Impact of hygroscopicity and composition of solder flux residue on the reliability of PCBA under corrosive conditions

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Summary

This paper provides an overview of the studies on the effect of solder flux chemistry on the surface insulation resistance due to its interaction with humidity. Hygroscopicity of contaminant, conductivity of electrolyte layer formed, and the leakage current under DC bias on the printed circuit board assembly (PCBA) was investigated for 5 weak organic acids usually found in flux systems namely: adipic, succinic, malic, glutaric, and palmitic. Additionally 5 no-clean wave and selective soldering fluxes were also investigated. The results showed difference in the climatic behaviour of the solder flux in connection with leakage current and corrosion, which is attributed to the properties of the weak organic acids in the flux. The results showed possibility of ranking the flux types based on the properties of the weak organic acids.

1 Introduction

The composition of solder flux applied during the PCBA manufacturing has a direct impact on the corrosion reliability of electronic device. Fluxes are usually composed of inorganic salts and/or acids, which provide oxide removal of the base metal upon application of solder, therefore flux remaining on the base metal is corrosive. In addition to that, it is usually hygroscopic and able to form electrolyte on a surface of printed circuit board assemblies. Thus most issues related to the solder flux originate in presence of high humidity in the atmosphere [1], [2]. An important aspect in relation to the functioning of the electronic device under high humidity is the reduction in surface insulation resistance [2–4].

The results from different testing of flux systems and weak organic acids (WOAs) used in the flux can be found in the literature A number of investigations have been reported on the effects of flux residues on the leakage current and corrosion as a function of humidity, temperature, flux type and its concentrations [2–8]. It is also shown that the soldering process and temperature has an effect on flux residue formation and thereby surface insulation resistance (SIR) [9]. Particular standards provide different test methods and climatic conditions for characterization of flux residue, however the comparison between the behaviour of the flux and constituent WOAs in the flux, and their effect on the reliability of the PCBA under high humidity conditions has not yet been reported.

The aim of the current study is to investigate the effects of different weak organic acids in the flux on the surface insulation resistance and herewith related issues under different humidity conditions, and compare the results with behaviour of actual flux.

2 Experimental

2.1 Test boards

The leakage current measurements were performed on the board having SIR (surface insulation resistance) comb pattern with air solder leveled (HASL) finish (Sn/Ag/Cu solder alloy), and dimensions of 13 x 25 mm, and pitch and spacing size of 0.3 mm. Detailed description of the test PCBA can be found elsewhere [10].
The test board for impedance measurement was a FR-4 laminate with two opposing conducting lines having width of 0.66 mm and the length of 5.8 mm, and the distance between the lines 1.3 mm. Base material of the conducting lines was copper, and on top of copper there was and intermediate layer of nickel 9±1 µm, and top layer of gold 6.5 ±1 µm.

2.2 Soldering flux

Table 1 contains summary of no-clean wave and selective soldering fluxes used for the investigation. The fluxes were selected for varying type of weak organic acid, acid number and solid content. All the flux types except of SF-5 were alcohol based. The ranking of the flux according to IPC J-STD-004 standard can be also seen in the table.

Table 1: No-clean wave soldering flux

ID	Solvent	IPC J-STD-004 Designation*	Acid number, mg KOH/g	Solid content, % wt/wt	Constituent acid (IC and FT-IR)
SF-1	VOC	ORL0	17.5	2.2	Succinic
SF-2	VOC	ORL0	26	4	Adipic and succinic
SF-3	VOC	REL0	15.8	2.2	Adipic
SF-4	VOC	ROL0	18.3	2.8	Palmitic
SF-5	Water	ORM0	36.85	4	Glutaric

*First two letters specify the film-former type: RO-rosin, RE-resin, OR-organic; third letter specifies the level of activator in the flux: L-low, M-medium; and the last number specifies halides content: 0-(<0.05 % wt/wt), 1-(>0.5%-2% wt/wt).

The composition of the flux is confidential and not provided by the manufacturer. The constituent acids given in the table were identified by ion chromatography and FT-IR microscopy.

2.3 Weak organic acids

Summary of physical properties of WOAs commonly used in the solder flux is shown in Table 2. One of the important parameters describing the WOAs is the dissociation rate, which is described as the ratio of the concentrations of the dissociated ions and the un-dissociated molecules. The negative of the logarithm of the acid dissociation constant (pKa) for the 1st and 2nd dissociation constants is given in Table 2. The larger the value of pKa, the smaller is the extent of dissociation and the lower the conductivity.

Table 2: Physical properties of WOAs [11]

Acid	pKa1	pKa2	Melting point, °C	Solubility in water at 20 °C, g/l
Adipic	$4.41_{18°C}$	$5.41_{18°C}$	151.5	$15_{15°C}$
Succinic	$4.21_{25°C}$	$5.64_{25°C}$	185	$83.5_{25°C}$
Glutaric	$4.32_{18°C}$	$5.42_{25°C}$	97.9	$1400_{25°C}$
Malic	$3.40_{25°C}$	$5.11_{25°C}$	132	$1440_{26°C}$
Palmitic	4.78		62.5	$0.00072_{20°C}$

Melting point temperature of the WOA is important because the no-clean flux is supposed to degrade during exposure to soldering temperature, and the remaining residue of no-clean flux has to be benign. Whereas solubility of WOA determines the amount of the acid which can be dissolved in water and it is important when the PCBA is exposed to humid conditions.

2.4 Quartz crystal microbalance

Quartz crystal microbalance (QCM) was used to determine the hygroscopicity of contaminants. QCM is a piezoelectric crystal with a resonant frequency, which enables to determine extremely small changes of mass loading on the crystal. The quantitative relationship between the change in frequency of piezoelectric crystal and a change in mass caused by the mass loading on a piezoelectric crystal surface was first derived by Sauerbrey [12]:

$$\Delta f = \left(\frac{-2 f_0^2}{A\left(\mu_q \rho_q\right)^{1/2}} \right) \Delta m = -C_f \Delta m \quad (1)$$

where f_0 (Hz) is a resonant frequency of the crystal; μ_q (g cm^{-1} s^{-2}) is shear modulus of quartz; ρ_q (g cm^{-3}) is density of quartz; A (cm^2) is surface area of the electrode; Δm (g) is the change in mass on the crystal. Sensitivity factor C_f for the crystal used in this work at room temperature was 56.6 Hz µg^{-1} cm^2, and the resonant frequency was 5 MHz.

Hygroscopicity of flux and WOAs was determined by putting 1.4 µL droplet of solution at concentration 1 g/L on the active gold electrode of the crystal, letting solvent to evaporate and exposing the crystal to elevated humidity inside the climatic chamber. The relative humidity (RH) was ramped from 20 % to 98 % at 25°C during 8 hours interval and elevated from 60 % to 100 % at 25°C in steps of 10 %. The increase of the mass on the crystal was associated to water adsorption to the surface of the crystal and the residue initially applied on the crystal. Abrupt change of the mass on the crystal was attributed to critical RH value of the substance on the crystal.

2.5 Leakage current measurement

During this test the leakage current was measured on standardized SIR pattern exposed to elevated humidity inside the climatic chamber. The SIR patterns were pre-contaminated with WOAs at a concentration of 100 µg cm^{-2}, and similar concentrations of solid flux residue were obtained. The current was measured as a function of applied potential, which was scanned from 0 V to 10 V at 2 mV/s sweep rate. The humidity inside the climatic chamber was elevated from 60 % RH to 100 % RH, in steps of 10 %, while the temperature was fixed at 25 °C. After every increase in humidity, the samples were left to equilibrate with environment for 2 hours, and thereafter the potential sweep measurement was performed. Leakage current measurements were performed at 60, 70, 80, 90, 95, 98, and 100 % RH at 25 °C.

2.6 Impedance spectroscopy

Impedance measurement was made using a “BioLogic VSP” multichannel potentiostat, Bio-Logic Instruments, France, with compliance voltage limits of ±10 V and 1 nA resolution connected in two-electrode cell configuration. The measurement was performed with AC signal with amplitude of 50 mV (Vrms ~35.36 mV) in frequency range from 10 mHz to 100 kHz. The average of 5 measures per frequency was recorded. Impedance and phase angle measurements were generated at the open-circuit potential. Impedance spectroscopy measurements were performed simultaneously with potential sweep leakage current measurements under the same climatic conditions.

3 Results

3.1 Hygroscopicity of contaminants

The WOAs and flux was applied on the active electrode of piezoelectric quartz crystal and exposed to two humidity conditions described earlier. The critical RH for WOAs and flux was determined from the mass change on the crystal. The summary of the results is given in Table 3. The first column of critical RH for WOAs contains data reported in literature [13].

Table 3: Hygroscopicity of WOAs and flux residue

WOAs				Solder flux	
	c.RH[13], %	$c.RH_{QCM}$, %			$c.RH_{QCM}$, %
Adipic	99.6	>98		$SF1_{(succinic)}$	98
Succinic	98	>98		$SF2_{(adipic\ and\ succinic)}$	96-100
Glutaric	84	83-89		$SF3_{(adipic)}$	99
Malic	86	75-84		$SF4_{(palmitic)}$	99-100
Palmitic	-	-		$SF\text{-}5_{(glutaric)}$	70-80

Prior and after the QCM measurement, the pictures of residues on the quartz crystal were taken. The images of quartz crystal pre-contaminated with 4 WOAs before and after exposure to relative humidity from 20 % to 98 % are shown in Figure 1.

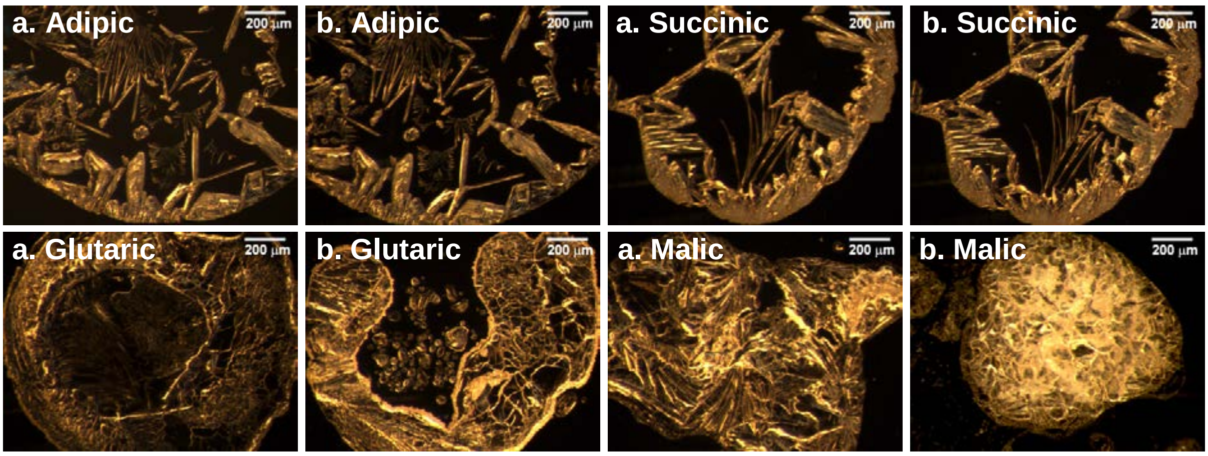
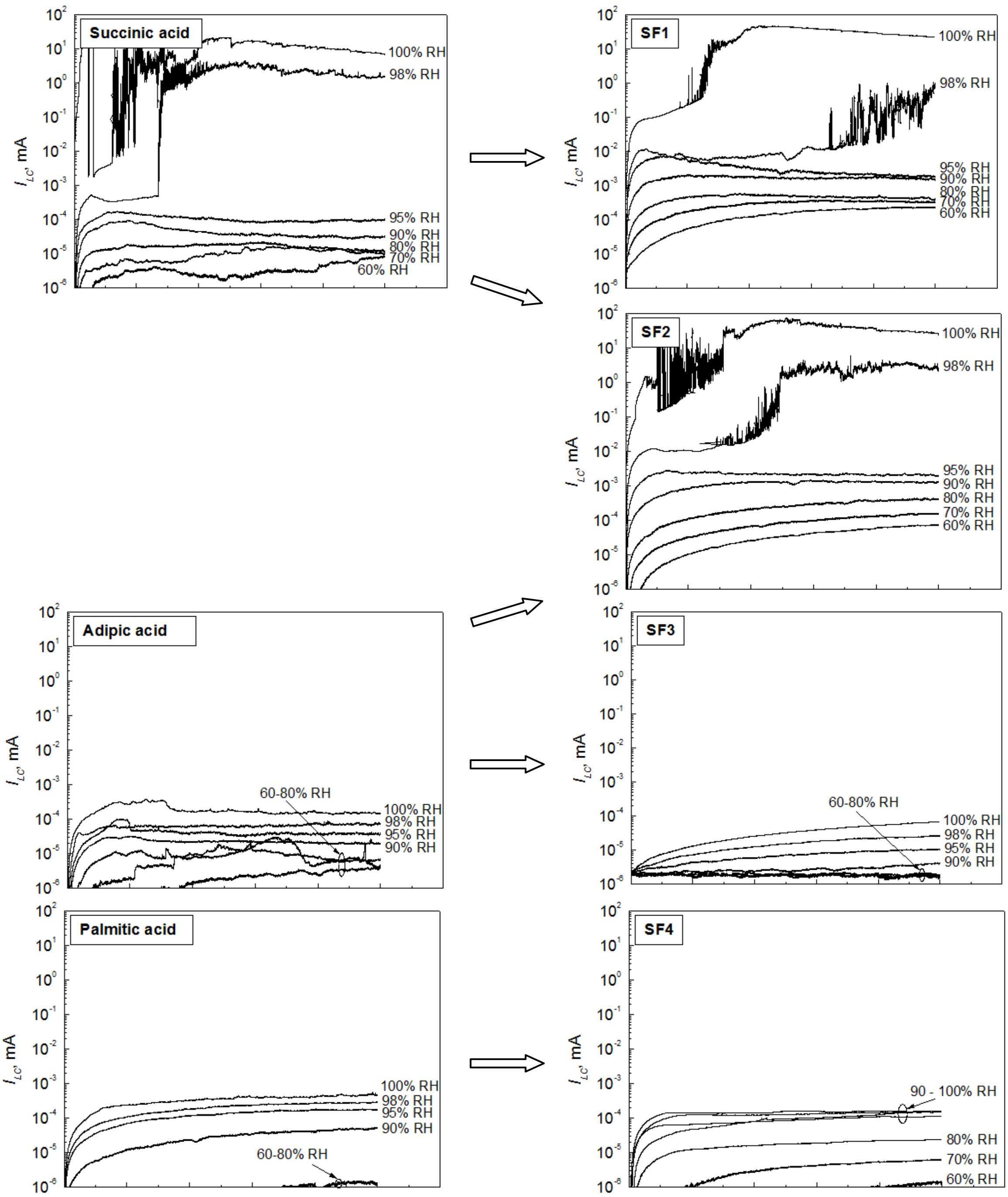


Figure 1: The images taken **a.** before and **b.** after the exposure to 98 % RH at 25 °C

The unchanged appearance of adipic and succinic acids indicated that 98 % RH at 25 °C was not enough to dissolve the acid into the water layer forming on a surface. However the changed appearance of glutaric and malic acids after exposure to 98 % RH at 25 °C indicated lower critical RH for those acids. The appearance of other residue including WOA and flux before and after the experiment was in agreement with the results from QCM.

3.2 Potential sweep leakage current

Leakage current measured on SIR pattern as a function of applied potential under RH levels from 60 % to 100 % at 25 °C is shown in Figure 2. Left side graphs show the curves for pure acids, while the set of graphs in the right side shows flux types with corresponding acids or mixture of acids. The current in the range of mA is attributed to short circuiting due to formation of tin dendrites and corrosion product bridging oppositely biased electrodes of SIR pattern. Whereas the current levels in the range of µA are indicating only the leakage due to the presence of conductive species on the SIR pattern; the magnitude of current also represents the corrosion rate of the SIR pattern.



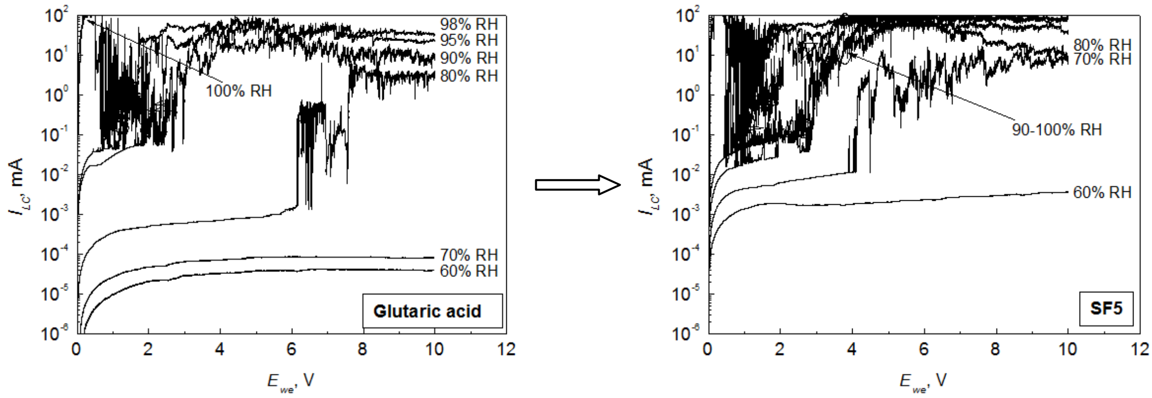


Figure 2: Potential sweep leakage current measurement on SIR pattern pre-contaminated with WOAs and flux at equivalent concentrations of 100 µg cm^{-2}

Succinic acid at concentration of 100 µg cm^{-2} on the SIR pattern exhibited dendrite formation at 98 % RH. Similar behavior was observed on the SIR pattern pre-contaminated with succinic acid containing flux. Adipic and palmitic acids showed to be less aggressive under test conditions used in this study. No short circuiting due to dendrite formation or corrosion was observed on these samples within the time of exposure to test conditions. Glutaric acid showed to be most aggressive, and started causing leakage current in the level of mA at 80% RH. Very similar behavior was observed for glutaric acid containing flux.

3.3 Impedance measurement

The impedance measurement on test board having two gold electrodes was performer under relative humidity levels from 60 % to 100 % at 25 °C. The representative graphs for succinic acid and SF-1 flux at 95, 98 and 100 % RH are shown in Figure 3.

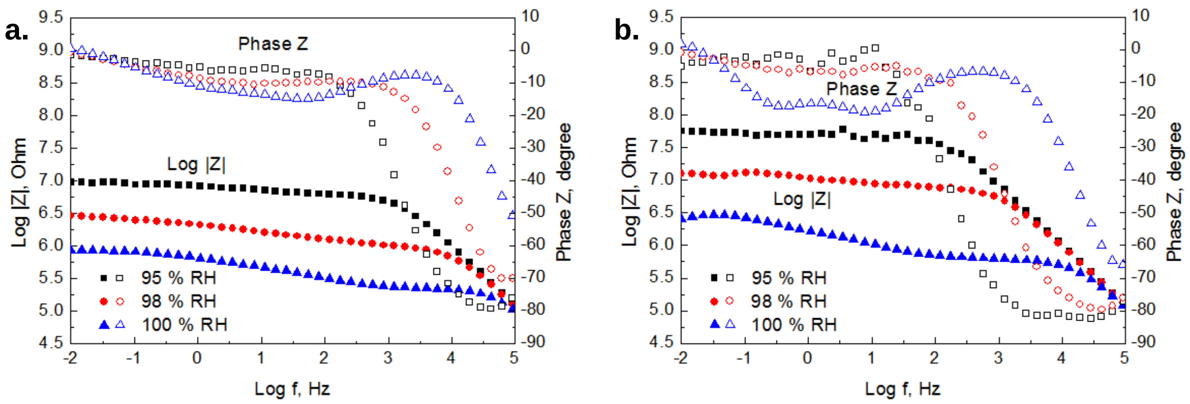


Figure 3: Representative Bode plots from impedance measurement between two gold electrodes: **a.** succinic acid; **b.** succinic acid containing flux SF-1

Impedance spectra enabled to characterize the conduction mechanism in the adsorbed electrolyte layers on the printed circuit board; however most important parameter for this analysis was the resistance of electrolyte layer between the two electrodes, since it determines leakage currents on the PCBAs. The latter parameter was dominant at low frequency domain. As it can be seen from the impedance values at 10 mHz in Figure 3, an increase of RH from 95 % to 100 % was followed by decrease of the resistance of electrolyte from 9.5 MOhm to 0.85 MOhm for succinic acid, and from 56 MOhm to 2.5 MOhm for SF-1 solder flux. The summary of the resistance of electrolyte for different humidity levels is given in Figure 4.

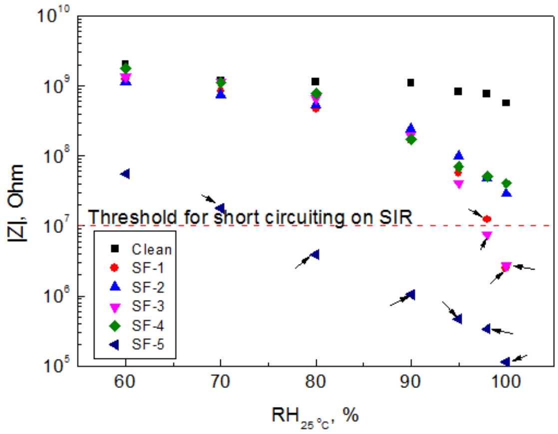


Figure 4: Resistance of electrolyte layer between two gold electrodes for different flux

The arrows in the graph indicate the condition when the short circuiting due to dendrites or corrosion product on the SIR pattern during the leakage current measurement was observed. The following relation between impedance measurement and leakage current measurement was seen: when the resistance of the electrolyte between two gold electrodes was dropping below approximately 100 MOhm, the dendrites formation on the SIR pattern was found. Thus 100 MOhm is marked as an approximate threshold for dendrite growth in Figure 4.

4 Discussion

Succinic acid has lower critical RH than adipic, is more soluble and has higher dissociation rate. Therefore it can be expected that the residue of succinic acid is more critical to be present on the PCBAs compared to adipic acid. The same behavior was observed during climatic testing conducted in this work. Succinic acid and succinic acid containing flux caused higher leakage current, and caused electrochemical migration and dendrite formation at 98 % RH, whereas adipic acid caused only a steady increase of leakage current with increase of humidity, and no dendrites were formed.
The behavior of palimitic acid was similar to that of adipic. It was giving comparable levels of leakage current, and no dendrites were observed within the time of exposure to test condition. Palmitic acid has very low dissociation rate and solubility in water, therefore this acid is not as critical as succinic or glutaric.
Glutaric acid has much lower critical RH for moisture condensation, and has high solubility in water. This resulted in significant increase of leakage current at lower humidity levels. The short circuiting due to dendrites formation was observed at 80 % RH for glutaric acid, and at 70 % RH for glutaric acid containing flux. The residues of this acid appeared to be the most critical among the acids tested in this work.

5 Conclusions

The results of flux residue investigations showed a different behaviour depending on the type of WOA in the flux. Under low humidity conditions the difference is mainly attributed to hygroscopic nature of constituent components of the flux. However, at high humidity and condensing conditions, the ionic conductivity and aggressiveness of electrolyte layer formed become the factors for consideration. Correlation between hygroscopicity of solder flux residue and hygroscopicity of the WOA in the flux was observed. The short circuiting due to dendrite formation was likely to occur at humidity levels higher than critical for moisture condensation. Analysis of the climatic behaviour of weak organic acids can be used for predicting the effect of flux residue on surface insulation resistance and herewith corrosion reliability of PCBA.

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7 References

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