Water film formation on PCBA surface
Investigation of aspects contributing to premature corrosion failures and safety measures for electronics reliability improvement

Kamila Piotrowska
June 2018

PhD Thesis

\[(EIV')' = q - \rho A \dot{v}\]

\[\sum \chi^2 = \left\{2.71\right\}\]
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"The miniaturization of electronics, which ultimately was driven by the marketplace, was started by NASA, because it costs money to get something into orbit. So you want to trim your electronics, miniaturize your electronics, miniaturize your satellites."

"Miniaturization of electronics started by NASA’s push became an entire consumer products industry. Now we’re carrying the complete works of Beethoven on a lapel pin listening to it in headphones."

Neil deGrasse Tyson
This thesis is dedicated to my parents
PREFACE

This thesis is submitted in candidacy for a PhD degree from the Technical University of Denmark. The project entitled “Water film formation on PCBA surface: Investigation of aspects contributing to premature corrosion failures and safety measures for electronics reliability improvement” was carried out at the Department of Mechanical Engineering, Section of Materials and Surface Engineering, under the supervision of Professor Rajan Ambat and Senior Researcher Morten Stendahl Jellesen. The PhD project is a part of the CreCon (Consortium for Climatically Reliable Electronics) industrial consortium under CELCORR (Centre for Electronic Corrosion, www.celcorr.com), and IN-SPE (Innovation Consortium for Sustainable Performance in Electronics) supported by the Innovation Fund Denmark. The duration of the PhD programme was October 2014 – June 2018.

During the time period May 2017 – December 2017, additional investigation was carried out as part of an external project in collaboration between CreCon and Robert Bosch GmbH (Automotive Electronics), apart from the PhD project.
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I am also indebted to all my colleagues from the section of Materials and Surface Engineering, especially Marianne Buendia, Ewa Adamsen, Gitte Salomon, Flemming Bjerg Grumsen, Lars Pedersen, and Rolf Jensen. Special thanks to the fellow PhD students and CELCORR team for countless hours of discussions, for their help, and for all the fun we had "after hours".

Privately, I am grateful and blessed to be surrounded by amazing people, many of whom I can call my close friends. You kept me sane and going throughout all these years. Thank you for all the knowledge, love, and fun you enrich my life with.

Last but not least, I express my deepest appreciation to my family for their unconditional love, support, and encouragement.
ABSTRACT

This PhD work was supported by the Innovation Fund Denmark through the IN-SPE (Innovation Consortium for Sustained Performance of Electronics) and by CELCORR (Centre for Electronic Corrosion) through the CreCon (Consortium for Climatically Reliable Electronics). The project is motivated by the climatic reliability issues that are faced by the electronics industry, which are related to the intermittent and permanent corrosion failures induced by the water layer formation on the PCBA surfaces. The demand for deep understanding of the water film build-up phenomenon on the electronic surfaces led to the investigations of synergistic effects of the related factors such as: materials' characteristics, manufacturing/process effects, process cleanliness, PCBA design, potential bias, and climatic variations such as changes in humidity and temperature. The assessment of the impact of these parameters was performed under accelerated testing (condensing conditions) and under the conditions relevant for the electronics operation, while also simulating the geographical changes in climate parameters worldwide. Number of material characterization and electrochemical testing methods were used for understanding the relationships between various parameters in determining the water film build-up on electronic surfaces and associated failures on a PCBA surface.

Chapter 1 provides an introduction to the climatic reliability issues and a motivation of the current PhD project. Chapter 2 reviews various factors influencing the water layer formation on the PCBA surface (e.g. humidity, surface characteristics, ionic contamination, temperature etc.) and the effect on corrosion reliability. Additionally, common failure mechanisms related to the mentioned factors are described together with the climatic reliability test methods. Chapter 3 summarizes the literature review and the objectives of this PhD project. Chapter 4 summarizes the materials and test methods employed in this thesis. The results of investigations are presented in the form of individual research papers published in peer reviewed journals or in the form of draft intended for publication in the journals. Chapter 5 contains a summary highlighting the objectives and conclusions of each paper.

The research results are summarized in 7 papers constituting chapters 6-12. Paper 1 (chapter 6) investigates the chemistry and morphology effect of the PCBA surface on the water film formation. Papers 2 and 3 (chapters 7 and 8) focus on the thermal decomposition of no-clean solder flux residues under simulated soldering conditions and related reliability issues. Papers 4-6 (chapters 9-11) investigate the interactions between no-clean solder flux residues and humidity under various temperature conditions, and the effects on the electrical performance and corrosion occurrence. Paper 7 (chapter 12) presents the effect of PCBA cleanliness under isothermal and non-isothermal conditions developed between the PCBA surface and outdoor, as well as under typical climatic profiles, and the related failure occurrence in electronics. Finally, chapters 13-15 provide the overall discussion, conclusion, and suggestions for future work.

Overall, the investigations showed the importance of PCBA laminate/solder mask surface chemistry and topography on the water film build-up and related failure occurrence due to the electrochemical process that may occur under humid and condensing conditions. Results show that with an optimized materials properties and surface characteristics, an extension of time-to-failure might be obtained upon the device exposure to transient condensing conditions.

The presence of ionic post-production contamination on the PCBA surface is often inevitable due to the thermal characteristics of a conventional wave soldering process and the use of no-clean flux technology. The acidic activators used commonly in the flux formulations do not decompose easily under the soldering conditions and often remain on the PCBA surface after the manufacturing process in the form of acids or anhydrites, highly susceptible to interact with moisture. The process-related
residues reduce the upper humidity boundary for water film formation on the PCBA surface and enhance the moisture adsorption processes. The contamination effect is more pronounced if the residues comprise of hygroscopic species or mixtures of contaminants, and under high temperatures, where the water film thickness is higher and favours the significant SIR reduction and the electrochemical migration. The types and importance of flux chemistries are investigated in detail, which shows the importance of activator chemistry in the no-clean flux system in determining the final residue compositions after the thermal treatments, its amount, and humidity-related corrosion failures in electronics.

The electrical properties of the water layer formed under transient conditions originate from the characteristics of the conductor bridging and electrochemical process at the electrodes (faradaic reactions and ion transport through the water layer), which were studied in detail in chapter 12. The extent of water film build-up is strongly dependent on the ambient humidity level, differential temperatures between ambient and PCBA surface, rate of the temperature change, cleanliness of the PCBA, and the PCBA design and enclosure characteristics. Even under potentially non-condensing conditions, the formation of a significant amount of water film can occur if highly hygroscopic residue remains on the PCBA surface due to the altered (reduced) humidity threshold for failures. The extent of water layer build-up is dictated by the ionic nature of the residues. Under condensing conditions, the presence of highly hygroscopic flux residues accelerate the formation of a continuous water layer and conductor bridging, leading to the risk of failure occurrence. The presence of thermal mass attached to the PCBA enhances the local moisture condensation and prolongs the wetting time of electronics, and this effect is further enhanced if hygroscopic residues remain on the PCBA surface.
DANSK RESUMÉ


Samlet set viste undersøgelserne vigtigheden af PCBA og laminat/loddemaske overfladekemi og topografi, når det kommer til opbygningen af vandfilm og relaterede funktionssvigt grundet den elektrokemiske proces der kan forekomme under fugtige og kondenserende forhold. Disse resultater viser hvordan tiden før funktionssvigt af en enhed udsat for transient kondenserende forhold kan forlænges ved optimering af materialeegenskaber og overfladekarakteristika.

Tilstedeværelsen af forurening i form af ioner på printkort-overfladen efter endt produktion er ofte uundgåelig som følge af de termiske karakteristika ved en konventionel proces og brugen af "no-clean" flus teknologi. De sure aktivatorer, der ofte anvendes i formuleringen af flus, har svært ved at dekomponere under de forhold der er ved lodning. Derfor forbliver disse også ofte på printkort-overfladen efter endt produktion, som syrer eller anhydrider, og reagerer let med fugt i omgivelserne. De procesrelaterede urenheder reducerer den øvre fugtighedsgrænse for dannelsen af vandfilm på printkort og øger vandadsorptionen. Effekten af kontamineringen er mere udtalt hvis urenhederne

LIST OF ABBREVIATIONS

AC – Alternating Current
ATR – Attenuated Total Reflection
a_w – water activity
BAM – Brewster Angle Microscopy
BET – Brunauer-Emmett-Teller
BSE – Backscattered Electron
CAF – Conductive Anodic Filament
CD – Circular Dichroism
CTE – Thermal Expansion Coefficient
DC – Direct Current
DP – Dew Point
DSC – Differential Scanning Calorimetry
ECM – Electrochemical Migration
EDS – Energy Dispersive X-ray Spectroscopy
EIS – Electrochemical Impedance Spectroscopy
FTIR – Fourier Transform Infrared
FR – Fire Retardant
GAB – Guggenheim-Anderson-de Boer
HASL – Hot Air Solder Leveling
IP – Ingress Protection
IPC – Association Connecting Electronics Industries
IR – Infrared
MCT – Mercury Cadmium Telluride
PCB – Printed Circuit Board
PCBA – Printed Circuit Board Assembly
PTH – Plated-Through Hole
QCM – Quartz Crystal Microbalance
RH – Relative Humidity
SE – Secondary Electron
SEM – Scanning Electron Microscopy
SIR – Surface Insulation Resistance
SM – Solder Mask
SMT – Surface Mount Technology
SPR – Surface Plasmon Resonance
Tg – Glass transition temperature
TGA – Thermogravimetric analysis
TH – Through-hole
THB – Temperature-Humidity-Bias
TOW – Time of Wetness
VOC – Volatile Organic Compound
WOA – Weak Organic Acid
XRD – X-Ray Diffraction
LIST OF PUBLICATIONS

LIST OF APPENDED JOURNAL PAPERS THAT CONSTITUTE THE INVESTIGATIONS IN THIS THESIS


OTHER CONTRIBUTIONS PUBLISHED DURING THE COURSE OF THE PHD PROJECT THAT DO NOT CONSTITUTE A PART OF THIS THESIS

JOURNAL ARTICLES


CONFERENCE PROCEEDINGS


Table of contents

1. Introduction ............................................................................................................................................. 1
   1.1. Background ........................................................................................................................................ 1
   1.2. Motivation and scope of the thesis ................................................................................................. 4
   1.3. Structure of the thesis ......................................................................................................................... 4

2. Water film formation on the PCBA surface .......................................................................................... 7
   2.1. Humidity ............................................................................................................................................. 7
       2.1.1. Characteristics of moisture ........................................................................................................ 7
       2.1.2. Interactions of humidity with electronics .................................................................................... 9
       2.1.3. Water layer formation on the clean PCBA surface ..................................................................... 10
       2.1.4. Absorption of moisture by electronic materials ......................................................................... 15
   2.2. Effect of PCBA surface morphology ............................................................................................... 17
   2.3. Effect of PCBA cleanliness ............................................................................................................... 20
       2.3.1. Solder flux residues .................................................................................................................... 21
       2.3.2. Atmospheric contamination ...................................................................................................... 28
       2.3.3. Interaction of moisture with hygroscopic contamination ....................................................... 31
   2.4. Effect of climatic conditions ........................................................................................................... 42
   2.5. Effect of enclosure design ............................................................................................................... 44
   2.6. Climate and contamination induced failures in electronics .......................................................... 45
       2.6.1. Degradation of surface insulation resistance (SIR) and high current leak ............................ 45
       2.6.2. DC Electrochemical migration (ECM) and dendrite formation ............................................. 46
       2.6.3. AC Electrochemical migration (ECM) and dendrite formation ............................................. 49
       2.6.4. Conductive anodic filament (CAF) formation .......................................................................... 50
       2.6.5. Polymer degradation ................................................................................................................ 51
       2.6.6. Galvanic corrosion ..................................................................................................................... 54
   2.7. Climatic reliability testing ................................................................................................................. 55
       2.7.1. Surface Insulation Resistance (SIR) testing ............................................................................ 55
       2.7.2. Electrochemical Impedance Spectroscopy (EIS) testing ......................................................... 57

3. Summary of the project and literature review ....................................................................................... 61

4. Materials and experimental methods ..................................................................................................... 75
   4.1. Electronic materials ......................................................................................................................... 75
       4.1.1. FR-4 laminates coated with solder masks .................................................................................. 75
       4.1.2. SIR test patterns ....................................................................................................................... 76
       4.1.3. Contamination .......................................................................................................................... 76
   4.2. Chemical characterization and elemental analysis .......................................................................... 77
4.2.1. Fourier Transform Infrared (FTIR) Spectroscopy ......................................................... 77
4.2.2. Nuclear Magnetic Resonance (NMR) Spectroscopy ......................................................... 77
4.2.3. Ion Chromatography (IC) .............................................................................................. 77
4.2.4. Energy dispersive X-Ray spectroscopy (EDS) .............................................................. 77
4.2.5. Standardized acid-base titration ....................................................................................... 77
4.2.6. Residues Reliability Assessment Testing (Residue RAT™) for contamination profiling. 78
4.2.7. Tin corrosion identification .............................................................................................. 78

4.3. Thermal characterization .................................................................................................... 78

4.4. Climatic testing ................................................................................................................... 78
4.4.1. Climatic chambers .......................................................................................................... 78
4.4.2. Flux activation treatment ................................................................................................. 78
4.4.3. Ovens .............................................................................................................................. 78
4.4.4. Gravimetric water vapour sorption/desorption testing .................................................... 79
4.4.5. Peltier cooling stage ........................................................................................................ 79

4.5. Electrical/electrochemical testing ...................................................................................... 79

4.6. Surface characterization and microstructure analysis ......................................................... 80
4.6.1. Contact angle – surface wettability ................................................................................ 80
4.6.2. Surface roughness ........................................................................................................... 80
4.6.3. X-ray diffraction (XRD) ................................................................................................. 80
4.6.4. Scanning electron microscopy (SEM) ............................................................................. 80
4.6.5. Optical microscopy ......................................................................................................... 80

5. Summary of appended papers ............................................................................................. 81
5.1. Effect of solder mask surface chemistry and morphology on the water layer formation under humid conditions ................................................................................. 81
5.2. Thermal decomposition of solder flux activators under simulated wave soldering conditions ......................................................................................................................... 82
5.3. Thermal decomposition of binary mixtures of weak organic activators used in no-clean flux systems and impact on PCBA corrosion reliability ........................................................................ 83
5.4. Parametric study of solder flux hygroscopicity: impact of weak organic acids on water layer formation and corrosion of electronics ........................................................................ 84
5.5. Humidity-related failures in electronics: effect of binary mixtures of weak organic acid activators .......................................................................................................................... 85
5.6. No-clean solder flux chemistry and temperature effects on humidity-related reliability of electronics .............................................................................................................................. 86
5.7. Residue-assisted water film formation under transient climatic conditions and failure occurrence in electronics .................................................................................................................. 87
APPENDED PAPERS

6. Effect of solder mask surface chemistry and morphology on the water layer formation under humid conditions ................................................................. 91
7. Thermal decomposition of solder flux activators under simulated wave soldering conditions ... 111
8. Thermal decomposition of binary mixtures of weak organic activators used in no-clean flux systems and impact on PCBA corrosion reliability ................................................................. 127
9. Parametric study of solder flux hygroscopicity: impact of weak organic acids on water layer formation and corrosion of electronics................................................................. 143
11. No-clean solder flux chemistry and temperature effects on humidity-related reliability of electronics .............................................................................. 191
12. Residue-assisted water film formation under transient climatic conditions and failure occurrence in electronics ................................................................. 213

13. General discussion .............................................................................................................................................. 241
14. General conclusions ........................................................................................................................................... 243
15. Suggestions for future work ........................................................................................................................ 247
1. INTRODUCTION

1.1. BACKGROUND

Today, the use of electronic devices occupies a major part of our lives. In the recent years, electronics underwent a size reduction (Figure 1.1) in order to create more compact devices exhibiting a large number of functions. Moreover, the exposure conditions of electronics broadened and nowadays the same products are being used worldwide in a variety of locations that impose different climatic conditions for devices’ operation, e.g. tropical, dry, arid etc. With an increased use of electronics, a large number of operational failures are reported. These failures can be intermittent or permanent, nevertheless all compromise the reliability of the device and can lead to huge economic loss. A vast majority of the failed products is due to the corrosion issues caused by the water film formation on the PCBA (Printed Circuit Board Assembly) surfaces as a result of the device’s exposure to humid conditions. Unlike conventional corrosion issues, in this case the corrosive medium is the ultra-thin water layer formed on the PCBA surface due to various factors, which will induce the electrochemical processes between the biased points on the PCBA surface. The electrochemical process leads to parasitic circuits (leak current and impedance changes) interfering with electrical functionality of the PCBA, although there can also be other corrosion modes due to multi-material use in electronics. The phenomenon of water layer build-up inside an electronic enclosure is affected by a number of factors related to the device manufacturing process, enclosure design, materials characteristics, exposure conditions, etc. There is, therefore, an increased demand for ensuring the product’s reliability, however, due to the technological developments, ensuring the reliability is complex and often difficult. The consequences of failing to provide a reliable product relate not only to the financial aspects, but also to diminishing the credibility of a producer, customer dissatisfaction, or even to the loss of human lives due to accidents.

![Figure 1.1: Size reduction of electronic devices and components over the years [1, 2].](image)

The rapid development in electronics manufacturing process and an increased user demand caused a miniaturization of the electronic devices. This means that spacing of various components and between the components on the PCBA surface are reduced. Over the last decade, size of the electronic components and PCBAs has reduced by over 70%. For some of the components, the miniaturization reached a level of even 90%. Furthermore, higher functionality requirements led to larger system integration and introduction of micro-circuits with distances down to few μm today. The decreased distance between the components increased the electric field \( E = V/d \), where \( E \) – electric field strength, \( V \) – voltage, \( d \) – distance between conducting lines). For humidity-related effects on electronics, the miniaturization trend is detrimental due to the easiness of connection between different biased points of the assembly when the water film forms on the PCBA surface.
The introduction of different PCBA manufacturing technologies and an expanded user environment contributed to the increased sensitivity of electronics towards harmful humidity effects and susceptibility to corrosion. An implementation of "no-clean" process for soldering purposes often results in certain amounts of post-production residue remaining on a PCBA surface, which in unpropitious conditions acts as a corrosion acceleration factor. Moreover, a number of contaminants originating from aggressive field applications or transport/storage can contribute to deteriorations in the device’s functionality. Due to the ionic and hygroscopic nature of the contaminants, the process-related residues may attract moisture from the device’s surroundings and cause a build-up of water layers, sufficient for causing an increase of leak current on a PCBA. The combination of small distances between the components, voltage applied to the device, water layer formation, and ionic nature of the electrolyte contribute to the reduction of surface insulation resistance (SIR) due to the current leaking. This subsequently leads to the corrosion occurrence in a form of electrochemical migration (ECM). In electronics, even a small degree of corrosion appearance may turn out to be destructive and possibly lead to the device’s malfunction or loss of operational capacity. The corrosion occurrence is therefore determined by a surface insulation resistance of the components, electrical properties of water film (defined by climatic conditions and residue), extent of ionic nature of the electrolyte (defined by climatic conditions and PCBA cleanliness), potential bias, PCBA geometry, enclosure design, etc.

Under highly humid conditions, a thin layer of moisture will form on all surfaces. However, electronic devices are typically exposed to cycling temperature conditions due to, e.g. day/night cycles. Under such situations, the difference between the temperature inside the device (therefore PCBA temperature) and outdoor temperature creates transient condensing conditions within an enclosure. The devices cannot rapidly respond to outdoor temperature changes and lag behind the external climate, which causes moisture condensation on a PCBA surface (Figure 1.2). This results in the formation of thick water layers that easily bridge the conductors, therefore creating an electrochemical cell for the corrosion occurrence. The PCBA design, cleanliness, and time of condensation further influence the condensation rate and become critical in the relation with reliability.

The interaction of moisture with the PCBA surface, electronic components, and residue associated with the processing steps are the key factors contributing to the occurrence of different failure modes and the overall deterioration of the device’s functionality. A variety of corrosion failure modes and humidity-related mechanisms can be found in the electronic devices (Figure 1.3), e.g. SIR reduction and subsequent electrochemical migration, galvanic corrosion, creep corrosion, or CAF (conducting anodic filament) formation. The formation of a conductive anodic filament is related to the absorption of water inside the PCBA. The occurrence of any corrosion mode can lead to catastrophic failures of electronic
devices, however the SIR reduction and electrochemical migration occurrence are typically named as the most important modes contributing to intermittent or permanent functionality issues and premature device breakdown.

Currently, certain solutions and strategies exist for prevention of water layer build-up and corrosion occurrence. Typically, these include the considerations of the assembly cleanliness that implies, e.g. an implementation of the expensive cleaning procedure in the production process or the installation of membranes protecting the enclosure against the entry of atmospheric contaminants. Many devices, especially units in consumer electronics, are conformally coated in order to combat the harmful effects of contamination, humidity, and temperature. Enclosing the electronics in casings will further delay the interaction between moisture and PCBA surface. However, these solutions will not improve the inherent humidity robustness of the PCBA, but will only delay the moisture-related issues. Safety measure in the form of conformal coating is an additional production step that increases the cost, while its protection level significantly depends on the initial cleanliness of the PCBA surface, coating thickness etc.

![Corrosion Modes Diagram](image)

Figure 1.3: An overview of typical corrosion modes contributing to failure occurrence in electronic devices due to exposure to humid conditions [3-6].

In order to improve the inherent reliability of the PCBA, the important aspect is to control the intermittent formation of significant levels of the water layer either by fully preventing or delaying the process. However, this requires detailed understanding of the synergetic effects of various factors such as humidity/temperature, contamination, potential bias, or PCBA design, and their influence on water layer build-up. Moreover, the combined effect of different corrosion accelerating factors must be considered for the prediction of device's susceptibility for failure. The information obtained could serve the electronic industries to develop methods and design guidelines that allow to avoid the formation of water layer of critical electrical properties sufficient for inducing deteriorations in the device operation. The aim of this PhD project is therefore to obtain the information about the role of various aspects contributing to the water layer build-up and premature corrosion failures of the electronic assemblies. The effects of different factors were studied individually and in combinations, in order to realistically assess the potential electrical functionality issues caused by the climatic exposure.
1.2. MOTIVATION AND SCOPE OF THE THESIS

The focus of the studies reported in this PhD thesis is related to the detailed empirical understanding of the role of various factors related to climate and device parameters that assist the water layer formation on the PCBA surface (Figure 1.4), and the potential prevention possibilities. Detailed investigation of the effect of surface chemistry and morphology was carried out under condensing conditions, where the impact of materials characteristics and PCBA design on the failure occurrence was assessed. Detailed studies were carried out under temperature and bias conditions for the reliability evaluation of various hygroscopic contaminants related to the PCBA processing step. The effects of transient climatic conditions and PCBA design were evaluated under different climatic conditions. Moreover, the combined effects of materials, contamination, humidity, temperature, and bias were studied together under humid and condensing conditions in order to provide an accurate overview of the complex set of aspects for reliability control and corrosion prevention.

![Figure 1.4: An overview of factors influencing the water film formation on the PCBA surface studied in this thesis.](image)

The work presented in this thesis aims to provide a set of insights and guidelines that can be applied by the electronics industry at the development stage for robust device. The climatic reliability improvement does not necessarily require an implementation of expensive safety measures – rather a careful choice of materials and chemicals for PCBA production, design considering the critical surface parameters and geometry factors, and consideration of the device exposure conditions, which overall can provide a longer lifetime, high reliability, durability, and safety.

1.3. STRUCTURE OF THE THESIS

The overview of the PhD thesis structure is presented in the Figure 1.5. The thesis is divided into 15 chapters. Chapters 1-3 contain an introduction to the scope of the work, present the available literature, and a summary of the literature information and the objectives of this thesis. Chapter 4 describes the materials and experimental methods used for the investigations. Chapter 5 presents a short summary of each appended paper highlighting its objectives and conclusions. The results are summarized in 7 papers constituting chapters 6-12. Chapter 6 investigates the effect of the PCBA surface...
characteristics on the water film formation and related differences in time-to-failure. Chapters 7 and 8 concern the thermal decomposition of no-clean solder flux residues composed of single or binary mixtures of organic activators under simulated soldering temperatures and related reliability issues. Chapters 9-11 present the study of interactions between the no-clean solder flux residues and humidity under various temperature conditions, and the effects on the electrical performance and potential corrosion occurrence. Chapter 12 investigates the effect of PCBA design, humidity, and contamination under condensing and non-condensing climatic conditions on the failure occurrence in electronics. Chapters 13, 14, and 15 present the overall discussion, conclusions, and suggestions for future work.

Figure 1.5: An overview of the PhD thesis structure.
2. WATER FILM FORMATION ON THE PCBA SURFACE

In this chapter, various factors influencing the water layer formation on a PCBA surface are reviewed such as humidity, PCBA surface characteristics, and PCBA cleanliness. The effects of climatic conditions and device design are briefly described. Further, some of the failure modes constituting the majority of field returns of electronics, which are directly linked to the water film formation on a PCBA, are reviewed. The chapter ends with a crisp information given on the climatic reliability testing applied for the evaluation of the water layer formation extend and aggressivity.

2.1. HUMIDITY

2.1.1. Characteristics of moisture

Water

Water is a dipole molecule of a small size (29 Å, H-O-H angle of ~105˚) and high mobility that makes it a good penetrant and space filler [7, 8]. Water molecules interact with solids due to the formation of non-covalent directional hydrogen bonds [9] – a type of intermolecular force bonding a weak partial positive charge on one atom in a molecule X with a weak partial negative charge on another atom within a molecule Y. Cohesion is the formation of hydrogen bonds between the water molecules, while adhesion is the formation of hydrogen connections between water and other molecules. Water can form a strong and complex network of hydrogen connections as a result of its bipolar nature: water molecules can act as a H-donor and H-acceptor, therefore numerous opportunities exist for its interactions with solids [7].

Water vapour pressure

The behaviour of water existing in the form of gas molecules can be mathematically described by an ideal gas law defined as:

\[ p \cdot V = n \cdot R \cdot T \]  \hspace{1cm} (Eq. 2.1)

where \( p \) is the pressure \( \left[ \frac{N}{m^2} = Pa \right] \), \( V \) is the gas volume \( [m^3] \), \( n \) is the mole number of gas molecules \( [mol] \), \( R \) is the universal gas constant \( \left[ 8.3145 \frac{J}{mol \cdot K} \right] \), and \( T \) is the absolute temperature \( [K] \).

In a closed container filled partially with bulk water, the water molecules constantly escape to the headspace in the form of gas molecules (water vapour). These vapour molecules are in a constant random motion and exert a pressure on the container walls. The moist air existing in the container headspace is then a two-component gas mixture due to the presence of air molecules and water vapour molecules. The total vapour pressure exerted on the container walls containing moist air \( (p_T) \) is a sum of the partial pressure of the dry air \( (p_{air}) \) and the water vapour partial pressure \( (p_w) \):

\[ p_T = p_{air} + p_w \]  \hspace{1cm} (Eq. 2.2)

Therefore, the ideal gas equation for the moist air can be defined as:

\[ p_T \cdot V = (n_{air} + n_w) \cdot R \cdot T \]  \hspace{1cm} (Eq. 2.3)

where \( n_{air} \) is the mole number of air molecules \( [mol] \), and \( n_w \) is the mole number of water molecules \( [mol] \). The more water molecules escape to the vapour state and the faster their motion, the higher vapour pressure of the moist air. The vapour molecules are in a dynamic equilibrium with the liquid water: they constantly condense from the gaseous to liquid state, and the liquid molecules constantly escape to the gas phase. At the certain point, no net change in the number of water molecules existing in the vapour state occurs, which is the equilibrium state (the rates of evaporation and condensation...
reactions are equal), and the pressure inside the container remains constant. This is the saturated vapour pressure, which is also a function of temperature.

**Raoult’s law**

The vapour pressure above the solutions of non-volatile solutes (e.g. salt solution) is dependent on the vapour pressure of the volatile component (solvent) and the mole fraction of the chemical component in the solution. The vapour pressure above the solution \( p_{\text{solution}} \) [Pa] is then equal to:

\[
 p_{\text{solution}} = p_0 \cdot X_{\text{solvent}}
\]  
(Eq. 2.4)

where \( p_0 \) is the saturated vapour pressure of pure water at the same temperature [Pa], and \( X_{\text{solvent}} \) is the mole fraction of the solvent in the solution (\( = \frac{\text{mole number of solvent molecules}}{\text{total mole number of all particles}} \)). The presence of a non-volatile compound in the solution decreases the vapour pressure above the solution, and it is always lower compared to the vapour pressure above pure liquid water. This is due to the fact that, in the solution, some of the water molecules interact with the solute and cannot escape to the vapour phase [10]. Moreover, the surface area of the solution is occupied by both water and solute molecules which inhibits the escape of water molecules to the vapour phase.

Figure 2.1: Variation of water vapour pressure ratio as a function of the: (a) solute mole fraction for salt solutions and an ideal solution, (b) salt solution concentration [11].

Figure 2.1 shows the variation in water vapour pressure ratio as a function of the solute mole fraction (Figure 2.1 (a)) and salt solution concentration (Figure 2.1 (b)). Ions dissociating in the solution reduce the water vapour pressure more than do the solutes that do not dissociate into the solution, and this reduction depends on the substance type.

**Absolute humidity (AH)**

Absolute humidity is the amount of water vapour in the air, and can be expressed as the ratio between the total mass of water vapour \( m_{H_2O} \) suspended in the given air volume \( V_{\text{air}} \):

\[
 AH = \frac{m_{H_2O}}{V_{\text{air}}} [\frac{\text{g}}{\text{m}^3}] 
\]  
(Eq. 2.5)

At a specific temperature, there exists a saturation water vapour content present in the air.

**Relative humidity (RH)**

Relative humidity expresses the amount of water vapour present in the air at a given temperature relative to the maximum moisture content possible to be present in the same temperature. RH is then the actual water vapour pressure and can be described then as a ratio between the actual partial pressure of water vapour \( p_w \) [Pa] and the saturation/equilibrium water vapour pressure \( p_0 \) [Pa] at a given temperature:
\[ RH = \frac{p_w}{p_0} \times 100 \]  
(Eq. 2.6)

RH is then expressed as a percentage of the total water vapour amount that could be held in the air at the given temperature. Higher water vapour content exists at higher temperature compared to lower temperature; therefore, for the same AH levels, the relative humidity of the cold air is higher than the RH of the warm air.

**Water activity \( (a_w) \)**

Water activity is a qualitative measure of the energy status of water contained in a system (e.g. in a form of salt solution or moisture absorbed by a material): the amount of relative energy that water contains when present in a system compared to the energy of pure water. For instance, \( a_w = 0.3 \) means that the water present in a system holds 30% of the energy that pure water would possess, but does not define the amount of "free" or "available" water amount in the system as it is not a quantitative measure.

The understanding of water activity is based on a second law of thermodynamics where the occurrence of certain phenomena is explained by the energetic feasibility of the system. The energy of water present in the system is directly related to its tendency to escape from the solution to the vapour phase (fugacity, mobility) and can be compared to the reference fugacity of a pure water \[12\]. Systems of higher energy allow for the water molecules to escape easier and to larger extend, which subsequently builds up higher pressure of vapour above the hydrated sample. Based on that, the \( a_w \) of the system can be expressed as following \[13\]:

\[ a_w = \frac{f}{f_0} = \frac{p_{\text{solution}}}{p_0} = \frac{RH_{eq}}{100} \]  
(Eq. 2.7)

where \( f \) is the fugacity of water contained within the solid \([Pa]\), \( f_0 \) is the fugacity of pure water \([Pa]\), and \( RH_{eq} \) is the equilibrium RH above the solid containing moisture \([\%]\), where all parameters are measured at the same temperature. The mobility of water molecules contained in most systems is lower than the mobility of water molecules in pure water \[13\]. Therefore, the vapour pressure gradient between the pressure above the hydrated solid sample compared to the vapour pressure in the ambient causes a movement of water molecules from high-energy system to low-energy system until an equilibrium is reached \[12\]. When the equilibrium is reached, the \( a_w \) of the system is equal to the RH surrounding the sample.

Water activity is typically measured using chilled mirror dew point, hygrometers, impedance, or FTIR (Fourier Transform Infrared) spectroscopy \[13\]. The \( a_w \) depends on the temperature and solid type \[13\]. In theory, water activity could be predicted using Raoult’s law, however, this would not be highly accurate due to the law’s assumption of the lack of interactions exhibited between the solute and water molecules (which does not hold true in almost any case). Alternate models for predicting water activity, accounting for non-ideality, are based on Norrish equation, Grover model, or Ross equation. The latter is discussed in section 2.3.3.

### 2.1.2. Interactions of humidity with electronics

A number of interaction types exist between water vapour and the components of electronic assembly, and the nature of such interaction determines the characteristics of water film formation on the PCBA surface and the potential effect on corrosion reliability of the device. Five main modes of interactions between humidity and electronic materials (Figure 2.2) can be distinguished and classified as the interactions taking place at the PCBA surface, interactions between water condensed on solids and the material, and water internally reacting (internalizing) with the bulk of the solid. Within the
mentioned modes, five types were suggested: adsorption of humidity onto the PCBA surface, capillary condensation into the confined spaces, deliquescence of hygroscopic compounds, crystal hydrate formation, and absorption into the bulk of amorphous substance [8, 14-16].

Figure 2.2: An overview of water-solid interactions [7].

The electronic devices are complex systems containing a variety of materials within their assemblies (metals, polymers, chemical residues), therefore all the mentioned water-solid interactions may occur upon the exposure of the assembly to humid conditions. The physical state of the solid (amorphous or crystalline [17]) determines the type of interaction with moisture [18] that will occur given the conditions for the phenomenon appearance are met. Humidity ingress into the materials or the formation of water layers alter the components’ properties, which subsequently may affect the product performance and lead to serious deteriorations of the device’s functionality or failure. It is important to understand these interactions with electronic components at a fundamental level, assess the risk and extent of their occurrence, and use that knowledge for the optimization of the production process, storage conditions, electronics design aspects, etc. to increase the humidity robustness of electronics.

2.1.3. Water layer formation on the clean PCBA surface

Adsorption

Adsorption is an interaction of moisture with the surface of the solid where the water molecules contact and adhere to a hydrophilic surface. The adsorbed water does not penetrate the surface but interacts with the chemical moieties on the surface via H-bonding, electrostatics, or charge transfer interactions [14]. Primarily, the formation of only few molecular layers occurs on the surface [8, 9, 19], followed by the interaction of other water molecules with the first strongly bonded water layers resulting in a 3D layer on the surface (without condensation of water) [19]. Upon the continued adsorption of water molecules, the pressure above the surface constantly equilibrates with the pressure of the surrounding.

In humid and non-condensing conditions, moisture adsorption on the perfectly clean surface results in the formation of tens of monolayers of water formed at saturated RH levels, which is not visible to the naked eye. The phenomenon is illustrated in the Figure 2.3 where water molecules adsorb to the metal surface upon increasing of the external humidity level. At low RH conditions, the water molecules form isolated islands that do not connect one to another (Figure 2.3 (a)), therefore the conductivity
between the two conductors at such conditions is expected to be low. Upon an increase of relative humidity, the initially formed water patches grow (Figure 2.3 (b)). When enough water accumulates on the surface, the water islands start to connect locally and form a path sufficient for producing the significant levels of leak current (Figure 2.3 (c) and (d)). The surface insulation resistance decreases as a result of ionic conducting layer formation capable of conducting the current. Upon a further growth of the water film, due to the increasing external humidity level, a uniform water layer forms (Figure 2.3 (e)) [20].

![Figure 2.3: Schematic representation of a relationship between water layer formation, relative humidity, surface insulation resistance (SIR), and leakage current. Adapted from [20].](image)

Adsorption of moisture on the clean surfaces does not bring significant amount of water into the system, which results in almost horizontal line at the baseline of moisture sorption curve (Figure 2.4). Typically, the bulk properties of the material adsorbing moisture are not critically affected by this interaction, however the properties of surface insulation/conductivity change [9] as following:

\[
SIR = (\sigma \cdot d)^{-1} \quad \text{(Eq. 2.8)}
\]

where \(SIR\) is the surface insulation resistance, \(\sigma\) is the conductivity [S/m], and \(d\) is the film thickness [m]. The larger amount of moisture adsorbed to the PCBA surface, the larger amount of ions and their mobility [21], therefore conductivity increases and the SIR values are reduced. However, the conductivity of adsorbed water layer is much lower than the conductivity of bulk water [22].

![Figure 2.4: Moisture adsorption on a surface of a solid displayed on a moisture sorption curve. Adapted from [14].](image)
In practice, adsorption of moisture takes place on all surfaces. The amount of water formed on the clean PCBA surface depends on the type of the materials facilitating this phenomenon [22]: the amount of polar functional groups, affinity of these moieties towards water molecules, spatial orientation of the functional groups, capabilities of creating weak bond connections, etc. Moreover, the external climatic conditions (temperature, relative humidity, pressure) to which the PCBA is exposed to, together with the surface cleanliness, define the adsorption occurrence and its extent [9, 19, 22-24].

The prediction of the nature and extent of water adsorption to the crystalline solid is typically challenged by two models: the Langmuir model and Brunauer-Emmett-Teller (BET) model. The Langmuir model is based on the assumption of a physical adsorption of a monomolecular layer to the identical and independent sorption sites and can be expressed as:

$$a_w \left( \frac{1}{M_w} - \frac{1}{M_0} \right) = \frac{1}{CM_0} \quad \text{(Eq. 2.9)}$$

where $M_w$ is the equilibrium moisture content $[\text{kg of } H_2O / \text{kg of dry matter}]$, $M_0$ is the monolayer moisture content $[\text{kg of } H_2O / \text{kg of dry matter}]$, and $C$ is the constant. The weight of a monolayer is of great importance as it indicates the amount of water strongly sorbed to the specific sites (moieties) of a solid material.

The extension of the Langmuir’s theory towards the adsorption of multi-molecular layers can be found in BET equation formulated in 1938 [12]. It is based on the measurement of water amount (weight) formed on a dry substance in relation to the external relative humidity level, and can be expressed as following [13]:

$$\frac{M_w}{M_0} = \frac{C a_w}{(1-a_w) + C_{hs} a_w} \quad \text{(Eq. 2.10)}$$

where $C_{hs}$ is the energy constant related to the heat of sorption $[\text{J per kg}]$. The BET theory has its limitations and the moisture sorption trend follows the linear behaviour only in a limited range of water activity from 0.05 to 0.45 (Figure 2.5) [12].

![Figure 2.5: Langmuir and BET models of adsorption isotherms (assumption: $a_w = 0.1$ for half monolayer coverage)  [19].](image)

The BET theory assumes that the first water layer is adsorbed to the surface with energy $E_0$ similar to the surface energy, and the subsequent layers bind to the underlying layer with the energies $E_1, E_2, E_3$ etc. equal to the energy of evaporation. The average number of molecular layers of water $N$ on a surface can be calculated as following [24, 25]:

$$N = \frac{a_w e^{(E_0-E)/kT}}{(1-a_w)[1+\left(\frac{E_0-E}{e^{kT}-1}\right)^{a_w}]} \quad \text{(Eq. 2.11)}$$
Certain PCBA materials (e.g., polymers) do not exhibit high affinity towards water molecules and adsorb moisture onto the surface to the moderate extent, therefore the value of adsorption energy is close to the heat of water condensation ($E = E_0$) and the above equation can be expressed as:

$$N = \frac{a_w}{1 - a_w} \quad (\text{Eq. 2.12})$$

Other PCBA materials (e.g., metals, ceramics) are hydrophilic and possess high surface energy where $E_0 \gg E$, and the averaged number of monolayers can be calculated as follows:

$$N = \frac{1}{1 - a_w} = \frac{a_w}{1 - a_w} + 1 \quad (\text{Eq. 2.13})$$

This implies that hydrophilic surfaces of high surface energy adsorb one extra monolayer of water compared to low energy surfaces, and that this additional monolayer can be held even at very low relative humidity levels [25]. The differences in the number of adsorbed monolayers of water for moderately and strongly adsorbing surfaces are shown in the Figure 2.6.

A relationship between the rate of atmospheric metal corrosion under thin water layers was established and is shown in the Figure 2.7. At the water layer thickness 100 Å-1 μm (region II), the water film formed is rather invisible and is defined as “humid atmospheric corrosion” region. With an increase of film thickness to ~1 mm (region III), a visible water layer forms and the corrosion is characterized as “wet atmospheric corrosion”.

Figure 2.6: The relationship between surface coverage by water and external humidity level for different PCBA materials. Adapted from [25].

Figure 2.7: The rate of atmospheric corrosion as a function of water layer thickness [26].
A further increase in the water film thickness (region IV) results in corrosion rate as in the bulk water. The values of film thickness are not absolute, as they depend on different factors. At the moisture layer thickness of ~1 µm, the maximum corrosion rate can be expected due to an easy access to environmental oxygen, however, the increase of liquid film thickness increases the diffusion layer and the corrosion rate decreases [26].

The detection of moisture adsorption and the formation of water monolayers requires the use of sensitive techniques such as ellipsometry, reflection/ATR (Attenuated Total Reflection) IR (Infrared) spectroscopy, Raman spectroscopy, Brewster Angle Microscopy (BAM), Circular Dichroism (CD), or SPR (Surface Plasmon Resonance).

The typical failure modes of electronics associated with the water film build-up and the reduction of surface insulation resistance are described in section 2.6.

**Capillary condensation**

Capillary condensation is the process of water vapour condensation in the confined spaces between the solid particles, inside the pores of the material, or in the surface defects/irregularities [14, 16, 27] (Figure 2.8). The phenomenon is a result of the initial moisture adsorption to the surface and takes place upon increasing of the ambient relative humidity. The adsorbed water collects and menisci form inside the pores, in the irregularities of the surface, or in the contact points between the particles (Figure 2.8).

![Figure 2.8: Schematics of capillary condensation phenomenon. Adapted from [28].](image)

The menisci develop high Laplace capillary pressure and high curvature, therefore the water vapour pressure (water activity) is reduced compared to the water vapour pressure in contact with a flat surface or in the surroundings [9]. Such reduced thermodynamic activity acts as a driving force for the condensation. The change in the water vapour pressure occurring as a result of a formed meniscus (curved liquid/vapour interface) is described by Kelvin-Thompson equation [13, 28, 29] where the pressure above a flat and non-curved surface is higher compared to the pressure above a curved surface:

$$\frac{p_w}{p_o} = e^{-\frac{2\pi \gamma m}{RT}} \quad \text{(Eq. 2.14)}$$

where $\gamma$ is the surface tension of water in the pore $\frac{N}{m}$, $V_m$ is the molar volume of the liquid $[m^3]$, and $r$ is the pore radius $[m]$. As the pore radius (particle size) decreases, the greater the curvature of the
meniscus resulting in the decrease of the actual vapour pressure and the more apparent occurrence of moisture condensation. This subsequently leads to the formation of bulk liquid in a system.

Capillary condensation can occur on non- and water-soluble materials where the formation of bridges between their crystals/particles is possible. In the former case of clean PCBA surface and non-soluble materials, 0.1% of water uptake can be associated to capillary condensation and implies the formation of liquid bridges at interparticulate contacts or inside the pores [9, 29], which becomes important while investigating the water vapour adsorption to the surface.

In the case of clean PCBA surfaces, the extend and kinetics of capillary condensation phenomenon is dependent on the type of solid (polarity/affinity to water molecules), size of interparticulate spaces, pore diameter, and ambient temperature [14]. The PCB substrate materials (laminates, Figure 2.16), are highly porous, and therefore the capillary condensation will differ depending on the pore size. Other PCB materials (e.g. solder mask, chip components) exhibit a high surface roughness, resulting from the manufacturing process or material characteristics, which increases the surface area available for the moisture to condense onto. If the surface cleanliness is altered by the ionic residues, the capillary condensation becomes dependent on the type and amount of contamination.

![Figure 2.9: Progress of capillary condensation described by different regions of adsorption isotherm. Adapted from [28].](image)

The interpretation of the capillary condensation phenomenon progress on the clean surfaces can be performed using an adsorption isotherm (Figure 2.9) where different adsorption models describe the gradual increase in surface coverage by water molecules upon an increase of ambient humidity levels.

### 2.1.4. Absorption of moisture by electronic materials

Absorption of moisture is a process in which water molecules permeate into another substance: water vapour moves into the internal structure of the amorphous solid. Amorphous solids, contrary to the crystalline substances, do not exhibit an ordered 3D structure, but rather a disordered and random molecular arrangement, and have a specific glass transition temperature (Tg). Tg is a glass transition temperature defined as a temperature at which the change in coordinated molecular motion takes place. The temperature depends on the glass formation process: fast cooling rates typically result in higher Tg compared to slow cooling rates [30].
Amorphous solids exist in two different states: “glassy” (non-equilibrium form of the state below Tg, most immobile and rigid state) and “rubbery” (more mobile and soft form, above Tg) [14], both of them exhibiting different relationship with water vapour. Exposing glassy solids of a rigid structure to the increasing ambient RH can facilitate the transition to the rubbery state of a softer texture (often related to the lowering of the Tg of that solid) [31].

Water ingress into the electronic materials results in altering the plasticity and reduction of Tg [32]. The base laminates, solder mask, components, or encapsulation materials become more susceptible for texture changes, crystallization, or shelf-life reduction. The changes of PCB properties induced by moisture ingress into the materials can lead to functional deteriorations of electronic devices (briefly described in section 2.6.) e.g. due to the altered dielectric properties. Moreover, the absorption of moisture to the base PCB materials prior to component assembling, occurring e.g. during the storage period, increases the post-soldering risk of a voids and cracks formation (pop-corn effect), and the risk of higher moisture uptake at the later stages of product use [33].

Figure 2.10: The examples of moisture absorption by various electronic materials: (a) effect of material type [34], (b) effect of exposure conditions [35].

The uptake and rate of moisture ingress into the materials depend on the type of solids, temperature, and ambient relative humidity level (Figure 2.10) [36]. Some of the saturation moisture sorption levels measured for various electronic materials constituting the base laminate substrates are given in Table 2.1.

Table 2.1: Moisture absorption saturation levels for various materials constituting the FR-4 substrate [33, 36, 37].

<table>
<thead>
<tr>
<th>Material</th>
<th>Moisture absorption level [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FR-4 epoxy resin</td>
<td>0.02 ; 0.05 ; 0.1 ; 0.7 ; 0.84 ; 0.87</td>
</tr>
<tr>
<td>Polyamide resin</td>
<td>0.9</td>
</tr>
<tr>
<td>Cyanate Ester resin</td>
<td>0.5</td>
</tr>
<tr>
<td>Thermount® reinforcement</td>
<td>0.44</td>
</tr>
<tr>
<td>Solder masked FR-4</td>
<td>0.87 ; 0.89 ; 0.92 ; 1.00</td>
</tr>
</tbody>
</table>
2.2. EFFECT OF PCBA SURFACE MORPHOLOGY

The surfaces of electronic materials (encapsulation, laminates, solder mask) differ in surface energy (originating from the chemical composition) and surface topography (Figure 2.11). As a result, the formation of water film on the surfaces of electronic materials varies and depends on both properties of the material.

![Figure 2.11](image1.png)

Figure 2.11: Differences in the surface topography of: (a) FR-4 epoxy laminate, (b) solder masked PCB, shown from the cross section point of view.

The effect of surface on water film formation can be described in terms of surface wettability where the sessile water droplet adheres to the surface forming a contact angle between the surface level and the tangent line at the droplet-air interface (Figure 2.12). Small contact angle forms when the liquid spreads on the surface, whereas large contact angle exists when the liquids beads on the surface [38, 39]. The angle values below 90° indicate well wetting properties exhibited by the hydrophilic material surface, while the angle values above 90° indicate poor wetting properties and the droplets form in a compact shape on the hydrophobic surfaces. Typically, the angles greater than 150° are exhibited by superhydrophobic surfaces.

![Figure 2.12](image2.png)

Figure 2.12: Schematics of contact angles formed on the surfaces of varying energies [38].

The contact angle (θ) of a droplet wetting the ideal solid surface was defined by Young and is dictated by the mechanical equilibrium of the droplet under an influence of three interfacial tensions [38]:

\[
\gamma_{LV} \cdot \cos \theta_Y = \gamma_{SV} - \gamma_{SL}
\]  
(Eq. 2.15)

where \( \theta_Y \) is the Young contact angle, \( \gamma_{LV} \) is the liquid-vapour surface tension, \( \gamma_{SV} \) is the solid-vapour surface tension, and \( \gamma_{SL} \) is the solid-liquid surface tension, expressed in [\( \text{N/m} \)]. Young’s contact angle assumes the droplet resting on ideal, topographically smooth, and chemically homogeneous surface. In practice, however, real surfaces always exhibit certain degree of roughness (Figure 2.13) – a random texture, or a periodic profile [40] – and the contact angles measured on such surfaces become meaningless in terms of Young’s equation.
Therefore, the contact angle on a real surface is an angle between the tangent to the liquid-vapour interface and the actual local surface of the solid – the line that represents the apparent solid surface (Figure 2.14) [42]. The actual and apparent angles can largely deviate.

\[
\cos \theta' = r_f \cdot \cos \theta_y
\]  
(Eq. 2.17)

Wenzel defined the relationship between roughness and wettability, and proposed the description of the apparent contact angle (\(\theta'\)) of a droplet placed on a rough surface [38, 43, 44]:

\[
\cos \theta' = \frac{r_f (\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}}
\]  
(Eq. 2.16)

where \(r_f\) is the roughness factor which is defined as a ratio between the actual surface area (which is higher than the apparent/projected one) and the geometrically projected area (which is lower than the actual surface area). The relationship between \(\theta_y\) and \(\theta'\) is then given by:

Surfaces of poor polarity (low surface energy) exhibit high water contact angles (poor wettability), contrary to the polar hydrophilic surfaces that exhibit high wettability. The wettability of the surface can be altered by the introduction of higher surface roughness [40, 45, 46]:

- hydrophilic materials become more wettable (which is attributed to water infiltration of the texture grooves as a result of capillary effect)
- hydrophobic materials become less wettable (a consequence of thin air layer trapped in the texture grooves).

An example of the rough surface texture effect on wetting and spreading of the liquid on hydrophilic and hydrophobic surfaces is shown in the Figure 2.15. On the high-energy surface (Figure 2.15 (a)), the
liquid easily spreads and fills the ridges, and higher degree of roughness facilitates the droplet penetration over the larger amount of grooves, resulting in lower contact angle. Hydrophobic surface (Figure 2.15 (b)), does not assist an easy liquid spreading, and promotes the formation of convex shaped-droplets. The effect is enhanced if the texture is increased and the air can be trapped underneath the droplets [42]. The value of the contact angle is a surface local property and does not depend on the droplet size [46].

The variety of electronic materials used for a PCBA production is huge, which suggests a number of complex chemistries and topographies that can be found for these surfaces [40]. As a result, the materials can exhibit different effects on the way water film forms on their surfaces, which is crucial to understand for a better reliability assessment. The examples of varying surface topographies of typical PCB materials are shown in the Figure 2.16.

![Figure 2.15](image_url): Spreading of liquid droplet on the rough hydrophilic and hydrophobic surfaces [40].

![Figure 2.16](image_url): Examples of varying morphology of: (a) typical FR-4 Printed Circuit Board laminates, (b) chip resistor terminal [47].
2.3. EFFECT OF PCBA CLEANLINESS

The formation of water layer and the potential for corrosion occurrence are determined by the PCBA cleanliness. The detrimental effect of the contamination depends on the [48]:

- type of contamination,
- quantity of contamination,
- location of the contamination on a PCBA surface.

The residual compounds are assessed as harmful for the electronic device if their presence leads to performance deteriorations, e.g. initiation of a premature damage during the storage time, functionality issues, or altering of the product reliability during the application. The contamination typically found inside the electronic devices originates either from the PCBA manufacturing process or from the service life (Figure 2.17).

![Figure 2.17: An overview of sources of the residues typically found on a PCBA surface [49].](image-url)

Manufacturing process of the PCBAs is complex and typically can be divided into:

- fabrication of a PCB (photolithography, drilling, electroplating, etching, cleaning) and
- component assembling process (soldering, cleaning).

A number of substances constitute the base FR-4 material (Table 2.2). During production, the PCBAs are exposed to a variety of chemical and mechanical treatments [49] which can potentially lead to the evolution of harmful ingredients from PCBA, or leave the original or decomposed fractions of destructive contaminants on a PCBA surface that can eventually lead to corrosion failures. The contamination originates from [48]:

- PCB substrate (e.g. outgassing of flame retardants from FR-4 laminates (Br)),
- components (e.g. outgassing from encapsulation materials, degradation),
- fabrication (e.g. drilling debris, etching salts, plating, cleaning agents),
- component assembling (e.g. solder flux residue, cleaning),
- coating and encapsulating,
- repair/rework and quality control (e.g. human contamination: fingerprints, sweat; solder flux residues).

Apart from the residues associated with the manufacturing process, the harmful halogenic contaminants are often found to cause the issues in the microelectronic devices. Typically, the polymeric materials (e.g. FR-4 laminates, mould compounds in the integrated circuits) undergo de-gassing where the halogenated fire retardants are evolved, causing a wire bond corrosion [50, 51].
Additional sources of contamination originate from the user environment, and vary depending on the season as well as the location the device is exposed to [48]:

- dust and dirt,
- air pollutants,
- salt fog,
- de-icing salts,
- microorganisms,
- maintenance and repair operations.

Any contamination type, originating from production or application site, that tends to interact with moisture, can significantly influence the formation of thick water layer if residing on a PCBA surface. Typical ionic contaminants contributing to the majority of field returns are discussed further in this chapter.

### 2.3.1. Solder flux residues

Upon the process of component assembling to the PCB (soldering), the metallic surfaces that are about to be soldered can undergo oxidation, which may result in poor mechanical properties of the solder joint due to lack of adhesion [53]. The solderability of the metals can be significantly improved with the use of solder flux systems prior to the soldering process. These chemicals clean the metallic surface from the contamination and oxides, and allow the molten solder to adhere to the metal, providing a mechanically robust joint [54, 55].

Solder flux systems come in a variety of forms, which are selected depending on the soldering process. For the wave soldering process, liquid type of flux is used. Flux can also be incorporated in the paste formulation (reflow process) or in the soldering wire (hand soldering).

The formulation of liquid solder flux system is complex, however typically it consists of:

- solvent (alcohols, ethers, esters, hydrocarbons, water etc.),
- additives (surfactants, stabilizers, inhibitors, antioxidants, dyes, plasticizers, thickeners etc.),
- vehicles/binders/film-formers (solids (rosin, resin), non-volatile liquids (polyols)), and
- activator (organic acids, amino acids, inorganic halide compounds, organohalides etc.).
Solvent serves as a carrier system for the ingredients and is a major component of liquid flux systems, while in the case of solder pastes (for reflow soldering) the major part consists of metal powder and film-former. The presence of the film-former in the flux formulation reduces the surface tension (for high wettability) and prevents solder balling. Moreover, it is supposed to encapsulate the eventual activator leftover present on the PCB surface after the soldering process. A number of additives serve to increase the surface wettability and disperse flux over the PCB surface more efficiently. The activators are the ingredients present as a minor fraction of the flux formulation, and serve to remove the oxide layer from the metallic surfaces prior to soldering. Typically, they are weak organic acids (WOAs) in most of the no-clean flux systems.

Flux formulation is categorized based on the IPC J-STD-004B standard [56] which defines the type of film-former (ROSin, RESin, ORganic, or INorganic), and the activity level (L – low, M – medium, H – high) which refers to the substances added for surface activation purposes. Further, the level of halide content is specified (0 – <0.05% wt/wt, 1 – 0.5-2% wt/wt).

Adaptation of “no-clean” solder flux technology for automated soldering allowed for cost saving and the use of environmentally-friendly chemicals in the PCB production. However, the main advantage was the lack of cleaning required after the soldering process as any flux residues remaining after production were claimed to be distributed all over the PCBA surface and be non-corrosive [55]. Moreover, if the flux applied was a low solid flux (<5% wt), it was claimed that the flux residue is possible to be largely removed by volatilization if activated to its maximum temperature, however, in practice, it is not always a case. In practice, high levels of flux residues can be found on a PCBA surface after production and, due to the hygroscopic nature of organic activators, they pose a significant concern for the long-term reliability of the devices.

The PCBA manufacturing process consists of several types of soldering depending on the types of the components to be soldered to the board. Depending on the soldering process characteristics, different levels of residues are expected to be left on the surface after production [57, 58].

Wave soldering process is used for mounting of the through-hole (TH) components. The component’s leads are inserted in the PCB through via holes, and then the board is passed through the fluxing tank where the liquid flux system is sprayed onto the bottom of PCB (Figure 2.18). Often, certain amount of flux goes through via holes and is left on the top part of the PCB [57]. Subsequently, the board is passed through the heating chamber, where various heating profiles are applied in order to activate the flux and remove oxide films from the metallic surfaces. Afterwards, the board passes the bath containing molten solder, and the components are soldered to the underside.

The top part of the PCBA, where certain amount of flux remains after the fluxing step (raised through via holes), experiences lower temperatures than the bottom [59]. Therefore, flux on the top part of the PCBA does not experience a sufficient thermal treatment in order to be removed and remains on the board as the hygroscopic contamination. Further, the fluxing step is often non-optimized – the time when a significant heating can be experienced by the flux is short and the thermal energy is mostly
consumed by the solvent evaporation rather than the removal of a solid part. It results in the presence of flux residues on a PCBA board after the wave soldering process as shown in the Figure 2.19.

In case of selective wave soldering process, certain PCB parts are covered with a stencil during the fluxing and soldering steps. It was found that during fluxing, large amount of flux can be trapped under the pallet (Figure 2.20) and not be exposed to the thermal treatment. Due to this reason, the amount of flux residues resulting from the selective soldering process significantly depends on the procedure of flux application and the precision of the PCB coverage. New flux application methods exist for the selective wave soldering process that allow for the local flux application, which significantly reduces the amount of residues remaining on the PCBA surface.

Figure 2.19: Examples of post-production flux contamination remaining on a PCBA after wave soldering process.

Figure 2.20: Examples of flux residues spread on a PCBA surface in the regular patterns after the selective wave soldering process (a). The red coloration in (b) shows the contamination profiling using the acidic indicator in a gel form.
In the reflow soldering process, the solder paste supplies both the solder alloy (in a powder form) and the solder flux. As illustrated in the Figure 2.21, the solder paste is applied on a land pattern (where the component is to be placed) using an automated system and a stencil. Subsequently, the required SMT (surface mount technology) components are mounted on top of the paste, and the whole PCBA is subjected to heating. The heat melts the solder paste, activating the flux which results in joining the component to the solder land.

![Figure 2.21: Illustration of the main steps comprising the reflow soldering process. Adapted from [53].](image)

Typically, the contamination left on a PCBA after the reflow soldering process is usually not visible with a naked eye as majority of the residues remain under the components. However, upon an exposure to harsh climatic conditions, activator initially concealed by a film-former is released from the remains placed under the components [57]. This results in a very local placement of the activator, resulting in a single component failure (e.g. integrated circuit breakdown). The examples of a post-production contamination remaining after the reflow soldering process on a PCBA surface are shown in the Figure 2.22.

![Figure 2.22: Examples of post-production flux contamination after reflow soldering process.](image)

From the corrosion reliability point of view, the residues originating from the manufacturing process and contributing to the failure occurrence in electronic devices are mainly weak organic acids (WOAs), serving commonly as active ingredients in the flux formulation. Number of acids are used in the electronics industry for liquid flux formulations and some of the commonly used dicarboxylic weak organic acids are shown in Table 2.3 together with the chemical and physical information relevant for their corrosion reliability assessment. The choice of acid for surface activation is typically dictated by e.g. solderability properties that the activator enhances.
The dicarboxylic acids in the no-clean low-solid solder flux systems are expected to undergo a decomposition/evaporation process at high soldering temperatures. The extent of flux removal from the PCBA surface depends on the type and amount of activator, thermal characteristics of a soldering profile (temperature and time), PCBA design (possible residue entrapment), etc. The thermal degradation of weak organic acids may lead to the vaporization of activators or decomposition. All acids are characterized by their decomposition temperatures (Table 2.3) where melting of the solid occurs (melting point) and the evaporation takes place (boiling point). Typically, acids of lower molar mass and odd number of methylene units in a chain (e.g. glutaric, suberic) melt at lower temperatures [71] than the acids of the lower even number of methylene units (e.g. succinic, adipic). However, the boiling points indicate that the evaporation tendency decreases with an increase of the molar mass, where it is easier to remove the activators of lower molecular weight from the PCBA surface.
The decomposition temperature and extent of acid’s removal is of a great importance for reliability assessment as the no-clean solder flux residues are expected to degrade and/or evaporate from the PCBA surface upon an exposure to the soldering temperatures. However, at high temperatures, weak organic acids were found to react with copper or copper oxide \cite{72} and form copper chelate complex compounds that require different thermal treatment for the removal from the PCBA surface. An increase of ambient temperature typically increases the reaction rate between copper and WOAs. The nature of the byproducts formed at these conditions, e.g. copper-acid complexes or acid anhydrides, differ from these of pure WOAs, and it may appear that the newly formed species exhibit higher affinity to moisture and larger susceptibility towards the corrosion occurrence.

The dicarboxylic acids used for surface activation are hygroscopic in nature and usually water-soluble up to certain extend. The hygroscopic properties vary between the acids and depend on their chemical structure. In humid environment, water from the surrounding air can be attracted by polar moieties of the dicarboxylic residues, dissolve, and dissociate them into ions, as shown below \cite{48}:

\[ R(COOH)_2 \rightarrow R(COO^-)_2 + 2H^+ \]

Typically, the more hygroscopic the solid, the lower relative humidity level needed for the initiation of moisture-acid interaction (deliquescence), and the higher its solubility in water \cite{7,73} (more detailed discussion on the specifics of deliquescence is provided in section 2.3.3.). Despite the differences in the extent of hygroscopicity between the WOAs, most of the activators attract moisture from the surroundings and facilitate water layer formation on a PCBA surface. Once the sufficient water amount is collected on the PCBA surface, the SIR drops due to the high conductivity of a formed electrolyte and the risk of corrosion occurrence increases \cite{63,74}.

The tendency of acids to dissociate (ionize) in the formed water layer determines their strength and is given by their 1st and 2nd dissociation constants (Ks). Acid’s strength is inversely proportional to the logarithm of Ks value – pKs (Table 2.3): lower value implies easier dissociation in the water film and higher conductivity of a formed electrolyte. Moreover, the solubility of WOAs in water specifies the amount of the residue possible to be dissolved at a given temperature. Both the acid strength and its solubility define the conductivity of a formed water layer: acids of high water solubility and high dissociation constants ionize easily and to a large extend into the water film, forming a well-conductive medium and increasing a risk of high leakage current upon the PCBA exposure to high humidity.

A number of acids originating from the rosin part of a flux formulation (serving as a vehicle/binder) \cite{75} can constitute a fraction of residue remaining on a PCBA surface after production. In contrast to the “resin” (which is a synthetic polymeric hydrocarbon material with a terpene-derivative based core), “rosin” is a product naturally derived from the pine trees, and consists of a mixture of few structurally closely related acids (isomers) insoluble in water (pKs values vary from 6.4 to 7.3). The acids are listed in Table 2.4 together with physical and chemical properties relevant for residue amount assessment. Depending on various factors, the ratio between the isomers in the rosin part of flux formulation can differ providing different physical properties and flux applications.
Despite the fact that rosin acids do not react with moisture due to their hydrophobicity [22], they are not considered a safe residue type in terms of potential failure appearance at a later stage of the device’s use. In practice, flux systems containing rosin (serving as a film-former and mild activator) are considered less aggressive than the water-soluble fluxes due to the encapsulation of flux residues by the rosin film at low temperatures after the soldering process. This immobilizes the ions and shields them from an exposure to humidity [22]. Rosin does not evaporate or decompose rapidly at typical soldering temperatures. Under certain circumstances, the residue encapsulation can be cracked by moisture (Figure 2.23), and allow the release of corrosive acidic residues that begin to interact with moisture and potentially lead to corrosion issues [76].

![DIRECTLY AFTER SOLDERING](image)

![AFTER EXPOSURE TO HARSH TEMPERATURE AND HUMIDITY CONDITIONS](image)

Figure 2.23: A schematic illustration of film-former cracking due to exposure to temperature and humidity.

A number of structural modifications can be performed on the rosin part for various flux purposes. Some examples of industrial modifications of abietic acid are shown in the Figure 2.24. For instance, the formation of esters with abietic acid leads to the reduced number of –OH groups and lowering of the softening point. Hydrogenation of rosin acid can improve its stability (depending on partial or full hydrogenation) and increase the compatibility with many polymers, which allows for further modifications depending on the desired properties. Dimerization of rosin increases both their softening point and stability. From a PCBA reliability point of view, modifications of the abietic acid are a concern, since the incorporation of maleic anhydride or fumaric acid into its structure is a common industrial practice. Fumaric and maleic acids are each other’s isomers (fumaric – E, trans; maleic – Z, cis) which can be differentiated due to their different physical and chemical properties (maleic is much stronger...
due to the intramolecular $H_2$ bonding occurrence, $pK_{a1,\text{maleic}} < pK_{a1,\text{fumaric}}$). Both acids contain double bonds in their structures which are more reactive than single bonds. As a result of the incorporation of maleic or fumaric acids into the rosin structure, new types of compounds with increased amount of carboxylic groups (and hence the increased acidity) are formed. The newly formed derivatives possess high boiling temperatures, and do not evaporate easily from the PCBA surface.

Figure 2.24: Examples of industrial modifications of rosin acid for various flux properties. Adapted from [77].

2.3.2. Atmospheric contamination

User environment contains a variety of contaminants (e.g. aerosol particles, corrosive gasses) originating either from the atmosphere (Figure 2.25) or formed during the device’s service life (e.g. as a result of polymer outgassing).

Figure 2.25: Micrographs (different scales) depicting a variety of atmospheric contaminants [11, 78].
Most of the particulate aerosol contaminants are hygroscopic and highly soluble in water, and, similarly to solder flux residues, can uptake moisture and enhance the formation of a conductive water film on a PCBA surface [79]. As a result, the potential corrosion occurrence in an electronic device is synergistically affected by temperature, relative humidity, and the chemical composition of atmospheric contaminants [80] that together define the extent of water film formation and its electrical properties. Examples of the field returned electronics with atmospheric contamination remaining on a PCBA surface is shown in the Figure 2.26.

![Figure 2.26: Examples of sand and dust collected inside an enclosure on a PCBA surface during the service lifetime.](image)

Apart from the risk of PCBA exposure to the particulate contamination, various gaseous pollutants (e.g. CO₂, NOₓ, SOₓ, H₂S) affect metallic parts of the assembly contributing to high leakage currents and triggering the corrosion occurrence under humid conditions [80]. High levels of sulphur gasses are present in industrial areas due to the fuel combustion sites. These are corrosive in nature or become corrosive by reacting with moisture (they transform into ions and enhance the solution conductivity). An example of power modules failure which occurred upon the exposure to harsh sulphur environment and was triggered by the electrochemical migration is shown in the Figure 2.27.

![Figure 2.27: An example of gaseous corrosion of a PCBA [5].](image)
Atmospheric contaminants form more complex chemical residues compared to solder flux systems. Considering the particles suspended in the air (with a diameter between few nanometres up to hundreds of micrometres, Figure 2.28), their chemical composition varies in time and space due to the different sources, seasons, and locations worldwide (Figure 2.29) [81, 82]. Coarse particles e.g. dust (2.5-15 µm) derive from natural sources, whereas fine particles e.g. smoke, pollution (0.1-2.5 µm) derive from anthropogenic sources [83].

The aerosol particles (dust) that are dangerous for the corrosion reliability of electronics are typically sea spray, sand or dust. These consist of sulphates, nitrates, and chlorides of ammonium, sodium, or potassium, and are considered highly hygroscopic. The highest concentration of aerosol particles is usually found in urban areas and close to the shoreline [82], which are rich in aerosols containing hygroscopic chlorides, contrary to the rural areas. In electronics, these airborne contaminants gather in a form of dust typically over a long period of service lifetime. The collection of dust takes place through the openings in the enclosure (e.g. cable feedthroughs), and can be accelerated by e.g. fans present in the device in order to provide a ventilation for heat dissipation.

Dust may act as a moisture trapping medium and therefore cause signal malfunctions in a similar manner to solder flux residues: by interacting with moisture from the surroundings and assisting the formation of water film sufficient in ions for the reduction of insulation resistance. The nature of dust interaction with humidity is determined by the chemical composition of dust, and the risk for PCBA failure increases with an increase of humidity above the critical RH level for deliquescence of dust hygroscopic particles. Deliquescence RH levels for various dust constituents are shown in the Table 2.5 and discussed in section 2.3.3. Generally, the dust composition is rather complex, and the prediction of safe humidity boundaries for electronics contaminated with dust becomes more difficult with an increase of composition complexity. A number of dust-induced failures in electronics was reported [84-87] including corrosion, mechanical (e.g. abrasion), and electrical (e.g. impedance reduction) modes. The only solution delaying the corrosion occurrence due to the dust ingress is the improvement of the equipment packaging design that can limit the ingress rate of fine dust particles, or introductions of a barrier coating (e.g. conformal coating) on a PCBA.
Figure 2.29: Variation in global distribution of atmospheric contamination: (a) composition dependence on a worldwide location, (b) amount of fine and coarse particles across the globe (grey area – no data) [88].

Several standards exist that deal with the corrosivity assessment of environmental contaminants, e.g. ANSI/ISA-S71.04 (copper corrosion rate), TOW classification (Time of Wetness, wetting time of a metal), or ISO 9223.

2.3.3. Interaction of moisture with hygroscopic contamination

The interaction between water vapour and the hygroscopic contamination occurs by means of adsorption, capillary condensation, and deliquescence (Figure 2.2). Solder flux residues or atmospheric particles which are crystalline in nature do not allow water molecules to enter into the lattice easily unless it is possible to form a crystalline hydrate [27], therefore absorption of water into the bulk is not possible. Capillary condensation and deliquescence lead to the formation of bulk water in the system which initiates the dissolution of a water-soluble residue [18] and water film formation on the PCBA surface.

Adsorption

Moisture adsorption to the PCBA surface contaminated with hygroscopic and water-soluble substances takes place prior to capillary condensation and deliquescence. Water interacting with the crystalline solid by adsorption leads to the formation of few molecular layers of water [27], but no dissolution [8, 9].

Capillary condensation

Capillary condensation occurs by similar mechanism as previously described (section 2.1.3.). The initial formation of bulk water in the surface irregularities or in between the particles is followed by deliquescence and further dissolution of the hygroscopic substance [15].

Deliquescence

Deliquescence is a moisture-induced phase transformation of the crystalline solid substance into the liquid state [7, 8, 15, 89]. Upon the initial adsorption and capillary condensation (Figure 2.30), more and more water gathers on the surface of the hygroscopic solid until the critical threshold RH value is reached. $R_{H_0}$ is the chemical potential of a saturated solution formed on the solid [89-92], which is also
called the critical relative humidity. At this point, a thin film of saturated solution forms on the surface and initiates the further dissolution of the residue [14, 15, 27, 93, 94].

![Diagram showing the increase of ambient relative humidity level and SIR reduction](image)

Figure 2.30: An overview of deliquescence phenomenon. Adapted from [7].

Every chemical reaction can be expressed in terms of the chemical potential \( \mu \) that is associated with the system, or the change of this system due to the chemical interaction with the solid. The chemical potential of pure water \( (\mu_w) \) in equilibrium with its vapour pressure is equal to [8]:

\[
\mu_w = \mu_0 + RT \cdot \ln p_0
\]

(Eq. 2.18)

where \( \mu_0 \) is the standard chemical potential. Comparing this system to the saturated aqueous solution formed on the deliquescing solid (at the same temperature), the vapour pressure above the saturated salt solution \( (p_{solution}) \) is lower than the pressure above pure water \( (p_0) \) [16, 90]. Therefore, the difference between the chemical potentials of both systems is expressed as:

\[
\mu_{solution} - \mu_w = RT \cdot \ln \left( \frac{p_{solution}}{p_0} \right) = RT \cdot \ln a_w = RT \cdot \ln \frac{RH_0}{100}
\]

(Eq. 2.19)

where \( \mu_{solution} \) is the chemical potential of a saturated solution formed on the solid. The lower vapour pressure above the saturated film solution is a consequence of high water solubility of the residue that causes a reduction in the vapour pressure of the saturated solution [8, 95] which is a state of lower thermodynamic activity (more favourable) [7]. The developed difference in pressures acts as a gradient and a driving force for water vapour condensation onto the solid once the critical relative humidity \( RH_0 \) (lower vapour pressure) is exceeded [14, 16, 92].

Upon the condensation of water and the water film build-up, the vapour pressure of a growing film raises to the level of a vapour pressure in the surroundings [8, 96], and the continuous accumulation of water eventually leads to the dissolution of remaining solid substance while maintaining the vapour pressure of the film at \( RH_0 \). At this point, if the substance remains on a PCBA surface, the SIR decreases as the amount of water collected increases. The driving force for the water vapour to condense further into the solution will remain as long as the undissolved substance is still present in the system and the ambient RH is higher than \( RH_0 \). Eventually, the complete solid dissolution occurs. The saturated solution undergoes a certain degree of dilution and once the vapour pressure over the solution reaches the atmospheric value – the equilibrium with the atmosphere is reached [8, 14, 90, 97]. The water activity \( a_w \) of the solution on the crystal remains constant during the deliquescence process if the kinetics of
moisture sorption does not exceed the dissolution rates and if the solution is kept at the saturation level throughout the process [10]. A typical moisture sorption profile, unique for each type of a deliquescent substance, is shown in the Figure 2.31.

Figure 2.31: The appearance of moisture sorption profile of a hygroscopic substance upon three water-solid interactions types. Adapted from [14, 27].

Deliquescence relative humidity depends on the type of contamination (its hygroscopicity, solubility, arrangement in the crystal lattice, number of species generated upon dissociation, which reduces the mole fraction of water, solute activity coefficient) and temperature. Many compounds of higher solubility tend to exhibit a deliquescent behaviour at lower RH₀ levels [7]. It was proven that an increase of ambient temperature raises the solubility of most chemical compounds, therefore effectively lowers the critical relative humidity for deliquescence (Figure 2.32) [92, 94, 95, 97-101]. However, an increase of ambient temperature acts inversely and decreases the solubility (therefore increases the RH₀) of the compounds with a negative heat of solution, e.g. some anhydrites [27], though not the weak organic acid activators. As derived from Clausius-Clapeyron equation in [8], the deliquescence relative humidity RH₀ (or water activity a₀) decreases with an increase of temperature (T):

\[
\frac{\partial \ln a_w}{\partial T} = -\frac{N \Delta H_s}{R T^2}
\]

(Eq. 2.20)

where \( N \) is the solubility \( \frac{\text{mol of substance}}{\text{mol of } H_2O} \), and \( \Delta H_s \) is the heat of solution. If the substance exhibits a positive heat of solution (increased solubility with an increase of temperature), the \( a_w \) and RH₀ decrease with the increase of temperature [8, 94]. The extent of the RH₀ reduction is dependent on the magnitude of the heat of solution [102].

Figure 2.32: Influence of temperature on the shift of critical RH for deliquescence [94].
Based on the substance solubility data, it was found that the critical relative humidity level of the water vapour pressure over a solution of deliquescent substance ($RH_0$) can be calculated at any temperature using the following equation [103]:

$$\frac{RH_0}{100} = \exp\left(-\frac{\beta \cdot N_i}{59.5}\right)$$  \hspace{1cm} (Eq. 2.21)

where $\beta$ is the amount of ions formed during the dissociation process.

Deliquescence is a thermodynamic property of the crystalline water-soluble species and characteristic for each compound. From the climatic reliability point of view, the critical RH level for ionic residue deliquescence is one of the most important parameters determining the safe humidity boundary for the operation of the electronic device to prevent the surface insulation resistance reduction and corrosion occurrence. An overview of RH levels for deliquescence of various contaminants typically found on a PCBA surface, e.g. solder flux residues, salt deposits, or dust particles, are given in the Table 2.5.

Table 2.5: Summary of deliquescence data for 25°C of typical contaminants found on a PCBA surface.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>RH for deliquescence</th>
<th>SOLDER FLUX ACTIVATORS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic acid</td>
<td>~99.99$e$; 99.9$b$; 99.9$c$</td>
<td></td>
</tr>
<tr>
<td>Suberic acid</td>
<td>&gt;98$e$; 99.8-99.9$b$; 99.4-99.8$h$; 99.8$g$; 99.6$e$; -99.9$c$; ≥99$s$</td>
<td></td>
</tr>
<tr>
<td>Adipic acid</td>
<td>&gt;98$e$; 98; ~99.9$c$; 99.1$g$; ≥98$s$; 99.5±1.8$b$; 97.6$g$; ≥94-98.8$h$; 98.85$k$</td>
<td></td>
</tr>
<tr>
<td>Succinic acid</td>
<td>97.3$i$</td>
<td></td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>83-89$p$; 84$d$; 83-88$q$; 88.2$g$; 89-99$s$; 90.1±1.8$p$; 88.9$d$; 85$p$; 83.5-88-88.5$q$; 87.8$b$; 85±5$p$; 89±2$e$; 88.3$n$; 83±4 / 80-85$v$</td>
<td></td>
</tr>
<tr>
<td>Glutaric acid</td>
<td>79$p$</td>
<td></td>
</tr>
<tr>
<td>Citric acid</td>
<td>75-84$q$; 86$q$; 80.5$q$; 78$p$; 72$q$; 75$q$</td>
<td></td>
</tr>
<tr>
<td>DL-Malic acid</td>
<td>INORGANIC SALTS</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>76$e$, 75$f$</td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>84$e$, 83.3$g$, 91$g$; 85±1$m$</td>
<td></td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>44$e$, 16$i$; 32$e$</td>
<td></td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>29$q$; 32.3$b$; 19.2-24$m$; 28.1$k$</td>
<td></td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>77.2$r$, 76.5-77.3$p$; 78.5$m$</td>
<td></td>
</tr>
<tr>
<td>Na$_2$NO$_3$</td>
<td>74$f$; 72.4$q$; 74.3±0.4$p$</td>
<td></td>
</tr>
<tr>
<td>NH$_4$NO$_3$</td>
<td>59.4$k$; 61.8$p$</td>
<td></td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>84$q$; 84.2±0.4$v$</td>
<td></td>
</tr>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>79$s$, 81.3$r$; 79.8$e$</td>
<td></td>
</tr>
<tr>
<td>NaHSO$_4$</td>
<td>52$r$</td>
<td></td>
</tr>
<tr>
<td>NH$_4$HSO$_4$</td>
<td>40$r$</td>
<td></td>
</tr>
<tr>
<td>(NH$_4$)$_2$H(SO$_4$)$_2$</td>
<td>69$e$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ - [104]; $^b$ - [105]; $^c$ - calculated in [105] for the range 20-40°C; $^d$ - [106]; $^e$ - [73]; $^f$ - [107]; $^g$ - [68]; $^h$ - [108]; $^i$ - [109]; $^j$ - [110]; $^k$ - [66]; $^l$ - [111]; $^m$ - [112]; $^n$ - [113]; $^o$ - [114]; $^p$ - [100]; $^q$ - [115]; $^r$ - [116]; $^s$ - [117]; $^t$ - [118]; $^u$ - [119]; $^v$ - [120]; $^x$ - [91]; $^y$ - [121]; $^z$ - given in [82]; $^\gamma$ - [11].
Deliquescence phenomenon can be detected by any method sensitive enough for phase transformation [7]. Among many, the typically employed techniques are dynamic gravimetric water vapour uptake measurement at constant temperature that allows for a generation of moisture sorption isotherms [122, 123] (e.g. using the electrodynamic balance) [97]. Another method relies on the measurement of water vapour activity above the saturated solution equilibrated with the solid and water phase (chilled mirror measurement of the dew point of the water vapour, the use of capacitance sensor/probe, water activity meter) [14, 89, 94, 97, 122]. Moreover, the visual assessment of deliquescence was employed using a microscope stage with temperature and humidity control [93, 123]. Impedance [101], conductivity [124], infrared and Raman spectroscopy [125-127], gravimetric measurements by QCM [128], and hygroscopic growth measurements are among the mostly used as well. More sophisticated methods include the RH-controlled X-Ray diffraction, rapid single-particle mass spectrometry, or laser light scattering [27].

**Deliquescence lowering**

The presence of more than one deliquescent component in the flux system or a mixture of hygroscopic salts originating from the environmental contamination creates a larger threat to the overall reliability of the electronic devices compared to the single-substance based systems. In fact, blends of deliquescent species are more susceptible for interactions with the surrounding moisture than either of their individual components [14]. Such mixtures deliquesce at the so-called “mutual RH level” (RH<brask>mix), lower than the deliquescence point RH<brask>0 of either of the single constituents [15, 89, 93, 97, 122].

The explanation of deliquescence lowering phenomenon can be supported with a phase diagram (Figure 2.33) for two deliquescent substances A and B which are in equilibrium with their aqueous solutions and the vapour phase. In a system saturated with the substance A, the solution exhibits water activity <brask>aw equal to the deliquescent point of the constituent A (e.g. RH<brask>0,A = 85%). At this point, the mole fraction of the substance B (<brask>XB) in the solution A is equal to 0. Upon an addition of the component B to the system, the solubility limit of the substance A and its <brask>aw decrease along the line 1. As proved by Raoult’s law, in an ideal solution the relationship between the solute concentration and the vapour pressure is inverse: the mole fraction of a solid affects the fraction of solvent molecules in the solution that can escape to the gas phase (definition of the vapour pressure). Therefore, higher mole fraction of the solid B accounts for an increase of molar concentration and higher proportion to the total vapour pressure, which results in a decreased ability for water molecules to evaporate into the vapour phase [27]. Similarly, if disturbing the saturated solution of the solute B of the initial activity equal to 0.78 (RH<brask>0,B = 78%) with an addition of the substance A, the solubility limit of the substance B and the water activity of the solution B decrease along the line 2. At the intersection of both solubility limit lines, both deliquescent substances reach a specific saturation point (marked with a yellow dot) and precipitate together [8, 93, 129].

---

1 In particular thermodynamic conditions (temperature, pressure), the saturated solution of a substance does not change its concentration. If no changes of the thermodynamic conditions occur, the solute does not precipitate and the solution is saturated with the substance – the maximum solubility is reached. In such saturated solution, the dynamic equilibrium between the solute and the solvent is developed, and the rate of dissolution reaction is equal to the rate of precipitation. For the particular reaction:

\[ A + 4B \rightleftharpoons 3C + 2D \]

the expression for the equilibrium constant is:

\[ K_c = \frac{[C]^3 \cdot [D]^2}{[A] \cdot [B]^4} \]
From the thermodynamic point of view, the Gibbs-Duhem equation explains this phenomenon describing the changes in the multicomponent system with the use of chemical potentials of all constituents at constant temperature and pressure, and assuming the equilibrium between the species and their electrolytes (saturation) [7, 8]:

$$ (n_w d\mu_w) + (n_A d\mu_A) + (n_B d\mu_B) = 0 $$

(Eq. 2.22)

where $n$ is the number of moles of water ($w$), solute $A$ ($A$), and solute $B$ ($B$), $\mu$ is the chemical potential of water ($w$) and ingredients $A$ ($A$) and $B$ ($B$). In the ternary system of $A$-$B$-water described above, the chemical potential of solution $A$ ($\mu_A$) remains constant until the second substance is introduced, which brings an additional source of chemical potential to the system ($\mu_B$). Therefore, in response to the system disturbance by the introduction of a second component, the chemical potential of water ($\mu_w$) and a chemical potential the solution $A$ ($\mu_A$) decrease upon the continuous addition of solute $B$ to the electrolyte $A$ [27] which directly influences the $a_w$ [10].

The ratio between solutes $A$ and $B$ at this specific water activity $a_{w,\text{mix}}$ (“mutual deliquescence RH” $\text{RH}_{0,\text{mix}}$) is called the eutonic composition [130]. As seen in the Figure 2.33, $\text{RH}_{0,\text{mix}}$ is always lower than the deliquescence $\text{RH}_0$ of either of the individual constituents in the system. The vapour pressure above the mixture solution at equilibrium is therefore also lower than the vapour pressures above individual saturated solutions $A$ or $B$ [8] unless a chemical reaction occurs between the components that exhibits higher equilibrium vapour pressure [7].

If the RH level of the environment is higher (Figure 2.33, region a) or lower (region d) than the $\text{RH}_{0,A}$ and $\text{RH}_{0,B}$, the substances $A$ and $B$ deliquesce and dissolve (region a), or stay as solids (region d), respectively. Below the lines 1 and 2 in the regions b and c, one of the solutes exists in excess and remains as solid, whilst still saturating the solution up to the possible extend. For instance, below the line 1, the solute $A$ saturates the solution $A+B$ and the residual amount exists as undissolved solid. The small fraction of the solute $B$ is completely dissolved in the solution at this point [7, 92, 93]. It is evident that the presence of even small amount of another hygroscopic component in the system can shift the deliquescence point and significantly lower the RH level for residue deliquescence.
The RH\textsubscript{0,mix} is dependent on the composition of the mixture, but not the ratio between the components [8, 14, 97]. The deliquescence RH of blends of substances is expected to decrease with an increase of the number of the constituents [68]. However, often the largest differences in the RH\textsubscript{0,mix} are observed between the single component and its binary mixture, whereas the difference is less pronounced as the number of constituents in the blend increased [97]. The amount of species dissolving into the water layer depends on the blend composition as well. If the composition is equal to eutonic composition, both solids dissolve completely at RH\textsubscript{0,mix} [93, 97, 123]. If the more hygroscopic component exists in a small amount, the dissolution of a less hygroscopic one takes place up to a small extent [97] until the RH level is raised sufficiently for the dissolution [8]. Initially only the eutonic composition deliquesces above the RH\textsubscript{0,mix} [10, 14]. The examples of deliquescence lowering are shown for moisture sorption isotherms of single components and their mixtures in the Figure 2.34.

![Figure 2.34](image)

Figure 2.34: Examples of deliquescence lowering shown for individual components and mixtures of two components [14, 123].

Figure 2.35 shows two examples of deliquescence lowering phenomenon depicted in the micrographs of two crystals (substances A and B) placed separately and in a physical contact with each other (simulation of the mixture). The crystals arranged separately remain intact at the mutual deliquescence point (RH\textsubscript{0,mix}) whereas the crystals placed in a contact deliquesce at the same RH level.

![Figure 2.35](image)

Figure 2.35: The visualization of deliquescence lowering phenomenon. Adapted from [8, 92].
The concept of deliquescence lowering is widely known and described in the food industry [89, 92, 93, 97, 122], where the typical food ingredients (sugars, organic acids, salts, vitamins) are tested towards assessment of their chemical and physical stability. Moreover, the pharmaceutical industry [8, 123] uses and expands this knowledge towards assessment of the drug’s possible degradation pathways or the proper choice/design of packaging. Environmental sciences broadened the existing expertise, which is currently being used for testing of a variety of atmospheric aerosols [109, 129-133], containing many of the dicarboxylic acids used in the electronics fluxing technology, for the determination of their composition and resulting hygroscopic growth at different climatic conditions and seasons [134]. Testing of the typical WOAs blends was reported in the literature [68, 135], however the concept is not yet recognized in the electronics industry for the assessment of the potential corrosiveness of flux systems based on blends of activators.

The estimation of the deliquescence relative humidity of the mixture (RH$_{0,mix}$) can be carried out using different approaches: Zdanovskii-Stokes-Robinson equation, Ross equation, and Raoult’s law. Among them, the one proposed by Ross in 1975 [7, 8, 14, 94, 136] is widely used and often meets the expected values. Derived from the Gibbs-Duhem equation [97], Ross equation assumes the same substance activity in the mixture as it exists in its individual solution. The water activity $a_w$ of the saturated solutions of each individual component in the mixture contribute to the overall $a_{w,mix}$ of the mixture:

$$a_{w,mix} = (a_{w,1})_1 \cdot (a_{w,2})_2 \cdot (a_{w,3})_3 \ldots (a_{w,n})_n$$ (Eq. 2.23)

where $a_{w,mix}$ is the water activity of the solution containing a mixture of different solids, and $a_{w,0}$ is the water activity of saturated solutions of solutes 1, 2, 3 etc. Ross equation assumes the presence of diluted solutions, ideal conditions, independent contributions of each component, and no interactions between the solutes [27, 96]. Ignoring the kinetic effects, Ross equation can be expressed in terms of the deliquescence relative humidity of each component in the mixture, assuming that $a_{w,0}$ is approximately equal to RH$_0/100$ [8]:

$$\frac{RH_{0,mix}}{100} = \frac{RH_{0,1}}{100}, \frac{RH_{0,2}}{100}, \frac{RH_{0,3}}{100}, \ldots, \frac{RH_{0,n}}{100}$$ (Eq. 2.24)

where RH$_0$ is the deliquescence relative humidity of solids 1, 2, 3 etc.

Moreover, Ross proposed an introduction of the empirical interaction parameter $\chi$ that represents the contribution of solute-solute interactions to the overall $a_{w,mix}$ the extend of non-ideality of the solution, and the deviation between the measured and calculated values [8, 27, 97, 136]:

$$\chi = \frac{a_{w,mix(measured)}}{a_{w,mix(calculated)}} = \frac{RH_{0,mix(measured)}}{RH_{0,mix(calculated)}}$$ (Eq. 2.25)

where the value of 1.0 for $\chi$ indicates no deviation. The values between 0.96-1.28 imply a rather good agreement between the experimental and calculated data, the trend decreasing if $\chi$ deviates strongly away from this range, indicating the presence of solute-solute interactions [89]. Ross equation was found to successfully predict the mutual RH point for binary systems [7] with the decreasing ability for correct estimations as the number of substances in the mixture increases, ranging the $\chi$ values from 0.84-2.0 [8, 89, 97]. This is due to the fact that in the blend of ingredients, every component should be in a physical contact with all the other constituents of the mixture [10] for the thermodynamics of a multi-component system to take place, which in practice is a difficult phenomenon to simulate if the number of ingredients increases [27, 94].

Furthermore, the common-ion effect was found to cause deviations for predicting the RH$_{0,mix}$ though the Ross equation was modified and developed in order to compensate for this effect [10, 27]. According to Le Chatelier’s principle, in the blend of compounds sharing the same ion, the common-ion will compete while equilibrating in the solution. Therefore, at the equilibrium state, the solution will be...
saturated with the common-ion while the solubility of counter-ions will decrease due to the lack of ability to dissociate at the same concentration\(^2\). The solubility of the less soluble solute decreases even further as a result of the common-ion presence [10]. Due to the overall decreased solubility, less ions will be dissociated in the solution and therefore the vapour pressure will be higher according to Raoult’s law [27]. This effect can cause a diminishing of deliquescence lowering, indicating that the obtained \(\text{RH}_{\text{0,mix}}\) values are higher (so is the vapour pressure) than those predicted by Ross equation for the blends sharing a common ion, especially of highly soluble ingredients [10]. An example is shown in the Figure 2.36 where the obtained \(\text{RH}_{\text{0,mix}}\) for NaCl-KCl mixture is higher (\(a_w = 0.72\)) than predicted (\(a_w = 0.64\)).

![Figure 2.36: An example of common-ion impact on deliquescence lowering in binary mixtures [10].](image)

The deliquescence lowering phenomenon is dependent on the type of the solutes. The chemical structures define their solubilities, which will directly determine their dissolution abilities once mixed together. The substance morphology was found to influence the deliquescence point of the ingredients [137]. Moreover, as in the case of single-ingredient based products, temperature increases the particles mobility that directly impacts their solubility [94, 95, 97, 100, 136]. From the corrosion reliability point of view, it is vital to study the effect of varying mixtures types e.g. in flux formulations, as the initially assumed safe humidity regimes may be shifted if any hygroscopic ingredient exists even in trace amounts in addition to the major one. Many additive compounds (polyglycols, non-ionic surfactants) present in flux formulations are known to contribute to low critical RH [22].

**Efflorescence**

Contrary to deliquescence, efflorescence is a process of water expulsion from the material and its induced crystallization (reverse phase transition) that takes place upon the decrease of ambient relative humidity level below the deliquescence \(\text{RH}_0\) (desorption) [7, 8, 97]. Adsorption and desorption are not fully reversible [13]. Crystallization of the substance is usually accompanied by an appearance of the hysteresis. This is shown on the typical moisture sorption-desorption isotherm in the Figure 2.37 where the reverse desorption branch lies above the forward adsorption branch. The presence of the hysteresis implies that the complete water removal from the particles occurs at lower RH levels than their

\(^2\) Only a specific maximum amount of each ion can exist in the saturated solution according to the solubility constant (\(K_s\)) equation:

\[
K_s = [\text{Cation}^+][\text{Anion}^-]
\]

where the multiplied concentrations of cations and anions cannot exceed the \(K_s\) value.
deliquescence due to capillary condensation effects, kinetic effects etc. [7, 8, 13, 91, 138, 139]. The explanation for the hysteresis occurrence comprises the ink bottle theory, the molecular shrinkage theory, the capillary condensation, and the swelling fatigue theory [12, 13], however their detailed description is beyond the scope of this thesis.

Figure 2.37: An example of absorption-desorption isotherm appearance with deliquescence occurring at 79.5\%RH and efflorescence at 35\%RH [91].

It was found that for atmospheric particles, crystallization may occur at higher relative humidity values due to the presence of insoluble impurities that induce crystallization at lower supersaturations [91], or efflorescence may not occur at all due to the water retention [140]. Efflorescence may change the crystal structure and therefore the properties of the solid.

Various types of moisture sorption isotherms were introduced. IUPAC classified and described 6 general types of isotherms [27] which are presented in the Figure 2.38. The curve appearance depends on the type and hygroscopicity of the material, sorption mechanism, and types of water-solid interactions taking place upon an increase of ambient humidity level.

Figure 2.38: Types of moisture sorption isotherms generated and characterized by IUPAC [27].

Type I, a Langmuir monolayer type, consists of sharp rises of the isotherm at specific RH apart from maintaining a plateau (convex shape, limiting values) as $a_w (p_w/p_0)$ increases to 1, characteristic for microporous solids of relatively small external surfaces (f.e. molecular sieves, porous oxides). Type II is in the form of sigmoidal curve indicating of H-bonding interactions at the surface of non-porous or microporous amorphous solid: monolayer (first inflection point) or multilayer adsorption. Type III
exhibits limited moisture sorption below the critical RH, above which a gradual curvature is formed, typical for deliquescent crystalline ingredients. The type IV exhibits a typical adsorption/desorption hysteresis loop associated with capillary condensation with the limiting water uptake at high $p_w/p_0$. The initial part of the curve is associated with the monolayer-multilayer adsorption (similarly to type II) and usually exhibited by mesoporous materials. Type V is a rather seldom, Brunauer-Emmett-Teller (BET) multilayer type of adsorption isotherm, related to type III, and characteristic for porous adsorbents. Type VI represents stepwise multilayer adsorption on a uniform non-porous surface [12-14, 141].

Similarly, various types of hysteresis loop appearance were found and described [141]. The type strongly depends on the type and state of the material, external conditions, etc [12]. Some examples are shown in the Figure 2.39.

![Different types of hysteresis loops](image)

Figure 2.39: Different types of hysteresis loops [141].
2.4. EFFECT OF CLIMATIC CONDITIONS

Today, the electronic devices are used in a number of applications and a variety of locations worldwide, therefore there is a wide range of climatic conditions that the electronics can experience. Typically, the components are highly prone to corrosion failure modes upon exposure to high humidity levels (e.g. seashore area). However, the water film formation and the subsequent malfunction can take place anytime during application at any climatic conditions due to the occurrence of unpredictable transient conditions as well as the PCBA surface characteristics [120, 142].

Ambient temperature and relative humidity define the dew point (DP) temperature, which is the PCBA temperature (lower than ambient temperature) at which water vapour starts to condense on its surface and forms a water film (Figure 1.2). The phenomenon is related to the fact that with a decrease of temperature, the air capacity to retain water vapour is reduced as well, which results in condensation of any excess moisture. Figure 2.40 shows the diagram the DP can be read from.

![Figure 2.40: Determination of dew point based on Magnus equation [143].](image)

Relative humidity and temperature cycles in the environment fluctuate throughout the day and throughout the seasons, and are different for different global locations. Depending on the location, the temperature difference between the ambient temperature and dew point temperature required for the condensation on a PCBA surface varies. For higher humidity conditions, the difference is small (e.g. for ambient 25°C/90%RH, the dew point is 23.2°C), which indicates that the dewing is highly likely to occur as the surface temperature is reduced only by ~2°C. However, even a slight reduction of PCBA temperature can lead to a thick water film build-up if sufficient time is given for it, therefore there exists an importance of the time interval of transient condition in determining the reliability. On the contrary, in dry environments (e.g. 25°C/40%RH) the DP temperature is ~10.5°C, which indicates that the PCBA surface must be reduced by ~15°C in order to create conditions for a condensation. Therefore, problems typically arise in areas of high temperature and high humidity where the air moisture content (AH) is high.
The temperature fluctuations occurring on a daily basis (e.g. due to warm day/cold night cycle) is another factor that contributes to the increased risk of thick water film formation. Despite the design and the microclimate inside an electronic device, the products typically cannot rapidly respond to the ambient temperature changes (Figure 2.41) due to the thermal mass, and the transient conditions are created inside an enclosure.

![Figure 2.41: Schematics of a typical temperature delay between PCBA and outdoor, contributing to condensation occurrence.](image)

These transient conditions are the most critical moment for the device robustness. If the device is switched on before the equilibration of ambient and enclosure temperatures is reached, the intermittent or permanent failures are likely to occur. The critical factors for condensation occurrence are the external climatic conditions, microclimate inside an enclosure, enclosure design, PCBA design, or thermal capacity of materials and components, and the presence of hygroscopic residues [144].
2.5. EFFECT OF ENCLOSURE DESIGN

The faulty design or improper choice of materials can facilitate an ingress of water vapour inside the device and assist the water film formation of a PCBA surface. The electronic devices are typically enclosed in the casing intended to protect the PCBA from the external contamination ingress. For the protection against moisture ingress, the enclosures contain openings for a free moisture flow, or are relatively tight. However, the latter solution may create a large time delay for the equilibration between the exterior and interior temperatures. One of the design solutions believed to be the most efficient in terms of protection against the moisture ingress and water layer formation on a PCBA surface is a hermetic sealing of the enclosure. However, this solution is costly and may create an even larger threat if the moisture is released from the components (e.g. FR-4 laminate) and cannot escape from the hermetically sealed casing. Typically, the enclosures are made from polymer materials, however polymers are permeable to moisture [145].

A number of design solution was introduced for a decrease of the risk of moisture condensation on the PCBA surface. Many devices contain desiccant materials that are porous and prone to absorb high amounts of moisture from the air. However, they possess a limited sorption properties and lifetime. Thermal solutions are another way to reduce the moisture accumulation inside the device. Self-heating may prevent the humidity condensation and is cost-efficient. Peltier elements may be introduced to the design either for cooling, collecting and removing the moisture from the interior of the device, or for heating up the air inside an enclosure [146].
2.6. CLIMATE AND CONTAMINATION INDUCED FAILURES IN ELECTRONICS

This chapter briefly discusses the mechanisms of typical failure modes occurring in electronics where the water film formation due to humidity has a major impact.

2.6.1. Degradation of surface insulation resistance (SIR) and high current leak

Surface insulation resistance is the material property, which is the electrical resistance between two conductors separated by dielectric material [22, 147], and is inversely proportional to the leakage current. The failures related to SIR degradation usually result from the water film formation due to the external climatic conditions (e.g. high humidity, temperature variations) or factors specific to the PCBA (e.g. surface features, presence of hygroscopic ionic contamination) [22]. The SIR reduction causes a majority of failures found in field returns and promotes the occurrence of corrosion phenomenon on the PCBA due to the fact that the SIR degradation is impacted by the electrochemical activity in the water layer (faradaic reactions).

Although thin water layers form on all clean surfaces even at low humidity levels (~60-70%RH), the resistance of surface remains high and the leakage current measured for these surfaces is typically below nA level. Such conditions typically do not influence the operational performance of the circuit as the thin water film is itself resistant [22]. However, in the presence of ionic residues remaining on a PCBA surface and RH levels above the critical RH for residue deliquescence [22], or upon water vapour condensation on the clean PCBA surface (due to e.g. day/night temperature cycles), leakage current significantly increases and SIR decreases due to the formation of thick water layer of high conductivity. If the device is operating under high voltage, this can lead to further SIR reduction. An exposure of the device to such detrimental conditions for a prolonged period of time can cause deteriorations in materials properties and an increased risk of failure occurrence.

Figure 2.42: SIR reduction: (a) effect of different climatic conditions and WOAs [148], (b) effect of different surface finishes (flux testing at 65°C/85%RH) [149], (c) effect of condensing conditions [80], (d) effect of TBH testing [150].
The extent of surface insulation resistance degradation depends on the contamination (type and amount), climatic conditions, temperature variations, potential bias, and PCBA type and design (e.g. spacing between the two conductors, surface finish) [75, 147, 151]. The influence of various factors on SIR drop (leakage current increase) is shown in the Figure 2.42. The evaluation of the effect of different parameters on surface insulation resistance is typically performed by SIR measurements according to different standards (more detailed description in section 2.7.1.).

The analysis of field returns for a verification of failures caused due to SIR reduction is difficult and often impossible. If the circuit malfunctioned due to water film formation, which only caused an increased leakage current but left no evident physical failure, it is problematic to trace during the PCBA inspection. Evaluation of the root cause in such situations requires a good knowledge about the device’s manufacturing and storage conditions, field exposure conditions, enclosure design, PCBA design, potential bias distribution over the assembly, PCBA cleanliness, etc.

In order to prevent significant SIR reduction and decrease the risk of corrosion occurrence, additional steps to the PCBA manufacturing process can be included, e.g. conformal coating application or post-soldering cleaning process. However, application of the conformal coating on a contaminated PCBA can adversely impact the reliability of the device as, in a long term, the effect of residue and humidity might cause coating delamination, blistering, and degradation of the protective coating (Figure 2.52), which, in the end, does not prevent moisture from reaching the PCBA surface [152]. Moreover, the application of a suitable cleaning process is difficult due to the challenges regarding the component compatibility with the chemicals constituting the cleaning liquids, or the possibility of the residual cleaning agents inducing corrosion of the metallic parts of a PCBA. Further, every extra process in PCBA production increases the cost of the device manufacturing and therefore, typically, the industry rather avoids incorporating additional safety measures.

2.6.2. DC Electrochemical migration (ECM) and dendrite formation

The electrochemical migration phenomenon is a growth of metallic filaments of dendritic shape across the two oppositely charged conductors on a PCBA surface in the presence of a conductive electrolyte and under the applied DC voltage bias. It is one of the most common failures reported in the electronics industry for devices operating under highly humid or condensing conditions. The phenomenon is associated with an initial SIR reduction (section 2.6.1.), facilitated by high humidity or contamination presence, which is followed by the ECM resulting in electrical shorts [22].

ECM occurs when two closely spaced conductors (e.g. component terminals, pins, etc.) are bridged by a conductive medium (e.g. water layer, Figure 2.3) which allows each of the electrodes to develop a solution potential under the applied DC bias. Typically, the PCBA electrode materials susceptible for ECM are Sn, Cu, Ni and Ag, and the bridging electrolyte is the water layer. Gold, platinum, and palladium conductors can be oxidized only in the presence of elements that can form strong complexes with the metal ions, e.g. Cl, Br, or I [22]. The hygroscopicity and solubility of a residue remaining between the electrodes defines the water film thickness and determines its capability to act as a good electrolyte for electrochemical processes. The electric potential difference developed between the two conductors in contact with an electrolyte is a driving force for the corrosion occurrence [153] which is initiated by an anodic dissolution at the positively charged electrode (Figure 2.43):  

\[ A(+) : M \rightarrow M^{n+} + ne^- \]  

(Eq. 2.26)
Metal ions migrate through a bridging medium (water film), under the influence of the electric field due to the potential bias between the two points, and deposit on a negatively charged cathode by the metal ion reduction process:

\[ C(-): M^{n+} + ne^- \rightarrow M \]  
(Eq. 2.27)

![Figure 2.43: Mechanism of dendrite formation. Adapted from [75, 154].](image)

The reduced metal forms as dendritic filaments due to the higher electric filed at the end of dendrite causing further deposition of metal ions. Upon a continuous dissolution of anode, ion migration, and their deposition at the cathode, the dendrites grow from cathode to anode. If the dendritic filament grows large enough to reduce the gap distance between anode and cathode, it can eventually result in conductor bridging and short circuiting. However, only a part of the current will be used for the metal reduction process at the cathode as other cathodic reactions can also take place due to the presence of water molecules and oxygen (equation 2.28 for oxygen reduction, equation 2.29 for dissociation of water):

\[ C(-): O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]  
(Eq. 2.28)

\[ C(-): 2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^- \]  
(Eq. 2.29)

At the anode, water oxidizes dissociating into hydrogen ions and oxygen:

\[ A(+): 2H_2O \rightarrow O_2 \uparrow + 4H^+ + 4e^- \]  
(Eq. 2.30)

Water dissociation at both anode and cathode, and the oxygen reduction at the cathode can significantly change the local pH levels due to the production of hydrogen and hydroxyl ions. The cathodic dissociation of water producing hydroxyl ions leads to the development of alkaline pH at the cathode, whereas the anodic water dissociation produces hydrogen (hydronium H_3O^+) ions which creates an acidic pH at the anode (Figure 2.44). Moreover, the hydrolysis of metal ions (e.g. tin) occurs where the hydrogen ions are additionally generated at the anode, enhancing the acidic nature of the electrode:

\[ A(+): Sn^{4+} + 4H_2O \rightarrow Sn(OH)_4 + 4H^+ \]  
(Eq. 2.31)

At a substantial water film thickness, this local pH change influences the possibility of electrochemical migration to occur due to the altered stability of the dissolved metal ions in the water layer [47]. Alkalization at the cathode can facilitate the process of hydroxide precipitation by increasing the hydroxyl ion concentration. The formation of neutral metal hydroxides disrupts the electrochemical metal migration – the hydroxides do not migrate under the electric field [53].
CHAPTER 2

Figure 2.44: The pH gradient development on a chip component under potential bias. The droplet coloration indicates the pH differences between anode (low) and cathode (high) as shown by the arrows [53].

The presence of ionic flux residues dissolved in the water film was found to increase the water layer conductivity which results in higher leakage current, however does not cause the ECM. Dust contamination on the component surfaces leads to the electrochemical migration, however if present together with flux residues, it causes more severe corrosion of the components [53].

Figure 2.45: Examples of ECM occurrence on a PCBA surface: (a) SEM image of dendritic growth between two capacitors [6], (b) optical image of ECM occurrence due to flux contamination remaining between electrodes of the SIR test coupons, (c) optical microscopic image of dendrite formation an electrode tip [155], (d) post-production contamination-induced dendrite growth between the pins, (e) and (f) dust-induced ECM occurrence during service life.

Factors influencing the occurrence, nature, and time for ECM are similar to the factors affecting the SIR reduction [22, 152, 156-160] such as: climatic conditions (temperature, humidity), contamination facilitating metal dissolution (type and amount), potential voltage, pH, solubility of the species formed upon ECM, PCBA design (conductor material, surface morphology, geometry/configuration, and spacing), or substrate composition (e.g. polymeric laminate, ceramics). Some examples of ECM occurrence between the conductors on a PCBA surface are shown in the Figure 2.45.
2.6.3. **AC Electrochemical migration (ECM) and dendrite formation**

The failure due to electrochemical migration caused by an alternating current is occurring seldom in electronics, therefore its features are yet not well known. However, in principle, the ion migration phenomenon develops as in the case of DC-induced ECM.

The schematic drawing shown in Figure 2.46 depicts the migration development. Due to the formation of water layer and AC voltage of a low frequency applied to the system, two closely spaced electrodes can develop a temporary potential, which defines one of them to be anode and the other one to be cathode. Subsequently, atoms from a positive electrode oxidize forming ions (Figure 2.46, t₀) which migrate through the electrolyte towards the cathode (Figure 2.46, t₁). Due to the characteristics of an AC current, the polarity reverses at a certain point (Figure 2.46, t₂) and the formed cations may migrate back to the electrode they originated from – now cathode (Figure 2.46, t₃ and t₄). Possibly, some of the formed ions will continue to migrate towards the originally developed negative conductor (Figure 2.46, t₂) due to the inertia [75].

![Figure 2.46: Schematics of a theoretical AC ECM occurrence. Adapted from [75].](image)

The dendrite growth resulting from the ion migration was reported to occur in systems at frequencies lower than 10Hz and in the presence of DC offset [75], which creates conditions for the conductors to develop a potential for a sufficient period of time. An example of ECM is shown in the Figure 2.47 (a) where the dendrite formation occurred under the AC conditions at extremely low frequencies, however in the presence of 2 V DC offset. The double exposure to DC peak voltage was stated to be a cause of a dendritic growth between the electrodes (Figure 2.47 (b)) as the AC/DC voltage applied to the system resembles more the traditional DC pulse voltage [75, 161].
Conductive anodic filament (CAF) formation

Conductive anodic filament (CAF) formation is a PCB failure related to moisture ingress into the PCB base material and voltage-induced electrochemical reactions resulting in the corrosion occurrence between embedded copper conduction lines and plated via holes. Similarly to the ECM where the electrode bridging takes place due to metal dendrite formation [22], in CAF the charged anodic and cathodic conductors are bridged by filaments composed of a metal salt precipitated along the degraded interfaces within the PCB laminate [35]. Typically, five stages of CAF formation can be distinguished: (i) initiation, (ii) separation of glass/epoxy interface, (iii) electrochemical reaction, (iv) salt deposition, and (v) completion of conductive pathway.

In the FR-4 type PCB laminates, several interfaces are present, e.g. Cu-resin, Cu-epoxy, epoxy-glass, glass-resin, and each of the interfaces can degrade under high humidity and high temperature (e.g. during the service lifetime) which causes moisture ingress [162], swelling, and debonding at the interfaces. The risk of failure due to CAF is proportional to the amount of moisture absorbed by a PCB. The water absorbed by the PCB acts as an aqueous medium (electrolyte) and copper conductors serve as electrodes. The potential of the circuit is a driving force for CAF occurrence due to the current leakage between copper conductors present on the same PCB layer or on the adjacent layers [162, 163].

In case of sufficient moisture uptake by a PCB and its entrapment along the faulty interfaces, the voltage running in the circuit initiates redox reactions at the conductors. An electrolysis (oxidation) of water at the anode (equation 2.30) takes place and results in the generation of hydrogen ions and oxygen evolution, creating a low local acidic pH at the anode. At the cathode, a water reduction occurs (equation 2.29) which is associated with a formation of hydroxyl ions and evolution of hydrogen, resulting in a high local alkaline pH at the cathode. The anodic and cathodic reactions create a pH gradient along the path (across the two electrodes) [162].

In the neutral pH, the copper electrodes are passivated and corrosion cannot occur, however, with the accumulation of hydrogen ions at the anode and creation of an acidic environment, copper oxidizes (equation 2.32) resulting in the formation of positively charged ions [164]. These ions subsequently migrate along the separated interfaces towards the cathode, precipitate due to the high pH and grow towards the anode (equation 2.33) [162, 163]. The process continues as long as the pH gradient is maintained and until the gap between the conductors is sufficient for leakage current to flow [165]. The growing filament is called the conductive anodic filament.

\[
Cu \rightarrow Cu^{n+} + ne^{-} \quad \text{(Eq. 2.32)}
\]

\[
Cu^{n+} + ne^{-} \rightarrow Cu \quad \text{(Eq. 2.33)}
\]

The defects are composed of copper salt of semiconductor properties [163]. Typical CAF formation paths (Figure 2.48) can occur between vias (hole-to-hole), via and conduction line (hole-to-line, hole-to-trace, trace-to-hole), or between conduction lines (line-to-line, layer-to-layer). The investigations of CAF appearance inside the PCB is typically performed by microscopy techniques (Figure 2.49).
CAF occurrence is influenced by several factors [35, 137, 167-169], namely: environment (temperature and humidity), applied voltage, presence of ionic residues and their concentration (from plating baths or solder flux residues), interfacial degradation, distance between the conductors, degree of polymer curing, or porosity of the material. The filament growth may lead to failures over a period of time such as a creation of an 'open' circuit (dissolution of Cu conductor and its precipitation along the interface depletes the conductor of Cu) or a creation of a 'short' (the conductive filament may bridge anode and cathode).

2.6.5. Polymer degradation

The electronic materials compose of polymers that are susceptible to moisture uptake. Moisture is absorbed by a variety of polymeric materials constituting the PCBA (packages, laminates) and causes swelling [171], inner delamination, and blistering issues (Figure 2.50). Absorption of moisture to FR-4 substrates can occur by two mechanisms, namely by wicking (enhanced moisture absorption due to voids and cracks at the glass fiber/resin interfaces) and capillary action (enhanced absorption due to voids and cracks in the bulk material) (Figure 2.51) [52, 172]. The absorbed water is bonded to the polymer chain and stored in a free volume of the bulk material. Material swelling caused by moisture bonded to the polymer creates additional free volume and as a result more water can then be absorbed by the swollen substrate [35].
Absorption of moisture to an electronic material takes place during the assembling process, storage, transportation, or operation time. It can affect the dielectric, mechanical, thermal, or dynamic properties of PCBA materials, e.g. [9, 35, 52, 95, 174, 175]:

- reduce the quality of lamination, coating, metallization (creates oxides), or solder masking,
- increase in free volume,
- decrease of Tg (moisture acts as a plasticizer),
- reduction of CTE (thermal expansion coefficient),
- increase in molecular mobility which can lead to decreased physical and chemical stability (f.e. change in plasticity),
- increase of strain on PTHs (plated-through holes),
- increase of dielectric constant (Dk) and dissipation factor (Df) (reducing circuit switching speed),
- interfacial degradation (leading to CAF),
- ionic corrosion (leading to both ‘open’ and ‘short’ circuits).

The example of the functional degradation of the conformal coating due to the moisture ingress is shown in the Figure 2.52.
Figure 2.52: Blistering and cracking of the conformal coating as a result of water vapour adsorption, ingress, and diffusion through the material to the PCBA surface.

If an electronic material containing entrapped moisture is subjected to high temperatures (e.g. during reflow soldering), the pressure built up by an expanding moisture in the interior can cause further damage to the product, e.g. delamination, or the occurrence of internal and external cracks ("pop-corn" effect) (Figure 2.53 and Figure 2.54) [52].

Figure 2.53: An example of external die-attach film voiding developed after the reflow process [171].

Figure 2.54: An example of internal moisture-induced stress cracking in electronic packaging. Adapted from [176].

The extent and rate of moisture absorption depend on the polymer type (amount of molecular moieties that can bond water molecules), its thickness, density, morphology, and the exposure climatic conditions [174]. The FR-4 laminates are porous materials and the pore sizes can vary largely from one product to another (Figure 2.16), therefore they may exhibit different sorption behaviours. In practice,
the surface of FR-4 is coated with a layer of polymeric solder mask that itself is absorbing large amounts of moisture [33] and does not protect the laminate substrate against the moisture ingress.

2.6.6. **Galvanic corrosion**

Galvanic corrosion is a less common phenomenon, compared to ECM or CAF formation, occurring in electronics and causing failures in the operational functionality. It occurs if two dissimilar metals are connected by an electrolyte which allows for an electron flow and therefore forms a closed circuit. The metals develop different electrochemical potentials when immersed in the medium, and their combination can typically be described as a “more noble metal” (higher el. potential, cathode) in contact with a “less noble metal” (lower el. potential, anode) [26]. The potential difference is a driving force for a corrosion occurrence, and the corrosion of an anode (“less noble metal”) occurs.

The susceptibility of Printed Circuit Board Assembly to galvanic corrosion is high due to the variety of metals and their alloys present, e.g. Sn, Ag, Au, Al, Ni, Cu. Typically, galvanic corrosion of wire bonds is found to be the primary reason for a loss of bonding strength between for e.g. golden wire and aluminium pad, encapsulated within an integrated circuit system (Figure 2.55 (a)). The debonding occurs as a result of the formation of intermetallics between the wire and the pad, which reduces the bond’s strength and causes the wire ball lift (Figure 2.55 (b)), and subsequent loss of connection. The loss of bond connection is facilitated by a presence of compound constituting the outgassing products from a variety of PCBA materials (section 2.3.), e.g. Br- and Cl-containing flame retardants [177, 178], I-based gaseous contaminants from housing materials [179].

Factors accelerating this type of corrosion are the detrimental climatic conditions (temperature, humidity) facilitating water film formation and process kinetics, high amount of ionic contamination which raises the thickness and conductive properties of an electrolyte, and large area ratio cathode : anode [49].

![Figure 2.55](image.png)

Figure 2.55 (a) localization of a bond pad in electronic component, (b) examples of various pad debonding failures [6, 180, 181].
2.7. CLIMATIC RELIABILITY TESTING

2.7.1. Surface Insulation Resistance (SIR) testing

Surface insulation resistance testing is commonly used in electronics industry for the evaluation of PCB quality after production (e.g. conformal coating performance), characterization of flux systems, or estimation of a long-term reliability [22, 147]. A number of standards describe the methodology used for assessment of the reduction of surface insulation resistance (SIR) of specially designed test coupons upon exposure to various climatic conditions (high temperature and humidity). Typically, it is an electrical test measuring a change in output current over a specific period of time usually performed at THB (temperature-humidity-bias) conditions - under applied voltage and at elevated temperature and humidity levels. Most of the tests include pre-conditioning of the comb patterns at certain environment. Moreover, despite the insulation resistance measurement is performed under high voltage, a stress bias is applied to test samples before or between the SIR measurements (Figure 2.56). The results are usually reported as surface insulation resistance rather than as leakage current [182] due to the fact that resistance measurement between two electrodes on the surface of a dielectric material includes both bulk and surface resistivity [22]. Some of the test coupons most commonly used in the standardized SIR testing are IPC-B-36 (cleaning alternatives), IPC-B-24 (residue), IPC-B-25(A) (multipurpose test board), and IPC-B-52 (cleanliness and residue evaluation), shown in the Figure 2.57.

![Figure 2.56: The overview of typical SIR measurement setup](image)

![Figure 2.57: Test comb patterns used for standardized SIR testing: (a) IPC-B-36, (b) IPC-B-24, (c) IPC-B-25A, (d) IPC-B-52](image)
In electronics industry, SIR testing is commonly used (Figure 2.58) for the assessment of electrical effect of typical residues associated with PCBA manufacturing process [184] – solder flux systems. The resistance reduction measurements of test patterns, contaminated with a flux residue, are performed over a specific period of time, and the decrease of SIR values is associated with water film formation and deliquescence of the residue. During testing, the dendrite growth typically occurs, and the determination of fail or pass SIR test relies, e.g. on the determination of a dendrite size. Short circuiting between the conductors is not the only fail scenario as even non-bridging dendrites negatively impact the surface insulation resistance values [184]. A summary of test characteristics of different standards is shown in the Table 2.6.

Figure 2.58: IPC standards tree for evaluation of electronic assemblies quality [185].

SIR testing is believed to be a feasible test capable of mirroring, to some extent, the field performance of PCBA and assessing the expected lifetime of the device. However, the result must be carefully interpreted as a simulation of real-life conditions (in terms of PCBA geometry or exposure climate) is often hard to achieve.
The examples of the SIR boards appearance after SIR testing of the commercial flux systems are shown in the Figure 2.59.

![Image of SIR boards](image-url)

Figure 2.59: Examples of SIR boards after IPC solder flux classification test (for ECM occurrence) [187].

### 2.7.2. Electrochemical Impedance Spectroscopy (EIS) testing

The AC electrochemical impedance spectroscopy allows to investigate the relevant bulk and interfacial properties of the electrochemical system perturbed with a small AC voltage by scanning across a wide frequency range [86]. The EIS method can distinguish between the water layer resistance (solution resistance) and impedance from interfacial electrochemical reactions. Therefore, it provides a detailed information on the conduction mechanisms and multiple electrode reactions [188], can identify the diffusion-limited reactions, and defines which impedance is dominant in the system [86]. It was
successfully employed for the investigations of the hygroscopic effect of ionic contaminants (dust [86, 118] and flux systems [188, 189]) at various climatic conditions where water film formation was facilitated by the ionic residues. Examples are shown in the Figure 2.60.

In AC impedance measurement, an AC voltage is delivered to the electrochemical system. Due to the typically small signal amplitude, it has a minimal impact (typically no dendrite growth) on the conductors (no polarization or corrosion occurrence) if sufficiently high frequency is applied. By scanning the system across the wide frequency range, a mechanistic information about various conduction processes can be obtained and quantified due to their different frequency-dependencies. On the contrary, DC SIR measurements cannot distinguish between the metal/solution interface reactions and ionic conduction in the electrolyte layer between the electrodes [188]. However, an estimate information of the system SIR, obtained typically through DC measurements, can be inferred from the AC results through a construction of an equivalent circuit and extrapolation of the resistance data [86] (value from the DC measurement can be found in the impedance spectrum at zero frequency).

![Figure 2.60: Bode plots showing result of impedance testing of dust particles and flux systems at different climatic conditions. Adapted from [86, 118, 190].](image)

The conduction processes that can be characterized by EIS measurements are [188]:
- ohmic conduction (represented by resistance $R$),
- dielectric displacement (represented by capacitance $C$), and
- diffusion (represented by Warburg impedance).

All circuit elements exhibit varying frequency-dependencies, but typically the main components comprise the equivalent circuit, therefore the information about major mechanisms can be extracted from the data fitting procedure. Examples of the equivalent circuits and the corresponding Bode and Nyquist plots are shown in the Figure 2.61. Purely resistive behaviour is marked with R and corresponds...
to the phase angle $\varphi$ of 0°. The construction of equivalent circuits is difficult for complex systems, requires experience, and a complete understanding of a system and occurring mechanisms.

The equivalent circuits represent every conduction process of the SIR system where the water film formation occurs, assisted by the presence of ionic flux residues, as shown in the Figure 2.62. The hygroscopic contamination remaining on the SIR surface initiates adsorption of moisture from the surrounding environment below the critical RH level for deliquescence, and a thin water film forms. Upon the applied potential and RH rise to the critical levels, the electrochemical process is triggered and facilitated by a growth of thick electrolyte and its high ionic conductivity. The ionic conduction is governed by the capacitance of SIR comb pattern (space between the conductors), expressed as $C_c$, and by ionic resistance of a water film expressed as $R_c$. The electrochemical reactions at the interface are marked with a green dotted line in the Figure 2.62, and express the transition from electronic conduction in the electrode to ionic conduction in the electrolyte film upon the growth of a thick electrolyte.

Figure 2.61: Electrochemical impedance spectra and associated equivalent circuits [188].

Figure 2.62: Equivalent circuits for DC and AC measurements of water film formation on the SIR pattern. Adapted from [188].
The reactions include charge transfer resistance $R_{ct}$ (associated with a faradaic reaction at the electrode surface), double layer capacitance $C_{dl}$ (associated with ionic current flow in the absence of faradaic reaction), and Warburg impedance $Z_w$ (associated with a diffusion-controlled faradaic reaction at the interface) [188]. The AC measurement can provide information about each process and quantify all circuit values separately, contrary to the DC testing which measures only the resistance associated with water film and the resistance associated with faradaic reactions occurring at the interface. The values for each resistance cannot be inferred from the DC SIR results separately, therefore no differentiation between the ionic conduction and the interface electrochemical reactions can be done.

Despite different characteristics of the obtained data, AC is more cost-efficient and non-destructive (samples are not destroyed upon the testing and possible to re-use, contrary to DC measurement [190]). However, DC indicates the voltage zone dangerous for the system and the expected current values. Both techniques are related to the electrolyte conductivity.
3. SUMMARY OF THE PROJECT AND LITERATURE REVIEW

This chapter provides an overview of the investigations carried out in the PhD thesis in relation to the literature review presented in chapter 2.

The effect of PCBA surface, assisting the water layer formation, was evaluated for a number of commercial electronic materials and described in terms of roughness, chemistry, and wettability, as described in chapter 2.2. The hydrophilicity and hydrophobicity of these surfaces were affected by their topography, which further significantly influenced the characteristics of droplet formation and the potential for failure occurrence under the condensing conditions. The results are presented in chapter 6.

The chemical and physical properties of typical no-clean solder flux residues described in chapter 2.3 have an effect on the amount and potential aggressivity of the flux residues remaining on the PCBA surface after the wave soldering process. The tendencies of solder flux residues to undergo a thermal decomposition under temperatures characteristic for a wave soldering process were studied at various temperatures and treatment time. A number of residue types tested in this thesis varied in the composition, specifically in the amount of activating components. The results are presented in chapters 7 and 8.

The impact of flux residues on the corrosion reliability is typically assessed using the standardized SIR testing described in chapter 2.7. However, the tests are performed under constant temperature and humidity conditions. The investigations in this PhD thesis focused on the assessment of the residue-moisture interaction under varying temperature and humidity conditions using both AC and DC techniques. The hygroscopicity of flux residues were assessed using gravimetric and electrochemical impedance techniques, and the corrosivity of the contamination was evaluated under varying DC potential bias. A variety of activators was used in the studies and, based on the results, flux residues were ranked in terms of hygroscopicity and resulting corrosivity, which is presented in chapters 9-11.

The importance of the external climatic conditions and fluctuations of PCBA temperature in relation to ambient conditions were briefly mentioned in chapter 2.4. In the thesis, the effect of transient climatic conditions and the residue presence are studied under various isothermal and non-isothermal conditions where the PCBA temperature reduction occurs. The results show how the PCBA surface conditions reduce the humidity threshold for failures even under potentially safe temperature variation where no risk of condensation exists. The presence of thermal mass on the electronic assembly accelerates and prolongs the local moisture condensation, extending the critical time for failure occurrence. The synergistic effects and importance of PCBA cleanliness, ambient humidity level, differential temperature range, cooling rate, and PCBA/enclosure characteristics were evaluated in terms of the electrical properties of a formed water layer and overall corrosion reliability of electronics. The results are presented in chapter 12.
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4. MATERIALS AND EXPERIMENTAL METHODS

4.1. ELECTRONIC MATERIALS

4.1.1. FR-4 laminates coated with solder masks

The investigations of water layer formation on the clean PCB surfaces (chapter 6) were carried out using FR-4 laminate materials reinforced with glass fibers and coated with solder masks of varying topographies. Five commercially available products were subjected for testing (Figure 4.1). One of the solder masks was used for the measurement of water layer thickness formed under the condensing conditions on a clean PCB substrate (chapter 12), and for the wettability assessment of pre-contaminated surface (chapter 9). Detail description is provided in the respective chapters.

![Figure 4.1: Photograph of test specimens subjected for the investigations of solder mask surface effect on the water layer formation (chapter 6).](image)

The visualization of in-situ water layer formation on the solder mask surface pre-contaminated with pure weak organic acids (chapter 9) was conducted on rough (Figure 4.2 (a)) and smooth surfaces (Figure 4.2 (b)). The observations of residue morphology changes resulting from its exposure to various temperature and humidity treatments were performed on a smooth solder mask surface (chapters 9 and 12).

![Figure 4.2: Pictures of (a) rough and (b) smooth solder mask surfaces used for visualization of in-situ water film build-up on specimens contaminated with solder flux residues (chapter 9).](image)

The assessment of decomposition behaviour of the residue entrapment under the components was studied in chapter 7 using a fabricated test rigs (Figure 4.3) constructed of laminate-laminate and laminate-copper.
Figure 4.3: Test rig used for decomposition studies of entrapped residues (chapter 7).

The in-situ AC measurements of water layer build-up on the solder mask surfaces (chapter 6) was performed using a test rig shown in the Figure 4.4.

Figure 4.4: Electrode pattern plated on the FR-4 substrate for in-situ impedance monitoring of the water film build-up (chapter 6).

More detail descriptions of the test substrates are provided in the respective chapters.

### 4.1.2. SIR test patterns

The surface insulation resistance patterns were used for PCBA level testing using the boards that comply with IPC-4101/21 specifications. The boards were produced using an FR-4 substrate. The comb pattern was a set of interdigitated lead-free electrodes comprising of HASL (hot air solder leveling) surface finish and Sn100C solder alloy. The dimensions of the SIR test pattern were 13x25 mm² and the distance between the electrodes was 0.3 mm. The test coupons were used for studying the synergistic effects of humidity, temperature, and hygroscopic contamination for various solder flux residue types (chapters 8-12).

Figure 4.5: Picture of the SIR pattern used for reliability testing (chapters 8-12).

### 4.1.3. Contamination

The investigations of the effects associated with the presence of process-related contamination on the corrosion reliability of PCBAs at various climatic conditions were studied for a number of solder flux
system formulations. Pure WOAs, representing a single-activator based systems or residues contributing to the moisture uptake and the formation of water layer, were studied in chapters 7, 9, and 12. Binary mixtures of various weak organic activators were studied in chapters 8 and 10. Additionally, a range of commercial wave solder flux systems was subjected to the thermal decomposition and reliability testing (chapters 7 and 11).

4.2. CHEMICAL CHARACTERIZATION AND ELEMENTAL ANALYSIS

4.2.1. Fourier Transform Infrared (FTIR) Spectroscopy

The Nicolet™iN™10 MX infrared imaging microscope (Thermo Scientific) was employed for identification of the functional groups in various materials and chemicals, which allowed for determination of the polymer comprising the solder mask coatings (chapter 6), thermal decomposition patterns of weak organic acids (chapter 7), and identification of the activator part in the commercial flux systems (chapter 11). The microscope was equipped with a MCT detector cooled with liquid nitrogen, and supported by Omnic Picta software. The samples were analysed using an attenuated total reflection (ATR) method.

4.2.2. Nuclear Magnetic Resonance (NMR) Spectroscopy

The Bruker Ultrashield 300 MHz spectrometer was used for $^1$H NMR spectroscopy measurements for identification of a particular activator chemistry present in the commercial flux systems. The technique allowed for the high precision estimation of the ratio between various activators in the flux formulations composed of binary mixtures of WOAs (chapter 11) with the use of MestReNova 11.0 software.

4.2.3. Ion Chromatography (IC)

The Dionex ICS-2000 (Thermo Scientific) with IonPac ICE-AS6 ion inclusion column was used for the ion chromatography analysis and quantification of the WOA ratio in the samples of binary WOA mixtures subjected to various thermal activation treatments (chapter 8).

4.2.4. Energy dispersive X-Ray spectroscopy (EDS)

The elemental analysis of the solder masks (chapter 6) and the corrosion products (chapter 9) were conducted using a field emission scanning electron microscope (FEG-SEM-Quanta 200FEG MKII, FEI) equipped with the Oxford Instrument energy dispersive X-ray (EDS) analyzer. The EDS analysis was performed at an acceleration voltage of 15 kV and Cu calibration using Oxford Instruments 80 mm$^2$ X-Max silicon drift EDS detector.

4.2.5. Standardized acid-base titration

The quantification of WOA content in the residue samples subjected to various thermal treatments (chapter 7) was conducted performing a standardized acid-base titration (IPC-TM-650 Test Method, number 2.3.13 "Determination of Acid Value of Liquid Solder Flux – Potentiometric and Visual Titration Methods").
4.2.6. Residues Reliability Assessment Testing (Residue RAT™) for contamination profiling

The visualization of the flux residue contamination level after the thermal treatments (chapter 8) was carried out using a patented product Residue RAT™ gel testing.

4.2.7. Tin corrosion identification

The visualization of tin corrosion on the PCBAs pre-contaminated with binary mixtures of WOAs (chapter 10) was performed with the use of colorimetric method, where the tin indicator contained in a gel form revealed the tin ions and tin hydroxides formed during the corrosion process. The reaction with tin indicator changes the colour of the gel from light yellow to blue, and the intensity of the colour represents the extent of corrosion.

4.3. THERMAL CHARACTERIZATION

The TGA technique was employed to investigate the degradation of binary mixtures of WOAs (chapter 8) in terms of weight loss as a function of temperature. The DSC measurements were employed for the assessment of endothermic melting transition and decomposition temperature of the residue. The tests were performed in Al₂O₃ crucibles in the temperature range 25-500°C with a heating rate of 10°C/min using NETZSCH STA 409 PC/PG instrument.

4.4. CLIMATIC TESTING

4.4.1. Climatic chambers

The "Espec PL-3KPH" climatic chamber was used for most of the tests performed under various humidity and temperature conditions. The operational range for temperature and humidity conditions is -40 °C to +100 °C and 20 %RH to 98 %RH. The accuracy of temperature and humidity control in the climatic chamber is ±0.3 °C and ±2.5 %RH, as specified by the manufacturer.

The observation of water film formation on the clean solder mask substrates (chapter 6) under condensing conditions was carried out in an air-tight box, filled with containers of deionized water in order to achieve a required humidity level.

4.4.2. Flux activation treatment

For the simulation of thermal activation of the wave solder flux systems comprised of single activator (chapter 7), the samples were treated at 175 ± 5°C and 250 ± 5°C for 45 seconds, representing the temperatures at the upper and lower side of the PCB surface during the wave soldering process, respectively. For some cases, the additional activation treatment was conducted at 350 ± 5°C, as well as an activation time of 10 minutes.

Binary (chapter 8) mixtures of organic activators were subjected to thermal decomposition studies upon the treatment at 175 ± 5°C and 245 ± 5°C for 45 and 90 seconds.

4.4.3. Ovens

The activator residues based on single WOA activator and few commercially used solder flux systems were subjected to radiative thermal treatment in Nabertherm LE4/11/R6 (chapter 7). Binary
mixtures of organic activators (chapter 8) were thermally activated in Techno HA-06 reflow oven (Technoprint).

4.4.4. Gravimetric water vapour sorption/desorption testing

The moisture uptake measurements were performed for residues composed of pure WOAs (chapter 9), binary mixtures of pure WOAs (chapter 10), and solder flux residues (chapter 11) at constant temperatures: 25°C, 40°C, and 60°C. The samples of each residue type were tested using Sartorius Research R 160 P electronic semi-microbalance with an accuracy of 0.01 mg upon exposure to varying relative humidity from 30~99%RH that afterwards decreased from ~99-30%RH, both ramps in the step of 5%RH.

4.4.5. Peltier cooling stage

The simulations of the temperature differences between the ambient air and test substrates were performed using a cooling Peltier element (Figure 4.6, model CP-031, TE Technology Inc.), which comprised of a Peltier element embedded in the aluminium block, and cooled down using a fan attached at the bottom. The control unit allowed for a creation of temperature control loop between the Peltier and test samples using a commercial computer software. The cooling experiments were used for the visualization of water film formation on the clean PCB surfaces (chapters 6 and 12) and contaminated surfaces (chapters 9 and 12).

Figure 4.6: Peltier cooling stage used for the investigations of water film formation on the clean (chapters 6 and 12) and contaminated surfaces (chapters 9 and 12).

4.5. ELECTRICAL/ELECTROCHEMICAL TESTING

The electrical/electrochemical measurements were performed with the use of the “BioLogic VSP” multichannel potentiostat. The workstation has 20 V compliance voltage with adjustable range (upper limits at -20 V and +20 V) and a 760 pA current resolution. The AC impedance technique was employed for studying the water film build-up on the clean (chapters 6 and 12) and contaminated surfaces (chapters 9-12) under various climatic conditions. The DC leakage current measurements were performed in order to study the corrosion susceptibility of various contamination types (chapters 8-12).
4.6. SURFACE CHARACTERIZATION AND MICROSTRUCTURE ANALYSIS

4.6.1. Contact angle – surface wettability

The contact angle technique was employed for the assessment of surface wettability of clean (chapter 6) and contaminated (chapter 9) PCB materials. The contact angle of the sessile droplet resting on the surface was evaluated using a camera equipped with a long-range microscope (ramé-hart instrument co. goniometer model 200-F1) and software DROPimage standard.

4.6.2. Surface roughness

The surface roughness assessment for various solder mask surfaces (chapter 6) was performed using a mechanical stylus profilometry. The surface profile measurements were carried out with a Hommel Tester T1000 (Hommelwerke GmbH, Germany) and Turbo Datawin software.

4.6.3. X-ray diffraction (XRD)

The changes in the activator crystal structure were investigated at elevated temperature and humidity levels (chapter 9), and the effect was analysed using the in-situ XRD technique. The measurements were carried out on a “Bruker D8” equipped with a parallel beam (Göbel mirror) and a secondary side divergence assembly in 1D, and an MRI temperature controlled dome stage.

4.6.4. Scanning electron microscopy (SEM)

The analysis of the solder mask surface microscale morphology (chapter 6) and the detailed corrosion morphology analysis (chapter 9) were carried out using a field emission scanning electron microscope (FEG-SEM-Quanta 200FEG MKII, FEI) with the EDS analyzer capability.

4.6.5. Optical microscopy

The optical inspection of the corrosion products after the climatic and electrochemical residue testing, observations of WOA morphology changes under various thermal and humidity treatments, and visualization of water film formation on the PCBA surfaces (chapters 9, 11, 12) were performed using a stereomicroscope Leica MZ 125 and Paint Shop Pro 7 software, “AD7013MZT Dino-Lite” digital microscope, and Alicona InfiniteFocus.
5. SUMMARY OF APPENDED PAPERS

5.1. EFFECT OF SOLDER MASK SURFACE CHEMISTRY AND MORPHOLOGY ON THE WATER LAYER FORMATION UNDER HUMID CONDITIONS

- Investigation of the effect of PCBA surface characteristics on water film formation under humid and condensing conditions.
- Five commercially available solder masked laminates were tested under this work.
- The effects of surface topography, chemistry, and bulk defects were assessed in terms of an influence on the surface wettability at ambient temperature.
- The build-up of thick water film under condensing conditions was monitored visually and the droplet bridging phenomenon was assessed via electrochemical measurements.

Findings:

- The wettability of solder mask surface is a result of synergistic effects of its surface chemistry, surface roughness, and a presence of bulk defects. Surface chemistry is a result of polymer type and various additives. PCBA surface roughness is determined by the application process of the solder mask and the fillers added to the solder mask layer. Bulk defects are the result of improper solder mask application process.
- High surface roughness of hydrophilic substrate and a presence of pin holes in the solder mask layer contribute to high surface wettability. The latter has the most pronounced effect than other factors related to surface features.
- Under condensing conditions, the appearance of droplets formed on smooth and rough surfaces differs (Figure 5.1 (a)). The failure (bridging of two conductors by water droplets) occurs faster on the rough surfaces, providing shorter time for SIR drop under transient condensing conditions (Figure 5.1 (b)).
- The studies show that the solder mask surface morphology is an important aspect in the process of water film formation, therefore it is important to define its characteristics properly. Suitable solder mask surface quality could delay the large SIR drop and the risk of corrosion under climatic conditions at which the chances for water layer formation are high.

![Figure 5.1](image-url)
5.2. THERMAL DECOMPOSITION OF SOLDER FLUX ACTIVATORS UNDER SIMULATED WAVE SOLDERING CONDITIONS

- Investigation of the decomposition behaviour of the activators commonly used in the wave solder no-clean flux systems: palmitic, suberic, adipic, succinic, glutaric, and DL-malic acids.
- Estimation of the residue amount remaining on the surfaces after subjecting pure acids and commercial fluxes to simulated wave soldering conditions.
- Contaminants tested at 25°C, 175 ± 5°C, and 250 ± 5°C, simulating the wave soldering conditions. Some tests conducted at 350 ± 5°C.
- The residue removal rate investigated on open substrates (glass, laminate w/ solder mask, laminate w/ 35 µm Cu) and from test rigs (Figure 5.2 (a)) simulating residue entrapment under the SMT components (laminate-laminate, laminate-copper).

Findings:

- Succinic and DL-malic acids underwent thermal degradation at high soldering temperatures and formed additional anhydride-like species, which have more aggressive chemical nature than the flux activators.
- Certain amounts of DL-malic, glutaric, and succinic acids evaporated at 250°C after 45 seconds treatment from the glass surface. Except for palmitic acid, all acids were removed at 350°C treatment in significant amounts.
- The prolonged time of heat treatment of the fluxes (10 minutes) did not suffice for their full evaporation. Almost no change was noted for testing at 175°C, and the treatment at 250°C allowed for more significant evaporation of succinic- and adipic-based flux systems. The presence and amount of film-former in other tested fluxes may restricted their residue removal rate even at experiment with prolonged heat treatment.
- Succinic acid evaporates from a variety of surfaces slightly easier than adipic acid. Almost total drop of residue amount for both contaminants occurred at 350°C for opened substrates of testing. No significant reduction in residue amount occurred for flux entrapped in test rigs even at 350°C (Figure 5.2 (b)).
- The best residue removal occurred from laminate-based materials. Copper-based substrates may react with WOAs not allowing for their full evaporation under set conditions.

Figure 5.2: (a) test rig constructed for studies of entrapped residues, (b) removal of entrapped succinic acid at elevated temperatures.
5.3. THERMAL DECOMPOSITION OF BINARY MIXTURES OF WEAK ORGANIC ACTIVATORS USED IN NO-CLEAN FLUX SYSTEMS AND IMPACT ON PCBA CORROSION RELIABILITY

- Investigation of the decomposition characteristics of three binary mixtures of weak organic activators: adipic : succinic, adipic : glutaric, succinic : glutaric. The ratios of each binary blend were 1:1, 1:5, and 5:1.
- The residue amount remaining on the surfaces after subjecting the binary blends to simulated wave soldering conditions was estimated as a function of binary mixture type, temperature, and exposure time. The decomposition preferences between two components of the binary blend was assessed. The effect of decomposition tendencies on the potential risk of corrosion occurrence was assessed at 25°C/90-99%RH under varying DC potential.
- Contaminants tested at 175 ± 5°C and 245 ± 5°C for 45 seconds, simulating the wave soldering conditions. Moreover, the extended time of thermal treatment (90 seconds) was applied in the study.

Findings:

- The typical range of temperatures and exposure time experienced by electronic units during the wave soldering process (175°C-245°C) is not sufficient for the removal of significant amounts of residues from the PCBA surface.
- The preferential evaporation of succinic acid, compared to the second constituent in the binary mixture, occurred for succinic : glutaric and adipic : succinic mixture types. Between both acids in the adipic : glutaric blend, the simultaneous degradation of two WOAs occurred regardless the thermal treatment.
- Under range of conventional wave soldering temperatures the decomposition behavior of binary mixtures of solder flux activators exhibits the increasing tendency for evaporation: succinic : glutaric > adipic : succinic > adipic : glutaric.
- Corrosivity of the residues subjected to heat treatments depends on the type of the binary mixture of WOAs and ratio between the constituents. The highest leakage current levels were found for succinic : glutaric blend type. However, a sufficient thermal treatment of the residues can lead to the diminishing of the corrosion effects.

Figure 5.3: (a) leakage current testing of SG (1:5 ratio) corrosive effects under different thermal treatments, (b) Residues RATTM images of varying residue amount for AS mixture (1:1 ratio) subjected to different heat treatments.
5.4. PARAMETRIC STUDY OF SOLDER FLUX HYGROSCOPICITY:
IMPACT OF WEAK ORGANIC ACIDS ON WATER LAYER FORMATION
AND CORROSION OF ELECTRONICS

- Investigation of the hygroscopic and corrosive nature of solder flux activators exposed to varied temperature and humidity conditions relevant to electronics operation.
- Six typical flux activators tested as pure compounds: palmitic, suberic, adipic, succinic, glutaric, and DL-malic acids.
- Hygroscopicity-dependence on a residue type and temperature was evaluated using the gravimetric vapour sorption and AC impedance techniques.
- The influence of flux residue on a corrosion reliability was assessed by DC measurements as a function of activator type and temperature.

Findings:

- The hygroscopic nature of flux residues is determined by the chemistry of the activating part of flux formulation (Figure 5.4 (a)) and temperature. DL-malic and glutaric acids exhibit the highest affinity to moisture due to the high polarity of their molecules. Palmitic and suberic acids minimally interact with humidity in the temperature range 25°C-60°C. Adipic and succinic acids show the intermediate behaviour.
- An increase of temperature strengthens the interaction between the acids and water vapour, leading to higher uptake of moisture by flux residues. An increase of temperature shifts the critical relative humidity level for deliquescence of flux activators towards lower RH range, and the solubility of the residues increases.
- At higher ambient temperatures, the formation of a conductive electrolyte is accelerated, and an increase in leakage current and subsequent electrochemical metal ion migration occur at lower RH levels. Among the tested flux activators, glutaric and DL-malic acids are corrosive at all temperatures studied in this paper, which is due to their high hygroscopicity and solubility (Figure 5.4 (b)). Palmitic and suberic acids are not corrosive until 60°C. Adipic and succinic acids induce the electrochemical migration only under high temperature and humidity conditions.

Figure 5.4: (a) the differences in the hygroscopicity of flux residues visualized in terms of surface wettability, (b) the differences in corrosivity exhibited by flux residues as a function of relative humidity.
5.5. HUMIDITY-RELATED FAILURES IN ELECTRONICS: EFFECT OF BINARY MIXTURES OF WEAK ORGANIC ACID ACTIVATORS

- Investigation of the hygroscopic and corrosive nature of solder flux residues artificially composed of binary mixtures of weak organic acids (WOAs), simulating an activating part of flux formulation.
- Three types of binary blends were tested: adipic : succinic, adipic : glutaric, and succinic : glutaric. Each mixture contained one component exhibiting higher hygroscopicity than another one.
- The ratios between two acids varied from containing minor to major fraction of more hygroscopic component, settling the hygroscopicity of the blends in the increasing order: 5:1 < 2:1 < 1:1 < 1:2 < 1:5.
- The hygroscopic behaviour was assessed using the gravimetric vapour sorption and AC impedance techniques, and described in respect to the binary blend type and the ratio between the two components.
- Corrosivity of the flux residues was evaluated by DC leakage current measurements, and the RH range for corrosion occurrence was defined for all mixtures and their ratios.

Findings:
- Hygroscopic nature (Figure 5.5 (a)) and corrosivity (Figure 5.5 (b)) of flux residue composed of binary mixtures of organic activators are defined by and dependent on the type of acids, ratio between the most and least hygroscopic component, and the ambient temperature.
- Solder flux systems containing binary mixtures of activators are more aggressive than systems comprised of single dicarboxylic acid. The presence of two activators shifts the critical relative humidity level for deliquescence towards lower range compared to deliquescence points obtained for individual acids. As a result, corrosion induced by the binary blends occurs at lower RH level than the RH for either of the individual mixture components.
- Mixtures containing highly hygroscopic component in higher amounts absorb more moisture, forming thick conductive water layers that lead to the increased leakage currents and electrochemical migration (ECM).
- An increase of ambient temperature strengthens the interaction between flux residues and water vapour, and further decreases the humidity level for residue dissolution into the water layer and corrosion occurrence.

Figure 5.5: (a) impedance reduction data obtained at 25°C/99%RH for three binary mixture types and ratios, (b) colorimetric visualization of tin corrosion extent (indicated by blue coloration) after leakage current testing at 25°C/90%RH of SIR samples deliberately contaminated with succinic : glutaric mixture of 5:1 (least hygroscopic) and 1:5 ratios (most hygroscopic).
5.6. NO-CLEAN SOLDER FLUX CHEMISTRY AND TEMPERATURE EFFECTS ON HUMIDITY-RELATED RELIABILITY OF ELECTRONICS

- Commercial flux systems tested towards the assessment of their hygroscopicity and corrosive nature as a function of activator chemistry and ambient temperature. Testing was performed under varying humidity and at temperature range relevant for electronics operation and exposure conditions.
- The residues of solder flux contained single WOA (adipic or succinic acid), binary, and ternary mixtures of weak organic acids that were primarily used as activators in the flux formulations.
- Hygroscopicity evaluation was performed using water vapour sorption and AC electrochemical impedance techniques.
- The susceptibility of flux residues for ion-induced corrosion was assessed using DC leakage current measurements. The humidity regions for corrosion were correlated to the hygroscopicity data.

**Findings:**

- The flux formulations based on mixtures of activating components exhibit stronger interaction with water molecules compared to the flux system residues based on single weak organic acid (Figure 5.6). The critical RH level for a dissolution and crystallization of flux residues composed of blends of activators is lower than the deliquesence RH of single-WOA formulations.
- Higher hygroscopicity of WOA mixtures results in higher water uptake which implies thicker water layer formation. Highly soluble residues composed of WOA mixtures easily saturate the water film forming highly conductive electrolyte layer.
- The corrosivity of solder flux systems based on blends of activators creates a larger threat to the overall reliability than the residues comprised of single-WOA due to the ionic-induced electrochemical migration occurring at lower relative humidity levels.
- The hygroscopic character of flux residues is greatly enhanced by the increase of external temperature. As a result, the deliquesence behaviour and initiation of corrosion occurrence are accelerated and take place at lower RH levels.
- The crystallization of the dissolved residues comprised of WOA mixtures is difficult and they tend to retain the uptaken water, compared to the residues composed of single WOA activator. As a result, the PCBA wetting time is prolonged, which is further enhanced if the ambient temperature increases.

![Figure 5.6: The impedance reduction as a function of elevated relative humidity at 25°C showing the effect of flux residues (SF) interacting with moisture: (a) three succinic acid-based flux systems, (b) three WOA mixture-based flux systems.](image-url)
5.7. RESIDUE-ASSISTED WATER FILM FORMATION UNDER TRANSIENT CLIMATIC CONDITIONS AND FAILURE OCCURRENCE IN ELECTRONICS

- Investigation of the synergistic effects of PCBA cleanliness, ambient humidity level, differential temperature between PCBA and ambient, and PCBA/enclosure characteristics on the water layer formation under transient climatic conditions.
- The impact of typical solder flux activators – adipic, succinic, and glutaric acids – on the water film formation and the resulting electrical properties was assessed at 25°C/80%RH under isothermal and non-isothermal conditions. The interaction between external climate and PCBA was evaluated upon exposure of electronics and enclosure to a day/night cyclic conditions of a geographical location.
- The effect of ambient humidity level (80%RH, 90%RH, and 95%RH) and cooling rate on the electrical properties of the water film build-up and conductor bridging on a clean PCBA were assessed.
- The AC impedance and DC leakage current techniques were employed to determine the electrochemical changes of the PCBA surface resulting from the build-up of a conductive electrolyte on the interdigitated test SIR surface, pre-contaminated with the organic contaminants.

**Findings:**

- The electrical properties of the formed water film depend on the ambient RH level and PCBA cleanliness, which define the extent of a conductor bridging. At constant ambient temperature and cooling rate, higher water vapour amount exists at 95%RH compared to 80%RH, which leads to the formation of thicker water film that bridges the electrodes easily (Figure 5.7).
- The presence of hygroscopic contamination decreases the critical RH level of PCBA surface and increases the water vapour content above it. Even under potentially non-condensing conditions and PCBA temperature reduction of only 0.5-2°C, it results in a more pronounced moisture adsorption and corrosion issues.
- Under non-isothermal conditions and a PCBA temperature reduction below the dew point, succinic and glutaric acids accelerate the formation of a continuous water layer and conductor bridging, and the resulting electrical properties are comparable to the results of moisture condensation on a clean PCBA at 95%RH.
- Under transient climatic conditions formed within an electronic enclosure for ~1h upon the changes of external conditions, the presence of glutaric acid leads to the formation of water film for a duration of ~4h. The presence of a thermal mass prolongs the PCBA wetting time to ~15min, increasing the extent critical period when the failure may occur.
APPENDED PAPERS
6. EFFECT OF SOLDER MASK SURFACE CHEMISTRY AND MORPHOLOGY ON THE WATER LAYER FORMATION UNDER HUMID CONDITIONS

Kamila Piotrowska, Rameez Ud Din, Morten Stendahl Jellesen, Rajan Ambat

Abstract - This work investigates the water film build-up on solder masked Printed Circuit Board Assembly (PCBA) laminates under humid conditions. The effects of solder mask surface chemistry, morphology, and roughness were investigated using different commercial laminates coated with solder mask. Chemical composition of the materials was analyzed using Fourier transform infrared spectroscopy. Microstructure and surface morphology were investigated using scanning electron microscopy, whereas the wettability was assessed using static contact angle technique, and correlated with the morphological observations. Solder mask surface waviness was characterized and quantified using a mechanical stylus profilometer. The formation of water film on a PCBA surface was monitored in-situ by optical microscopy and electrochemical impedance spectroscopy and correlated with the observations of surface features. The results show that the solder mask surface chemistry and morphology significantly influence the water film formation, which is important for corrosion reliability of electronics exposed to humid conditions.

Keywords - Corrosion, electronics reliability, humidity, printed circuit board assembly (PCBA) manufacturing, solder mask.

I. INTRODUCTION

Today, electronics industry adopts an increased packing density on printed circuit board assembly (PCBA) surfaces and device miniaturization, which in combination with an exposure of electronic equipment to a variety of climatic conditions, due to the widespread user environment, introduce a number of serious humidity-related reliability issues [1]. Exposure to moisture results in occurrence of a variety of failure modes due to the corrosion [2], which can be permanent or intermittent, depending on the climatic conditions and device’s characteristics. Water film of varying thickness forming on the PCBA surface is found to be the critical factor determining the reliability under such unpropitious circumstances, which is to a great extent determined by the PCBA surface and its architecture, presence of hygroscopic residues, humidity level in the environments, or the temperature fluctuations. The formation of water layer inside the electronic device was reported to cause a number of operational failures, for example, loss of electrical connection, polymer swelling, loss of adhesion, crack formation, or multiple corrosion modes (electrochemical migration (ECM), leakage current, short-circuiting) [3-15]. The water film build-up on the PCBA surface is the key factor determining the corrosion effects; therefore, it is important to understand the process of water layer formation and electrochemical behaviour.

Under humid conditions with no temperature variations, thin water films (up to few molecular layers) form on all clean surfaces, whereas under condensing conditions, caused by temperature differences, thicker water layer builds up [15, 16]. The formation of thin water layer in humid environment depends on the relative humidity (RH) level and the PCBA surface - FR-4 laminate material typically covered with a solder mask coating [17]. The chemistry of solder mask defines its polarity, which reflects the affinity of water molecules to adsorb to such surface via hydrogen bonding. The PCBA surface polarity varies due to the different polymer matrix, e.g. epoxy, phenolic, or acrylic [18, 19], and a number of additives of varying morphologies and concentration [20-24] incorporated into the material with a primary function to improve various properties [17, 22, 25-30]. High PCBA surface energy is associated with a presence of polar compounds (e.g. additives) that raise a risk of water adsorption to the surface. Moreover, the presence of hygroscopic ionic residues (e.g. flux residues, dust, and corrosive gases) on the PCBA surface reduces the critical RH level for water layer build-up [31-33], which substantially leads to an increase of water film thickness and higher risk for corrosion occurrence.

Although the presence of solder mask between the conductors was proven to raise the surface insulation resistance (SIR) of the system and decrease the chances for (ECM) occurrence [34], improper characteristics of the PCBA surface morphology and roughness were reported to influence the water layer formation and subsequent corrosion issues [35-37].

The corrosion failures occurring on the PCBA surface may, in addition to the inaccurate choice of materials and PCBA design, be accelerated by detrimental climatic conditions (high humidity, temperature variations) [4, 38-41] that lead to the build-up of thick water films. The difference between the relative temperature of the PCBA surface in comparison to an external temperature results in a creation of transient climatic conditions within an enclosure (due to e.g. day/night cycles), playing a vital role in the water layer build-up [42]. Under transient conditions, the device cannot rapidly respond to prompt changes and lags behind the outdoor climate, causing condensation on the surface and an increased risk of failure occurrence due to the corrosion. Such phenomenon is often observed in industrial electronics where the non-hermetic enclosures contain a number of openings (for cooling, cabling, etc.) capable of providing the moisture ingress path and water film formation on a PCBA surface. Moreover, the polymeric casing of the device can be permeable to humidity, resulting in the humidity ingress inside the device by diffusion through the enclosure’s walls [43, 44]. Consumer electronic devices using water-resistant but not waterproof technology (e.g. IPX6) are protected against the direct water ingress via openings. However, the devices may still be permeable to humidity (e.g. moisture diffusion through the enclosure walls), and the formation of water film on a PCBA surface is a possibility.

Limited literature studies deal with the characteristics of solder mask in relation to corrosion reliability, and the focus typically lies in the assessment of its effect on the PCBA solderability [45], susceptibility toward solder balling [46], mechanical properties [47], or the moisture sorption capabilities [48]. Current investigations provide a detailed analysis of the solder mask surface characteristics on the water film formation and its subsequent effect on electrical properties that may affect the corrosion reliability of the PCBA.

Solder mask surface composition was investigated by Fourier transform infrared (FTIR) spectroscopy, and the surface morphology was studied using scanning electron microscopy (SEM). The wettability of the specimens was assessed using the static contact angle method and correlated with the results of surface composition and topography analysis. Mechanical stylus profilometry was employed for the quantification of surface roughness parameters. The formation of water layer under condensing conditions was visualized using optical microscopy and monitored by means of electrochemical
impedance spectroscopy. The \textit{in-situ} water film build-up observations were correlated with the results of surface roughness analysis.

II. MATERIALS AND EXPERIMENTAL METHODS

BARE PCB MATERIALS

Five commercially used FR-4 laminate materials reinforced with glass fiber and covered with a layer of solder mask were chosen for the investigations. The overall thickness of the boards was within the range of 1.45-1.72 mm with a solder mask thickness up to ~20 µm. These printed circuit board (PCB) materials constitute the control units in industrial electronic devices (e.g. roof windows, water pumping systems, frequency converters). Based on visual assessment of the surfaces, all specimens were divided into five representative groups (A-E) from macroscopically very rough to smooth as presented in the Table 6.1.

Table 6.1: Overview of test specimen visual characteristics.

<table>
<thead>
<tr>
<th>Solder mask</th>
<th>Visual appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>very rough</td>
</tr>
<tr>
<td>B</td>
<td>rough</td>
</tr>
<tr>
<td>C</td>
<td>moderately rough</td>
</tr>
<tr>
<td>D</td>
<td>smooth</td>
</tr>
<tr>
<td>E</td>
<td>smooth/glossy</td>
</tr>
</tbody>
</table>

For the impedance measurements, two test specimens were prepared as shown in Figure 6.1. Two copper conduction lines were deposited on each specimen by means of electroless copper plating. The other areas were masked using adhesive tape. Subsequently, the solder paste was applied on the plated tracks using a stencil and soldered in a reflow oven. The geometry of the formed electrodes was with a width of ~1 mm and pitch distances of ~500 µm, ~750 µm, ~1 mm, and ~2 mm. The final accurate distances between the electrodes were as follows: 520 (±40) µm (specimen A), 510 (±50) µm (specimen D), 720 (±30) µm (A), 760 (±30) µm (D), 970 (±30) µm (A), 1.03 (±0.03) mm (D), 2.03 (±0.04) mm (A), 1.97 (±0.04) mm (D). Two cables were soldered onto the connecting pads. This connection part was separated from the measurement electrodes in order to prevent AC signal interference.

Figure 6.1: Schematic of the electrode pattern constructed for impedance measurements. Dimensions are given in mm.
All the test panels were thoroughly cleaned prior to each testing. Initial rinsing with ultrapure Millipore water for approximately 30 seconds (resistivity of 18.5 MΩ at 25°C) was followed by rinsing with isopropyl alcohol (analytical purity of 99.8%) three times and drying with pressurized air. All cleaned boards were stored in a desiccator (RH level RH<15%).

SOLDER MASK SURFACE COMPOSITION AND MICROSCALE MORPHOLOGY

Fourier transform infrared (FTIR) spectroscopy
The type of polymer constituting the test samples was identified by FTIR spectroscopy using a Nicolet™iN™10 MX infrared imaging microscope and OMNIC software. The detector used for measurements was an MCT detector cooled with liquid nitrogen. All the spectra were recorded in the range of 4000 cm\(^{-1}\) - 675 cm\(^{-1}\). The type of polymer was inferred from the observation of the transmittance peaks in the particular regions of the obtained spectra.

Scanning electron microscopy and energy-dispersive X-Ray spectroscopy
Surface microscale morphology, cross-sectional analysis, and elemental analysis of the solder masks were carried out using a field emission SEM (FEG-SEM-Quanta 200 FEG MKII, FEI) with an Oxford Instrument energy-dispersive X-ray (EDS) analyzer capability. The EDS analysis was performed at an acceleration voltage of 15 kV and Cu calibration using Oxford Instruments 80 mm\(^2\) X-Max silicon drift EDS detector.

The cross sections of the laminates with solder mask were prepared via metallographic methods. The samples were prepared in the transverse direction and mounted in cold-setting epoxy, subsequently allowed curing for 24 h. The samples were then subjected to mechanical grinding using silicon carbide papers up to 4000 grit followed by polishing using 3 µm and 1 µm diamond paste.

SOLDER MASK SURFACE ROUGHNESS
The evaluation of surface roughness of the materials was carried out using a mechanical stylus profilometry. The measurements provided three surface roughness parameters: mean (R\(_A\)), root mean square (R\(_MS\)) deviation of the profile from the centerline, and mean (R\(_Z\)) peak-to-valley height. Value R\(_A\) is the arithmetic average of the absolute values of the profile height deviations (peaks and valleys) over the length of assessment. Value R\(_MS\) is the root mean square average of these profile deviations and can serve as an indication of the largest surface defects levels, whereas R\(_Z\) is the arithmetic average of the highest peak values and the lowest valley values within a sampling length.

The profile measurements were carried out with a Hommel Tester T1000 (Hommelwerke GmbH, Germany) and Turbo Datawan software. The assessment profile was measured along 8 mm with a cutoff value of 0.8 mm and measuring range of 320 µm. Surface roughness parameters were calculated within the software. The representative profiles of two substrates (A and E) were obtained with the assessment length of 16 mm.

WATER LAYER FORMATION ON THE SOLDER MASK SURFACE

Surface wettability
The interaction of water with the surfaces was characterized in terms of the droplet tendency to spread over a solid surface using contact angle measurement. Surface wettability was estimated in the ambient conditions using static contact angle method of sessile 5 µL Millipore water droplets. The applied droplet stabilized on the surface at a concentric shape after approximately 30 seconds. Then,
the tangent line was drawn to the curvature of the droplet shape and intersecting at the point on solid surface. The angle was assessed using a camera equipped with a long-range microscope (ramé-hart instrument co. goniometer model 200-F1) and software DROPimage standard.

**In-situ observation of water layer formation under condensing conditions**

The solder mask specimens of 25 x 25 mm dimensions were pasted to the CP-031 cooling Peltier element (TE Technology Inc., MI, USA) using a heat-transfer paste. The materials’ surface temperatures were recorded and monitored using a calibrated Pt1000 temperature sensor connected to a data logging system (Model 2700 Multimeter, Keithley Instruments). During the experiment, the samples were cooled down using Peltier stage from ambient temperature (22.6-23.6°C) to 9.4-10.1°C within 12 minutes in order to create condensation on the solder mask surfaces. This allowed for visualization of the water layers build-up on the surface. The experiments were carried out at 70 (± 5)% RH and the temperature 24 ± 1.5°C, which set the dew point temperature at the range of ~15.5-20.7°C. The in-situ images of water film formation on test materials were taken using a “AD7013MZT Dino-Lite” digital microscope.

**Impedance measurements**

The impedance measurement was conducted in order to assess the influence of surface waviness on the water layer formation and the resulting change of electrical response under in-situ monitored condensing conditions. Clean samples of copper-plated FR-4 with solder masks (Figure 6.1) were pasted to the Peltier cooling element (CP-031 Peltier stage, TE Technology Inc.) using a thermally conductive paste, placed in the climatic chamber, and exposed to 80 (± 1)% RH and 24°C which implied the dew point in the range of 18.4-19.0°C. Once the conditions inside the test chamber settled, the specimens were cooled down to 17.0-17.5°C within 15 minutes. The dew point was exceeded in order to assure moisture dewing on the solder mask samples and a build-up of thick water layer. This range of temperatures was then maintained using a feedback loop, coupled with the Peltier stage, for the substrate temperature control until the failure was noted (water droplets bridging between conduction lines).

In the course of water condensation, the AC signal was applied through the copper-plated tracks (Figure 6.1). The impedance as a function of time was recorded using a Biologic VSP multichannel potentiostat (Bio-Logic Instruments, France). The signal amplitude of 25 mV ($V_{rms} = 17.68$ mV) at a frequency of 10 kHz was applied. This frequency is governed by the capacitive character of the SIR electrode system. With water layer build-up in between the electrodes during condensation, the measured impedance output (reduction) becomes dominated by the resistive character of water layer forming in between the conducting lines [49]. A gradual reduction in impedance signal corresponded to the water layer build-up. At a certain point, the signal abruptly decreased indicating that the formed water droplets bridged the two electrodes and the time-to-bridge was noted. All eight specimens were subjected for similar cooling rate, controlled and monitored by a set of sensors, and the repetitions included removing and remounting the specimens to the Peltier stage in separate measurements.

**Test chambers**

The observation of water layer formation on the solder mask materials under condensing conditions were conducted in an air-tight box, filled with deionized water at the bottom in order to achieve a required humidity level. For impedance measurements, the samples were exposed to required humid conditions using climatic chamber Espec PL-3KPH. According to the specifications, the accuracy
of humidity and temperature is within ±0.3°C/±2.5%RH for the conditions used in this paper. The climate inside both test chambers (temperature and RH) was monitored with the use of EL-USB-2-LCD+RH/temperature data logger mounted next to the test samples.

III. RESULTS

SOLDER MASK SURFACE COMPOSITION AND MICROSCALE MORPHOLOGY

The FTIR spectra recorded in a transmittance mode for all the solder mask specimens are presented in Figure 6.2. All spectra showed characteristic bands of epoxy (oxirane) ring \([25, 50-54]\) at 1184 cm\(^{-1}\) (stretching \(\nu_{\text{C-O}}\)), 1023 cm\(^{-1}\) (stretching \(\nu_{\text{C-O-C}}\)), 950-827 cm\(^{-1}\) (symmetric and asymmetric ring deformations), together with the peaks originating from the aromatic ring at 1734 cm\(^{-1}\) (overtones), 1607 cm\(^{-1}\) and 1508 cm\(^{-1}\) (stretching \(\nu_{\text{C=C}}\) and \(\nu_{\text{C-C}}\) respectively), 1040-1000 cm\(^{-1}\) (\(\delta_{\text{Ar-C-O}}\), overlapping). Moreover, the weak wide band at 3600-3250 cm\(^{-1}\) indicated the presence of hydroxyl group.

The reported bands may overlap with the peaks originating from various additives present in the solder mask (e.g. fillers and fire retardants) \([55, 56]\). Therefore, the peak at 1296 cm\(^{-1}\) might indicate the presence of P=O groups, peaks at around 1100 and 880 cm\(^{-1}\) come from both symmetric and asymmetric stretching vibrations of P-O-P bands, and those at 1110-1028 cm\(^{-1}\) from P-O-C bands \([57]\).

The results of surface microscale morphology studies are presented in Figure 6.3, where the representative micrographs of each solder mask (A-E) are shown. All test specimens contained various inorganic fillers of different loadings, sizes, and morphologies, present in the subsurface or protruding out of the solder mask as marked with circles in Figure 6.3. The relative amount and type of fillers, together with a presence of any surface features as determined from SEM/EDS analysis are summarized in Table 6.2.

Solder masks A, B, and C (Figure 6.3 (a)-(c)) contained a relatively high amount of surface fillers compared to D and E (Figure 6.3 (d) and (e)). Moreover, the size of fillers present in C specimen was the lowest, although they occurred in high amount. All the solder masks exhibited the presence of bulk surface defects - pin holes - with the size varying from hundreds of nanometers to a few microns in diameter. Examples of voids are marked with arrows on the micrographs presented in Figure 6.3. In
particular, the solder masks B and E contained the surface defects of a size in the range of 0.8-4.5 µm, and the specimens A, C, and D were found to contain the voids size of 0.2-1.3 µm.

In order to investigate the size, shape and loading characteristics of the fillers present in each solder mask, the metallographic cross sections of PCBs were prepared and the representative micrographs for each solder mask are presented in Figure 6.4. In general, the PCB structure consists of two main parts, namely, the solder mask coating and the FR-4 laminate as base material, as shown in Figure 6.4 (a). The laminate consists of epoxy resin reinforced with woven glass fibers, whereas the solder mask consists of base polymer matrix containing a number of additives, e.g. fillers, and a thickness up to ~20 µm.

Table 6.2: Summary of the solder mask (SM) features obtained by SEM/EDS analysis.

<table>
<thead>
<tr>
<th>Solder mask</th>
<th>Fillers</th>
<th>SM features</th>
</tr>
</thead>
</table>
| A           | BaSO₄, SiO₂, Mg₃Si₄O₁₀(OH)₂, Mg-O-type | - high filler loading  
- very few surface defects |
| B           | BaSO₄, SiO₂ | - high filler amount  
- high amount of surface defects  
- high amount of fine filler particles and low amount of larger particles  
- few surface defects |
| C           | BaSO₄, SiO₂ | - low filler content  
- few surface defects |
| D           | SiO₂ | - low amount of fillers  
- high amount of surface defects |
| E           | BaSO₄, SiO₂, Mg₃Si₄O₁₀(OH)₂ | - low amount of fillers  
- high amount of surface defects |
The cross-section analysis revealed the loading and morphological differences of various fillers present in solder mask. In general, the solder masks A, B and C (Figure 6.4 (b)-(d)), were found to possess large filler particles within the solder mask layer, in addition to smaller ones, that caused the surface roughness to locally raise as the particles were situated just below the surface. The solder masks D and E (Figure 6.4 (e) and (f)) were found to possess smooth surfaces compared to A, B, and C masks.

![Figure 6.4: SEM micrographs of solder mask cross sections: (a) overall structure, (b) A, (c) B, (d) C, (e) D, (f) E.](image)

**SOLDER MASK SURFACE ROUGHNESS**

The results of the surface roughness analysis obtained by mechanical profilometry are presented in Figure 6.5. Roughness parameters for all the solder masks showed the differences in the surface waviness profile and ranked the specimens from rough to smooth following the trend A > B > C > D > E. The results complied with visual observations of roughness variations between the test substrates.

Based on visual observations and stylus measurements, the largest difference between the solder masks’ roughness was observed for A and E samples. Therefore, the representative surface profiles were obtained for both substrates, which are presented in Figure 6.6. A large contrast between the surface waviness profiles was observed. The roughest solder mask A was found to contain many irregularly occurring peaks and valleys within its profile (Figure 6.6 (a)), which deteriorated highly from the zero level. On the contrary, the smoothest mask E (Figure 6.6 (b)) did not show such highly deviating profile distortions.
Figure 6.5: Surface roughness parameters measured for different solder masks: (a) $R_A$ values, (b) $R_{MS}$ values, (c) $R_Z$ values. Each point represents an average with the deviation bar given for 10 measurements.

Figure 6.6: Surface roughness profiles of solder mask specimens: (a) A and (b) E.

WATER LAYER FORMATION ON THE SOLDER MASK SURFACES

**Surface wettability**

Wetness of all the solder mask surfaces was investigated by means of static water contact angle, and the data are presented in Figure 6.7 shown in the decreasing order of values. Regardless of the solder mask type, all the surfaces showed the water contact angle values below 90°, indicating high wettability for water droplets. Substrates B and E appeared to exhibit similar low angle values, whereas solder mask D deviated the most from other substrates in terms of surface wetness. Generally, solder
masks exhibited highest 86° and lowest 59° contact angles in the following trend D > A > C > E > B, indicating as well the trend in surface energy of these substrates, as shown in Figure 6.7.

![Figure 6.7: Static contact angle of water on solder mask substrates. Each point represents an average with the deviation bar given for 5 measurements.](image)

**Observation of in-situ water layer formation**

The evaluation of the influence of surface roughness on the water layer formation was investigated in-situ on all solder mask specimens. The reported photographs in Figure 6.8 display the representative appearance of water droplets on the surfaces of solder masks (A-E).

In general, the difference in the appearance of water film build-up during the condensation experiment was caused by the varying surface roughness between the test substrates. The condensation on different solder masks, in terms of tendency of water for spreading and bridging, showed the following trend, from highest to the lowest wettability, A~B > C > D~E, respectively.

The water layer build-up on solder masks A and B (Figure 6.8 (a) and (b)) consisted of water droplets formed irregularly in the grooves of the surface. Moreover, upon continuous dewing of moisture on the surfaces, spreading of the formed water islands occurred, followed by bridging of the droplets one to another and the creation of large water islands on the surface. On the contrary, the formation of water droplets on the masks D and E (Figure 6.8 (d) and (e)) varied significantly from other samples, and in the end of experiment, the water islands were found to possess more concentric and regular shape than the droplets formed on substrates A and B. Water layer build-up on the specimen C (Figure 6.8 (c)) exhibited a behavior lying between A/B and D/E masks.

**Water layer formation and impedance change**

The observations from in-situ water film formation were supported by impedance measurements. Two representative Cu/Sn electrode-plated specimens were chosen based on the surface roughness differences, namely the laminate with a very rough solder mask (A) and smooth (D) solder mask surfaces. These specimens were subjected to moisture condensation experiment, while monitoring the impedance between the Cu/Sn electrodes. The gradual decrease of impedance signal in the course of condensation was observed. An abrupt decrease of impedance ~50 to 100 kΩ/s indicated that the formed water droplets bridged the two opposing electrodes, as shown in the representative impedance
Figure 6.8: Representative photographs of the solder masks appearance before and after cooling: (a) A, (b) B, (c) C, (d) D, (e) E. The temperature of the samples at the moment of photo capture is indicated in the right top corners. The regions appearing white are due to the camera light reflection.
curves in Figure 6.9 (a) and (b) for two pitch distances. The time-to-bridge was noted for all the pitch distances of both solder masks as given in Figure 6.9 (c).

The results show that an increase in the pitch distance between the electrodes was proportional to the time of bridging. The application of identical condensing conditions for all specimens ensured the amount of water gathered between the electrodes to be similar for a given pitch distance of both masks. However, the rapid bridging appeared on the rough surface (A) compared to the smooth surface (D), for any tested pitch distance, as presented in Figure 6.9 (c). The overview of the appearance of the solder mask area between the electrodes at the end of the condensation experiment (Figure 6.9 (d)) shows the moment the rough surface allowed for droplets bridging while the smooth surface, at the time of the measurement, allowed only for the formation of concentric droplets not connecting the electrodes.

Figure 6.9: (a) and (b) representative impedance plots for solder masks A and D with the pitch distance ~500 µm and ~2 mm; (c) time-to-bridge the electrodes during condensation (each point represents an average with the standard deviation for 3 measurements); (d) an overview of the rough and smooth electrodes appearance during the condensation experiment.

IV. DISCUSSION

The results presented in this paper relate the effect of surface topography on the water film build-up on PCBA surface that could have an adverse effect on the reliability due to the possibility of SIR reduction and introduction of corrosion failure modes. The surface composition and morphology of the solder mask were found to influence the wettability. Under condensing conditions, the roughness was
associated with the differences in droplet appearance on the solder mask surface, which was mirrored during the electrochemical measurements.

The wettability effect is primarily dependent on two factors - surface energy (related to the surface chemistry) and surface microscale roughness [58]. According to Bohr et al. [59] and Wenzel [60], an increase of surface roughness increases the wettability of hydrophilic surfaces (<90°), and decreases the wettability of hydrophobic surfaces. Despite a generally complex composition of the solder mask [20-24], the FTIR analysis showed a very similar pattern of absorption peaks due to the epoxy-type of matrix constituting the solder mask polymer [18, 19]. Since the epoxy-based material itself is generally considered hydrophilic (~70°) [61-63], the differences in wetting between the specimens arose due to the presence of fillers on the surface, its roughness, and the presence of bulk defects. The type and amount of fillers on the surface defined the surface energy, whereas the filler loading below the solder mask surface influenced its roughness.

An addition of inorganic fillers to the solder mask matrix is a common practice and serves to influence various material properties, e.g. thermal conductivity, adhesion, or a fracture toughness [22, 23, 27, 28, 30, 64-72]. However, the size and loading of the fillers play a vital role in defining the surface morphology [73]. According to the EDS analysis, the fillers found in the solder mask materials were: SiO₂ (in the form of silica or quartz), BaSO₄, and talc (Mg₅Si₄O₁₀(OH)₂) which complies with literature data [22, 23, 27, 28, 64, 67, 69-71, 74, 75]. Both silica and talc are used as matting components [71, 74], whereas silica itself also provides better thermal conductivity [76]. Furthermore, Mg-O-based particles were found on the surface of solder mask A, which potentially occur in the form of Mg stearate [29], Mg hydroxide [70], or Mg oxide [30, 67], the latter used for the improvement of thermal conductivity [77].

Although the same filler types (SiO₂, BaSO₄, and talc) were found for A and E masks, and the presence of talc would be expected to decrease wetting properties [78], this is in agreement with only solder mask A showing high contact angle compared to E mask. This can be due to the fact that solder mask A additionally contained Mg-O-based particles appearing in the form of hydrophobic magnesium stearate [79], and the addition of waxing hydrocarbons is a common practice in the PCB manufacturing process in order to reduce the solder balling [29]. Further, solder mask E was found to contain a large amount of micro-sized bulk voids, compared to nanometer-sized voids for A masks, that lead to a decrease of contact angles for E specimen. Voids in the solder masks are common and can be an effect of moisture outgassing during curing or non-optimized dispense process of the solder mask [72].

Compared to solder mask A, mask C did not contain neither talc nor Mg-O-based particles, and exhibited lower contact angles (~71°) compared to the solder mask A, which can be explained by higher surface hydrophilicity of C mask compared to A that contained hydrophobic talc and Mg-O-based particles. Further, comparing solder masks B and C, however both contained the same types of fillers, high distribution of fine filler particles on the surface of C mask could have caused masking of its pin holes and evening of the surface. Therefore, lower contact angles were observed for B solder mask, which showed a large amount of micro-sized voids causing high wettability.

Although the solder mask D contained only SiO₂, it was found to exhibit higher contact angles than solder mask A that contained hydrophobic talc and Mg-O-based filler on its surface. This phenomenon can be explained by a low surface roughness of D specimen, compared to A, B, or C masks. Typically, the filler size varies between 0.1 to 20 µm [30, 66]. Our study showed that the presence of large filler particles (in the case of solder masks A, B, and C) was up to 6 µm and were situated below the solder mask surface, which increased the surface microscale roughness. The D and E masks, due to the small filler size and low loading compared to A, B, and C masks, lacked major profile deteriorations, and exhibited a non-disturbed surface roughness. According to Wenzel [60], low surface roughness of a
hydrophilic surface (<90°) does not further decrease the contact angle as much as the rough surface does, therefore both D and E masks were expected to exhibit higher contact angles compared to A, B, and C substrates due to the low surface roughness of D and E. As mentioned before, solder mask B did not follow the expected behaviour due to the presence of large pin holes within its surface, and solder mask A, despite its highest roughness and therefore low contact angles expected, did not follow this trend due to high surface hydrophobicity.

The wettability investigations were related to microscale features of the surfaces and non-condensing conditions. Similar phenomenon was observed in [15] where the build-up of first adsorbed water layers occurred in the form of separated islands that grew and expanded, bridging other islands at high RH. The observations of water layer formation under heavy condensing conditions were in correlation with visual assessment, stylus measurements, and SEM analysis of cross sections of the specimens. The in-situ experiment revealed that in case of rough surfaces (solder masks A, B, and C), the pinning effect caused filling up of the valleys of the materials and creation of irregular water islands in the course of moisture dewing. This further led to the spreading of water droplets and their eventual bridging. The water droplets formed on smooth surfaces were of a concentric shape and did not tend to spread and bridge as easily as in the case of rough surfaces. The observations were supported by the AC measurements that allowed for monitoring of condensation as the signal was not masked by the polarization effect of corroding electrodes. The droplets build-up on the rough solder mask surfaces lead to the shorter time for bridging of electrodes which is in agreement with the literature [35, 80] where rough surface topographies were stated to contribute to the ECM occurrence and reduction of the overall time to failure. The existence of ridges within the rough material's profile implies the formation of localized areas (typically pores, grooves, valleys, or surface defects) where the capillary forces facilitate the formation of thick water layers [81]. They are believed to form a favoured path for the growing dendrites in the course of ECM due to accumulation of thick water layers in the concave part of the surface. From the reliability point of view, such phenomenon is critical [82] and may lead to short time-to-failure of the metallic components (e.g. IC legs) on a PCBA.

From a manufacturing point of view, the solder mask morphology may be dictated by its influence on solder balling [83] - solder balls do not adhere well to the rough surfaces as they form a convex meniscus. In practice, the industrial standards (f.e. IPC-SM-840 “Qualification and Performance Specification of Permanent Solder Mask and Flexible Cover Materials”) specify the evaluation of the solder mask performance (in terms of physical, soldering, electrical, or mechanical aspects), the allowed number of pin holes, or a surface tension. However, no information is reported or required regarding the morphology of the solder mask. As presented in our investigations, the solder mask roughness/topography is an important parameter for a PCBA reliability. A suitable surface morphology could delay the SIR drop under transient conditions at which the chances for thick water film build-up are high, and prolong the device’s lifetime. As the pitch sizes in electronics industry decrease [84], the susceptibility towards corrosion increases [14, 85], therefore a suitable choice of materials is necessary in order to define the safe design regimes for a risk-free product. In practice, exposure of devices to humid environment and situations causing condensing conditions are transient, therefore a fraction of an hour delay in bridging the conductors by the water film could significantly enhance a long term reliability of the device. Once the device is “on” for a certain amount of time, the internal heating of the device will remove the water film, therefore the condensing conditions cease. The merit of this work lies in the fact that by a proper choice of solder mask surface morphology it is possible to delay the water film bridging that leads to the reduction of surface insulation and related corrosion failure issues.
V. CONCLUSIONS

1) The solder mask surface wettability is influenced by the surface roughness, filler types, and presence of bulk defects (pin holes), the latter having the most pronounced effect than other factors related to surface features. Low contact angles (high wettability) were observed for substrates characterized by high surface roughness and occurrence of large amount of large voids. High contact angles (low wettability) were found for samples containing hydrophobic fillers (talc and Mg-O-type).

2) Large filler particles situated below the solder mask surface locally increase its roughness, which under condensing conditions allows for water droplets to spread easily and bridge in irregular shapes with the nearby formed water droplets. The results indicate that, from the corrosion reliability point of view, the failure may occur faster on the PCBAs with rough solder mask surfaces.

3) The impedance technique complied with in-situ observations of water film formation on the PCBA surfaces. The results imply that under the same condensing conditions, shorter time for electrode bridging occurs on the rough solder mask surface compared to the smooth one, which can have detrimental effect on the reliability of the device exposed to transient conditions.

VI. REFERENCES


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7. THERMAL DECOMPOSITION OF SOLDER FLUX ACTIVATORS UNDER SIMULATED WAVE SOLDERING CONDITIONS

Kamila Piotrowska, Morten Stendahl Jellesen, Rajan Ambat

Abstract - Purpose – The aim of this work is to investigate the decomposition behaviour of the activator species commonly used in the wave solder no-clean flux systems and to estimate the residue amount left after subjecting the samples to simulated wave soldering conditions.

Design/methodology/approach – Changes in the chemical structure of the activators were studied using Fourier transform infrared spectroscopy technique and were correlated to the exposure temperatures within the range of wave soldering process. The amount of residue left on the surface was estimated using standardized acid-base titration method as a function of temperature, time of exposure and the substrate material used.

Findings – The study shows that there is a possibility of anhydride-like species formation during the thermal treatment of fluxes containing weak organic acids (WOAs) as activators (succinic and DL-malic). The decomposition patterns of solder flux activators depend on their chemical nature, time of heat exposure and substrate materials. Evaporation of the residue from the surface of different materials (laminate with solder mask, copper surface or glass surface) was found to be more pronounced for succinic-based solutions at highest test temperatures than for adipic acid. Less left residue was found on the laminate surface with solder mask (~5-20% of initial amount at 350°C) and poorest acid evaporation was noted for glass substrates (~15-90%).

Practical implications – The findings are attributed to the chemistry of WOAs typically used as solder flux activators. The results show the importance of WOA type in relation to its melting/boiling points and the impact on the residual amount of contamination left after soldering process.

Originality/value – The results show that the evaporation of the flux residues takes place only at significantly high temperatures and longer exposure times are needed compared to the temperature range used for the wave soldering process. The extended time of thermal treatment and careful choice of fluxing technology would ensure obtaining more climatically reliable product.

Keywords - Corrosion, flux, quality control, flux chemistry, climatic reliability of electronics, thermal decomposition.

I. INTRODUCTION

The manufacturing process for printed circuit board assemblies (PCBAs) requires a careful choice of soldering materials, as well as process control including the selection of no-clean flux systems. The reliability of the solder joints depends not only on the soldering method and the solder material itself, but also on the flux properties and its reactions with the components of the assembly [1]. The solderability could be significantly improved by the use of flux systems, as they clean the components
to be joined from contaminating films and oxides, and protect them from reoxidation until the soldering is completed [1-5].

With the introduction of no-clean flux systems for automated lead-free soldering (wave, reflow or selective), the assumption is that the process-related residues would be distributed all over the surface of the assembly at a negligible level. However, significant levels of no-clean flux residues are always present on PCBAs after the soldering process. Although the residues are expected to be benign, in practice, the chemical nature of flux residues on PCBAs is of significant concern for the long-term stability and reliability of electronic devices. At the soldering temperatures, any thermal degradation, or the presence of transition products of flux species, must be either non-corrosive or else it must be possible to remove them completely [2]. However, the decomposition pattern of the solder flux systems depends strongly on the amount of flux applied, its solid content and chemical properties, time and temperature, the heating rate of the fluxing step, type of soldering process, geometry and design of the PCBAs, etc. [6-10].

Typically, flux systems used in the electronics industry consist of activators (organic acids, halides, etc.), solvents (alcohols, ethers, esters, hydrocarbons, water, etc.), vehicles/binders (rosin, resin, non-volatile polyols, etc.) and additives (surfactants, inhibitors, antioxidants, plasticizers, etc.) [11, 12]. From the corrosion/reliability point of view, the species responsible for corrosion failures in electronics are mainly the flux activators. Typically, these are weak organic acids (WOAs) which are ionic and hygroscopic in nature; therefore, they significantly reduce the critical relative humidity level for water film formation on the PCBA surface [13-15]. This results in the reduction of surface insulation resistance on the PCBA surface or other corrosion failure modes [10, 15-21].

Flux residue distribution and level depend on the type of soldering process [22, 23]. From the climatic/reliability point of view, process-related residues resulting from the wave soldering process are considered to be more dangerous than reflow soldering process. This is because of the fact that the wave soldering process uses liquid flux, unlike flux paste for the reflow soldering process. The use of flux paste in the reflow soldering process limits the residue to be localized below the components, whereas in the wave soldering process, it is spread all over the PCBA surface. In the wave soldering process, flux is sprayed onto the bottom side of the PCBA; however, some amount of flux can also reach the top part of the PCBA as spray droplets infuse through via holes. The top part of a PCBA during the wave soldering process experiences only 175°C, which is significantly less compared to the bottom part (about 250°C) [24]. In the selective wave soldering process, significant amounts of liquid flux can be trapped under the pallet and not exposed to thermal treatment sufficient for their removal or decomposition. It was reported previously that solder flux activators may not decompose completely within the temperature range of the soldering step [25].

The formation of residues from WOA-based flux systems can be determined by the acid's ability to melt and evaporate from the PCBA surface under high soldering temperatures. Such a property depends on the acid's boiling point, therefore, influencing the rate of acid removal during the soldering process. Similarly, the interaction of the humidity with the residue depends on the deliquescence behaviour of the acids, which is a function of the hygroscopicity and solubility of activators in water. A typical decomposition path for WOA flux activators is a full or partial formation of anhydrides – species with the ability to attract moisture from the surroundings higher than the organic acids from which they are derived, and which could influence the PCBA reliability by reacting with copper oxides and forming complex compounds [26].

Available information in the literature on the relative decomposition and the level of residues formed from no-clean WOA activators is limited. Most of the reported investigations focus on
organometallic complex formation from flux activators in reaction with metal surface [26] or focus on the hygroscopic effect of WOAs and related impact on the surface insulation resistance [26-31]. A number of papers deal with the effect of flux on electrical signals in general, with no differentiation between the acid types [27, 32-34] although the corrosive behaviour was proven to be dependent on the chemical structure of the activators and their decomposition products [29].

The present investigation reported herein focused on understanding the decomposition pattern of WOA flux activators and their relationship to chemistry, amount and type of residue formed. The amount of flux residue was quantified as a function of simulated wave soldering temperature, time of heating and substrate material. Monitoring of the structural changes of WOA activators as a function of temperature was carried out using Fourier transform infrared spectroscopy (FTIR) and pure acids. Quantification of the residue amount was conducted using a standardized acid-base titration method for both pure acids and commercial flux systems. Residue evaporation from the surface was studied on different substrate materials (laminate with solder mask, copper and glass) and fabricated test rigs.

II. MATERIALS AND METHODS

WEAK ORGANIC ACIDS AND FLUX SYSTEMS USED FOR INVESTIGATION

Six WOAs serving as activators in typical no-clean flux systems commonly used in the electronics industry [2, 21, 26, 28, 31] were used for the investigation. The activators studied were DL-malic acid, succinic acid, glutaric acid, adipic acid, suberic acid and palmitic acid. All of them were used as pure analytical grade crystals supplied by Sigma Aldrich. Table 7.1 shows the melting and boiling points of various WOAs, together with their chemical structures.

Table 7.1: Organic acids typically found in solder flux systems – summary of physical and chemical properties [35, 36].

<table>
<thead>
<tr>
<th>WOA name</th>
<th>Chemical structure</th>
<th>SUCCINIC ACID</th>
<th>GLUTARIC ACID</th>
<th>ADIPIC ACID</th>
<th>SUBERIC ACID</th>
<th>DL-MALIC ACID</th>
<th>PALMITIC ACID</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Melting point</td>
<td>Melting point</td>
<td>Melting point</td>
<td>Boiling point</td>
<td>Boiling point</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>185-189°C</td>
<td>95-98°C</td>
<td>151-154°C</td>
<td>140-144°C</td>
<td>130-132°C</td>
<td>61-63°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>235°C</td>
<td>302-304°C</td>
<td>337°C</td>
<td>345.5°C</td>
<td>150°C (decomp.)</td>
<td>351-352°C</td>
</tr>
</tbody>
</table>

The required amounts of pure WOAs were dissolved in isopropyl alcohol to obtain the 2.5 and 5% wt/v solutions similar to the levels of WOA found in commercial flux systems. These solutions were used for the thermal decomposition studies of pure WOAs.

Additionally, six commercially available no-clean flux systems were investigated for their decomposition behaviour. Table 7.2 shows the investigated flux systems with the flux classification according to J-STD-004 carrying information on the WOA activators. The type of activator was obtained either from the safety data sheets or by using FTIR and ion chromatography analysis. All of them were liquid-type volatile organic compound (VOC)-based fluxes used in wave or selective soldering processes.
### Table 7.2: Commercial flux systems used for investigations and their characteristics.

<table>
<thead>
<tr>
<th>Flux symbol</th>
<th>Acidic constituent</th>
<th>J-STD-004 standard designation*</th>
<th>Acid value [mg KOH/g]</th>
<th>Solid content [%wt]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF1</td>
<td>Succinic acid</td>
<td>REL0</td>
<td>18.5-19</td>
<td>1.9</td>
</tr>
<tr>
<td>SF2</td>
<td>Adipic acid</td>
<td>REL0</td>
<td>14.2</td>
<td>8.5</td>
</tr>
<tr>
<td>SF3</td>
<td>Succinic + glutaric + adipic acids</td>
<td>ORL0</td>
<td>33.5</td>
<td>4</td>
</tr>
<tr>
<td>SF4</td>
<td>Succinic + resin &amp; rosin fumarated acids</td>
<td>ROL9</td>
<td>23.4</td>
<td>-</td>
</tr>
<tr>
<td>SF5</td>
<td>Succinic acid</td>
<td>ORL0</td>
<td>14.2</td>
<td>1.5</td>
</tr>
<tr>
<td>SF6</td>
<td>Adipic acid</td>
<td>REL0</td>
<td>22</td>
<td>2.2</td>
</tr>
</tbody>
</table>

*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; the last number specifies halides content: 0-(<0.05% wt/wt).*

### SUBSTRATE MATERIALS AND TEST RIGS

Different substrate materials and test rigs were used for decomposition studies of WOAs and fluxes. The aim was to investigate the effect of materials similar to the laminate and metallic surfaces present on the PCBA. Simple FR-4 laminate materials covered with ~20 µm of solder mask (panel of dimensions 90 x 90 x 1.6 mm) and FR-4 laminate covered with a thin copper layer of 35 µm (panel of dimensions 80 x 100 x 1.6 mm) were used to study the thermal decomposition from opened areas of evaporation. For comparison, a borosilicate glass dish of 16 cm² surface area was used.

To study the effect of trapped residue, two types of test rigs were fabricated to simulate the flux flow under components on a PCBA and its subsequent evaporation and decomposition. The test rig consisted of two panels, one above the other, as shown in the Figure 7.1, separated by a fixed distance of 500 µm. Material for the top panel was changed depending on the requirements (FR-4 or copper). Material at the bottom was FR-4 laminate. The surface area under the small lid for both test rigs was 16 cm².

![Figure 7.1](image-url): Test rig used for decomposition studies of entrapped residues: (a) top view, (b) side view (dimensions given in mm).

The required WOAs or fluxes were applied on the substrate surface by spraying to simulate the wave soldering flux spray process. One spray of the activator solution over the piece of laminate material (~80 cm²) resulted in a mass change of approximately 0.25 g. Therefore, samples of one (0.25 g) and two sprays (0.5 g) were tested, of 2.5% and 5% wt/v concentrations. For studying the flux removal rate from the opened substrates (~80 cm² for laminates, 16 cm² for glass dish), the contaminating solutions were applied all over the surface area by spreading the sprayed solution. For testing of entrapped
residue using fabricated test rigs, the solutions with desired WOAs or fluxes were injected in between the gap (surface area of 16 cm²). The contaminated test objects were placed in the oven and subjected to a radiative thermal treatment using a wave soldering profile.

**FLUX ACTIVATION TREATMENT**

All of the pre-contaminated samples were thermally activated at two temperatures, namely, 175 ± 5 and 250 ± 5°C, representing the temperatures at the upper and lower sides of the PCB surface during the wave soldering process, respectively [24]. As a reference, the residue obtained at room temperature was quantified. The time of thermal treatment was 45 s, which simulated the soldering part of the wave soldering profile. For some cases, an additional activation treatment at 350 ± 5°C was conducted to get a better understanding of the decomposition behaviour, as well as an activation time of 10 min.

**ANALYSIS TECHNIQUES**

*Fourier transform infrared spectroscopy*

The chemical structures of the residues were analyzed by FTIR using a Nicolet™iN™10 MX infrared imaging microscope and OMNIC software. The samples were analyzed using the attenuated total reflection method. The detector used for measurements was an mercury cadmium telluride (MCT) detector cooled with liquid nitrogen. All spectra were recorded in the range of 4000-675 cm⁻¹ with a resolution of 4 cm⁻¹.

*Standardized acid-base titration*

To evaluate the acid content in the residue sample, a standardized acid-base titration was conducted (IPC-TM-650 test method, number 2.3.13 "Determination of Acid Value of Liquid Solder Flux – Potentiometric and Visual Titration Methods"). This quantified the volume of 0.1M KOH solution in isopropyl alcohol needed to neutralize the amount of acid present in 1 g of the solder flux sample. After thermal treatment of the activators, the residue was rinsed with 50 mL of isopropanol and gathered in Erlenmeyer flask. The acid–base equilibrium indicator (phenolphthalein) was then added, and the whole mixture was titrated with a potassium hydroxide (KOH) solution. The titrant was added until the mixture changed colour from transparent to pale pink. Each experiment was repeated three times. The acid value was calculated using the following formula:

\[
\text{Acid value} = \frac{V \cdot M \cdot 56.11}{m}
\]

(Eq. 7.1)

where \(V\) is the volume of the titrant used (mL), \(M\) is the molarity of the titrant solution (mol/L) and \(m\) is the mass of the sample (g). The acid value is expressed as mg of KOH used to neutralize the amount of acid present in 1 g of the solder flux.

**III. RESULTS**

**FOURIER TRANSFORM INFRARED SPECTROSCOPY ANALYSIS**

Six analytically pure samples of WOA powder (1 g) were tested at room temperature and after activation at 175 ± 5 and 250 ± 5°C. Adipic, suberic, glutaric and palmitic acids did not show any change in their infrared spectra after heating the samples up to 250°C for 45 s. For succinic and DL-malic acids, slight changes in the IR spectra were observed. Figure 7.2 shows a comparison of the spectra obtained for succinic and DL-malic acids at three different temperatures. The highlighted regions in the spectra
show the observed changes in the peaks’ appearances after the thermal treatment. All the spectra showed absorption peaks at around 2950-2870 cm\(^{-1}\) that are assigned to the symmetric and asymmetric C-H stretching vibrations coming from the single bonds in the CH\(_2\) organic acid chain. Changes in the succinic acid spectrum were observed at vibrational frequencies of 1785, 1325 and 1303 cm\(^{-1}\). For DL-malic acid, the absorption peaks in the region of 1408-1173 cm\(^{-1}\) showed some distinct changes in the shapes of the peaks. For DL-malic acid, the fingerprint region between 1500-500 cm\(^{-1}\) showed different patterns for all three temperature conditions. Additionally, a peak at around 1736 cm\(^{-1}\) disappeared for the thermally treated samples.

Figure 7.2: The FTIR spectra in the wavenumber from 675 to 3600 cm\(^{-1}\) to the left and with zoom of 675 to 1900 cm\(^{-1}\) to the right: (a) succinic acid, and (b) DL-malic acid.

**FLUX RESIDUE QUANTIFICATION**

*Effect of activator type and activation treatment*

The values of acid number (acid content) of the residues obtained by titration of 1 g samples of 5% wt/v solutions with KOH solution of fixed concentration (following the IPC standard) for six different WOAs are shown in the Figure 7.3. The acid number is presented as a function of temperature for the samples tested on a Petri dish. Standard deviations for three repetitions are given for each data set. For all WOAs, only negligible changes in the acid values were found after heating the acids at 175°C. After the thermal treatment at 250°C, DL-malic and succinic acids showed a significant decrease in the acid number. Heating at 350°C resulted in a clear drop of the residue amount for DL-malic, succinic, glutaric and adipic acids. However, no changes were observed for any given test temperatures for suberic and palmitic acids.

Figure 7.3: Acid values for six different WOA residues obtained after activation at various temperatures on a Petri dish.
To evaluate the relative effect of the heating time on the acid evaporation from actual flux systems, samples of liquid solder fluxes (1 g) based on succinic acid (SF1), adipic acid (SF2), a mixture of succinic, glutaric and adipic acids (SF3), and a mixture of succinic and resin/rosin fumarated acids (SF4) were applied onto a Petri dish and thermally treated at 175 ± 5 and 250 ± 5°C (Figure 7.4) similar to the treatment provided for the WOAs. The prolonged heat exposure time of 10 min was used to assess its impact on the residue removal. Although the 45 s treatment did not significantly lower the levels of residues, the prolonged heating for 10 min at 250°C removed the residues significantly. However, thermal treatment at 175°C for 10 min did not show a significant change in residue levels.

![Figure 7.4: The acid levels in the residue formed from typical flux systems after thermal treatment at various temperatures and time intervals.](image)

**Substrate effect and trapping of residues during heating**

The influence of a substrate material on residue formation and its trapping under the components was investigated for two different WOAs (succinic and adipic acids) using different materials and test rigs shown in the Figure 7.1. Figure 7.5 presents the percentage of the acid amount left plotted against various heat treatment temperatures. The melting points (mp) and boiling points (bp) of the respective acids are indicated on the graphs.

Three types of samples were tested:

(i) 0.5 g of 5% wt/v solution,
(ii) 0.5 g of 2.5% wt/v solution, and
(iii) 0.25 g of 2.5% wt/v solution.

The residue amounts for (ii) and (iii) showed similar evaporation trends, therefore only those for (iii) are shown in the Figure 7.5.

For both acids, a significant decrease in residue amount was observed only after a 350°C thermal treatment. The values decreased to the level from 5 to 45% of the original values for most substrate materials, whereas the case of evaporation from trapped regions using test rigs showed less significant decrease to the level of 40-80% of the original values. A considerable amount of residues was left, even after the activation treatment at 250°C. The highest and fastest decrease in the acid levels was found for the laminate substrates and the test rig consisting of laminate with laminate on the top.
A similar investigation was carried out using actual flux systems, namely, SF1, SF2, SF5 and SF6 containing the above tested acids. For individual experiments, a sample of the liquid flux (0.25 g) was subjected to the thermal treatment followed by standardized titration (Figure 7.6). Figure 7.6 (a) and (c) show that the succinic acid-based fluxes (SF1 and SF5) appeared to be easily removed with residue levels decreasing to 75% of the initial values at 175°C, whereas for adipic-based SF2 and SF6 the level decreased only to 85-95% of the initial values (Figure 7.6 (e) and (g)). At higher temperatures, namely, 250 and 350°C, the residue levels were significantly reduced for succinic acid-based flux systems, unlike for the adipic acid-based ones. Evaporation from the test rigs with closed areas takes place very slowly; therefore, a significant decrease was found only at the high temperatures close to 350°C for succinic-based SF1 and SF5 (Figure 7.6 (b) and (d)) trapped between the laminate-laminate combination (drop to 30-45% of the initial values). For adipic-based flux systems, SF2 and SF6 (Figure 7.6 (f) and (h)), residue removal was significantly less for the same test rig (it only dropped to approximately 70% of the initial values).
Figure 7.6: Influence of different materials on acids' removal from fluxes: (a) and (b) SF1, (c) and (d) SF5, (e) and (f) SF2, (g) and (h) SF6.
IV. DISCUSSION
FOURIER TRANSFORM INFRARED SPECTROSCOPY ANALYSIS

Investigation of the chemical structures of pure acids as a function of temperature did not show any changes in structure for adipic, suberic, glutaric and palmitic acids. The boiling points for those acids are above 300°C, therefore, only limited levels of evaporation take place below this temperature. The FTIR spectra of succinic and DL-malic acids showed differences depending on the treatment temperature. The observed changes can occur because of the possible partial formation of other species, namely, organic acid anhydrides [37]. At such high temperatures, simulating soldering temperatures, evaporation of water from the acid molecule will take place. Dicarboxylic acids (WOAs) may undergo decomposition in several ways – sometimes very complex – when exposed to high temperatures [10], but everything depends on their boiling points, and chemical nature [26]. The thermal decomposition of WOAs depends on the amount of methylene units within the molecule, which determines the chain length: acids of lower molecular weight decompose easier than the higher ones [37]. All dicarboxylic acids may form anhydrides at their specific temperatures, although the formation of adipic and higher anhydrides may require the existence of particular conditions in addition to very high temperatures [38].

For succinic acid, the formation of anhydride takes place at 235°C [31]. Changes in IR spectra observed around 1300 cm\(^{-1}\) indicated C-O bond formation for cyclic acid anhydrides (1300-1176 cm\(^{-1}\)). The single peak became divided into two, probably because of the fact that C-O bonds in symmetric acid become differentiated in the anhydride and non-symmetrically arranged in space or because of the fact that there was still acid present in the heated sample. The growing peak at around 1785 cm\(^{-1}\) can be assigned to C=O vibrations in the five-unit ring of succinic anhydride (1870-1818; 1800-1750 cm\(^{-1}\)) [39, 40]. The obtained spectra can point to the existence of both succinic acid and its anhydride in the sample after thermal treatment (Figure 7.7 (a)). It was stated [37] that the dicarboxylic acids of an even number of methylene units (i.e. C2-succinic) should undergo the decomposition/decarboxylation process at higher temperatures than the acids of the next higher odd number of carbon units (i.e. C3-glutaric). However, the formation of glutaric anhydride was not observed in this study although the resulting five-membered (for succinic) and six-membered (for glutaric) anhydride rings are energetically most favourable to produce [38].

![Diagram](image)

**Figure 7.7:** Possible pathway for thermal decomposition products of (a) succinic, (b) DL-malic acids.

In the case of DL-malic acid, more changes in the spectra were observed. This acid decomposes at 130-150°C to CO, CO\(_2\), maleic acid and maleic anhydride (Figure 7.7 (b)). During dehydration at high temperatures, the water molecule is formed in the first step from the hydroxyl group and hydrogen atom
of the nearest CH$_2$ group, which results in the formation of species with a double bond. It is hard to distinguish these species clearly in the IR spectra, but the decrease of peak intensity at around 3500 cm$^{-1}$ indicated the slow disappearance of hydroxyl groups from the sample (probable dehydration). Even if double bonds did occur, they would have appeared just below 3000 cm$^{-1}$ [40] and have overlapped those coming from the single C-H bonds, making them impossible to distinguish. Changes in vibrational frequencies at 1737 cm$^{-1}$ and between 1408-1173 cm$^{-1}$ indicate changes in C=O and C-O bonds, respectively, and can point into the partial formation of the anhydride [39]. The differentiation of peak shape and intensity at around 980-837 cm$^{-1}$ could be because of changes in the hydroxyl groups.

**RESIDUE AMOUNT QUANTIFICATION**

**Effect of activator type and activation treatment**

Heat treatment of WOA samples on a Petri glass dish at 175 and 250°C resulted in significant amounts of acids remaining on the surface. This could have been the result of the rather short treatment time (45 s), as the thermal energy was mostly used to evaporate the solvent, followed by the acid. The obtained results presented a good correlation between the acid value and changes in acid chain length: the longer the chain/molecular weight, the higher the boiling temperature [41]; therefore, less amount will be evaporated in a given time. It was also stated that the boiling point increases with an increase in the carbon atoms in even numbered molecules of dicarboxylic acids (succinic, adipic and suberic) [37], the trend which was followed by the obtained results on acid amounts after thermal treatment, though the melting points of these acids decreased in the same order.

At 350°C, for DL-malic, succinic, glutaric and adipic acids, there was a significant decrease in the amount of acid present. This was most likely because of the fact that their boiling temperatures are lower than 350°C [31] but higher than 235°C, and their partial evaporation was more likely to proceed at 350°C than at 175 and 250°C. For suberic and palmitic acids, there was a similar acid amount left at all tested temperatures, which correlated with their high boiling points (345.5°C and 351-352°C, respectively [35, 36].

The extended thermal treatment time did not result in total evaporation of the residue, as was expected. After heating at 175°C for 10 min, there was no significant change in the acid amounts, which might have been because of the need for higher temperatures for evaporation and decomposition. Only at 250°C, a drop in residue amount was observed. For succinic acid-based flux, SF1, the amount of residue was reduced by 90%, which could be associated with its boiling point of 235°C, whereas for adipic acid-based flux, SF2, residue levels went down by 88%. Flux systems SF3 and SF4 based on the mixture of acids showed a drop-in residue amount by 60% of their initial values at 250°C. Possibly, there was an influence of rosin content in the SF4 flux composition, which does not allow a simple residue removal at soldering temperatures (comparing to SF1). The boiling points of the typical acidic isomers constituting rosin are 413-440°C [35, 36]. These are higher than the temperatures experienced during the soldering process [24]. Overall, the results show that residue removal depends significantly on the exposure temperature. However, the kinetics play a big role; therefore, the time of exposure to a particular temperature is of great importance as well.

**Substrate effect and trapping of residues during heating**

Substrate influence on evaporation of residues from flux systems was investigated with the use of two representative pure WOA solutions and four commercial flux systems containing those acids. It is possible to remove significant amounts of activator (WOAs) from the surfaces having opened areas for evaporation. Thermal treatment of residues at 350°C for 45 s on laminate sheet always resulted in their
lowest amounts for all samples tested. For the laminate material covered with a thin layer of copper, the contamination amount was always higher in comparison to the laminate surface. Thermal treatment of residues on a Petri glass dish left the highest amounts of acids in all the cases. This could be because of the fact that their heat capacities/thermal conductivities differ, which will result in their uneven heating up [42]. The thermal conductivity of an FR4 substrate is very low and varies from 0.25 W/m·K [43] to 0.35 W/m·K [44], whereas for copper, the values are much higher 355 W/m·K [43] or 398 W/m·K [44]. However, the specific heat capacity of copper is around 385 J/kg·K, whereas for laminate it is 880 J/kg·K [45] - 1210 J/kg·K [46]. This means it should be relatively easier to evaporate the residue from the copper surface. However, a significant level of residue on the copper surface might be because of the fact that it is only a copper coating of 35 µm. Therefore, the whole copper-coated laminate material is believed to possess poorer thermal conductivity properties than pure copper sheet. Further, it is suspected that the organic residue left on the copper surface reacted with copper or copper oxide at high test temperatures. The reaction with copper can result in the formation of colourful copper complexes or chelates/ring compounds [26]. As a result, the developed species include a copper atom in the centre of the new compound, with the bonded organic functional groups originating in the acid structure. It was noticed during the experiment that the copper surface underwent a little darkening and a change of colour to green-blue after 45 s of thermal treatment with contamination present. It was reported [47, 48] that the products of copper reactions with organic species are blue or green which is, in fact, what was observed in this study. The fact that the formation of copper complex species took place explains the poor evaporation rate and, therefore, the high amount of residues left after the thermal treatment.

In general, the study indicated that any contamination placed on the PCBA materials may experience different thermal treatment, even though the temperature used for the activation is the same. Because of the combined effect of the thermal properties of the materials and flux components, and kinetics of decomposition, significant differences in residue amounts can be found. Evaporation of entrapped contaminants from the test rigs was even less effective compared to the opened areas.

V. CONCLUSIONS

1) Among all the tested WOAs, succinic and DL-malic acids underwent thermal degradation at high soldering temperatures and formed additional anhydride-like species, some of which had a more aggressive chemical nature than the flux activators.

2) Of all the activators, only certain amounts of DL-malic, glutaric and succinic acids evaporated at 250°C after 45 s treatment from the Petri dish glass. Except for palmitic acid, other acid types evaporated at 350°C treatment in significant amounts. The trend in evaporation was the result of the difference in boiling points of these organic species.

3) The prolonged time of heat treatment of the fluxes (10 min) was not sufficient to ensure their full evaporation. Almost no change was noted for testing at 175°C, and the treatment at 250°C allowed for more significant evaporation of succinic- and adipic-based flux systems.

4) Testing of different materials and test rigs showed that it was slightly easier to evaporate succinic acid-based mixtures than adipic acid-based ones. Almost a total drop of residue amount for both
contamination types occurred at 350°C for opened substrates when testing. Evaporation from closed areas did not result in a significant reduction of contamination amounts even at 350°C.

5) Residue removal from a laminate surface was found to be more effective compared to a copper-coated surface because of the reaction between WOAs and copper surface.

6) In general, the results showed that the decrease in flux residue levels occurred only at significantly high temperatures and longer time of exposure times compared to the range used for the soldering process.

VI. REFERENCES


8. THERMAL DECOMPOSITION OF BINARY MIXTURES OF WEAK ORGANIC ACTIVATORS USED IN NO-CLEAN FLUX SYSTEMS AND IMPACT ON PCBA CORROSION RELIABILITY

Kamila Piotrowska, Feng Li, Rajan Ambat

Abstract - No-clean solder flux systems are commonly used for the wave soldering purposes of Printed Circuit Board Assemblies (PCBAs), and typically weak organic acids (WOAs) serve as activators in the flux formulations. After the soldering process, significant levels of hygroscopic residues are usually left on the PCBA surface, which may be detrimental from the corrosion reliability point of view. The aim of this work is to investigate the decomposition behavior of binary mixtures of organic activators commonly used in the no-clean flux formulations upon the exposure to thermal treatments simulating the wave soldering temperatures. Three mixture types of varying ratios between the acids were studied: adipic : succinic, adipic : glutaric, and succinic : glutaric. Differential scanning calorimetry and thermogravimetric analysis were used to study the characteristics of WOA mixtures degradation in terms of weight loss as a function of temperature. The amount of residue left on the surface after the heat treatments was estimated by gravimetric measurements as a function of binary mixture type, temperature, and exposure time. Ion chromatography analysis was employed for the identification of the decomposition preferences between the activators in binary blends. The aggressivity of the left residue was assessed using the acidity indication gel test, and effect of reliability was investigated by DC leakage current measurement performed under varying humidity and potential bias conditions. The results show that if the residues comprise of binary mixture of weak organic activators, the final ratio between the components, the residue level, and the corrosive effects depend on the relative decomposition behavior of individual components. Among the WOA investigated under the conventional wave soldering temperature, the evaporation and removal of succinic acid is more dominant compared to adipic and glutaric acids.

Keywords - Corrosion, humidity, soldering, solder flux, quality control, thermal decomposition, binary mixtures.

I. INTRODUCTION

The manufacturing process of electronic units – printed circuit board assemblies (PCBAs) – is required to assure the overall reliability by a careful choice of the soldering materials and process characteristics [1]. Solder flux systems, used for the component assembling process, improve the solderability of metallic surfaces by reacting with them and removing the oxides. This results in good wettability [2, 3], and the formation of oxide-free and mechanically robust joints [4, 5]. The durability of the solder joint depends on the type solder flux (reactivity with the metal) and the soldering material [6]. However, the majority of the reported failures in the electronics industry originate from the post-production residues of the soldering materials remaining on the PCBA surface. Their presence facilitates
the formation of water layer on a PCBA surface under humid conditions [7, 8], which leads to electrochemical process resulting in leak current and failure modes such as electrochemical migration (ECM). The potential threat to the overall device reliability is therefore a function of the flux chemistry and its thermal decomposition characteristics under the soldering temperatures.

The introduction of no-clean technology for automated soldering purposes aims to increase the reliability by using the soldering chemicals that evaporate or decompose during the soldering process [9]. Moreover, any process-related residues remaining on a PCBA surface are assumed to be non-corrosive [10] and present in a minimal level. However, the assemblies are often contaminated with the significant amounts of no-clean solder flux residues that do not decompose completely under the soldering temperatures [6, 8, 11]. The decomposition of solder flux system and the final residue distribution and levels are a function of the soldering process (e.g. heating time and temperature profile) and the flux itself (e.g. chemical properties, form, and solid content) [12]. Flux paste is used for the reflow soldering process, and the eventual contamination is typically localized below the components. For the automated wave soldering process, liquid formulations are used, where the flux is sprayed onto the bottom of PCBA. However, often some amount of flux infuses through the via holes reaching the top part of the assembly [13]. The thermal profiles of both sides are different as the top part experiences only 175°C, whereas the bottom part can reach even 250°C. This means that the residues on the top part do not experience the same thermal treatment and may not undergo the same decomposition or evaporation profile [8]. From the corrosion reliability point of view, the residues originating from the wave soldering process contribute to the majority of the reported failures, therefore are considered to be more critical than the residues formed under the reflow conditions.

Solder flux systems used for the wave soldering purposes contain a number of ingredients: (i) solvent – a medium carrying all the flux components, (ii) activator – typically weak organic acids (WOAs), (iii) vehicle/binder – non-volatile resin or rosin, and (iv) additives – corrosion inhibitors, foaming agents, surfactants, etc. [1, 14]. Activators are the chemicals that react with the metal oxides and allow for the formation of a strong metallurgical bond between the joint and molten solder. However, these are also the flux components that contribute to the corrosion failures in electronics exposed to humid conditions [9, 15-19]. Due to the hygroscopic nature of WOAs, the adsorption and absorption of moisture to the PCBA surface is facilitated [15] at the critical relative humidity (RH) levels characteristic for each WOA. This results in the formation of water layer with varied conductivity, depending on the type of WOAs [20]. Under bias conditions, the presence of an electrolyte between the conductors leads to the leak current and reduction of surface insulation resistance (SIR), which eventually may result in the corrosion occurrence such as electrochemical migration (ECM) [9, 16, 21-25]. The chemistry of process-related residues remaining on the PCBA surface after the soldering process and the surrounding temperature/humidity conditions are the factors directly associated with the extent of corrosion [7].

The potential risk of corrosion occurrence on the PCBA surface is dictated by the tendency of the residues to decompose during the soldering process [1], which is related to the melting and boiling temperatures characteristic for each flux activator. Moreover, the range of temperatures that can be experienced by the residues upon the soldering process defines the residual contamination level [22]. The physicochemical properties of activators, namely the critical RH, solubility, and dissociation constant (pKₐ) become meaningful in the connection to humid conditions where the risk of electrochemical migration exists [7, 19].

Literature data offers limited information on the particular residue levels that can be expected on the PCBA surface under different thermal conditions of a wave soldering process. The reported studies
do not tend to discuss the evaporation tendencies and related corrosive effects in relation to the flux chemistry (activators) [24-27], but describe the general SIR effects for the flux systems as a whole. Limited number of papers characterize the impact of activating flux components on corrosion reliability, however, only for the systems comprised of single WOA activator. This paper shows the decomposition tendencies of binary mixtures of weak organic acid activators, which are discussed from the chemistry point of view. The importance of flux chemistry and sufficient thermal treatment in relation to the corrosion effects were evaluated in terms of SIR response under humid conditions. The differential scanning calorimetry and thermogravimetric analysis were used to assess the characteristics of WOA mixtures degradation under increasing temperature. The quantification of WOA residues was carried out using a gravimetric method for different mixture types, ratios, and thermal treatments simulating the wave soldering conditions. The ion chromatography analysis was used to rank the WOA activators according to their decomposition preferences when two acids comprise a binary mixture. The corrosivity of residues formed at different soldering temperatures was evaluated using DC leakage current measurements performed under varying humidity and potential bias conditions on the SIR comb patterns.

II. MATERIALS AND METHODS

ACTIVATOR MIXTURES USED FOR INVESTIGATIONS

Three weak organic acids, commonly found in the no-clean flux formulation for the automated wave soldering process, were selected to compose various binary mixtures. The acids were: adipic acid, succinic acid, and glutaric acid. Table 8.1 summarizes the chemical and physical characteristics of the chosen activators relevant for this study.

<table>
<thead>
<tr>
<th>Name</th>
<th>ADIPIC ACID</th>
<th>SUCCINIC ACID</th>
<th>GLUTARIC ACID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C₆H₁₀O₄</td>
<td>C₄H₆O₄</td>
<td>C₅H₈O₄</td>
</tr>
</tbody>
</table>
| Chemical structure | HOOC
\[-\text{CONH2}\-\text{COOH} | HOOC
\[-\text{CONH2}\-\text{COOH} | HOOC
\[-\text{CONH2}\-\text{COOH} |
| Melting point [°C] | 151-154 | 185-189 | 95-98 |
| Boiling point [°C] | 337 | 235 | 302-304 |
| pKₐ₁; pKₐ₂ | 4.44 ; 5.43 | 4.21 ; 5.65 | 4.34 ; 5.3 |
| Solubility at 25°C | 24; 24.97 | 70.03; 88.81; 88 | 540.1; 1400; 1397; 1429 |

Three types of binary blends were prepared for the investigations using the chosen acids:

(i) adipic acid : succinic acid (AS),
(ii) adipic acid : glutaric acid (AG),
(iii) succinic acid : glutaric acid (SG).

Each mixture was prepared from analytically pure acids supplied by Sigma Aldrich. Required amounts of WOAs were prepared in order to obtain the binary blends of the following ratios:

a) 83.3 wt% : 16.7 wt% (5:1)
b) 50 wt% : 50 wt% (1:1)
c) 16.7 wt% : 83.3 wt% (1:5)

The binary mixtures constituted of two components where one of them exhibited higher affinity towards moisture (hygroscopicity) than another one, therefore the increasing order of hygroscopicity for the blend ratios was established as follows: 5:1 < 1:1 < 1:5 [19]. Required amounts of pure WOAs were dissolved in isopropyl alcohol (analytical purity of 99.8%) in order to obtain 0.3% wt/v and 2.5% wt/v solutions of binary mixtures of each ratio. The 0.3% wt/v concentration solutions was used for the residue quantification studies, and the 2.5% wt/v solutions were used for the corrosivity assessment conducted on the interdigitated surface insulation resistance patterns.

SURFACE INSULATION RESISTANCE (SIR) TEST BOARDS

The DC electrochemical measurements were performed on Pb-free surface insulation resistance comb patterns (Figure 8.1) with a hot air solder leveling (HASL) surface finish and Sn100C solder alloy. The dimensions of the comb pattern were 13 mm x 25 mm, and therefore the active surface area was 325 mm$^2$. The distance between the electrodes was 0.3 mm.

The test SIR boards were carefully cleaned prior to each testing by rinsing with deionized water (conductivity of 18.2 MΩ·cm at 25°C) which was followed by rinsing with isopropyl alcohol (analytical purity of 99.8%) three times and drying with a pressurized air.

CLIMATIC CHAMBER

The DC electrochemical tests were carried out using the SIR interdigitated patterns in the controlled environment in the climatic chamber Espec PL-3KPH. The fluctuations in the temperature and relative humidity are stated to be within the range of ±0.3°C/±2.5%RH in the conditions -40°C to +100°C/20%RH to 98%RH. The airflow was ~1.5 m/s.

THERMAL DECOMPOSITION TREATMENT

The samples pre-contaminated with the binary mixtures of organic activators were thermally activated at two temperatures, namely 175 ± 5°C and 245 ± 5°C, both treatments lasting for 45 or 90 seconds. The chosen temperature ranges represent the temperatures experienced by the PCBA top and bottom surfaces during the conventional lead-free wave soldering process [13]. The pre-contaminated samples were subjected to a radiative thermal treatment in the Techno HA-02 oven. As a reference, the residue obtained upon evaporation at room temperature was subjected for testing.

ANALYSING TECHNIQUES

The thermal degradation analysis was conducted with a combination of thermogravimetric analysis and differential scanning calorimetry. The chemical and quantitative investigations were performed
with a use of gravimetric method, ion chromatography, and Residue RAT™ gel testing. The aggressivity of residues was assessed by DC leakage current measurements.

**Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)**

The TGA technique was employed to study the characteristics of WOA degradation in terms of weight loss as a function of increasing temperature. The DSC measurements allowed for the estimation of the endothermic melting transition and the decomposition temperature of particular residue types. The binary mixtures of pure acids were subjected to both analyses in Al₂O₃ crucibles in the temperature range 25-500˚C with a heating rate of 10˚C/min using NETZSCH STA 409 PC/PG instrument.

**Gravimetric measurements for residue quantification**

The amount of contamination after various thermal treatments was estimated using gravimetric measurements. The 0.3% wt/v solutions of binary blends were applied on a Petri dish and evaporated at ambient conditions, which resulted in the dry residue level of ~100 µg/cm². This level of contamination is often found on the PCBAs which underwent a poorly controlled wave soldering process. Subsequently, the respective Petri glass dishes with the residues were subjected for heating in the Techno HA-02 oven at various temperatures simulating the wave soldering conditions. The weight of the specimens was monitored and determined before and after the thermal treatment using the Sartorius Research R 160 P electronic semi-microbalance with an accuracy of 0.01 mg.

**Ion chromatography (IC)**

The Dionex ICS-2000 (Thermo Scientific) with IonPac ICE-AS6 ion inclusion column was used for the ion chromatography quantification analysis. The ratios of WOAs in respective binary mixtures were estimated after the samples with ~100 µg/cm² residue were subjected to various thermal activation treatments on the Petri glass dish. The decomposed acids were dissolved in the mixture of ethanol and Millipore water (10%:90% v/v) directly after the activation treatment, and a mild stirring was performed for ~2 min in order to ensure that both WOA residues are transferred to the extraction solution. Subsequently, the solutions were subjected for the IC testing, and the identification and quantification of WOAs was inferred from the peaks in a chromatogram where the retention time was assigned to the particular acid types.

**Residue aggressivity assessment**

The visualization of the flux residue contamination level after various thermal treatments was carried out using a patented product Residue RAT™ (Residues Reliability Assessment Testing) gel testing [34]. The residue levels were ~100 µg/cm² and ~200 µg/cm², in order to show the effect of initial contamination level on the evaporation tendencies. This method of visualization makes use of the pH change and is based on the reaction between gel indicator with acidic contaminants. The gel was heated and applied on the Petri dishes containing the decomposed residues. After the colour change was observed after around 2 min due to the reaction between an indicator and WOAs, the photographs were taken.

**Corrosion reliability testing**

The corrosive effects of activated and non-activated binary mixtures of organic activators were evaluated using the DC leakage current measurements performed on the surface insulation resistance (SIR) patterns. Clean SIR comb patterns were pre-contaminated with solutions of binary acid blends,
and the approximate concentration left on the SIR surfaces was \( \sim 100 \, \mu\text{g/cm}^2 \) after solvent evaporation at room temperature. Subsequently, the boards were subjected for the thermal treatments in the Techno HA-02 oven, then placed in Espec climatic chamber, and exposed to humidity levels of 90%RH, 95%RH, and 99%RH at constant 25°C. The leak current was measured with varying potential from 0 to 10 V at a sweep rate of 2 mV/s using Bio-Logic VSP potentiostat. The detailed description of the test method can be found elsewhere [7, 19].

### III. RESULTS

#### THERMAL DEGRADATION OF RESIDUES

The TGA and DSC results for testing performed for the three binary mixtures of a 1:1 ratio are shown in Figure 8.2. The TGA curves were initially smooth, however, a sudden decrease occurred at high temperatures. The transition from 100 wt% to 0 wt% was observed at the temperature ranges 175-285°C, 190-293°C, and 175-270°C for AS (Figure 8.2 (a)), AG (Figure 8.2 (b)), and SG (Figure 8.2 (c)) blends, respectively.

The DSC scans showed four endothermic peaks: the first two peaks (marked in Figure 8.2 with black arrows) are associated with the melting temperatures of WOAs constituting the mixtures. The other two peaks (marked with colourful arrows) occur at high temperatures and, within both peaks, the one appearing at higher temperature is attributed to the sample weight decrease to 0 wt% as shown in the TGA curves.

![Figure 8.2: TGA and DSC results for binary mixtures: (a) AS (ratio 1:1), (b) AG (ratio 1:1), (c) SG (ratio 1:1).](image-url)
**FLUX RESIDUE QUANTIFICATION**

*Effect of mixture type and activation treatment*

The results of gravimetric assessment of the residue amount performed for the samples subjected to 175 ± 5°C and 245 ± 5°C treatments for 45 and 90 seconds are presented in Figure 8.3. Treatment at 175°C and 45 seconds did not result in a significant removal of the residues. Upon the 175°C and 90 seconds temperature exposure, the highest amount of residual activator amounts were found for AG type of mixture (~70%). Between AS and SG blends, lower amount of residues was found for the latter mixture type (~40% compared to ~60%). The 245°C thermal treatment for 45 seconds allowed for the removal of significant amount of SG mixture type compared to other blend types. The prolonged treatment time at 245°C removed most of the residues composed of AS and SG mixtures of activators, however the contamination levels for AG under the same thermal treatment resulted in ~20% residue remaining on the surface. The differences in evaporation tendencies between different ratios of the same blend type were negligible. The overall tendency of binary mixtures for evaporation followed the increasing order: AG < AS < SG.

![Graphs showing residue left percentage at different temperatures for different mixtures](image)

Figure 8.3: Quantification of the residue amount for binary mixtures: (a) AS, (b) AG, (c) SG of initial contamination level ~100 µg/cm² subjected for various thermal treatments.

The estimation of weight ratio between the acids constituting various binary mixtures that were subjected to various thermal treatments is shown in Figure 8.4. In case of AS blend type (Figure 8.4 (a)),
the preferential evaporation occurred for succinic acid in respect to adipic acid upon the exposure to different heat treatments. For the thermal treatment of AG mixture type (Figure 8.4 (b)), the ratio between both constituents remained at the similar level indicating the simultaneous degradation. In case of SG type of binary blend (Figure 8.4 (c)), the amount of succinic acid progressively decreased in respect to glutaric acid upon the exposure to simulated soldering temperatures.

Figure 8.4: Ion chromatography results of weight ratio estimation of WOA constituents in binary mixtures subjected to various thermal treatments: (a) AS, (b) AG, (c) SG for ratios (1) 1:5, (2) 1:1, (3) 5:1.

**Effect of initial residue amount**

The results from investigations of the effect of initial residue amount on the decomposition trend at various heat treatments is presented in Figure 8.5. The evaporation pattern was studied for the initial contamination levels of ~100 µg/cm² and ~200 µg/cm². The data for 100 µg/cm² was taken from Figure 8.3.
Overall, the higher initial level of contamination present on the surface did not result in a significant decrease of the activator amount at the given conditions of thermal treatments: 175°C (45 and 90 seconds) and 245°C (45 seconds). However, the extended time of heat treatment at 245°C (90 seconds) resulted in the residue amount decrease to 20-50% for all binary blends and ratios. The highest amount of residue remaining on the surface was found for AG mixture type (~45-52% of the initial amount).

Figure 8.6 shows the images of residues remaining on Petri glass dishes after various thermal treatments, visualized by Residue RAT gel test method. The initial residue levels were

![Figure 8.5: Thermal decomposition trend for ~100 µg/cm² and ~200 µg/cm² initial contamination levels at various thermal treatments.](image)

![Figure 8.6 Residues RAT™ images of flux residue profile of AS mixture (1:1 ratio) after various thermal treatments for initial contamination levels of ~100 µg/cm² and ~200 µg/cm².](image)
~100 µg/cm² and ~200 µg/cm². The reported images present the varying amount of contamination, which is indicated by the red coloration. The residues evaporated at room temperature and not subjected to any thermal treatments showed distinct red coloration. Heating the 100 µg/cm² samples at 175°C (45 and 90 seconds) and at 245°C (45 seconds) showed a reduced contamination amount, although still significantly high. The 200 µg/cm² samples did not show significant reduction in the residue level for the mentioned heat treatments, and the coloration level did not differ from the samples not subjected to any thermal decomposition. Both samples of initial contamination level 100 µg/cm² and 200 µg/cm² showed very significant degradation of acid amount only at 245°C (90 seconds) treatment.

CORROSION RELIABILITY TESTING

The effect of residue decomposition on the electrical performance and corrosion reliability of the PCBA was assessed upon the DC testing and the results are shown in Figure 8.7. The exposure to varying potential from 0 to 10 V at a sweep rate of 2 mV/s resulted in the total time of ~1.5 h per each humidity level. An abrupt increase in leakage current above µA level indicated the corrosion occurrence in the form of electrochemical migration.

Figure 8.7 Results of DC leakage current measurements for SIR patterns pre-contaminated with ~100 µg/cm² of binary mixtures: (a) AS, (b) AG, (c) SG for ratios (1) 1:5, (2) 1:1, (3) 5:1 after various thermal treatments.
In case of AS mixture type (Figure 8.7 (a)), no corrosion for untreated and activated residues was observed at any humidity level. Similarly, mixtures AG of 5:1 ratio (Figure 8.7 (b3)) and SG of 5:1 ratio (Figure 8.7 (c3)) exhibited lack of corrosive effects.

The residue-induced electrochemical migration disappeared in the case of SG blend type of 1:5 ratio (Figure 8.7 (c1)) under the treatment of 175°C and 245°C, both for 90 seconds. However, the corrosivity of AG mixture of 1:5 ratio (Figure 8.7 (b1)) was found to diminish only for the treatment at 245°C for 90 seconds, despite the RH level. The overall time to failure (ECM) was similar when comparing AG and SG mixture types of a 1:5 ratio and observed at all test humidity levels.

In case of 1:1 ratio of AG mixture (Figure 8.7 (b2)), the base leakage current levels decreased significantly and progressively upon the exposure to higher temperatures and extension of exposure time, with the lowest current level recorded for the treatment at 245°C for 90 seconds. The corrosive behaviour for this ratio type was noted only at the saturated humidity level for untreated residues, however, the ECM did not occur at this RH level once the residues were thermally treated. In case of the SG blend type of 1:1 ratio (Figure 8.7 (c2)) a significant decrease in current was observed upon the exposure to more pronounced thermal treatment and time. The untreated residues corroded at 95%RH and 99%RH, however, the base current levels and electrochemical migration occurrence diminished the corrosive behaviour.

IV. DISCUSSION

This paper shows the importance of flux chemistry on the residue decomposition pattern when mixture of acid activators is present on the PCBA, and the necessity of the sufficient thermal treatment for the reliability assurance. The corrosion failures on a PCBA facilitated by the process-related residues are related to the contamination levels, chemical nature, and humid conditions upon which the electronics operate.

The results of DSC/TGA testing (Figure 8.2) of the thermal degradation of WOA mixtures showed an increasing order of the decomposition tendency: AG < AS < SG, which was also mirrored in the residue quantification and IC experiments (Figure 8.3 and Figure 8.4). The temperature range for evaporation found by DSC/TGA was 190-293°C, 175-285°C, and 175-270°C for AG, AS, and SG mixtures, respectively, which meant that the blends containing succinic acid (AS and SG) can be removed easier from the surface. This was confirmed by our quantification studies, where the amount of residual AG was the highest among other mixture types, regardless of the thermal treatment. It is also in agreement with the study reported by Conseil et al. [8] where succinic acid showed the lowest temperature necessary for degradation. The presence of adipic acid in the mixtures indicated that higher temperatures are needed for the residue degradation [8]. The overall ranking for the evaporation tendencies between the single WOAs increases as follows: adipic < glutaric < succinic.

The treatment at 175°C left significantly high amounts of residual acids (~40-90%) regardless of the heating time. Only the treatment at 245°C for 90 seconds was sufficient to remove most of the AS and SG residues, although for AG ~20% of residues were present. The temperature range for residue evaporation closest to the typical wave soldering temperatures was found for the SG mixture (175-270°C), which explains the evaporation tendency of this contamination type at a given temperature conditions, compared to the AG mixture (190-293°C).

The DSC/TGA curves showed the maximum evaporation rate (weight loss to 0 wt% in the TGA curves) at the second DSC degradation peak (Figure 8.2). The evaporation tendencies observed in this study are related to the chemical structure of WOAs [35] which is also mirrored in their boiling points
(Table 8.1). The thermal decomposition depends on the amount of methylene units within the molecule, which determines the chain length [36]. Succinic acid contains the shortest chain length (2 units) among the tested WOAs, therefore it is easier to be removed from the surface. Contrarily, adipic acid is a heavy molecule with the highest number of methylene units (4 units), therefore the hardest one to remove from the surface. Glutaric acid comprises of 3 methylene units, which places its evaporation tendencies in between the other two activators. Under the given thermal conditions applied in this study, its decomposition trend was, however, similar to adipic acid (Figure 8.4 (b)) as both of their boiling points exceed 300°C compared to 235°C for succinic acid (Table 8.1). This shows that the chemical structure/nature of the activators is vital for the flux degradation purposes, and determines the residual levels of activators on the PCBA surface after the soldering process, therefore the influence on humidity-related reliability issues.

The typical soldering temperatures used in this study for the estimation of degradation tendencies between various contamination types turned out to be insufficient for the reduction of the residue amount. Typically, the temperatures experienced by the top and bottom part of the PCBA (175°C and 250°C, respectively) last only for ~45 seconds [1, 9, 13, 17, 20, 37] during the soldering profile. The levels of activators present on the surface after 45 seconds treatments were still relatively high (Figure 8.3, Figure 8.5, Figure 8.6), and only the prolonged time of heating at 245°C resulted in the significant residue amount degradation. This finding is in agreement with literature data on single WOA where it was proven that the range of soldering temperatures and treatment time do not result in full activator degradation [1, 8].

Lack of corrosion effects was exhibited by the AS residue type (Figure 8.7 (a)), and AG and SG mixtures of 5:1 ratio (Figure 8.7 (b3) and (c3)). In the case of highly corrosive 1:5 ratios of both AG and SG mixture types (Figure 8.7 (b1) and (c1)), the residue-induced electrochemical migration exhibited by the untreated residue was detected at the humidity levels of 90-99%RH. It complies with the literature data for RH levels for ECM occurrence found for these mixture and ratio types [19].

Upon the thermal treatment, the corrosive effects disappeared only when the residues were treated for 90 seconds at 175°C and 245°C (SG) or only 245°C (AG). Based on the evaporation tendencies between the two constituents comprising the binary mixture, measured by the IC method (Figure 8.4 (b)), the activated AG residues comprised of 1:5 ratio at any given treatment. Therefore, its diminished corrosivity at 245°C (90 seconds) was only the effect of the reduced residue amount. On the other hand, the SG mixture of the initial 1:5 ratio underwent the progressive decrease in the amount of succinic acid (compared to glutaric acid) (Figure 8.4 (b)) in the course of thermal degradation. As shown in the literature data [19, 38], the hygroscopicity of a single WOA is less pronounced compared to its binary mixture, and the higher content of more hygroscopic compound (glutaric acid) increases the corrosivity. It was shown in the case of 245°C (45 seconds) treatment, where the initial 1:5 ratio dropped to 0.3:5, increasing the hygroscopicity of the residues and initiating the corrosion occurrence. Between 175°C (90 seconds) and 245°C (45 seconds) treatments, which resulted in similar residue level (~40%), the latter showed slightly higher hygroscopicity, therefore exhibited the corrosion effects compared to the former one. However, the resulting lack of corrosive effects of SG 1:5 ratio at 175°C and 245°C (90 seconds) were the result of the decreased residue amount despite an increased hygroscopicity of the residual solid. Similar effect of the residue amount decrease on the reduced susceptibility to ECM was observed for the ratio 1:1 for both AG and SG (Figure 8.7 (b2) and (c2)). However, the corrosivity of the latter was more pronounced compared to AG, which is a result of generally higher hygroscopicity of SG [19].
Overall, the results show the importance of flux chemistry of the residues composed of acid mixtures, their relative levels, and different physical properties, in determining the contamination levels present on the PCBA after the soldering process, and effect on humidity-related reliability issues. Results also showed that a proper optimization of the activator mixture (type and ratio) in the flux formulation, based on the physical characteristics determining the residue removal and required activity in relation to solderability, provides a way for achieving the two conflicting objectives: solderability and humidity-related reliability.

V. CONCLUSIONS

1) The typical range of temperatures experienced by electronics during the wave soldering process (175°C-245°C) for 45 seconds is not sufficient for the removal of significant activator amounts. The prolonged time of thermal treatment or higher temperatures may increase the acid decomposition rate and therefore the PCBA reliability.

2) The type of acids constituting the binary mixture is of great importance as it determines the ratio of the final residue mixture after the thermal treatment, its amount, and corrosive effects. The preferential evaporation of succinic acid, compared to the second constituent in the binary mixture, occurred for succinic : glutaric and adipic : succinic mixture types. Between both acids in the adipic : glutaric blend, the simultaneous degradation of two WOAs occurred regardless the thermal treatment.

3) Under the range of wave soldering temperatures, the decomposition behavior of binary mixtures of solder flux activators exhibits the increasing tendency for evaporation: succinic : glutaric > adipic : succinic > glutaric : adipic. At 175°C and 90 seconds of exposure, the amount of residue, compared to the initial amount, was ~40%, ~60%, and ~70% for succinic : glutaric, adipic : succinic, and adipic : glutaric, respectively. At 245°C and 90 seconds of exposure, only adipic : glutaric mixture remained on the surface at significant levels (~20%).

4) Corrosivity testing under humid conditions showed that the residue-induced corrosion failures depend on the type of the binary mixture of WOAs, which determined the corrosivity of the final residue mixture after the thermal treatment. The highest leakage current levels were found for succinic : glutaric blend type. However, a sufficient thermal treatment of the residues can lead to the diminishing of the corrosion effects.

VI. REFERENCES


2010.


9. PARAMETRIC STUDY OF SOLDER FLUX HYGROSCOPICITY: IMPACT OF WEAK ORGANIC ACIDS ON WATER LAYER FORMATION AND CORROSION OF ELECTRONICS

Kamila Piotrowska, Rameez Ud Din, Flemming Bjerg Grumsen, Morten Stendahl Jellesen, Rajan Ambat

Abstract - The presence of solder flux residues on the printed circuit board assembly surface is an important factor contributing to humidity-related reliability issues that affect device lifetime. This investigation focuses on understanding the hygroscopic nature of typical wave solder flux activators – weak organic acids – under varied temperature conditions. In-situ X-ray diffraction measurements assessed the effect of high temperature on the crystal structure of organic activators. The hygroscopicity studies were carried out under relative humidity (RH) levels varying from 30% to ~99% and at temperatures 25˚C, 40˚C, and 60˚C. Water absorption levels were determined using the gravimetric method, and the influence on reliability was assessed using electrochemical impedance and leak current measurements performed on the surface insulation resistance comb patterns. The corrosion studies were correlated with the hygroscopicity results and solubility data. Corrosion morphology was analysed using the optical microscopy and scanning electron microscopy. The results show that the hygroscopic nature of typical solder flux residue depends on its chemical structure and temperature. An increase of temperature shifts the critical RH level for water vapour absorption towards lower RH range, accelerating the formation of a conductive electrolyte and the occurrence of ion transport-induced electrochemical migration. The overall ranking of flux activators with the increasing order of aggressivity is: palmitic < suberic < adipic < succinic < glutaric < DL-malic acid.

Keywords - Corrosion, solder flux, humidity, hygroscopicity, climatic reliability of electronics.

I. INTRODUCTION

No-clean solder flux systems are commonly used in the electronics industry for the Printed Circuit Board (PCB) assembly process. Today, most fluxes are halide-free organic-activator based with the functionality of de-oxidizing metal surfaces and providing good wetting properties for the molten solder [1-4]. Typically, the activators used in the no-clean flux formulations are dicarboxylic weak organic acids (WOAs), which are likely to decompose/evaporate from the soldering surface leaving a negligible amount of non-corrosive residue [3]. Therefore, no additional cleaning process is expected to be required in order to maintain the device’s reliability. However, in practice, significant levels of flux residues are left on the Printed Circuit Board Assembly (PCBA) surface, which was reported to cause the corrosion reliability issues under exposure of electronics to humid conditions [5, 6].

Typically, the no-clean flux systems for the wave soldering process consist of resin or rosin serving as the vehicle, diluted by inorganic or organic solvents (e.g. alcohols, hydrocarbons, water). Additionally, a number of additives are present in the flux formulation (e.g. plasticizers, surfactants) [7]. From the corrosion reliability point of view, the species contributing to the deteriorations in the PCBA...
performance are activators - WOAs [6-8]. Different WOA types exhibit different physicochemical properties that determine the PCBA susceptibility towards corrosion.

Most organic activators are water-soluble and ionic in nature. The acid’s strength (the tendency to ionize into the solution) is reflected in their dissociation/ionization constants (Ka) [9]. Lower value of pKa indicates stronger acidity and easier ionization in the solution. Further, the hygroscopic nature of WOAs [10] implies they tend to absorb moisture from the surrounding due to the presence of polar functional groups within their structure [11, 12]. Many hygroscopic species hold the absorbed water molecules within their lattice and do not release water easily even if the external conditions change. Between the pKa and hygroscopicity, the latter was stated to influence the electrical response and account for high leakage currents, whereas the ionic properties are believed to become meaningful only in connection with hygroscopicity [13].

Another important factor for reliability is WOA solubility, which determines the amount of residue possible to be dissolved in water at the given temperature. This becomes an important parameter for corrosion effects on the PCBA surface, as the water film formed under humid conditions is thin; therefore, small amounts of highly soluble WOA can saturate the solution. Since most of the post-production contamination left on the PCBA surface is ionic in nature, both the solubility and ionization constants are proportional to the solution conductivity. Highly water-soluble residues tend to produce increased leak currents and cause PCBA corrosion [8].

The presence of WOA as a residue on the PCBA surface decreases its critical relative humidity for water film formation; therefore, moisture adsorption to the contaminated PCBA takes place at lower relative humidity (RH) than the RH level required for moisture condensation on a clean surface [6-8]. The adsorption is followed by absorption once the humidity exceeds a threshold value [14, 15] as the solid deliquesces and dissolves into the water layer [16, 17], leading to the formation of droplet saturated with ions. The dilution of the formed solution takes place until an equilibrium vapour pressure between the solution and the surrounding is reached [14, 18, 19]. As stated by Adams et al. [13], the more hygroscopic species exhibit lower critical relative humidity for deliquescence, and the better their solubilities. Higher hygroscopicity results in an increased conductivity of the thin water layers [20] and leads to the reduction of surface insulation resistance (SIR) between the conductors [6], high leak current, and likely the occurrence of electrochemical migration (ECM) [21, 22]. The critical relative humidity for deliquescence (dRH) depends on the type of contamination and is specific for each crystalline solid [23] and the temperature [24-26].

Literature studies focus on the investigation of WOAs’ hygroscopicity and corrosivity in terms of climatic conditions and WOA type. Typically, the method employed is the standardized SIR testing [27-31] applied in a variety of climatic conditions, all of which are constant (e.g. 40°C/93%RH, 85°C/85%RH). As stated by Verdingovas et al. [8], the measurements performed under DC (direct current) voltage and constant conditions may not reveal the potential corrosive nature of a particular flux chemistry since the test is carried out under one particular temperature and relative humidity level. Moreover, the AC (alternating current) impedance measurement offers advantages in recognizing the hygroscopic nature of the flux residue that is not masked by the polarization effect of the corroding electrode (as in the case of DC measurements) and can serve as a behaviour monitoring tool, although is seldom used in electronics for testing the WOA effect [32].

In this study, the hygroscopicity and corrosivity of commonly used solder flux activators were evaluated under exposure to varying RH and temperature conditions relevant to the electronic devices. The effect of high temperatures on the crystal structure of the acids was investigated at ambient humidity levels and different gas atmospheres using the in-situ X-ray technique. Different gas
atmospheres were used in order to evaluate the effect of humidity presence on the changes in crystal structure upon the temperature increase. The hygroscopicity was assessed under varying humidity levels using visual observations (contact angle and in-situ water layer formation), gravimetric water vapour sorption/desorption, and AC electrochemical impedance technique. The static contact angle and in-situ water layer formation were employed for visualization of WOAs tendencies to wet the surface and form the solution droplets, which relates to the WOAs hygroscopic nature at ambient conditions. The gravimetric sorption method and electrochemical impedance measurements were used in order to describe the varying WOA hygroscopicity in terms of deliquescence RH and were related to the acid type and temperature. The corrosivity was assessed through DC measurements using SIR comb patterns, and the results were correlated with the hygroscopicity studies and solubility data.

II. MATERIALS AND METHODS

WOAS USED FOR INVESTIGATION

Six WOAs commonly used as wave solder flux activators [8, 33, 34] were chosen for the studies. The acids were: palmitic, suberic, adipic, succinic, glutaric, and DL-malic, supplied by Sigma Aldrich as pure crystals of analytical grade. Required amounts of pure WOAs were dissolved in isopropyl alcohol (analytical purity of 99.8%) in order to obtain the 5% wt/v solutions, similar to the level of WOA found in the commercial flux systems. Table 9.1 summarizes the physical and chemical properties of WOAs used for the investigations.

Table 9.1: Summary of physical and chemical properties of WOAs. The molecular formulas, chemical structures, and pK values taken from [35]. The pKa values are given for the materials in their standard state. Solubilities are given in g/L.

<table>
<thead>
<tr>
<th>Name</th>
<th>Palmitic acid</th>
<th>Suberic acid</th>
<th>Adipic acid</th>
<th>Succinic acid</th>
<th>Glutaric acid</th>
<th>DL-Malic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C15H32O2</td>
<td>C8H14O4</td>
<td>C6H10O4</td>
<td>C4H8O4</td>
<td>C4H8O4</td>
<td>C4H8O5</td>
</tr>
<tr>
<td>Chemical structure</td>
<td>H2C(2H24)COOH</td>
<td>HOC(2H24)COOH</td>
<td>HOC(2H24)COOH</td>
<td>HOC(2H24)COOH</td>
<td>HOC(2H24)COOH</td>
<td>HOC(2H24)COOH</td>
</tr>
<tr>
<td>pK&lt;sub&gt;a&lt;/sub&gt;; pK&lt;sub&gt;c&lt;/sub&gt;</td>
<td>4.78 ; - 4.52 ; 5.33</td>
<td>4.44 ; 5.43</td>
<td>4.21 ; 5.65</td>
<td>4.34 ; 5.3</td>
<td>3.4 ; 5.2</td>
<td></td>
</tr>
<tr>
<td>Solubility at 25°C</td>
<td>0.00004; 0.0008206; 0.000687</td>
<td>11.9; 5.9; 4.4; 24; 24.97</td>
<td>70.03; 88.81; 88; 540.1; 1400; 1397; 1429</td>
<td>591.8; 1400</td>
<td>0.65; 0.64</td>
<td></td>
</tr>
<tr>
<td>Solubility at 40°C</td>
<td>0.0145; 4.08; 5.8; 47.85; 51.2</td>
<td>48.8; 52</td>
<td>135.7-139.4; 160.06; 157; 162</td>
<td>646.6; 642.9; 1800</td>
<td>646</td>
<td></td>
</tr>
<tr>
<td>Solubility at 60°C</td>
<td>0.012; 9.76; 176.83; 176</td>
<td>147.3; 358</td>
<td>263.6; 335; 754.8; 729.7</td>
<td>756.9; 5297</td>
<td>2700; 733</td>
<td></td>
</tr>
</tbody>
</table>

a - [35]; b - [36]; c - [37]; d - [38]; e - [39]; f - calculated from [40]; g - [41]; h - [42]; i - [43]; j - [44]; k - [45]; l - [46]; m - [47]; n - [11]; o - calculated from [48]; p - [49]; q - [34]; r - [50].
TEST BOARDS

The DC and AC electrical measurements were performed on the SIR comb patterns. The base material of the test specimen was Pb-free Sn100C with a hot air solder leveling (HASL) surface finish. The dimensions of the test pattern were 13 mm x 25 mm, and the distance between the electrodes was 0.3 mm (Figure 9.1).

Two FR-4 laminates with the solder mask were used for the assessment of WOA hygroscopicity described in terms of wettability and in-situ water layer formation at ambient conditions. Additionally, the morphology changes of the residue were visualized on the solder mask materials after exposure of the pre-contaminated samples to different temperatures and high RH levels. The laminate specimens of size 45 mm x 45 mm x 1.48/1.58 mm contained different surface morphology (rough and smooth) and were previously used for the studies of their topography effect on the water film formation [51].

Prior to all experiments, the test boards were cleaned by initial rinsing with deionized water for approx. 30 seconds, which was followed by rinsing with isopropyl alcohol (analytical purity of 99.8%) for about 10 seconds. The procedure was repeated six times and followed by drying with pressurized air.

CLIMATIC CHAMBER

Except for wettability assessment, all the experiments were performed in the climatic chamber Espec PL-3KPH. The fluctuations in the temperature and relative humidity levels for this chamber were stated to be within ±0.3°C/±2.5%RH in the range of -40°C to +100°C/20%RH to 98%RH. The airflow in the chamber was ~1.5 m/s.

HYGROSCOPICITY OF WOAS

Surface wettability

The wettability investigation of solder mask surface contaminated with different WOAs was conducted under ambient conditions using static water contact angle method of sessile 5 µL Millipore water droplets. The contamination level on the solder mask was ~1-1.2 mg/cm² confined to the test surface area. The angle was assessed using a camera equipped with a long-range microscope (ramé-hart Instrument Co. Goniometer Model 200-F1) and software DROPimage standard. The contact angle was measured by drawing a tangent line (at the liquid/air interface) that subsequently crossed the horizontal line determined by the surface (at the interface solid/liquid). The angle measurement was taken approx. 5 seconds after applying the water droplet on the pre-contaminated surface.

In-situ water layer formation

The formation of water layers on the solder mask surface under condensing conditions was assessed in relation to the WOA type and solder mask surface finish. Each FR-4 substrate with solder mask was pre-contaminated with the WOA solution using an automatic pipette, and the resulting residue level after solvent evaporation was ~3 µg/mm². The contaminated samples were pasted to the
cooling Peltier element (model CP-031, TE Technology Inc.) using a heat-conductive thermal paste and subsequently exposed to 80%RH 24-24.5°C in the Espec climatic chamber, which set the dew point at ~21-22°C. The test specimens were cooled down to 10.9-11.4°C within 10 minutes in order to provoke a condensation on the PCB surfaces. Throughout the experiment, the photographs of condensation progress were collected with the use of DinoLite digital microscope.

**X-ray diffraction (XRD)**

The in-situ X-ray diffraction (XRD) technique was employed in order to investigate the effect of elevated temperature and ambient humidity level on the changes in the activator crystal structure. The measurements were carried out on a “Bruker D8” equipped with a parallel beam (Göbel mirror) and a secondary side divergence assembly in 1D, and an MRI temperature controlled dome stage.

The measurements were performed at ambient conditions and at nitrogen-rich conditions. The heat treatment included the temperature elevation from 25°C to 65°C in the steps of 1°C, followed by the temperature reduction back to 25°C. The overall time duration of the experiment was 8.5h. The thermocouple for temperature control loop was mounted between the glass plate containing the acid powder and the alumina rods. The XRD scans were conducted at each temperature step: 1 scan per step and 5 scans at 65°C.

**Gravimetric water vapour sorption/desorption**

The ability of organic residues to sorb (adsorb and absorb) and desorb moisture was assessed using weight gain measurements under cycling humidity at constant temperatures: 25°C, 40°C, and 60°C. The samples of 30 (± 0.72) mg, 75 (± 0.54) mg, and 150 (± 1.19) mg for each crystalline WOA were placed in the aluminium crucibles and stored in a desiccant box (RH<15%) for 24-120h prior to the testing. Subsequently, the samples were exposed to varying relative humidity from 30-~99%RH that afterwards decreased from ~99-30%RH, both ramps in the step of 5%RH. The weight of the specimens was monitored at each RH step and determined periodically using Sartorius Research R 160 P electronic semi-microbalance with an accuracy of 0.01 mg. When the gravimetric equilibrium was reached at the particular RH step [52], the final weight gain for this specific RH was determined and the samples were returned to the chamber for further exposure to the higher RH level. The mass values obtained at each RH were used to generate water vapour sorption and desorption isotherms at each test temperature. The moisture content $M_c$ was expressed as a percentage of the WOA’s initial mass and calculated using equation 9.1 as follows [53]:

$$M_c(\text{wt\%}) = \frac{m_w - m_d}{m_d} \cdot 100$$  \hspace{1cm} (Eq. 9.1)

where $m_w$ is the weight of the wet sample after the exposure to certain test condition, $m_d$ is the initial weight of a dry specimen. The relative humidity levels for deliquescence (dRH) and efflorescence (eRH) were defined from the range of RH where there was abrupt increase (for dRH) and decrease (for eRH) in the mass of absorbed water.

The measurements at 40°C and 60°C carried a risk of vapour condensation once the crucibles were placed in the chamber back from the weight measurements. Therefore, after each weight measurement, the samples were kept for ~10-15 minutes in the climatic chamber to reach the required temperature, but enclosed in additional containers in order to avoid condensation. The condensation tape was placed in various places of the extra containers in order to track the possible occurrence of undesired condensation.
AC electrochemical impedance measurements

The electrochemical impedance measurements were performed in order to assess the residue-water vapour interaction at various temperatures, namely: 25°C, 40°C, and 60°C. The test SIR patterns were pre-contaminated using an automatic pipette with the solutions of six WOAs, which resulted in the residue level of ~100 μg/cm² after the evaporation of isopropanol at room temperature. Prior to exposing samples to the required test conditions, the pre-contaminated specimens were stored in the desiccator box for 24-96h at low RH (<15% RH). Subsequently, the comb patterns were placed in the Espec climatic chamber and exposed to increasing humidity (30-99%RH) followed by decreasing humidity (99-30%RH), each ramp lasting 12h. The rate of humidity ramp was ~0.1%RH/min. Prior to the elevation of humidity, the samples were kept at 30%RH level for 6-16h in order to stabilize the impedance signal.

The AC measurements were performed with the use of “BioLogic VSP” multichannel potentiostat. A signal amplitude of 25 mV (V_{rms} = 17.68 mV) at a frequency of 10 kHz was applied. This frequency is governed by the capacitive character of the SIR electrode system at the humidity levels not exceeding the critical RH for WOAs deliquescence (dRH) [54]. With an increase of RH level and deliquescence of the residue, the water film thickness increases as well; therefore, the measured impedance output (decrease) is a result of a resistive character of water layer forming in between the conducting lines. A drop of impedance to ~5-10 kΩ indicated a total dissolution of the residue into the water layer. During the desorption cycle, the efflorescence (crystallization) takes place and the water film thickness decreases, which results in impedance increase back to the original values.

Residue morphology

The evaluation of the temperature and high humidity effects on the WOAs' morphology changes were investigated on the FR-4 laminates with solder mask. The WOA solutions were applied using an automatic pipette, which resulted in a residue level ~2 µg/mm². Subsequently, the pre-contaminated samples were kept in the Espec climatic chamber for 6h, separate set at 25˚C/99%RH and 60˚C/99%RH. Afterwards, the samples were stored in a desiccant box (RH<15%) for 72-120h. The pictures before and after the test were taken with the use of Alicona InfiniteFocus.

CORROSIVITY OF WOAS

DC leakage current measurements

The leakage current measurements were performed in order to assess the climatic conditions at which the corrosion induced by each weak organic acid occurs. The SIR patterns were pre-contaminated with WOA solutions using an automatic pipette and the resulting residue level after solvent evaporation was ~100 μg/cm². Subsequently, the specimens were exposed to constant temperature and varying humidity levels in the Espec climatic chamber: from 50%RH to 99%RH in the steps of 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95%, 98%, and 99%, separate specimen per RH level. The samples were kept at the set conditions for 1h prior to the electrical testing in order to assure the equilibration between the climate and the residue. The leakage current was measured as a function of the applied potential varying from 0 V to 10 V at 2 mV/s rate using “BioLogic VSP” multichannel potentiostat. The test temperatures were 25°C, 40°C, and 60°C.

Corrosion inspection

The corroded samples after the leakage current testing were subjected for optical inspection using a stereomicroscope Leica MZ 125 and Paint Shop Pro 7 software. The detailed corrosion morphology
analysis was carried out using field emission scanning electron microscope (FEG-SEM-Quanta 200FEG MKII, FEI) with an Oxford Instrument energy dispersive X-ray (EDS) analyser capability. The EDS analysis was performed at an acceleration voltage of 15 kV and Cu calibration using Oxford Instruments 80 mm²X-Max silicon drift EDS and BSED detectors.

III. RESULTS

HYGROSCOPICITY OF WOAS

Surface wettability

The results of surface wettability studies are shown in the Figure 9.2. As a reference, the contact angle of clean solder mask surface is also provided.

![Figure 9.2: Water contact angle for the clean and pre-contaminated solder mask surfaces.](image)

Compared to the clean surface, most of the WOAs exhibited higher wettability (lower contact angles), ranging from ~70° to ~9° in the following order: adipic > succinic > suberic > glutaric > DL-malic. However, the contact angle values below ~25° are hardly reliable. On the contrary, palmitic acid showed a hindering effect raising the water contact angle above 90°. The results served as a qualitative comparison and reflected the wettability differences between WOAs under humid conditions.

![Figure 9.3: The appearance of water droplets on clean and pre-contaminated specimens](image)
The representative photographs obtained during the contact angle measurements are shown in Figure 9.3. The tendency to highly wet the PCBA surface is seen for glutaric and DL-malic acid (Figure 9.3 (f) and (g)) where the water droplets spread almost completely. The poorest propensity for wetting the surface was exhibited by palmitic acid (Figure 9.3 (b)), which seemed to hamper surface wettability.

**In-situ water layer formation**

The visualization of water layer formation on the pre-contaminated solder mask surfaces exposed to condensing conditions at ambient temperature is presented in the Figure 9.4. The differences in water droplets appearance were the effect of diverse hygroscopic properties of WOAs and the solder mask surface finish.

Among the tested samples, palmitic acid showed a hindering behaviour and did not significantly dissolve into the formed water droplets (not shown). Suberic and succinic acids exhibited similar behaviour to adipic acid (Figure 9.4 (a) and (b)), where the appearance of droplets formed upon water vapour condensation on the contaminated area (dashed circles in the figures) did not differ compared to the clean area. Contrarily, both glutaric and DL-malic acids initially absorbed high amount of moisture which, in the course of condensation, resulted in the formation of thick droplets of saturated solutions as shown in Figure 9.4 (c) and (d) for glutaric acid. Further, the formed water droplets appeared to spread over and bridge easily on the rough surface (Figure 9.4 (a) and (c)), while the droplets had more concentric shape on the smooth surface (Figure 9.4 (b) and (d)) and did not allow easy bridging.

**Hygroscopicity as a function of temperature**

The results from in-situ X-ray measurements showing the phase transformation during the heat treatment are presented in the Figure 9.5. Among all the activators tested, the phase changes occurred only for glutaric acid. Upon the temperature increase to 65°C at ambient humidity levels (Figure 9.5 (a)), the peaks associated with the phase existing at 25°C disappeared and the formation of new peaks was observed at ~56°C. During the temperature ramp back to ambient, the peaks formed at high temperatures were found to decrease in intensity and the reappearance of original peaks took place at
~40°C. Keeping of the ambient temperatures after the heat treatment resulted in glutaric acid returning to the same phase as the one exhibited in the beginning of the experiment. Identical experiment conducted in the nitrogen and humidity-free atmosphere (Figure 9.5 (b)) resulted in the same phase transformations observed upon the temperature changes.

![Figure 9.5: The XRD results obtained for glutaric acid during the in-situ phase measurement upon temperature elevation and subsequent reduction at: (a) ambient conditions, (b) nitrogen atmosphere.](image)

The sorption and desorption capabilities of each WOA are presented in Figure 9.6 in the form of isotherms that correspond to the equilibrium amount of water vapour sorbed as a function of steady-state RH at constant temperature. Each plot represents an isotherm constructed of the values obtained for a set of 3 samples of 30 mg, 75 mg, and 150 mg, resulting in 9 values per point.
Figure 9.6: Moisture sorption isotherms of: (a) palmitic acid, (b) suberic acid, (c) adipic acid, (d) succinic acid, (e) glutaric acid, (f) DL-malic acid at (1) 25°C, (2) 40°C, (3) 60°C. The inset in (d3) shows the moisture intake prior deliquescence. Each point represents an average with the deviation bar given for 9 measurements.

Negligible residue dissolution was observed for palmitic, suberic, and adipic acids (Figure 9.6 (a), (b), and (c)), at any given test temperature, although the amount of water vapour sorbed by each acid progressively increased with an increase of temperature and humidity. Similarly, succinic acid exhibited such behaviour at 25°C and 40°C, although the acid deliquesced at 60°C in the RH level between 95-99%RH (Figure 9.6 (d)). On the contrary, both glutaric and DL-malic acids dissolved at all test temperatures (Figure 9.6 (e) and (f)). Compared to glutaric acid, DL-malic absorbed more moisture at any given relative humidity and temperature. The saturated moisture sorption level at 99%RH varied...
for glutaric and DL-malic acids in the decreasing order: \( \text{MC}_{\text{sat}, 60^\circ C} > \text{MC}_{\text{sat}, 25^\circ C} > \text{MC}_{\text{sat}, 40^\circ C} \). The summary of saturated moisture sorption levels for all WOAs is presented in Table 9.2.

Table 9.2: Saturated moisture sorption levels for all WOAs at different temperatures. The average and standard deviation values are given for 9 measurements.

<table>
<thead>
<tr>
<th>Weak Organic Acid</th>
<th>25°C</th>
<th>40°C</th>
<th>60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic acid</td>
<td>0.05 (+ 0.06)</td>
<td>0.19 (+ 0.07)</td>
<td>0.82 (+ 0.15)</td>
</tr>
<tr>
<td>Suberic acid</td>
<td>0.09 (+ 0.04)</td>
<td>0.21 (+ 0.05)</td>
<td>0.38 (+ 0.11)</td>
</tr>
<tr>
<td>Adipic acid</td>
<td>0.09 (+ 0.05)</td>
<td>0.26 (+ 0.09)</td>
<td>1.23 (+ 0.42)</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>0.12 (+ 0.03)</td>
<td>0.43 (+ 0.04)</td>
<td>292.05 (+ 41.15)</td>
</tr>
<tr>
<td>Glutaric acid</td>
<td>224.83 (+ 13.43)</td>
<td>142.34 (+ 12.58)</td>
<td>282.09 (+ 24.39)</td>
</tr>
<tr>
<td>DL-Malic acid</td>
<td>309.41 (+ 16.12)</td>
<td>232.27 (+ 22.16)</td>
<td>381.12 (+ 21.30)</td>
</tr>
</tbody>
</table>

For every solid, the crystallization (efflorescence) was accompanied by an appearance of a hysteresis loop where the desorption (reverse) branch lied above the sorption (forward) branch; therefore, the efflorescence point (eRH) for deliquescent WOAs was found in the lower range of RH than the RH for deliquescence (dRH). Moreover, the range of relative humidity levels for deliquescence and efflorescence decreased with an increase of test temperature for glutaric and DL-malic acids.

The summary of impedance measurements is shown in Figure 9.7. While a distinct and steady decrease in impedance output was observed for palmitic, suberic, adipic, and succinic acids at 25°C (Figure 9.7 (a), (b), (c), and (d)), a more pronounced one was observed at 40°C and 60°C. The point of impedance drop for the mentioned acids shifted to lower RH levels with an increase of temperature.

Figure 9.7: Impedance plots obtained at different temperatures on the SIR boards pre-contaminated with \(~100\) \(\mu g/cm^2\) of: (a) palmitic acid, (b) suberic acid, (c) adipic acid, (d) succinic acid, (e) glutaric acid, (f) DL-malic acid. The inset in (a) shows the determination of dRH from impedance sorption curves. Solid line – sorption, dashed line – desorption.
On the contrary, the impedance signal for glutaric and DL-malic acids was found to abruptly decrease at all test temperatures. Similarly to four other WOAs, the RH level observed for the impedance drop indicating WOA dissolution shifted towards lower RH with an increase of temperature, except for the case of glutaric acid at 60˚C. Moreover, the crystallization of a dissolved residue was accompanied with an appearance of a hysteresis loop, and the efflorescence point was found in the lower range of RH than the RH for deliquescence (dRH). However, in case of DL-malic acid, the inverted hysteresis behaviour was observed.

The point on the impedance sorption curves where the signal significantly decreased from the original values indicating WOAs dissolution (dRH) was defined by drawing two tangent lines as indicated in the Figure 9.7 (a). Further, the efflorescence point (eRH) was defined on the desorption branch of impedance, where the signal returned to the original values upon decreasing of a surrounding relative humidity level. For DL-malic acid, the steady gradual decrease of impedance signal occurred prior to an abrupt drop due to the dissolution; therefore, for this acid, the deliquescence RH was defined as indicated in the Figure 9.7 (f). The efflorescence RH for DL-malic acid was assessed as in the case of other acids. The summary of RH levels for deliquescence (dRH) and efflorescence (eRH) derived from the impedance curves for all acids are presented in Table 9.3.

Table 9.3: Summary of relative humidity levels for deliquescence (dRH) and efflorescence (eRH) for all WOAs at different temperatures obtained from impedance measurements. The average and standard deviation values are given for 3 measurements.

<table>
<thead>
<tr>
<th>Weak Organic Acid</th>
<th>25°C</th>
<th>40°C</th>
<th>60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic acid</td>
<td>-</td>
<td>-</td>
<td>91.0 ± 3.7</td>
</tr>
<tr>
<td>Suberic acid</td>
<td>-</td>
<td>-</td>
<td>92.8 ± 1.5</td>
</tr>
<tr>
<td>Adipic acid</td>
<td>97.4 ± 1.1</td>
<td>-</td>
<td>91.5 ± 0.8</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>94.2 ± 0.4</td>
<td>91.3 ± 0.6</td>
<td>91.3 ± 1.2</td>
</tr>
<tr>
<td>Glutaric acid</td>
<td>84.7 ± 2.8</td>
<td>52.9 ± 4.3</td>
<td>73.9 ± 3.3</td>
</tr>
<tr>
<td>DL-Malic acid</td>
<td>75.4 ± 4.5</td>
<td>70.1 ± 0.8</td>
<td>72.6 ± 2.8</td>
</tr>
</tbody>
</table>

The changes in WOAs morphology induced by temperature and high humidity are shown in the Figure 9.8. After the samples treatment at 25˚C/99%RH, no significant changes were observed for palmitic, suberic, and adipic acids as shown for the latter in Figure 9.8 (a). On the contrary, succinic, glutaric, and DL-malic acids dissolved into the formed water layer forming droplets of saturated acid solution, and subsequently recrystallized into small densely concentrated (succinic and glutaric acids, Figure 9.8 (c)) or large and separated (DL-malic acid, Figure 9.8 (e)) islands.

The test at 60˚C/99%RH revealed the changes in residue appearance of all WOAs. Distinct morphology changes were observed for palmitic, suberic, and adipic acids (Figure 9.8 (b)), whereas succinic, glutaric, and DL-malic acids dissolved and subsequently recrystallized into small (succinic and glutaric acids, Figure 9.8 (d)) or large (DL-malic acid, Figure 9.8 (f)) islands, similarly as for the treatment at 25˚C/99%RH.
CORROSIVITY AS A FUNCTION OF TEMPERATURE

The results of leakage current measurements are shown in the Figure 9.9 as representative graphs obtained for 3 repetitions for WOA corrosivity testing at applied test temperatures. Typically, an abrupt increase of current above a µA level indicates the process of electrochemical migration taking place, and the formation of dendrites that may consequently lead to cathode-anode bridging (short circuiting).

In the case of palmitic and suberic acids, no significant increase in the current level was observed at any test temperature implying no electrochemical migration took place; therefore, the graphs are not shown. The observation was further confirmed by a microscopic analysis where no visible corrosion was found on the samples subjected for SIR testing.

Both adipic and succinic acids did not exhibit significant leak current at 25°C, although the acids were dissolved into the water layer at 40°C and 60°C and showed ECM (Figure 9.9 (a) and (b)). Electrochemical migration was accelerated by the temperature and occurred at lower humidity levels when higher test temperatures were applied. Succinic acid exhibited migration at lower RH levels compared to adipic acid at 40°C and 60°C. The surface morphology of the corroded samples showed no difference between these acids at 40°C and 60°C. Representative micrographs are presented in the Figure 9.10, which shows the dendrite formation due to the ECM occurrence. Deposition of dendrites preferentially occurred at the tips of the electrodes (Figure 9.10 (a) and (b)). The recrystallized contamination is marked with yellow arrows on the micrograph (b). Figure 9.10 (c) shows the SEM back-scattered electron (BSE) image of the succinic-contaminated sample after the test at 60°C/99%RH. The EDS analysis of the corroded area showed the laminate pores filled up with the depositing electrode material (Sn) while the dendrites progressively grew. Similar appearance of dendritic paths on the laminate was found for adipic acid-contaminated specimens tested at 60°C/99%RH.
Figure 9.9: Leakage current measurements on SIR comb patterns pre-contaminated with ~100 μg/cm² of: (a) adipic acid, (b) succinic acid, (c) glutaric acid, (d) DL-malic acid at (1) 25°C, (2) 40°C, (3) 60°C.
Both glutaric and DL-malic acids showed ECM at all test temperatures (Figure 9.9 (c) and (d)). At higher temperatures, generally the RH range for ECM was lowered. For both acids, the corrosion morphology showed the deposited metal ions in the laminate pores in the pathway of dendrite filament formation (Figure 9.11 (a)). The extent of corrosion was highest for DL-malic acid (Figure 9.11 (b) and (c)), which resulted in the highest amount of dendrites. The EDS analysis identified tin, copper, and nickel as major elements constituting the dendrites.

**Figure 9.10**: Micrographs of succinic acid-induced corrosion after leakage current measurement at: (a) and (b) 40°C/99%RH, (c) 60°C/99%RH.

**Figure 9.11**: Micrographs showing the extent of corrosion after leakage current measurement at 25°C/99%RH for samples contaminated with: (a) glutaric acid, (b) and (c) DL-malic acid.

**IV. DISCUSSION**

Solder flux systems used nowadays for automated soldering process are believed to decompose upon thermal treatment during the assembling process; however, high levels of flux residues are typically present on a PCBA surface after production. A number of electronic devices were reported to fail due to the corrosion induced by the flux contamination remaining on a surface and a resulting moisture condensation on a PCBA surface. Today, the devices operate under a variety of temperatures worldwide, and their susceptibility towards corrosion is dependent not only on the flux contamination, but also on the exposure conditions which modify the corrosivity of the residue. The results presented in this paper show the importance of investigating the corrosive behaviour of activators in solder flux systems as a function of temperature and humidity conditions relevant to electronics operation. Water film formation on the PCBA surface was influenced by the climatic conditions (temperature and humidity) \[54\] together with the hygroscopic nature and the solubility of the residue, which are also temperature-dependent. The hygroscopicity of WOAs was stated \[13\] to be more vital in terms of corrosion occurrence than their solubility, as the ionic nature of the solution (extent of solubility) is
significant only when associated with hygroscopicity, i.e. the threshold RH level for dissolution must be reached. The more hygroscopic the solid, the lower is its dRH and the higher solubility in water [8, 13, 24]. A highly water-soluble hygroscopic WOA residue dissolves into the condensed water layer creating a well-conductive pathway, which will subsequently allow for the conduction of ions and an increase of leakage current [54] finally resulting in a failure mode such as electrochemical migration.

HYGROSCOPICITY-RELATED INFLUENCE ON RELIABILITY

The hygroscopicity of solder flux residue is related to the affinity of WOA molecules to attract water from the surrounding, which depends on the chemical structure of contamination, i.e. type, amount, and spacing between the polar functional groups, chain length, symmetry of the molecules, or crystal lattice packing. Another important property of WOAs, solubility, is related to the physicochemical properties of both the solute and the solvent. An increase of the substance polarity induces its easier dissolution in a polar solvent (i.e. water). Most of the tested WOAs possess two polar carboxylic functional groups, which increases their affinity towards water. An increased number of methylene bridges within the chain separates the polar carboxylic groups decreasing the polarity and tendency to hold water molecules within the crystal lattice – between the WOAs, it occurs in the “odd-even” manner [55, 56].

Among the tested acids, only glutaric possesses a center of symmetry along the inner methylene group that orients both carboxylic groups in one direction, allowing for easier interaction with water. Taking into consideration all molecular and structural features, the hygroscopic nature of WOAs increases in the following order [8, 33]: palmitic < suberic < adipic < succinic < glutaric < DL-malic, the trend which was mirrored in our hygroscopicity assessment and corrosivity studies at all applied test temperatures.

An increase of temperature affects the mobility of water molecules and raises the solubility of WOAs (Table 9.1) [18, 26, 57-59]. From a number of complimentary techniques used in this research, it was noted that an increase of test temperature increases the degree of interaction between the residue and water vapour. Despite a range of exposure temperatures applied in this study, the hygroscopicity trend between the acids remained the same.

The in-situ XRD measurements showed the effect of only high temperatures (and ambient humidity level) on the crystal structure of the activators. Among the tested acids, the phase changes occurred only for glutaric acid (Figure 9.5). The changes in the diffraction angle for the sample tested at increased temperatures and ambient atmosphere (Figure 9.5 (a)) were associated with the interlayer spacing changes [60] and the conversion from β to α phase. The testing conducted at nitrogen-rich atmosphere and ambient humidity confirmed that the phase changes observed at ambient atmosphere were not associated with the potential removal of water molecules from the crystal lattice at increased temperature levels. The cross and arrow symbols shown in the Figure 9.5 point the peaks associated with two phases of glutaric acid present at 25°C and 65°C, confirmed by the literature data.

In agreement with the molecular structure of the acids, both glutaric and DL-malic acids were found to be the most hygroscopic among the tested WOAs. Their tendency to highly wet the pre-contaminated surface (Figure 9.2 and Figure 9.3) comply with the literature studies [27] where water-soluble hygroscopic residue typically exhibited low contact angles. The results from gravimetric, impedance, and morphology studies revealed that both acids dissolve into the water layer at all test temperatures and absorb more moisture than other WOAs, leading to the formation of thick droplets on the surface. An increase of temperature led to lowering of their critical RH for deliquescence and efflorescence [18,
Between glutaric and DL-malic acids, the latter was found to be slightly more hygroscopic leading to higher moisture uptake (Figure 9.6).

Contrarily, palmitic acid exhibited a completely reverse behaviour due to its single carboxylic functional group and long hydrocarbon chain inducing its poorest hygroscopicity among the tested WOAs. Although it underwent a certain degree of interaction with water vapour at higher temperatures (Figure 9.6, Figure 9.7, and Figure 9.8), palmitic acid did not significantly dissolve into the water layer and caused a hindering effect on the formation of water droplets as confirmed by wettability studies (Figure 9.3) and in-situ water film formation (Figure 9.4). Suberic, adipic, and succinic acids exhibited intermediate hygroscopic behaviour among the tested WOAs and interacted with water vapour up to a certain degree; however, not undergoing a significant dissolution even at high temperatures (except for succinic acid at 60°C).

The hysteresis phenomenon was observed during gravimetric sorption and impedance measurements at all temperatures, and indicated that a complete water removal from the residue occurs at lower RH levels than their deliquescence and is characteristic for deliquescent solids [24, 62-65]. The explanation for the hysteresis occurrence comprises the ink bottle theory, the molecular shrinkage theory, the capillary condensation, and the swelling fatigue theory [25, 66], though they are not a part of this study. However, for DL-malic acid, the impedance testing resulted in an inverted hysteresis where the crystallization seemed to occur faster (at higher RH levels) than deliquescence at all test temperatures, contrary to the results from vapour sorption studies. This phenomenon is explained by the size and concentration of droplets containing a dissolved contamination, presented in the Figure 9.8 (e) and (f). Upon desorption of water from the solution formed in the course of deliquescence and subsequent dilution, the droplets comprised of a large size though occurred in low quantity and widely separated. Although, according to the gravimetric sorption studies, the droplets held high amount of water upon desorption and residue crystallization (Figure 9.6 (f)), the distribution of conductive water droplets along the SIR pattern did not provide high conductivity, falsely indicating a release of water upon lowering the ambient RH and resulting in the appearance of inverted hysteresis on the impedance curves.

**CORROSIVITY OF WOA ACTIVATORS**

The results from leakage current measurements follow the hygroscopicity tendencies observed for the weak organic acids in water vapour sorption and impedance studies. Both glutaric and DL-malic acids, upon deliquescence, allowed for the formation of thick water layers. Because of their highest solubilities and low pK\(_a\) values (Table 9.1), the conductivity of the water films was high and accounted for high leak currents [33]. This caused heavy electrochemical migration (Figure 9.11). The leakage current measurements of palmitic acid revealed no corrosive nature, which complies with its structural features (one carboxylic functional group, long chain), poorest hygroscopicity observed in this study, lowest solubility, and highest pK\(_a\) value (Table 9.1). Similarly to hygroscopicity results, suberic, adipic, and succinic acids followed identical trend during the corrosivity measurements. Despite a low amount of water absorbed by all three WOAs and rather poor wetting [67], a sufficient amount of adipic and succinic acids dissolved at high humidity and temperatures causing corrosion (Figure 9.9). Succinic and adipic acids exhibit higher solubility and lower pK\(_a\) (Table 9.1) than suberic acid which explains the leakage current results. For the corrosive contaminants, higher temperature acted as an accelerator for ECM [68] which is of a great importance for the reliability assessment of electronics that operate under different temperatures worldwide.
Although the gravimetric sorption, impedance, and leakage current techniques supported each other for testing of all WOAs, that was not the case for glutaric acid at 60°C. Glutaric acid exhibited the highest solubility among all WOAs at 60°C (Table 9.1), which might have contributed to the limiting conductivity of a formed water film. Because of the partial dissociation of the acid, as the concentration of a weak electrolyte increases, the dissociation equilibrium shifts in the opposite direction and reduces the solubility [49].

The degree of ionization is not proportional to the concentration of an electrolyte, but depends on the degree of dissociation, and in the case of glutaric acid, the limiting conductivity was reached at very high concentration at 60°C and remained until ~80%RH. With a subsequent dilution of a saturated solution at higher RH levels (>80%RH), the dissociation degree increased which led to an increased conductivity. As the AC and DC techniques reflect the conductivity characteristics of a solution, the resulted limiting conductivity falsely indicated the deliquescence occurring at high RH levels (Figure 9.7 (e) and Figure 9.9 (c3)), contrary to the results of water vapour sorption measurement (Figure 9.6 (e3)) which is not conductivity-dependent.

The summary of RH range for deliquescence obtained from gravimetric sorption and impedance measurements were plotted together with the RH range for ECM occurrence found by leakage current testing, and is presented in the Figure 9.12.

![Graphs](image)

**Figure 9.12**: Summary of dRH values obtained from gravimetric sorption and impedance studies coupled with the results of RH range for corrosion occurrence: (a) adipic acid, (b) succinic acid, (c) glutaric acid, (d) DL-malic acid.

For adipic and succinic acids (Figure 9.12 (a) and (b)), the occurrence of ECM took place at higher RH levels than the interaction with water vapour (indicated by impedance data) due to their low solubility. The water vapour absorption only at high humidity level was sufficient to lead to corrosion occurrence. On the contrary, the RH levels obtained from AC impedance and leakage current measurements for
highly hygroscopic glutaric and DL-malic acids (Figure 9.12 (c) and (d)) indicated that the beginning of interactions between WOA and water vapour (impedance data) and the corrosion occurrence take place simultaneously, which is due to the high polarity and high solubility of both activators.

The literature offers a large amount of data for dRH of different WOAs at 25°C (Table 9.4); however, limited information is available on WOA performance at higher temperatures. According to [69], the critical relative humidity level of the water vapour pressure over a solution of hygroscopic substance can be calculated for any temperature using the following equation 9.2:

\[
\frac{dRH}{100} = \exp \left( \frac{-p.C}{55.5} \right)
\]  
(Eq. 9.2)

where \(dRH\) is a critical relative humidity for deliquescence of the substance, \(\beta\) is the amount of ions formed during the dissociation process, and \(c\) is the solubility of the substance at a given temperature. According to the solubility data given in the Table 9.1, the dRH for WOAs were calculated for different test temperatures and are presented in Table 9.4 together with available literature data.

The assessment of dRH value found by means of impedance, previously successfully employed for studying the dRH of different contaminants [54, 80], was more accurate (compared to the data in Table 9.4) for glutaric and DL-malic acids for any test temperature, however, was less accurate for other acids. Less sensitive, gravimetric vapour sorption technique resulted in similar accuracy as impedance data. The leakage current results estimated the RH range for corrosion for all WOAs. Differences in the values obtained for eRH originate in the limitations of impedance and gravimetry techniques. The former represents a kinetic effect and lags behind the equilibrium state, especially because water vapour desorption is a very slow process. The latter is an equilibrium measurement where enough time is given for the solid to equilibrate with the surrounding pressure.

Overall, this study shows the importance of studying and understanding the flux chemistry and its hygroscopicity which depends on the test temperature. High temperatures cause the acid dissolution at lower RH levels, which then act as a corrosion accelerating factor. All WOAs exhibited hysterisis

<table>
<thead>
<tr>
<th>Palmitic acid</th>
<th>Suberic acid</th>
<th>Adipic acid</th>
<th>Succinic acid</th>
<th>Glutaric acid</th>
<th>DL-Malic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>99.79; a</td>
<td>97.14; b</td>
<td>99.55-99.57;</td>
<td>98.41-98.75;</td>
<td>77.3-90.73;</td>
</tr>
<tr>
<td>~99.9; a</td>
<td>99.96; a</td>
<td>99.95-99.97;</td>
<td>98.41-98.75;</td>
<td>77.3-90.73;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>~99.99; b</td>
<td>97.14; b</td>
<td>≥98; 99.8-99.9;</td>
<td>≥98; 99.8;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>99.99; c</td>
<td>99.95-99.97;</td>
<td>99.8-99.9;</td>
<td>99.8-99.9;</td>
<td></td>
</tr>
<tr>
<td>~99.9; a</td>
<td>99.97-99.1;</td>
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<td>64.50-89;</td>
<td></td>
</tr>
<tr>
<td>~99.9; b</td>
<td>99.97-99.2;</td>
<td>96.81-97.38;</td>
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<td></td>
</tr>
<tr>
<td>60°C</td>
<td></td>
<td></td>
<td>61.48-87.68*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* - calculated using equation 9.2; a - [8]; b - [59]; b - calculated in [59] for the range 20-40°C; c - [70]; d - [13]; e - [71]; f - [49]; g - [72]; h - [73]; i - [74]; j - [11]; k - [75]; l - [76]; m - [77]; n - [78]; o - [26]; p - [79]; s - [62].
behaviour upon water vapour sorption/desorption cycle, characteristic for deliquescent hygroscopic substances, which implies that under cycling humidity it is harder to dry once dissolved acid - these hygroscopic species tend to keep uptaken water molecules. The results presented here can serve as a guideline for choosing the flux chemistry considering the device exposure conditions, or for defining the safe climatic boundaries that should be met by the enclosures in order to provide a reliable and corrosion-free environment.

V. CONCLUSIONS

1) Weak organic acids (WOAs) typically used as solder flux activators exhibit different hygroscopic nature that depends on their chemical structure and ambient temperature. An increase of temperature strengthens the moisture-residue interactions leading to higher degree of acid dissolution and a shift of critical RH level for acid deliquescence and efflorescence towards lower humidity range.

2) The corrosive properties of WOAs are associated with their hygroscopicity and solubility changes upon varying temperature. Leakage current measurements revealed the RH range for electrochemical migration complied with the deliquescence RH found by means of impedance technique for highly soluble glutaric and DL-malic acids. An increase in temperature raised the solubility of the organic activators leading to the increased leakage current and accelerated corrosion occurrence due to WOAs deliquescing at lower RH levels.

3) Climatic testing of flux activators resulted in the following order of hygroscopicity and corrosivity: palmitic < suberic < adipic < succinic < glutaric < DL-malic acids for all test temperatures. Palmitic acid was found to be the safest WOA due to its poor hygroscopicity or very low solubility. On the contrary, glutaric and DL-malic acids were associated with the formation of thick water layers and severe corrosion occurrence.

VI. REFERENCES


10. HUMIDITY-RELATED FAILURES IN ELECTRONICS: EFFECT OF BINARY MIXTURES OF WEAK ORGANIC ACID ACTIVATORS

Kamila Piotrowska, Vadimas Verdingovas, Rajan Ambat

Abstract - The ionic residues of activator compounds used in the no-clean solder flux systems often remain on a Printed Circuit Board Assembly surface after the soldering process and may compromise the corrosion reliability of electronic device upon exposure to humid environment. The solder flux formulations contain weak organic acids (WOAs) activators of different types, sometimes present in the form of mixtures of varying compositions. This paper presents the results of parametric hygroscopicity studies of binary mixtures of weak organic acids that simulate the activating part of the typical no-clean solder flux formulation. Three types of binary blends of varying ratios between the acids were tested: adipic : succinic, adipic : glutaric, and succinic : glutaric. The hygroscopic and corrosive behaviour of the mixtures were investigated under relative humidity (RH) varying from 30% to ~99% and at test temperatures of 25°C, 40°C, and 60°C. The moisture sorption and desorption isotherms were determined using a gravimetric method, while AC electrochemical impedance was employed for monitoring the solid-liquid transition of residues. The influence of residues on corrosion reliability was investigated using DC leakage current measurements on a contaminated surface insulation resistance comb patterns with tin solder alloy. The results of corrosion testing were correlated with hygroscopicity studies and visualized by ex-situ colorimetric analysis using a tin ion indicator in a gel. The results show that the critical humidity level for moisture absorption shifts to lower RH values for mixtures, compared to pure WOAs. Water absorption behaviour varied based on the relative content of WOAs in the mixtures and ambient temperature, which also influenced the leak currents and electrochemical migration.

Keywords - Corrosion, solder flux, binary mixtures, humidity, hygroscopicity, climatic reliability of electronics.

I. INTRODUCTION

No-clean halide-free solder flux systems are widely used in electronics industry for automated Printed Circuit Board (PCB) assembling process. At high soldering temperatures, chemically active flux components remove the surface contaminants and activate the metal surface thereby improving the wettability for the solder [1, 2]. The “no-clean” technology relies on the fact that the activating species in flux formulation are less corrosive compared to those in washable systems [3] and possible to be removed during the soldering process [4], or remain at a minimal level on the surface [5]. The amount of remaining flux residues depends on the flux formulation (activator type [6], solid content [7]) and characteristics of the soldering process (temperature, time duration [6]). In practice, however, the Printed Circuit Board Assemblies (PCBAs) are often contaminated with significant amounts of process-

related flux residues [8, 9] influencing the corrosion reliability of electronics exposed to humid conditions [3].

The commonly used wave solder flux systems contain a number of ingredients that can be grouped as: (i) solvent (organic, inorganic, or a mixture of both), (ii) vehicle/binder (resin, rosin), and (iii) activator (organic acids) [10]. The post-production contamination left on a PCBA surface and contributing to the risk of corrosion occurrence are activators – typically the weak organic acids (WOAs) [7] – which were reported to cause a number of PCBA operational failures [11-16]. The corrosivity of residues strongly depends on the acid type and climatic conditions upon which the electronics operate. Most of the WOAs are soluble and ionisable in water which results in their high susceptibility to form electrolyte solutions of high conductivity, and can lead to the increased leak current and ion-induced electrochemical migration (ECM) [6, 7].

Under humid and non-condensing conditions, thin water layers adsorb to all clean surfaces [17-19], and the thickness of adsorbed water layer depends on the exposure conditions and substrate type. The PCBA surface energy increases due to the presence of polar contamination. As most of the WOAs used in the solder flux formulations are hygroscopic in nature [20], they interact with moisture from the atmosphere due to the presence of carboxylic functional groups within their structure [21], adsorbing minimal amounts of water to the surface by virtue of hydrogen bonding [22]. A transition of the residue from solid to aqueous phase [23-25] takes place at the critical relative humidity (RH) level, the condition when sufficient amount of water is absorbed to the contaminated surface and WOAs deliquesce occurs. As a result, the water layer formed on a PCBA surface increases the leakage current and likelihood of corrosion occurrence. Deliquescent behaviour is characteristic for the crystalline water-soluble substances and depends on the substance type [26] and temperature [27]. The compounds of high water solubility typically tend to exhibit a deliquescent behaviour at lower RH levels [19, 23]. An increase of ambient temperature raises the solubility of substances, therefore effectively lowers the critical relative humidity at which the deliquesce occurs [27-30]. The hygroscopic nature associated with the particular flux chemistry and electronics operational temperature defines the humidity boundary above which the failure is likely to occur.

Majority of the investigations reported in literature focus on the interaction between single WOA activator, or a flux system as a whole, and the surrounding moisture, and tend to describe the impact on surface insulation resistance (SIR) changes [11, 31-33] and ECM occurrence. However, the water absorption behaviour of WOAs and the temperature effects are rarely available. Further, many of the no-clean solder flux formulations contain mixtures of activators in a form of binary or ternary blends. Introduction of multiple activating components in the flux system changes the interaction characteristics between the residue and humidity, therefore alters the boundary for the failure occurrence due to the modified chemical nature of the flux. It is therefore vital to study the hygroscopic behaviour of various mixtures between the acids in order to evaluate their impact on electronics reliability. Moreover, the investigations should focus on the combined effect with temperatures that are relevant to the electronics operational conditions and the climatic conditions upon which the electronics operate.

The aim of this paper is to investigate the binary WOA mixtures and their interaction with humidity under varying temperature conditions relevant to the electronics applications. Deliquesence and efflorescence behaviour, water absorption capability, and the effect on corrosion reliability were studied in detail. The combinations of acids in the studied blends were relevant to the presently used no-clean flux systems, and WOAs content in the binary mixtures was systematically varied in order to understand the effect of composition over a range of ratios between the constituents. The hygroscopicity
studies were performed using the moisture gravimetric vapour sorption method and AC electrochemical impedance technique. The effect on corrosion reliability was investigated using DC leakage current measurements performed on the SIR pattern, which was followed by a visualization of tin corrosion using the colorimetric tin indicator gel method [34].

II. MATERIALS AND METHODS

WOA MIXTURES USED FOR INVESTIGATION

The activators selected for the studies were based on the actual activating binary compositions commonly found in the no-clean solder flux systems used presently for the wave soldering purposes. Three types of binary mixtures were studied:

(iv) adipic acid : succinic acid (AS),
(v) adipic acid : glutaric acid (AG),
(vi) succinic acid : glutaric acid (SG).

Each blend type was prepared from analytically pure acids supplied by Sigma Aldrich. Required amounts of pure WOAs were prepared in order to obtain the binary mixtures of the following ratios:

d) 83.3 wt% : 16.7 wt% (5:1)
e) 66.7 wt% : 33.3 wt% (2:1)
f) 50 wt% : 50 wt% (1:1)
g) 33.3 wt% : 66.7 wt% (1:2)
h) 16.7 wt% : 83.3 wt% (1:5)

The mixtures constituted of two components, one of them exhibiting higher hygroscopicity than another one, therefore the increasing order of hygroscopicity for the blend ratios was established: 5:1 < 2:1 < 1:1 < 1:2 < 1:5. The addition of a more hygroscopic component is a common practice for the improvement of solderability properties. Required amounts of pure WOAs were dissolved in isopropyl alcohol (analytical purity of 99.8%) in order to obtain the 5% wt/v solutions of binary mixtures of each ratio, and used for the AC/DC testing using the SIR patterns.

SURFACE INSULATION RESISTANCE (SIR) TEST BOARDS

The AC and DC electrochemical measurements were carried out using Pb-free SIR test patterns (Figure 10.1) with a hot air solder leveling (HASL) surface finish and Sn100C solder alloy. The dimensions of the comb pattern were 13 mm x 25 mm, and the distance between the electrodes was 0.3 mm. Prior to each experiment, the SIR specimens were carefully cleaned by rinsing with deionized water (conductivity of 18.2 MΩ·cm at 25°C) which was followed by rinsing with isopropyl alcohol (analytical purity of 99.8%) three times and drying with pressurized air.

Figure 10.1: The overall view on the SIR test pattern.
CLIMATIC CHAMBER

All experiments were carried out in the controlled environment in the climatic chamber Espec PL-3KPH. The fluctuations in the temperature and relative humidity are stated to be within the range of ±0.3°C/±2.5%RH in the conditions -40°C to +100°C/20%RH to 98%RH. The airflow was ~1.5 m/s.

HYGROSCOPICITY OF BINARY MIXTURES

Gravimetric water vapour sorption/desorption

The water vapour sorption and desorption behaviour was investigated by gravimetric measurements at varying humidity and constant temperatures of 25°C, 40°C, and 60°C. The 150 mg powder samples of each binary blend type and ratio were prepared by weighting the acids separately, placing them in the same aluminium crucible, and mixing the whole content for about 2 minutes in order to provide the maximum degree of physical contact between the crystals of both WOAs. The prepared samples were kept in a desiccant box (RH<15%RH) 24-72h prior to the exposure. The samples were subsequently subjected to RH ramps from 30~99%RH and from ~99-30%RH in the steps of 5%RH at each test temperature. Throughout the experiment, the sample weight was periodically monitored at each RH step using Sartorius Research R 160 P electronic semi-microbalance with an accuracy of 0.01 mg. The final weight gain at each humidity level was determined after the gravimetric equilibrium was reached [35] and the specimens were returned to the chamber for exposure to higher RH. The moisture content $M_c$, specific for each climatic condition, was calculated using equation 10.1 [36] and expressed as a percentage of the sample's initial mass:

$$M_c(\text{wt}%) = \frac{m_w - m_d}{m_d} \cdot 100$$

(Eq. 10.1)

where $m_w$ is the weight of the wet sample after the exposure to specific test condition, $m_d$ is the initial weight of a dry specimen. The moisture content values obtained at each RH level were used to generate the water vapour sorption and desorption isotherms for each test temperature. The relative humidity levels for deliquescence (dRH) and efflorescence (eRH) were defined from the range of RH where an abrupt increase (for dRH) and decrease (for eRH) in the mass of water vapour occurred.

The measurements at 40°C and 60°C had a risk of moisture condensation on the crucibles that were returned to the chamber after the weight measurements. Therefore, after each weight measurement, the crucibles were kept for ~10-15min in the climatic chamber set to required conditions, but enclosed in additional containers in order to equalize the specimens' temperatures with the surrounding conditions.

AC electrochemical impedance measurements

The electrochemical impedance experiments were performed in order to assess the interaction of particular mixture type and ratio with the surrounding moisture, and verify the RH range, particular for each mixture type, at which the deliquescence occurs at 25°C, 40°C, and 60°C. The SIR patterns were pre-contaminated with 5% wt/v solutions of each mixture type and ratio, which resulted in the residue level of ~100 μg/cm² after the solvent evaporation at ambient conditions. The pre-contaminated samples were stored in the desiccator box for 24-72 h (<15% RH) prior to the testing. Subsequently, the specimens were placed in the climatic chamber and kept at 30%RH level for 4-6 hours in order to stabilize the impedance signal and reach an equilibrium between the specimens and the chamber. After reaching the equilibrium, the RH was elevated (30-99%RH) and subsequently decreased (99-30%RH) in the rate of ~0.1%RH/min.
The AC measurements were carried out using "BioLogic VSP" multichannel potentiostat. The signal amplitude of 25 mV ($V_{\text{rms}} = 17.68$ mV) was applied at a fixed frequency of 10 kHz, which is governed by the capacitive character of the SIR electrode system at the humidity levels not exceeding the critical RH for WOAs deliquescence and water layer formation [20, 37]. Upon deliquescence of the contamination and absorption of water to the surface, the thickness of a formed film increases, which results in the impedance reduction due to the resistive character of water layer forming in between the conducting lines. A drop of impedance to $\sim5$-$10$ kΩ indicated a total dissolution of the residue into the water layer. Upon efflorescence (crystallization), occurring upon decreasing of the RH (99-30%RH), the thickness of water layer decreases and the impedance signal returns to the initial values.

**CORROSIVITY OF BINARY MIXTURES**

**DC leakage current measurements**

The DC electrical testing was carried out in order to assess the RH range for the ECM occurrence for the particular blend type and ratio at 25°C, 40°C, and 60°C. The humidity exposure conditions were determined from the hygroscopicity studies for each mixture type. The SIR test substrates were pre-contaminated and stored in a similar manner as for the AC measurements. The exposure to constant temperature and varying RH was conducted in the Espec climatic chamber where the samples were kept at the set conditions for 1h prior to the testing in order to assure the equilibration between the climate and the residue. The leakage current was measured as a function of the applied potential varying from 0 V to 10 V at 2 mV/s rate.

**Colorimetric visualization of tin corrosion**

The visualization of tin corrosion on the SIR patterns pre-contaminated with different binary mixtures of WOAs was performed using a tin ion indicator gel. This method of tin corrosion visualization is based on the reaction of tin ion indicator with tin corrosion products, and the application of the indicator in a form of a gel. The detailed description of the test method including application examples can be found elsewhere [34], therefore only a short description will follow.

The preparation of the gel with indicator was done in the following steps: (i) agar gel (type A7921, Sigma-Aldrich) was added into Millipore water with a conductivity of 18.2 MΩ·cm at 25°C at the concentration of 10 g/L, (ii) the water containing agar gel was heated to a temperature above 80°C for homogeneity of the solution, and (iii) tin ion indicator was added into solution, while the solution was being stirred.

After the gel was ready, it was applied either by a pipette on the SIR patterns. The gel acts as a medium for application of the indicator, while it also helps to immobilize the corrosion products, as a result of increasing viscosity of the gel as it cools down after application on the test boards with SIR patterns. The presence of tin in its oxidation state $+2$ and $+4$, due to corrosion occurrence, was visualized by colour change of the gel from light yellow to blue/violet as a result of chelate complex formation with tin ions. For consistency of the results, the corresponding photographs were taken within 5-7 min after application of the gel.
III. RESULTS

HYGROSCOPICITY OF BINARY MIXTURES AS A FUNCTION OF TEMPERATURE AND BLEND RATIO

The results of gravimetric water vapour uptake measurements are shown in the Figure 10.2, and are presented in the form of sorption and desorption isotherms corresponding to the equilibrium amount of water vapour sorbed as a function of a steady-state RH at constant temperature.

Figure 10.2: Moisture sorption isotherms of binary blends: (a) AS, (b) AG, (c) SG at (1) 25°C, (2) 40°C, (3) 60°C. Each point represents an average with the deviation bar given for 3 measurements.
Comparing three mixture types, AS did not exhibit a deliquescent behaviour at 25°C and 40°C (Figure 10.2 (a1) and (a2)), although the amount of water vapour sorbed progressively increased at higher temperature. Moreover, no differentiation between the sorption levels for various ratios could be made. At 60°C (Figure 10.2 (a3)), the AS blend significantly dissolved into the water layer leading to ~400 wt% uptake at saturated humidity level.

On the contrary to AS, both AG and SG mixtures were deliquescent at all test temperatures (Figure 10.2 (b) and (c)). Between the two, SG mixture underwent slightly higher degree of moisture absorption than AG at any test temperature and RH level. Moreover, mixture ratios containing larger fraction of a more hygroscopic component took up more water compared to the ratios constituting largely of low hygroscopic component in the following order: 5:1 < 2:1 < 1:1 < 1:2 < 1:5. For AG and SG blend types, the saturated moisture sorption level at 99%RH varied in the decreasing order: $M_{c_{\text{sat}},60^\circ C} > M_{c_{\text{sat}},25^\circ C} > M_{c_{\text{sat}},40^\circ C}$ as presented in the Table 10.1.

### Table 10.1: Saturated moisture sorption levels for different mixture types and ratios at different temperatures.

<table>
<thead>
<tr>
<th>Mixture type</th>
<th>Ratio</th>
<th>$M_{c_{\text{sat}}}$ (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25°C</td>
</tr>
<tr>
<td>Adipic : Succinic</td>
<td>5:1</td>
<td>0.26 (± 0.01)</td>
</tr>
<tr>
<td>(AS)</td>
<td>2:1</td>
<td>0.27 (± 0.09)</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>0.30 (± 0.05)</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>0.31 (± 0.01)</td>
</tr>
<tr>
<td></td>
<td>1:5</td>
<td>0.33 (± 0.07)</td>
</tr>
<tr>
<td>Adipic : Glutaric</td>
<td>5:1</td>
<td>40.00 (± 6.78)</td>
</tr>
<tr>
<td>(AG)</td>
<td>2:1</td>
<td>62.25 (± 6.45)</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>135.00 (± 13.25)</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>160.00 (± 7.58)</td>
</tr>
<tr>
<td></td>
<td>1:5</td>
<td>211.00 (± 10.36)</td>
</tr>
<tr>
<td>Succinic : Glutaric</td>
<td>5:1</td>
<td>89.00 (± 3.50)</td>
</tr>
<tr>
<td>(SG)</td>
<td>2:1</td>
<td>120.00 (± 11.78)</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>190.06 (± 8.32)</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>208.75 (± 1.66)</td>
</tr>
<tr>
<td></td>
<td>1:5</td>
<td>243.12 (± 2.56)</td>
</tr>
</tbody>
</table>

The range of relative humidity levels for deliquescence (dRH) was found to be the same for both AG and SG mixtures and independent on the ratio type. Moreover, the dRH decreased with an increase of ambient temperature. For blends that underwent deliquescence phenomenon, the crystallization (efflorescence) was accompanied by a hysteresis behaviour where the desorption branch lied at higher $M_c$ levels than the sorption branch. As a result, the efflorescence point (eRH) was found in the lower range of RH than the critical RH for deliquescence, and, similarly to dRH, was found to decrease with an increase of test temperature. Moreover, the crystallization occurred at lower RH range for SG compared to AG at 25°C and 40°C.
The results of AC electrochemical impedance testing, used as a complementary technique to the gravimetric vapour sorption measurement, are presented in the Figure 10.3. The highlighted RH range on the impedance graphs represents the deliquescence regions found by means of gravimetric technique (Figure 10.2).

Figure 10.3: Summary of the impedance testing conducted on the SIR comb patterns pre-contaminated with ~100 μg/cm² of binary mixtures at different ratios: (a) AS, (b) AG, (c) SG at (1) 25°C, (2) 40°C, (3) 60°C.

In case of AS mixture, the distinct changes in impedance signal occurred at 25°C and 40°C at high humidity levels (Figure 10.3 (a1) and (a2)), indicating a low degree of interaction with water vapour though no deliquescence. The interaction with moisture was more pronounced at 40°C than at ambient temperature. However, at 60°C, the AS type of residue dissolved into the water layer (Figure 10.3 (a3)), causing a significant reduction of impedance at the RH range noted as deliquescence from the gravimetric measurements.

On the contrary to AS mixture type, AG and SG blends exhibited deliquescent behaviour in the tested RH range at all test temperatures causing significant drops in impedance values (Figure 10.3 (b) and (c)). With an increase of temperature to 40°C, the shift in dRH towards lower RH values was found for all ratios except for 5:1 type (containing the lowest fraction of a more hygroscopic component). At 60°C, the impedance signal indicating activators’ dissolution decreased significantly although not at the RH
range for deliquescence noted from water vapour sorption measurement. Similarly to the results obtained via gravimetric sorption test, the efflorescence (crystallization) was accompanied by an occurrence of a hysteresis loop upon desorption of water molecules from the deliquesced residue.

**Figure 10.4:** Summary of the impedance values obtained at 10 kHz frequency at saturated humidity conditions (~99%RH) for all mixtures and ratios at (a) 25°C, (b), 40°C, (c) 60°C. Each point represents an average with the deviation bar given for 3 measurements.

Figure 10.4 presents a summary of AC testing where the average impedance values obtained for series of measurements at saturated humidity levels (~99%RH) were plotted for different mixtures and ratios at all test temperatures. Among all blend types, AG and SG caused larger impedance drops at saturated humidity compared to AS mixture. All AS ratios caused minimal impedance decrease at 25°C/99%RH and 40°C/99%RH, similarly to the clean SIR surface. At 60°C/99%RH, all mixtures except for AS 5:1 ratio dissolved into the water layer causing an almost complete reduction in the impedance output.

**CORROSIVITY OF BINARY MIXTURES AS A FUNCTION OF TEMPERATURE AND BLEND RATIO**

The data obtained via DC measurements is presented in the Figure 10.5, Figure 10.6, and Figure 10.7 where the leak current on the SIR patterns was plotted against the applied potential at different relative humidity levels for each test temperature. An abrupt increase in current above μA level is typically an indication of a residue-induced electrochemical migration where the corrosion progresses due to the water layer build-up and consequent dendrite formation between opposing electrodes that eventually cause a short circuit.
Figure 10.5: Leakage current measurements for SiR boards pre-contaminated with ~100 µg/cm² of AS mixture: (a) 5:1 ratio, (b) 2:1 ratio, (c) 1:1 ratio, (d) 1:2 ratio, (e) 1:5 ratio at (1) 25°C, (2) 40°C, (3) 60°C.
Figure 10.6: Leakage current measurements for SIR boards pre-contaminated with ~100 µg/cm² of AG mixture: (a) 5:1 ratio, (b) 2:1 ratio, (c) 1:1 ratio, (d) 1:2 ratio, (e) 1:5 ratio at (1) 25°C, (2) 40°C, (3) 60°C.
Figure 10.7: Leakage current measurements for SiR boards pre-contaminated with ~100 μg/cm² of SG mixture: (a) 5:1 ratio, (b) 2:1 ratio, (c) 1:1 ratio, (d) 1:2 ratio, (e) 1:5 ratio at (1) 25°C, (2) 40°C, (3) 60°C.
Generally, a higher test temperature was accompanied by the ECM taking place at lower RH. Moreover, the RH range where the dendrite formation occurred strongly depended on the ratio between different hygroscopic components in the binary blend: the higher content of a more hygroscopic one induced the ECM occurring at lower RH levels. The corrosion of highly hygroscopic ratios took place at the RH range for deliquescence (known from moisture sorption and impedance measurements), or lower than dRH. The overall tendency for corrosion occurrence, regardless the ratio type, increased in the following order: AS < AG < SG.

The summary of the RH range values for which the dendrite formation took place in the course of SIR testing is presented in the Figure 10.8 for all the blend and ratio types, together with the highlighted dRH range obtained from weight gain testing. In most cases, the RH for ECM was lower than the RH for ECM for individual constituents of such blend type [20], as shown in the Figure 10.8. Any ratio type of AS mixture (Figure 10.8 (a)) caused a dendrite growth at RH levels lower than those for adipic or succinic acid separately. In cases of more hygroscopic ratio types (e.g. SG 1:5, Figure 10.8 (c)), the uptake of water vapor for ECM occurrence at 40˚C and 60˚C was sufficient at RH range lower than dRH obtained from gravimetric sorption measurements.

![Graph showing RH range for dendrite formation](image)

Figure 10.8: Summary of RH range for dendrite formation at all test temperatures and ratio types: (a) AS, (b) AG, (c) SG.

The corrosivity of the binary mixtures under humid condition and applied DC voltage was further visualized using a tin ion indicator gel, which was earlier presented for a use in corrosion profiling on the printed circuit boards [34]. A representative set of micrographs in Figure 10.9 was obtained on the
SIR patterns pre-contaminated with SG mixture type of varying ratios. These micrographs correspond to the leakage current measurements at dRH and 25°C. The corrosion level was found to increase with increasing amount of more hygroscopic component in a blend. The corroded samples of 5:1 ratio showed many areas where pitting occurred (Figure 10.9 (a), marked with red arrows), though no tin corrosion product deposition was seen on the laminate between the conductors. The ratios containing higher content of glutaric acid in the blends resulted in increase of corrosion attack, and accordingly higher deposition of tin corrosion products on the laminate and occurrence of dendrites (Figure 10.9 (d) and (e)). Overall, an increase of blue coloration, indicating the amount of tin corrosion products spread throughout the surface of the SIR pattern, can be seen for increasing the ratio of more hygroscopic – the glutaric acid – in the binary blend of SG.

Figure 10.9: Colorimetric visualization of tin corrosion extent over SG samples subjected to leakage current testing at 25°C/90%RH. The representative micrographs of SIR patterns contaminated with binary mixture of varying component ratios: (a) 5:1, (b) 2:1, (c) 1:1, (d) 1:2, (e) 1:5. Red arrows indicate pitting and dendrite formation.

IV. DISCUSSION

Overall, the results presented in this paper show the importance of understanding the humidity interaction with mixtures of weak organic acids used in the solder flux systems as activating components. Further, this study indicates the relevance of the binary mixtures composition in determining the moisture absorption behaviour and the effect on corrosion reliability of electronics when the residues are present on the PCBA surface. Mixing of two activators is a common practice that serves to improve the solderability properties, however, the results presented in this study show that it is significant to optimize the ratio between the activators for better humidity-related reliability performance. An optimized level of activators with relative difference in aggressiveness might provide both humidity reliability and solderability requirements.
Effect of Activator Type

Hygroscopic nature of flux residue is a result of its chemical structure, e.g., spatial arrangement of polar functional groups, hydrocarbon chain length. All tested weak organic acids are dicarboxylic and therefore polar compounds with a close structural relationship to each other. The difference lies in the chain length (succinic – C4, glutaric – C5, adipic – C6) which defines the molecules center of symmetry and the distance between the functional groups, therefore the hygroscopicity of the compounds. Between the three tested acids, their structural features described in our previous study \[20\] rank them in the following order of increasing hygroscopicity: adipic < succinic < glutaric. The same trend occurs in the solubility of mentioned WOAs: the most hygroscopic - glutaric acid - exhibits the best solubility in water and the lowest RH level for deliquescence \[7, 19, 20, 23\]. From the corrosion point of view, high solubility of a very hygroscopic ionic substance contributes to the high leakage current and can lead to the migration phenomenon of a large extent due to the formation of highly conductive water layer on a PCBA surface \[38, 39\].

Two of the tested binary mixtures (AG and SG) contained glutaric acid as a more hygroscopic component compared to adipic and succinic acids being the less hygroscopic ones. The results of gravimetric and electrochemical measurements showed that both AG and SG blends dissolve into the water layer at all investigated temperatures (Figure 10.2 (b) and (c), Figure 10.3 (b) and (c)). The SG mixture type showed higher moisture sorption capabilities than AG which complies with the hygroscopicity ranking. The SIR testing commonly used for evaluation of the effect of ionic contamination \[11, 40, 41\] followed the results of hygroscopicity studies for the mixtures and showed that both blends containing glutaric acid can cause electrochemical migration at all test temperatures (Figure 10.6 and Figure 10.7). The ECM occurrence and extent depended on the ratio between the constituents of a binary blend. The larger fraction of glutaric acid present in the AG and SG mixtures contributed to higher moisture sorption capabilities and, therefore, higher possibility of causing the ECM.

On the contrary, the AS mixture type did not exhibit a significant water absorption at 25°C and 40°C. However, the amount of moisture uptaken at 40°C/99%RH was sufficient for the formation of water layer conductive enough for the occurrence of ECM (Figure 10.5 (a2)-(e2)) by most of the tested ratios except for the least hygroscopic 5:1. However, at 60°C the residue dissolved into the water film (Figure 10.2 (a3), Figure 10.3 (a3)) leading to corrosion at lower RH levels (Figure 10.5 (a3)-(e3)). The results comply with the behaviour of succinic acid described in previously reported study \[20\].

The presence of a hysteresis loop in moisture sorption isotherms and on impedance plots complies with the findings for other deliquescent solids \[42-44\] and implies that the complete evaporation of water molecules from the saturated residue solution takes place at RH lower than the RH level for deliquescence. Broader shape of a hysteresis loop related to the water absorption has a significant influence on the reliability of electronics under transient humidity conditions. A broader loop shape indicates lower crystallization humidity (efflorescence) which leads to the extended wetting of the PCBA surface even if the surrounding humidity level has fallen below the deliquescent point of the surface contamination. Literature offers multiple descriptions on the origins of hysteresis behaviour including the ink bottle theory, the molecular shrinkage theory, the capillary condensation, and the swelling fatigue theory. However, the detailed investigation of this phenomenon was not a part of this study, but could be found elsewhere \[45\].
EFFECT OF BINARY BLEND

In a system saturated with a substance A, a component is in equilibrium with its aqueous solution and the vapour phase, and its water activity is equal to $dRH_A$. Upon addition of a component B to the system, the solubility limit of substance A and its activity decrease as much as the mole fraction of the substance B increases. As proven by Raoult’s law, in an ideal solution the relationship between the solute concentration and the vapour pressure is inverse: the mole fraction affects the fraction of molecules in the solution that can escape to the gas phase. Higher mole fraction of a component B accounts for an increase of molar concentration, and therefore higher proportion to the total vapour pressure, and decreased ability of water molecules to evaporate to the vapour phase [46]. Similarly, if disturbing the saturated solution of a solute B of initial $dRH_B$ by an addition of a substance A, the solubility limit of the substance B and its water activity decrease. The vapour pressure above the mixture solution at equilibrium is therefore also lower than the vapour pressures above saturated solutions A or B [47], unless a chemical reaction occurs between the components that has a higher equilibrium vapour pressure [23]. The phenomenon is called “deliquescence lowering” and results in mixtures deliquescenting at the so-called “mutual RH level” ($dRH_{mix}$), lower than the critical RH for deliquescence of any individual component of a measured binary system [24, 26, 47-51]. The results of our study comply with the theory, as shown in the Figure 10.10: the RH levels for deliquescence of binary mixtures were lower than the levels found for individual weak organic acids according to the results from gravimetric moisture sorption testing [20].

![Figure 10.10: Summary of RH levels for deliquescence obtained from gravimetric vapour sorption test.](image)

The mutual $dRH_{mix}$ is constant, depends on a mixture composition, but is independent on a ratio between the constituents in the mixture [24, 47]. It was confirmed by our current study where different ratios of the same mixture type exhibited the same RH range for deliquescence, but the water uptake level increased with an increase of the amount of hygroscopic components. This had its effect on corrosive behaviour of the blends where certain ratios caused the migration at lower RH compared to other mixtures (Figure 10.8). The consequences on reliability are unequivocal: the presence of even small amount of another hygroscopic component in the system, existing as impurity or trace compound, can significantly shift the deliquescence point of a whole and induce the corrosion occurrence at lower humidity than initially assumed for a major component [52]. Moreover, if the ratio between flux activators is not controlled, highly hygroscopic component constituting larger fraction of the mixture may lead to a greater extent of corrosion.
The estimation of deliquescence relative humidity of the mixture (\(d\text{RH}_{\text{mix}}\)) can be performed using different equations, though among many, two were chosen in this study for \(d\text{RH}_{\text{mix}}\) predictions. Ross equation (equation 10.2) proposed in 1975 [53] was found to often meet the expected values [54]. It assumes the same substance activity in the mixture as it exists in an individual solution, independent contributions of each component, and no interactions between the solutes [46, 55]. For a binary mixtures such activity can be expressed as critical RH of each individual component [47]:

\[
\frac{d\text{RH}_{\text{mix}}}{100} = \frac{d\text{RH}_A}{100} \cdot \frac{d\text{RH}_B}{100}
\]

(Eq. 10.2)

where \(d\text{RH}_{\text{mix}}\) is a deliquescence relative humidity of the mixture, \(d\text{RH}_A\) and \(d\text{RH}_B\) are deliquescence relative humidity values of solids A and B.

Another equation 10.3 is based on the solubility values for different solution constituents and, assuming the ideal solution behaviour and neglecting any interactions between the species, the saturation concentration of each substance in a mixture is equal to the values in saturated solutions of each pure compound [56]:

\[
\frac{d\text{RH}_{\text{mix}}}{100} = \exp(-M_{\text{H}_2\text{O}} \sum s m_s)
\]

(Eq. 10.3)

where \(d\text{RH}_{\text{mix}}\) is a deliquescence relative humidity of the mixture, \(M_{\text{H}_2\text{O}}\) is a water molar mass, and \(m_s\) are the molalities of each substance in the mixture, calculated from the solubility data given in [20] for the lowest and highest values.

The RH range for deliquescence (\(d\text{RH}_{\text{mix}}\)) obtained in the current study via gravimetric sorption and impedance methods were plotted together with \(d\text{RH}_{\text{mix}}\) calculated values using equations 10.2 and 10.3 as shown in the Figure 10.11. In case of Ross equation, the values used for \(d\text{RH}\) of individual components are given in our previous study [20] as (i) literature data, (ii) data from gravimetric sorption, and (iii) data from impedance testing. In case of equation (3), the solubility data was taken from [20].

The data obtained in the current study is highlighted with yellow colour in order to differentiate it from the data obtained through calculations. In case of the AS mixture type, which was deliquescent only at 60°C, the calculation of \(d\text{RH}\) using Ross equation for literature data and the calculations using the equation 10.3 comply with RH range obtained in this study (Figure 10.11 (a)). Similarly, both equations appeared to correctly predict the RH range for mutual RH for deliquescence of the SG blend, though the RH ranges were wide and not precise (Figure 10.11 (c)). For the AG blend, only Ross equation using the literature data used complied with the \(d\text{RH}_{\text{mix}}\) obtained in this study (Figure 10.11 (b)). In all cases, Ross equation based on the impedance data given in [20] did not follow the observations from this study. Moreover, Ross equation based on the \(d\text{RH}\) obtained from sorption test in [20] could be used only in case of the SG blend at 60°C.

The deviations for predicting the \(d\text{RH}_{\text{mix}}\) using Ross equation may derive from the common-ion effect [57]. According to Le Chatelier’s principle, in the blend of compounds sharing the same ion (as dicarboxylic acids) the common ion will compete while equilibrating in the solution. Therefore, at the equilibrium, the solution saturates with the common ion while the solubility of counter ions is decreased as they lack the ability to dissociate at the same concentration. Due to the overall decreased solubility, less ions will be dissociated in the solution and therefore the vapour pressure will be higher according to the Raoult’s law [46]. This effect can cause a diminishing of deliquescence lowering, where the mutual RH values are higher (so are the vapour pressures) than those predicted by Ross equation for the blends sharing a common ion [57].

Another important factor that might have contributed to the deviations in the predicted and measured \(d\text{RH}\) levels is the way all experiments were performed. In the blend of ingredients, every
component should be in a physical contact with all the other constituents of the mixture in order for the thermodynamics of a multi-component system to take place [57]. In practice, the requirement is difficult to meet, especially when the number of components increases [46, 47, 54].

![Figure 10.11](image)

Figure 10.11: Mutual RH levels for deliquescence for the tested binary mixtures: (a) AS, (b) AG, (c) SG. Experimental and calculated data.

**EFFECT OF TEMPERATURE**

As proven in our previous study [20], an increase in temperature increases the solubility of weak organic acids [49, 58], leading to a stronger degree of interaction between the flux residue and the water vapour. Higher test temperature lead to lower RH level for deliquescence and efflorescence for both AG and SG mixtures, and accelerated the occurrence of ECM [33]. However, the results from gravimetric sorption, impedance, and leakage current measurements did not comply with each other at 60˚C for both blends containing glutaric acid. This is due to the fact that electrical measurements rely on solution’s conductivity for which a limit was reached at the highest test temperature. Glutaric acid exhibits the highest solubility among all WOAs at 60˚C, and at low RH levels have saturated the formed water layer and led to the decrease of a degree of dissociation. The limiting conductivity remained until ~80%RH, and the increase of relative humidity allowed for a dilution of a saturated solution where the dissociation degree increased and led to an increased water film conductivity. The AC/DC measurements, relaying on the solution conductivity, falsely indicated the tendency for deliquescence and therefore did not comply with the water vapour sorption data for AG and SG mixtures at 60˚C.
V. CONCLUSIONS

1) The presence of two WOAs in the binary mixture shifts the RH levels for deliquescence and corrosion occurrence towards lower values, compared to either of WOAs constituting the blend. The difference between the critical RH levels of single activators and deliquescence RH of binary mixtures is within 10%RH.

2) The highly hygroscopic ingredient forming a mixture with less aggressive component associates formation of a thicker water layer and leads to electrochemical migration occurring at lower RH level. For the same mixture type, the RH level at which ECM occurs for most and least hygroscopic ratios may be 25%RH different.

3) An increase of temperature strengthens the interaction between the residue and water molecules, shifting the critical RH level for deliquescence and efflorescence towards lower humidity range, and thereby accelerates the corrosion occurrence. The deliquescence shifted of 5-15%RH when increasing the temperature from 25˚C to 40˚C, and the shift of 15-25%RH was found for the temperature increase from 40˚C to 60˚C.

4) The presence and shape of a hysteresis loop in vapour sorption isotherms and impedance curves indicate the wetting of the PCBA surface occurs even if the surrounding humidity level has fallen below the deliquescent point of the surface contamination.

VI. REFERENCES

[9] H. Schimanski, O. Yezerska, P. Plagemann, and J. Hagge, "Investigation of the influence of electrochemical migration (ECM) on the reliability of electronic assemblies after rework using lead-free


11. NO-CLEAN SOLDER FLUX CHEMISTRY AND TEMPERATURE EFFECTS ON HUMIDITY-RELATED RELIABILITY OF ELECTRONICS

Kamila Piotrowska, Magdalena Grzelak, Rajan Ambat

Abstract - The use of no-clean flux technology for the wave soldering process of Printed Circuit Board Assembly (PCBA) influences the humidity-related robustness of the electronic devices due to the ionic residues remaining on the PCBA surface after soldering. This paper investigates the effect of various no-clean solder flux chemistries on the formation of water layer on the PCBA surface studied as a function of climatic conditions relevant for the electronics industry. The activating part of the commercial flux formulations used for the investigations was based on single weak organic acid (WOA) and WOA mixtures. The hygroscopic nature of flux residues, reflecting its ability to uptake moisture and lead to the water film build-up, was investigated using the gravimetric moisture sorption test and AC electrochemical impedance. The effect of flux composition and ambient climatic conditions on the corrosion reliability was studied using DC leakage current measurements upon varying potential bias, humidity, and temperature levels. Study shows that solder flux residues containing mixture of WOA activators in their formulation facilitate the formation of water layer on the PCBA surface at lower humidity levels, compared to the residues composed of a single activator, and absorb higher amount of moisture. Corrosion occurrence is accelerated by the presence of highly hygroscopic residues of WOA mixtures, compared to significantly less corrosive contaminants comprised of single activator. Increase of ambient temperature enhances moisture interaction with flux residues and changes its deliquescent behaviour, leading to the formation of thicker water layer and severe ion-induced corrosion at lower humidity levels.

Keywords - Solder flux residue, quality, activator mixtures, humidity, temperature, corrosion, electronics reliability.

I. INTRODUCTION

Cleanliness of the Printed Circuit Board Assembly (PCBA) is important for the humidity-related robustness of electronics devices. The presence of contamination originates largely from the manufacturing process [1, 2], which involves the use of various chemical treatments for etching, plating, or cleaning purposes, and for subsequent soldering process of component assembling. However, the majority of the reported failures in the electronics industry are related to the effect of flux residues [3], arising from the use of solder flux systems, which are present on the PCBA surface after production. These constitute the largest threat to the electronics reliability [4] as they alter the humidity boundary within the enclosure due to their interaction with moisture, and, as a result, they facilitate the formation of water layer on the PCBA surface [5-9]. The build-up of electrolyte medium on electronic surfaces can easily trigger the electrochemical processes and corrosion occurrence, which eventually leads to
premature failures of the devices. The threat to the overall device reliability is a function of flux chemistry and its hygroscopic properties, which change with temperature and humidity conditions.

The concept of "no-clean" solder flux technology, used for automated PCBA assembling process, was introduced for environmental safety reasons [10] and such fluxes are supposed to be easily removed/decomposed at soldering temperatures [11]. Any remaining residues should contain non-corrosive activating compounds [3] (compared to washable flux systems) that do not require cleaning afterwards. However, in practice, the assemblies are often contaminated with significant amounts of no-clean solder flux residues that do not decompose completely under the range of soldering temperatures [12-14]. The elimination of the post-soldering cleaning step from the PCBA production [15] leads to the substantial amount of flux residues remaining on the surface [12] and creates reliability issues for the devices operating under varying humidity and temperature conditions [3, 16].

No-clean wave solder flux systems comprise majorly of a solvent which serves as a carrier for surfactants and a variety of additives [17]. The activators are typically weak organic acids (WOAs), e.g. succinic, adipic, or glutaric acids, which are hygroscopic [18] and often highly water-soluble [5, 19]. The WOAs interact with water molecules from the surrounding and assist their adsorption to the PCBA surface. At the specific critical relative humidity level [5, 20], WOAs deliquesce and dissolve into the formed water layer. The build-up of a conductive pathway under bias conditions [12] reduces the surface insulation resistance (SIR) and leads to current leakage, which triggers the occurrence of corrosion failures [21-24], e.g. electrochemical migration (ECM), even under mild humidity conditions. The level of current leak and the extent of corrosion depend on the electrical properties of the formed electrolyte, which are directly related to the dissociation constant (pKₐ) and solubility properties of the residues [5, 19]. Flux activators are ionic in nature, however many of them do not dissociate fully into the water layer and, as a result, they form weak electrolytes (e.g. adipic acid) [25]. Contrarily, highly ionisable acids form strong electrolytes (e.g. glutaric acid) and saturate the formed water layer easily with ions, creating a highly conductive electrolyte, which is detrimental in terms of corrosion reliability of electronics. Therefore, even if the quantity of the contaminants remains relatively equal, process-related residues containing highly hygroscopic activator significantly change the safe operating humidity boundary for electronics and magnify the effects of varying temperature.

Our earlier investigations focused on the hygroscopicity assessment of activators, typically used in the electronics industry, that comprise of a single [5, 11] or mixture of weak organic acids [19]. The corrosive nature of these activators was evaluated and correlated to the chemistry and climatic effects. The studies allowed for ranking of the activator types in terms of aggressivity, however, the effect of solder flux residues as a whole is rarely conducted [3] and explained from the chemistry point of view. Moreover, studies lack the combined effects of solder flux formulation and various climatic conditions on the reliability assessment.

Data reported in the literature contains of studies of the flux effects on reliability in terms of SIR changes [26, 27] or ECM occurrence, however the effects of activator chemistry is seldom discussed [28-30]. Further, the temperature/humidity effects are typically evaluated based on standardized SIR constant test conditions (e.g. 40°C/93%RH, 85°C/85%RH). In order to obtain the comprehensive understanding of the flux chemistry effect together with climatic conditions, the investigations should focus on the effect of temperatures and varying humidity levels that are relevant for the electronics operational conditions. The temperature changes can occur due to the climatic conditions upon which the electronics operate or conditions developed within the electronic enclosure (due to e.g. heat dissipation).
This paper investigates the climate-dependent hygroscopicity trends of the commercial solder flux systems by simulating various conditions of humidity and temperature relevant for electronic devices. The investigated flux types consisted of chemistries based on single WOA and mixture of WOAs as activators. The activator part of the fluxes (WOAs) was identified using Fourier Transform Infrared (FTIR) spectroscopy and Nuclear Magnetic Resonance (NMR) spectroscopy. Hygroscopicity evaluation was conducted under exposure to varying humidity and temperature conditions using gravimetric sorption test which allowed the estimation moisture uptake levels. The AC impedance technique was employed for the assessment of the residue-moisture interaction and related electrical effects as a function of humidity at different temperatures. The evaluation of the influence of flux chemistry on leakage current level and ECM occurrence was investigated using contaminated SIR test coupons under DC bias conditions.

II. MATERIALS AND METHODS

COMMERCIAL SOLDER FLUX SYSTEMS

Nine no-clean solder flux systems, commercially used for automated wave soldering process, were selected for the investigations based on their composition, acid number, and solid content.

<table>
<thead>
<tr>
<th>Flux symbol</th>
<th>WOA type (FTIR)</th>
<th>WOAs ratio (NMR)</th>
<th>J-STD-004 standard designation*</th>
<th>Acid number [mg KOH/g]</th>
<th>Solid content [%wt]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF1</td>
<td>Adipic</td>
<td>-</td>
<td>ORL0</td>
<td>24.0 ±1.2</td>
<td>3.8</td>
</tr>
<tr>
<td>SF2</td>
<td>Adipic</td>
<td>-</td>
<td>ROL0</td>
<td>15.8</td>
<td>2.2</td>
</tr>
<tr>
<td>SF3</td>
<td>Adipic</td>
<td>-</td>
<td>REL0</td>
<td>15.8</td>
<td>2.2</td>
</tr>
<tr>
<td>SF4</td>
<td>Succinic</td>
<td>-</td>
<td>ORL0</td>
<td>22.4</td>
<td>3.6</td>
</tr>
<tr>
<td>SF5</td>
<td>Succinic</td>
<td>-</td>
<td>ROL0</td>
<td>19.7</td>
<td>5.0</td>
</tr>
<tr>
<td>SF6</td>
<td>Succinic</td>
<td>-</td>
<td>REL0</td>
<td>18.75</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td>SF7</td>
<td>Adipic + succinic</td>
<td>A : S = 1 : 1.7 (37% : 63%)</td>
<td>ORL0</td>
<td>26.0</td>
<td>4.0</td>
</tr>
<tr>
<td>SF8</td>
<td>Adipic + glutaric</td>
<td>A : G = 1 : 5.5 (15% : 85%)</td>
<td>ORM0</td>
<td>36.85</td>
<td>4.0</td>
</tr>
<tr>
<td>SF9</td>
<td>Succinic + adipic + glutaric</td>
<td>S : A : G = 1 : 1.1 : 1.5 (27.5% : 30% : 42.5%)</td>
<td>ORL0</td>
<td>31.5 ± 2.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

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

Table 11.1 contains the summary of relevant information provided by the manufacturer, namely the classification of the flux according to the J-STD-004 standard, acid number, and solid content. The acid number is related to the amount of acid in the flux formulation, and it is defined as the amount of KOH required for the neutralization of 1 g of flux sample. The solid content relates to both the activator (WOA) and a film-former (rosin, resin) which can be rosin (RO), resin (RE), or organic (OR). All the fluxes were VOC-based except for SF8 which was water-based. The specific information about the activator part of the flux composition was not provided in the datasheet, therefore was analysed by means of...
Fourier Transform Infrared (FTIR) spectroscopy. Fluxes SF1-SF6 were chosen in order to study the effect of flux formulations based on single WOA. Fluxes SF7-SF9 were chosen due to their content of WOA mixtures, instead of one activator type. For the flux systems containing WOA mixtures, Nuclear Magnetic Resonance (NMR) spectroscopy was employed for a precise evaluation of the ratio between the constituting WOAs. The results of both FTIR and NMR analyses are given in the Table 11.1 and described in the results section.

**IDENTIFICATION OF WOA TYPE AND RATIO IN THE FLUX SYSTEMS**

**Fourier Transform Infrared (FTIR) spectroscopy**

The type of WOA in each flux system was determined with the use of FTIR technique which allows for the detection of multiple diagnostic bands in the IR spectrum. The acid identification was based on the inference from the observation of the transmittance peaks in the particular regions of the obtained spectra. The measurement was conducted on the flux residues after solvent evaporation at room temperature using Nicolet™iN™10 MX infrared imaging microscope with a MCT detector cooled with liquid nitrogen. The samples were analysed using an attenuated total reflection (ATR) method. The spectra were recorded in the range of 4000 cm⁻¹-675 cm⁻¹ with a resolution of 4 cm⁻¹.

**Nuclear Magnetic Resonance (NMR) spectroscopy**

The estimation of ratio between the acid constituents in the flux systems was carried out using ¹H NMR spectroscopy. The proton carries a property of a spin state that implies it is a rotating sphere of charge creating its own magnetic field. The NMR technique relies on the creation of an external magnetic field allowing the proton to absorb the electromagnetic radiation, which causes the transfer of the spin state from base to higher energy level (the nucleus is then in resonance with an applied magnetic field). The energy difference between the two spin states takes place at the wavelength that corresponds to the radio frequency. When the nucleus returns to the base energy level, the energy is emitted at the same frequency. The response (signal intensity, its resonant frequency, and the absorption energy) is characteristic for the particular proton for each molecule, therefore the ratios between different activators in the flux formulation could be estimated with a high precision.

The spectra were recorded at 298 K on Bruker Ultrashield 300 MHz spectrometer in the deuterated dimethyl sulfoxide-d₆ (DMSO-d₆) solution. The chemical shifts of the recorded peaks are reported in δ (ppm) with a reference to the solvent residual signal (δH = 2.50 ppm for DMSO-d₆ [31]). All the signals originating from WOAs in the flux systems were recognized based on ¹H NMR spectra for pure acids as references. The ratio was calculated by means of the vertical integration of the specific peaks after the signals were assigned to the exact WOA using MestReNova 11.0 software.

**SURFACE INSULATION RESISTANCE (SIR) TEST BOARDS**

The AC and DC electrochemical measurements were conducted across a test interdigitated surface insulation resistance (SIR) lead-free comb patterns with a HASL surface finish and Sn100C solder alloy. The dimensions of the pattern were 13 mm x 25 mm and therefore the active surface area was 325 mm². The distance between the electrodes was 0.3 mm (Figure 11.1).
Prior to each experiment, the test boards were cleaned with Millipore deionized water (resistivity of 18.2 MΩ at 25°C) and isopropyl alcohol (analytical purity of 99.8%) three times, which was followed by drying with a pressurized air.

CLIMATIC CHAMBER

The AC/DC electrochemical tests and water vapour sorption experiments were conducted under controlled environment in the climatic chamber Espec PL-3KPH. The fluctuations in the temperature and relative humidity are within the range of ±0.3°C/±2.5%RH in the conditions -40°C to +100°C/20%RH to 98%RH. The airflow in the chamber was ~1.5 m/s.

HYGROSCOPICITY OF FLUX SYSTEMS

Gravimetric water vapour sorption/desorption

The estimation of moisture sorption capabilities of flux residues was characterized using gravimetric water vapour sorption and desorption measurements at varying humidity and at constant temperatures of 25°C, 40°C, and 60°C. The commercial flux samples were evaporated at ambient conditions, followed by drying in desiccant box (RH<15%RH) for 21 days. Subsequently, the 1 g dry samples of each flux residue were prepared and placed in Petri glass dishes, then exposed to 30-99%RH in the steps of 5%RH at each test temperature. The weight of samples was controlled at each RH level using Sartorius Research R 160 P electronic semi-microbalance with an accuracy of 0.01 mg. When the gravimetric equilibrium was reached at each particular RH [32], the final weight gain was determined and the specimens were returned to the chamber for further exposure to the higher RH level. The mass of the samples, specific for each condition, was used for determination of moisture content \( M_c \), expressed as a percentage of the WOA's initial weight, using equation 11.1 [33]:

\[
M_c(\text{wt}) = \frac{m_w - m_d}{m_d} \cdot 100
\]

(Eq. 11.1)

where \( m_w \) is the weight of the wet sample after an exposure to certain test condition, \( m_d \) is the initial weight of a dry specimen. The \( M_c \) values were used to generate water vapour sorption and desorption isotherms for each test temperature. The relative humidity levels for deliquescence (dRH) and efflorescence (eRH) were defined from the range of RH where an abrupt increase (for dRH) and decrease (for eRH) in the mass of water vapour occurred.
The measurements at 40°C and 60°C had a risk of moisture condensation on the glass dishes that were placed in the chamber after the weight measurements. Therefore, after each measurement, the containers were kept for ~10-15 min in the climatic chamber set to required conditions, but enclosed in additional containers in order to equalize the specimens’ temperatures with the surrounding conditions.

**AC electrochemical impedance**

The AC measurements were conducted in order to investigate the interactions between particular solder flux composition and the surrounding humidity at 25°C, 40°C, and 60°C. Based on the available data, the average content of flux activator in the commercial solder flux systems was ~2.5% wt, therefore the SIR comb structures were pre-contaminated with 13 µL of liquid flux which provided a level of ~100 µg/cm² of the residue on the 325 mm² of the SIR pattern after the solvent evaporation at ambient conditions. Since SF8 was water-based, 13 µL of the flux was transferred to the container for the water evaporation at ambient conditions. Subsequently, 13 µL of isopropanol (analytical purity of 99.8%) was added to the solid residue of SF8 for its dissolution, and then the solution was applied onto the SIR pattern. The pre-contaminated SIR specimens were stored in the desiccator box for ~6 weeks (<15%RH) prior to the testing. Subsequently, the patterns were placed in the climatic chamber for 6 hours at 30%RH and at desired temperature in order to stabilize the impedance signal. Afterwards, the RH was elevated (30-99%RH) and subsequently decreased (99-30%RH) at a rate of ~0.1%RH/min while the AC voltage was applied and the impedance signal was monitored.

The impedance experiments were performed using “BioLogic VSP” multichannel potentiostat. The signal amplitude of 25 mV (V<sub>rms</sub> = 17.68 mV) was applied at a fixed frequency of 10 kHz. This frequency is dominated by a capacitive character of the SIR electrode pattern used in this study at the RH levels not exceeding the RH for WOAs deliquescence [8]. Upon an increase of relative humidity level in the climatic chamber, the deliquescence of the flux residue and adsorption of water to the surface occurred, leading to the increase in thickness of the formed water layer which resulted in impedance reduction due to the resistive character of water layer forming in between the electrodes of the SIR. A drop of impedance to ~5 kΩ indicated a total dissolution of the residue into the water layer. Upon efflorescence (crystallization) occurring during the RH decrease (99-30%RH), the thickness of water layer decreased and the impedance signal returned to the original values once the residue reached the crystallization point at low RH.

**DC leakage current**

The leakage current measurements were carried out for the assessment of RH levels at which the risk of ECM occurrence exists at 25°C, 40°C, and 60°C. The surface insulation resistance patterns were pre-contaminated with flux solutions in a similar manner as for the AC impedance measurements. The samples were then kept at room conditions to ensure solvent evaporation, and subsequently stored in desiccator box for ~6 weeks (<15%RH) in order to ensure the complete removal of volatile compounds. The dried residue remaining on the SIR comb pattern was subsequently subjected for DC leakage current testing upon exposure to constant temperature and varying RH conducted in the Espec climatic chamber. The leakage current was measured as a function of the applied DC potential varying from 0 V to 10 V at 2 mV/s rate.
**Optical microscopy**

The morphology of the SIR coupons after DC testing was observed under optical microscope. The micrographs were obtained using Leica MZ125 stereomicroscope equipped with Leica DFC450 C digital camera.

### III. RESULTS

**IDENTIFICATION OF WOA TYPE AND RATIO IN THE FLUX SYSTEMS**

The identification of the activator type within the no-clean solder flux systems was carried out using FTIR spectroscopy. The set of FTIR spectra of the test flux systems is shown in Figure 11.2 together with a reference spectra of WOAs identified within the flux formulation. The correlation between the activator present in solder flux and the acid was done by a comparison of the fingerprint region (1500-675 cm\(^{-1}\)) in the respective spectra. Every spectrum contained the typical absorption peaks attributed to the free carboxylic functional groups which appear at the vibrational frequencies of 3300-2500 cm\(^{-1}\) (stretching ν\(_{\text{C}=\text{O}}\)), 1690 cm\(^{-1}\) (stretching ν\(_{\text{C}=\text{O}}\)), 1460-1395 cm\(^{-1}\) (in-plane bending δ\(_{\text{C}=\text{O}}\)), 1195-1320 cm\(^{-1}\) (stretching ν\(_{\text{C}=\text{O}}\)), ~920 cm\(^{-1}\) (out-of-plane bending δ\(_{\text{O-H}}\)) [34, 35]. The diagnostic peaks were assigned to the appearance of stretching C-O bonds that, in case of each WOA, absorb at slightly different frequency (1277 cm\(^{-1}\) – adipic, 1307 cm\(^{-1}\) – succinic, 1300 and 1260 cm\(^{-1}\) – glutaric). The phenomenon is related to the distinct changes in the chemical structure (chain length) of acids, the resulting symmetry, and spatial arrangement of the molecules.

![Figure 11.2](image-url)

Figure 11.2: The FTIR spectra of tested solder flux systems and corresponding weak organic acids: (a) SF1, SF2, SF3, and adipic acid, (b) SF4, SF5, SF6, and succinic acid, (c) SF7, succinic, and adipic acids, (d) SF8, glutaric, and adipic acids, (e) SF9, succinic, adipic, and glutaric acids. Black arrows point the diagnostic peaks in the flux spectra indicating the presence of specific activators.
The identification of WOAs within the tested flux systems revealed that SF1-SF3 contained adipic acid (Figure 11.2 (a)), whereas fluxes SF4-SF6 were succinic acid-based formulations (Figure 11.2 (b)). The SF7 was found to contain a mixture of succinic and adipic acids, glutaric and adipic acids were found in SF8, and succinic, adipic and glutaric acids in SF9 (Figure 11.2 (c)-(e)). Additional peaks appearing in the FTIR spectra originated from different C-C and C-H stretching vibrations, and bending modes of a carboxylic acid core chain and rosin/resin acids [35]. However, the detailed analysis of specific peaks is beyond the scope of this paper.

The composition of three selected flux systems (SF7-SF9) was based on WOA mixtures, therefore the ratio between the acids was estimated using 1H NMR spectroscopy. The chemical shifts for particular protons in adipic, succinic, and glutaric acids were defined by performing the analysis for pure substances. Subsequently, the spectra for three fluxes were recorded, and the chemical shifts inferred from flux spectra were assigned to the particular protons within each WOA. The integration of peaks, assigned to specific hydrogen atoms in each particular WOA, was used to estimate the ratio between the acids, and the results are presented in the Figure 11.3.

The spectrum of SF7 (Figure 11.3 (a)) shows the integration of peaks originating from four methylene bridges of adipic acid (marked with yellow colour) by 1.49 ppm (multiplet) and 2.20 ppm (triplet) to 4H and 4.06H, which refers to four internal hydrogen atoms around the molecule’s rotation axis and four protons bonded to external carboxylic groups, respectively. Based on that relation, the integrated value of the singlet assigned and calculated for succinic acid was 6.84H (marked with blue colour) which defines four hydrogen atoms of inner methylene bridges. The ratio adipic : succinic was therefore calculated to be 1 : 1.7 (37% : 63%). Similarly, the spectra analysis was carried out for SF8 (Figure 11.3 (b)) and SF9 (Figure 11.3 (c)), and the ratio between WOAs were 1 : 5.5 (15% : 85%) for adipic : glutaric in SF8, and 1 : 1.1 : 1.5 (27.5% : 30% : 42.5%) for succinic : adipic : glutaric in SF9. The peaks originating from three methylene bridges of glutaric acid were marked with pink colour.
HYGROSCOPICITY OF FLUX SYSTEMS

The summary of gravimetric water vapour sorption and desorption measurements performed at different temperatures is shown in the Figure 11.4 in a form of moisture sorption isotherms. The curves are constructed from the equilibrium water amount sorbed by the residue (Mc) as a function of steady-state humidity. The moisture sorption levels at saturation (~99%RH) are shown in Table 11.2, and the data for deliquescence and efflorescence RH levels is shown in the Table 11.3.

Comparing different flux formulations, minimal moisture amounts were sorbed by the flux systems based on adipic acid (SF1-SF3) at any temperature (Figure 11.4 (a)). Solder fluxes (SF4-SF6) based on succinic acid showed larger tendency towards vapour sorption (Figure 11.4 (b)) than adipic-based flux systems. Both adipic- and succinic-based fluxes (SF1-SF6) seem to deliquesce at the same high RH levels at all temperatures (Table 11.3), however, based on the visual assessment, the flux residues did not fully dissolve into the water layer. The poorest sorption properties were exhibited by succinic-based SF5 (Table 11.2).

Figure 11.4: Moisture sorption and desorption isotherms of flux systems exposed to varying humidity: curves for (a) SF1, SF2, and SF3, (b) SF4, SF5, and SF6, (c) SF7, SF8, and SF9 at (1) 25°C, (2) 40°C, (3) 60°C.
On the contrary to SF1-SF6, fluxes SF7-SF9 based on the WOA mixtures, exhibited clear deliquescent behaviour at all test temperatures (Figure 11.4 (c)) absorbing significantly more moisture compared to adipic- or succinic-based flux formulations. Moreover, flux systems with mixture of WOAs were found to interact strongly with water vapour at lower critical RH levels compared to single WOA based fluxes (SF1-SF6). Adipic+glutaric-based SF8 showed the lowest critical RH for deliquescence (Table 11.3) and highest sorption capabilities (Table 11.2) among all tested flux systems. The other two flux systems based on WOA mixtures (SF7 and SF9) absorbed comparable amount of water vapour.

An increase of temperature enhanced the interactions between all flux residue types and water vapour, which eventually led to an increase in the amount of sorbed moisture for all flux systems, as shown in Table 11.2. Moreover, an increase in temperature shifted the humidity level for deliquescence and efflorescence to lower RH values, which was more pronounced for the fluxes based on mixture of WOAs (Table 11.3).

Table 11.2: Saturated moisture sorption levels for all flux systems at different temperatures. The average and standard deviation values are given for 3 measurements.

<table>
<thead>
<tr>
<th>Flux symbol</th>
<th>WOA constituents</th>
<th>25°C</th>
<th>40°C</th>
<th>60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF1</td>
<td>Adipic acid</td>
<td>5.3 (± 1.3)</td>
<td>8.2 (± 2.4)</td>
<td>12.1 (± 2.4)</td>
</tr>
<tr>
<td>SF2</td>
<td>Adipic acid</td>
<td>4.1 (± 2.3)</td>
<td>6.9 (± 3.3)</td>
<td>9.0 (± 3.3)</td>
</tr>
<tr>
<td>SF3</td>
<td>Adipic acid</td>
<td>5.7 (± 2.4)</td>
<td>7.7 (± 2.3)</td>
<td>16.1 (± 5.0)</td>
</tr>
<tr>
<td>SF4</td>
<td>Succinic acid</td>
<td>9.4 (± 2.3)</td>
<td>18.6 (± 4.2)</td>
<td>51.7 (± 3.6)</td>
</tr>
<tr>
<td>SF5</td>
<td>Succinic acid</td>
<td>1.6 (± 0.5)</td>
<td>2.6 (± 0.5)</td>
<td>4.9 (± 3.1)</td>
</tr>
<tr>
<td>SF6</td>
<td>Succinic acid</td>
<td>13.3 (± 5.6)</td>
<td>25.9 (± 6.3)</td>
<td>48.3 (± 4.1)</td>
</tr>
<tr>
<td>SF7</td>
<td>WOA mixture</td>
<td>18.0 (± 6.3)</td>
<td>41.9 (± 6.2)</td>
<td>96.0 (± 4.3)</td>
</tr>
<tr>
<td>SF8</td>
<td>WOA mixture</td>
<td>72.2 (± 9.6)</td>
<td>92.3 (± 14.3)</td>
<td>120.1 (± 8.3)</td>
</tr>
<tr>
<td>SF9</td>
<td>WOA mixture</td>
<td>13.4 (± 4.4)</td>
<td>45.1 (± 6.3)</td>
<td>106.7 (± 8.3)</td>
</tr>
</tbody>
</table>

Table 11.3: Summary of relative humidity levels for deliquescence (dRH) and efflorescence (eRH) for all flux systems at different temperatures obtained from moisture sorption/desorption isotherms.

<table>
<thead>
<tr>
<th>Flux symbol</th>
<th>WOA constituents</th>
<th>25°C</th>
<th>40°C</th>
<th>60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF1</td>
<td>Adipic acid</td>
<td>95-99</td>
<td>85-90</td>
<td>90-95</td>
</tr>
<tr>
<td>SF2</td>
<td>Adipic acid</td>
<td>95-99</td>
<td>85-90</td>
<td>90-95</td>
</tr>
<tr>
<td>SF3</td>
<td>Adipic acid</td>
<td>95-99</td>
<td>85-90</td>
<td>90-95</td>
</tr>
<tr>
<td>SF4</td>
<td>Succinic acid</td>
<td>95-99</td>
<td>90-95</td>
<td>90-95</td>
</tr>
<tr>
<td>SF5</td>
<td>Succinic acid</td>
<td>95-99</td>
<td>90-95</td>
<td>90-95</td>
</tr>
<tr>
<td>SF6</td>
<td>Succinic acid</td>
<td>95-99</td>
<td>90-95</td>
<td>90-95</td>
</tr>
<tr>
<td>SF7</td>
<td>WOA mixture</td>
<td>95-99</td>
<td>90-95</td>
<td>90-95</td>
</tr>
<tr>
<td>SF8</td>
<td>WOA mixture</td>
<td>95-99</td>
<td>90-95</td>
<td>90-95</td>
</tr>
<tr>
<td>SF9</td>
<td>WOA mixture</td>
<td>95-99</td>
<td>90-95</td>
<td>90-95</td>
</tr>
</tbody>
</table>
Flux systems that exhibited a pronounced deliquescent behaviour were found to crystallize upon the reduction of humidity level. As a consequence, the moisture sorption isotherm appeared in a form of a hysteresis loop with a reverse (desorption) branch lying above a forward (sorption) branch.

The summary of AC electrochemical impedance measurements conducted at different temperatures is shown in Figure 11.5 where sorption and desorption curves are plotted for solder flux systems based on adipic acid (Figure 11.5 (a)), succinic acid (Figure 11.5 (b)), and mixtures of WOAs (Figure 11.5 (c)). The RH levels for deliquescence obtained from the gravimetric sorption results are highlighted in the impedance graphs.

At 25°C a slight decrease in impedance values was observed for fluxes SF1-SF6 (Figure 11.5 (a1) and (b1)), and more pronounced impedance reduction occurred at higher temperatures (Figure 11.5 (a2)-(a3) and (b2)-(b3)). All adipic- and succinic acid-based fluxes exhibited similar pattern of impedance decrease at all temperatures. The RH levels for deliquescence found by means of gravimetric sorption test (highlighted in yellow) complied with the regions of RH when the impedance signal decreased.

Figure 11.5: Impedance plots obtained for the solder flux systems applied onto the SIR comb patterns and exposed to varying humidity: (a) SF1, SF2, and SF3, (b) SF4, SF5, and SF6, (c) SF7, SF8, and SF9 at (1) 25°C, (2) 40°C, (3) 60°C.
Contrary to single WOA-based solder flux system, fluxes SF7-SF9 based on WOA mixtures (Figure 11.5 (c1)-(c3)) caused a sudden drop of impedance to low values at the particular RH levels. An increase in temperature shifted the critical RH for deliquescence (dRH) and efflorescence (eRH) towards lower humidity levels, especially in the case of SF8 (adipic + glutaric) when comparing the sorption curves at 25°C and 40°C. However, the sorption curve at 60°C followed the sorption behaviour similarly as in the case of 25°C. The SF7 (adipic + succinic) did not exhibit significant impedance drops at 25°C and 40°C, compared to the behaviour of SF8 and SF9 flux systems.

Similarly to water gravimetric vapour sorption results (Figure 11.4), the efflorescence branch of the impedance curve (Figure 11.5) showed the characteristics of water expulsion from the dissolved residue upon decreasing of a surrounding RH in the form of a hysteresis loop. The occurrence of a hysteresis in both gravimetric and impedance sorption curves showed that the crystallization of the acids or their mixture occurred at lower RH range compared to the deliquescence RH and the gap generally increased at higher temperatures.

CORROSIVITY OF FLUX SYSTEMS

The results of DC testing show the effect of flux residues in inducing the electrochemical leak current and corrosion (electrochemical migration) under varying temperature and humidity conditions. The magnitude of the residue effects is shown as the leakage current data and the morphology of the samples after corrosion testing.

DC leakage current

The results of DC testing performed as a function of applied voltage at varying relative humidity levels for all flux systems tested at different temperatures are shown in the Figure 11.6, and the summary of important data is given in Table 11.4. A sudden increase of current above the µA level, measured under non-condensing conditions, is the result of flux residue deliquescence and subsequent build-up of water film, which is sufficient for electrochemical processes occurring at the electrodes, and resulting in ion-induced electrochemical migration. Dissolution of tin, migration through the electrolyte layer, and deposition at the cathode cause a formation of metallic dendrites, shown in the Figure 11.7, which is also reflected in high levels of current if short-circuiting of the electrodes occurred. The magnitude of a residue effects under humid conditions is directly mirrored in the base current level and current peaks, which become more pronounced if the contaminant reacts easily with the water vapour.

Flux systems based on adipic acid (Figure 11.6 (a)) and succinic acid (Figure 11.6 (b)) were found to exhibit corrosive behaviour at 60°C, and succinic-based SF4-SF6 caused the metal migration between the RH range of 90-95%RH compared to adipic-based fluxes that caused an ionic-induced corrosion at lower range of 95-99%RH (Table 11.4). On the contrary, the WOA mixture-based solder flux systems (Figure 11.6 (c)) contributed to a rise in leakage current at all temperatures, and caused a dendritic growth at lower RH levels than the levels found for single WOA-based fluxes. Further, an increase in ambient temperature lowered the RH level for corrosion (ECM) occurrence. An overall ranking of flux systems in terms of increasing tendency for initiating the electrochemical migration was: adipic-based (SF1-SF3) < succinic-based (SF4-SF6) < adipic+succinic-based (SF7) < adipic+glutaric-based (SF8) < adipic+succinic+glutaric-based (SF9).
Figure 11.6: Results of leakage current testing carried out on the SIR patterns for solder flux systems exposed to varying humidity, temperature, and potential bias conditions: (a) SF1, SF2, and SF3, (b) SF4, SF5, and SF6, (c) SF7, SF8, and SF9 at (1) 25°C, (2) 40°C, (3) 60°C.
According to the data shown in Table 11.4, the current levels exhibited by adipic- and succinic-based flux systems (SF1-SF6) at 25°C and 40°C were comparably high and increased for the latter at 60°C. In the case of flux systems based on WOA mixtures (SF7-SF9), the current levels were found to be significantly higher than the values obtained for single WOA types. The highest current was recorded for SF8 (adipic+glutaric) and SF9 (adipic+succinic+glutaric) reaching the levels of 25 mA, which is the safety limit imposed by the measurement specifications. The increased temperature led to high leakage current levels.

### Table 11.4: Summary of relative humidity levels for ECM occurrence (RH\text{ECM}) and maximum leakage current (I\text{LC,max}) at ~99%RH obtained from DC measurements for flux systems at different temperatures.

<table>
<thead>
<tr>
<th>Flux symbol</th>
<th>WOA constituents</th>
<th>RH\text{ECM} [%]</th>
<th>I\text{LC,max} [mA]</th>
<th>RH\text{ECM} [%]</th>
<th>I\text{LC,max} [mA]</th>
<th>RH\text{ECM} [%]</th>
<th>I\text{LC,max} [mA]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF1</td>
<td>Adipic acid</td>
<td>-</td>
<td>6.1\times10^{-4}</td>
<td>-</td>
<td>0.001</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>SF2</td>
<td>Adipic acid</td>
<td>-</td>
<td>7.6\times10^{-4}</td>
<td>-</td>
<td>8.6\times10^{-4}</td>
<td>95-99</td>
<td>1.1</td>
</tr>
<tr>
<td>SF3</td>
<td>Adipic acid</td>
<td>-</td>
<td>2.7\times10^{-4}</td>
<td>-</td>
<td>6.3\times10^{-4}</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>SF4</td>
<td>Succinic acid</td>
<td>-</td>
<td>7.4\times10^{-4}</td>
<td>-</td>
<td>7.8\times10^{-4}</td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td>SF5</td>
<td>Succinic acid</td>
<td>-</td>
<td>3.7\times10^{-4}</td>
<td>-</td>
<td>3.6\times10^{-4}</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>SF6</td>
<td>Succinic acid</td>
<td>-</td>
<td>6.3\times10^{-4}</td>
<td>-</td>
<td>6.6\times10^{-4}</td>
<td>22.9</td>
<td></td>
</tr>
<tr>
<td>SF7</td>
<td>WOA mixture</td>
<td>95-99</td>
<td>9.8\times10^{-4}</td>
<td>5.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SF8</td>
<td>WOA mixture</td>
<td>85-90</td>
<td>22.3</td>
<td>70-75</td>
<td>22.4</td>
<td>60-65</td>
<td>25.0</td>
</tr>
<tr>
<td>SF9</td>
<td>WOA mixture</td>
<td>75-80</td>
<td>25.0</td>
<td>60-65</td>
<td>25.0</td>
<td>55-60</td>
<td>25.0</td>
</tr>
</tbody>
</table>

**Surface morphology of electrode pattern after DC testing**

Representative optical micrographs, shown in Figure 11.7, present the extent of corrosion on the contaminated SIR specimens subjected for DC testing at 25°C. The pictures indicated the presence of dendrites resulting from the ECM. Tin dendrites grew towards the anode and led to bridging of the oppositely biased electrodes (short-circuiting) which was also reflected in the high current levels.

No dendrites were found on the SIR substrates pre-contaminated with adipic- and succinic acids containing flux systems (SF1-SF6, Figure 11.7 (a) and (b)). Similarly, the test boards containing adipic+succinic-based residue (SF7) did not show severe corrosion (Figure 11.7 (c)). However, a significant amount of dendrites and anode pitting were found on the SIR coupons containing SF8 (adipic+glutaric) and SF9 (adipic+succinic+glutaric) (Figure 11.7 (d) and (e)). The optical observations of dendrite formation and corrosion extent correlated with the results of leak current and occurring current peaks corresponding to the ECM occurrence.
IV. DISCUSSION

The results presented in this paper show the importance of the combination of solder flux chemistry (activator type and mixtures) and temperature on the humidity-related corrosion reliability of electronics. This study shows how the critical humidity levels for moisture absorption to the PCBA surface and residue crystallization are directly related to the activator part of the flux system and vary within normal operational temperature range for the electronic systems. The use of WOA mixture is a common practice in developing a flux formulation, however, present investigation shows the importance of optimizing the relative acid levels and types for a better control of humidity-related reliability problems. The chemistry of residues not only defines the humidity boundaries for moisture uptake, but also the extent of absorption, which determines the water layer thickness and the risk of conductor bridging. The electrical properties of the formed water film are related to the solubility of the residues. High ambient temperatures, relevant for the electronics operation conditions, accelerate the formation of a liquid film on the PCBA surface and its extent, and increase its ionic content leading to the formation of highly conductive electrolyte and a risk of serious failure occurrence, as demonstrated in this paper.

EFFECT OF FLUX CHEMISTRY ON CRITICAL RELATIVE HUMIDITY AND CRYSTALLIZATION HUMIDITY LEVELS

The results of gravimetric water vapour sorption and AC impedance measurements showed the differences between the tendencies of various flux systems to interact with moisture and deliquesce, which are directly related to the chemistry of residues and temperature levels (typically related to external climate conditions or internal heating of the device). The affinity of ionic residues towards water molecules (hygroscopicity properties) depends on the chemical structure of the contaminant, and polar molecules tend to interact with water easily [5]. An increase in ambient temperature strengthens
the interaction between ionic residues in a flux system and moisture by increasing the mobility of molecules [36-38]. The rise of temperature shifts the critical relative humidity level for deliquescence towards lower RH values, which is highly important for the reliability of electronics that operate under a wide range of climatic conditions.

Solder flux systems based on adipic and succinic acids (SF1-SF6) exhibited similar variations in the levels of relative humidity for deliquescence (Figure 11.4) at all temperatures, which complied with the RH levels for deliquescence reduction (highlighted in Figure 11.5). The rise in ambient temperature shifted the dRH from 95-99%RH at 25°C to 90-95%RH and 85-90%RH at 40°C and 60°C, respectively, accelerating the dissolution of the residue into the water layer. Similar levels of eRH for both flux types were found by gravimetric water vapour sorption, however, the crystallization behaviour in impedance curves differed significantly from the gravimetric sorption data. This is due to the fact that the data obtained in gravimetric measurements relates to the equilibrium conditions, whereas impedance technique is a dynamic test and the equilibrium upon crystallization may be impossible to reach in the course of testing [5]. Overall, the flux systems based on adipic- and succinic acids showed similar trends in impedance reduction which indicated comparable tendencies to interact with water vapour. Both acids belong to less hygroscopic activator types commonly used in the no-clean solder flux systems [5], however succinic acid is generally considered to be slightly more prone for the interaction with moisture [3]. Regardless, the corrosion issues induced by the residues comprised of adipic or succinic acids can be typically observed only at high humidity levels [5].

On the contrary, more pronounced deliquescent behaviour was found, at all temperatures, for the flux systems based on the mixtures of weak organic acids (SF7-SF9) [19]. The deliquescence of fluxes containing WOA mixtures as activators occurred at lower range of humidity levels than for adipic- or succinic-based systems (Figure 11.4). The WOA mixture-based flux systems dissolved into the water layer at all temperatures as represented by a drop of impedance signal to low values, which is more significant than the impedance reduction recorded for single WOA-based fluxes. The interaction of WOA mixture-based fluxes with moisture, as shown in impedance curves at the critical RH levels for deliquescence obtained via gravimetric method (highlighted in Figure 11.5), complied with the gravimetric sorption data in the case of 25°C and 40°C for SF7 and SF8, and at 60°C for adipic+succinic-based SF7. The discrepancy in impedance measurements for SF8 and SF9 at 60°C is related to the content of glutaric acid in their activating parts that reaches the limiting conductivity at 60°C [5, 19], falsely indicating no dissolution at the critical RH levels found by means of gravimetric sorption. Although, based on the sorption data, the critical RH for deliquescence for the ternary mixture-based SF9 (adipic+succinic+glutaric) was found to be higher than for binary-based flux system SF8 (adipic+glutaric), the impedance results did not show a distinct deliquescence point. It is believed that a continuous interaction and sorption of water vapour at all humidity levels occurred for SF9.

An increased hygroscopicity of WOA mixture-based flux formulations, compared to single-WOA fluxes, is the effect of "deliquescence lowering" [19]. The vapour pressure above the solution of the binary or ternary blend of deliquescent solids is lower than the vapour pressures above the solutions or either of the individual constituents of the mixture [36]. The addition of a second and third component in the solid-water system, comprised primarily of a single ingredient, accounts for an increase in molar concentration of the solution, decreasing the ability of water molecules to escape to the vapour phase (definition of vapour pressure) [39]. The water activity above the solution of multi-component system (and therefore the critical RH level for deliquescence) is therefore lower than the critical RH level for single WOA-based systems [36, 40-42]. It complies with our results where lower critical RH levels for deliquescence were found for the flux residues composed of WOA mixtures compared to the RH levels
found for adipic or succinic-based systems [5], which could have a significant effect on the humidity-related reliability issues if these residues are present on the PCBA surface. The residues composed of multiple hygroscopic components (WOA mixtures) become dangerous at the RH levels which are not critical for the adipic- or succinic-based flux systems in terms of interaction with moisture, therefore increase the risk of water film formation at low humidity. Temperature further enhances the hygroscopicity creating a larger threat. Moreover, if transient conditions develop within the electronic enclosure upon rapidly changing external conditions (e.g. in the morning when the device lags behind in equilibrating with the external temperature increasing due to the sun light) [6, 43], the presence of highly hygroscopic residues can reduce the level of temperature difference necessary for condensation occurrence on the PCBA surface [6].

Most of the reported data showed the appearance of a hysteresis loop upon the decrease of ambient RH, which implied that the expulsion of water molecules from the saturated residue solution and subsequent crystallization (efflorescence) occurred at lower range of RH than the critical RH levels found for deliquescence [44-46]. As a result, it has a significant influence on electronics reliability under transient conditions developing upon rapidly changing external conditions. The residue dissolved in the course of deliquescence tends to retain water and, as a result, extends the wetting time of the PCBA surface, even if the external RH level falls back below the deliquescent point of the residue. The prolonged wetting time of the PCBA surface critically increases the risk of deterioration in electronics performance, which is further enhanced by higher temperatures that shift the crystallization point to lower RH and broaden the hysteresis loop. Broadening of the hysteresis loop was also found for highly hygroscopic WOA mixture-based fluxes compared to the adipic or succinic acid flux systems.

**EFFECT OF FLUX CHEMISTRY ON MOISTURE SORPTION AND THE RESULTING WATER LAYER THICKNESS**

The hygroscopic nature of flux residues defines the degree of interaction with moisture, which then determines the extent of water layer formation upon deliquescence of ionic contamination. The amount of moisture condensed becomes critical in terms of conductor bridging: highly hygroscopic flux activators sorb large amounts of water and result in the continuous water film formation that can easily bridge the opposite electrodes, leading to the leak current and a risk of short-circuiting by ECM occurrence.

The averaged thickness of water film was calculated using the sorption data (Table 11.2) for the flux systems at ~99%RH and the contamination level of 100 µg/cm² (Figure 11.8). The presented data assumes no absorption of the formed water layer into the bulk material (SIR specimen). The calculated thickness remained at ~50-200 nm level for the adipic acid based contaminants (SF1-SF3), regardless the temperature. In case of succinic-based flux systems, the initial thickness of ~200 nm at 25°C increased to 500 nm at 60°C for SF4 and SF6, however no significant change was observed for SF5. Higher amount of sorbed moisture for most of the succinic-based flux systems, compared to adipic-
based systems, is due to the more pronounced affinity to water molecules exhibited by succinic acid [3, 5]. Adipic acid exhibits poorer interaction with moisture due to its lower polarity (longer hydrocarbon chain). The water layer thickness was found to be ~200 nm at 25°C for two flux systems based on WOA mixtures (SF7 and SF9), however, with the rise of ambient temperature, the thickness increased significantly (above 1 µm) compared to the flux systems comprised of single WOA (SF1-SF6), which is in agreement with the hygroscopicity studies.

The effect of temperature is important for many of the electronic products operating under various thermal conditions, which is shown to have a huge impact on the extent of water film growth critical for the PCBA reliability. The temperature enhances the contaminant-moisture interaction [36-38], and, as the results show, synergistic effect of flux chemistry and temperature defines the potential for failure occurrence.

EFFECT OF FLUX CHEMISTRY ON LEAK CURRENT
AND ELECTROCHEMICAL MIGRATION

The results of leakage current from the SIR testing are in agreement with the results of hygroscopicity investigations. Between adipic- and succinic acid containing systems, the latter appeared to exhibit corrosive behaviour at lower RH levels at 60°C (90-95%RH compared to 95-99%RH for adipic) which originates from its slightly higher hygroscopicity and better solubility [5][3]. On the contrary, three WOA mixture-based flux systems (SF7-SF9) induced high leak current and ionic dissolution of tin at all test temperatures. The RH range for ECM for the WOA mixture-based fluxes was lower than for the single WOA-based flux systems due to the “deliquescence lowering”. Further, an increase of temperature shifted the humidity level for ECM occurrence to lower RH values due to the increased solubility of the flux residues [36, 47]. Between the three WOA-mixture based fluxes, SF9 (adipic+succinic+glutaric) was found to induce ECM at lower humidity levels compared to SF7 (adipic+succinic) and SF8 (adipic+glutaric) which is in agreement with the impedance results (Figure 11.5). Although the water vapour sorption results for SF9 suggested a low moisture uptake and relatively high critical RH level for deliquescence, it was sufficient for the dissolution of SF9 and creation of a conductive electrolyte capable of initiating the severe corrosion of the SIR pattern (Figure 11.7). The ratios between WOAs in the flux systems SF7 (adipic+succinic) and SF8 (adipic+glutaric) were found in our previous studies [19] to be the most corrosive ratio types, which complies with our current DC testing results. The overall tendency of the flux activators to increase the leak currents and cause corrosion issues is increasing as follows: single WOA-based fluxes < binary WOA mixture-based fluxes < ternary WOA mixture-based fluxes.

Overall, the results presented in this paper show the importance of flux activator chemistry and temperature on the variations in critical RH levels for absorption and desorption of water by the residues. The reliability can be enhanced by a proper choice of optimized flux formulation that does not contribute to detrimental humidity effects on the PCBA surface.
V. CONCLUSIONS

1) Solder flux residues based on the mixtures of weak organic activators interact stronger with moisture, which results in lower RH range for deliquescence and crystallization compared to the residues composed of a single weak organic acid. The difference in critical RH levels for deliquescence between single WOA based residues and WOA mixture based residues is up to 5-15%RH at 25°C and 30-45%RH at 60°C.

2) Higher hygroscopicity and solubility of WOA mixtures result in higher water uptake (higher water film thickness) and accelerated occurrence of electrochemical migration. At 60°C the thickness of water layer is ~1 µm for residues composed of WOA mixtures, compared to ~100-500 nm in case of single WOA based contamination. Residues comprised of the ternary mixture of WOAs showed higher susceptibility for corrosion compared to binary mixtures of WOAs.

3) An increase of ambient temperature increases the affinity of flux residue to moisture, reducing the critical relative humidity for deliquescence, crystallization, and initiation of ECM. The deliquescence of single WOA based residues shifted of 5-10%RH when increasing the temperature, whilst the shift of 5-25%RH was found for the highly hygroscopic WOA mixture based residues.

4) Highly hygroscopic residues based on WOA mixture tend to retain the uptaken water and prolong the wetting time of the PCBA surface, compared to the residues composed of single WOA activator. The formation of liquid film is enhanced at high temperatures where the residues absorb high amount of moisture.

VI. REFERENCES


12. RESIDUE-ASSISTED WATER FILM FORMATION UNDER TRANSIENT CLIMATIC CONDITIONS AND FAILURE OCCURRENCE IN ELECTRONICS

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Abstract - Electronic devices are exposed to a variety of climatic conditions worldwide. The day/night temperature fluctuations between the device interior and external conditions can lead to the formation of transient conditions within the enclosure that enhance the possibility of water layer build-up on the Printed Circuit Board Assembly (PCBA) surfaces. This paper deals with the parametric investigation of the effects assisting the formation of water film on a PCBA surface under transient climatic conditions, which alter the functionality of electronics. Studied parameters included the external humidity level, PCBA cleanliness, temperature difference between ambient and PCBA, and the rate of temperature/humidity change. The effect of ionic residues commonly associated with the soldering operations – weak organic acids – on the water film formation was investigated at 25°C/80%RH under isothermal and non-isothermal conditions. For non-isothermal conditions, the PCBA temperature was reduced to the level above and below the dew point. The impact of external climate on wetting of the contaminated PCBA surface was demonstrated by its exposure to day/night cyclic conditions of a geographical location, and the overall effect on corrosion reliability of the electronic circuit was assessed. A combination of AC impedance and DC leakage current techniques was employed to determine the electrochemical changes of the PCBA surface resulting from the build-up of a conductive water film. The results show that the presence of highly hygroscopic flux residues increases the water vapour content above the PCBA surface leading to moisture condensation under potentially non-condensing conditions, and results in the corrosion issues.

Keywords - Humidity, temperature, enclosure, solder flux, corrosion, condensation, reliability of electronics.

I. INTRODUCTION

Present development of electronic devices is trending towards high-density packing, component and device miniaturization, as well as finer pitch distances. These requirements aim to obtain the reduced weight and size of the product body, increase the thermal dissipation, lower the cost of manufacturing process, and achieve a flexible device from the design point of view [1]. However, the miniaturization tendencies may create adverse results in connection with electronics exposure to harsh climatic conditions, printed circuit board assembly (PCBA) cleanliness issues, and other factors that altogether enhance the water film build-up [2, 3]. Under humid conditions, potential bias, and in the presence of ionic contamination, the formation of water layer on a PCBA surface is likely to occur and lead to moisture-induced intermittent or permanent failures [4-8].

Electronic devices operate in a variety of geographical locations worldwide and are used in a broad range of applications. During the day/night cycle, the electronics is exposed to changes in temperature
and humidity conditions [9, 10]. The critical moment for the creation of transient conditions within the enclosure occurs while the climate outside the device, especially the temperature, changes [2, 11]. If the temperature of a surrounding air rapidly rises (e.g. in the morning time), the internal and PCBA surface temperatures may lag behind in equilibration, depending on the thermal capacity of the interior parts and enclosure tightness. Due to the thermal lag, the internal conditions of the enclosure will be different from the outside conditions until the equilibrium is reached [12]. If the retained humidity inside the enclosure is high enough, depending on the temperature conditions, dewing can occur on the PCBA [13].

The dew point (DP) depends on the temperature and relative humidity (RH) levels. At high external temperature and RH conditions, the DP is high and the slight difference between the ambient and PCBA temperatures may lead to the condensation. The range of temperature difference between the inside and outside of the device determines the thickness of the dewed water film, e.g. larger difference and longer exposure result in thicker water film. Water layer formation on the PCBA surface is also determined by the rate of temperature and humidity change, depending on the climatic conditions at the geographical locations. Due to the temperature and humidity cycling process, an increased risk of the corrosion occurrence within the electronic assembly was reported [11, 14-17] as often the transient conditions forming within the enclosure lead to the formation of thick water layers on the electronic surfaces.

The problem of water film build-up on the PCBA surface becomes more critical if other accelerating factors are present, e.g. the presence of ionic residues originating from the manufacturing process or application sites [10, 18-24]. Moreover, the electronic enclosures often contain a number of openings for electrical connectors or drainage [10], therefore provide a path for humidity and dust ingress, which creates a risk of moisture condensation on the electronic surfaces. The risk will be increased further if the PCBA contains a heat sink which acts as a thermal mass leading to a delay in temperature equilibration under transient conditions. The altered PCBA cleanliness, due to the presence of the contamination associated with the soldering process (WOAs – weak organic acids from no-clean flux systems) or the particulate contamination originating from the user environment [19, 25-31], was reported to greatly accelerate the condensation and corrosion risks. Ionic residues, due to their highly hygroscopic nature [2, 19] and high moisture sorption properties, facilitate the formation of an electrolyte layer even at low humidity levels. The extent of residue-assisted water film formation is determined by the chemical nature of surface contaminants [11, 32] and the contamination level. Highly hygroscopic residues deliquesce at lower critical RH levels and are more water-soluble, compared to the less hygroscopic contaminants [23]. The transient climatic conditions created within the device in combination with the contaminated PCBA surface cause an extremely high risk for the electrochemical (ECM) migration occurrence [32-37] and the risk of device failures [29, 34, 38]. Other factors influencing the formation of water film on a PCBA surface include surface finish and surface roughness, material porosities, or the component spacing [39-43].

This paper reports a parametric study of various factors influencing the build-up of water layer on a PCBA surface and the resulting operational performance of electronics upon the PCBA temperature reduction. The effect of various parameters was studied synergistically, including the ambient humidity level, PCBA cleanliness, temperature difference between ambient and PCBA, and the rate of temperature/humidity change. Effect of the rate of surface cooling on water film formation and its electrical property was studied on the clean surfaces at various external relative humidity levels (80%RH, 90%RH, and 95%RH) simulating the geographical variation in the rate of external humidity change. The water layer build-up on the surfaces was monitored using the electrochemical impedance measurements and was correlated to the gravimetric measurement of water amount. The impact of
hygroscopic residues on the water film formation was studied under isothermal and non-isothermal conditions for the PCBA temperature reduction above and below the dew point. Under condensing conditions (below the DP), the AC parameters were collected for various cooling rates and residue types. The effect of ionic residues under potentially non-condensing conditions (above the DP) was assessed using the AC impedance and DC leakage current testing for various acidic activator types. The DC testing was directly related to the surface insulation resistance, and the resulting leakage current levels represented the magnitude of WOA effects. Further, the interaction between varying external conditions and the ionic contamination was assessed under the real climatic profile where the risk of transient conditions occurrence is high.

II. MATERIALS AND METHODS

TEST BOARDS

The AC and DC electrochemical measurements under water film formation conditions were performed across the interdigitated surface insulation resistance (SIR) coupons (Figure 12.1 (a)) with the Pb-free HASL (hot air solder leveling) surface finish using Sn100C solder alloy. The dimensions of the pattern were 13 mm x 25 mm and therefore the active surface area was 325 mm². The distance between the electrodes was 0.3 mm.

Figure 12.1: The overall view on the test boards: (a) surface insulation resistance test coupon, (b) FR-4 laminate board coated with solder mask.

The thickness measurements of water layer build-up on the clean surface and the observations of changes in WOAs’ morphology upon the reduction of PCB temperature at humid conditions were performed on the clean FR-4 glass-reinforced laminate substrates coated with a ~20 µm layer of solder mask (Figure 12.1 (b)). The dimensions of the base material were 50 mm x 50 mm resulting in the total surface area of 2500 mm².

Prior to each measurement, all boards were thoroughly cleaned by rinsing with deionized water, followed by cleaning with isopropyl alcohol (analytical purity of 99.8%) and drying with pressurized air. The procedure was repeated three times in order to obtain a perfectly clean surface.

IONIC CONTAMINANTS

The effect of PCBA cleanliness on the water film formation and failure occurrence were studied using the weak organic activators commonly found in the wave solder flux formulations. The contaminants were chosen based on the differences in their hygroscopic properties [23, 24]: adipic acid,
succinic acid, and glutaric acid. The acids were supplied by Sigma Aldrich as pure crystals of analytical grade. Required amounts of pure WOAs were dissolved in isopropyl alcohol (analytical purity of 99.8%) in order to obtain their 2.5% wt/v solutions, similar to the level of activators found in the commercial wave solder flux systems.

**CLIMATIC CHAMBER**

The experiments were carried out in the controlled environment in the climatic chamber Espec PL-3KPH. The fluctuations in the temperature and relative humidity levels were stated to be within the range of ±0.3°C/±2.5%RH for the conditions studied in this paper. The airflow was ~1.5 m/s.

**PELTIER COOLING STAGE**

The simulation of the temperature differences between the ambient air and surface of the test PCBA was carried out using a cooling Peltier stage (model CP-031, TE Technology Inc.), which comprised of a Peltier element embedded in the aluminium block. The stage was powered up by a voltage supply and was connected to the TC-720 OEM (TE Technology Inc.) control unit that was further connected via USB to the computer. The test samples were pasted to the Peltier stage using a heat-transfer paste. The temperature of the test samples was monitored and controlled using the MP-3193 thermistor (TE Technology Inc.) pasted to the sample. The thermistor was connected to the TC-720 OEM control unit which allowed for the creation of a temperature control loop between the Peltier and test samples using commercial computer software. The heat generated by the working Peltier stage was dissipated by the air flow induced by the fan attached to the cooling unit at the bottom. The fan was powered up by a separate power supply.

**ELECTRICAL/ELECTROCHEMICAL MEASUREMENTS**

The AC electrochemical impedance and DC leakage current measurements were performed using a "BioLogic VSP" multichannel potentiostat. The impedance technique was employed in order to monitor the water film build-up on the clean and contaminated SIR surfaces under various transient conditions. The leakage current measurements were conducted in order to assess the potential for corrosion occurrence on a PCBA surface which temperature was reduced above the DP (non-condensing conditions). The effect of contamination was studied on the SIR test coupons deliberately pre-contaminated with the solutions of WOAs using an automatic pipette, and the resulting residue level after solvent evaporation was ~100 μg/cm². The contaminated samples were stored in the desiccator box for 24h at low RH (<15% RH) prior to the exposure to desired test conditions. All electrical/electrochemical measurements were performed in the Espec climatic chamber.

The AC signal amplitude of 25 mV (V_{rms} = 17.68 mV) at a frequency of 10 kHz was applied. This frequency regime is governed by the capacitive character of the dry SIR electrode pattern at the humidity levels not exceeding the critical RH for deliquescence of the contamination present on the PCBA surface [30]. With an increase of RH level and the reduction of PCBA temperature, the residue deliquescence takes place, and the water layer thickness and electrolyte conductivity increase. Similarly, the water film build-up on a clean surface which temperature was reduced below the dew point results in the formation of thick water layer due to the condensation. As a result, the measured impedance output decreases and a resistive character of water layer forming in between the conductors dominates. A drop of impedance to ~5-10 kΩ and the increase of phase angle towards ~-5° at the studied frequency
indicated the residue dissolution into the water layer and the formation of a conductive electrolyte resembling a “bulk water behaviour”.

The leakage current measurements were performed under 5 V DC potential bias. This testing allowed for the assessment of potentially corrosive effects of the contamination dissolving into the water layer. Due to the fact that the PCBA temperature reduction below the DP results in the condensation and certain corrosion occurrence, the DC technique was used only to track the residue effects upon the PCBA temperature reduction above the DP and at RH level not exceeding the deliquescence point (where the risk of corrosion occurrence potentially does not exist). The output measured during the DC testing was related to the surface insulation resistance, and the resulting leakage current directly reflected the interaction of residues with the water vapour. An abrupt increase of current above µA level indicates that the formation of water layer, facilitated by the residues, resulted in the occurrence of corrosion – electrochemical migration.

WATER LAYER THICKNESS MEASUREMENTS

The measurements of water film thickness were performed on a clean laminate material (Figure 12.1 (b)) using a gravimetric method. Moisture condensation on the clean PCB surfaces upon their temperature reduction below the DP resulted in the formation of water film, which, at the end of each test, was carefully collected using a fast-absorbing filter paper. Subsequently, the weight of a wet paper was immediately measured and compared with the mass of a dry paper obtained prior to the experiment. Based on a mass difference, the averaged thickness of the formed water film on a PCB surface was calculated. The average of 3-5 measurements for each test condition was performed. The measurement carried a risk that the water layer formed upon the condensation may not be fully collected from the surface due to the difficulty of the technique. However, based on the visual assessment of the surface after collection of the water film and additional experiments, the error in the reported thickness data is expected to be within 5%.

WATER FILM FORMATION ON THE CONTAMINATED PCBA SURFACE

The presence of residues on a PCBA surface changes its properties when interacting with water vapour under humid conditions. As a result, the temperature needed for the dew formation is significantly reduced for the contaminated surfaces, which depends on the residue type and temperature difference between ambient and PCBA. In our study, the residue effects were studied at 25°C/80%RH due to the fact that at these conditions no corrosion induced by either of the tested ionic contaminants can be expected to occur if transient conditions do not exist [23].

The test setup used for the investigations of the residue-assisted water film formation on the PCBA surface is shown in Figure 12.2. The SIR pattern and FR-4 laminate were pasted to the Peltier cooling element and the setup was placed in the Espec climatic chamber. The water film formation was evaluated electrically (SIR board) whereas the morphology of the residue was visualized on the FR-4 laminate.
The residue effects were studied under: (i) isothermal conditions, (ii) non-isothermal conditions with the PCBA temperature reduction above the DP, (iii) non-isothermal conditions with the PCBA temperature reduction below the DP, and (iv) transient climatic conditions of a geographical location.

**Isothermal conditions**

The residue interaction with water vapour was assessed at constant 25°C/80%RH ambient conditions and PCBA surface temperature equal to 25°C. Both AC and DC data were recorded separately for the contaminated SIR specimens. The samples were kept in the climatic chamber at 25°C/30%RH for 30 min prior to the measurements, then the relative humidity was raised from 30%RH to the desired humidity level within 1h at constant temperature, and maintained thereafter. The PCBA and chamber conditions were monitored throughout the process using a set of temperature and RH sensors. The electrical properties of the SIR samples were then monitored for the total of ~20h.

The interaction between ionic contaminant and water vapour may result in moisture adsorption to its surface or deliquescence, depending on the residue type and ambient humidity level. As a result, the morphology of residues remaining on the PCBA surface changes due to e.g. dissolution into the water layer and subsequent crystallization. Under isothermal conditions, the morphology changes of the residues were investigated on the FR-4 laminates coated with solder mask (Figure 12.2). The solutions of activators were applied on the PCB material using an automatic pipette, which resulted in a residue level of ~40 µg/mm². The temperature sensor was pasted onto the FR-4 substrate next to the contamination area, which allowed for the temperature control of the PCB in order to maintain constant 25°C. Subsequently, the pre-contaminated samples were placed in the Espec climatic chamber and the desired conditions were settled as described before. After the ~20h exposure, the FR-4 samples were stored in the desiccator box for 72-168h at low RH (<15% RH). The pictures of the residue before and after the test were taken with the use of Alicona InfiniteFocus.

**Non-isothermal conditions (reduction of PCBA temperature above the DP)**

The effect of process-related residues on the water layer build-up was then evaluated under non-isothermal conditions with the PCBA temperature reduction above the dew point, which implied that
any potential condensation occurrence is a result of ionic nature of contamination. The testing was performed at constant 25°C/80%RH chamber conditions which settled the DP temperature at 21.3°C.

The samples were kept in the climatic chamber where the conditions were set at 25°C/80%RH as described before, and with the constant PCBA temperature of 25°C. After the stabilization of chamber conditions, the PCBA temperatures were decreased from 25°C while remaining in the non-condensing region above the dew point (Figure 12.3 (a)).

![Figure 12.3: (a) conditions for testing the effect of residues on the water film formation under non-isothermal conditions with the PCBA temperature reduction above DP, (b) cooling profiles used for testing.](image)

The PCBA set temperatures were reached by a decrease from ambient 25°C to the final 24.5°C, 24°C, 23.5°C, 23°C, 22.5°C, and 22°C, with the cooling rate 0.1°C/min (Figure 12.3 (b)). After the set temperatures were reached, they were maintained for 3-7 days, and the deviation of ±0.01-0.03°C from the final set temperatures was recorded throughout this time period for all experiments. During the cooling step and thereafter, the impedance, phase angle, and leakage current signals were monitored. Each set PCBA temperature testing comprised of a separate experiment and required the use of new SIR laminates. The visualization of residue morphology changes upon the interaction with water vapour was carried out on the FR-4 laminates (Figure 12.2), similarly as described in section for isothermal testing. The desired PCB set temperatures were reached according to the profiles shown in Figure 12.3 (b). Each set PCB temperature testing comprised of a separate experiment and required the use of new laminate substrates. After 3 days of exposure, the samples were kept in the desiccator box for 72-168h at low RH (<15% RH), and subsequently the pictures of the residue after the test were taken with the use of Alicona InfiniteFocus.

Non-isothermal conditions (reduction of PCBA temperature below the DP)

The effect of residues on the water film build-up was studied under non-isothermal conditions with the PCBA temperature reduction below the dew point (21.3°C), which implied that the condensation occurrence is a result of both ionic contamination and dewing force.

The samples were kept in the climatic chamber where the conditions settled at 25°C/80%RH as described previously, and with the constant PCBA temperature of 25°C. Subsequently, the PCBA temperatures were decreased from 25°C to the final temperatures (Figure 12.4 (a)) within 12 minutes (Figure 12.4 (b)). The time of cooling was set to 12 minutes in order to exclude the time factor from the
observations. The constant cooling time implied different temperature reduction rates, depending on the final PCBA temperature. The water vapour density on the PCBA surface and the resulting water layer formation was therefore influenced by the residue type and the cooling rate. Throughout the cooling period, the impedance and phase angle were monitored. Each PCBA set temperature testing comprised of a separate experiment and required the use of new SIR pattern.

![Figure 12.4: (a) conditions for testing the effect of residues on the water layer formation under condensing conditions, (b) cooling profiles for testing.](image)

The in-situ observation of the SIR pattern appearance during the reduction of PCBA surface temperature below the dew point was carried out with the use of AD7013MZT Dino-Lite digital microscope.

**Transient climatic conditions in a geographical location**

The effect of WOA residues on the water layer build-up under transient climatic conditions was investigated under varying temperature and humidity conditions for the PCBA placed inside a simulated electronic enclosure. The enclosure used for investigations was made of aluminium with dimensions of 260 mm x 160 mm x 90 mm. The IP rating [44] for this enclosure type is 66 which indicates a “dust tight” casing capable to withstand water projected from powerful jets for a given amount of time. The through-holes of 1 or 3 mm diameter size were drilled in the casing material (one side) in order to simulate a leakage path for humidity due to the opening (usually due to the cable feedthrough, sealing imperfections, or drain hole presence). On the opposite side of the drilled through-hole, an opening for the cables was provided and the gasket for cable sealing. The overall geometry of the casings is shown in Figure 12.5.

The calibrated sensors Pt1000 (temperature) and HIH4021 (humidity) were placed inside the aluminium enclosures, attached to the PCBA surfaces and aluminium thermal mass (Figure 12.5 (b)), and connected to a data logging system (model 2700 Multimeter, Keithley Instruments). The thermal mass was introduced for the investigations in order to mitigate the behaviour of actual PCBA containing large thermal components attached to it (e.g. heat sink) that delay the PCBA temperature equilibration with the external conditions. An additional set of sensors was used to monitor the humidity and temperature conditions inside the enclosures.
Figure 12.5: Top view of 2D schematics of the PCBA/enclosure configurations used for testing of the water layer build-up on the PCBA surfaces under transient climatic conditions: (a) PCBA in Al enclosure, (b) PCBA on thermal mass in Al enclosure.

The contaminated SIR patterns were placed at the center of the enclosure and attached to the thermal mass of a defined 40m$^3$ volume. The enclosures containing test SIR specimens were sealed and subsequently exposed to varying climatic conditions in the Espec chamber where the climatic conditions in humid geographical location of Copenhagen (Denmark) were simulated. According to the hourly data generated in global humidity index [45], the 24h climate measured on 28.07.2008 was used for the housing exposure (Figure 12.6).

Figure 12.6: Climatic profile in Copenhagen, Denmark (July 28, 2008). Data of ambient temperature (T), relative humidity (RH), and dew point (DP). The time period for the occurrence of transient conditions in a profile is highlighted in pink.

The chosen climatic conditions represent the critical T and RH changes in the morning time (~03:50-04:50, highlighted in pink) that commonly pose a threat for the PCBA reliability when the outside temperature rapidly increases and the dew point temperature is only 1°C lower than the ambient. If the
temperature of the device placed in a humid area lags behind an outdoor climate due to the casing barrier and thermal mass presence, the risk of condensation can occur. Throughout the 24h exposure, the impedance and phase angle data were collected for different ionic contaminants present on the SIR surface.

**WATER FILM FORMATION ON THE CLEAN PCBA SURFACE**

The studies of water film formation characteristics on the clean PCBA surface were performed under non-isothermal conditions with the PCBA temperature reduction below the dew point in order to provoke condensation on the surface. The effect of ambient humidity level and the PCBA cooling rates were evaluated. The schematics of the test setup used for the investigations is shown in Figure 12.2. The water film formation was evaluated electrically (SIR board) and quantified using a gravimetric method (FR-4 laminate board).

The SIR and FR-4 laminate specimens were subjected for water layer build-up at 25°C and various relative humidity levels (Figure 12.7 (a)), namely 80%RH, 90%RH, and 95%RH. The dew point (DP) at each test condition was calculated according to the formula given in [46]: 21.3°C (at 80%RH), 23.2°C (at 90%RH), and 24.1°C (at 95%RH). The desired chamber conditions were reached similarly as described before.

In order to provoke condensation on the clean surfaces, the PCBA temperatures were reduced from 25°C to the set temperatures below the dew point (Figure 12.7 (b)), accordingly to the ambient relative humidity level. The time of cooling was set to 12 minutes which implied that different PCBA set temperatures constitute individual cooling rates. The water vapour density on the PCBA surface and the resulting water layer formation were therefore the effect of ambient relative humidity level and the cooling rate.

![Figure 12.7: (a) conditions for investigations of the water film formation on a clean PCBA surface, (b) cooling profiles for various test conditions.](image)

Throughout the cooling period, the impedance and phase angle outputs were monitored, and each experiment required the use of new SIR pattern. At the end of each test, the water film formed upon moisture condensation on the laminate surface was carefully collected with the filter paper and weighted in order to evaluate the average water layer thickness, which was then correlated with the AC data.

The observations of SIR pattern appearance during the condensation were conducted *in-situ* using AD7013MZT Dino-Lite digital microscope.
III. RESULTS

ISOTHERMAL CONDITIONS

The results from electrochemical testing of the residue effect on the water film formation performed under isothermal conditions at 25°C/80%RH (without PCBA temperature reduction) are presented in Figure 12.8. A slight decrease of impedance values and increase of phase angle values were recorded for all the investigated contamination types throughout the measurement. However, the interaction with the water vapour was insufficently strong to result in residue dissolution. The leak current values for succinic and adipic acids based test patterns remained below nA level, and slightly higher current level (1-10 nA) was observed for the SIR pattern containing glutaric acid. However, no dissolution into the water layer and lack of corrosion were concluded from the DC results.

Changes in WOAs morphology associated with the interaction between the residue and humidity are shown in Figure 12.9 as representative optical micrographs taken before and after the exposure of the contaminated laminate surfaces to 25°C/80%RH. Among the tested contamination types, the changes in residue appearance occurred only in the case of glutaric acid (Figure 12.9 (c)).
NON-ISOTHERMAL CONDITIONS (REDUCTION OF PCBA TEMPERATURE ABOVE THE DP)

The results of AC and DC testing performed at ambient 25°C/80%RH for the contaminated SIR samples for which the temperatures were gradually reduced from 25°C to the set temperatures above the dew point (non-condensing region) are shown in Figure 12.10. For a reference, the data recorded for a clean SIR pattern is shown in Figure 12.10 (a).

No significant changes in the impedance, phase angle, and leak current data were observed for the clean and adipic acid contaminated SIR patterns at the PCBA temperature range 24.5°C-22°C (Figure 12.10 (a) and (b)). The impedance decreased and phase angle values progressively increased for the conditions where the larger temperature difference occurred between PCBA and ambient temperature, however, the changes were not significant. The leakage current recorded for adipic acid containing system was slightly higher compared to the clean SIR surface, however it remained at the nA level. The effect of succinic acid (Figure 12.10 (c)) tested under the AC conditions showed a similar trend as in the case of clean SIR and adipic acid containing system. However, the impedance reached low values upon the PCBA temperature reduction to 22°C, which indicated the advanced water layer formation and “bulk water behaviour”. The leakage current measured for succinic acid at the surface temperature of 22°C did not show signs of ECM.

On the contrary, the results for glutaric acid testing (Figure 12.10 (d)) showed significant changes in the AC and DC signals occurring for every PCBA surface temperature tested, indicating the dissolution of the acid into the formed water film. The decrease in impedance values and increase in phase angle were more pronounced and lasted for a longer period of time in cases where larger temperature differences between the PCBA surface and ambient air occurred. The DC signal followed the trend of AC output, increasing initially to the mA levels sufficient for the occurrence of ECM. After a certain time interval, the impedance, phase angle, and leak current values returned to the original values for the PCBA temperatures 24.5°C-23°C. At the PCBA temperatures below 23°C, the “bulk water behaviour” occurred, which was inferred from the very low impedance and high phase angle values maintained throughout the time of testing.

The changes in WOA morphology induced by the PCB temperature reduction above the dew point are shown in the Figure 12.11. No significant changes in the residue appearance occurred for adipic acid at the PCBA temperature range tested (Figure 12.11 (a)-(f)), namely 24.5°C-22°C. The residues composed of succinic acid did not undergo a noticeable change in appearance at the PCBA set temperature range 24.5°C-22.5°C (Figure 12.11 (g)-(k)). However, the morphology has changed upon the PCBA temperature reduction to 22°C (Figure 12.11 (l)) where the dissolved residue recrystallized into the islands of acid of various sizes, closely spaced. On the contrary, for the glutaric acid, every PCB temperature decrease has caused morphology changes (Figure 12.11 (m)-(r)), and the recrystallized islands of residue were of a small size and densely concentrated.
Figure 12.10: Impedance, phase angle, and leakage current data obtained under non-isothermal conditions at ambient 25°C/80%RH and PCBA temperature reduction above the dew point for clean SIR pattern (a), and SIR-patterns pre-contaminated with 100 μg/cm² of WOAs: (b) adipic acid, (c) succinic acid, (d) glutaric acid. The final PCBA temperatures after cooling are indicated, and the “bulk-water behaviour” for the SIR patterns indicated by the AC results is highlighted in yellow.
### Figure 12.11

The overview on WOAs' morphology before and after temperature decrease from 25°C to temperatures above dew point: (a)-(f) adipic acid, (g)-(l) succinic acid, (m)-(r) glutaric acid. The final PCB temperatures after cooling are indicated.
NON-ISOTHERMAL CONDITIONS (REDUCTION OF PCBA TEMPERATURE BELOW THE DP)

The results of AC testing of the water film formation associated with a clean PCBA surface under non-isothermal conditions and PCBA temperature reduction below the dew point (21.3°C) are presented in Figure 12.12. The time of cooling was kept constant, while the factors of a cooling rate and ambient humidity levels were investigated during testing. The final impedance (Figure 12.12 (a)) and phase angle (Figure 12.12 (b)) values obtained at the end of the 12 minute cooling experiments were plotted against the averaged water film thicknesses obtained via the gravimetric measurement of water loading on the FR-4 laminate for the respective cooling experiments. The impedance and phase angle values for dry clean surfaces at all ambient humidity levels were in the range of ~480–520 kΩ and -86˚ (±2), respectively, before the condensation occurred. Each point on the graph represents the results obtained for different final PCB temperatures after cooling (different cooling rates). Changes in impedance and phase angle values, and the related substantial water coverage, occurred at PCBA temperatures of 21˚C, 23˚C, and 24˚C respectively for 80%RH, 90%RH, and 95%RH humidity levels.

The decrease of impedance progressed gradually and was linear for the ambient conditions of 80%RH and 90%RH until the low values were reached, contrary to 95%RH where the PCBA temperature decrease led to low impedance values regardless the cooling rate. The phase angle data followed the same trend with a shift towards less negative values. The "bulk water behaviour" (impedance reaching ~5–10 kΩ and phase angle values shifting to ~-5˚) was observed for a large range of thickness values (6–40 µm).

The photographs in Figure 12.13 show the appearance of water droplets formed on the SIR surface upon the moisture condensation and PCBA surface temperature reduction from 25°C to 21°C (after 12 minutes of cooling) under the ambient humidity level kept at 80%RH, 90%RH, and 95%RH. The appearance of water film formation corresponds to the respective impedance and phase angle values shown with black arrows in the Figure 12.12 (a) and (b). For the lowest RH level, the formation of water droplets was not observed at the end of experiment (Figure 12.13 (a)). At higher humidity levels, the visible water layer was built up in the course of condensation, however significantly higher amount of water vapour condensed at 95%RH (Figure 12.13 (c)) leading to a more pronounced conductor bridging, compared to 90%RH (Figure 12.13 (b)).
Figure 12.13: Optical images with an overview on the clean SIR surfaces upon the moisture condensation and PCBA temperature reduction from 25˚C to 21˚C at: (a) 80%RH, (b) 90%RH, and (c) 95%RH.

Figure 12.14 shows the results of AC impedance testing for moisture condensation on the contaminated SIR patterns at ambient 25˚C/80%RH with the PCBA temperature reduction below dew point (13-21˚C). For a reference, the results obtained for the clean SIR surface at 80%RH were shown together (data from Figure 12.12). Based on the AC impedance results, significant decrease of impedance (Figure 12.14 (a)) and increase of phase angle values (Figure 12.14 (b)) were observed upon the PCBA surface temperature reduction below the DP (21.3˚C) for all the acids. Between the tested activators, glutaric and succinic acids contributed highly to low impedance and high phase angle values, and, therefore, a "bulk water behaviour", compared to adipic acid. Compared to the impedance results obtained under condensing conditions for the clean PCBA surface at 80%RH, the values obtained for WOAs were significantly lower considering the corresponding PCBA set temperatures.

An in-situ overview of the SIR patterns appearance upon the moisture condensation on clean and contaminated SIR surfaces is shown in Figure 12.15 for the PCBA temperature reduction from 25˚C to 20˚C within 12 minutes. In case of the clean PCBA surface (Figure 12.15 (a)), small water droplets were
formed upon cooling. Compared to the clean surface, more significant amount of water droplets was formed on the contaminated specimens (Figure 12.15 (b), (c), and (d)), with the large droplet islands formed for succinic acid and thick continuous water film built up on the glutaric acid containing SIR comb pattern.

Figure 12.15: The optical micrographs obtained (1) before and (2) after moisture condensation at 25°C/80%RH and PCBA temperature reduction from 25°C to 20°C for: (a) clean SIR pattern, and SIR specimens pre-contaminated with 100 µg/cm² of (b) adipic acid, (c) succinic acid, (d) glutaric acid.

TRANSIENT CLIMATIC CONDITIONS

The results of investigations on the interaction between external climate and the PCBA containing residues are shown in Figure 12.16. The chosen 24h profile of Copenhagen (Figure 12.6) represents the critical temperature and humidity changes that can occur in the morning time (~03:50-04:50, highlighted in pink in Figure 12.16) when the transient conditions develop inside an electronic enclosure if the external temperature rapidly increases, and the PCBA lags with the temperature equilibration.
The impedance and phase angle data obtained for a clean SIR (Figure 12.16 (a)), shown here for a reference, showed no significant change in the output upon the PCBA exposure to varying temperature and humidity conditions. The SIR samples contaminated with adipic (Figure 12.16 (b)) and succinic acids (Figure 12.16 (c)) showed distinct changes in the AC data between 4-6h of the 24h profile, which corresponds to the rapid change of external conditions in the morning time.

![Figure 12.16: Impedance and phase angle data as a function of contamination type and thermal mass (TM) presence obtained under exposure of PCBA in aluminium enclosure with 1 mm and 3mm leak size to climate profile in Copenhagen: (a) clean SIR pattern, and SIR-patterns pre-contaminated with 100 µg/cm² of WOAs: (b) adipic acid, (c) succinic acid, (d) glutaric acid. The time period for the occurrence of transient conditions, extracted from the climatic profile in Figure 12.6, is highlighted in pink.](image)

On the contrary, the presence of glutaric acid on the SIR pattern significantly decreased the impedance values (Figure 12.16 (d)), indicating the residue dissolution into the formed water film, in the time period associated with the development of potentially transient conditions within the enclosure (highlighted in pink). The phase angle followed the trend and reached levels close to 0°. Considering that, according to the climatic profile given in Figure 12.6 where the transient conditions lasted for 1h (~03:50-04:50), the water layer formed on the SIR surface contaminated with glutaric acid remained present for ~3.5-4h, even though the transient period has theoretically passed. Moreover, prior to the dissolution of residue related to the occurrence of transient conditions at ~03:50-04:50, additional decrease in AC impedance values occurred at ~02:40-03:50 (highlighted in green in Figure 12.16 (d)), corresponding to the time period in the climatic profile where the high external humidity conditions were present (Figure 12.6).
Considering different through-hole sizes, the critical period of time when the impedance values remained low occurred ~30 min earlier and lasted ~10 min longer for the 1 mm diameter opening, compared to the 3 mm diameter hole. In the presence of thermal mass attached to the PCBA, the wetting period began ~7-9 min earlier than wetting of the PCBA with no thermal mass. Upon the moisture desorption from the PCBA surface, the presence of thermal mass increased the time of water layer presence on the SIR of ~15 min in case of the casing with 3 mm opening hole. For the enclosure with 1 mm diameter through-hole, the differences in wetting time of the SIR with and without the thermal mass were negligible.

IV. DISCUSSION

Investigations presented in this paper focused on showing the relationship between four parameters determining the characteristics of water layer build-up on the PCBA surface under exposure to climate conditions, and assessing their effects on the extent of water film formation. The parameters studied were external humidity level, PCBA cleanliness (residue effects), temperature difference between ambient and PCBA, and the rate of temperature/humidity change. The study shows that the shift in one of these parameters (e.g. residue type, cooling rate) significantly changes the electrical properties of the formed water layer. The results clearly demonstrate that the PCBA dew point temperature depends on the PCBA cleanliness [11], and the resulting extent of water layer build-up is related to the ionic nature of the residues [47]. Under transient conditions, when the risk of condensation occurrence is high due to the small difference between ambient and dew point temperatures (e.g. $\delta=1^\circ$C as shown in our study), the altered DP of the contaminated PCBA surface could significantly change its humidity robustness due to the water film existing on the PCBA for an extended period of time.

Under the applied AC voltage for the impedance testing, when the conditions are dry and non-condensing, the clean SIR system follows the simple RC circuit behaviour [26] and at the high frequency (e.g. $10^4$ Hz used in this study) acts as a capacitor [30]. The capacitive nature is related to the geometry of the comb pattern and permittivity of the laminate embedded between the electrodes of the pattern. The impedance values under these conditions are high and the phase angle values oscillate around -90˚ which indicates a capacitive behaviour. Upon the adsorption of moisture to the PCBA surface, as a result of RH increase or the PCBA temperature changes, the water layer is formed, which changes the electrical properties of the system. The water film acts as a conductive electrolyte and provides a pathway for the current flow, reducing the capacitive nature of the bulk SIR system and enhancing the resistive conduction behaviour. Upon the continuous water layer growth, the pathway becomes more conductive and the charge can be transferred between the electrodes [48]. Therefore, throughout the results presented in this study, the impedance and phase angle values associated with a “dry” PCBA at 25°C/80%RH (the water layer formation not induced by the PCBA temperature reduction, Figure 12.8) complied with the expected behaviour of a capacitive SIR nature (phase shift ~-85˚). Upon the moisture adsorption to the SIR specimens and the water layer build-up (increased conductivity between the conductors), the impedance values decreased and phase angle values raised towards less negative values which reflects the change in electrical properties from capacitive-dominated mode to the resistive character of the system [48-51]. This change also coincides with the higher leak current possibilities and electrochemical migration. With the significant increase of film thickness, the conductivity of a water film increased, which was reflected in the results by a pronounced impedance reduction to 5-10 kΩ and phase angle values approaching ~0˚ (“bulk water behaviour”).
The investigations in this paper included two types of non-condensing conditions that elucidate the effect of hygroscopic residues on the PCBA surface:

(i) isothermal conditions, and
(ii) non-isothermal conditions with the PCBA temperature reduction above the dew point.

In case of isothermal conditions, the interaction between the residue and water vapour depends on the critical relative humidity of the residue [23] which defines the DP of the SIR surface. In case of non-isothermal conditions, the hygroscopicity effect of the residues was shown in reducing the required gap between actual and dew point temperatures, which results in the accelerated moisture condensation occurrence when hygroscopic residues are present. As a result, the boundary for humidity robustness of the PCBA is changed when the contamination is present on its surface.

Moreover, additional investigations were performed under:

(iii) non-isothermal conditions with the PCBA temperature reduction below the DP, and
(iv) transient climatic conditions in a geographical location.

In the case of non-isothermal conditions where the PCBA temperature was reduced below the DP, the presence of residues and the rate of temperature change (cooling rate) were shown to impact the extent of water film build-up through the conductor bridging characteristics. The risk of water layer formation due to the interaction between external climate and the contaminated PCBA under the critical transient conditions was shown to be highly dependent on the residue hygroscopicity. The chemistry of activator initiated the build-up of water film, and defined the wetting period of the contaminated PCBA.

**ISOTHERMAL CONDITIONS**

At 25°C/80%RH and equal PCBA and chamber temperatures (25°C), no significant changes in the AC and DC data were observed for any contaminant (Figure 12.8) which implies no dissolution into the water film occurred. The morphology visualization (Figure 12.9) showed that glutaric acid clearly exhibited a stronger interaction with the surrounding moisture, compared to the other acids; however, the results of electrochemical suggest that no deliquescence and corrosion occurred. Under isothermal conditions tested in this study, the ionic nature of the WOA residues were not sufficient to induce the pronounced formation of water layer. Among the investigated WOA types, glutaric acid is the most hygroscopic and soluble in water [23, 26, 52], and interacts with water vapour easily which can explain its morphology changes at 80%RH.

**NON-ISOTHERMAL CONDITIONS WITH THE PCBA TEMPERATURE REDUCTION ABOVE THE DEW POINT**

The results obtained for testing of the residue effects under non-isothermal conditions and PCBA temperature reduction above the DP showed an agreement between the AC/DC measurements (Figure 12.10) and visualization of the contaminants morphology (Figure 12.11). No changes in the electrical properties and residue morphology were observed for adipic acid at any tested PCBA temperatures, and the results of electrochemical testing were comparable to those of a clean PCBA surface. Succinic acid showed the significant SIR reduction and dissolution into the water layer only upon the PCBA temperature decrease to 22°C, where the “bulk water behaviour” (low impedance and high phase angle values) was maintained throughout the 3 days of testing. On the contrary, the SIR patterns containing glutaric acid showed a pronounced decrease of impedance values, increase in phase angle, and the corresponding ECM occurrence at the PCBA temperatures 24.5-23°C, however the values returned to the initial levels within ~2.5 days. In case of larger temperature differences between
ambient and PCBA (22.5°C, 22°C), glutaric acid residues dissolved into the water layer and exhibited "bulk water behaviour" throughout the whole test time (3 days). The discrepancy in facilitation of the water layer build-up exhibited by the three contaminants originates from their hygroscopicity [23, 26]: at ambient 25°C adipic acid deliquesces only at very high humidity levels and dissolves into the water film to a small extent. Slightly higher hygroscopicity is exhibited by succinic acid, however, glutaric acid significantly differs from the other two residue types due to the high polarity of its molecules and high solubility in water. The presence of highly hygroscopic glutaric acid changed the humidity boundary of the PCBA surface and led to the accelerated formation of a water film upon the PCBA temperature reduction.

![Figure 12.17:](image)

According to the Mollier diagram, the moisture content expressed as an absolute humidity (AH) was 18.3 g/m³ for the ambient conditions of 25°C/80%RH applied in this study (Figure 12.17). Upon the PCBA temperature reduction, the same amount of water vapour was contained within the air surrounding the sample, therefore, in order to equilibrate and compensate for the surface temperature decrease, the relative water vapour content (relative humidity) above the contamination has increased [53]. As a consequence, when the PCBA temperature reached, e.g. 24.5°C, the relative humidity level above the contaminated sample increased to 82.5%RH, which strengthened the interaction between the water vapour and glutaric acid, and the potential for moisture condensation on the SIR surface raised. In case of PCBA temperature decrease from 25°C to 24.5-23°C, the initial impedance decrease due to the water film formation and subsequent return to the higher values is believed to be the results of RH equilibration with the chamber conditions after ~2.5 days (due to e.g. strong air flow). In case of the PCBA temperature reduction from 25°C to 22.5°C and 22°C, the formed electrolyte layer resembled the "bulk water behaviour" as the actual relative humidity levels above the SIR surface reached 92%RH and 95%RH (Figure 12.17). At such high humidity level of 95%RH, the amount of water vapour sorbed by glutaric acid rises significantly to 100 wt% (compared to 0.05 and 0.1 wt% for adipic and succinic acids, respectively) [23] which is sufficient for a formation of a continuous liquid film and occurrence of "bulk water behaviour", critical from the electronics reliability point of view. The results show that highly hygroscopic contamination types can reduce the critical RH level of the SIR surface and increase the water vapour content above it. Even under potentially non-condensing conditions, if the temperature of
the contaminated PCBA is reduced of only few degrees, the risk of water layer formation and corrosion occurrence is high. In actual practice, this shows that for an electronic device with the PCBA soldered using glutaric acid containing flux system, the condensed water film can be created on the surface of electronic unit at low transient temperature reduction conditions, compared to the flux systems with adipic or succinic acids.

**NON-ISOTHERMAL CONDITIONS WITH THE PCBA TEMPERATURE REDUCTION BELOW THE DEW POINT**

In case of clean surfaces (Figure 12.12), no correlation between the impedance or phase angle change and the averaged water layer thickness can be done - the “bulk water behaviour” (low impedance and high phase angle) was observed for the large range of thickness values (6-40 µm) which is directly associated with the ambient relative humidity level. The amount of water vapour available to be adsorbed to the PCBA surface upon condensation is proportional to the RH at constant temperature. For the tested humidity conditions at 25°C, the moisture content expressed as an absolute humidity (AH) [54] was 18.3 g/m³, 20.6 g/m³, and 21.7 g/m³ according to the Mollier diagram, for 80%RH, 90%RH, and 95%RH, respectively. Considering the same cooling rate (e.g. 25°C→21°C) and cooling time (12 minutes) applied at the tested RH levels for a clean SIR, the resulting impedance, phase angle, and averaged water film thickness values differed (Figure 12.12, shown with black arrows). A continuous water layer was formed at 95%RH (Figure 12.13 (c)) which resulted in the “bulk water behaviour” as inferred from the impedance data, compared to the data obtained at 80%RH and 90%RH. The observations are related to the characteristics of water film formation between the electrodes where the high moisture content at 95%RH allowed for advanced conductor bridging [3]. The water vapour density on the PCBA surface, and the resulting impedance and phase angle responses for the clean surface, were therefore a function of the absolute humidity level which defined the tendencies of the water film to bridge the electrode pattern (Figure 12.13). Moreover, the considered PCBA temperature reduction (25°C→21°C) indicated that the dew point was exceeded of 0.3°C, 2.2°C, and 3.1°C for 80%RH, 90%RH, and 95%RH, respectively, and that largest temperature difference between the PCBA and surrounding air (3.1°C) additionally contributed to the enhanced condensation and the observed impedance decrease.

The conductor bridging primarily depends on the surface roughness, type of the insulation material, and thermal conductivity of the materials [39, 55]. Similarly as shown for the clean surfaces, where the increase of ambient RH (AH) resulted in the increase of moisture condensation and electrode bridging characteristics, the presence of ionic residues (Figure 12.14) changed the critical RH of the surface, increased the water vapour content above the surface, and lead to the electrolyte formation and conductor bridging [3, 47]. In a thick water film, the charge transfer occurs easily and a system exhibits low resistance against it [48]. Between the tested activators, glutaric and succinic acids led to a significant impedance reduction and phase angle increase, similarly as in the case of moisture condensation on a clean PCBA at 95%RH (Figure 12.12). As discussed by Tencer [47], both parameters of deliquescence and surface coverage by the residue are vital for the formation of a conductive layer and electrode bridging. The contamination effect was visualized in Figure 12.15 where the reported photographs showed the advanced water film formation in case of succinic and glutaric acids, compared to the clean and adipic acid contaminated surfaces where only few water droplets can be observed under the same cooling conditions. The results show that highly hygroscopic contamination further enhances
the existing condensing conditions, leading to the accelerated water film formation and advanced conductor bridging.

TRANSIENT CLIMATIC CONDITIONS

The extent of water film formation on the SIR surfaces subjected to transient climatic conditions (Figure 12.16) was influenced by the contamination type. Under the 24h climatic profile of Copenhagen (Figure 12.6), the transient conditions were expected to occur for the ~1h period in the morning time (~03:50-04:50) due to the high humidity level and rapid increase of external temperature. During that critical period, the dew point raised to critically high levels and the difference of only 1°C was noted compared to the ambient temperature. In case of clean surface (Figure 12.16), the tested climatic profile did not result in a significant build-up of the water film. For the adipic and succinic acids, the effect was poorly pronounced. The residue contribution to the formation of water layer during the critical period of temperature change was observed only in the case of highly hygroscopic glutaric acid under a given climatic profile. The results are vital from the electronics application point of view: the effect of a temperature lag between outdoor and PCBA, almost unavoidable in a real life and primarily leading to a water film formation, is enhanced by the presence of hygroscopic ionic contamination [10].

The critical transient conditions, enhanced by the presence of glutaric acid on the PCBA surface, lasted for a shorter time period in the case of enclosure with larger through-hole (3 mm diameter) compared to the smaller leak size (1 mm diameter). As a result of natural convection occurring upon the temperature difference development between the chamber and internal enclosure conditions [10], a larger opening allowed for a less disturbed airflow and the PCBA could equilibrate with the external conditions faster. The presence of thermal mass increased the PCBA wetting time of ~15 min in case of enclosure with 3 mm diameter hole, however no effect of thermal mass was noted for the profiles obtained for casing with 1 mm diameter opening. The internal thermal mass attached at the bottom of test PCBA created an additional thermal gradient between the PCBA and external conditions [56] prolonging the wetting time of SIR pattern.

Overall, the results show the dependency of the water layer build-up on various parameters, which synergistically alter the extent of moisture adsorption and the electrical properties of the formed water film. The local RH increase due to the temperature difference between PCBA and ambient [11], ambient RH level, PCBA cleanliness, rate of temperature/humidity change, and the enclosure characteristics defy the robustness of the system by contributing to the tendency of a conductor bridging and subsequent risk of failure occurrence. Even potentially non-condensing conditions may be detrimental for the device if harsh process-related contamination is present on a PCBA surface. Maintaining the PCBA cleanliness and a control of internal climate of the device (e.g. towards less abrupt temperature changes) could influence the response of the device interior conditions to external climate fluctuation and condensation risk, delaying the potential deterioration in electronics performance.

V. CONCLUSIONS

1) Water vapour condensation on the clean PCBA surface and the resulting electrical properties of the water film are dependent on the ambient RH level and the rate of temperature change, which define the characteristics of conductor bridging. At constant ambient temperature, higher amount of water vapour exists at 95%RH than at 80%RH which, at the same cooling rate, leads to the formation of a continuous water film and easy conductor bridging.
2) The altered PCBA cleanliness decreases the critical RH level of the surface for condensation, increasing the water vapour content above it, and its extent is dictated by the ionic nature of residues. Under non-isothermal conditions and PCBA temperature reduction above the dew point (non-condensing conditions), high affinity to water and solubility of glutaric acid are sufficient to provoke the condensation of water vapour and subsequent corrosion issues for \( \sim 2.5 \) days if the PCBA temperature drops of 0.5-2°C from ambient 25°C.

3) Under non-isothermal conditions when the PCBA temperature decreases below the dew point, the presence of succinic and glutaric acids accelerate the formation of a continuous water layer and conductor bridging, and the resulting electrical properties are comparable to the results of moisture condensation on a clean PCBA at 95%RH.

4) Under transient conditions generated for \( \sim 1\)h within an electronic enclosure, the presence of highly hygroscopic glutaric acid prolonged the duration of PCBA surface wetting to \( \sim 4\)h. The presence of a thermal mass attached to the PCBA further extended the time for water layer existence of \( \sim 15\)min, increasing the extent of failure.

VI. REFERENCES


13. GENERAL DISCUSSION

This chapter contains a short discussion combining the investigations presented in the appended papers. The reliability of electronics exposed to humid conditions can be enhanced by a proper choice of materials for PCBA manufacturing which affect the process of water layer formation. The results presented in this thesis showed the synergistic effect of factors like PCBA surface, PCBA cleanliness, PCBA design, humidity, temperature, and enclosure characteristics, and their importance on corrosion failures in electronics.

The investigations showed that the range of temperatures experienced by the PCBAs during the wave soldering process is insufficient for the full decomposition and removal of the solder flux from the surfaces. Significant amount of residue is possible to be evaporated at temperatures higher than peak soldering temperatures (175°C and 250°C) and under extended time of thermal treatment compared to the conventional 45 seconds heating time. The removal of short-chain acid activators (e.g. DL-malic, succinic, glutaric acids) is easier compared to the acids of longer hydrocarbon chain (e.g. adipic, suberic, palmitic acids). If the residues comprise of binary mixture of weak organic activators, the physicochemical properties of both acids determine the decomposition tendency, the ratio and amount of the final residue mixture after thermal treatment, and the corrosive effects. Some of the activator types used in the no-clean flux formulations form anhydride compounds upon dehydration at high soldering temperatures, which are more aggressive and interact with moisture easier than the respective acids. The removal of contaminants from the metallic surfaces becomes more difficult as most of the weak organic acid activators tend to react with copper surface and form chelate complex compounds, which do not evaporate easily at wave soldering temperatures. Significant difference in the amount of contamination was found on various surfaces where the combined effects of thermal properties of the materials and flux chemistry define the evaporation tendency. Removal of the entrapped contaminants from under the components is far less effective compared to the opened areas on the PCBA surface. The residues remaining on a PCBA surface after the soldering process are detrimental for the electronics corrosion reliability, unless a sufficient thermal treatment or optimized residue type (and ratio between the corrosive components) are provided.

Although the acid activators used in no-clean solder flux systems are believed to be non-corrosive, the investigations in this thesis showed the importance of activator part of the flux formulation and temperature conditions on the climatic reliability issues. The studies showed that the presence of ionic contamination, originating from the soldering manufacture process, can facilitate the formation of water layer on a PCBA surface and lead to dramatic deteriorations in electronics reliability. The susceptibility of solder flux systems to assist the absorption of moisture from the surrounding is dependent on the activator part of the flux formulation and its hygroscopic properties. Most of the activators used commonly in the modern no-clean flux systems are characterized by critical RH levels at which deliquescence and residue dissolution into the formed water layer occur. The presence of multiple weak organic activators in a flux shifts this critical humidity boundary to lower values and increases the overall hygroscopicity of the residue. High hygroscopicity of the flux residues is often associated with lower critical RH levels and higher solubility in water. The absorption of water molecules continues until complete dissolution and subsequent dilution of the saturated solution occur. The extent of water layer formation depends on the hygroscopicity of the residues: highly polar molecules will absorb large amount of water from the surrounding at lower humidity levels compared to less hygroscopic activators. Mixing of highly hygroscopic acids with less hygroscopic ingredients facilitates the formation of thick water layer. The build-up of thick water film increases the leakage currents levels and bridging extent,
and therefore the potential for metal ion migration and short-circuiting. The electrical properties of the formed water layer will be influenced by the solubility and ionization properties, and good water-solubility and ionization constant of the residues increase the current level and can result in a failure mode such as electrochemical migration. Therefore, process cleanliness is a crucial factor in maintaining the corrosion reliability. Moreover, the selection of proper no-clean flux system with a formulation optimized in terms of chemistry and activator levels, and in relation to product’s characteristics (PCBA design, user environment conditions) is recommended for better humidity reliability and solderability requirements.

The temperature effect on the reliability of contaminated PCBA surfaces was assessed for all the known and commonly used flux chemistries under various temperature conditions relevant for the electronics operation. An increase of test temperature strengthens the degree of interaction between the residue and water vapour, leading to the acid deliquescence and dissolution at lower RH levels, increasing the water layer thickness, and accelerating the occurrence of corrosion. Temperature influences also the crystallization behavior of deliquesced residues, and higher ambient temperatures decrease the efflorescence RH level, which then become more difficult to dry under cycling humidity conditions.

Most of the flux activator types exhibit typical deliquescent behavior, which also implies that the residue dissolved in the course of deliquescence tends to retain water and extends the wetting time of the PCBA surface, even if the external RH level falls back below the deliquescent point of the residue. The prolonged wetting time of the PCBA increases the existence of water layer on the surface and potential for failure.

Another important parameter for the electronics reliability is the PCBA surface characteristics, namely surface chemistry and topography, that influence the possibility of SIR reduction and occurrence of corrosion failure modes. Due to the addition of inorganic fillers to the solder mask matrix, the PCBA surface energy is defined, and the filler loading below the solder mask surface defines its roughness. From the reliability point of view, the presence of hydrophobic fillers (e.g. waxing hydrocarbons) and high roughness of a hydrophobic surface is a good solution, as both parameters decrease the wettability of the PCBA surface. Under heavily condensing conditions, the build-up of water layer on the rough PCBA surface leads to the shorter time for bridging of electrodes and ECM occurrence, compared to the smooth surfaces. The roughness factor is further affected by the presence of hygroscopic residues that enhance the droplet bridging extent. From the reliability point of view, such phenomenon is critical, and a proper choice of materials characteristics could delay the SIR drop under transient conditions and enhance a long term reliability of the device.

The conductor bridging characteristics were shown to depend not only on the PCBA surface and cleanliness, but on the ambient humidity conditions and the differential temperatures between PCBA and ambient. The presence of hygroscopic residues reduces the humidity threshold for failures, and leads to condensation and corrosion issues even under potentially non-condensing conditions. Under transient conditions, developed within the electronic enclosure, the altered PCBA cleanliness leads to the extended wetting time, and the local moisture condensation is enhanced by the presence of thermal mass due to its high heat capacity and a thermal lag development.
14. GENERAL CONCLUSIONS

Effect of PCBA surface
1) The formation of water layer on the PCBA surface depends on the surface energy and roughness, which are mainly dependent on the solder mask additives. It was found that the type of fillers (e.g. hydrophobic fillers or waxing additives) defined the surface energy, whereas the micro-scale roughness of the solder mask was a result of filler loading below the surface. Both parameters influence the wettability and, therefore, the characteristics of water layer formation.

2) Increased wetting properties were exhibited by the hydrophilic PCBA surfaces, which arose due to the presence of polar fillers and high surface roughness. High wettability was further enhanced by a large amount of micro-sized bulk defects that locally decrease the contact angle. Contrarily, the addition of hydrophobic fillers (e.g. talc) and high surface roughness decrease the spreading tendency of the water droplets, which increases the PCBA reliability.

3) Under heavy condensing conditions, the differences in droplet appearance on the solder mask surface are mainly associated with the surface roughness. From the corrosion reliability point of view, the build-up of water layer on the rough PCBA surface leads to the shorter time for bridging of electrodes and possibility of ECM occurrence, compared to the smooth surfaces.

4) The effect of high surface roughness is further enhanced if the PCBA cleanliness is altered by the presence of hygroscopic residues that trigger more pronounced adsorption of moisture under condensing conditions and lead to the extended conductor bridging.

Effect of PCBA cleanliness
1) Full decomposition of solder fluxes residues from the PCBA surface did not occur under the range of conventional temperatures of the wave soldering conditions, leaving behind significant level of WOA residues. The significant decrease in flux residue amount occurred only at high temperatures (350°C) or for extended time of exposure compared to the parameters used typically for the soldering process.

2) Among the tested weak organic activators, DL-malic, succinic, and glutaric acids evaporate easier from the surface, compared to adipic, suberic, and palmitic acids. If the residues comprise of binary mixtures of acid, the preferential evaporation of succinic acid, compared to adipic and glutaric acids, occur.

3) Residue removal from the FR-4 laminate surface was found to be more effective compared to a copper-coated surface. Weak organic acids react with copper at high temperatures and form chelate complex compounds of altered evaporation tendencies. The presence of film-former in some of the tested fluxes may restrict their residue removal rate even upon the prolonged heat treatment.

4) Evaporation of the residues from test rigs simulating the entrapment under the components did not result in a significant reduction of contamination amounts after thermal treatment at 350°C. Heating of the residues remaining on opened substrates resulted in almost complete contamination removal at 350°C.
5) Among all the tested WOAs, succinic and DL-malic acids underwent thermal degradation at high soldering temperatures and formed additional anhydride-like species, some of which have more aggressive chemical nature than the flux activators.

6) Most of the weak organic acids typically used as solder flux activators are hygroscopic in nature, and deliquesce at specific critical RH levels, leading to the formation of water layer on the PCBA surface. The corrosive properties of WOAs are associated with their hygroscopicity and solubility properties. DC leakage current measurements revealed the RH range for electrochemical migration complied with the deliquescence RH for highly soluble glutaric and DL-malic acids. Overall, the climatic testing of WOAs resulted in the following order of hygroscopicity and corrosivity: palmitic < suberic < adipic < succinic < glutaric < DL-malic acids.

7) The presence of highly hygroscopic glutaric and succinic acids decreases the critical RH level of the PCBA surface. Under non-isothermal conditions and PCBA temperature reduction in the non-condensing region (above the dew point), glutaric acid provokes condensation and corrosion issues on the PCBA, even if the PCBA temperature drops of 0.5-2°C from ambient 25°C. Under non-isothermal conditions when the PCBA temperature decreases below the dew point, they accelerate the formation of a continuous water layer and extent of conductor bridging, leading to accelerated failure occurrence. Under transient conditions generated for ~1h within an electronic enclosure, the presence of highly hygroscopic glutaric acid prolonged the duration of PCBA surface wetting to ~4h.

8) The presence of multiple WOA comprising the flux residues shifts the RH levels for deliquescence and corrosion occurrence towards lower values, compared to residues based on single activator. The difference between the critical RH levels of single activators and deliquescence RH of binary mixtures was found to be within 10%RH.

9) The extent of moisture sorption and the risk of corrosion occurrence depends not only on the mixture type but also the ratio between the components. The presence of highly hygroscopic ingredient in a blend with less aggressive component associates the formation of a thicker water layer and leads to electrochemical migration occurring at lower RH level.

10) An increase in temperature shifted the critical RH levels for deliquescence and efflorescence towards lower values, accelerating the formation of water layer on the PCBA surface. Due to the increased solubility of the residues at high temperatures, the water film saturated easily in ions and the electrochemical migration occurred at lower RH levels.

11) Hygroscopic deliquescent residues are characterized by the appearance of hysteresis loop in their vapour sorption isotherms. This indicates the extended wetting of the PCBA surface occurs even if the surrounding humidity level has fallen below the deliquescent point of the surface contamination.

**Effect of transient conditions and PCBA parameters**

1) The formation of water layer and conductor bridging characteristics were shown to depend not only on the PCBA surface and cleanliness, but on the ambient humidity conditions, the differential temperatures between PCBA and ambient, and the cooling rate.
2) The presence of a heavy thermal mass (e.g. heat sink) on a PCBA placed in the enclosure delays the temperature change of the electronic assembly, contributing to the prolonged PCBA wetting. If the hygroscopic residues remain on the PCBA surface, the temperature delay extends the time for water layer existence on the PCBA and therefore dramatically increases the potential for failure occurrence.

**Recommendations for improving the humidity robustness of electronics based on the thesis work**

1) The solder mask material should comprise of a hydrophobic matrix and contain hydrophobic fillers. In case the PCBA substrate is hydrophobic, high surface roughness could further enhance this character. If the surface is hydrophilic, the lowest roughness level is recommended.

2) The amount of PCBA bulk defects (pin holes), originating from a non-optimized process, should be kept at minimum.

3) For the soldering purposes, the use of flux formulations based on single activator is recommended. The activator hygroscopicity and solubility in water should be minimal. In case the flux system contains multiple acid activators, the type of blend and ratio between the components need to be optimized.

4) The lowest amount of solder flux sprayed onto the PCBA surface during the soldering process is recommended. The thermal treatment time or a range of soldering temperatures should be increased as much as possible.

5) Large temperature differences and quick temperature/humidity changes between the PCBA, enclosure, and outdoor should be avoided by allowing a good enclosure ventilation and lack of large PCBA components that act as a thermal mass and cause a temperature delay.

6) The interior humidity level of the electronic enclosure should be kept low due to the risk of severe condensation if the PCBA temperature drops below the dew point and the air contains high amount of moisture.
15. SUGGESTIONS FOR FUTURE WORK

PCBA surface effects on water film formation

The dependency of water film formation on the PCBA surface characteristics (chemistry and morphology) should be studied in a more systematic way. The chemically homogenous surfaces should be fabricated and vary in surface composition and roughness over a large scale. The bulk defects should be avoided in order to exclude their effect on the wettability performance. The water film formation on the fabricated specimens under various condensing conditions should be studied. Perhaps, certain chemistry and roughness levels could be associated with the significant delay of a potential ECM occurrence. The outcome can be very useful and provide more specific production guidelines for PCBA materials and design.

The phenomenon should be studied on a variety of metals and polymers, constituting the complex electronic assemblies.

Moreover, the effect of water film formation under condensing conditions should be extended to vertical PCB arrangements, where the surface morphology and gravity define the characteristics of bridging the electrodes by the forming water droplets.

Contamination effects on water film formation

The flux activators studied in this work constitute the vast majority of the acids used in the commercial wave solder flux systems. However, there is a need of studying new activating chemistries under varying climatic conditions, and finding a compromise between the solderability properties and climatic reliability.

The decomposition tendencies and interaction with humidity should be studied for other flux constituents, e.g. surfactants, binders, solvents, foaming agents, etc. Moreover, the thermal decomposition of residues originating from reflow soldering should be investigated. The subsequent film-former cracking and residue exposure under humid conditions should be quantified and assessed in terms of corrosion reliability.

The investigations of the contamination hygroscopicity and corrosivity under the temperatures relevant to electronics operation should be extended to atmospheric contamination (e.g. dust from various locations worldwide). The inorganic/organic compositions should be studied alone and in combination with solder flux residues.

The hygroscopic and corrosive properties of the contaminants present in electronic devices should be also studied for different contamination levels and for the recrystallized residue (the residue which has already undergone several deliquescence and efflorescence cycles).

Moreover, the contamination behaviour of the contaminants should be studied for the temperatures lower than 25°C, imitating the electronics operating at e.g. winter conditions or cold locations worldwide.

The dry-out time for the residue that underwent deliquescence could be studied as a function of various dry conditions.

Effect of transient conditions on water film formation

The water film formation under potentially non-condensing conditions should be extended to mixtures of activators and atmospheric contaminants, which can likely lead to the change of humidity boundary for failure due to the formation of water layer on the PCBA surface. The potential for condensation should be investigated for a wide range of contamination types (e.g. various flux
components, dust, road salt deposits) and levels in order to assess the critical RH and residue levels for corrosion occurrence.

The condensing conditions (for clean and contaminated surfaces) could be investigated at the temperature range lower and higher than 25°C where the absolute humidity levels (moisture content) are significantly different.

The investigations can be expanded to cycling temperature conditions, where the potential for condensation occurrence might be studied as a function of various volumes and heat capacities of thermal masses, temperature levels, enclosure designs and materials, or time. Moreover, a number of climatic profiles from different locations worldwide could be studied together with the contamination, PCBA, and enclosure effects.

All the above should be investigated for various PCBA geometries (e.g. pitch distances, electrode widths, electrode materials) and materials constituting the electronic surfaces (e.g. solder masks, FR-4 laminates).