Conduction mechanisms in contaminant layers on printed circuit boards

by J. R. White

AC impedance methods have been utilized to explore surface conduction mechanisms on printed circuit boards (PCBs) containing various types of solder flux contaminants. Residues from water-soluble, rosin-based, and no-clean fluxes were analyzed and evaluated for their potential impact on reliability. Impedance data for intentionally contaminated PCBs having several circuit line geometries were obtained at different relative humidities. An equivalent circuit model is presented that fits the data obtained. It is used to evaluate and distinguish among ohmic, kinetic, and diffusion effects and to predict the environmental conditions that may be detrimental for various line geometries.

Introduction

Historically, PCBs have been assembled (via component soldering operations) with rosin-based fluxes, which require PCB cleaning in freon-based solvents. With the acceptance of the Montreal protocol for the reduction of chlorofluorocarbon emissions, many manufacturers have changed to solder pastes and fluxes which are either water-soluble or are "no-clean" (intended to be left on the PCBs, without cleaning). This has led to increased emphasis on the reliability of the fully assembled PCB, because of the propensity for these materials or their residues to promote failures due to metal migration [1–3].

To assess the impact of residues on reliability, representative PCBs are typically placed in a controlled temperature and humidity chamber. A dc bias ranging from 5–100 V is applied to alternate circuit lines for several hundred hours. The resistance between the lines is monitored, and if there is a drop in the resistivity or if there are signs of dendritic growth, the contamination level is deemed to be unacceptable. The major drawbacks to this type of testing are that it takes an exceedingly long time and is destructive; if dendritic growth occurs, the PCBs are no longer useful.

The use of ac impedance methods offers several advantages for assessing the risks associated with surface contaminants compared to conventional dc methods. The

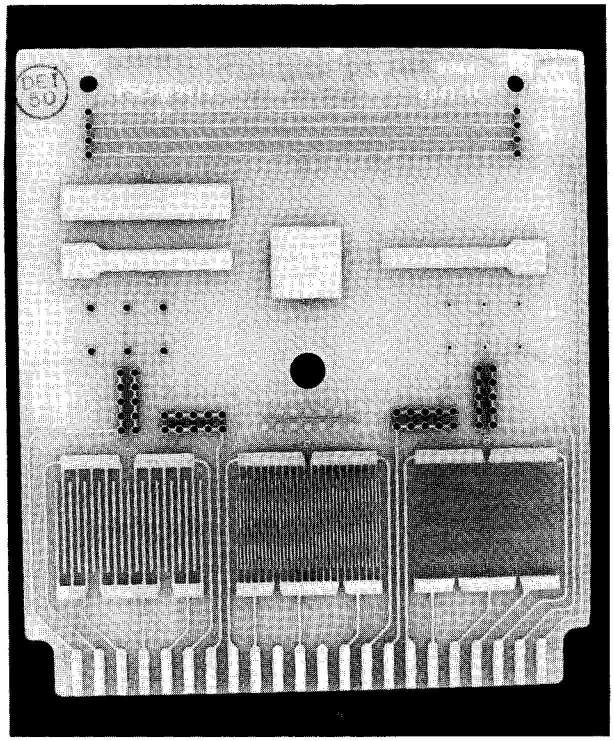


Figure 1

Photograph of an IPC-B-25 PCB test vehicle. Reproduced with permission.

impedance measurement required is comparatively short (minutes vs. weeks) and the applied voltages used are too low to induce dendritic growth during testing. Further, the ac impedance methods facilitate modeling of the interfacial parameters, which is useful as a predictive tool. Such methods have been utilized to study the raw materials for PCB assembly (e.g., solder paste) [4, 5] and to compare and elucidate conduction pathways in PCBs, by comparing surface conduction to bulk conduction processes—both between adjacent plated-through-holes and between conductors on opposite sides of a PCB [6].

Presented here are representative ac impedance data for PCBs containing a variety of residues that are encountered in their production. An equivalent circuit model is presented which facilitates the evaluation of electrochemical parameters and the influence of environmental conditions and circuit line geometries on the parameters, making it possible to identify conditions under which a specific residue may present a reliability risk.

Experimental techniques

The PCBs used in this study were standard epoxy/fiberglass multipurpose test vehicles, purchased from the Institute for Interconnecting and Packaging Electronic Circuits (IPC, part number IPC-B-25) (**Figure 1**). They contained three sets of interdigitated copper conductors, approximately 60 μm in height and 1.54 cm long. The spacing between the lines was 165, 305, and 635 μm for test patterns A, B, and C, respectively. Prior to testing, the PCBs were cleaned in 60°C DI water followed by three DI water rinses to remove ionic contamination, and by a mixture of methanol and CCl_2F_2 to remove trace organics.

Several of the PCBs were intentionally contaminated with known volumes of commercially available soldering fluxes. The selected fluxes were representative of a multitude of formulation possibilities, and while the results discussed here are generally applicable, they may not apply to every formulation available. Flux R was a rosin-based (nonaqueous) flux, containing approximately 30% by weight nonvolatiles, composed primarily of natural product, water white rosins [7]. Flux N was a no-clean flux, containing approximately 3% nonvolatiles, which consisted primarily of adipic acid. Flux W was a water-soluble flux, containing approximately 95% nonvolatiles, composed primarily of a nonylphenoxypolyethoxyethanol surfactant (92%) and diethylamine hydrobromide (3%).

A quantity (750 μl) of each flux was applied to a masked area around the interdigitated test sites of the PCBs. Dilutions, in 2-propanol, of 1:100, 1:10, and 1:100 were used for fluxes W, N, and R, respectively. The PCBs, with the flux contamination and a control PCB which had no intentional contamination, were placed in a temperature and humidity chamber maintained at a temperature of 50°C. Impedance data were taken at 20, 50, 80, and 90% relative humidity (RH). The chamber was allowed to equilibrate for 24 hours each time the RH was changed. The impedance data were taken with an EG&G Princeton Applied Research (PAR, Model 388) impedance system. The ac voltage amplitude was 50 mV, and no dc bias was used. A $5.66 \times 10^8\ \Omega$ resistor was placed in parallel with the PCB being examined in order to prevent the sensitivity limit of the potentiostat from being exceeded. Equivalent circuit modeling was accomplished with a linear least-squares-fit procedure [8].

Results and discussion

The equivalent circuit model used to interpret the impedance data from a PCB test vehicle is shown in **Figure 2**. The capacitance C_{epox} and resistance R_{epox} are assumed to characterize the bulk of the test vehicle. The other parameters are assumed to characterize the surface contaminant layer that is present between its copper lines. The portion associated with those parameters corresponds to an equivalent circuit of a typical electrochemical interface [9]. The resistance R_{Ω} describes the ohmic resistance of the surface contaminant layer, and C_{dl}

represents the double-layer capacitance at the interface of the contaminant layer and the surface of the copper lines. The resistance R_{ct} is the charge-transfer resistance associated with a faradaic reaction occurring at the copper/contaminant interface (it is assumed that there are no faradaic processes occurring in the absence of a contaminant layer). The parameter Z_ω is the Warburg impedance, detectable when a faradaic reaction occurs under diffusion control. It is a complex, frequency-dependent term described by

$$Z_\omega = \sigma\omega^{-1/2}(1 - j), \tag{1}$$

where σ is the Warburg coefficient.

The nature of the contaminant layers chosen in this study represents three distinct cases, which may all be described by this equivalent circuit. First is the case for which there is no contaminant layer present and the only conduction pathway is through the epoxy/fiberglass substrate. This is the simplest case and may be described simply as a parallel combination of R_{epox} and C_{epox}, since $R_\Omega \rightarrow \infty$.

The second case is the no-clean flux case. Here, the contamination layer is a crystalline solid (primarily adipic acid) and does not form a continuous layer between the copper conductors. As water is adsorbed onto the PCB, with increasing humidity some of the adipic acid dissolves and dissociates to form an ionic, conducting medium. Thus, R_Ω decreases, providing an alternate surface pathway to bulk conduction.

The third case is represented by the water-soluble flux. Unlike the no-clean contamination, the water-soluble flux does leave a continuous, conducting layer between the copper conductors. Further, a detectable faradaic component is present which exhibits diffusion control at lower frequencies.

Relevant Bode plots obtained via test circuit A are shown in **Figure 3**. The data points represent experimental data, and the corresponding fits to the equivalent circuit are shown as solid lines. At higher frequencies, only the capacitive behavior of the epoxy dielectric is observable and is independent of the nature of the surface layer. At lower frequencies, the dependence of the impedance upon the characteristics of the contamination is more pronounced.

The rosin flux and control cases both show comparatively large impedance values at low frequencies, with those associated with the rosin flux being somewhat greater than those of the control. Although the values are near the detection limit, this is a significant increase, attributable to the hydrophobic nature of the rosin flux, and is in agreement with insulation resistance testing performed on these materials [10]. In the absence of rosin flux (or any intentional contaminant), the epoxy surface is free to adsorb water, permitting surface conduction to occur if there are trace ionic contaminants available. The rosin flux functions by passivating the surface in two ways: First, it prevents or reduces water adsorption on the epoxy/fiberglass; second, it covers (passivates) the surface of the copper conductors. Essentially, it blocks surface pathways, leaving conduction through the bulk epoxy/fiberglass as the only pathway. Therefore, in practice,

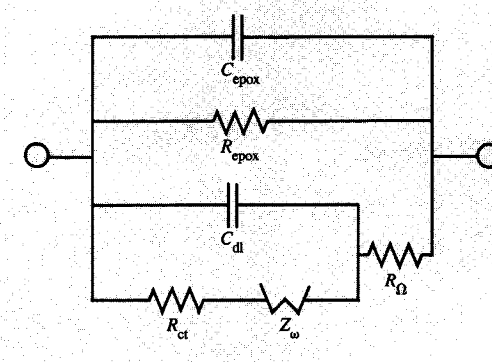


Figure 2

Equivalent circuit model used for characterizing ac impedance data.

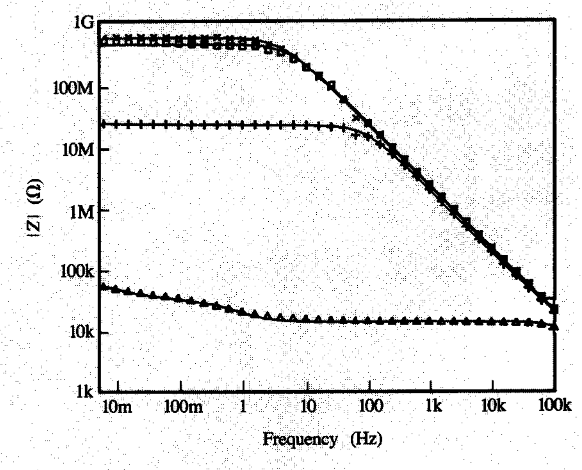


Figure 3

Bode plots obtained using test pattern A in the presence of (x) rosin flux, (+) no-clean flux, and (Δ) water-soluble flux, and (□) in the absence of flux. The data were obtained at 90% RH and 50°C. The solid lines show the fit from the equivalent circuit model.

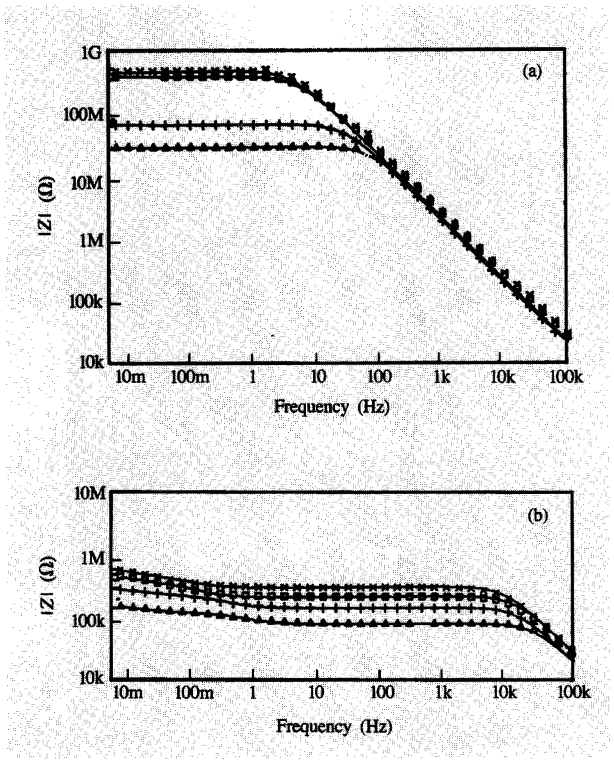


Figure 4

Bode plots obtained at several relative humidity levels via test pattern B: (x) 20% RH, (□) 50% RH, (+) 80% RH, and (Δ) 90% RH, in the presence of (a) no-clean flux and (b) water-soluble flux.

leaving rosin flux residues on the PCB may be desirable because of the resulting tendency toward surface passivation.

For these reasons, the rosin flux case was used to evaluate the parameters associated with bulk conduction in the epoxy (assuming that $R_\Omega \gg R_{epox}$, thus eliminating the surface pathways). Values for R_{epox} and C_{epox} were determined to be $7.5 \times 10^9\ \Omega$ and 8.0×10^{-11} F, respectively, and were used throughout for the modeling of other cases. The value of R_{epox} is similar to values obtained by dc insulation resistance testing [10]. A value for the capacitance of 4.4×10^{-11} F is expected for this line geometry, assuming a dielectric constant of 4.0 for the epoxy/fiberglass PCB. This is reasonably good agreement, considering that these low capacitance values are near the sensitivity limit for the instrument and that there may be additional capacitance from the circuitry or leads.

The water-soluble flux is clearly the most conductive medium, followed by the no-clean flux. From the fit with the model, R_Ω and C_{dl} were determined to be $1.4 \times 10^4\ \Omega$ and 1.6×10^{-5} F, respectively, for the water-soluble flux case. This flux, which is a nonvolatile liquid, provides a relatively thick, continuous layer with an intimate contact with the copper conductors. Thus, it exhibits a significantly higher capacitance than the other cases and is more representative of values normally encountered for an aqueous electrolyte interface.

The capacitance obtained for the no-clean flux case is not significantly different from that for the rosin or control samples, supporting the observation that the residue is primarily a crystalline solid, which does not form an intimate contact with the copper surface. The surface conduction pathway relies on a thin layer of adsorbed water to dissociate the acid, thus providing a conductive medium. The effect of this residue is to reduce the surface ohmic resistance. The value of R_Ω was determined to be $2.0 \times 10^7\ \Omega$ from the plot in Figure 3. No charge-transfer or diffusional components were observed for this case. Thus, the plot still resembles a simple *RC* network, which now contains the term R_Ω.

The dependence of the impedance on RH is shown in **Figure 4** for the water-soluble and no-clean flux cases. At high humidity, the no-clean flux case shows intermediate values of Z, attributable to the adsorption of water and subsequent dissolution and dissociation of adipic acid [Figure 4(a)]. As the humidity decreases, Z increases to values close to the control and rosin flux cases. This is further evidence that this type of contaminant is reliant on ambient moisture, which must be adsorbed on the surface in order to provide potentially deleterious conduction pathways. In contrast, the water-soluble flux case shows much lower values of Z at all humidity levels [Figure 4(b)], indicating that ambient moisture is not necessary for surface conduction pathways to exist. Thus, any significant level of this type of contaminant has the potential to cause reliability problems. The slight increase in Z with humidity demonstrates some propensity for the layer to absorb water and swell, becoming somewhat more conductive at elevated humidity levels.

The only case that clearly exhibits a Warburg impedance (diffusion control) is that of the water-soluble flux. Representative Bode and Nyquist plots are shown in **Figure 5**. The diagnostic for diffusion control is a linear plot of $Z_{imaginary}$ vs. Z_{real}, with a slope of 1, in the low-frequency region. Figure 5(a) demonstrates this behavior, with a slope of 1.1 for the low-frequency points.

The effect of the Warburg impedance was observed, qualitatively, as an increase in Z at frequencies below 10 Hz in the Bode plots [Figure 5(b)]. The effect was somewhat masked as coarser line patterns were used, and can be justified by the following relationship for the total real impedance [9]:

$$Z_{real} = R_\Omega + R_{ct} + \sigma\omega^{-1/2}, \qquad (2)$$

where R_{ct} and σ are both inversely proportional to the electrode area A [9]. Therefore, as the electrode area is decreased, the impedance attributable to these parameters increases. R_{Ω} is the frequency-independent solution (surface layer) resistance, which may be described by the conductance L (Ω^{-1}) of the layer, namely

$$L = \kappa(A/l), \tag{3}$$

where κ is the intrinsic conductivity $(\Omega^{-1}\text{-cm}^{-1})$ of the layer and l is the distance between the conductors. Because the grids of test patterns A, B, and C were increasingly coarse, their A/l ratios were lower, respectively. While a decrease in A makes the effects of R_{ct} and σ more pronounced, an increase in l decreases the conductance L, effectively increasing R_{Ω}. The latter is a more dominant effect. Therefore, the use of finer test grids tends to minimize the ohmic contributions to the total impedance, thus making the study of kinetics more facile (**Figure 6**).

The two cases which displayed low values of R_{Ω} were the water-soluble and no-clean flux cases. The occurrence of a relatively low-impedance pathway between conductors on a functional PCB may alter the impedance (current-carrying) characteristics of the conductors and may be cause for concern. However, if metal migration occurs across this pathway, a short circuit failure is possible. For metal migration to occur, a conductive pathway must be present, and metal dissolution (charge transfer) must occur at the anodic conductor. Only the water-soluble flux case demonstrated a propensity for faradaic charge transfer. Although the no-clean flux case demonstrated relatively low values of R_{Ω}, there were no observable charge-transfer processes occurring; the plots appeared as simple RC networks.

This may be explained by the relative stability of copper in the presence of adipic acid (no-clean flux) compared to Br^-(dimethylaminehydrobromide, from the water-soluble flux). Corrosion data from a copper rotating-disk electrode in equimolar solutions of adipic acid and dimethylamine hydrobromide has indicated lower open-circuit corrosion rates for the former.* Since the interfacial kinetics are sufficiently poor (i.e., the corrosion rate is low) and the contaminate/copper interface is not well defined, one would not expect metal migration to occur when no-clean flux contamination is present on a PCB, even though the

*J. R. White, unpublished results.

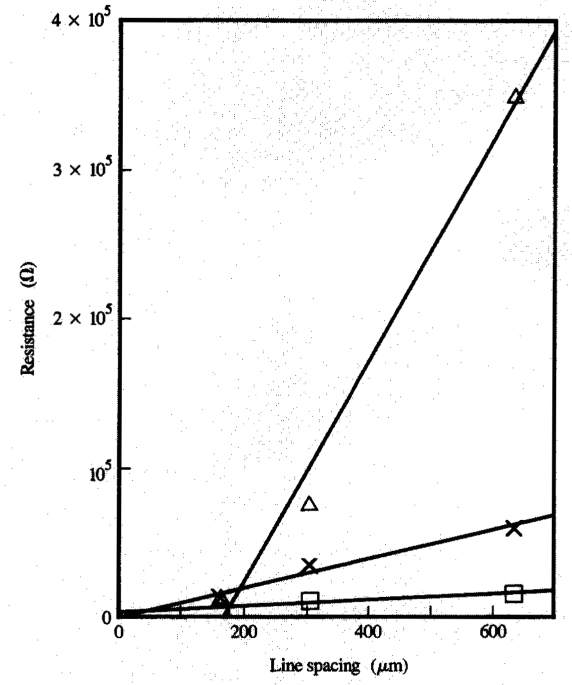
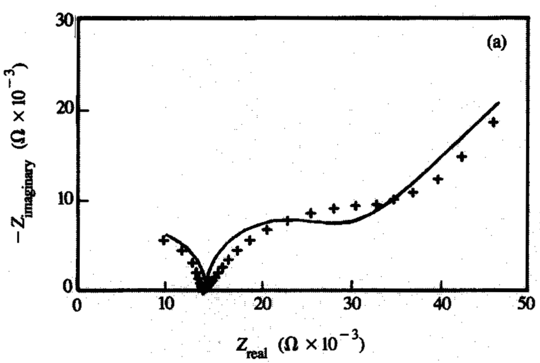


Figure 6

Resistance vs. conductor line spacing for water-soluble flux at 90% RH: (Δ) R_{Ω}, (□) σ, and (x) R_{ct}.



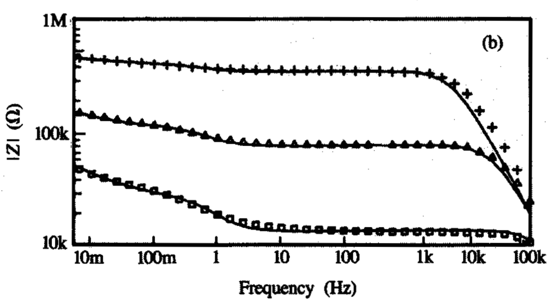


Figure 5

(a) Complex plane plot for water-soluble flux case at 90% RH, via test pattern A. (b) Bode plot for water-soluble flux at 90% RH: (□) pattern A, (Δ) pattern B, and (+) pattern C.

value of R_Ω is relatively low. This has been demonstrated during standard insulation resistance (IR) testing of cards contaminated with no-clean flux in a humid environment, under dc bias [10].

Conclusions

The utility of ac impedance methods for evaluating surface conduction mechanisms in PCBs has been demonstrated. Different responses were observed as a function of humidity and conductor line geometry, for various types of fluxes. An equivalent circuit model was used to evaluate the impedance results obtained. It consisted of a parallel combination of parameters associated with the bulk epoxy/fiberglass substrate and the surface electrochemical processes. As the surface pathways become more dominant, the results can be more effectively characterized by the model of Figure 2 than by a simple parallel *RC* network.

Residues of water-soluble fluxes are, in general, a reliability concern since they provide conductive pathways through which metal migration may readily occur. Such pathways display a significantly lower impedance than those associated with the other fluxes examined, and exhibit diffusion-controlled charge transfer. The impedance is not strongly dependent upon humidity, since the residues are intrinsically conductive and do not rely on water absorption to provide conduction.

In contrast, the no-clean flux residues do rely on an increase in humidity level and associated water adsorption to provide potentially harmful conductive pathways. However, the kinetic data obtained show that, while conductive pathways may be present, metal migration is not likely to occur because of the sluggish kinetics at the copper/flux interfaces.

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