

Relation between PCBA cleanliness and climatic reliability

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Abstract

Flux residues and other ionic residues left on a printed circuit board assembly (PCBA) from the manufacturing process are a potential threat to climatic reliability for electronic devices in service today. The current use of no-clean flux systems should in principle only leave benign surface contaminants during wave and re-flow soldering process, however results show that the variation in temperature on the PCBA surface during soldering due to thermal and process conditions can result in considerable amounts of localized residues.

Components of the flux residue (especially the carboxylic acid content) in contact with water layer - formed due to humidity - can cause higher leakage current (reduction in surface insulation resistance (SIR)) between biased points on the PCBA. Active residues like carboxylic acids are hygroscopic and therefore influence the amount of water adsorption under humid conditions. Subsequent dissolution of the active part of the flux into the adsorbed water layer then influences the SIR followed by detrimental electrochemical processes at biased metallic connections. These mechanisms have a direct impact on the reliability and lifetime of electronics.

Presently used cleanliness test methods provide information only on the overall changes in the SIR and leakage current, but not on the localized concentration levels, and their effects on climatic reliability. A number of test methods have been developed in our laboratory together with standard chemical and spectroscopic methods, which provides detailed information on the localized residues levels, nature of residue, its effects on leakage current (SIR), and corrosion reliability especially on electrochemical migration (ECM). ECM is a major reliability threat for electronic devices due to the possibility of forming metallic dendrites short circuiting the anode and cathode.

This paper provides an overview of these methods together with investigations related to various types of flux and other contaminations at minute levels on ECM. Contaminations investigated in this paper are flux residue, Cl^- , Br^- , SO_4^{2-} , and H_2PO_2^- ions.

Electrochemical migration testing of chip capacitors were carried out using an in-house built Single Component Electrochemical Migration (SCECM) at a potential bias of 6V. Corrosion morphology was investigated using SEM and EDS. Results show that the effect is dependent on the nature of contamination, which is in contrast to the IPC standard rules presently followed irrespective of the type of contamination.

Keywords: *Electronic products, Contamination, Residue detection, Electrochemical Migration.*

1. Reliability and corrosion of electronics

Corrosion problems experienced by electronic systems can be generalized as caused by the following key factors. These are miniaturization together with: (i) unfavorable material combinations, (ii) DC or AC electric field applied to the system in use, (iii) process related ionic residues on the PCBA surface, and (iv) service related factors such as high humidity, gases, aggressive ions, dust, etc. Service related as well as process related residues or contamination left on a PCBA surface is a key factor accelerating corrosion. Figure 1 sketches the variety of factors likely to influence electronic corrosion.

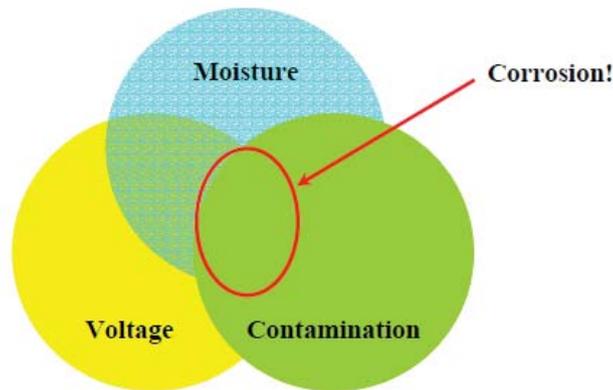


Figure 1 Combination of factors accelerating corrosion in electronics.

The probability of seeing condensation of a moisture layer large enough to bridge positively and negatively charged conductors on a PCBA increases with the decreasing distance between the components, and this will constitute a corrosion cell formation. Corrosion of metals (points on PCBA) connected by water layer can occur as a result of the applied potential or due to galvanic corrosion if dissimilar metallic materials are coupled. The incorporation of many different and very complex components in electronic circuits adds to this reliability threat. The metallic materials used on a PCBA often consist of a multitude of materials, often selected for their electrical, mechanical, or magnetic properties rather than for their corrosion-related performance. This increases the risk for electrolytic migration or galvanic corrosion due to connections introduced through the moisture layer or condensed water layer.

The basic corrosion process taking place at the anode (positive electrode) and cathode (negative electrode) can be described by the following reactions:



The cathode reaction is the reduction of oxygen, while the reaction at the anode will dissolve the metal constituting the electrode and possibly cause failure after an extended time of application. Due to the applied bias potential, which often greatly exceeds the equilibrium potentials of the metals, and the resulting high electric field between closely spaced conductors, the corrosion mechanism in electronics are often more complex and diverse than expressed by the two above equations.

Depending on the magnitude of applied potential, other reactions can contribute to the anodic/cathodic reactivity at the electrodes, and dissolved ionic contamination in the moisture can in this regard have large effects on the corrosion behaviour of the system by reacting with metal-ions or take part in the electrode reactions. The transfer of charge through a medium and at the electrodes is necessary for the corrosion reactions to be sustained, and the magnitude of this leakage current will depend on the aggressiveness and conductivity of the medium. Three basic factors must be present and interact as a prerequisite for a substantial leakage current to flow between conductors, and they are:

- A potential difference (intrinsic or applied bias)
- A bridging electrolyte (high humidity or local condensation)
- Dissolved conductive species (ionic contamination)

The potential difference is the basic driving force for the charged species to travel between conductors, while the electrolyte provides the medium or path, in which the motion takes place. Ionic contamination will increase the ability of the electrolyte to conduct current. Degradation of the electronic components will – if not prevented - in time often have detrimental effects on the signal transmission in the circuit, causing alteration or termination of the electric signal and ultimately failure of the device.

When taking precautions to decrease corrosion in electronics it is therefore important to minimize the contribution from any of the factors given in figure 1. In this regard the contamination control is the most feasible approach and lowering contamination levels will largely increase the corrosion reliability of a given product.

A major source of contamination is the solder flux residues in its original or decomposed form. Flux residues are one of the most common and harmful residue sources that affect the reliability of PCB assemblies, and field failures regularly occur due to flux residues that have not been activated properly. The most common flux residues are activating species such as chloride (if halogen containing flux is used) and weak organic acids, but also additives and surfactants like polyglycols have been found to create problems in electronic assemblies [1,2]. The use of no-clean flux systems should in principle only leave benign surface contaminants during wave and re-flow soldering process, however results show that the variation in temperature on the PCBA surface during soldering due to thermal and process conditions can result in considerable amounts of localized residues [3].

Besides the effect of flux following contaminants are investigated and results presented in this paper:

- Hypophosphite (a likely residue from PCB plating processes as e.g. the ENIG (electroless nickel gold) process.
- Bromide (likely to exist as a contaminant due to degassing from brominated flame retardants used in PCB laminate) [4].
- Chloride and sulphate, contaminants likely to happen during service life.

Presently the mechanistic knowledge on electronic corrosion is limited, especially the relation between failures as effects of process related residues and contamination coming from service conditions.

2. Present cleanliness testing of electronics

The most common method for evaluating cleanliness levels of PCBA is the IPC ROSE test (IPC - Association Connecting Electronics Industries) - IPC-TM-650 Test Method 2.3.25, detection and measurement of ionizable surface contaminants by resistivity of solvent extract (ROSE). ROSE testing was developed in the early 1970s as a process control tool to measure the amount of conductive residue remaining on printed wiring assemblies processed with rosin-based fluxes. In the late 1970s, the laboratory test method was automated and several manufacturers produced ionic cleanliness test equipment. The ROSE test method can be generically described as immersion of the test substrate in a solution of room temperature isopropanol (75%) and deionized water (25%).

This method of determining the ionic contamination provides no information of the type of ions present in the solution, so the resistivity change is referenced to a NaCl-equivalent, i.e., an amount of NaCl that would yield the same decrease in resistivity of the solution [5]. Results are displayed as $\mu\text{g NaCl}/\text{cm}^2$ of the tested PCB, and a general threshold acceptance level of contamination is $1.56 \mu\text{g NaCl}/\text{cm}^2$ for assembled PCBs [6].

The IPC ROSE testing has the advantages that it is cheap, easy, non-destructive as a production line process control. The disadvantages are that the output of the test is solution conductivity as a whole and it will not give any clue on level of local contamination on the PCBA tested. The IPC ROSE-test will only provide an average value of the residue-levels present on the overall PCB surface, as localized contamination just dissolves into the bulk solution.

Ion Chromatography (IC) has more recently become an important technique for evaluating ionic cleanliness as a more precise analytical method than ROSE testing, which can also be done locally. According to IPC-TM-650, method 2.3.28, standard IC extraction uses the same isopropanol (75%) and DI water (25%) solution as ROSE testing, but the extraction time is 60 minutes and extraction temperature is 80°C . These conditions will extract more residues than the 10-minute, room temperature ROSE extraction.

For more simple and rapid testing of flux residue, a spin off product from the research work at Centre for Electronic Corrosion (Celcorr) could be used – called residues RAT (Reliability Assessment Testing). It is a gel with indicator calibrated to show coloration at flux levels considered harmful.

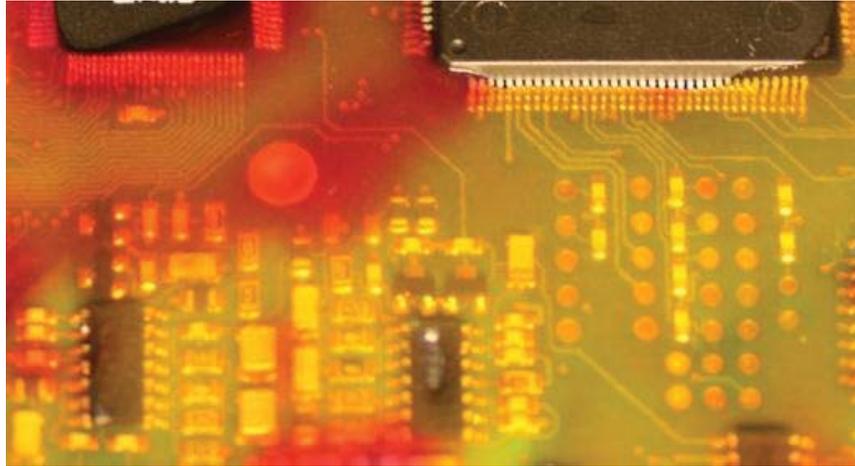


Figure 2 PCBA with sprayed "Residues rat" gel to reveal unreacted flux residues.

The "Residues Rat" product is sprayed onto the surface of an electronic device in the form of a gel. Shortly after contact with the surface of the PCBA, the mixture will reveal unreacted flux residues from the soldering process. Such residues are detected as a visual colour change in the gel, due to chemical reactions with species within the gel. The application by spraying, combined with the high viscosity of the gel, ensures that the colour change is fixed to the site where the residue was originally present, and no smearing of the residues occurs, even on vertical surfaces. This gives a picture of both the amount and distribution of residues, which can be observed either by naked eye or using photo documentation. No other tools or instruments are required for the analysis, thereby making it very cheap and fast.

Safe limits for contamination on printed circuit board assemblies are given in IPC J-STD-001D "Requirements for soldered electrical and electronic assemblies" [7]. The IPC J-STD-001D is a process document that establishes a set of criteria for the manufacturing of electronic assemblies to a degree of reliability dependent upon the end use of the product. The criteria encompass a broad spectrum of products from general purpose electronics (designated as Class 1), to dedicated service electronics (designated Class 2), and to high performance electronics (designated Class 3).

3. Materials and methods

Investigations of electrochemical migration (ECM) are carried out by using a setup holding the tiny electronic components by placing a single component between two adjustable probes, which acts as connections to each end of the component. The in-house made set up for this is called Single Component Electrochemical Migration (SCECM) setup [8]. The probes are connected to a potentiostat (model: VSP BioLogic) controlled by a software programme EC-Lab V9.97. Condensation is simulated by applying a droplet of pure DI water on the top surface of the capacitor.

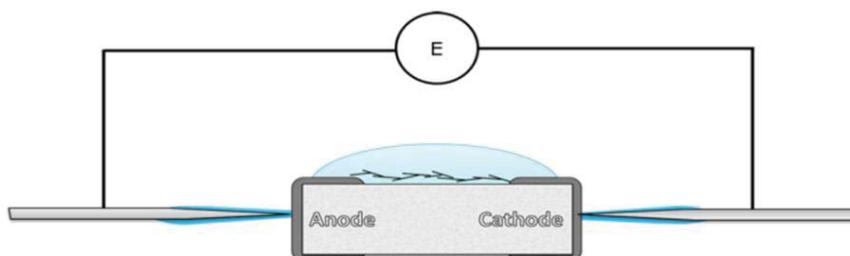


Figure 3 Schematic of the single component electrochemical migration cell (SCECM).

The electronic components used for investigation in this work are commercially available capacitors size 0805. The dimension of the chip capacitors are 2.0×1.2×0.45 mm. The component chosen for this investigation represents a large number of chip capacitors used in PCBA applications. Capacitors are placed in a three-component ECM setup and current is monitored on all 3 channels under a bias of 6 V. The setup is placed under a video microscope enabling in situ video. These sequences can simultaneously be compared with migration data in terms of current. In order to have a constant time of evaporation for the applied droplet, the component is placed in a sealed plastic box in a relative humidity controlled atmosphere. The actual RH control was achieved by placing two small baths containing a saturated NaCl solution inside the box and the relative humidity was measured to be 65 % RH at 22 °C.

Solutions of KCl, KBr, K₂SO₄ and NaH₂PO₂·H₂O, were prepared to match the IPC ROSE standard chloride equivalent by taking care of the top surface area of capacitor and droplet volume. The stock solution is made 100 times more concentrated than the amount of chloride set from the standard IPC J-STD-001D and from this stock solution the rest is diluted.

$$156\mu\text{g NaCl}/\text{cm}^2 * 0.024\text{cm}^2 = 3.744\mu\text{g NaCl}$$

$$\frac{3.744\mu\text{g NaCl}}{2\mu\text{L}} = 1.87\text{g/L}$$

An amount to 1.87g NaCl/L gives a contamination of 156 µg NaCl/cm² on the surface area of the capacitor which is 0.024cm² with a droplet volume of 2µL.

Table 1 Contaminants tested; Cl⁻ from KCl, SO₄²⁻, from K₂SO₄, Br⁻ from KBr, H₂PO₂⁻ from NaH₂PO₂.

[NaCl] / ug/cm ²	[Cl ⁻] / g/l	[SO ₄ ²⁻] / g/l	[Br ⁻] / g/l	[H ₂ PO ₂ ⁻] / g/l
156	1.1300	1.1300	1.1300	1.1300
15.60	0.1130	0.1130	0.1130	0.1130
1.56	0.0113	0.0113	0.0113	0.0113
0.31	0.0023	0.0023	0.0023	0.0023
0.15	0.0011	0.0011	0.0011	0.0011

The concentration of chloride ions in KCl solution can be compared to the ROSE test values as given in Table 1. Similar concentrations of anions are investigated for sulphate, bromide and hypophosphite.

The flux solution tested is a commercially available no clean wave solder flux, Cobar 390-RX-HT (low solids) from Cobar Europe BV.

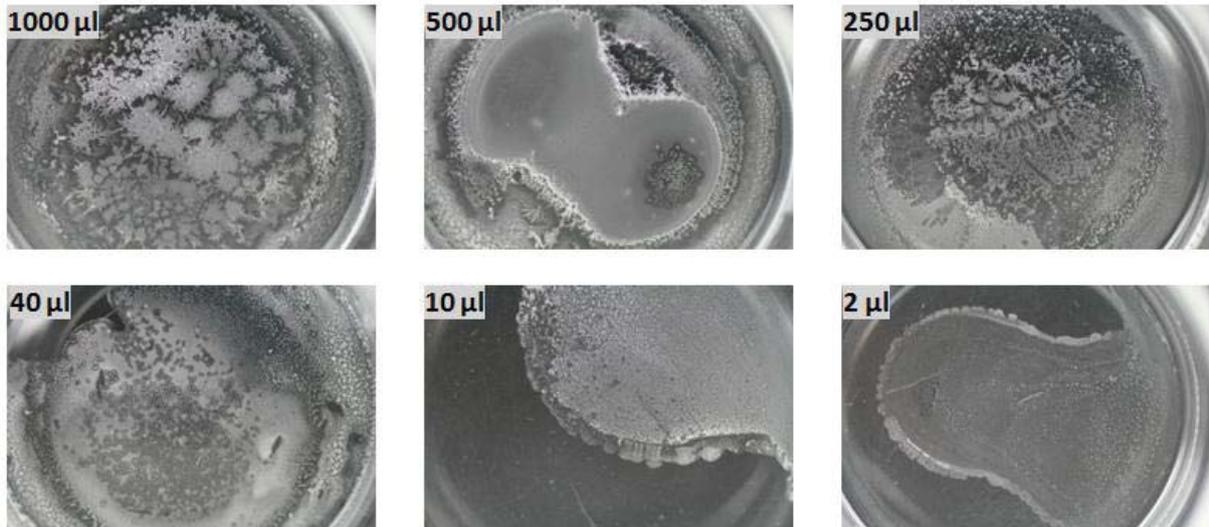


Figure 4 Flux residues after evaporation of solvent. The corresponding volumes of the flux are listed on the images ranging from 2 – 1000 µl.

Flux residues have been prepared as follows. Various amounts of flux have been left in separate petridishes for evaporation (Figure 4). Hereafter 8 ml miliQ water was added to each petridish and solution extracted for ECM experiments.

Ion Chromatography (IC) analysis was performed using a Dionex ICS-2000 system with an anion column type sn:O6080155, suppressor ASRS, 4mm, and a KOH eluent. The volume of solution needed for IC analysis is 0.5 ml fed via an autosampler. A standard calibration curve of adipic acid dissolved in miliQ water was made.

Microstructural characterization of the components after SCECM experiments was done using SEM (JEOL 5900 instrument), and chemical analysis was carried out using EDS (Oxford Link ISIS) analyzer attached to the SEM.

4. Results and discussion

The results from the investigation of the process and service life related ionic contaminants are presented as ECM results in the following. Ionic residue contaminated samples were also investigated using SEM/EDS.

4.1 ECM results

The graph in Figure 5 illustrates the increase in tendency for more migration with increasing ion concentration, especially for hypophosphite where a limit of 0.0113 g/l (eqv. to the ROSE test value of 1.56 NaCl eqv. /cm²) causes 6 out of 9 capacitors to migrate. For chloride and bromide there seems to be a maximum probability at 0.113 g anion/l thereafter less migration occurs.

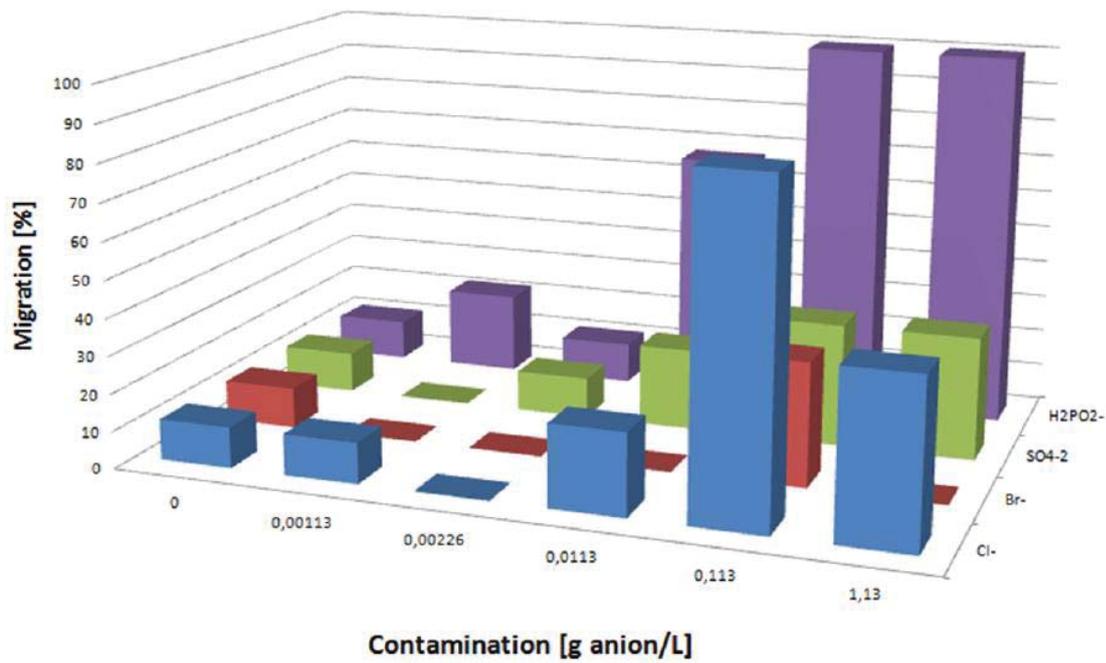
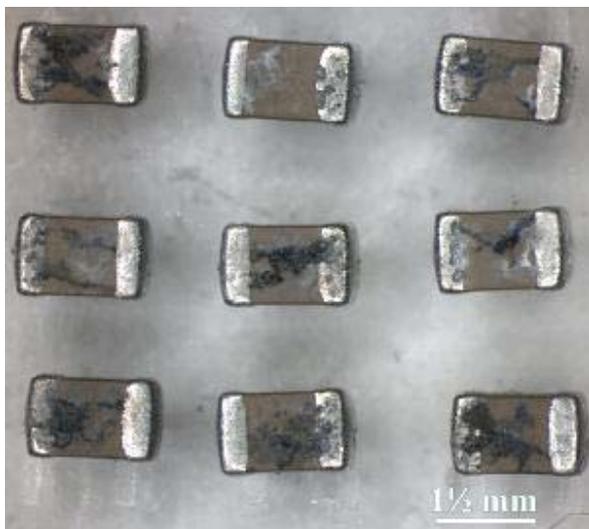


Figure 5 Probability of ECM versus ionic contamination.

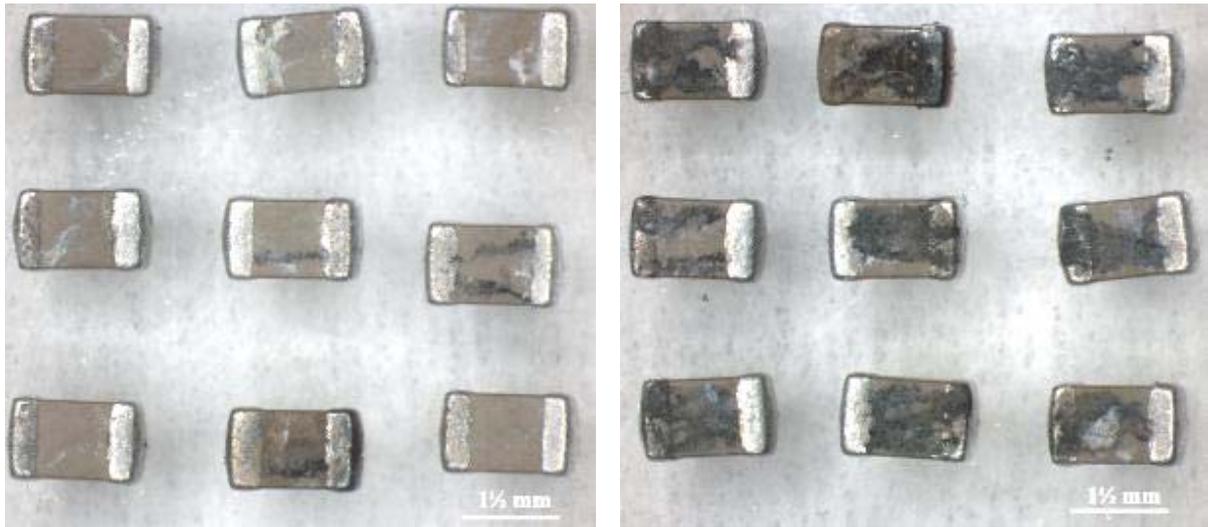
Results in general shows a clearly tendency of increasing migration risk with increase in concentration of ions. This is more pronounced for the hypophosphite ion. For chloride and bromide there seems to be a peak of maximum probability at 0.113 g anion/l thereafter the probability for migration decreases.



a.) KCl



b.) KBr



c.) K_2SO_4

d.) NaH_2PO_2

Figure 6 Light optical micrographs of samples after testing with ions with concentration equivalent to $15.6 \mu\text{g}/\text{cm}^2$.

The micrographs given in Figure 6 shows the severe migration at $15.6 \mu\text{g}/\text{cm}^2$ (equivalent to $0.113 \text{ g anion}/\text{l}$) especially for Cl^- and H_2PO_2^- . The capacitors suffering from migration when contaminated with SO_4^{2-} and Br^- show a thinner dendrite formation and less corrosion products.

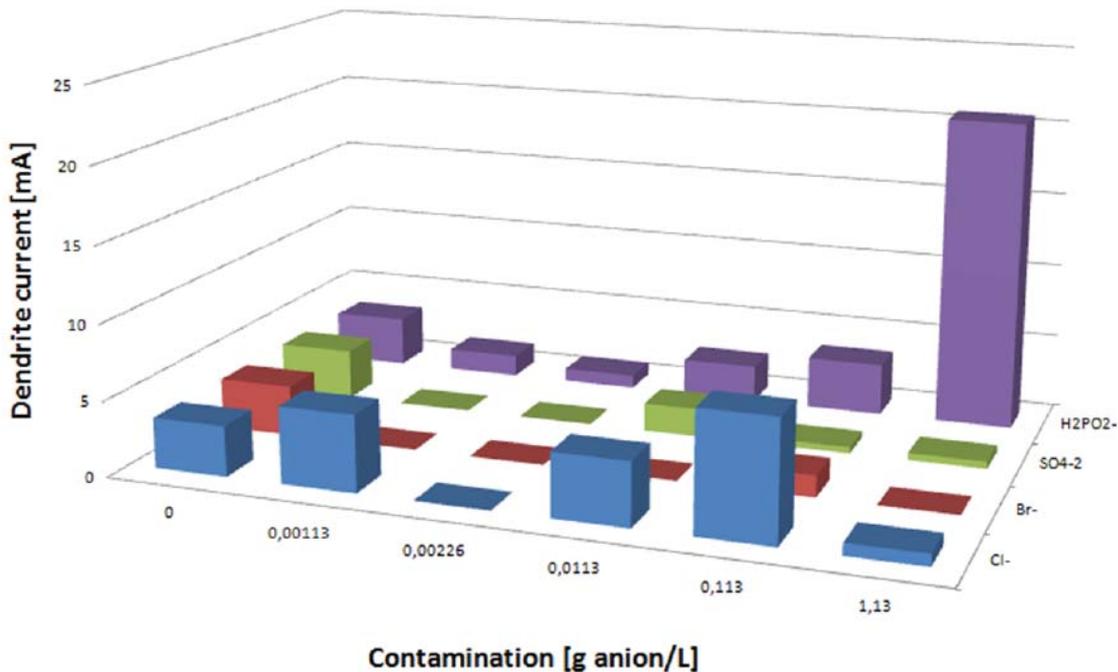


Figure 7 Dendrite current of migrated components versus contamination.

The current flow as the dendrite causes shorting is sketched in Figure 7 as the dendrite current. It shows the tendency for stable and current dendrites being formed at high concentrations of hypophosphite and chloride whereas only thin dendrites and corrosion products are formed when contaminating samples with bromide and sulphate.

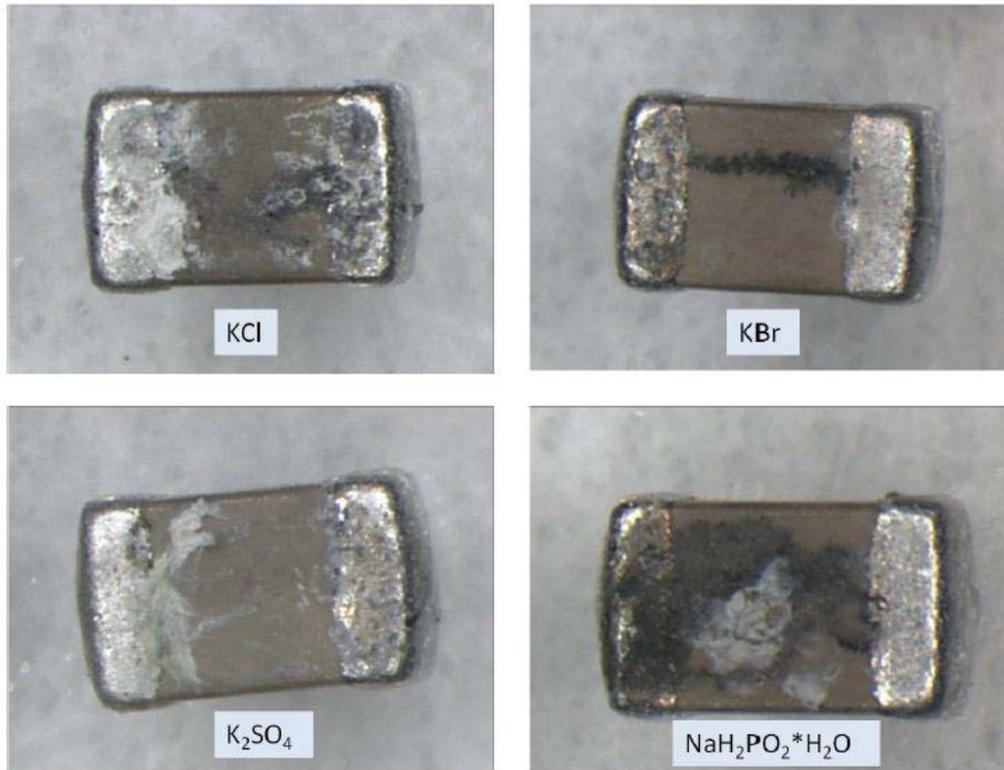


Figure 8 Comparison of selected (the most representative out of 9 repetitions) chip capacitors after testing with ions concentration equivalent chloride leakage current of $15.6 \mu\text{g}/\text{cm}^2$.

Figure 8 shows the typical features of the capacitor after electrochemical migration in presence of different ions. Aggressiveness of the hypophosphite ions toward migration is very clear from the picture. The dendrite formation of the hypophosphite contaminated capacitor is thick and broader (which can pass high level current without burning off) compared to dendrite formed in KCl or KBr solutions. On the other hand SO_4^{2-} contaminated capacitor did not show any dendrite formation at this concentration indicating that the corrosion product is more stable compared to the deposition of the ions determined by the stability of Sn in presence of sulphate ions. Higher corrosion effects also could be seen on the samples exposed to NaCl and hypophosphite.

Figure 9 shows the effect of the level of flux residue on electrochemical migration failures. Similar to other active ions described before, increased concentration of flux residue resulted in dendrite formation, which did not happen at lower concentrations. However, in comparison with IPC standard chloride equivalent, the amount of flux residue at which ECM occurs is about 5.2 times of the $1.56 \mu\text{g}/\text{cm}^2$ NaCl equivalent. This is understandable as the carboxylic acid in the flux residue produces relatively weaker ions both in relation to conductivity/leakage current as well as to corrosion. An effect of passivation was also observed for tin in presence of carboxylic acids [9].

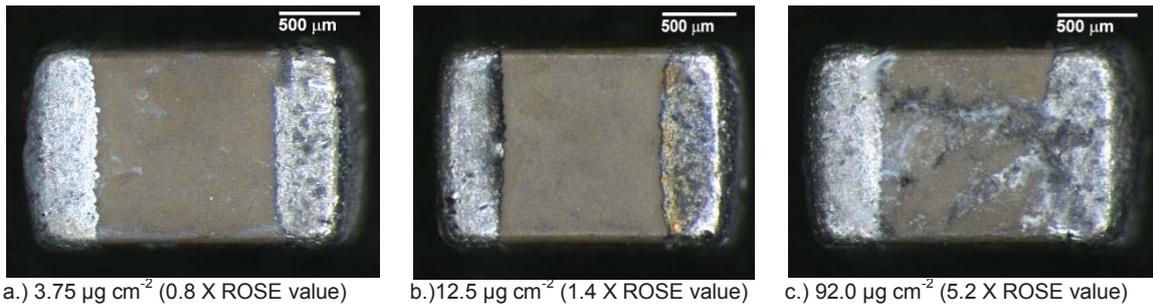


Figure 9 Light optical micrographs of representative flux contaminated capacitors.

Figure 10 shows the reliability plot showing how the cumulative failure develop out of 18 components tested in each case depending on the amount of flux residue. As the curve move from full reliability 1.0, the cumulative damage increases as the steepness determines the rate of drop, while the position of the curve with respect to the X-axis shows the time scale interval for the cumulative damage. Results presented in figure 10 clearly shows that increased flux amounts reduced the time scale as well as increased the steepness of the curve for reliability drop. This is more pronounced when the concentration level is $92.0 \mu\text{g cm}^{-2}$.

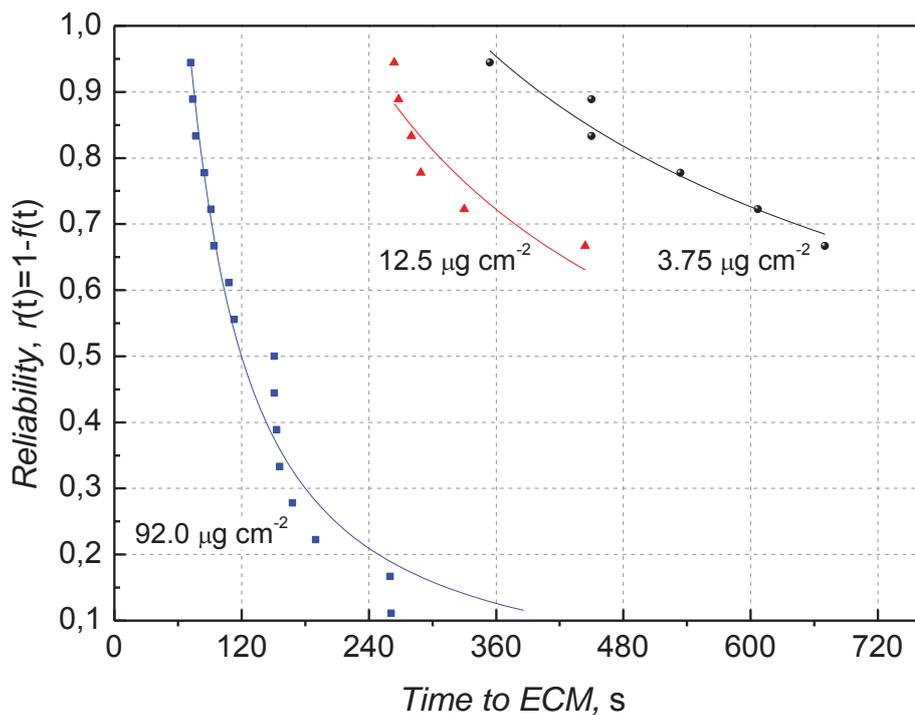


Figure 10 Time to ECM and probability of failure as a function of unreacted flux residues.

This level of flux residue exceeds the ROSE test value more than 4 times. With smaller amounts of flux residue less than 40 % of the specimens show migration and the time to ECM increases.

Table 2 Amount of flux residue and corresponding carboxylic concentrations found using IC.

Flux residue [$\mu\text{g cm}^{-2}$]	Carboxylic acid concentration, [mg/l]
3.75	38
12.5	79
92.0	232

Results from our work (which is not shown in this paper) indicate that, similar to the behavior of chloride and hypophosphite, it is likely that a maximum of flux residue levels exists above which migration is probably drastically reduced. Irrespective of the type of residue, such increase and decrease in probability as a function of residue content is related to the stability of tin ions in solution defined by the Pourbaix diagram [10] and as explained in literature [11]. As the corrosion increases, the amount of tin ions in the solution increases, which leads to the precipitation of hydroxides that will inhibit electrochemical migration.

4.2 SEM/EDS analysis

A cross section of a chip capacitor terminal is given in Figure 11 revealing an inner layer of Cu, a strike of Ni and Sn as top layer at chip capacitor terminals.

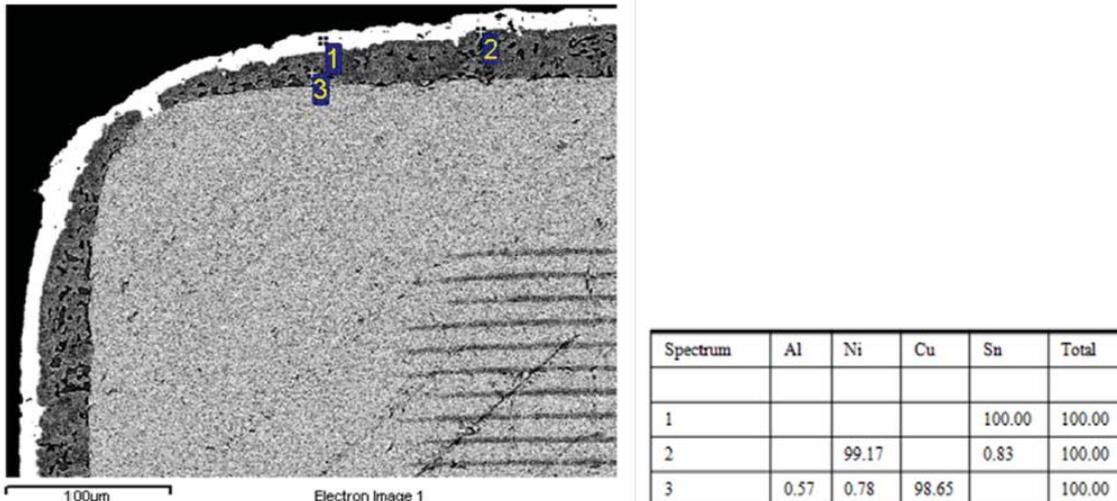


Figure 11 Cross section of chip capacitor as investigated using SEM/EDS.

SEM/EDS analysis of migrated samples exposed to various anion at a concentration of 0.113 g/l (eqv. to 15.6 $\mu\text{g/cm}^2$) shows that dendrites consists of primarily Sn with traces of Ni (Figure 12).

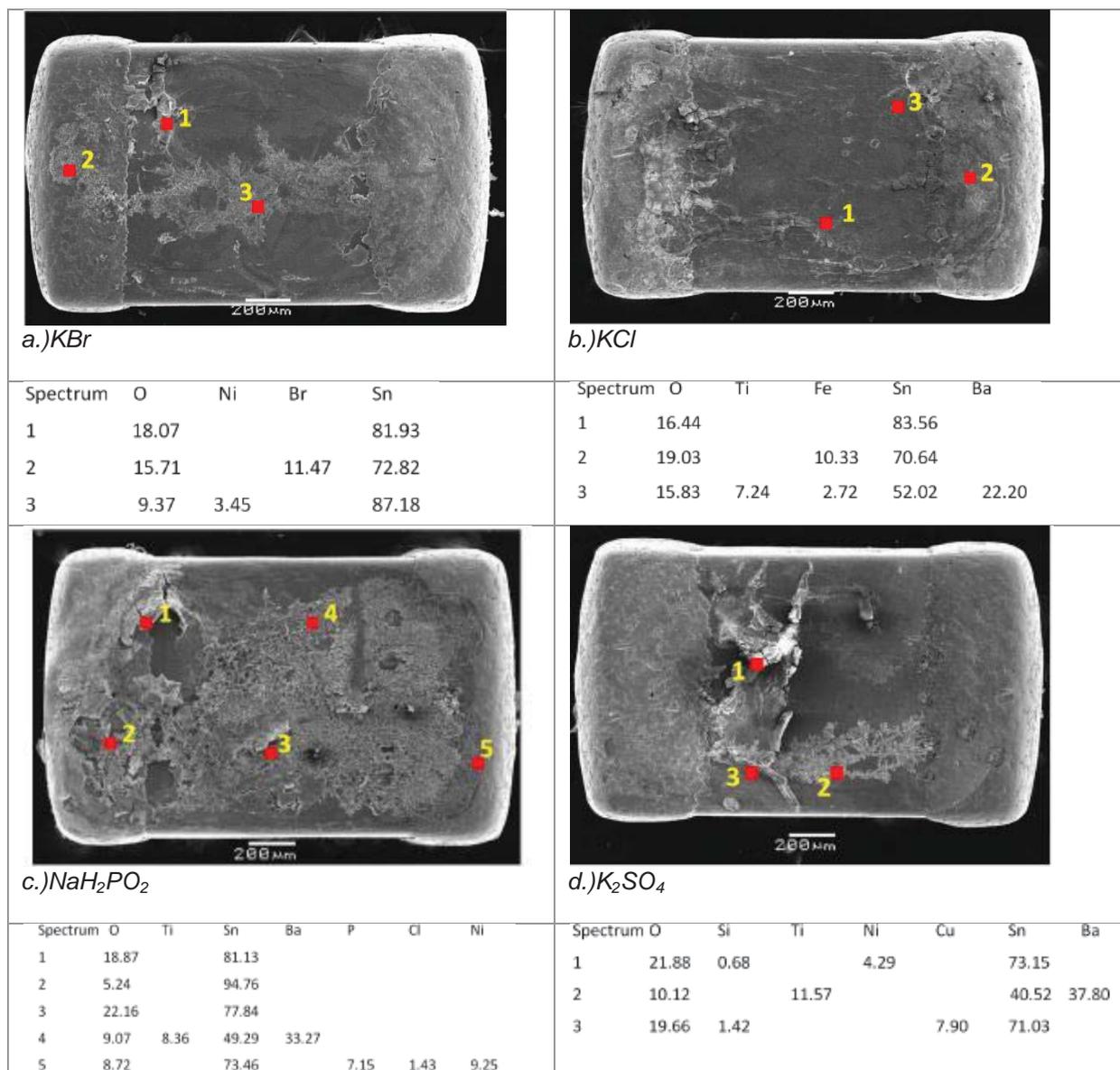


Figure 12 SEM/EDS analysis of migrated samples exposed to various anion at a concentration of 0.113 g/l (eqv. to 15.6 $\mu\text{g NaCl}/\text{cm}^2$). All EDS spectrum results are given in wt.%.

In the case of sulphate contaminated capacitor, copper is exposed, indicating that the corrosion must have penetrated both tin and nickel layers of the terminal. However, all the samples showed significant level of corrosion, which led to dendrite formation irrespective of the contamination type.

5. Conclusion

1. Results show that residue levels are of high importance in determining the level of leakage current and electrochemical migration susceptibility on the PCBA surface when a water layer is present, the formation of which is also a function of the type of contamination.
2. Probability of migration varies with level of contamination; however the tendency for migration drastically increases above the IPC standard value of $1.56 \mu\text{g}/\text{cm}^2$ NaCl equivalent.

3. Electrochemical migration showed an initial increase with contamination levels followed by a decrease irrespective of the type of contaminations, but the concentration at which reversal occurs is ion dependant.
4. A strong vs. weak ions effect is found when comparing the results from chloride, sulphate, bromide, and hypophosphite with weak ionic residue such as flux.
5. Among the strong ionic residues tested, the hypophosphite ion was most aggressive towards electrochemical migration.

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