N°XXX

PERFORMANCE OF CONFORMAL COATINGS ON ELECTRONIC PRINTED CIRCUIT BOARDS UNDER HARSH ENVIRONMENTAL CONDITIONS

Umadevi RATHINAVELU, Morten S. JELLESEN, Per MØLLER and Rajan AMBAT

Department of Mechanical Engineering, Technical University of Denmark, Denmark, umra@mek.dtu.dk

Electronic devices are presently used under service conditions that were never thought of few years back. The demand for industrial electronics is not lifetime performance, but reliability, since replacing electronics can be a costly task. Miniaturization at all levels is one of the key factors reducing corrosion reliability. Over the last 10 years, size of the electronics has been reduced by over 70%. For flip chip ICs, miniaturization amounts to ~ 90%. The closer spacing increases the electric field ($E = V/d$), which makes corrosion cell formation easier during local condensation under humid environments.

One approach to protect electronic devices from harsh environments is by applying conformal coatings on printed circuit boards (PCBAs). Conformal coatings are meant to provide a high degree of insulative protection and are usually resistant to many types of solvents and severe environments encountered in the product life cycle. Various types of conformal coatings are available for this applications namely silicone based, polyurethane or acrylic. However, in practice performance of the conformal coatings depends on various factors such as adhesion to PCB surface, water permeation, and permeability to other environments such as gases.

Focus of this paper is the investigation of the performance of selected (silicone and polyurethane based) conformal coatings used for Printed Circuit Board Assembly (PCBA) using a Printed Circuit Board (PCB) with Dual Copper Electrodes (DCE) as substrate for coating. DCE's are coated with desired conformal coating of known thickness using a spin coater. Water permeation was studied using potentiostatic DC polarization technique by measuring the current between DCE electrodes under the coating exposed to desired environments. Adhesion testing was carried out using standard pull-off adhesion tester before and after exposure to the environment both in the laminate area and close to electrodes. Effect of solder flux residues on the permeability, adhesion, and subsequent under-film corrosion was investigated. Scanning electron microscope and FIB-SEM was used for investigating the corrosion under the conformal coatings after exposure to environments. Results show that the adhesion and performance of the coating was greatly affected by the process related flux residues. Type of coatings determined the permeability to environment, while contamination at the interface has drastically increased the corrosion attack once the coating is delaminated.

Key words: Conformal coating, permeability, adhesion, acrylic.

Introduction

Electronic systems are presently used for a wide range of applications today and hence they are exposed to broad environmental conditions from mild to harsh such as clean room to offshore conditions. Demand for miniaturization and increased boundaries related to application environments have introduced increased reliability problems for corrosion in recent years. Therefore corrosion protection measures are sought for PCBAs to eliminate environmental impact.

In view of increasing the reliability of the PCBAs, conformal coatings are applied on the circuit boards as the final step in production. Conformal coatings are synthetic resins or polymers that are applied to the printed circuit boards, in order to protect the circuit from contaminants like moisture, dirt, harsh solvent, high atmospheric humidity, chemical agents etc. They also serve to isolate the closely spaced conducting lines and increase the reliability of the circuit board. Hence conformal coating is widely used by the electronic industries in order to ensure environmental reliability. There are several factors involved in selecting a particular coating for a specific application. These factors include circuit preparation, environmental performance requirements, application of the coating, coating adhesion promotion, coating thickness control, prevention of bridging between components, coating removal or circuit repair, thermal expansion considerations, and cost effect.

There are different types of conformal coating available in the market. The basic types of resin system are categorized as follows.

- Acrylic resin
- Epoxy resin
- Urethane resin
- Silicone resin
- Parylene

The acrylic, epoxy and urethane are organic resins. These resin systems are primarily made up of monomers, oligomers, de-forming agents, fillers, and wetting agents. Various combinations of each are added to the formulations to adjust the particular cured and uncured properties. Solvents are typically added to adjust the viscosity [4].

Moisture penetration into these coatings under severe environment causes significant degradation in the performance of the coating. Adhesion of the coating to the PCBA surface is an essential factor determining the performance of the coating under humid environmental conditions. In the case of a poor adhesion, permeated water or gases can collect easily at weak spots by de-lamination of the coating. Formation of such occluded environment can accelerate corrosion to a significant level than without coating. If the conformal coating is not adhered well enough on a PCBA, corrosion problem in effect will be much higher than without coating once the environment penetrates the coating. Therefore it is important to know the effect of various process related contamination on PCBA surface on the adhesion and performance of the conformal coating in various environmental conditions. This paper investigates the performance of acrylic based conformation coating using a PCBA with dual copper electrodes to act as the conducting lines (similar to PCB lines) below the coating. Performance of the coating under biased condition was studied in various environments using DC potentiostatic polarization experiments by monitoring the current flow between electrodes, adhesion testing before and after experiments, ion-chromatography for contamination analysis, and microscopic analysis.

Materials and experimental methods

PCB with Dual Copper Electrodes (DCE):
A test PCB with two copper electrodes as shown in Figure 1 was used as a substrate for the investigation. This multi-purpose PCB was designed and manufactured with the help of Vestas Windsystems A/S and GPV Chemitalic A/S for environmental reliability studies under the CELCORR (www.celcorr.com) programme. The copper electrodes are with 2mm width and separated by 2mm distance. The base of the board is an FR-4 laminate with solder mask, and overall dimension of the PCB is 50mm X 55mm.

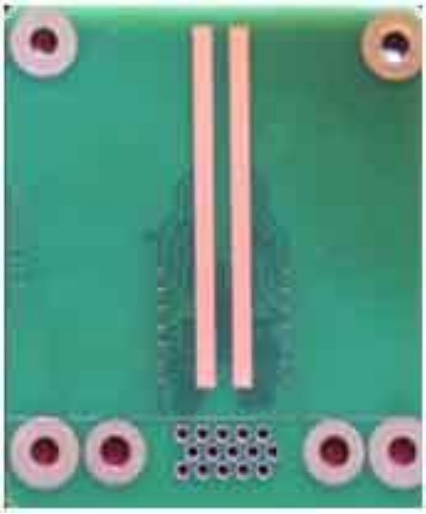

Figure1. Dual-Copper Electrode system

DCE's are connected to a number of micro wires enabling one to measure the resistance changes at various locations, however in the present study only two wires are connected to the external potential source to apply bias to the electrodes.

Acrylic coating:
Acrylic resins are a group of related thermoplastic or thermosetting plastic substances derived from acrylic acid, methacrylic acid or other related compounds. They are easy to apply and have high moisture resistance and stable dielectric property. Their service temperature is from -60˚C to 135˚C. The acrylic coating used in this study was a modified acrylate resin, which has a temperature resistance up to 130˚C.

Activating the copper electrodes:
The as-received dual electrode PCBs were oxidized at the copper surface due to atmospheric exposure. The oxidized copper surface was degreased in an alkali bath and after which immersed in a cyanide bath for de-oxidation. After each treatment the Dual copper electrode system was rinsed in water and dried.

Introducing flux residue to test PCB:

In order to introduce flux residue to the test PCB (Figure 1), a known amount of no-clean wave soldering flux solution was sprayed all over the top surface and was heated to 255°C in the oven, in order to activate the flux for 45 seconds. The temperature used for heating in this case corresponds to maximum temperature during lead free wave soldering process.

Application of conformal coating:

The conformal coating was applied on the PCB with a spin coater WS-650S. A known amount of conformal coating solution was placed and the PCB was allowed to spin with required rpm to obtain a defined thickness. Amount of acrylic coating used was 3 ml and rotated at a speed of 120 rpm for 10 minutes to get a coating thickness of 50 to 65 µm .The coating was then cured at room temperature at least for one hour.

Potentiostaic DC polarization experiments:

Using coated PCBs, potentiostaic DC polarization experiments were conducted as a function of time at 3V potential bias either by full immersion in 10 ppm NaCl solution or under cyclic humidity of 96% Relative Humidity and 60°C Temperature. Current between the electrodes was measured as a function of time using a Gill–AC Bi stat ACM potentiostat. The increase in current between the electrodes shows the permeation of the moisture through the coatings.

Ion Chromatography:

Dionex Ion chromatography system was used to analyze the composition of the flux residues. The residue extracted solution was fed into the AS40 automated sampler and analyzed using the ICS-2000 anionic and ICS 1500 Cationic column. The result gives the quantity of acid and ester component present in the extract.

Adhesion strength evaluation:

The adhesion of the conformal coating to the test PCB at various locations before and after environmental exposure was tested using an Instron 3343 tensile testing machine using a specially fabricated fixture as shown in Figure 2. The dolli used for gluing on the conformal coating is shown in Figure 3.

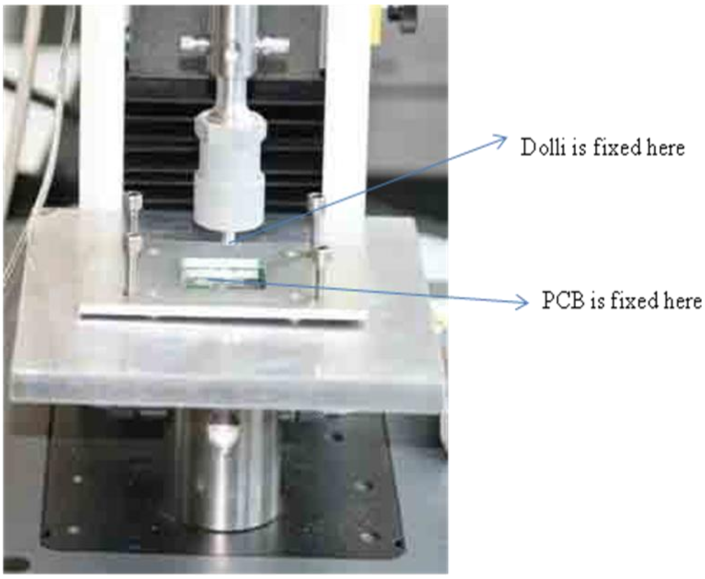

Figure 2. Fixture for measuring the adhesion strength of the conformal coating on Printed Circuit Board Assembly

Figure 3. Dolli used of 5mm diameter

In order to conduct the test, aluminum dolly was attached to the coating with a strong adhesive. The adhesive used in the present work was 2011 Araldite. The surface of the dolli was degreased with acetone prior to gluing and rubbing on a scotch-Brite pad and cleaned with a dry tissue and then cleaned with acetone again in order to remove the contaminants caused due to rubbing. The microstructure resulting from using a three-dimensional abrasive conditioning pad such as Scotch Brite pad is more conducive for adhesion [3]. The diameter of the aluminum dolly used was 5mm (Figure 3). After attaching the aluminum dolly to the coating, the adhesive is allowed to cure for minimum 12 hrs duration. After the curing process, the dolly was pulled using the fixture on the tensile testing machine at the load rate of 10N per minute and load – displacement curve was measured.

Results and Discussion

Surface Morphology of PCB Laminate and Flux residue

The PCB laminate of the DCE system is made of Flame Retardant (FR)-4 laminate. The SEM picture of the FR-4 laminate without solder mask at higher magnification is shown in figure 4(a). The micrograph in figure 4(a) shows that the epoxy laminate without solder mask has a porous surface morphology that can easily trap any flux residue. These pores can easily pick up the flux sprayed during production and also other contaminants. Once the contaminants are trapped in the pores, they are difficult to remove. A picture of the laminate with flux residue formed at room temperature is shown in figure 4(b). Large amounts of flux residues trapped inside the surface pores of the laminate could be seen. However, the application of the solder mask make the surface more uniform as shown in figure 4(c). As shown in Figure 4(d) laminate with solder mask also traps flux residues, however to a significantly lower level compared to one without solder mask. Flux residues remaining on the solder mask on the PCB laminate can cause several problems such as decrease in surface insulation resistance due to increased availability of conducting ions when water layer forms in humid environments, aggressive ions for corrosion, and adhesion problems related to conformal coatings. A conformal coating on PCBs with improper adhesion is more dangerous from the corrosion point of view than one without coating as interface delamination occurs easily with poor adhesion and corrosive environment. Delamination due to permeation of water can cause severe corrosion underneath because occluded environment between two potentially biased points is more dangerous than open environments due to the localization of electrochemical reactions.

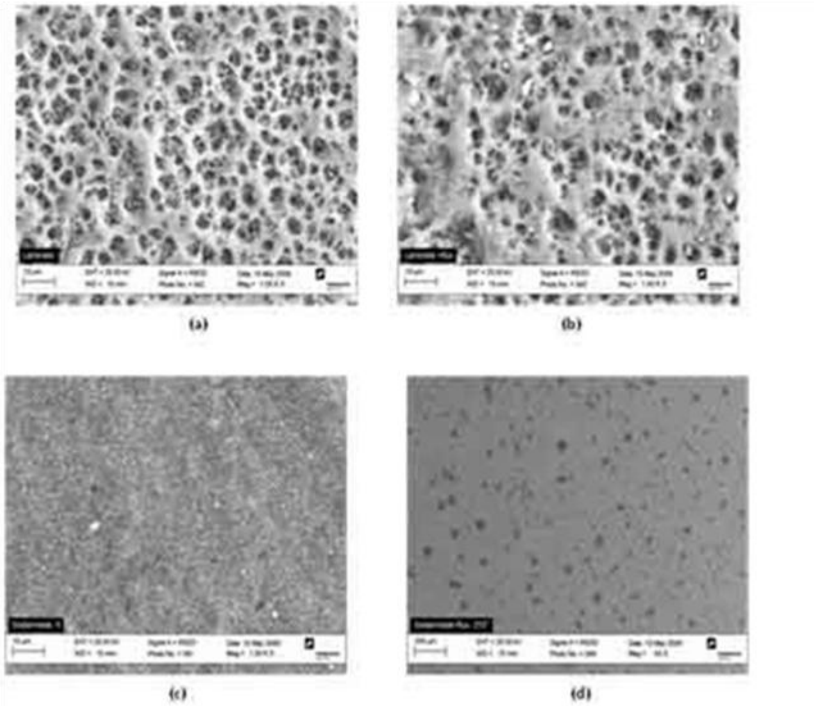

Figure 4. SEM picture of the laminate: (a) FR-4 Laminate, (b) Laminate with flux sprayed, (c) Laminate with solder mask, (d) Laminate with solder mask and flux deactivated at 255°C in oven.

Figure 5 shows typical morphology of the solder flux residue. In general, the no-clean wave solder flux used for the present investigation consists of mainly adipic acid as the activator component, a resin, and isopropyl alcohol as the carrier [7]. In figure 5, the acid crystals are embedded inside the resin, some of which are exposed, while others are covered by the resin. The resin part of the residue is not expected to contribute directly to corrosion problems, but it will be a good site for trapping of solid contaminants such as dust. Due to collection of dust particles with time the resin surface can also becomes hydrophilic.

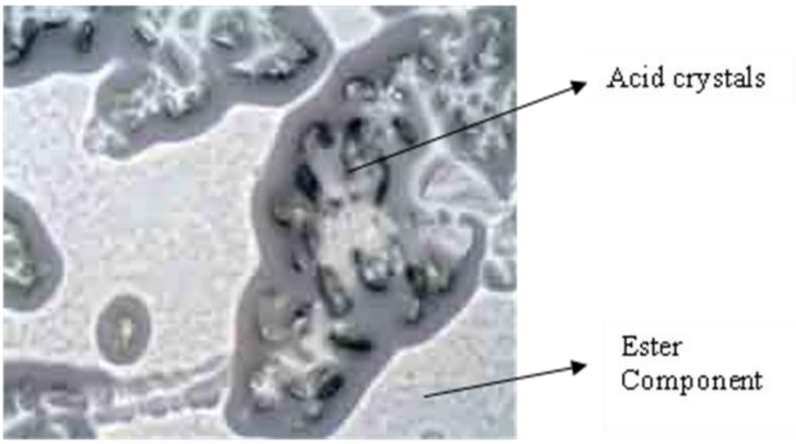

Figure 5. Optical Micrograph of morphology of flux at room temperature.

Quantification of flux residues

In order to quantify the amount of flux residue that could be possibly present on various parts of the PCBAs, a known quantity of flux was heated to different temperatures for 45 seconds and the left-over residue was analyzed using ion-chromatograph. A time scale of 45 seconds was used because it comparable with the overall time scale of the wave soldering profile from the time at which the PCBAs enter into the soldering oven to its exit after the soldering and cooling stage. Figure 6 shows the percentage of acid components (adipic acid and succinic acid) in the residue as a function of heating temperature. For ion-chromatographic analysis, flux residue was extracted from the glass plate using 3ml of water and a waiting time of 30 minutes. The amount of adipic acid and succinic acid activators in the flux residues remains almost constant up to a temperature of 230°C, above which first succinic acid shows a reduction in amount, while the quantity of adipic acid reduces only above 250°C. In general the results show that substantial amounts of flux residues with activator components could be expected on PCBAs after the soldering process. This is especially important for the top side of the PCBAs as the temperature on top side reaches only 170°C during the wave soldering process.

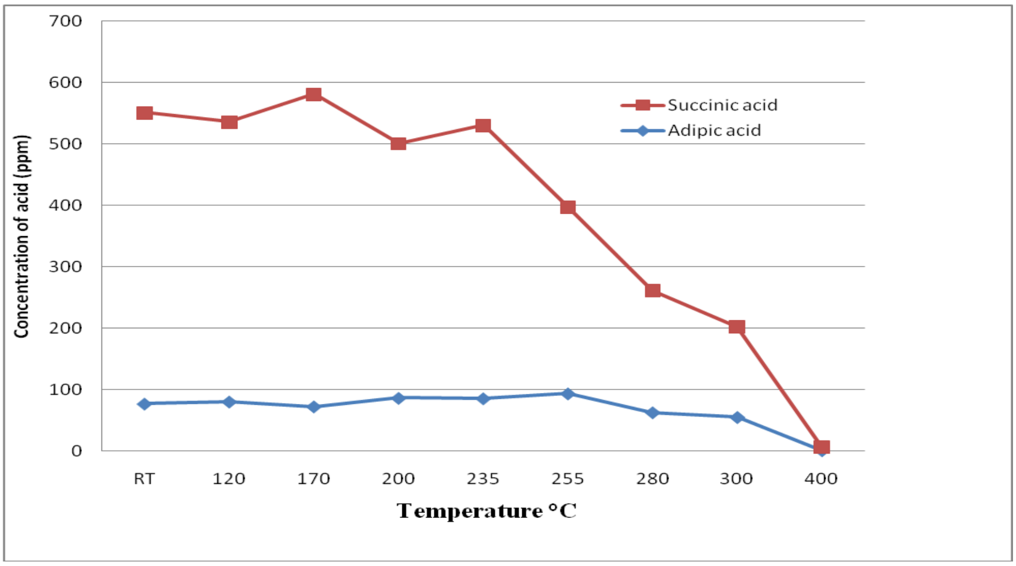

Figure 6. Percentage of acid component present in the flux as function of deactivation temperature.

For quantifying the amount of flux residue at various stages of the soldering process in practial PCB assembling process, a number of PCBs were taken out from the manufacturing line at various stages after the flux spraying. PCBs are removed from the oven after: (i) flux spraying, (ii) flux spraying followed by pre-heating, and (iii) flux spraying followed by pre-heating and final soldering. The amount of flux residues on the PCBs removed at various stages was analyzed using ion-chromatograph. Flux residues were extracted for analysis using 30ml of 1:1 Iso-propyl alcohol and water mixture by dipping for 30 minutes with mild brushing. Figure 7 shows the amount of various components in the flux residues from PCBs. It is assumed that the flux residues were 100% immediately after the spraying process. After the pre-heating stage, the amount of acid components were reduced to 60%, while after the soldering, the quantity was further reduced to 20 – 10%. On the other hand quantity of resin component remained almost constant even after the soldering process. The implication of having more resin in the residue is described before, whereas large amounts of activator components after pre-heating stage (about 60%) clearly shows that at various parts of the PCBs (especially on the top part) where the temperature during soldering stage is less than the maximum value can trap higher amounts of residues. In this respect top part of the PCB after wave soldering is more critical from for environmental reliability.

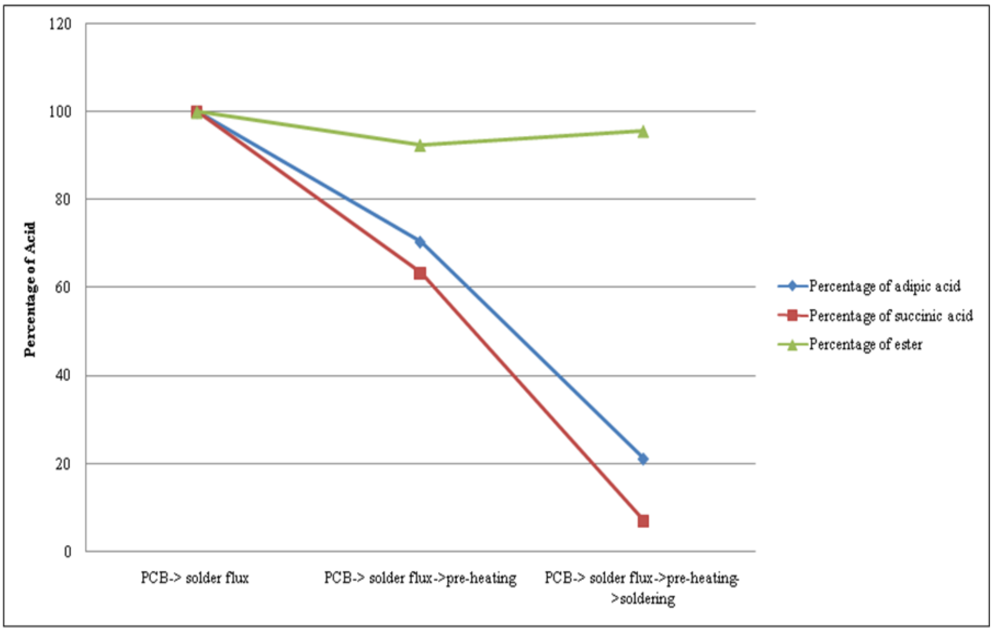

Figure 7. Percentage of flux residue at various stages of wave soldering process

<u>Influence of flux residue on performance of acrylic conformal coating on PCBA</u>

The permeability of the coating to gases and humidity, and adhesion of the coating are two significant properties of the conformal coating which plays major role in ensuring reliability of the PCBAs. The ability to allow penetration of the media (gaseous, liquid or vapor) through the solid is called the permeability of the solid material and it is an intrinsic property of each material. The permeability or transmission rate of gases and vapors through any polymeric material is dependent upon two factors; the solubility of a gas or vapor and the rate of diffusion through the barrier. The solubility function is dependent upon the chemical relationship between the permeant molecule and the polymer: and the rate of diffusion is dependent upon the size of the permeant molecule and the amorphous configuration of the barrier polymer [1]. There are various factors that affect the permeability of a polymer; they are characteristics of polymers, environment, temperature, humidity, and pressure. The characteristics of polymers include pendent chains, degree of chain motion, degree of crystallinity, polarity, degree of cross-linking, and the presence of pin holes and micro voids. When moisture permeates through the coating, a water layer is formed between the conducting lines of the PCB and the coating, which causes decrease in surface insulation resistance of the board.

Adhesion of conformal coatings is mainly affected by the improper cleaning of the PCBA surface prior to coating. Examples of assembly processing parameters affecting adhesion include flux, solder, PWB material, PWB solder mask, soldering process, and PWB surface finish. The end-use environment like temperature and humidity extremes, sand, salt-water, gases, petroleum based fluids, etc also affect the adhesion of the conformal coating. Improper adhesion of the coating to the PCB surface makes it easier for the moisture to reach the PCB surface, and results in lower surface insulation resistance and other failure effects.

Investigation of performance of acrylic coating using potentiostaic DC polarization

Climatic chamber exposure at constant humidity and temperature

The copper electrodes on the DCE system were coated with the acrylic conformal coating to a thickness of about 50 µm. A potential bias of 3V was applied between the electrodes and exposed in a climatic chamber to 96% Humidity and 60 °C for a duration of 84 hours. In one of the DCE system, the no-clean flux was sprayed all over the top surface and deactivated at 255°C in the oven and then conformal coated, in order to study the influence of flux residues on the performance of the coating. Figure 8 represents the leakage current measured on the DCE system with the presence of deactivated flux and without flux on the PCB surface. The leakage current observed was around $4\ X10^{-6}$ to $2\ X10^{-6}$ mA and there was not much difference in the leakage current with respect to the flux contaminant. However, during the initial duration of the experiment, less than a decade of higher current was observed in the case of clean PCB surface compared to the PCB with deactivated flux on it. However, both curves showed a slight increase in leakage current after 40 hours. It is possible that the time of exposure (84 h) is not enough to observe any real change in leakage current. Based on this information presently long term investigation is being carried out.

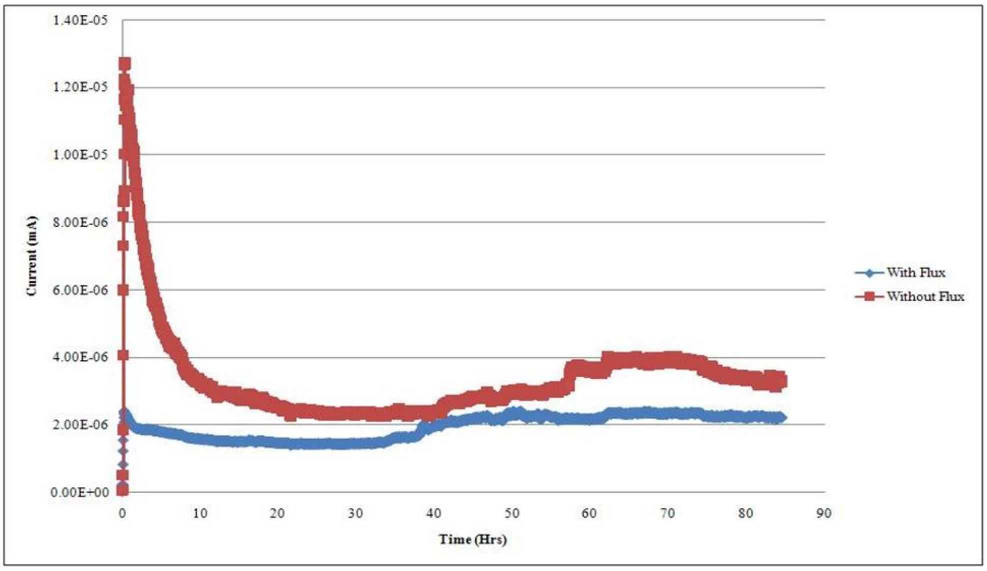

Figure 8. Leakage current between the copper electrodes biased with 3V potential and coated with the Acrylic conformal coating and exposed to 60°C and 96 %Humidity.

<u>*Constant immersion in NaCl Solution*</u>

The DCE system coated with the acrylic (about 50 µm thickness) is biased to a potential of 3V and immersed in 10 ppm NaCl solution for a duration of 82hours. One of the DCE system was coated without flux residues, but another one was with flux residue followed by conformal coating. Figure 9(a) shows the leakage current measured on the DCE system without flux, immersed in 10ppm NaCl solution. Similarly, Figure 9(b) shows the leakage current measured on the DCE system with flux deactivated and immersed in 10ppm NaCl solution. The leakage current measured for the DCE with flux is much higher than one without flux and further increases with exposure after 20h. Current measured for the system with flux was of the order of 10^{-2}mA, while one without flux showed a current value of 10^{-7} to 10^{-8} mA indicating a high insulation resistance. Visual observation showed severe corrosion on DCE with flux and an increase in current above 20h. Increase in current might be attributed to the formation of Conductive Anodic Filament (CAF) between the electrodes. However, the higher current levels from the beginning of the experiment for DCE with flux might be attributed to a defective coating, but probably resulting from the presence of flux residue on PCB surface. In the case of DCE with flux, severe corrosion was also observed near to via holes indicating that more flux residue might have trapped in and around via holes. For the DCE system with flux, coating was completely delaminated after immersion in the NaCl solution. It shows that the flux on the surface reduces the adhesion and integrity of the conformal coating, and thereby causes increase in leakage current as the NaCl solution can easily reach the surface of the copper electrodes.

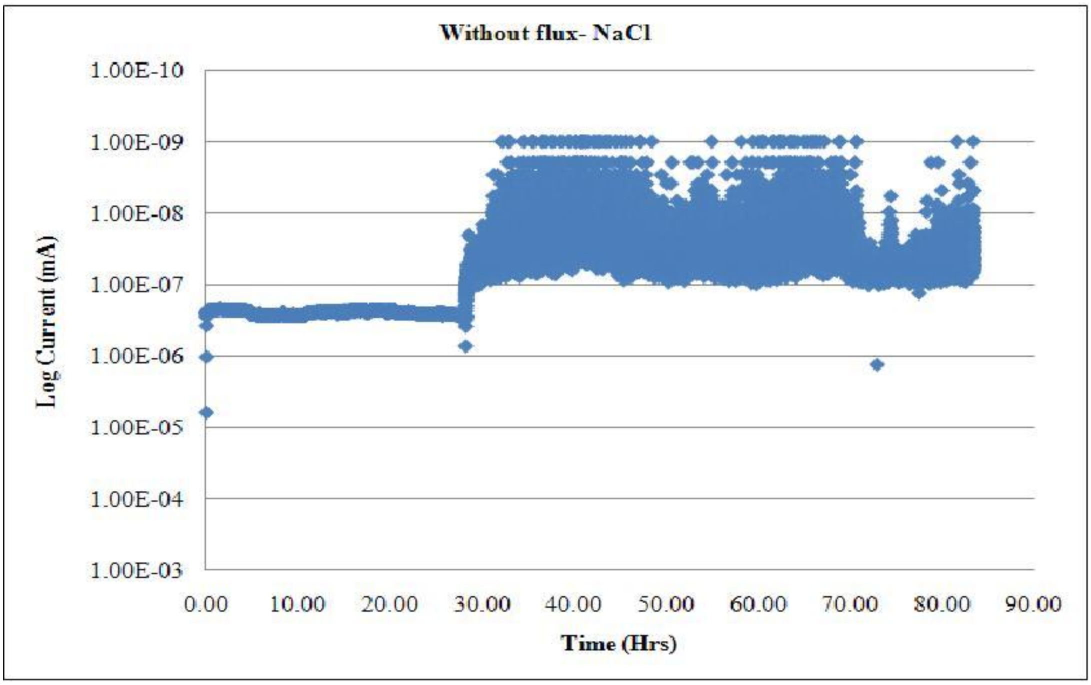

Figure 9(a). Leakage current between the copper electrodes biased with 3V potential and coated with the Acrylic conformal coating and immersed in 10 ppm NaCl.

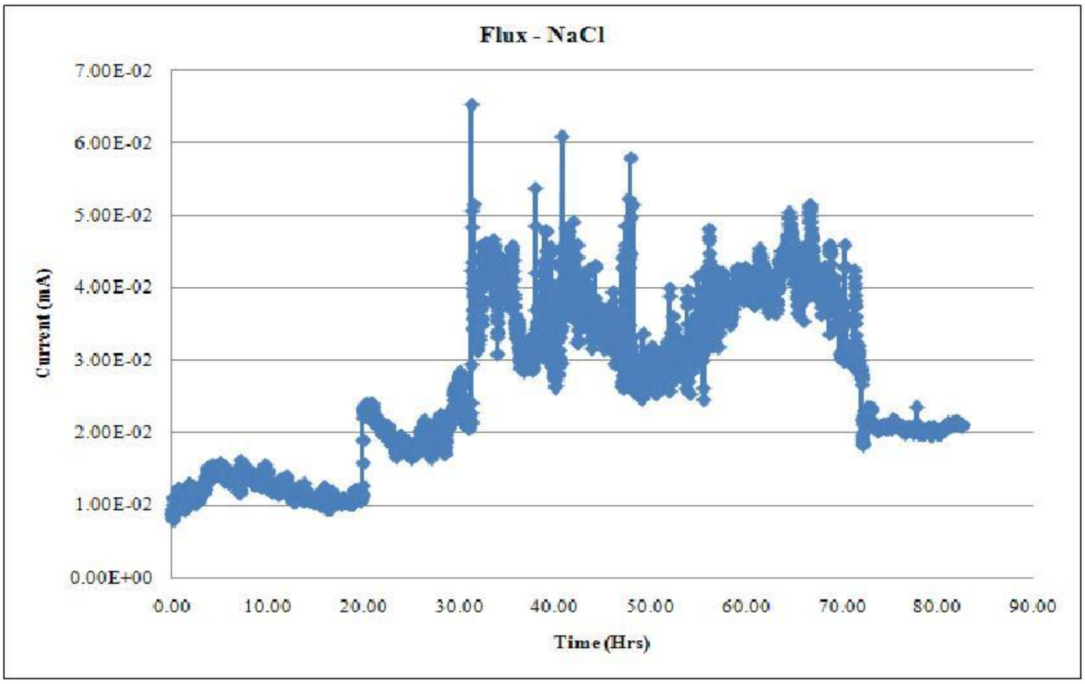

Figure 9(b).Leakage current between the copper electrodes biased with 3V potential, deactivated with flux and coated with the Acrylic conformal coating and immersed in 10 ppm NaCl.

Adhesion measurement

Adhesion measurement of the conformal coating using Instron tensile testing machine using the technique described in section 2.7 shows that maximum load and displacement is lower for one with flux residue. Figure 10 shows adhesion strength measurement for the DCE system with and without flux residue. As expected the adhesion strength of the coating on the PCB with flux contamination is less compared to the adhesion strength of the coating on the clean PCB. The maximum load values and extension are given in table 1. However more statistical data is required to confirm the effect of flux residue. .

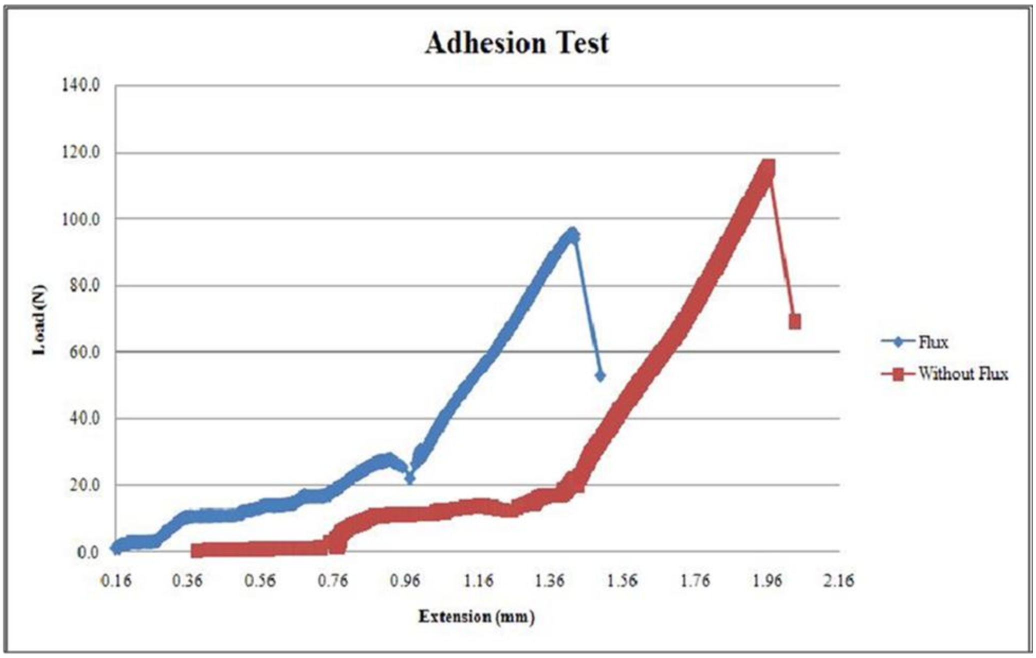

Figure 10.Adhesion strength measurements on Acrylic conformal coating

Table 1: Adhesion strength and extension of the acrylic conformal coating with and without flux on DCE prior to coating.

	Maximum Load (N)	**Extension (mm)**
With flux	95.44	1.24
Clean	115.66	1.56

Conclusion

The influence of flux residues and severe environmental conditions on the performance of the acrylic based conformal coating is the basic idea of this investigation. The coatings are evaluated by measuring the leakage current under exposure to environment and the adhesion strength of the coating. Overall, it was found that the flux residues affect greatly the adhesion of the coating and reduces the surface insulation resistance of the PCBA. The influence of climatic condition of 60°C and 96% of humidity seems to be the same in the case of flux deactivated DCE system and clean system, however, immersion in NaCl solution causes higher leakage current and much reduced adhesion strength for the DCE system with flux deactivated compared to coating on clean PCB.

Acknowledgements

Current research has been conducted as part of the CELCORR consortium. Authors would like to acknowledge the Danish Ministry of Science, Technology and Innovation for the funding of the CELCORR project. Project partners Danfoss A/S, Grundfos A/S, Vestas A/S and PRI-DANA Elektronik A/S, Danish Technological Institute and IPU are acknowledged for their commitment to this project. Pia Wahlberg form the Danish Technological Institute is acknowledged for the FEG-SEM images used in this work.

References:

[1] Permeability properties of plastics and elastomers, by Liesl K.Massey, published by William Andrew, (2003).

[2] http://www.jgpp.com/projects/circuit/documents/ccamtf_jtr_appendix_e.pdf dated 15 June 2009

[3] http://www.defelsko.com/technotes/DollyPreparation.htm dated 15 June 2009

[4]"Conformal coating over existing process residues", Barry Ritchie, www.loctite.com.

[5] P.E.Tegehall and B.D.Dunn, ESA Journal, 16 (1992) p255-p273.

[6] Sheng Zhan and Micheal H.Azarian, IEEE transactions on electronics packaging manufacturing, vol 29(3) (2006) p 217-223.

[7] P.Westermann , "Investigation of process related residues during PCB manufacturing", M.Sc.Thesis, The Technical University of Denmark, Sept (2008).