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Are Lead-free Assemblies Especially Endangered by Climatic Safety?

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Abstract
The ever-increasing use of high frequency in high density interconnect (HDI) assemblies, combined with the worldwide move toward lead-free manufacturing, has initiated a closer scrutiny towards effective flux removal processes. Since adequate climatic operating conditions cannot always be assumed, system signal integrity maybe vulnerable to failure through induced capacitive effects of hygroscopic activator residues. Furthermore, such contamination, particularly with the new lead-free solder paste formulations, is no longer-detectable by ion-equivalent measurement alone.

Most failures of electronic components in humid environments are caused by electrochemical migration and corrosion induced leakage currents. In this paper, the origins and effects of such failure mechanisms are examined. In addition, the influence of alloy types, with particular reference to lead free formulations, is also discussed. The critical importance of contamination free surfaces in high frequency circuits is outlined. Finally, different methods to determine climatic reliability are discussed, in which a new and innovative test method is described.

Failure Mechanisms

As mentioned above one can differentiate two main forms of humidity and pollution effects on electronic components, namely electrochemical migration and corrosion induced leakage currents. In order for a climatic reliability failure of the electronic circuitry to occur four main factors need to be simultaneously present. These include, but are not limited to:

- Differences in the electrical potential,
- Sufficient atmospheric humidity,
- Suitable metal alloys that can electrochemically migrate, and
- Remaining contamination on the surface.

Electrochemical Migration

Effect of Humidity

Electrochemical migration, one of the most common failure mechanisms, can be initiated by as little as a few mono-layers of humidity. The latter can start the corrosion process at critical humidity levels of 60-70% RH at ambient temperature, which in turn depends on the polarity of the substrate and its respective surface energy. Hygroscopic pollutants are known to lower the critical humidity level to as little as 30% RH. This implies that, for example, under most common climatic conditions (i.e. standard office climate) even the functionality of common household electronics (i.e. computers) is endangered.

Historically, electronic assemblies were mostly used in controlled environments, in which the risk of electrochemical migration was limited. However, now that electronics are applied in the harshest and critical environments, the risk of migration is indeed increasing.

Furthermore, the exposure of the electronic circuits to atmospheric pollutants, such as dust, inorganic particles, as well as harmful gases like sulphur and nitrous oxides (i.e. SO_x, NO_x) dramatically accelerate this type of failure mechanism. The pollutants then act as condensation seeds and promote the adsorption of humidity.

Effect of Metal/Alloy

Besides the above-mentioned critical humidity film, a metallic alloy with a tendency to migrate is also required. This is evidently related to the composition of the alloy. For the simplest cases, the tendency of a metal to migrate in pure, condensed water can be confirm with a so-called “Pourbaix” diagram, which correlates the pH value against the electrical potential. An example is shown in Figure 1. It should again be pointed out, that such Pourbaix diagrams are representative for the pure water only.

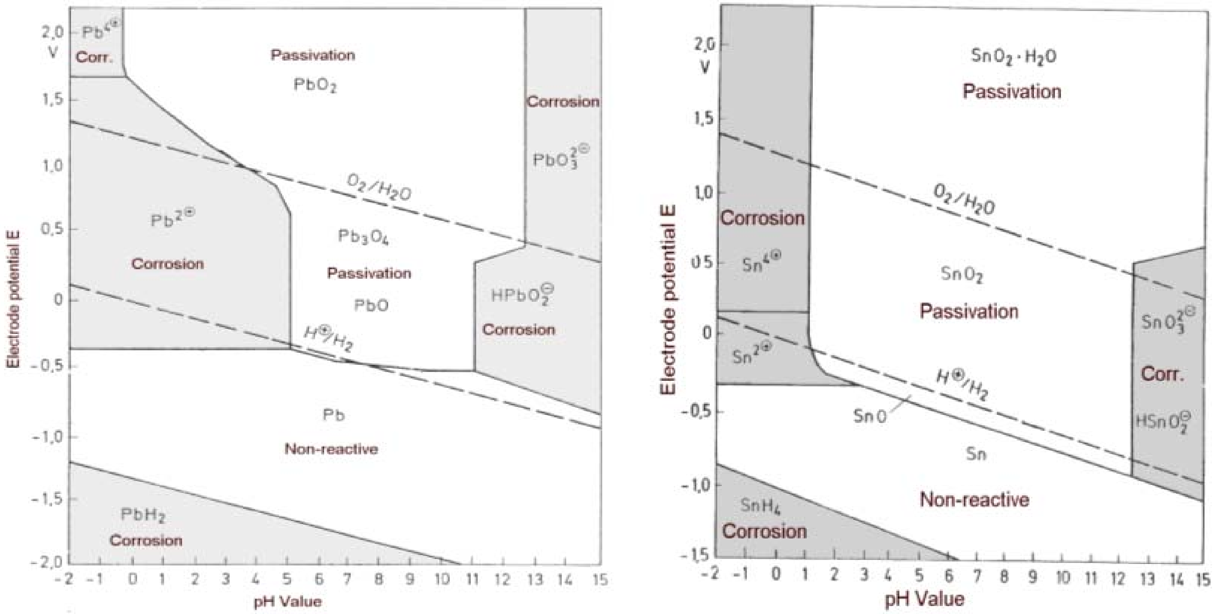

Figure 1 - Pourbaix Diagrams for Tin and Lead

Electrochemical Migration Mechanism

The electrochemical migration process consists essentially of three steps as shown graphically in Figure 2 below:

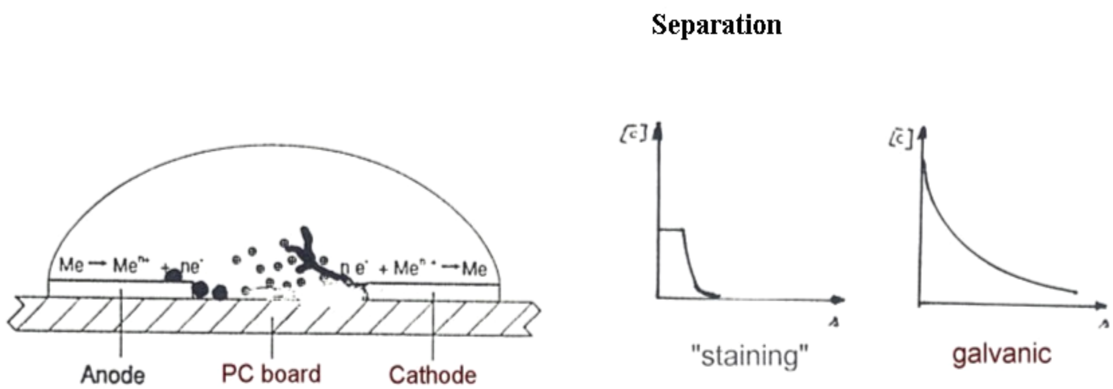

Figure 2 - Mechanism of Dendrite Growth

The first step, <u>*Anodic metal dissolution,*</u>

Anodic metal dissolution, is a process by which the metal atoms (M) are transformed into their metal ion state (M^+) at the anode (M to $M^+ + e^-$) and begin to migrate towards the cathode.

The driving force for this transformation of metal-to-metal ion is the electrolysis ($2\ H_2O + 2e^-$ to $2OH^- + H_2$ or $2\ H_2O + O_2 + 2e^-$ to $4\ OH^-$), of the humidity film on the surface, caused by the operating voltage during normal board operation (Figure 3). It is known that the electrolysis process occurs at voltages above 1.5V. With most circuitry operating upwards of 3.3V, this phenomenon is therefore prone to occur.

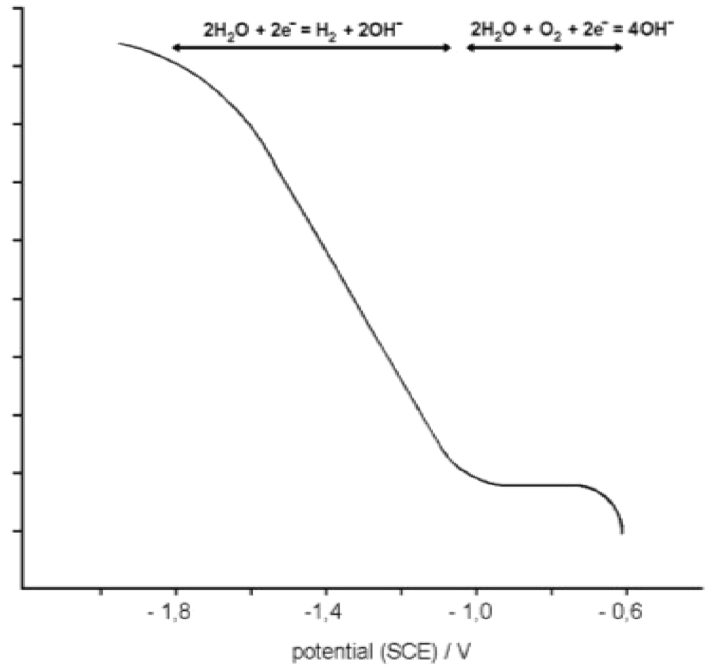

Figure 3 - Electrical Dissociation of Water

The second step, *Diffusion of the metallic ions*,

Metal diffusion characterizes the migration of dissolved metal ions (M^+) from the anode to the cathode. The metal ion concentration gradient between the anode and the cathode is determined by the operational current density, the size of the active anodic area and the rate of diffusion of the metal ions, respectively. The conductivity of the electrolyte depends only on the solubilized metal ions. Interestingly, the degree of contamination on the surface of the PCB does not affect the rate of diffusion.

The third step, *Deposition of the metallic ions,*

During the deposition of the metallic ions the dissolved metal ions are deposited at the cathode ($M^+ + e^-$ to M). The deposition is dominant at places with high electrical field strength. If the conductivity of the solution is small, (i.e. due to a small concentration of ions) which then lead to a dendritic growth shape of the bridge structure. Should the metal concentration be higher, one will observe the growth of band like bridge structures as depicted in Figure 4.

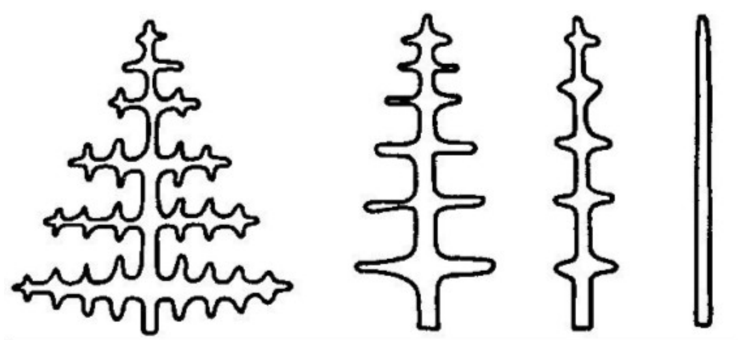

Figure 4 - Dendrite Morphology

Corrosion Induced Leakage Currents

This failure mechanism also promotes the building of bridges, similarly to electrochemical migration. The most significant difference however is the underlying cause for the formation of leakage currents. In other words, this effect occurs mostly in contaminated atmospheres. For example, in the presence of sulphuric gases and a humidity of around 60%, this phenomenon is readily visible with copper and copper alloys. It in turn promotes the formation of copper sulphate layers up to the point, at which an electrical short-cut occur. NO_x gases support the oxidation of SO_2 to sulphuric acid, an example of the corrosive influences of industrial gases. In addition to these corrosion induced leakage currents, corrosion induced cut-offs can also occur as illustrated in Figure 5. In particular, the glass conductor lines of hybrid assemblies are very susceptible, since sulphuric compounds themselves already promote the corrosion process.

Contamination Induced Leakage Currents

In addition, the intrinsic conductivity and electro-diffusion effects of most contamination, generally lowers the surface insulation resistance. This hygroscopically induced moisture absorption phenomenon can for example intensify due to dissociated hydronium ions (i.e. from activators), to further result in malfunctions and complete assembly failures.

In extreme cases the board material overheats along creep age paths, smoldering and even fires might occur. Similarly, activator residues can change the impedance of connecting surfaces and through-holes, causing statistical fluctationing virtual pad geometry enlargements.

To ensure fully reliable and functioning assemblies, the authors therefore suggest that the only reliable method is to ensure surface cleanliness.

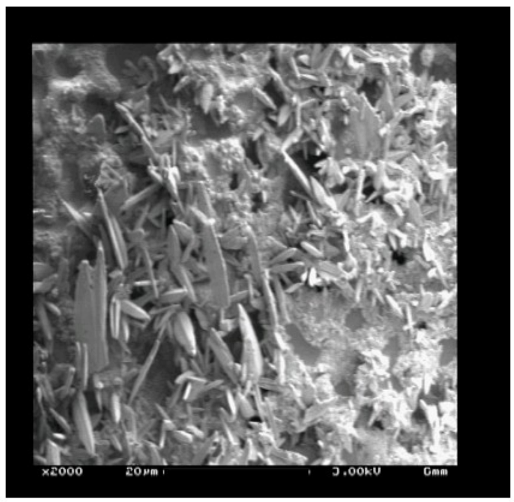

Figure 5 - SEM Structure of Silver Sulphate Needles Caused By a Corrosion Induced Short Cut on a Hybrid

The Reliability of Lead Free / Silver-Based Solders

Silver as opposed to Tin (Sn) and Lead (Pb) forms hydroxides that are readily water-soluble. These hydroxides [(Ag OH)] form in the process of the silver diffusion to the metal surface (i.e. solder joint), and are subsequently but consistently present at low concentrations. (See Figure 6.)

As mentioned previously, these silver hydroxides readily diffuse in moisture films, which in turn form at a relative humidity as low as 60%. The latter value is known as the upper moisture range of not air-conditioned environments.

Climatic reliability studies[1] carried out by Tabai Espec in Japan revealed the formation of short-lived dendrites with a brief life span of 10 to 15 minutes due to electrochemical migration, as illustrated in Figure 7. Tests performed on un-cleaned comb structures (at 85^oC/85% RH) with a permanently applied voltage of 50 VDC showed on the contrary, that silver-free eutectic tin-lead solders did **not** follow the same, temporary failure pattern.

With only low concentrations of silver hydroxides present, "delicate" dendrites, characteristic of their minimal current carrying capacity, are formed. These dendrites lower the surface resistance primarily in the final stage of their growth, before being burned off by the ensuing short circuit. The original surface resistance is then re-established.

Due to the fact that the rate of renewed silver supply to the surface of the solder joint is slower than the attack by the electrochemical migration, these bridges are short lived and do not transform into constant short-circuits. This behaviour in turn, results in inexplicable defect patterns in the circuitry that can neither be predicted nor discovered by discontinuous resistance measurement.

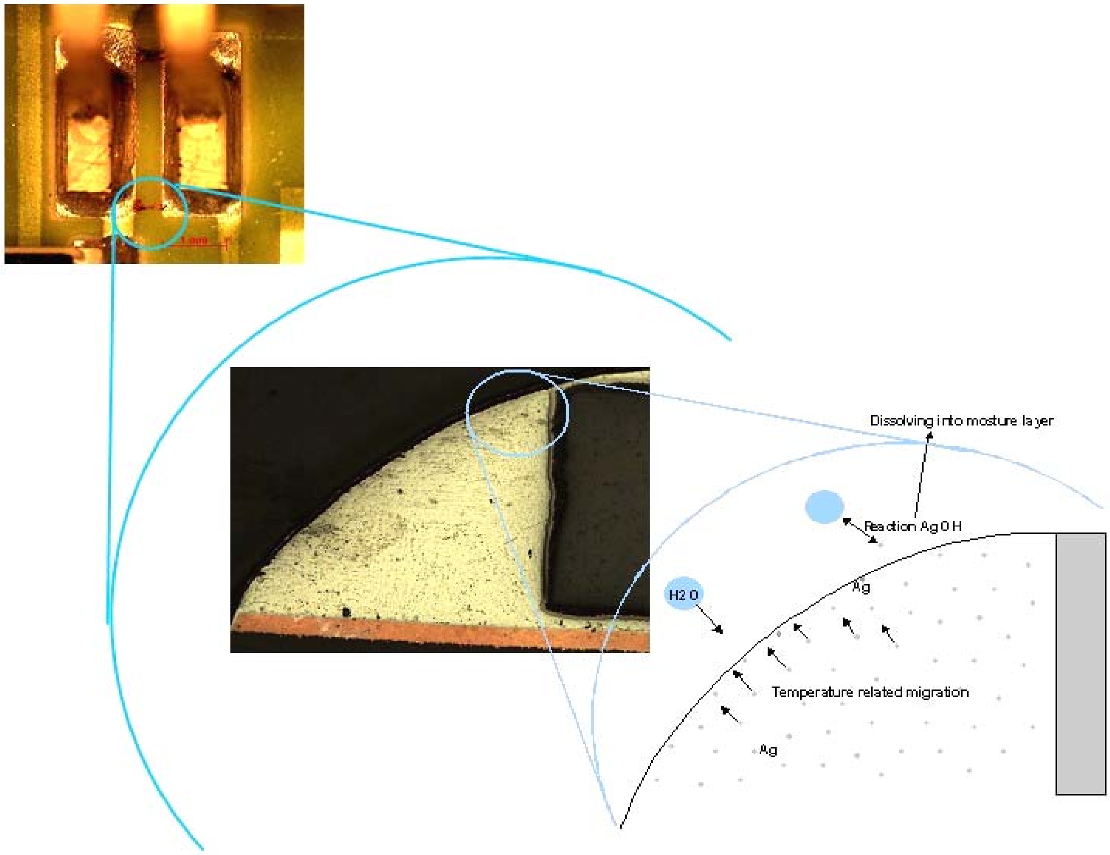

Figure 6 - Mechanism of Silver Electrochemical Migration

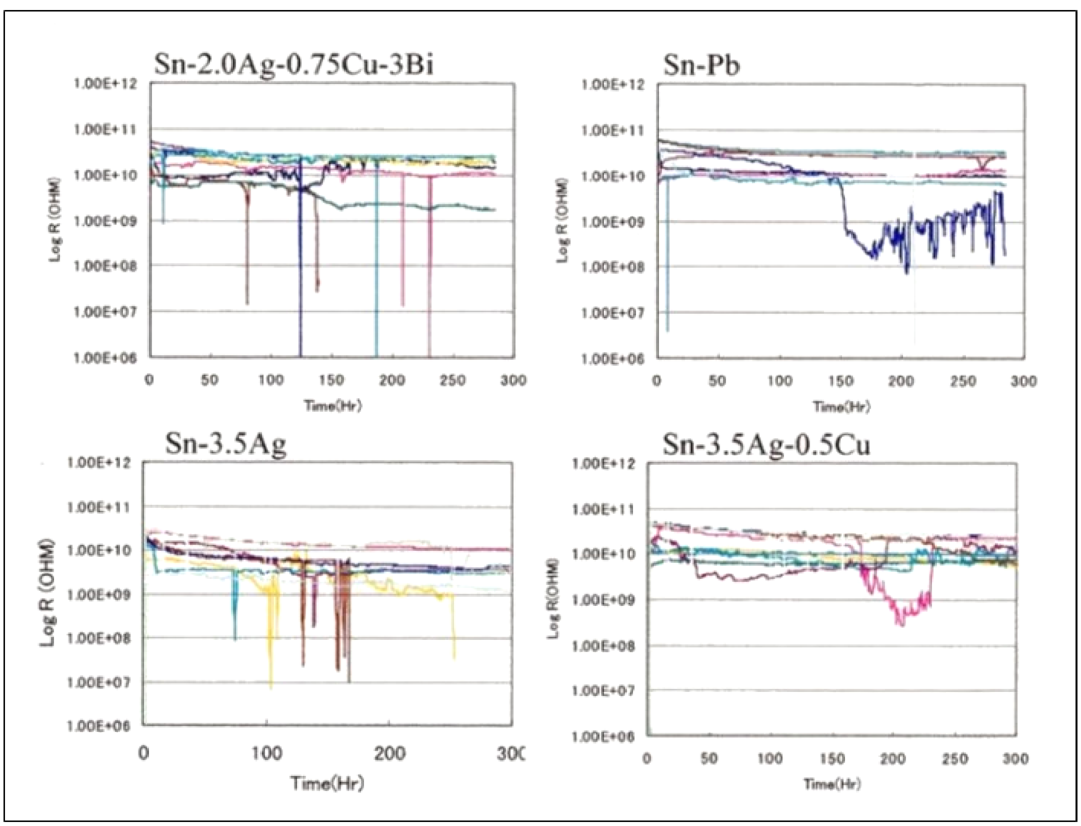

Figure 7 - Formation of Short Life Dendrites with the Persistence of 10 To 15 Minutes As A Result Of Electrochemical Migration in Different Alloys

The Reliability of High Frequency Circuitry

The use of high frequency assemblies particularly in the automotive and telecommunication industries are increasing rapidly. Given this trend, more and more assemblies are being exposed to a wide variety of differing climatic influences, including harmful gases and moisture which can effectively threaten their functional reliability and consequently the products and devices in which they are housed. Moreover, the sensitivity of these circuits to environmental interference is accentuated by the use of high-ohmic components. High-frequency circuits between 30 MHz and 5 GHz, are highly susceptible to environmental influences.

To maintain signal integrity the systems not only require an adequate ohmic-insulation resistance, but also must have stable impedance. Therefore, capacitive surface effects must be taken into account as early as during the design stages of electronic circuits.

Similarly, activator residues can change the impedance of connecting surfaces and through-holes, causing statistical fluctationing virtual pad geometry enlargements.

Determination of Cleanliness

Reductions in the Surface Insulation Resistance (SIR) and capacitive potential that occur as a result of flux activator residues can be shown under a scanning electron microscope (SEM) Figure 8. How can one determine the cleanliness of surface though?

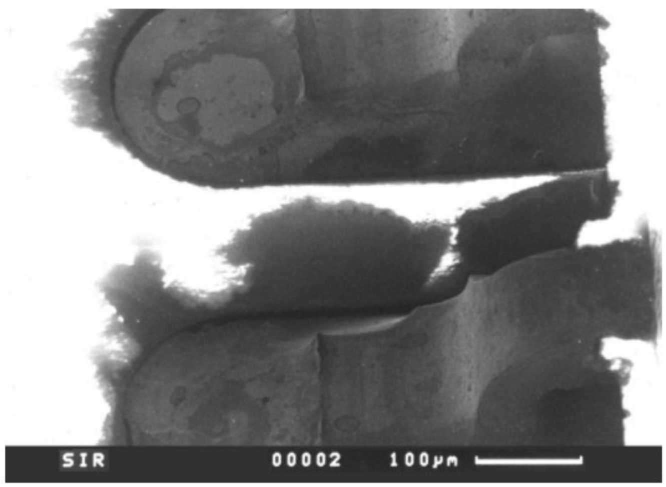

Figure 8 - Charge Contrast Representation of Electrically Conducting Contamination That Are Not Optically Visible

Ionic Contamination

Regular ionic contamination tests are performed according to standard IPC TM 650. This test is usually more relevant to wave solder technology, since it measures ionic contamination over the entire surface of the electronic circuit board.

With more modern reflow technologies such as SMT, the flux is limited to the pad areas and is not distributed over the whole assembly. Thus, to get a meaningful interpretation of ionic contamination, one should only take into account the solder pad area, which is in effect the area where the flux has been deposited on.

Flux Residue Test

Employing a procedure that specifically targets flux activator components can be mentioned as another useful method to determine whether flux activators are present or not. This can be accomplished by using a solution, which promotes a selective colorization reaction of these activator residues, as shown in Figure 9.

The Zestron Flux Test allows the observer to not only determine if activator residues are still on the surface, but also to understand their distribution behavior. Therefore, a conclusion with regard to short or long term failure can easily be done visually, as shown Figure 10.

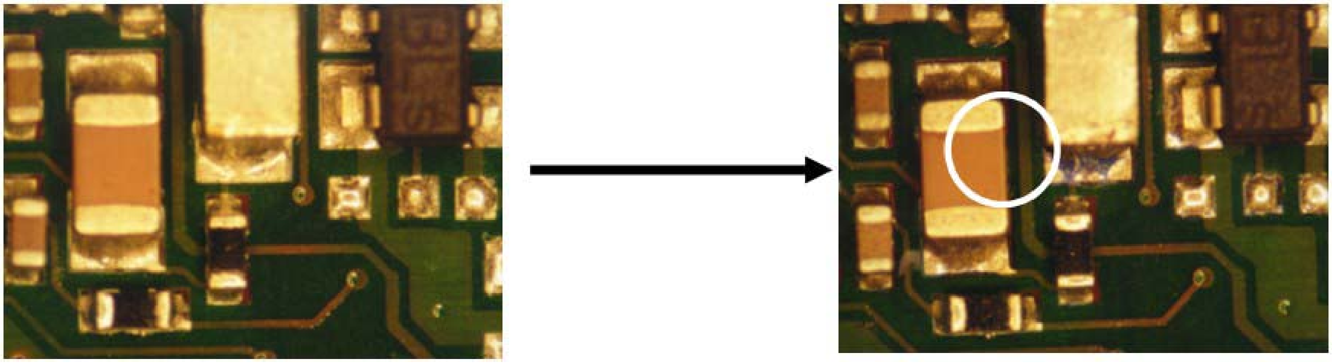

Figure 9 - Flux Residue Test

Long Term Short Term

Figure 10 - Long / Short Term Climatic Reliability Related to Flux Residue Distribution

Impedance Spectroscopy

An alternative direct and non-destructive measurement to directly determine resistivity values of a component, can be performed through Impedance Spectroscopy. The surface resistance under chip resistors and capacitors can be determined as shown in Figure 11. The "Bode" figures clearly show the improvement that cleaning provides with respect to surface resistivity.

BODE Diagram

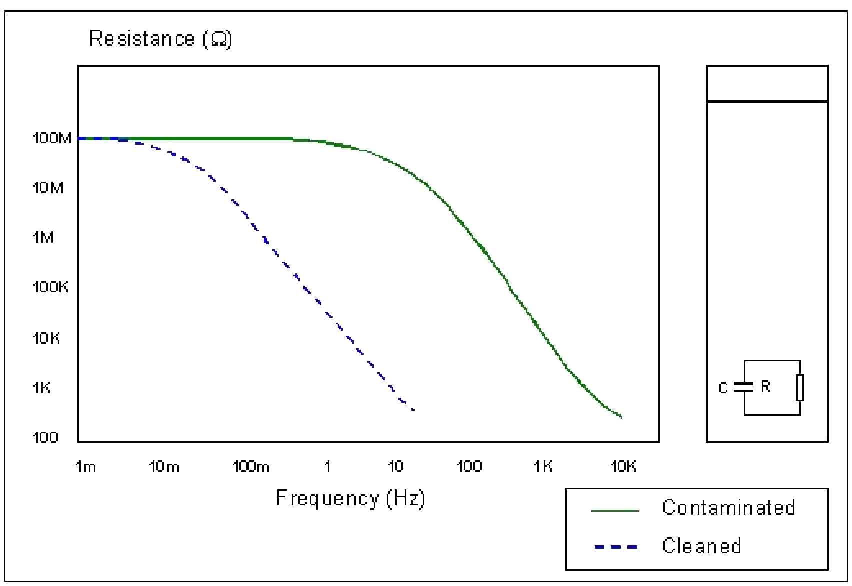

Figure 11 - Detection of Contamination under Chip Capacitors By Means of Impedance Spectroscopy

Surface Insulation Resistance (SIR) and Climatic Chamber Testing
PCBs or test comb structures are placed in a controlled environment (Climatic Chamber) and exposed to the test conditions, harmful gasses, etc. The surface insulation resistance of the test comb structure is mainly used to qualify fluxes and solder pastes and determined over time as shown in Figure 7.

Parameters in the Climatic Chamber that can be varied are temperature, relative humidity, and the duration of the actual test. Numerous standards exist for climatic exposure and surface insulation resistance testing. For example, there are industry standards such as IPC TM 650 or IEC 68, specific industry standards such as Belcore / Telcordia, and even company specific standards. For example, testing under bias gives a more accurate continuous picture of the surface insulation behavior of the substrate being tested.

Description of Water Stress Test
Under moist climatic conditions, the mechanism for electrochemical migration is similar to that found during condensation conditions. For most metal alloys the electrochemical migration pattern occurs in thin moisture films that are in close proximity to the actual surface area. For that reason, the correlation between electrochemical migrations under dewation conditions and during full water immersion is feasible.

The Water Stress Test is an innovative, new test for accelerated climatic reliability testing, for uncoated and/or coated electronic circuits. The PCB is placed in a bath of water and operated in the functional or the stand by mode. The stand by mode is normally chosen since it is far less time consuming and cumbersome.

The power consumption of the board over time, measured through the current, gives an indication of the formation of dendrites or leakage currents.

The Water Stress Test, Figure 12, consists typically of a bath of de-ionized water into which the PCB in question is immersed. The PCB requires a power supply, to be run in a “stand-by” mode for example. A plotter is commonly used to record the change of current through the PCB over time.

The failure characteristic and the functionality of the conformal coat can now be determined by simple visual analysis.

This test therefore provides an indication of whether for example the climatic reliability is endangered by any remaining contamination on the board, determines if a coating against humidity is required, and if an existing coating is a reliable barrier against the effects of humidity.

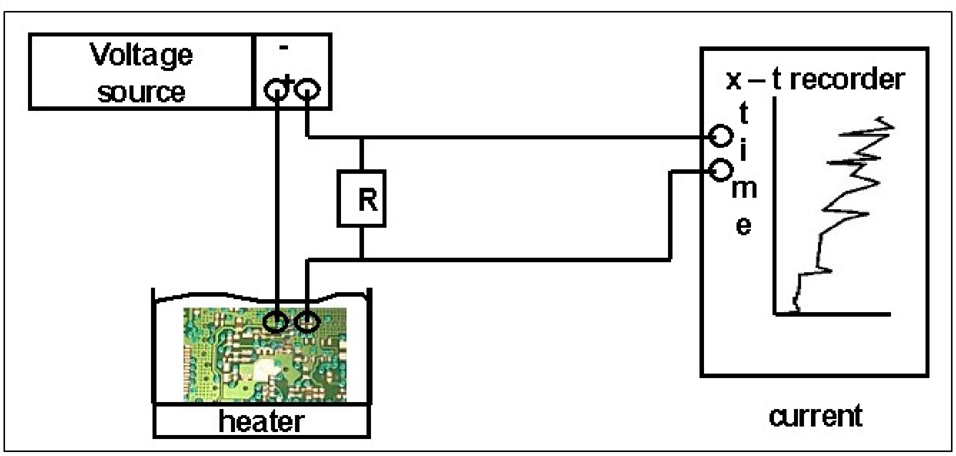

Figure 12 - Water Stress Test

To ensure a greatly accelerated failure mechanism, an electronic circuit / PCB is totally submerged in a de-ionized water solution. The water bath must be stationary in order to avoid a surface rinsing and movement effect, which can obviously affect the results. Under calm submerged conditions the pH values and ion concentration profiles that are formed, correspond to the conditions that would be found under condensation conditions. It should be noted here that the water stress test is merely a “point of weakness” analysis of the electronic circuitry and not a lifecycle test.

In order to determine potential weak points the PCB is run either in the stand by mode, or in the operational mode. The cable connections must be covered in water resistant wax to prevent short circuits between these connections.

The sensitivity of the electronic circuitry to water ingress is determined by analysis of the resulting current plot and also visual analysis of the PCB after the test.

The test timeframes recommended for the weak point analysis of coated boards is 10 hours and that of uncoated boards is 2 hours. This timeframe was determined through numerous experimental studies and is an internal standard.

Subsequent to the performed test sequence, the authors recommend to subject the electronic circuit to a functional test.

The following aspects have to be taken into account:

- Stand-by or functional mode current history,
- Microscopic visual analysis for bridges,
- The distribution of corrosion products, and
- Analysis of the corrosion products and bridges.

Analysis of Coated Boards

Under ideal conditions the stand by current does not change when the PCB is submerged into the test solution. Furthermore, the ensuing visual macroscopic investigation shows no de-lamination of the coating, in particular in the area of the solder joints, after a test period of 10 hours. If this is the case then a complete climatic reliability, for the lifetime of the circuit, can be expected.

If the during the testing the current shows a increase in the stand-by current after immersion into the test solution, then the increase in the stand-by current is directly proportional to the defects in the coating. In such a situation the climatic reliability analysis is analogous to the uncoated board climatic reliability analysis. Furthermore, the coating imperfections due to the corrosion products should be clearly visible.

Conclusion

The climatic reliability of electronic circuitry is becoming ever more critical due to their increased functionality (medical, safety systems, etc.) and the harsher environments they have to operate in (aerospace, automobile, etc.). In addition, with the ever-increasing use of high frequency in high density interconnect assemblies, increasing package component densities, decreasing component standoffs, and the introduction of lead free solders, the issue of climatic reliability and contamination effects is becoming an important consideration.

This paper outlined the electrochemical migration and induced leakage current failure mechanisms. The interesting observation of short-term dendrite formation with silver containing alloys was described. The susceptibility of high frequency assemblies to failure due to surface contamination was outlined. Lastly, different methods for determining climatic reliability were briefly discussed as well as a new climatic reliability test, the Water Stress Test was described in more detail.

All the above must be seen in the context of the importance of the cleaning process in the whole electronic assembly production process and the positive effects cleaning can have on the whole product quality and long term climatic reliability. Cleaning is becoming increasingly more important, if not vital, to mitigate the above effects in critical high value applications especially.

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