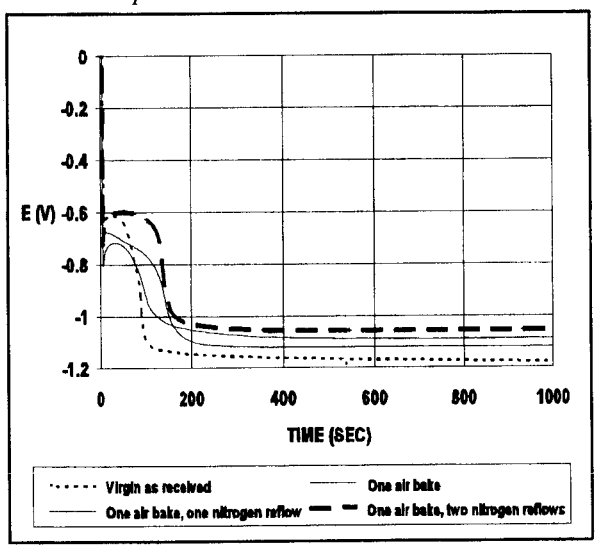

Figure 16. *Effect of thermal assembly process steps in nitrogen atmosphere.*

followed by an increasing in the voltage indicates that the OSP probably lost the uniformity due to the stratification. The potential of a tail part of SERA curve obtained after treatment was significantly higher than value obtained for freshly coated sample.

Commercial manufacturing of the surface-mount boards requires multiple passes through the reflow machines. Gutierrez [14] recently reported on SERA study of a different "thin" OSP, prior to reflow-cycle, as well as after one and two cycles. His results are shown in Figures 15 and 16. The effect of the thermal assembly process steps, in air atmosphere, is shown in Figure 15. This graph illustrates the effect of each thermal operation, i.e., air bake, air bake and one IR reflow etc. Figure 16 represents thermal process steps under the nitrogen atmosphere.

From these tests, it is clear that both organic coatings have deteriorated during the thermal stress. The "thick" coating protects copper from oxidation better than "thin" one. However, the presence of oxide film as well as the stratification of an organic layer should be correlated to the solderability of OSP protected boards.

Conclusions.

Results presented here clearly show that the SERA technique can be utilized to assess the thermal stability of OSPs and monitor the extent of oxidation of copper substrates. Further efforts are currently under way to establish the correlation between the extent of copper substrate oxidation and solderability.

Acknowledgments.

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