

Corrosion in electronics

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Abstract

The risk of corrosion in electronics is significant due to miniaturization together with factors such as bias voltage, globalization of production, high demands for usage, and the use of multi-material combinations. This paper focuses on important production and user related issues affecting the overall corrosion reliability of electronic products. An example of a production related parameter is the inevitable contamination resulting from fluxing and soldering. During use, many factors can influence corrosion reliability such as humid environments, presence of aggressive ions such as chloride, corrosive gases, and temperature variations. Comprehensive analyses of products affected by production related contamination, corrosion, and climatic effects are presented.

Center of Electronic Corrosion (CELCORR) is a consortium project set to tackle corrosion and climatic effects on electronic products. The CELCORR programme is funded by Danish Ministry of Science, Technology, and Innovation. Industrial partners are: Vestas Windsystems A/S, Danfoss A/S, Grundfos A/S and GPV Chemitalic A/S. In this way CELCORR is an integrated programme combining research, technology development, and innovation to improve corrosion reliability of electronics.

Keywords: Electronic products, Contamination, Residue detection, Reliability.

1. Introduction to corrosion in electronics

Corrosion involves interaction with the environment. Electronic devices are presently used under service conditions that were never thought of few years back. Especially consumer electronics are used under highly variable environmental parameters (e.g. mobile phones brought to the seaside or sound system installations in kitchens or bathrooms). Industrial electronics also experience a variety of environments due to their wide spread use. In many cases precautions for protecting electronics against aggressive conditions are not met. The demand for electronics is not lifetime performance, but reliability, since replacing electronics is a costly task. Furthermore corrosion failures can be difficult to diagnose and cause unexpected production loss due to plant shut down. The increased use of electronics has also increased the demand for corrosion reliability.

Overall size of electronic equipment and therefore the component size has been decreasing at a faster rate. The size of integrated circuits has decreased by a factor of 10 over the last couple of years, which means that the spacing between the circuit components is ~ 200 nm. For components on a PCB, the minimum spacing is around 5 μm , while in mid-90's it was 100 μm . The reduction in size and distance between components makes the system more susceptible to corrosion problems. To generate a fault in the conducting path of such constructions, a material loss in the order of picograms is sufficient. [1] Therefore, even a small environmental impact can cause huge damages if the components are not well protected. When the device is in use, the large voltage gradients between points on a PCB will accelerate corrosion problems significantly.

2. Contamination and parameters effecting corrosion

An electronic device from manufacturing to use will pass through several steps that could have impact on its corrosion reliability during use. These are: PCB and equipment design, various stages of production process, storage, transport, and use. With increased requirements to electronic products reliability, corrosion resistance is an important property to consider already at the design and production phase. An important factor is the control of contamination at all stages of manufacturing process (component level, PCB level, and device level) so that the inherent reliability of the product

could be increased. Contamination can also be a problem during storage, transportation, and use.

In the following section contamination issues are discussed in detail. Contamination accelerating corrosion problems in electronic devices can be divided into two categories, one occurring from the manufacturing process, while the other is due to device exposure to external environment during storage, transport, and in use. Controlling the contamination from the manufacturing process could enhance the inherent corrosion reliability of the device, while the contamination from external environment at all stages should be regulated for long term corrosion reliability. Conditions during use can not only cause new contamination to the product, but also could modify the already existing contaminants from the manufacturing process to initiate corrosion attack.

2.1 Contamination resulting from production

Process related residues (contamination) on PCB surfaces result from all stages of manufacturing process starting from base PCB production to components mounting, soldering, inspection and testing, device assembly, and packing. Base PCB manufacturing is a complicated process involving the use of plating and etching baths with complex chemistries and organic compounds (e.g. additives to the plating baths and solder mask), which could introduce tiny levels of contamination especially at regions where solution entrapment is easy such as via holes. Next step in the manufacturing process is the components mounting and soldering. Cleanliness of the component itself is an issue; while the soldering process will further introduce additional contamination due to presently used no clean fluxing. In addition, PCB handling between the production stages and during assembly using bare hands (with out gloves) etc. could also introduce contamination in the form of fingerprints. All these factors could have great impact on the corrosion reliability.

An particularly important factor is the residue resulting from no clean flux especially from the wave soldering process as this is generally the last step in the PCB manufacturing processes. The flux systems in general contain isopropyl alcohol, an oil component such as organic ester, and an organic acid such as adipic acid meant for activating the metal surface. As the job of the flux is to activate the metal surface (achieved by the acid component) as well as to protect the activated surface against further oxidation (achieved by oil component by forming a blanket), flux should be stable at the peak temperature of the soldering process $\sim 230 - 240$ °C. [2] This results in significant amounts of undecomposed flux on the PCB surface, although the meaning of no clean flux is to leave no significant residue. [3] Results of several investigations clearly show significant amounts of flux residues on the PCB surface after soldering process, which consists of both oil component and organic acid as discussed below. Device failures are also seen resulting from exposure of these residues to humid environments causing corrosion under potential bias on the PCB. If residues dissolve in condensed water layer, they will increase the conductivity. This creates a risk of leakage currents on the PCB under humid conditions. Figure 1 shows an example of flux residues, which appears white after exposure to high humidity during use in the field.

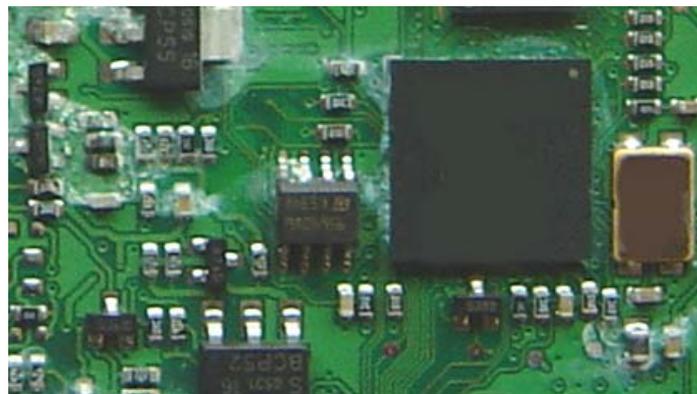


Figure 1. White residues, visible after exposure to high humidity in the field. The electronic product has failed. [4]

Detailed analysis of the chemical content of the flux residue in the above case using localized FT-IR technique showed both the oil component (an organic ester) and adipic acid to exist at a significant level. SEM-EDX analysis of the corrosion products revealed a high amount of lead, tin and copper in the corrosion products. Electrochemical migration is suspected to be the reason for corrosion failure. This observation and further information about the user environment led to the conclusion that

corrosion of the PCB took place in the user environment. The failure was initiated by flux residues and high humidity at the customer due to a failure in the air control system.

As described earlier, other process related contaminations that can introduce corrosion is plating bath leftovers (e.g. acidic species hidden locally, in for example PCB viaholes). Human handling related contamination is another problem and also sealing of electronics using polymer material as outgasing from polymers is well known. Also the flame retardant used in the PCB laminate contains bromated phenols, and it has been found that the water layer formed on a PCB surface invariably contains significant amounts of bromide. [5] Finally a clean environment within the electronic producing factory obviously plays a vital role, and requires humidity and dust levels to be controlled strictly.

2. 2 Contamination from environment during storage, transportation, and use

Corrosion behaviour of any material is determined by the external environment to which it is exposed. Important environmental parameters related to user environment for electronic devices are humidity, temperature, aggressive chemicals and ions, dust and corrosive gases. Corrosion of electronics most often involves moisture and ionic contamination from the environment. Thickness of the moisture films formed on the PCB surfaces depend on the relative humidity and the temperature. Temperature variation can also create cycles of wet and dry conditions, often referred to as Time of Wetting (TOW).

For large electronic installations, RH surrounding the equipment area is usually maintained in the range of 30 to 60%; consumer electronics, of course, are exposed to a broader range as it is difficult to put a limit for the user environment. The power dissipated in most equipment, however, elevates the internal temperature sufficiently that exposure to greater than 70% RH during operation is unusual, except for humid outdoor exposures. Within this range, several monolayers of water are still present on clean metal surfaces. [6] Some electronic products are advised to be left turned on in order to experience less water condensation and hence lower corrosion rates than expected from the relative humidity of their surroundings. If local temperature variations of components under working conditions are known, so called water traps and drainages can be included in the design phase of an electronic product. Electronics devices exposed to outside environment needs such design measures to withstand humid environment.

Even for indoor electronic devices, humidity and temperature variations can cause failures due to corrosion. Most corrosion studies involving airborne substances have been done on metals in outdoor environments, whereas corrosion studies in indoor environments are considerably more limited. Some typical indoor airborne data are given by Rice and colleagues [5] who examined the corrosion rates of copper, silver, nickel, cobalt, and iron at eight indoor locations in the United States and found the rates to be dramatically less than those outdoors for all the metals except silver. This reduction was clearly due in part to the lower indoor concentrations of corrosive gases (sulphur dioxide, nitrogen oxides, and chlorine- containing species). As stated in [6], measures of airborne concentrations are informative, but they tell little about conditions on surfaces where corrosion is taking place. These are determined by the rates of arrival and sticking probabilities of the atmospheric species at a surface and by the amount of adsorbed water on the surface. It is the combination of adsorbed moisture and accumulated atmospheric species that provides the local environment for corrosion to occur. Dust, cleanliness and contaminants play a vital role in this respect.

In the case of electronic devices, corrosion is further accelerated by the presence of potential bias on the PCB. Contamination from the local environment can increase the conductivity of the water layer to increase the leakage current and subsequently corrosion.

3. Localized electrochemical techniques for investigating electronic corrosion

Microelectrochemical set up

One major difficulty for electrochemical corrosion testing of electronic components is that the measurement needs to be carried out at tiny areas with sizes ranging from few mm to μm . The corrosion group at Technical University of Denmark make use of microelectrochemical systems for this purpose. A popular idea involves the use of a pipette connected to a system to control the solution

flow at the tip. Through addition of reference and counter electrodes, the pipette system becomes a microscopic electrochemical cell, which can then be used with high precision to determine the electrochemical characteristics of a small region of interest. The resolution of the technique is determined by the size of the pipette tip. The microelectrochemical systems in our laboratory have resolution ranging from $\sim 1 \text{ mm} - 10 \mu\text{m}$. The set up has also been used in combination with high resolution video microscope for in-situ visualization of corrosion.

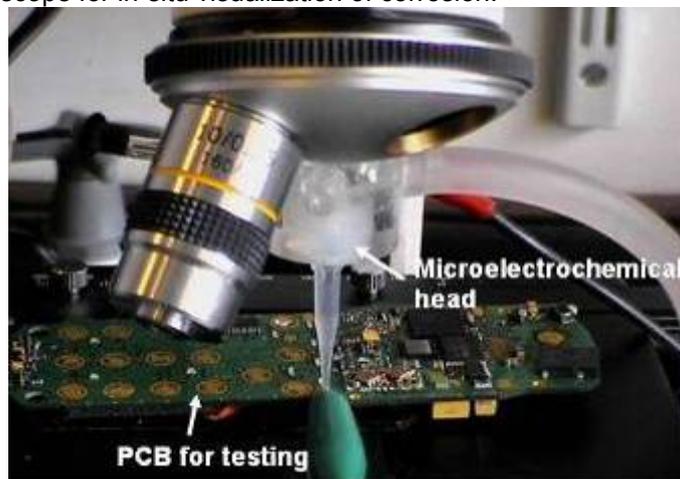


Figure 2. Microelectrochemical set up.

Figure 2 shows a picture of the microelectrochemical set up with a tip resolution 1 mm. The setup consists of an electrochemical head containing the solution, counter and reference electrodes, which is attached to the carousel of an optical microscope. The cell is connected to a pipette, which makes contact with a local region of the working electrode (in this case the PCB used for investigation). The lateral resolution of the technique is determined by the dimensions of the pipette tip. Presently the set up is used for electrochemical testing of components and metal contacts on the PCBs, tiny passive components, via holes etc.

Localized Surface Insulation Resistance measurement system

Cleanliness of the PCB surface is most important in reducing the corrosion problems. Therefore, identifying and quantifying residues on a PCB surface is extremely important. Localized pockets of contamination are not identified when analyzing whole board areas using standard extraction techniques such as ROSE test. Such methods give only the overall contamination level on the PCB surface, and it also difficult use for the PCBs with components as the PCB has to be fully immersed in solution. The most effective way for residue detection is to have a system for localized analysis of residue or its effect. Such a Localized Surface Insulation Resistance measurement system built in our laboratory is shown in figure 3. The system consists of a pair of inert electrode (in this case platinum electrodes) with specific dimensions and geometry fixed on a holder made of acrylic material. The measurement head is then fixed on to the carousel of an optical microscope for the X,Y,Z translation and for precise movement control.

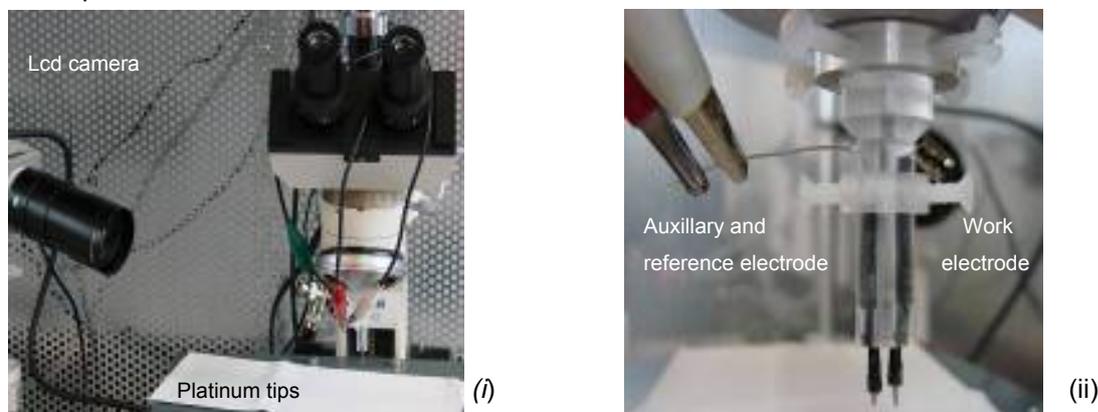


Figure 3. Set-up for leakage current measurements mounted on microscope stage with a lcd camera (i) The two platinum tips (ii) are connected to a potentiostat.

The distance between electrodes is approx. 3.5 mm, but it can be adjusted for various length scales on the PCB surface. With 3.5 mm distance between electrodes one can determine contamination effects down to an area of about 0.3-0.5 cm². Measurement area can be reduced by decreasing the distance between electrodes.

Localised residue levels are measured using this equipment by an indirect electrochemical method by measuring the leakage current resulting from the dissolution of the residue into a tiny amount of water equivalent to condensation in humid environment. Current is measured at high voltage enough to avoid polarization effects to a level where the current between the electrode is limited by the solution resistance. In this way the technique give direct correlation to leakage current that could be expected if there is condensation on the PCB during use. Leakage current between the electrode is measured at 10 V potential difference using a potentiostat system and recording the resulting current for 2 minutes. Using the cell dimensions, current can be converted to surface resistance or conductivity if needed.

4. Analysis of contamination resulting from manufacturing process

4.1. Localized leakage current measurements

Figure 4 shows the leakage current analysis using Localized Surface Insulation measurement system in few clean water drop-lets, and contamination extracted to a drop-let from human finger print, as received component, freshly wave soldered PCB, and PCB after exposure to outside environment for some time. The ionic residues were extracted simply by putting few drop-lets of DI water (about 0.1 ml) at locations needed (also for components) for 30 minutes. The solution was then extracted and the leakage current was measured. Current values reported in Figure 4 are the plateau current values from a current – time curve measured for 2 minutes.

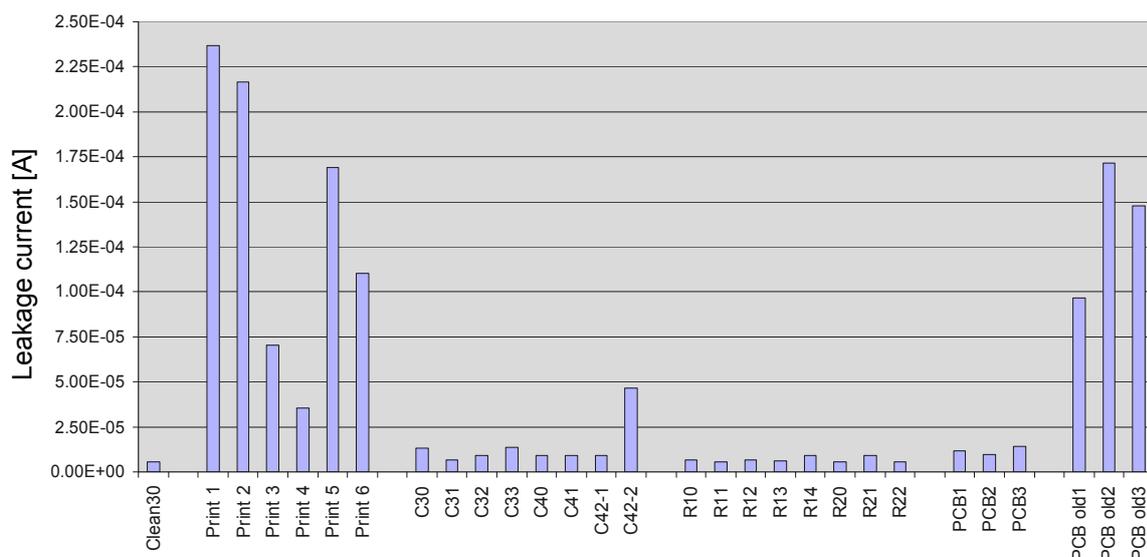


Figure 4 Leakage current measurements using localized system on finger prints, components, and PCBs.

Clean drop-lets itself showed a current close to 1 micro-amps at 10 V potential difference. In effect chromatographic water should be perfect insulator, but this is seldom as exposure environment can always create tiny levels of contamination as well carbon dioxide exposure to generate carbonic acid. However, contamination from finger prints showed on the average a 100 times increase in leakage current due to ionic contaminants resulting from the chemicals in finger prints. This clearly shows the damaging effect of finger prints on the PCB surface and importance of using gloves during the production of PCBs. It is interesting to note that the current levels resulting from finger print is slightly higher than that for the old PCB (after use in external environment). All the components tested did not show significant level of contamination represented by the low levels of leakage current. Leakage current for components was about 10 times higher than that for clean drop-lets, while for the freshly

soldered PCB showed slightly more leakage current than that for the component (it is not evident in the figure). However, use of PCB outside for some time has increased the leakage current by 100 times due to the contamination from the external environment.

Localized leakage current measurement system can also be used for failure analysis of corroded PCBs by identifying the levels of contamination at the localized corroded area. This together with ion chromatographic analysis provides information on the environment and leakage current that causes the corrosion problem.

4.2 Spectroscopic analysis of flux residue

As shown in Figure 1 flux residues combined with high humidity conditions during use can cause electronic products to fail. The temperature profile during wave soldering has a large influence on the quantity of flux residues left on a PCB. A typical temperature profile for the wave soldering process is shown in figure 5.

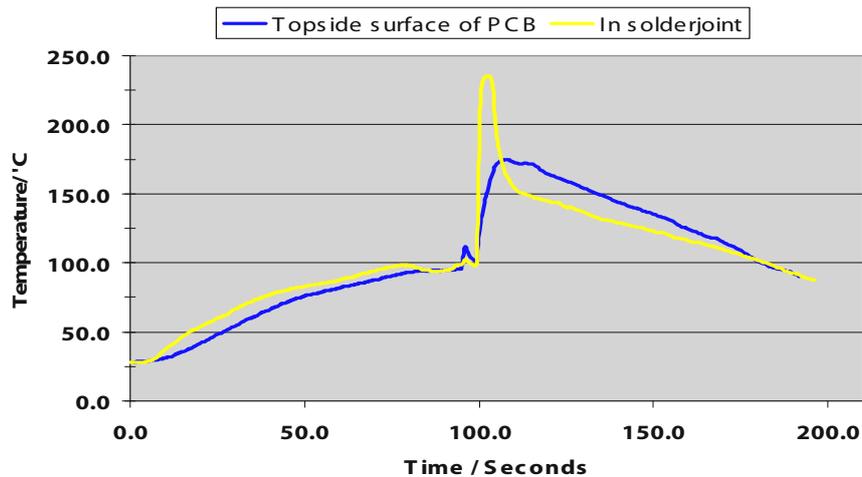


Figure 5. Temperature profile of a wave soldering process at bottom side (soldering side) and top of the PCB.

As the solder wave is only in direct contact with the bottom side of the board during wave soldering, any flux residue residing on the topside will not undergo the same temperature cycle as the bottom side (Figure 5), which is designed to keep the amount of flux residues on an absolute minimum or render them benign in subsequent field applications. [7]

Precautions have to be taken during fluxing in wave soldering processes in order to avoid the deposition of flux on the topside of the assemblies. However during fluxing of the assemblies it is desirable to deliver flux all the way up the plated through-holes in order to ensure reliable solder joints, so it can be very difficult to avoid that some portion of the flux ending up on the topside of the PCB. Especially the spray-fluxing has been found to increase the risk of flux-deposition in unwanted locations due to the powerful propulsion of the liquid, which can eject flux out through the unsoldered through-holes. Furthermore the spray creates a mist of flux in the atmosphere around the assembly enhancing the risk of flux condensing on the top-surface. [8]

In order to investigate the chemical change and nature of flux residues as a function of various temperatures corresponding to the heating profiles in Figure 5, samples of the flux were burned at various temperatures and analysed using FT-IR. Figure 6 shows a collection of FT-IR spectra for the flux residues at various temperatures starting from room temperature to 400 °C.

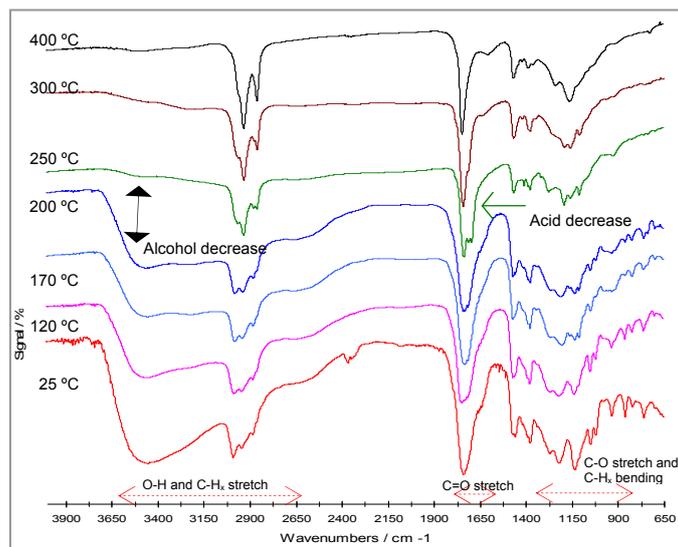


Figure 6. FT-IR spectra of flux residues at various temperatures.

Apart from a decrease in the alcohol concentration (isopropyl alcohol base in the no clean flux), heating of the flux does not seem to have any significant effect on the chemical composition of the residue until temperatures in excess of 200 °C are reached. Any substantial volatilization or conversion of the adipic acid is not observed until 250 °C, where the O-H and the C=O stretching vibrations of the acid notably decrease, but even at this temperature the C=O peak clearly indicates the presence of adipic acid in the residue. At 300 °C most acid seems to have gone, and the remaining and strong C-H₂ stretching vibrations strongly indicate that the residue at higher temperatures consists of long-chain hydrocarbons. The intense C=O stretching vibration at 1735 cm⁻¹ along with the C-O stretching vibrations at ~1230-1145 cm⁻¹ strongly implies that the residue could be a thermally stable ester oil remaining from the flux. The specific type of ester can however not be determined from these experiments, and further investigation is needed to confirm this.

Quantitative analysis of the amount of adipic acid in the flux residue after exposure to various temperatures has been performed using Ion chromatograph (Dionex ICS -2000). Amount of adipic acid in the residue as a function of burning temperature is shown in figure 7. It is clear that in agreement with FT-IR, adipic acid levels in the residue remains unchanged until 300°C. This is significant as it shows that the presently used wave soldering peak temperature of approx. 230 – 240°C will leave significant amounts of acid component from the flux on the PCB surfaces. This is presently under investigation. Also the effect of these residues on the corrosion is being investigated.

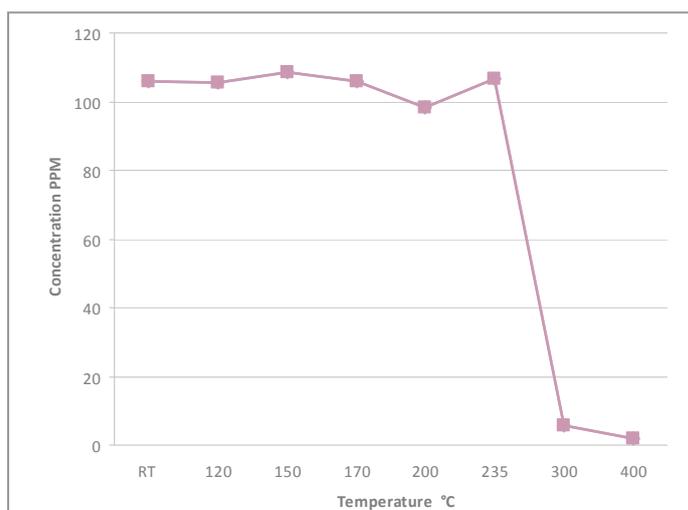


Figure 7. Amount of adipic acid in the residue as a function of temperature measured using Ion chromatography.

4.2 Conditions affecting electronic products during use

4.2.1 Humidity and bias

As described before, for electronics during use, the coexistence of high humidity and large voltage gradients between points on a PCB can accelerate the corrosion problems significantly.

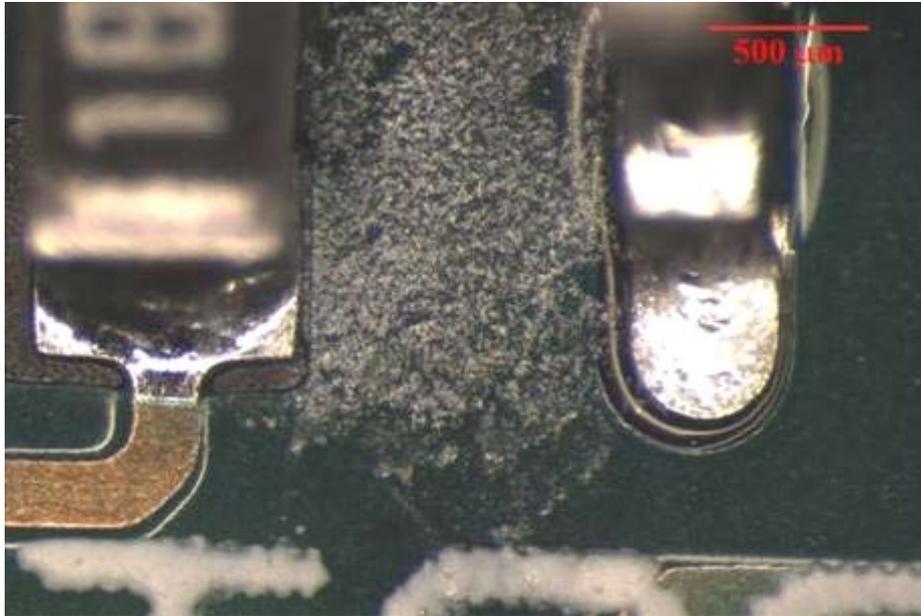


Figure 8. PCB assembly suffering from corrosion in between components due to high humidity and large voltage gradients.

A closer look at the failure shown in fig. 8 reveals that Pb from the Sn/Pb solder alloy has caused electrolytic migration in the humid environment and created a short circuit. Migration is caused by both tin and lead. Bulky dendrite was observed due to the presence of high levels of lead.

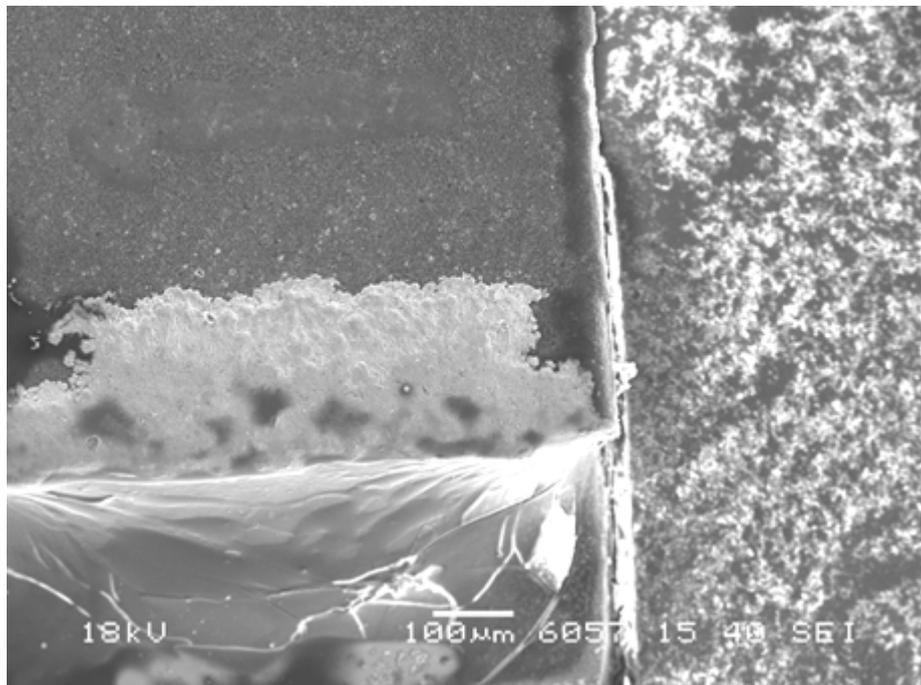


Figure 9. SEM micrograph of migrated Pb from soldering of components on a PCB assembly.

Such failures are commonly found for many PCB manufactured with lead solder alloys under exposure to humid conditions Dendrite growth between the adjacent points due to electrolytic migration is commonly observed in these cases.

4.2.2 Dust contamination

Dust collection on the PCB and components is an important aspect in the corrosion of electronics. Dust can increase corrosion due to two factors namely: (i) it is good source for ionic contaminants, and (ii) it will attract water so that condensation can take place at lower humidity. A study related to electronic corrosion showed that under dusty environment corrosion in electronics can occur at humidity levels lower than 50%, which is otherwise not possible. Size, composition, and nature of dust particles varies from place to place and industry to industry depending on the product produced, and cleanliness followed. For example in a paper factory or textile industry, large amounts of cellulose fibres can be expected in the dust particles.

The particles collecting on surfaces also absorb water easily, which make the surfaces conductive. In fact it has been stated that the leakage current and corrosion caused by surface contamination are more harmful than the effect of gaseous impurities in the air. [9]

In an industrial environment, the dust consists of mainly inorganic particles. The damaging effect of these dust particles to electronics depends on their composition.

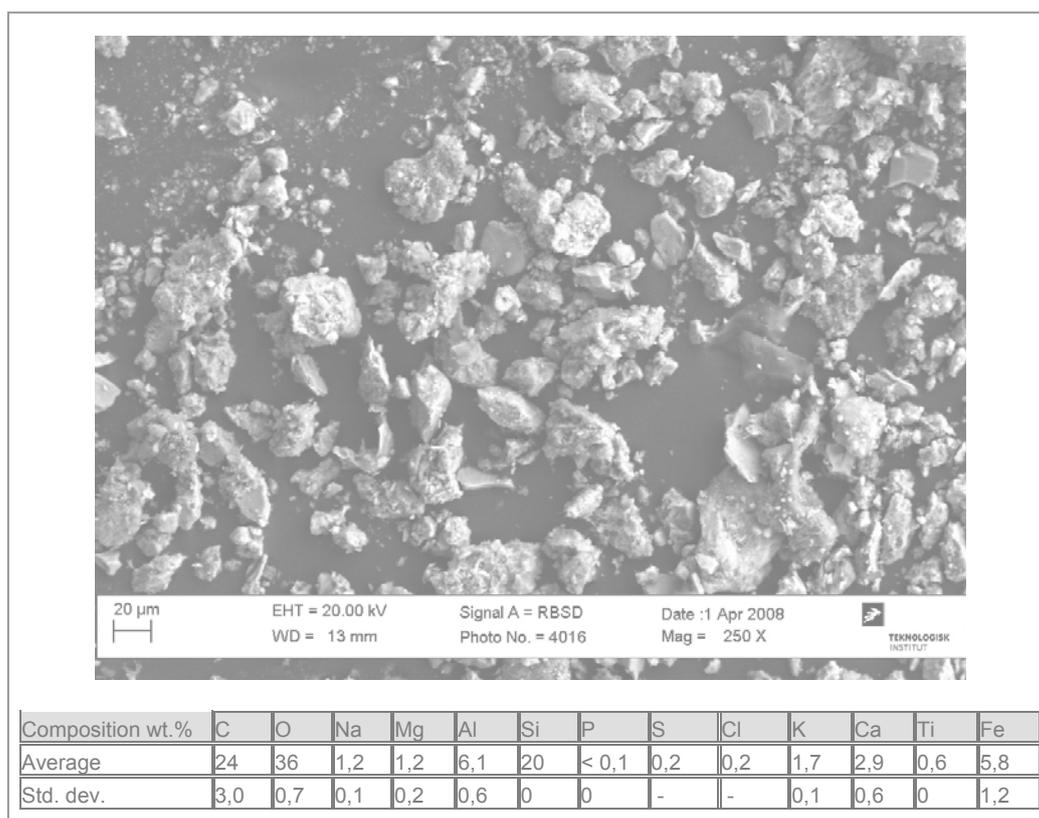


Figure 10. Dust particles collected on an electronic device after use in industrial environment.

Failure analysis of an electronic device failed in industrial applications showed clearly visible signs of dust inside the cabinet. A sample was collected and investigated using SEM/EDX (figure 10). EDX analysis revealed that the dust particles are inorganic in this case with higher amounts of aluminium, silicon, iron, and calcium, and many other elements such as K, Cl, Mg etc. points to the fact that probably it come from building materials. In this case for example, condensation of water can results in dissolution of many of these metal ions that can increase the conductivity of the medium and corrosion.

Dust particles usually contain elements of Si, Al, Mg, O and C. Many dust particles include elements of Na, K, Ca, S, O and Cl. [10] Carbon/soot particles and particles containing rust/metal dust are considered being the worst. [5] Investigations of dust and humidity parameters are presently being carried in CELCORR. Protection of electronic devices and especially their inside from solids or filtering of the air are effective means to minimize the risk of corrosion.

5. Summary

1. Corrosion reliability of electronics is a serious issue today that needs to be tackled. An important aspect is the contamination resulting from all stages of manufacturing process and service environments. Contamination from the manufacturing process to a larger extent can be predicted, however, service environments are too complex due to the wide spread of use of electronics today.
2. No clean flux usage during the soldering process leaves significant levels of residues especially the oil and acid component on the PCB surface. Such residue will have significant effect on corrosion reliability. Problem is compounded due to the fact that temperature profile on the PCB during soldering is not uniform with top part at about 170 °C, while the bottom part reaches up to 235 °C. This cause more flux residues on the top part. Study found that quantity of both acid and oil component in the residue remains unchanged up to a temperature of 300°C.
3. Sources of contamination can also be human handling such as finger prints. Finger prints on PCBs found to increase the local leakage current by a factor of 100 showing that it is important from the corrosion reliability point of view to use gloves for all the manufacturing process.
4. Service related parameters affecting the corrosion are humidity, aggressive ions and gases, temperature, and dust particles. Aggressive ions like chlorides and gases like sulphur dioxide are very damaging to electronic assembly. Dust particles could be site for water trapping (means corrosion can occur at lower humidity) and source for aggressive ions.

New novel test techniques developed namely microelectrochemical set up and Localized leakage current measurement set up have found to be good tool for electrochemical testing of electronic components and assemblies for corrosion and contamination testing. Direct leakage current data can be obtained from a localized area that could be correlated with service conditions.

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