Abstract

The miniaturization of electronic systems and the explosive increase in their usage has increased the climatic reliability issues of electronics devices and components especially having metal/alloys parts exposed on the Printed Circuit Board Assembly (PCBA) surface or embedded within the multi-layer laminate. Problems are compounded by the fact that these systems are built by multi-material combinations and additional accelerating factors such as corrosion causing process related residues, bias voltage, and unpredictable user environment. Demand for miniaturised device has resulted in higher density packing with reduction in component size and closer spacing thereby increasing the electric field, while thinner metallic parts needs only nano-grams levels of metal loss for causing corrosion failures.

This paper provides an overview of the climatic reliability issues of electronic devices and components with a focus on the metals/alloys usage on PCBA surface together with cleanliness issues, humidity interaction on PCBA surface, and PCBA design and device design aspects.

Key words: Electronics, reliability, corrosion, cleanliness, humidity

Introduction

During the past couple of decades, use of electronic devices has increased in gigantic proportions. Mobile phones are obvious examples of how devices integrate more and more complex functions, such as camera, GPS and several wireless communication technologies. The integrated device is expected to be cheap, while the applications necessitate it to be robust, durable, and reliable at all environmental conditions including severe conditions to which the user can expose them. Industrial electronics is another sector where the electronic controls and other devices are used irrespective of the type of industries and environmental conditions. Vast majority of these electronics systems are not produced with serious consideration on the climatic reliability aspects. Climatic reliability issues of electronics leading to corrosion can introduce intermittent malfunctions and permanent failures, which cause severe economic loss.

Miniaturization and intend for high density packing is another reason for increased corrosion reliability problems for the electronic devices. In order to provide additional functionalities and increase in the number of components per unit area on a PCBA, PCBs are made today with multilayers (common to see 8 -12 layers). The line width, distances, and sizes of the components on the PCBAs are reduced considerably. Over the last 10 years, size of the electronics has been reduced by over 70%. For the flip chip ICs, miniaturization amounts to ~ 90%. Material loss of the order of nano-grams can cause reliability problems.

The average size of dew droplet formation on a surface at different temperatures varies from 20 – 50 µm at about 50% RH [1]. Hence smaller distance on the PCBs makes it easy for the local electrochemical cell to form, due to the formation of water layer connecting the two electrical points, thickness of which is determined by the humidity levels, conditions on the PCBA surface including cleanliness, roughness, and the relative temperature to the atmosphere.

This paper provides an overview of the climatic reliability issues of electronic devices and components with a focus on the metals/alloys usage on PCBA surface together with cleanliness issues, humidity interaction on PCBA surface, and PCBA design and device design aspects.

Overview of electronic corrosion and key factors

Corrosion issues on a PCBA surface under humid conditions can be summarized as shown in Figure 1. Three factors inherent on a PCBA surface, which are essential ingredients to cause corrosion,
are: (i) presence of metals/alloys, (ii) potential bias/electric field, and (iii) the humidity levels determining the thickness of the water layer. These three factors together can cause formation of conventional electrochemical cells, which are either electrolytic or galvanic in nature as shown in Figure 2 [2]. Typical example of a electrolytic type corrosion cell formation on PCBA surface is the closely spaced conduction lines with opposite bias which is connected by water layer, while galvanic type cells are formed for example by the coupling between the gold and underlying electroless nickel and the copper layer on a ENIG contact. Numerous other examples of both types can also be found on the PCBA.

However, pure water layer on a clean PCBA surface only has limited conductivity to introduce any significant leak current or corrosion effects. However, PCBA surface is seldom clean due to the process related residues [3-5] (as shown in Figure 1), which dissolves into the water layer. Water layer with dissolved ionic residues are more conducting, which cause first level corrosion effect such as the increased levels of leak current causing functionality problems. However, the leak current is generated by the faradic reactions involving dissolution (from positive electrode) and building up of metal ions in the solution layer, which over a long period of time (also depends on level of potential bias, thickness of water layer, and materials involved) will results in Electrochemical migration (ECM). Electrochemical migration results in the formation of metal dendrites between the two adjacent electrodes connected by the water layer resulting in an electric short. Electric short caused by the dendrites can be intermittent or permanent. Other forms of corrosion can also occur depending on the materials and other parameters involved. However ECM is a common failure mode on a PCBA surface if metals such as Sn, Pb, Ag, Cu, and Au are involved. Presence of ionic residues on the PCBA surface also influence the formation of water layer as all ionic residues are hygroscopic in nature, therefore absorbing the water at relatively low levels of humidity than on a clean surface, while thickness of the water layer also changes with the amount of contamination. Following sections will provide more detailed discussion on various aspects related to the electronic corrosion.

**Corrosion failure mechanisms**

Corrosion failure mechanisms of electronics can be divided into two major categories: (i) the electrochemical corrosion in aqueous environment and (ii) the gaseous corrosion caused by the corrosive gases. Other factors such as the wear and vibration can superimpose on corrosion causing tribo-corrosion types such as the fretting. Gaseous corrosion at room temperature or slightly elevated temperatures can also be assisted by aqueous conditions, and therefore it is difficult to differentiate between the electrochemical corrosion mechanisms and gaseous corrosion. Some of the important failure mechanisms on outer surfaces of the PCBA are discussed briefly below, while the Conductive Anodic Filament (CAF) failure mode usually found inside the laminate is not included in the discussion.

![Figure 1: Schematic showing various factors on a PCBA surface causing leak current followed by corrosion such as ECM.](image-url)
Figure 2: Two types of electrochemical cell formation possible on a PCBA surface. Left: Galvanic cell due to coupling between two different metals through water layer and Right: Electrolytic cell formation between similar metal/alloy parts due to opposite potential bias.

**Gas phase corrosion**

Various gases such as sulphur gases, ozone, ammonia etc can cause corrosion of various parts on a PCBA depending on the material content. However, a detailed discussion is beyond the scope of this paper, therefore only a generalized discussion on the corrosion of silver due to sulphur gases is described as an example. Presence of low levels of sulphur gases can create severe corrosion problems on Ag and Cu parts. Moisture from the humidity can assist gaseous corrosion due to the dissolution gases into the water layer generating various acid species. Therefore at ambient temperatures, it is difficult to distinguish between the chemical corrosion due to sulphur gases and the electrochemical corrosion. Figure 3 shows corrosion of silver parts on a PCBA due to sulphur containing gases from a pig farm environment. Formation of silver sulphide dendrite can be seen all over the surface [6]. Usually sulphur corrosion on PCBAs is found at sulphur gases levels lower than 50ppb.

**Anodic corrosion and Electrochemical migration**

Electrochemical migration is a typical form of corrosion found on electronic systems. Electrochemical migration occurs due to the presence of a potential gradient between the two closely spaced conductors on a PCBA such as terminals of a capacitor, resistor, or legs of integrated circuit for example connected by a thin layer water due to humidity. Under such conditions, metal ions dissolves into the solution layer from the positive electrode (anode) which due to the effect of high electric field migrate towards the oppositely charged negative electrode (cathode), and deposit there in the form of a dendrite depending on the local chemistry of the solution. Therefore, whether a specific metal ion deposit on the cathode or not depends on the stability of the ion in the aqueous solution and local chemistries generated between the electrodes at high potential levels. Therefore, only few metals are susceptible to electrochemical migration such as Sn, Pb, Cu, Ag, Au etc., while other metals just precipitate as hydroxides or other compounds as corrosion products. A typical example of a non-migrating metal used in electronics is aluminium. In humid environment with chlorides, aluminium dissolves and forms hydroxide (or hydroxy chlorides) instead of migrating to the cathode regions. On the other hand metals like Cu, Ag, Sn, Pb etc. migrate upon dissolution and deposit at the cathode at least over a range of potentials and pH under which particular ion is stable predicted by the Pourbaix diagram [7]. A detailed discussion on the mechanism of ECM is beyond the scope of this paper, but can be found elsewhere [8]. Figure 4 shows a picture of ECM by dendrite formation between two copper conduction lines at 2.5 V and 10 V potential difference and on a chip capacitor at 10 V. Formation of dendrite can cause electric short compromising the functionality of the device intermittently or permanently.

**Cathodic corrosion**

Some metals used for electronic systems are soluble in acidic and alkaline environments over a wide range of potentials and pH. For example, the Pourbaix diagram [7] for Al and Zn shows solubility in acidic and alkaline environments above the equilibrium dissolution potential, which itself is a function of pH in the alkaline range. In a micro-galvanic cell, oxygen reduction takes place at the cathode, which produce OH- ions. Production of OH- ions at the cathode surface shifts the pH to alkaline values, which cause the metals like aluminium to dissolve.

Therefore, although in principle the metals should be cathodically protected, due to the change in pH a new dynamic equilibrium is created at the cathode surface at which certain metals could dissolve. Among the metallic materials used for electronic applications, aluminium metallization lines on the IC chips are susceptible to this type of corrosion. A schematic of the anodic and cathode corrosion process is shown in Figure 5.
Galvanic corrosion

This type of corrosion is attributed to the use of metals/alloys with widely varied electrochemical properties. On PCBAs, galvanic corrosion manifest in many ways and considered as dreadful for the connectors and switches. For connectors and switches, the corrosion products formed by the galvanic corrosion induce high resistance in the circuit. Usually the connectors are made of multi-layer metallic coatings as described before. The metallic layers have distinctly different electrochemical properties. A typical example is the ENIG parts on the PCB.
Figure 6 shows a mobile phone key-pad made by the ENIG process and corrosion due to galvanic coupling between layers. As shown in Figure 6d, the immersion gold (IM Au) layer is porous that exposes part of the EL Ni layer. The large difference in electrochemical potential between EL Ni and IM Au cause corrosion of EL Ni (Figure 6c), while the Au layer acts as powerful cathode. As the corrosion proceeds, pitting of EL Ni layer exposes Cu at deep pit areas. Even in the absence of porosity on the top coating, the gap between metallic component and resist edge can be a point where all the metallic layers get exposed to the solution. Palladium has been introduced as a substitute for gold, but Pd has faster cathodic reaction kinetics than gold. Therefore, use of Pd can enhance the galvanic corrosion problems. Metals in the various PCB finishes (Cu, Sn, Ag, Ni, Au, and Pb) have large difference in the electrochemical potential for galvanic corrosion (Figure 6e).

The bonding process ICs use different metals, which can generate galvanic corrosion problems if moisture ingress occurs due to any damage in the encapsulation material. Often a gold/aluminium bonding is used for IC chips and the combination is seldom safe from the corrosion point of view due to the large difference in the electrochemical potentials. The lead frame is also coated with solderable coatings, which are generally noble than the base material. Therefore, any mechanical defects in the coating can cause corrosion problems.

Fretting corrosion

The most reliable material for the electronic switches is gold. However, gold is expensive so from time to time electronic industries have been trying to use tin coated copper switches. The tin coated copper surface is solderable as well. The most important problem with the electronic switches and contacts is the relative motion between the contacting parts due to the small amplitude vibrations. The vibratory motion can be relatively low (10-200 micron) and caused by the floor vibration, the thermal stresses etc. The relative movement of contacting part due to the vibration destroys the oxide film on the contacting surface. The new surface generated reacts with the environment to form a new film, which will be destroyed during the subsequent movements. In this way, a large number of oxide debris will be produced, which will affect the electrical properties by increasing the contact resistance. This results in current spikes and damage to the electronic device.

Due to the fretting corrosion, the switches in an oscillating movement (10 cycles/min) have experienced an increase in the connection resistivity from 1 milliohm to 1 ohm within 20 min. It is obvious that the use of gold, which is not producing an oxide layer, as the connection material could solve this problem except for the cost. Another way of solving the problem is to have a good design for switches and contacts for ensuring mechanical stability.

Corrosion susceptible materials and components

The materials used today in the electronic devices include all classes of materials such as the polymers, plastic, and elastomers, ceramics, and metals and alloys. Among them the most important for the corrosion reliability are the metals and alloys.
A number of metals and alloys including the noble gold to metals such as silver, tin, lead, aluminium, copper, nickel, iron etc., and a combination these are used in the form of alloys (eg. solder alloys or components terminals) or multi-layer coatings (eg. PCB surface finish such as ENIG).

Polymers and plastic used in the electronic device are also susceptible to degradation in various climatic conditions, but to a lesser degree, and not life threatening as the corrosion problems related to metallic parts. However, polymers and plastic parts on the device can act as a medium for the adsorption of humidity, gases, and ions accelerating corrosion inside or outside of the assembly. A typical example is the transport of water molecules through the interface between the glass fibers and matrix in glass epoxy laminate and the resulting CAF formation between embedded copper conduction lines. Similarly, the surface morphology of the polymer or ceramic parts can also have an impact on the water layer formation due to the presence of porosity and roughness acting as capillaries for the absorption of humidity. Another aspect is the content of the polymers and plastics, and the possibility of release of chemical species during processing or service that could have influence on reliability. A typical example is the use of various types of fire retardants, which can release fractionalized compounds causing corrosion reliability issues (See section on “Fire retardant and degassing”).

Metallic materials on the PCBA are of prime interest for the corrosion reliability as electrochemical corrosion can occur on these parts leading to material loss or several other problems, which leads to the failure of the device in a short span of time. Basically metals/alloys used on the PCBA vary in their reactivity towards the environment, determined by its nobility. Metals like gold are noble (find in metallic form in the earth crust), while metals like Cu, Ni, Sn, Pb, Ag etc. are less noble than gold and has a tendency to go back to its native state as stable compounds once they come in contact with an environment. Even gold can corrode under some conditions on the PCBA surface involving high potential bias and contaminations such as chlorides. From the aqueous corrosion point of view, many of the tiny components or conduction lines are made of active metals/alloys, which also can have opposite potential bias when the device is functional. Together with humidity it can cause corrosion as shown in Figure 1 & 2. Some of the important components on a PCBA, which are susceptible to various types of corrosion, are briefly described below with a discussion on the materials make up of them and possible climatic reliability issues.

Bare printed circuit board and manufacturing process

Printed circuit board (PCB) in general is the substrate for mounting and connect between electronic components, while it mechanically support the components and other devices from mechanical and thermal vibrations. A printed circuit board consists of conductive path-ways embedded in a glass epoxy polymer or other types of laminates. The conduction lines on a PCB are made of copper, while the non-conducting substrate is for example made from glass epoxy polymer. However, the surface of the PCB on which the components to be mounted will have an added surface finish to the base copper lines, where the type of surface finish depends on the type of application or product. A PCB can be single sided, double sided, or multi layered.

Functional electrical circuits or PCBAs are formed by interconnecting packaged integrated circuits with other devices using printed circuit boards. As such, these boards can be viewed as the second-level packaging. Individual devices are attached to the PCB using mainly two types of soldering techniques namely wave soldering and reflow soldering process. Wave soldering is used for through-hole components with legs, while the reflow is used for surface mount components. Manual hand soldering is used only for the special components that cannot be soldered using either of the above process. Tin-lead alloys were the predominant choice for soldering until recently, however due to the ban on lead, toady lead free soldering technology is in place.

Printed circuit board surface finish and metallic combinations: Most commonly employed PCB surface finishes are: electroless nickel-gold (ENIG), immersion tin, hot levelled solder finish (either Sn-Pb solder or lead free solder alloy), immersion silver, and copper finish. In the case of a gold surface finish PCB (ENIG), gold is not directly plated on to copper as they can easily form diffusion couples producing various types of intermetallics at the interface. In order to avoid this problem, gold surface finish PCBs is ENIG type meaning that the copper and gold layer is separated by 5-6 micrometers of electroless nickel. Nickel layer provides both diffusion barrier and the necessary hardness especially for contact applications. A thin layer of gold is plated on the nickel layer using an electroless process called immersion gold plating. In this case the gold layer is plated on to the surface by ion exchange process with palladium activated nickel. In the case of immersion Au finish, thickness of the gold layer is extremely low to the level of 50 – 100 nanometers. But gold layer on the electronic contacts are usually much thicker of the order of 500 nm – 1 µm. In case higher thickness is achieved by electroplating process.

For a tin finish, immersion tin is mainly used, produced by plating a thin layer of tin onto the copper conducting lines. Tin layer in this case is usually not more than 1 µm. Immersion tin plating process is similar to immersion gold plating process,
which is carried out by electroless process using an ion exchange mechanism. Hot-levelled PCB surface finish PCBs are made by coating the solder material (lead containing or lead free) on to the copper lines by dipping the whole PCB consisting of solder mask into a molten solder bath followed by removal of excess material using an air knife. The thickness of the layer in this case is of the order of 1 micrometer.

Irrespective of the overall surface finish, low voltage, low-force connectors and contacts are usually present on a PCB for connecting the device with other parts of the device [9,10]. A variety of different configurations exist, but the most used substrates are copper, brass, bronze, or copper-beryllium. The use of copper alloys ensures some susceptibility to environmental degradation. To reduce interfacial resistance and corrosion, the substrate is plated with a nickel diffusion barrier and then with a precious metal (e.g., gold, palladium) [9,11].

Printed circuit board and electronic corrosion: Important effects of a bare PCB on the corrosion reliability are the following: (i) source of contamination, (ii) water permeation through laminate and related corrosion issues, and (iii) corrosion issues related to multimetallic layers on the surface. Due to miniaturization, features on the PCBs are tiny and the smallest distances between the conducting lines on the external surface and interior of the PCB is approximately 100 µm. Thickness of the conduction lines are also of similar magnitude.

Sources of contamination: Although at tiny levels, left over chemical species from the PCB manufacturing process can influence the corrosion process by increasing the conductivity of the water layer formed on the PCB during service. Overall cleanliness of the PCB after manufacture is ensured by ROSE test (Solvent extract test, IPC-TM-650 2.3.25 ROSE test standard) which defines an overall allowed contamination level of 1.56 µg/cm² NaCl equivalent. However, contamination at localized sites can be significantly higher if there is local condensation especially at sites where hygroscopic residues are present. Important trapping sites for process chemicals on a PCB surfaces are via holes (plated through holes), edges of conducting lines or any other features where entry of the cleaning solution is difficult. Figure 7 shows examples of trapped chemicals in via holes (Figure 7a&b) mainly constituting ionic residues such as chloride, sulphates, hypophosphite etc. Via holes can also act as a water trapping sites due to the capillary effect during service, while it also maintain water for longer times compared to the flat regions during thermal cycling. Therefore, the chances of forming a thicker layer of water at high humidity surrounding a set of vias is more compared to the flat regions.

Aspect ratio of the vias is an important factor in achieving cleanliness. High aspect ratio vias has higher chances of trapping contamination than low aspect ratio vias due to the difficulty of entry for the cleaning solutions. Similarly it is quite common to find defective plating inside the vias (example wicking) for higher aspect ratio vias. This can expose the underlayers and glass fibers of the polymer to the opening of the vias acting as a site for easy water transport. This can cause formation of conductive anodic filament (CAF) between buried conduction lines.

Release of chemicals from the PCB laminate is another issue especially during the reflow or wave soldering due to the increase in temperature as high as 250 – 270°C. Most important in this case is the possibility of release of fractionated chemicals mainly from the fire retardant chemistries. Typical examples are the release of bromine resulting from the use of fire retardant Tetrabromobisphenol (TBBA) (See section on “Fire retardant and degassing”).

Permeation of water through laminate: Water permeability of polymer laminate is an important aspect in determining the corrosion of buried conduction lines in the case of multilayered PCBs. For FR4 types of laminate, easy pathway for water is along the glass fibre interface, which will be contaminated with various species along its way through the polymer. In this case, the fiber-epoxy interface is also the preferential solution connecting path for two conduction lines situated inside the PCB to form corrosion cell. Water permeated to the polymer can act as a conductive media causing corrosion between the conducting lines especially when the PCB is working, which introduce potential bias between the lines. Typical corrosion issue related to water entry into the polymer is the corrosion of copper conduction lines due to conductive anodic filament formation as described above. Major PCB factors controlling this corrosion
are the amount of water, fibre matrix interface to act a connecting path, and presence of ionic residues. Typically CAF is found between two oppositely charged via holes due to the possibility of gap between vias and epoxy to collect water and the possibility of acting several fibre-matrix interface as a pathway for the solution layer between the vias over all length of the hole.

*Corrosion of multimetallic surface finish:* Depending on the surface finish of the PCB, there is a possibility of two or more different metals/alloys comes in contact, which can together interact with the environment leading to galvanic corrosion (See section "Galvanic corrosion"). Galvanic coupling between the various metallic layers is a clear possibility especially for the features that are open on the PCB surface namely electronic contacts such as the pin contacts or edge contacts. Other features usually get buried below the solder joints after the component mounting, therefore expected to have comparably less effect on corrosion.

*Component assembling and soldering:* Next level of packaging is the introduction of components by the soldering process to produce final assembly for the device. Additional materials and process related parameters are introduced at this stage, namely: (i) solder alloy to join the component on to the board, (ii) components with various shapes and material content, and (iii) chemicals (solder flux) used during the soldering process. Soldering carried out by wave, reflow soldering, or in some cases by selective soldering/hand soldering depending on the nature of the components. Apart from the solder alloy and components, an important factor to contribute from this stage to the corrosion reliability is the solder flux residues from the soldering process. The type, quantify, composition, and morphology of the flux residue introduced from the wave, reflow, and hand soldering process are different, and therefore interact differently to the humid environments (See section cleanliness issue, leak current, and corrosion). Figure 8 shows a picture of the wave solder flux residue on a PCBA resulting from the use of no-clean weak organic acid (WOA) based flux.

*Electrical components and corrosion reliability*

*Chip capacitor:* Practically capacitors for electronic applications are available in variety of forms, but the discussion here is limited to the most commonly used type today namely surface mount chip capacitor (SM capacitor). These are flat components which can be directly surface mounted on to the PCB by the reflow soldering process. Due to its bipolar nature, the chip capacitors are found to cause corrosion problems on a PCBA, especially the failure mode electrochemical migration. Also, the open circuit nature of a capacitor makes it very sensitive to leakage currents (e.g. if a condensed layer of water bridges the two electrodes). As the stored electrical energy can be released from the capacitor even after the potential bias has been switched off, a capacitor can cause corrosion failures after the electronic device has been switched off.

![Figure 8: A view of the wave solder flux residue on a PCBA.](image)

An example, SEM picture of the cross section of a SM capacitor is given in Figure 5[2]. The ceramic part of the SM capacitor is commonly based on titanium dioxide or barium titanate (BaTiO₃), with small additions of other elements to increase the dielectric constant. The electrodes of the comb pattern are made from nickel or silver-palladium [12]. The connecting electrodes has copper layer, which is covered with a layer of nickel followed by a top layer of tin as shown in Figure 9. Both copper and nickel layers are made by thick film technique, where as the tin layer is made either by solder dip process or barrel plating.

![Figure 9: Cross section of a SM chip capacitor showing comb electrode pattern and end electrodes.](image)

The outer layer of tin has very rough surface morphology due to the barrel plating process. For more details on the manufacturing of multilayer
ceramic chip capacitors the reader is referred to Kahn et al. [12].

SM capacitor and corrosion reliability issues: The bi-polar nature of the chip capacitors with closely spaced electrodes makes them vulnerable to the formation of tiny electrolytic corrosion cells by humid water layer. Usually the surface morphology and integrity of the top tin layer is important from the corrosion point of view as this is the layer usually get exposed to the corrosive environment on a PCBA. Any damage to the top tin layer will result in galvanic coupling between the buried layers (e.g. Ni and Cu). Electrochemical migration is the predominant corrosion type observed on capacitors, which leads to an electric short of the component. If the water layer on the capacitor is conductive enough (due to contamination on the PCB), corrosion can take place on the positive electrode. In this case, as the electrodes are made of Sn, it dissolves as Sn$^{2+}$ or Sn$^{4+}$ ions depending on the potential bias, and migrate towards the cathode to deposit there in the form dendrites causing electrochemical migration (See section on “Electrochemical migration”). Growth of dendrites finally lead to electric short between the two electrodes creating intermittent malfunction or permanent damage to the electronic equipment depending on the number of capacitors involved, and the conductivity and thickness of the dendrites formed.

However, severe electrode corrosion without migration is also possible, which will eventually lead to lack of electrical connection either between electrodes and the capacitor plates or between the electrodes and PCB solder pad. Another corrosion possibility for capacitors is the internal ECM between parallel plates or between electrodes and plates if there is damage in the ceramic layer for the humidity to enter. Figure 10a shows the dendrite formation on a SM capacitor in chlorides, Figure 10b shows heavy corrosion of electrode and damage of underlying layer of Cu and Ni at high chloride levels, and Figure 11 shows ECM formation due to the damage of the ceramic layer and connection to the internal parallel plates. Probability of ECM formation on a chip capacitor was found to be a function of the potential bias and NaCl concentration. Probability of ECM was found to be about 60% at a NaCl concentration of 1.56 µg/cm$^2$ (equivalent to IPC standard), while reduction of concentration by half (0.85 µg/cm$^2$) reduced the probability to 5 - 10%. Increase in NaCl concentration above 1.56 µg/cm$^2$ did not change the probability significantly. All experiments are carried out using drop-let test methods, while probability is calculated out of 18 experiments in each case for a 98% confidence level.

The height of the chip component on a PCBA is also an issue sometime if one assumes that the water layer formation or condensation takes place on the top of the component [2]. In this case as shown in Figure 8, the component with low height has shown more susceptibility to migration than the component with more height. This is due to difference in the flow of solder material for the low height component, which leads to flow of solder alloy on to the top of the component as shown in Figure 12. The lead free solder material is more prone to electrochemical migration than the electrode material of the chip component ie. pure Sn.

![Figure 10: SM chip capacitor after ECM test in NaCl: (a) 1.56 µg/cm$^2$ NaCl showing dendrite, and (b) 15.6 µg/cm$^2$ NaCl showing severe corrosion of the positive terminal. For both, anode is on the right side.](image)

![Figure 11: ECM between top electrodes and internal comb pattern of a SM capacitor due to damage of the ceramic layer.](image)

![Figure 12: Effect on height of SM chip capacitor on the flow of solder material: (c) SM capacitor with lower height showing spread of solder material to the top and (d) component having more height shows no sign of solder material flow.](image)
**Resistors:** Although there are various types of resistor design, miniaturization together with the new assembling technologies have led to the surface mount chip resistor design, where tiny resistors can be directly placed on the PCB for assembly and soldered by the re-flow soldering. This is the commonly used resistor today, and also an important component from the corrosion point of view.

Chip resistor consists of a number of materials. It has a sintered ceramic body (1 in Figure 13a & c), a resistive material layer with a glass coat on the top (2 in Figure 13b & c), and two ends are connected to the end terminals [2].

![Figure 13: SM chip resistor: (a) bottom view, (b) top view, and (c) schematic of cross-section.](image)

The electrodes of the SM resistor are made of three metallic layers with Ag first attached to the ceramic body followed by a nickel layer and a Sn layer at the top. Thickness of these metallic layers varied with low thickness towards the corners and edges. On the top of the component, a resistive element is applied by thick film technique which is commonly made from the metal oxides or ceramic/metallic composites (cermet) [13] covered by a protective silica layer. The Ag layer is used to connect the resistive layer to the terminals through a back up nickel layer. Terminals are tin coated by a solder dip process and consists of tiny levels of Pb (2-3 wt.%). Both silver and nickel layers are made by the thick film technique. Due to the solder dip process, surface morphology of electrodes is very rough.

**SM resistor and corrosion reliability issues:** From the corrosio point of view, resistors are bi-polar components similar to capacitors, therefore it could form tiny electrolytic cells if both sides of the electrodes are connected by a condensed water layer. Electrically this changes the overall resistance in the circuit as the water layer act as a resistance in parallel, and the conductivity of the solution determines the resistance. However, the principle of corrosion in this case is similar to that explained for the capacitor where the Sn migration is commonly observed, therefore the failure mechanisms are essentially similar.

If the inner layers are exposed, corrosion of nickel and silver is also possible under the potential bias, which electrochemically migrates to produce dendrites. However, corrosion in this case is also possible without bias due to the galvanic coupling between tin, nickel, and silver depending on the layers exposed. Undermining of the tin layer due to corrosion was also observed leading to severe corrosion of the layers underneath.

However from the reliability point of view, in general the resistors are found to be more resistant to ECM than capacitors. A possible explanation is the self heating due to the resistance however the effect is also same for resistors with lower values for which heating is not an issue. Therefore, more possible explanation (at least for the top part) is due to the glass passivation layer on which dendrite growth might be difficult compared to ceramic layer on the SM capacitor.

**Switches, connectors, and contacts:** From the materials and corrosion point of view, a common feature of switches, connectors, and contacts is the use of multilayer metallic coated parts. A most commonly used material combination for connectors are nickel – gold on various substrates. On a PCB edge connector, the material combinations are copper on the PCB is plated with a 3-5 µm of nickel followed by gold of various thickness depending on the application. The immersion gold ENIG contacts have very thin gold layer of an order of 50 – 100 nm. Some of the edge connectors have a higher thickness of gold, in this case electroplated gold up to a thickness of approximately 1 µm. The thickness of the gold is dictated by the need to avoid porosity in the coatings, which leads to exposure of nickel under layer, and possibility of fretting due to the movement of the contacts.

Various types of pin contacts use hard gold up to a thickness of 3 µm with a nickel under layer of similar thickness. In this case, the substrate in general can be copper alloy such as bronze or steel or other hard alloys. Another type of material combination commonly employed for pin contact is the hard silver plating on copper alloy substrate. Thickness of the silver layer in this is about 3 µm. In some cases tin is also used for contact applications as a top layer. Various other types of contacts systems are also used for example roll bonded or plated silver on steel, silver on bronze and other substrates especially for switches as domes. Table 1 shows some of the commonly used substrate
materials and surface coatings for the contact and connector applications.

**Corrosion reliability issues of contact and connectors:** The main corrosion issues related to the material combinations described above for contacts and connectors is the possibility of galvanic coupling in humid environments. In this case integrity of the top layer is very important for e.g. a porous gold layer can lead to the exposure of underlying nickel. Galvanic coupling between gold and nickel lead to severe corrosion as the large cathodic area of noble gold will accelerate corrosion at regions where the nickel is exposed to the environment. A similar situation can arise due to the combination of other materials.

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<th>Table 1: A summary of materials and coatings used for contact and connector applications</th>
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<td>Basic Materials</td>
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<td>Connection Surface</td>
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Another aspect is the fretting due to the movement of the mating parts of the contact or connector that cause wear to the top layer followed by exposure of under layer to the environment. This can lead to wear and galvanic corrosion or corrosion of the top layer by the action of wear and exposure to the external environment leading to fretting corrosion problems.

**Integrated circuits:** Integrated circuits (IC’s), are as the name suggests consisting of several components which are integrated into one single device. Integrated circuit is usually encapsulated, sometimes hermetically. From materials point of view, an IC is made mainly using silicon based materials, although other metals such as gold, silver, copper, zinc, aluminium or their alloys are used for various purposes such as connecting leads, bumps etc. Connectors are for electrical contact between the different active elements on the silicon wafer. The most common materials used for conductors today is aluminium alloyed with small quantities of copper, titanium, or tungsten [14,15] to avoid electromigration and for higher strength. As circuit dimensions decrease below the 0.25 µm level, copper is beginning to replace aluminium.

The external lead frame is often made from Cu/Zn37, CuFe2, FeNi42 (alloy 42) or CuNiZn (Vacon) alloys [16] or from multiple metallic layers [17]. The end of the lead, which needs to be bonded to the wafer is selectively treated with nickel, gold, palladium, or other inert metals. The other end has treated with a solderable coating for connecting to the PCB. The ICs are protected by encapsulating in a polymer.

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<tr>
<th>Table 2: Materials used for IC applications.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dielectrics</strong></td>
</tr>
<tr>
<td>AIN</td>
</tr>
<tr>
<td>Alumina (96%)</td>
</tr>
<tr>
<td>BeO</td>
</tr>
<tr>
<td>Cordierite</td>
</tr>
<tr>
<td>Mullite</td>
</tr>
<tr>
<td>Polyimide</td>
</tr>
<tr>
<td>PTFE</td>
</tr>
<tr>
<td>SiO2 (CVD)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
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<td></td>
</tr>
</tbody>
</table>

Also the mounting design of the IC to PCBA has evolved over the years from simple ceramic flat packs to pin grid arrays (ICs with several legs to fix on to the PCB) followed by leadless chip carrier packages. From 1990s flip-chip ball grid array packages are widely used. FCBGA package, ICs are mounted upside-down (flipped) and connected to the package balls through a package substrate that is
similar to a printed-circuit board rather than by wires. Ball grid arrays at the bottom of the IC for mounting and electrical connection to the IC are made of the solder materials. Table 2 provides a summary of materials used for various parts of the IC. For metallic materials and alloys, Table 2 also indicates that the reactivity of the material increased from bottom to top.

**IC and Corrosion reliability issues**: Corrosion possibilities related to an IC microcircuit can be divided into two categories; (i) corrosion of materials inside the IC device, and (ii) corrosion of external features such as IC legs or ball grid arrays. Corrosion of materials situated inside the IC depends very much on the ingress of humidity through the IC encapsulation. In the case of hermetically sealed (CHP) IC's this is more due to any damage in the ceramic layer for water to penetrate, otherwise corrosion problems are significantly less. However, for non-hermetically sealed ICs (PEM), ingress of water through the plastic layer for a long period of time or damage to the encapsulation can produce various corrosion reliability issues. Once water enters into the interior of the IC, various corrosion types are possible due to the combination of metallic materials (Table 2). Mainly these are: (i) anodic corrosion or cathodic corrosion, (ii) electrochemical migration, and (iii) galvanic corrosion, although other forms of corrosion can also be seldom seen. Corrosion of aluminium metallization and wire bond lifting are two of the most common reliability problems related ICs [18]. Figure 14 shows a picture of bond pad corrosion due to galvanic coupling between gold and aluminium [19].

![](image1.png)

**Figure 14: Corrosion of bond pad due to galvanic coupling between gold and aluminium**

FCBGA use solder balls consisting of solder alloy (Sn/Pb) and they are susceptible to electrochemical migration and formation of dendrite if there is water layer connecting between two biased points. Similarly galvanic corrosion is a possibility when materials such as Au, Ag, Cu, Pd etc. are in contact with aluminium or any other combination with different reactivates as shown in Table 2. Corrosion and contact failure of Au ball bonds on aluminium metallization has been reported due to the out gassing of bromine from the moulding compound.

**Cleanliness issues, leak current, and corrosion**

If the condensed water layer on the PCBA remains pure, it will seldom create any problem due to the low conductivity of pure water. However, water layer formed on the PCBA surface will not remain clean due to the process related contamination left on the PCBA surface, and any service related contamination due to the service environments. Sources of process related contaminants can be many starting from the bare PCB manufacturing process to assembling, and handling. Figure 15 shows possible process related contamination sources and types of contaminations.

Among the various contamination sources, the no-clean solder flux residue introduced from the soldering process (wave, re-flow, selective or hand soldering) is a major source, and mostly the reason for the leak current and corrosion related failures when dissolved into the water layer. No-clean solder flux residue can be of many types depending on the activating chemicals, resin part, and the solvent. Among the constituents, most important is the activating compounds, which are usually weak organic acids (WOAs) or halogen based chemicals such as chlorides and bromide added in the form of amine salt. There are a number of weak organic acids used namely adipic acid, glutaric acid, succinic acid, malic acid etc. Effect of these acids on corrosion reliability can be different as also for the halide residues both in terms hygroscopicity and aggressiveness towards corrosion. Therefore some flux types depending on the acid type could in general causes more leak current and corrosion effects than others. Table 3 shows the critical relative humidity measured for common acids types in the flux systems, leak current levels above the critical relative humidity, and the ECM susceptibility levels.

Some generalizations could be made on the contamination types irrespective of the sources of contamination. This based on the polar nature of the contamination and its effects on corrosion reliability issues. These are:

- **Ionic contamination** left on the PCB easily dissolves into ions in condensed moisture to generate an aggressive corrosion medium by increasing the electrical conductivity of the moisture and/or by dissolving protective metal-oxide layers to promote migration phenomena as in the case of halides [19]. Further, ionic contaminants are hygroscopic in nature decreasing the critical relative humidity of the PCBA surface. Among the ionic contamination some of the ions are weak in increasing the conductivity of water layer on PCBA, while others form strong electrolytes. Typical example of weak ion is WOA ions from flux residue, while strong ions are chloride and bromide.

- **Non-ionic contamination** can have adverse effects on the reliability of electronic assemblies in the sense that the contaminants can be hygroscopic
and act as moisture- or dust-trapping agents. This condition will increase the adsorption and condensation of moisture on the surface of PCBs and provide a medium for ionic species to dissolve and for leakage current to flow.

The increased adsorption of moisture will promote the formation of continuous moisture-layers and increase the layer-thicknesses leading to higher susceptibility of electrochemical metal migration and other corrosion related failures. Often observed non-ionic hygroscopic residues are oils and surfactant chemicals like polyglycols from HASL or water soluble solder fluxes [20,21].

Figure 16 shows possible ionic residues on the PCBA surface categorized into weak and strong ions. This is important from the corrosion point of view as strong ionic residue can generate 10-100 times more leak current than weak residues at similar levels on a PCBA surface. Strong ionic residues such as halide also cause more aggressive corrosion. Therefore it is important to understand the type of residue in addition to the presently used IPC-TM-650 2.3.25 ROSE test defining the level of ionic residues as 1.56 µg/cm² NaCl equivalent.

Figure 15: A schematic of the process related contamination sources.

Figure 16: Schematic showing weak and strong ionic contaminations seen on PCBA surface.
Table 3: Properties of various WOAs of similar quantities under humid conditions.

<table>
<thead>
<tr>
<th>Weak organic acid</th>
<th>Measured Critical Relative Humidity</th>
<th>Leak current levels</th>
<th>ECM susceptibility of chip capacitors with WOA residues</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adipic</td>
<td>No wetting until 98% RH</td>
<td>0.001 µA(60% RH) to 0.1 µA(98% RH)</td>
<td>No ECM until 98% RH for potential bias 2 – 10V</td>
</tr>
<tr>
<td>Succinic</td>
<td>No wetting until 98% RH</td>
<td>0.01 µA(60% RH) to 1 µA(98% RH)</td>
<td>No ECM until 98% RH for potential bias 2 – 10V</td>
</tr>
<tr>
<td>Glutaric</td>
<td>~81-87</td>
<td>0.001 µA(60% RH) to 1 mA(98% RH)</td>
<td>ECM above ~90% RH and potentials above ~4V</td>
</tr>
<tr>
<td>Malic</td>
<td>~80-84</td>
<td>0.1 mA(60% RH) to 10 mA(98% RH)</td>
<td>ECM above ~70% RH and potentials above ~2 V</td>
</tr>
<tr>
<td>NaCl</td>
<td>~70-75</td>
<td>----</td>
<td>----</td>
</tr>
</tbody>
</table>

Effect of soldering process on flux residue: Hand solder flux usually introduces more residues content due to the improper heating and amount flux introduced depending on the expertise of the technical personnel. Another factor is the distribution of flux residue on the surface, which is a function of the temperature distribution and trap sites such as below the components or crowded areas. Temperature distribution on the surface is a function of the local material mass on the PCB surface and their thermal properties. Usually areas close to large copper layers below the solder mask, big components etc. have higher flux residue due to the more absorption of heat so that the temperature will be significantly lower than the peak soldering temperature. In the case of wave soldering process, automated soldering process is done on the bottom side of the PCB by the solder wave, where the temperature reaches the peak soldering temperature, while the upper part of the PCB typically attain only 170°C. Flux spraying process prior to the soldering process will leave large number drop-lets on the top of PCB, which will not be decomposed fully due to the lower temperature. Therefore after the wave soldering process, there is more chance to find higher amounts of flux residue on the top part of the PCB. The flux residue formed in this case mainly consists of parts of activator components carboxylic acids and the part of the resin components.

Reflow soldering process on the other hand use flux paste introduced on to the PCB by a screen printing process prior to component mounting and soldering process. The flux residue formed after the reflow soldering process in general has a different morphology than the wave solder residues. In this case the resin component tightly covers the leftover of activator components (carboxylic acids) so that they are not exposed as much as in the case of wave soldering process. However, reflow flux residue can release active component upon exposure to humidity which opens up the otherwise concealed residue.

Importance of flux types: Composition of the no-clean flux also plays a big role in the amount of residue left on the PCB surface as well as the reactivity of the flux residue towards humidity and corrosion. In general the use of higher acid content flux systems (for WOA flux types) results in residues with higher WOA content, and therefore more leakage current when it is dissolved into the water layer. Acid type in the flux also can influence as some WOAs are more hygroscopic than others, while also influence the corrosion in different ways (Table 3). Figure 17 shows the effect of acid number on the ECM susceptibility of residues after heating the flux to ~170°C (similar to top part of the wave soldering PCBAs during soldering) tested using the C3 cleanliness test system [22]. Two effects can be seen from the figure: (i) in general an increase in acid number reduces the TTF for ECM and (ii) reactivity of fluxes having similar levels of acid content showed different behavior due to different types of acid types used.

Halogen fluxes in general leaves more active residues due to the presence of halogen ions. Further due to the strong ionic nature of halides for eg. Chloride is highly hygroscopic with a relative critical humidity ~70% RH. Halides are strong ions causing higher leakage current levels compared to the equivalent levels of WOAs. They are highly aggressive towards corrosion, which will increase the probability for ECM to higher levels even at quantities defined by the IPC standard level of 1.56 µg/cm² of NaCl.

Another aspect related to liquid flux types is the solvent used due to the difference in the viscosity. Flux made with organic solvents (such as alcohols) is easy to evaporate compared to water based flux types. This is important especially with low standoff components where the flux residue can get trapped under the component. Failures have been
reported due to trapping of the residue under the low standoff components, and one solution suggested in this case was the use of highly volatile organic solvent flux systems instead of water based flux [23]. On the other hand for selective soldering using pallets, use of organic solvent flux systems could easily spread the flux to neighboring areas due to high wettability. Due to this reason usually after the selective soldering, more residues are found outside of the selective soldered area [23]. Corrosion failures also have been reported on components situated outside of the pallet area due to the spread of no-clean flux [23].

![Figure 17: Effect of acid number of wave solder flux system on ECM susceptibility.](image)

<table>
<thead>
<tr>
<th>Time to ECM short using C3 testing (Sec)</th>
<th>Acid number of flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
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<td>25</td>
<td>25</td>
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<tr>
<td>30</td>
<td>30</td>
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<tr>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>40</td>
<td>40</td>
</tr>
</tbody>
</table>

Figure 17: Effect of acid number of wave solder flux system on ECM susceptibility.

<table>
<thead>
<tr>
<th>Contamination Source</th>
<th>Number of capacitors with ECM and short circuiting</th>
<th>Percentage of ECM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass plate</td>
<td>2 of 6</td>
<td>33 %</td>
</tr>
<tr>
<td>Halogen free laminate</td>
<td>0 of 6</td>
<td>0 %</td>
</tr>
<tr>
<td>Standard FR4 laminate</td>
<td>6 of 6</td>
<td>100 %</td>
</tr>
<tr>
<td>TBBA</td>
<td>6 of 6</td>
<td>100 %</td>
</tr>
</tbody>
</table>

Table: Results of ECM testing of SM chip resistor after heating on various types of laminate and glass plate. ECM testing was carried out after heating by drop-let methods and solution used was pure water.

Fire retardant and degassing

Degassing from the fire retardant chemical used in the laminate and other packaging polymers sometimes generate corrosion issues. Most important in this case is the halide based fire retardant commonly used namely Tri-bromo Bisphenol (TBBA). Literature shows that the decomposition of temperature of TBBA is ~250°C.
and release some of the bromine containing species including HBr. As shown in Figure 18, it is found that when the chip components are placed above TBBA containing laminates and heated to 270°C for 45 seconds showed more susceptibility to ECM compared to the one exposed to the laminate with halide free fire retardant.

It is also important to know how the fire retardant is placed in the polymer. Some cases TBBA is added as chemically bound (as in FR-4 laminate), while in other cases it is present as loosely bound (as in plastics used for encapsulating connectors etc. for example). Loosely bound form of TBBA in general can release more brominated species compared to the bound one.

A commonly used halide free fire retardant is red phosphorous. Some times red phosphorous is used in combination with Al₂O₃ as a cover so that red phosphorous will not be released easily. However, cases have been reported due to the release of red phosphorous through the Al₂O₃ layer to cause corrosion attack on the Ag and Cu parts. It is also seen that the red phosphorous used as fire retardant in polyamides causing corrosion issues on silver parts on PCBA due to the release of phosphorous species. Releases phosphorous species can react with humidity forming phosphorous based acids such as phosphoric acid.

Summary

Climatic reliability of electronic devices is becoming a serious issue, thus needs more consideration starting from the design stage and proceeding onto the device level manufacturing processes. Proper understanding of the user environment profile is an additional factor, which especially will help in designing robust climatically reliable industrial electronics. At present corrosion reliability issues and related factors are given little consideration while designing electronics. However, a number of factors at the design stage and related to manufacturing process can be tried with the available knowledge on influencing parameters. Some of which are described below.

Improving climatic reliability: Some aspects to care

Material choice

Some thoughts to materials choice if possible is an important issue in controlling the corrosion reliability. This is due to the fact that the different metals/alloys have different reactivity towards environmental conditions as well the possibility of coupling if they are put together such as in multi-layer coatings. A number of cases of material use in PCBA applications can be viewed here with a focus on corrosion reliability, however it is beyond the scope of this paper. Therefore few examples are provided below to show the importance of material choice.

It is important to know the user environment in critical cases before the selection of PCB surface finish for example. In a sulphur containing environment such as in pig farm, a silver finish PCBA can easily fail due to the higher sensitivity of silver towards sulphur. Ozone containing environment is also not good for the silver. Although high levels of ozone is not found in the atmosphere, its level can be easily increased in a closed electronic box due to the switching devices generating electric sparks, which could convert atmospheric oxygen to ozone.

Another aspect related to the material choice is the multi-layer coatings used for contact and connectors. Typical example is ENIG with 50-100 nm layer of gold, which is insufficient to avoid porosity and exposure of underlying nickel to cause galvanic corrosion. Therefore when the connectors are made with a top noble layer such as old, it is important to optimize the gold thickness for better performance. Similarly if new coating combinations are selected, it is important to know relative electrochemical potential difference between them defining the galvanic coupling possibility.

PCBA design

Today PCBA design is based more on other reliability aspects such as mechanical, electrical, and electronics, and it is clear that it is not easy to change many of these design aspects, however consideration of corrosion issues during the PCBA design sometimes can lead to simple changes that could enhance the corrosion reliability.

Important aspects which could be considered during PCBA design for improved corrosion reliability are:

1. Avoid short distances where it is not necessary.
2. Selective and hand soldering can generate more residues, and therefore avoid as much as possible.
3. Variation of thermal mass of the PCBA surface due to variation in the distribution of copper can introduce temperature variation on the PCBA surface during soldering resulting in increased flux residues at low temperature area.
4. PCBAs get heated up during working and therefore drive away humidity. PCBA designs with uniform temperature distribution perform better than designs showing hot and cold areas.
5. Knowledge on local flux contamination in critical areas in connection with design is more important than the overall flux residue content as leak current and corrosion effects are highly localized.
6. Know your laminate and plastics before use. Glass epoxy laminate structure is important in driving water inside of the laminate, while type
of fire retardant used is important in connection with application.

**Cleanliness of PCBA**

While it is important to start with a clean PCB for mounting, selection of flux system is important in achieving higher corrosion reliability. Although other considerations are needed for flux selection such as wettability and solder joint integrity, following are the factors if possible could take care from the corrosion point of view:

1. Halide flux residues in general are more aggressive towards leak current and corrosion due to the strong ionic nature.
2. Acid content and acid type of the flux is important as it could influence the hygroscopicity, leak current, and the corrosion effects.
3. Localized content of flux residue is more important than the overall residue content. Fast and reliable techniques are available for the localized testing of critical areas for residue levels in additions to the IPC-TM-650 2.3.25 ROSE test.
4. It is also important to know the distribution of ions in residues at least to the level of whether it is weak or strong ions as the behaviour towards them to the leak current and corrosion is different.

**Use of conformal coating**

Conformal coating can be used as protective layer against corrosion on the PCBAs. Number of conformal coatings types are available for example acrylic, silicone, polyurethane, epoxy etc. However, irrespective of the coating, it is difficult achieve a uniform defect free coating on the PCBAs due to the inhomogenity of the surface. Therefore presence of any localized contamination on the board prior to coating can have an adverse effect on adhesion under the humid conditions. Presence of flux residue at the coating – PCB interface cause corrosion failures within a short time interval compared to a clean surface. Corrosion is more severe in this case than without coating due to the localized chemistry of the solution generated underneath of the coating. It is very important therefore to achieve more cleanliness levels before introducing the conformal coatings.

**Acknowledgements**

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