

## **Decomposition studies of no-clean solder flux systems in connection with corrosion reliability of electronics**

*Hélène Conseil, Morten S. Jellesen, Vadimas Verdingovas, Rajan Ambat*  
*Materials and Surface Engineering, Department of Mechanical Engineering,*  
*Technical University of Denmark*  
*Building 425, Kongens Lyngby, Denmark, [helco@mek.dtu.dk](mailto:helco@mek.dtu.dk)*

### **Summary**

One of the predominant factors for accelerated corrosion in electronics is the intrinsic contamination on Printed Circuit Board Assemblies (PCBAs) originating from the soldering process used for component mounting. However, the amount, distribution, and morphology of flux residue vary considerably with specific soldering process and parameters, while most important factors are the flux chemistry and its decomposition characteristics. Active parts of the flux residue can cause increased water absorption due to their hygroscopic nature and in solution they will increase leakage current and corrosion such as electrochemical migration resulting in intermittent or permanent failures. This paper summarizes the investigations on decomposition of some typical no-clean flux systems (WOA based) which are used today for the electronic manufacturing. The change in flux chemistry was studied as a function of temperature (simulating the manufacturing process) using Differential Scanning Calorimetry (DSC), Ion Chromatography (IC), Fourier Transform Infrared Spectroscopy (FT-IR), and an aggressivity test method using a patented gel method. Effect of flux residue on the corrosion reliability was investigated by exposing the contaminated PCBA parts to varying humidity and measuring the resulting leakage current. Results revealed a significant influence of flux chemistry including the amount of WOAs, while aggressiveness of the residue seems to vary with content and type of WOAs, and their nature of decomposition.

### **1 Introduction**

It is well known that among various solutions, the solderability improvement in PCBA manufacturing can be achieved by appropriate selection of flux types. The main attention is towards the robustness of soldering joints and effective removal of existing oxides on the metal surface to be soldered. Adequate attention is not paid towards the chemical nature of flux types and therefore the potential acceleration of corrosion caused by remaining flux residues [1]. The most commonly used flux systems contain (i) Solvent – a medium for mixing all the components of the flux, often a mix of organic alcohols [2,3], (ii) Activators – mainly weak organic acids, or halogenides, and (iii) Vehicle – a non-volatile compound such as a resin or ester which is stable through all temperatures involved in the soldering process. The activating species have been found to create reliability issues in electronic assemblies [4, 5] especially under humid condition [6]. The assumption behind the process is that the aggressive chemicals used in the flux solution will burn off during the soldering process and only leave a minimum residue of aggressive nature. The

flux systems used today, which are mostly no-clean flux systems, should in principle only leave benign surface contaminants during wave and re-flow soldering processes. However, in practice this seldom happens, and mostly substantial amounts of flux residues including the activator components are found on the PCBA [7, 8]. Also, results show that variation in process conditions like temperature of the PCBA surface during soldering is of great importance and can result in considerable variation in amounts of localized residues [9].

## **2 Materials and method**

### **2.1 Materials and heat treatment**

The activating species, such as adipic, glutaric, succinic, and malic acids have been characterized, after dilution in isopropyl alcohol (5 wt. %). Three typical wave soldering no-clean flux systems, which are used today for electronic manufacturing [10] have been investigated. From the technical datasheet provided by manufacturers, they have been selected in function of their acid type. SFa contains 96-99% of isopropyl alcohol and 1-3% of succinic acid, its acid number is 17.5 mg KOH/g, SFb contains Isopropyl alcohol and adipic acid, its acid number is 14.7 mg KOH/g, and SFc contains 95% of water, and 1-5% of glutaric acid, its acid number is 36.85 mg KOH/g. The pure weak organic acids (WOA) and solder fluxes are analysed after different heat treatments namely: (i) at room temperature (RT), (ii) at  $170 \pm 5$  °C (approx. temperature on top of the PCBA during wave and selective soldering) and (iii)  $250 \pm 5$  °C for 45 s (equivalent to maximum temperature during soldering). The temperature values were chosen as a simulation of a conventional lead-free soldering process. Humidity tests were carried out in a climatic chamber. The PCBAs were exposed to RH from 60% to 100 %, and the temperature was kept constant at 25 °C.

### **2.2 Experimental techniques**

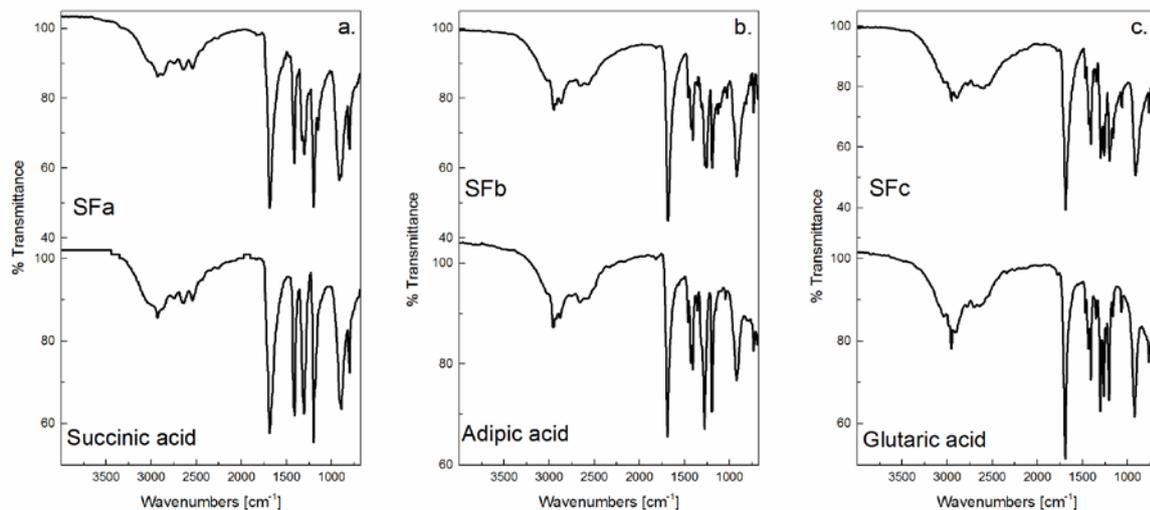
Change in flux chemistry is investigated as a function of temperature using a gel method for revealing active component (patented Residues RAT process from EC-RAT, Denmark), acid value titration, Ion chromatography (IC), and Fourier Transform Infrared Spectroscopy (FT-IR). Thermal decomposition is observed using Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA). The effect of flux residues on the corrosion reliability was investigated by exposing a contaminated Surface Insulation Resistance (SIR) pattern to varying humidity under a bias voltage, and measuring the resulting leakage current.

## **3 Results and Discussion**

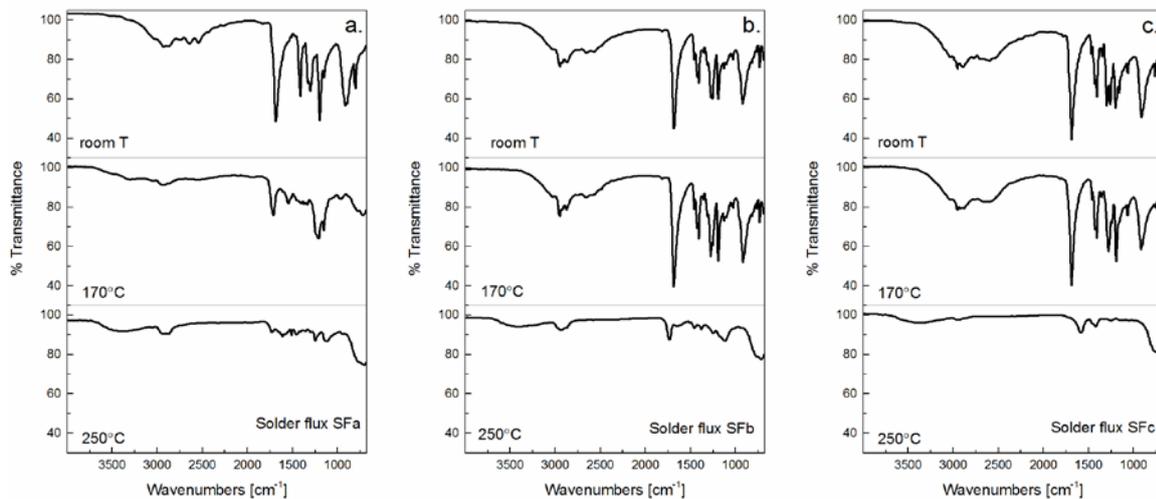
### **3.1 FTIR analysis**

The spectra of fluxes are compared with the spectra of different pure weak organic acids, and it is then possible to determine the type of acid contained in each fluxes. Figure 1 shows that SFa, SFb and SFc spectrum closely match with succinic, adipic

and glutaric acids respectively. Investigation of the chemical change and nature of flux residue as a function of temperature (Figure 2) shows that after heating at 170 °C, no degradation of the fluxes based on adipic and glutaric acid is observed, however we can distinct different changes in the spectrum of the flux based on succinic acid. Heating at 250 °C results in several changes of the FT-IR spectra. The intensities of the CH<sub>3</sub>-stretches have decreased relative to the asymmetric CH<sub>2</sub>-stretch (at ~ 2950 and 2870 cm<sup>-1</sup>), which is still existing and intense. The O-H-stretch absorption from the acid (2750-2550 cm<sup>-1</sup>) also dramatically decreases, and viewed alongside the decrease in the 'acidic' C=O intensity (at 1710 cm<sup>-1</sup>), indicating that a substantial amount of the acid is degraded at this temperature [11].



**Figure 1:** FTIR spectra of a) SFa and succinic acid, b) SFb and adipic acid, c) SFc and glutaric acid

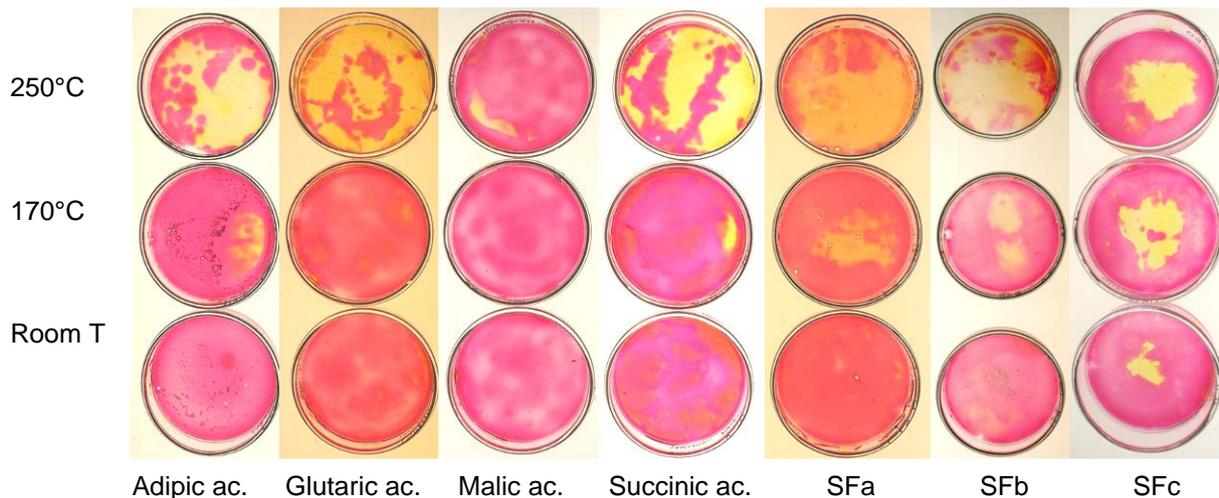


**Figure 2:** FTIR spectra after thermal decomposition of a) SFa, b) SFb and c) SFc

### 3.2 Residues RAT tests

Figure 3 shows images of pure acids and solder flux residue samples heated at different temperatures, after addition of Residues RAT gel. The Residues RAT gel makes use of pH change due to the presence of acid in the flux residue by using an

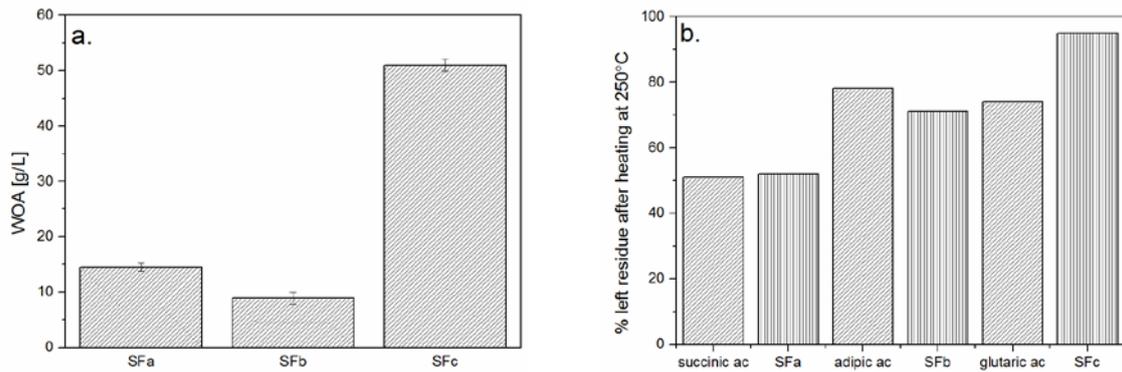
indicator in the gel in an optimized manner [12]. The images show clear red coloration for all the residues evaporated at room temperature. At 170 °C, all of them give more or less same residue levels as at room temperature, showing very little degradation of acid as should be expected. However, after heating at 250 °C, the amount of residues varied depending on the type of acid or flux system. These observations have been confirmed by Ion-Chromatography analysis. In general Malic acid showed more intense colour, while on the flux side SFc with glutaric acid showed more intense colour. Both could be correlated either to the higher amount of residue or more aggressive acid.



**Figure 3:** Residues RAT test images of flux residue after different heat treatments

### 3.3 Ion-Chromatography analysis

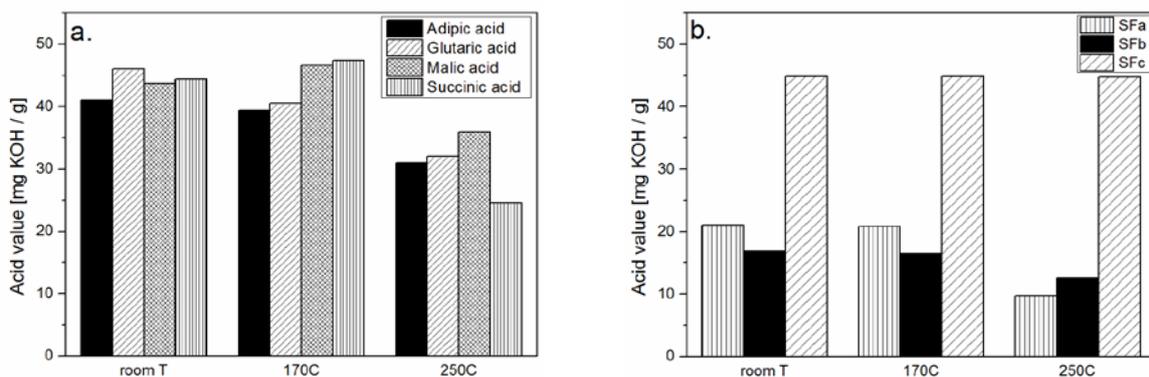
The concentration of WOA in the solder flux residues is shown in figure 4a. We can observe that SFc contains a high amount of WOA, 5 wt. %, SFa and SFb contain 1.4 and 0.8 wt. % of WOA respectively. The results, in figure 4b, show that after heating at 250 °C for 45 seconds, the amount of WOA has decreased to ~50% for the flux based on succinic acid (SFa), to ~25% for the flux based on adipic acid (SFb) and to ~5% for the flux based on glutaric acid (SFc). These results can be correlated with the degradation temperature of the fluxes, measured by DSC. Flux based on adipic acid shows the highest degradation temperature, which is above the solder temperature, and thus SFb is expected to leave a highest amount of residues. The flux based on succinic acid, which shows the lowest degradation temperature, 10 °C below the solder temperature, will leave 50 % of residues. The flux based on glutaric acid, which is water based, shows a different behaviour, the solvent does not evaporate during the time of the soldering (45 sec). These results are also in agreement with TGA results for pure acids showing that above the melting point a progressive evaporation of acid occurs without any decomposition.



**Figure 4:** Ion Chromatography results – a) Concentration of weak organic acid in the solder fluxes at RT and b) % left residues (heated at 250 °C) of the pure acids and the solder fluxes

### 3.4 Acid value determination

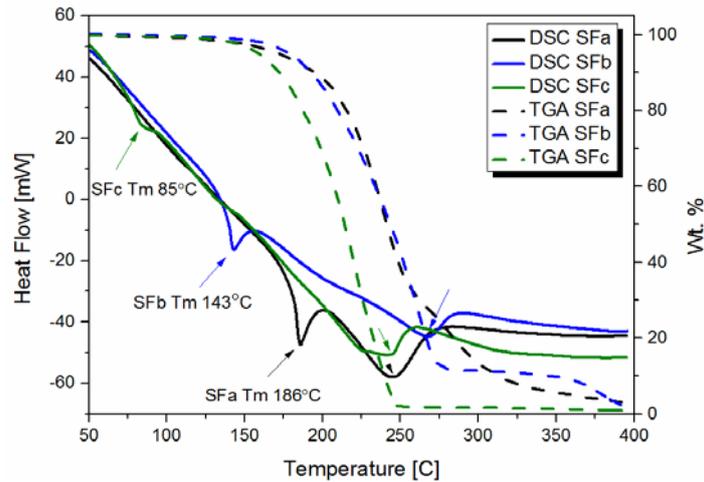
Figure 5 shows the acid value of pure acid and of fluxes after different heat treatments, which are an indication of aggressiveness of the acid residues. It can be observed that all types of acids and flux systems leave significant levels of acids, as shown in figure 4, or decomposition of acids into lower chain acids. However, no evidence for the latter was found in IR spectroscopy.



**Figure 5:** Acid value of a) acid solutions (5 wt. %) and b) solder fluxes after different heat treatment

### 3.5 Thermogravimetric analysis and Differential Scanning Calorimetry

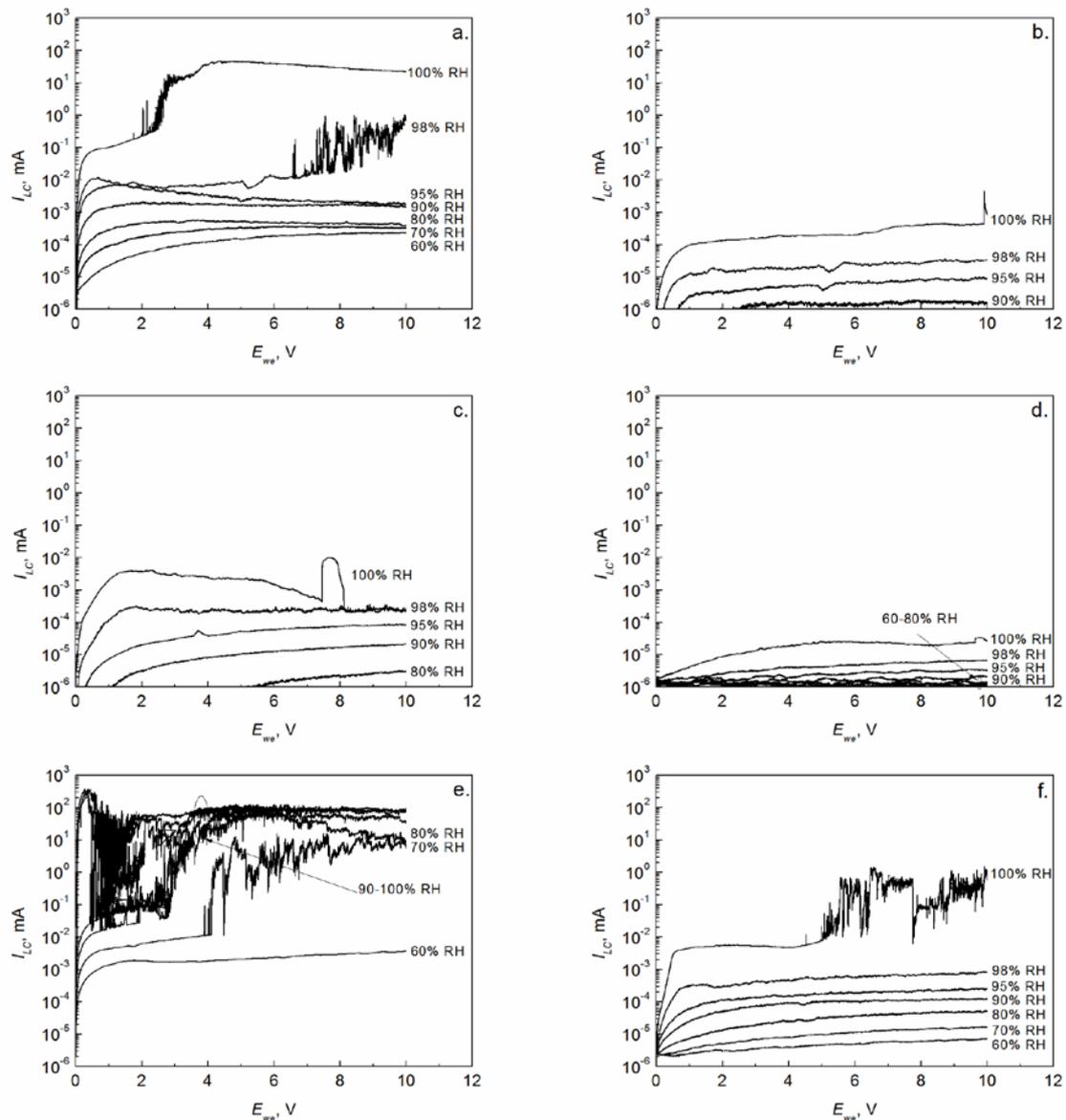
The TGA scans for pure acids [13] (not shown) are essentially smooth curves showing a sudden sharp decrease starting at ~180 °C, and ending with a 0% weight residue at higher temperature, which show that these WOA melt and evaporate without decomposition [14]. The TGA scans for the soldering fluxes shown in figure 6 reveal same type of degradation behaviour showing an evaporative regime, levelling off at a higher temperature with a lower amount of residue given as a weight % of the original sample weight. It corresponds to the resin part, which is decomposed at higher temperature, for the fluxes SFa and SFb. DSC scans show two endothermic peaks. The first one, which does not correspond to any weight loss, corresponds to the melting temperature of the sample. This peak is followed by another peak at higher temperature, which corresponds to a maximum rate of weight loss in the TGA and represents the decomposition temperature of the acids.



**Figure 6:** TGA and DSC curves of a) SFa, b) SFb, and c) SFc, (analysis in alumina crucibles (unsealed), from 30 to 400 °C, at a heating rate of 10 °C/min)

### 3.6 SIR leakage current results

Figure 7 represents the leakage current dependency of bias voltage obtained on SIR patterns pre-contaminated with a certain volume of solder flux. The potential bias on the SIR patterns was applied at 2 mV/s sweep rate, and increased from 0 V to 10 V. The relative humidity increased from 60 % to 100%, while the temperature was kept constant. With increasing relative humidity, the water layer on the PCBA surface increases and it is reflected as a leakage current increase. The leakage current increased tremendously for the fluxes based on succinic and glutaric acids (Fig 7 a-e), to a level of 100 mA. However, the leakage current of SFa after heating decreased considerably, below the level of  $\mu\text{A}$  (Fig 7 b). The leakage currents of SFc were still very high after heating (10 mA at 10 V and 100% RH) (Fig 7 f). SFb seemed to be the least aggressive residue, with a leakage current of 0.1  $\mu\text{A}$  at 10 V and 100%RH, at room temperature and after heating (Fig 7 a-b). The flux system SFc showed electrochemical migration (ECM) at high humidity both for RT and high temperature residue, while SFa showed migration only for RT residue. This is indicated by the sudden increase in current at higher humidity levels and potential values. This effect can be directly correlated to the presence of more aggressive acid in the flux system especially for SFc due to the presence of glutaric acid. The leakage current over the SIR pattern from pure acids and solder flux based on the same acid behave the same way, both at room temperature and after heating [13] (leakage current results for pure acids are not shown).



**Figure 7:** Representative leakage current dependency of bias voltage and relative humidity at 25 °C of SFa a) evaporated at RT and b) heated at 250 °C, SFb c) evaporated at RT and d) heated at 250 °C, and SFC e) evaporated at RT and f) heated at 250 °C

## 4 Conclusions

1. Residues RAT testing, acid value determination, and ion chromatography results showed that the amount of acid residue or flux residue left and its aggressiveness is a function of acid type and temperature.
2. Results showed that no significant decomposition of fluxes and acids takes place within the temperature regime of soldering process, which is also confirmed by IR spectroscopy showing solely the original acid in the residue.
3. TGA and DSC results showed only an evaporation regime indicating that above the melting point and until peak temperature of soldering process (~250 °C) only evaporation takes place without significant levels decomposition. For

flux system, the major evaporation is expected to be due to the low vapour pressure solvent leaving higher amounts of aggressive residues.

- Humidity testing showed that the level of leakage current and ECM depends on the type of flux system, implying the type of acid. Glutaric based flux showed higher levels of leakage current and ECM.

## 5 Acknowledgments

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