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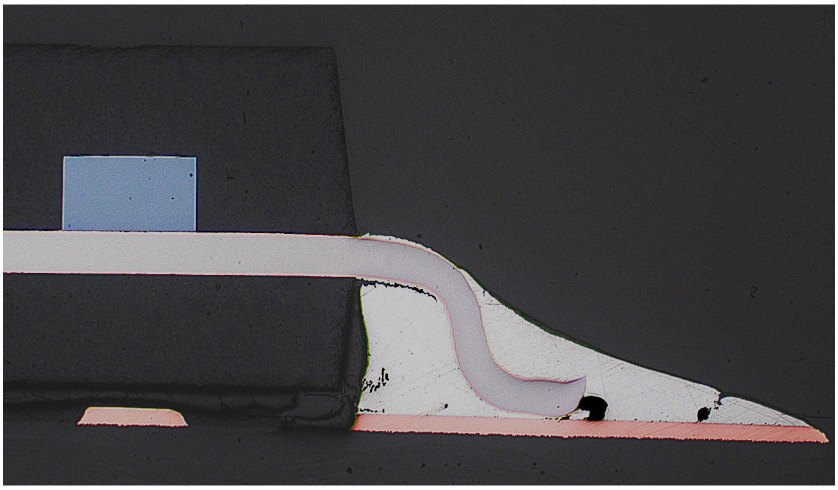

Lead-Free Soldering Processes in the Electronic Industry
Industrial Implementation at SMEs

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ABSTRACT AND KEYWORDS

Following the implementation of the new European environmental directives, Restriction of the Use of Certain Hazardous Substances (RoHS) and Waste Electrical and Electronic Equipment (WEEE), which involve the ban of lead from electronic and electrical products, this work presents process development work, production and reliability testing of real products from several partners with commercial solders that have been tested and monitored to ensure the reliability of the new lead-free solders and compare them to the leaded ones. It aims to help the implementation of the lead-free solders in the soldering processes and supply the SMEs more information about real products and conditions that might be compared with theirs.

The reliability tests and characterisation on the real products from several companies showed that the lead-free boards demonstrated a good performance under testing, being equivalent or better than the tin/lead ones. The defects or anomalies found in most of the joints (voiding and pad lifting) result from the manufacturing process. Most of the faults were found in through-hole devices and were due to component failures and not from the joint integrity. The degradation after the reliability tests of both types of solders is similar.

The SMEs are engaged in taking this opportunity to reach a higher level. Some of the companies embraced this “forced” transition to upgrade and improve their facilities, bringing better capabilities and opportunities in their businesses.

The objective of this work is to be a tool of information to the SMEs of the electrical and electronic sector, in order to help them in the transition to lead-free soldering.

Lead-free solder– Soldering – Electronics – Reliability – PCB – RoHS

RESUMO E PALAVRAS CHAVE

No decorrer da implementação das recentes directivas ambientais Europeias: Restrição do Uso de Substâncias Perigosas (RUSP) e Resíduos de Equipamentos Eléctricos e Electrónicos (REEE) surge a proibição do uso de chumbo em produtos eléctricos e electrónicos. Este trabalho apresenta o estudo de desenvolvimento de processo, produção e testes de fiabilidade em produtos reais de diversas empresas. Vários tipos de soldas comerciais foram usadas e testadas de modo a permitir a comparação em termos de performance das soldas sem chumbo face às com chumbo. O presente trabalho tem como objectivo o apoio às PMEs (Pequenas e Médias Empresas) durante a implementação da soldadura sem chumbo nos seus processos industriais e fornecer-lhes mais informação sobre produtos reais que lhes permita comparar com a sua própria produção.

Os testes de fiabilidade e a caracterização feita nos produtos em estudo demonstraram que as placas soldadas sem chumbo possuem uma boa performance em teste e são equivalentes ou melhores que as placas soldadas com soldas com chumbo. Os defeitos e anomalias encontradas nas juntas soldadas resultam do processo de fabrico. Na sua maioria, as falhas encontradas nas placas são devidas a falha de componentes e não da integridade das juntas. A degradação das soldas após teste é similar nos dois tipos de solda.

As PMEs estão motivadas em aproveitar esta transição “forçada” para melhorar as suas capacidades, equipamentos e oportunidades de negócio.

O objectivo final deste trabalho é fornecer informação às PMEs do sector eléctrico e electrónico, de modo a apoiar a sua transição para a soldadura sem chumbo.

Solda sem chumbo – Soldadura – Electrónica – Fiabilidade – PCB – RUSP

CONTENTS

CHAPTER ONE

Introduction

CHAPTER TWO

Electronic industry issues related to European directives

CHAPTER THREE

Soldering in electronics

CHAPTER FOUR

Lead-free process validation of commercial solders in industrial boards

CHAPTER FIVE

General overview – environmental and economical impacts

CHAPTER SIX

Final conclusions and future work

LIST OF ACRONYMS AND SYMBOLS

CTE – Coefficient of Thermal Expansion
EDS – Energy Dispersive Spectroscopy
EEE – Electrical and Electronic Equipment
ENIG – Electroless Nickel, Immersion Gold
EU – European Union
HASL – Hot Air Solder Levelled
IC – Intregrated Circuit
IPC – Association Connecting Electronic Industries
ISQ – Instituto de Soldadura e Qualidade
IT – Information Technologies
LCF – Low Cicle Fatigue
LF – Lead-free
MELF – Metal Electrode Leadless Face
OSP – Organic Surface Preservative
PBB – Polybrominated Biphenyl
PBDE – Polybrominated Diphenyl Ether
PCB – Printed Circuit Boards
PPM – Parts Per Million
RoHS – Restriction of the Use of Certain Hazardous Substances
SEM – Scanning Electron Microscope
SMD – Surface Mount Device
SME – Small and Medium Enterprises
TL –Tin/lead
TMF – Thermo-Mechanical Fatigue
VOC – Volatile Organic Compounds
WEEE – Waste Electrical and Electronic Equipment

Ag – Silver
Au – Gold
Bi – Bismuth
Cu – Copper
In - Indium
Ni – Nickel
N_f – Number of cycles to failure
Pb – Lead
S – Spreading coefficient
Sn – Tin
T_{sd} – Soldering temperature

Zn – Zinc

θ – Contact or wettability angle

γ_{VS} – Vapour/solid surface tension

γ_{LS} – Liquid/solid surface tension

γ_{LV} – Liquid/vapour surface tension

ΔT – Range of the thermal cycle

LIST OF TABLES

LIST OF FIGURES

CHAPTER ONE

Introduction

1.1 Objectives

This work results from the implementation of the new European environmental directives, particularly the Restriction of the Use of Certain Hazardous Substances (RoHS). From all the restrictions imposed by the Restriction of the Use of Certain Hazardous Substances (RoHS) and Waste Electrical and Electronic Equipment (WEEE) directives, banning of lead from electronic and electrical products had one of the biggest impacts on this industrial sector (see sub-chapters 2.1.1 and 2.1.2). Small and Medium Enterprises (SME) that have to strive with the huge competitiveness of the market are now facing a new obstacle, the substitution of solder alloys and all the consequences that this change implies.

This work presents process development work, production and reliability testing of real products from several partners with commercial solders that have been tested and monitored to ensure the required reliability of the new lead-free solders and compare them with the previous lead containing ones. It aims to help the implementation of the lead-free solders in the soldering processes and supply to the SMEs more information about real products and conditions that might be compared with theirs, and not only results obtained from ideal conditions as in the laboratory.

Finally the objective of this work is to be a tool of information to the SMEs of the electrical and electronic sector, in order to help them in the transition to lead-free soldering.

1.2 Workplan

The present work is based in an industrial research project and compiles in a brief manner several of the main results obtained with electric and electronic industrial assemblers from Portugal, Spain and United Kingdom.

The first part of this thesis brings an analysis of the European directives and their impact in industry, and some information about the basic principles of soldering in electronics. A description of the work carried out and results are presented in the second part. Finally the economical and environmental impacts will be evaluated, and the discussion and conclusions of the work will be presented.

Several industrial products were selected from each of the industrial partners for the work presented in the second part of this thesis. These products were manufactured and all data recorded, including the level of the defects found for each type of solder tested. The boards were visually inspected before and after the reliability and functionality testing. Some joints from each board were then selected and characterised by optical and electronic microscopy. In the following figure 1 it is presented a summary of this work:

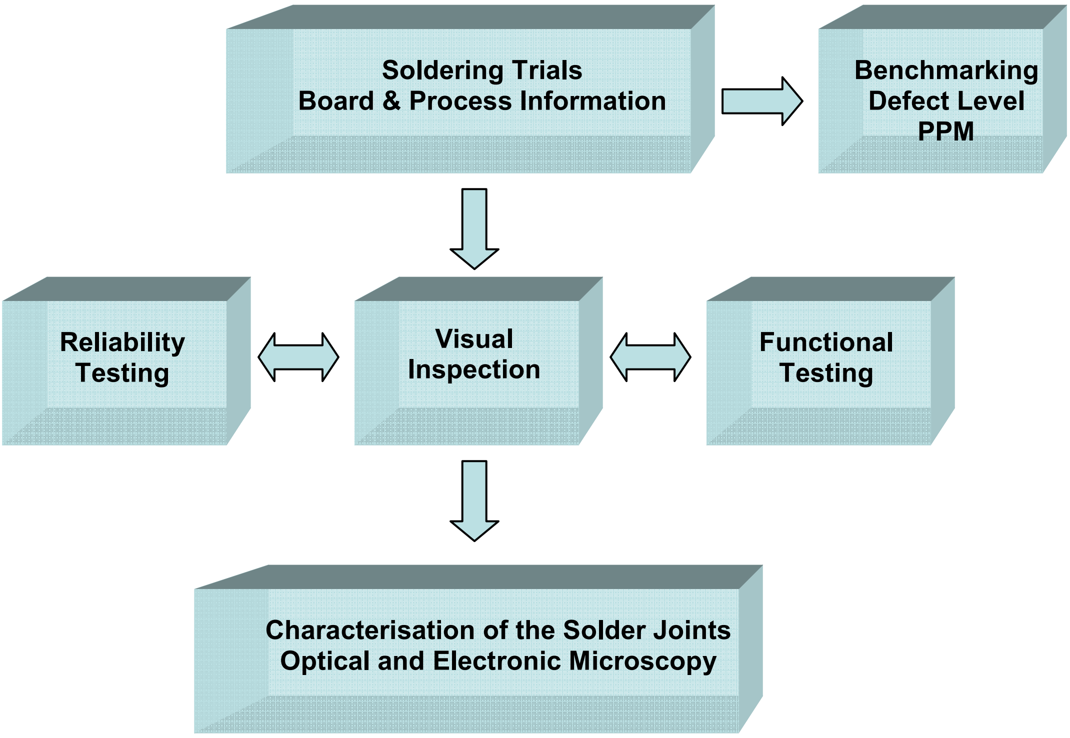


Figure 1 – Description of the experimental work carried out.

CHAPTER TWO

Electronic industry issues related to European directives

2.1 European directives

2.1.1 RoHS

The Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment – RoHS Directive – implements the provisions of the European Parliament and Council under the Directive 2002/95/EC. The RoHS Directive bans the introduction on the EU market of new Electrical and Electronic Equipment (EEE) containing more than the permitted levels of lead, cadmium, mercury, hexavalent chromium and both polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE) flame retardants from 1st July 2006. The directive applies both to electric light bulbs and to household luminaries among other products stated in the WEEE directive, e.g. microwaves, computers, telephones; however there are some exempted applications for these substances, e.g. lead in the glass of cathode ray tubes. The two categories of the WEEE Directive that are not included within the scope of the RoHS are medical devices and monitoring & control instruments. The Directive also does not apply to the re-use of equipment that was put on the market before the same date.

Manufacturers will need to ensure that their products - components and sub-assemblies of such products - comply with the requirements of the RoHS Directive. The Directive will also enforce those who import EEE into the European Union, those who export to other Member States and those who re-brand other manufacturer's EEE as their own. A maximum concentration value will be permitted in the manufacture of new EEE, up to 0.1% by weight in homogeneous materials for **[1]**:

- Lead;
- Mercury;
- Hexavalent chromium;
- PBB (polybrominated biphenyl);
- PBDE (polybrominated diphenyl ether).

And of up to 0.01% by weight in homogenous materials for:

- Cadmium.

Homogeneous material means a material that cannot be mechanically disjointed into different materials. As an example, an electric cable is not a homogeneous material because it can be divided in two parts: copper core and the plastic outer shell.

The following decision tree **[2]** has the objective of helping the companies to decide whether or not a product might come within the scope of the RoHS Directive.

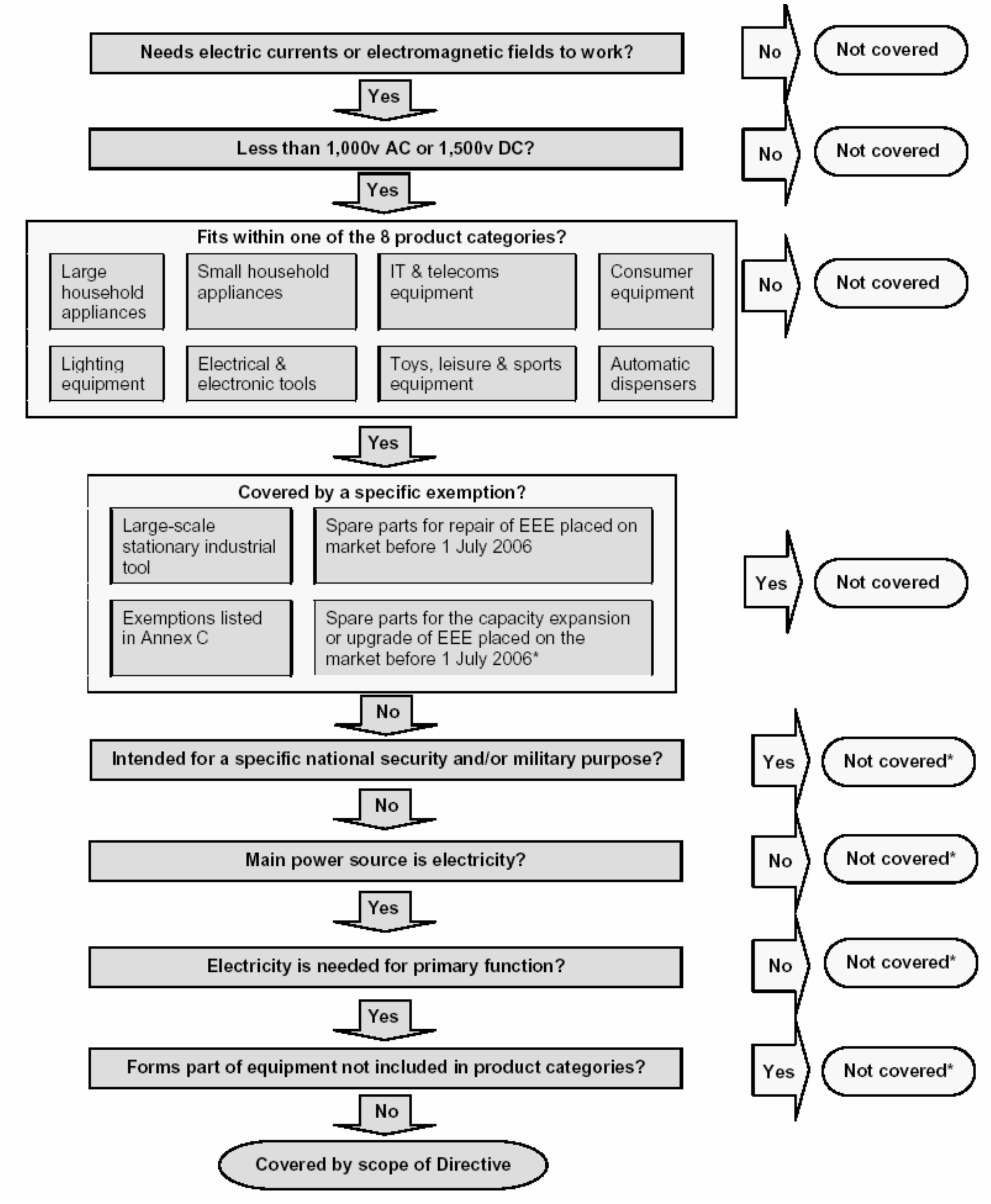


Figure 2 – Decision tree to decide if a product is within the scope of the RoHS Directive **[2]**.

* Legal council required

2.1.2 WEEE

The Waste Electrical and Electronic Equipment Directive (WEEE Directive) is the European Community Directive 2002/96/EC on waste electrical and electronic equipment. Electrical and Electronic Equipment means equipment which is dependent on electric currents or electromagnetic fields in order to work properly and equipment for the generation, transfer and measurement of such currents and fields falling under the categories set out in Annex IA of the Directive and stated below; and designed for use with a voltage rating not exceeding 1000 Volt for alternating current and 1500 Volt for direct current.

The purpose of this directive is the prevention of WEEE, and in addition, to regulate/stimulate the reuse, recycling and other forms of recovery of such wastes so as to reduce the disposal of waste. It also seeks to improve the environmental performance of all operators involved in the life cycle of electrical and electronic equipment, e.g. producers, distributors and consumers and in particular those operators directly involved in the treatment of waste electrical and electronic equipment **[3]**.

The WEEE directive will affect those involved in manufacturing, selling, distributing, recycling or treating electrical and electronic equipment and applies to ten categories of products:

- Large household appliances;
- Small household appliances;
- IT and telecommunications equipment;
- Consumer equipment;
- Lighting equipment;
- Electrical and electronic tools (with the exception of large-scale stationary industrial tools);
- Toys, leisure and sports equipment;
- Medical devices (with the exception of all implanted and infected products);
- Monitoring and control instruments;
- Automatic dispensers.

The directive imposes the responsibility for the disposal of WEEE on the manufacturers of such equipment. Those companies should establish an infrastructure for collecting WEEE, in such a way that "Users of electrical and electronic equipment from private households should have the possibility of returning WEEE at least free of charge". Also, the companies are compelled to use the collected waste in an ecological-friendly manner, either by ecological disposal or by reuse/refurbishment of the collected WEEE. This way private householders will be able to return their WEEE to collection facilities free of charge; producers (manufacturers, sellers, distributors) will be responsible for taking back and recycling electrical and electronic equipment and producers will be required to achieve a series of demanding recycling and recovery targets for different categories of appliance. The WEEE Directive obliged the twenty-five EU member states to transpose its provisions into national law; to establish and maintain a registry of producers putting electrical and electronic equipment onto the market and required that those Member States ensure a target, by 31 December 2006, of at least 4 kilograms of WEEE- waste of electrical and electronic equipment per inhabitant per year is being collected from private households. The current status on the implementation and transposition of the directive is available in the Perchards report **[4]**. In Portugal the two directives were transposed into the decree-law 230/2004 in September 2004, all producers and importers based in Portugal must be registered, and must show their registration number on invoices and transport documents. Registration shall be carried out by a body set up by producer associations and by the collective compliance system, under licence from the National Waste Institute. The Waste Institute will also be responsible for supervising compliance and approving individual or collective compliance systems.

Producers must register in every individual EU country. Without the WEEE registration a product cannot be placed on the EU market! **[5]**

2.2 Lead-free industrial implementation concerns

The main issue that comes from the prohibition of lead alloy solders is the increase of the melting point that is inherent to the alternative solders. This increase of the melting point of the solders has several important implications to the manufacturing process, as is described bellow.

Surveys were carried out before the implementation of the RoHS directive to the electric and electronic industry participating in the project, in order to investigate their concerns and possible problems. The results showed that the main concerns were related to **[6]**:

- Investment in new equipment or upgrades;
- Thermal limitations of some components and materials;
- Thermal profile and temperatures to be used;
- Low cost reliable solders;
- Reliability of the products;
- Bath contamination on wave soldering;
- Solderability on rework process;
- Differences in the joint appearance that has a great impact in inspection.

Some of these concerns have become a reality with the transition to the lead-free process, others have been overcome or even not found at all, e.g. decrease of the products reliability under single standard tests. A lot of work has been done in this area and a lot more still has to be done, not only to achieve the implementation of the directives but to take the electric and electronic sector to another level.

CHAPTER THREE

Soldering in electronics

3.1 Basic principles of soldering

Soldering is one of the oldest processes that use melting to join two metals. Soldered pottery and jewellery has been found that is more than 3000 years old. It is defined to be all the joining processes that do not melt the base material, the joint is produced by heating and adding another metallic alloy, which melting point is lower than the “solidus” temperature of the base material. The alloy penetrates the joint, filling it, by capillarity **[7]**. Soldering simply consists of the relative positioning of the parts to be joined, of wetting the surfaces with molten solder and allowing the solder to cool down until it has solidified.

Soldering is a very important technique in the assembly of electronic products and everyday hundreds of millions of soldered joints are being produced. It has many advantages:

- The solder joint forms itself by the nature of the wetting process, even when the heat and the solder are not supplied precisely to the places to be soldered;
- The temperature is relatively low;
- It is very versatile in terms of joints dimensioning, so that it is possible to obtain good results even if a large variety of components are used on the same soldered product;
- Connections can be disconnected if necessary, which implies that repair is possible;
- Processes can easily be automated, allowing in-line production **[8]**.

Efficient functioning of electrical and Electronic equipment is in many ways dependent on the correct interconnection of electrical components. This interconnection relies to the most part on soldering. Soldering itself is a vast and complex system; it can be approximately divided in: design, manufacture and use. In the design stage the shape, dimensions, thermal behaviour of components, all the configuration, thermal requirements of the board, among other parameters, should be studied.

In electronics, Printed Circuit Boards (PCB) are commonly used to mechanically support and electrically connect electronic components using conductive copper paths laminated onto a non conductive substrate. Some PCB’s are composed of one up to more than twenty-four conductive layers separated by other layers of insulating material laminated together. The most common substrates are: FR2 - composed of multiple plies of paper impregnated with flame retarding phenolic resin, which is cheap, has good electrical performance; FR3 – the same as FR2 but the paper is impregnated with an epoxy resin providing better electrical and mechanical properties, which is used in TV, computer and telecommunication applications; and FR4 – multiple layers of woven glass cloth impregnated with epoxy resin, used in double sided and multilayer boards in military, advance computer systems and automotive. Some materials like Kapton are being used for flexible boards. The Kapton is a polyimide film that is resistant to soldering temperatures and it is very flexible; this flexibility allows to adapt the shape of the circuit to that of the end product (e.g. photo camera) or to connect parts that are moving during the functioning of the equipment (e.g. compact disc players). The conductive layers are almost invariably made of copper in all types of boards **[8]**. Layers may be connected together through drilled holes (vias), to form an electrical connection. These vias can be electroplated or alternately small rivets can be inserted. In every PCB small copper traces or tracks are visible on the surface, these traces are made by adhering a layer of copper over the entire substrate and then removing the unwanted copper by etching, using a mask, leaving only the desired copper traces. Multilayer boards have traces inside the PCB that are obtained by bonding several etched thin boards together by a lamination process. Pads to which components will be mounted are normally plated, because bare copper oxidizes quickly, reducing solderabillity. Platings like OSP (organic surface preservative), Immersion silver and ENIG (electroless nickel with immersion gold) are used **[9]**.

An illustration of the parts that constitute a joint is shown in figure 3.

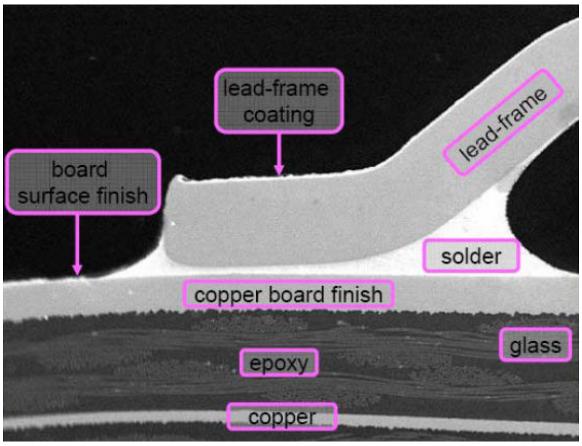


Figure 3 - Example of parts on a board **[10]**.

In the manufacturing stage, components and board have to pass through the soldering machine under the selected process conditions. The solderability of components should match the characteristics of several parameters: solder alloy, flux, soldering equipment, thermal load, rework (if needed) and much more. The usage stage of the product also brings in the issue of reliability. This means that the product not only has the desired properties after production, but can also be expected to ensure failure free working during the life of the equipment.

Soldering in electronics is a vast and interesting subject that incorporates various sciences such mechanics, chemistry, materials (metallurgy, polymers…). In this chapter several subjects of these sciences/disciplines will be approached.

3.1.1 Physics and chemistry of soldering

All the various soldering processes have their own characteristics. They only differ in the way in which the heat, solder flux and the solder alloy are applied. Apart from these differences they all have to comply with some requirements in order to produce good joints. These pre-requisites are the basic aspects of the soldering processes. The main physical properties for the solders are:

Phase-transition temperature

The phase-transition temperatures have important implications. All products have a specific service temperature, temperature in which the product will work. The melting temperature of a solder must be at least two times higher than the upper limit of the expected service temperature, in order to avoid failure during service **[11]**.

Table 1 – Temperature extremes, during usage, in solder joints for typical electronics applications **[11]**.

Applications	Temperature Extremes (ºC)
Consumer Electronics	0 to 60
Computers	15 to 60
Telecommunications	-40 to 85
Commercial Aircraft	-55 to 95
Military Aircraft	-55 to 125
Automotive – passenger Compartment	-55 to 65
Automotive – Under the hood	-55 to 150

Electrical conductivity

Electrical conductivity is the movement of electrons under an electrical field, and is predominant in metals. In solders this is primarily contributed by the flow of electrons. Resistivity (the inverse of electrical conductivity) increases with increasing temperature, due to the reduction of the mean-free-path of the electron mobility; can also increase with plastic deformation **[12]**.

Thermal conductivity

Thermal conductivity is the property that characterises the ability of a material to transfer heat. Like electrical conductivity, thermal conductivity decreases with increasing temperature. Because the movement of the electrons is also responsible for the heat transfer in materials (together with phonons) **[13]**.

Thermal expansion

The components (board, lead, solder, copper pads) that compose a board all have different coefficients of thermal expansion (CTE). Heat is generated from electronic devices during the power on, following the Joule law. The heat will gradually dissipate to external environment while power off, these temperature fluctuations, such as temperature variations in the external environment or power on-off, promote the difference of those CTE's, increasing the stress and strain on the solder joints, damaging them and leading to failure. This damaging phenomenon is called thermo-mechanical fatigue (TMF) **[11]**.

Surface tension

Wetting is an essential pre-requisite for soldering (θ in figure 4). Wetting means that the contact angle between a liquid and a solid is zero or so close to zero that the liquid spreads over the solid easily; non wetting means that the angle is greater than 90º so that the liquid tends to form a ball and rolls off from the surface. A good wetting between solder and bare material is a necessary and essential pre-requisite for soldering.

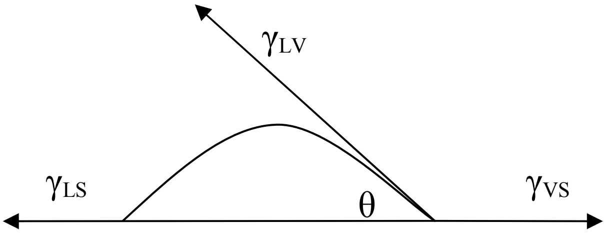


Figure 4 – spreading of a liquid on a solid surface.

The contact or wettability angle, θ, can be calculated by the Young's equation:

$$\cos\theta = \frac{\gamma_{VS} - \gamma_{LS}}{\gamma_{LV}} \quad (1)$$

With,

γ_{VS} – Vapour/solid surface tension

γ_{LS} – Liquid/solid surface tension

γ_{LV} – Liquid/vapour surface tension

The spreading coefficient, S, can be defined as:

$$S_{L/S} = \gamma_{VS} - \gamma_{LS} - \gamma_{LV} \quad (2)$$

Lower values of θ and higher values of S are favourable for a good solder, i. e., the lower the surface tension of the molten solder (γ_{LS}) or the higher the surface tension of the pad (γ_{VS})

better is the wetting. Fluxes in soldering have the role to maximise the surface tension of the pad **[14]**. Any contamination on the surface of the substrate will act as a barrier to wetting. On pads that have oxide layer the solder will not wet the pad ($\theta > 90^\circ$; $S < 0$). If, however, the surface of the pad is clean and oxide free, the solder atoms can be closer to the substrate atoms and thus diffusion will occur forming an alloy layer, which ensures good electrical contact and good adhesion.

During their service lifetime solders are exposed to external conditions and factors that may affect their performance. Some of these factors are listed below.

Plastic deformation

Occurs when a solder suffers a mechanical or thermal stress, producing an irreversible plastic deformation. Usually initiated by shearing and it may proceed globally in the entire structure or locally in the grains depending on the stress level, strain rate, temperature and material characteristics. Strain hardening results from plastic deformation **[11]**.

Recovery and recrystallisation

Recovery is a softening process; the solder tends to release the stored strain energy. It is driven by thermodynamics and starts at a rapid rate, continuing at a slower rate. Recrystallisation occurs typically at temperatures one third to one half of the melting point of the material and involves a greater energy release from strained materials than recovery. New strain free crystal structures are formed through the nucleation and growth process **[11]**.

Stress fields

Stresses can be applied by various means, most metallic alloys are weaker in shear than in tension or compression. Shear is the most common stress in service life of solders.

Creep

Creep is a time-dependent and permanent deformation of materials when subjected to a constant load or stress and temperature. In metals, this phenomenon is considered important for temperatures greater than 0.4 of the melting temperature. Creep can lead to failure due to the long exposure of a constant load or stress, this can happen by microstructural and/or metallurgical changes: grain boundary separation; formation of internal cracks and voids **[15]**.

Fatigue

Fatigue occurs under alternating stresses. It usually starts as several small cracks that grow under repeated stresses, leading to failure. The stress that an alloy can tolerate under cyclic load is much less than that under static loading **[15]**. Low cycle fatigue (LCF) often occurs in solder joints because this type of failure normally is created from repeated stresses of thermal origins and follows the simplified Coffin-Manson relation **[16]**:

$$N_f(\Delta T)^{\gamma} = Cte \qquad (3)$$

With, N_f – Number of cycles to failure; ΔT – Range of the thermal cycle and γ – Constant, characteristic of the material (typically around 2)

3.1.2 Thermal aspects

In soldering one of the most important parameters is the soldering temperature (T_{sd}). As regarding T_{sd} there is a dilemma: the parts to be soldered should be heated to a temperature high enough to be wetted by the solder but on the other hand, the temperature that the components suffer during the assembly process should not be so high that can affect their operating characteristics. This issue has become more problematic with the introduction of lead-free solders. The components have to withstand temperatures higher than 217ºC (lead-free solder melting point), instead of 183ºC (lead solder melting point) with the eutectic tin/lead solders. Some components are not prepared for this process changeover and cannot stand the higher temperature demands (Fig. 5).

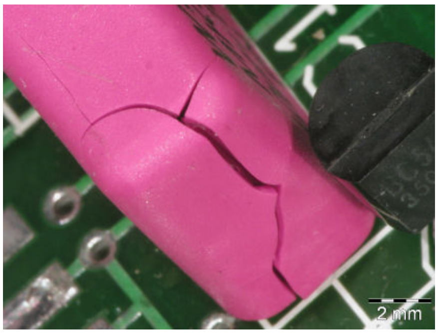


Figure 5 – Example of a capacitor that was not suited to lead-free soldering temperatures **[6]**.

Each component has its size, geometry, heat capacity and other characteristics that should be kept in mind. To achieve a good solderability over the whole board a well designed temperature profile has to be used, especially with lead-free and the consequent decrease of the process window. As can be seen in figure 6, the process window ΔT changed from 40-45ºC to 10-15ºC leaving almost no margin between the melting point and the damaging point **[8]**.

Lead-free solder have smaller process windows because the temperatures of the reflow soldering process are basically determined by the melting point of the solder alloy. For adequate soldering, every point in the board has to reach at least the melting point of the alloy. This means that we have to deliver at least 20ºC higher than the melting point for even distribution of temperatures. On the other hand, components have a maximum temperature that they can endure without damage. Thus, in the lead-free solders with higher soldering temperature the gap to max component temperature is decreased **[6]**.

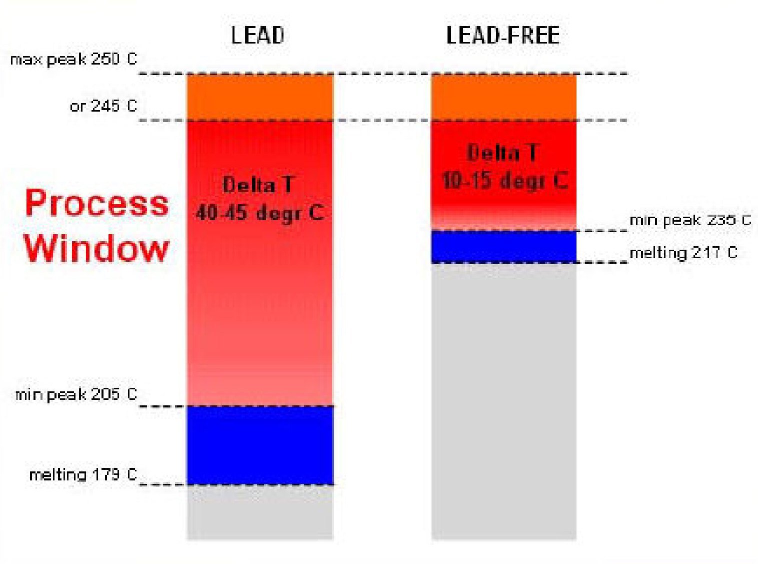


Figure 6 – Lead-free and lead soldering process window **[17]**.

Pre-heating is very important in all lead-free soldering processes in order to facilitate wetting, reduce contact time, prevent thermal shock from room temperature to soldering temperature and to activate the flux agent **[8]**. To avoid the thermal differences in the board pre-heat should be use in all processes (reflow, wave, selective soldering…).

Temperature profiling is essential in order to assure that the peak temperatures of the components are not being compromised. Using a set of thermocouples attached on the boards can give valuable information about the temperatures distribution among board, components and solder. This is an excellent tool for setting up the process.

3.2 Fluxes

One of the primary purposes of fluxes is to prevent oxidation in the base material (substrate). Solders can attach very well to copper (Cu), but poorly if copper oxide is present, which form quickly at high temperatures. Fluxes are to a large extent inert at room temperature, but become strongly reducing at high temperatures, mitigating the formation of metal oxides. The second objective of fluxes is to act as a wetting agent in the soldering process, increasing the surface tension of the substrate and promote wettability. And the third objective is to aid the heat transfer to the joint area.

Fluxes can be: water-soluble fluxes (no VOC's are required for removal) or rosin (also called colophony) fluxes. The water-soluble fluxes can be organic or inorganic; rosin fluxes can be: non-activated, mildly activated and activated. These last two fluxes contain rosin combined with an activating agent (an acid), which increases the wettability of metals by removing existing oxides. In the water-soluble fluxes cleaning is always necessary; in the rosin it depends on the “degree” of activation, some 'no-clean' fluxes which are mild enough do not require removal at all **[8]**.

3.3 Solder alloys

The use of soldering as a metallurgical joining technique dates back to the time of the Mesopotamian civilization (4000 BC). It was later borrowed by the Romans for their aqueducts. Use of lead (Pb) based solders in plumbing and other areas continued through the centuries due to its versatility. In the modern era, the main applications of solder are in plumbing and in electronics packaging, in which the solder joint acts as electrical, mechanical and thermal connectors, their reliability is very important for the whole functionality of the product.

Solders based on the tin/lead eutectic possess a desirable combination of these attributes, and because both tin (Sn) and lead (Pb) have high availability and are relatively inexpensive, they have been the most used solders. However, in the past years, the demand to find an alternative solder without lead has accelerated due to various reports on the harmful effects of lead on the environment that has resulted in legislation to regulate lead usage. Various tin based solders are been investigated for replacement. Some characteristics that need to be satisfied are e.g. **[11]**:

- Low melting points to prevent component damage during soldering;
- Good wettability on the substrates and metallisations for proper joint formation;
- Good electrical conductivity;
- Good strength and ductility for solder joint integrity.

One of the best performing and now fully commercialised alloys are the Sn/Ag/Cu ternary alloys.

3.3.1 Alloys

Lead containing solders have been used extensively in microelectronic applications to form electrical interconnections between packaging levels, to facilitate heat dissipation, to provide mechanical/physical support and to serve as a solderable surface finish layer on PCB’s and lead frames **[18]**. This wide use of lead containing solders is due to the low melting point of the tin (Sn)/lead (Pb) alloy (183ºC), good wettability, good mechanical and electrical properties, and relative low cost.

As mentioned before, due to European restrictions lead has been banned from solder alloys and a new era has begun. The demand for new lead-free alloys was a priority concern and several alloys were tested and are currently being experimented. Compared to the tin/lead eutectic or near-eutectic composition, the lead-free alloys had to be produced in a (Sn) based system, a minimum of 60 weight percent of tin, due to practical issues. These issues include metallurgical bonding capability on substrates, wetting ability during reflow process, alloying between elements, natural resources availability, manufacture, toxicity and cost. Some studies showed that 0.5% and (Ag) at 3% in the Sn/Ag/Cu ternary system produced significant effectiveness in lowering the melting point, (Cu) at 0,5% alone reduced the melting point by around 4ºC and (Ag) at 3% 10ºC.

Since the discovery of alternatives to lead containing solders the research in this area has increased significantly. New ternary and quaternary systems containing new elements like zinc (Zn), nickel (Ni), bismuth (Bi) and indium (In) have been used and tested. In the following table some examples of solder alloys commercially used are presented:

Table 2 – Examples of commercial solder alloys compositions and their melting points **[6]**.

Solder	Alloy	Melting Point (ºC)
Lead	63Sn/37Pb	183
	60Sn/40Pb	183-187
	62Sn/36Pb/2Ag	179
Lead-free	96.5Sn/3.5Ag	221
	99.3Sn/0.7Cu	227
	96.3Sn/3.2Ag/0.5Cu	217-218
	96Sn/3.8Ag/0.7Cu	218

3.3.2 Metallurgy

Lead alloys

Alloys of this simple eutectic system are composed of primary dendrites of either tin-rich or lead-rich solid solution surrounded by eutectic. As shown in figure 7, the eutectic occurs at 61.9% tin (183ºC) and consists of lead-rich and tin-rich phases either lamellae or globules, depending on the solidification rate. The higher the solidification rate the greater the probability of formation of a globular eutectic. These solders have relatively fast solid state reactions with other elements such as copper, leading to the formation of intermetallic compounds in the vicinity of the solder.

As can be seen in the tin/lead binary phase diagram (Fig. 7), molten eutectic tin/lead solder during solidification separates into two different solids, a lead-rich phase and a tin-rich phase. The resulting microstructure is shown in figure 8.

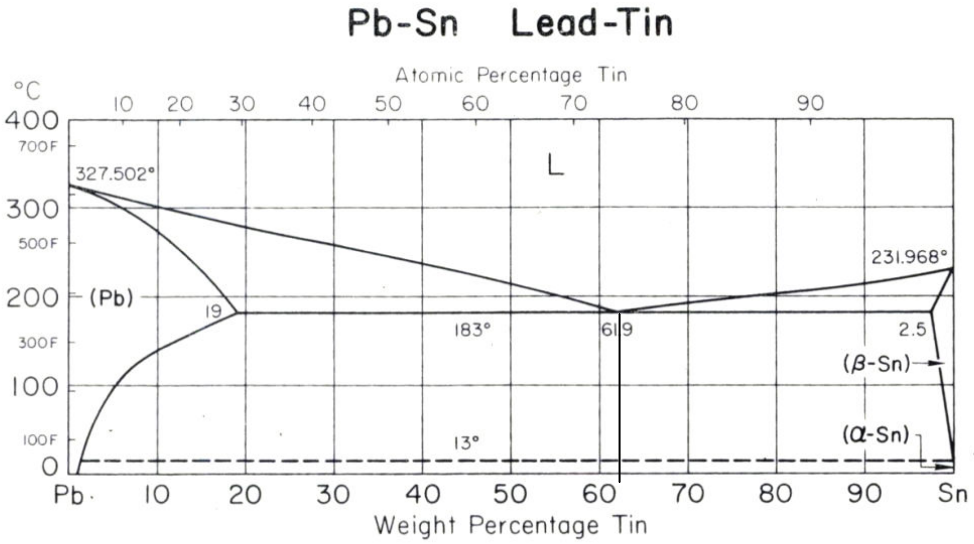


Figure 7 – Lead/tin phase diagram **[19]**.

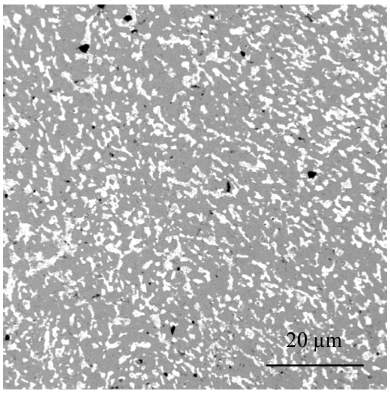


Figure 8 - Eutectic tin/lead microstructure SEM image (1700X) at moderate to rapid cooling rate. Bright areas are Pb-phase and darker areas are Sn-phase **[20]**.

Sn/Ag/Cu alloys

Tin/silver eutectic formation is very important for lead-free solders in electronic industry. As shown in the phase diagram (Fig. 9), the eutectic composition for this alloy is located at 96.5 wt% (Sn) and 3.5 wt% (Ag), with a melting point of 221ºC.

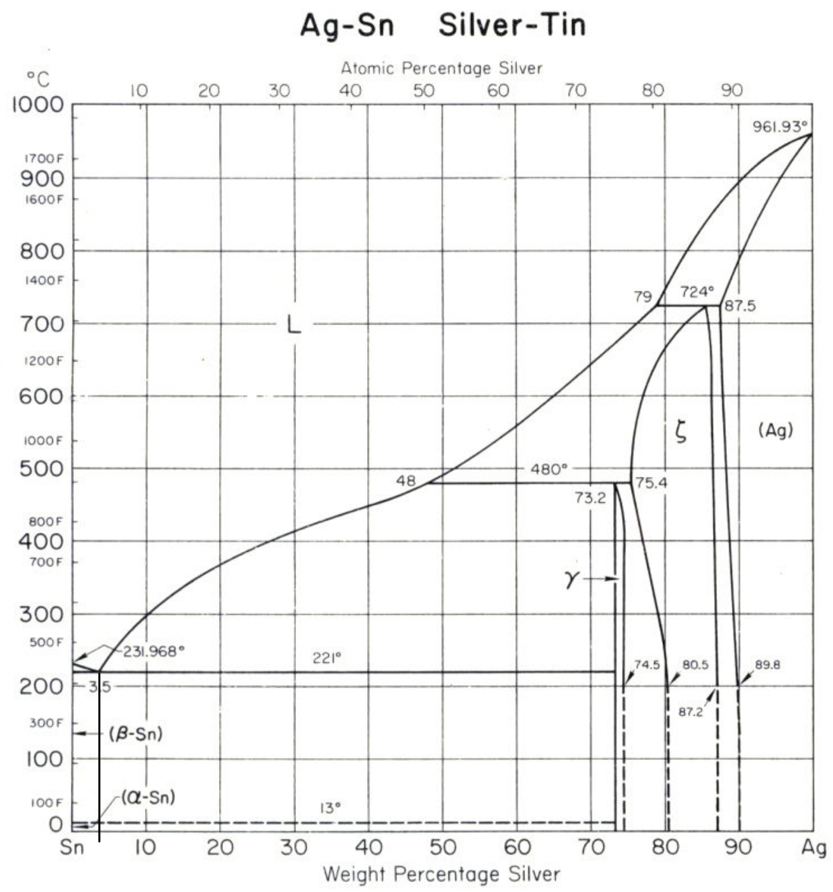


Figure 9 – Tin/silver binary phase diagram **[19]**.

During solidification, when the temperature reaches below the eutectic tie-line, the (Sn) solid phase and γ intermediate phase form heterogeneously together from the liquid (L).

$$L(96.5\%Sn)\xrightarrow{221^{\circ}C}\beta-Sn(100\%Sn)+\gamma(73.2\%Sn) \qquad (4)$$

As the (Sn) phase grows, the excess (Ag) atoms in the liquid are rejected from the tips of the (Sn) phase, and will diffuse laterally in a short distance to the γ phase (Ag_3Sn). On the other hand, the excess of (Sn) atoms rejected from the γ phase will diffuse to the tips of the near (Sn) phase. In the image is shown a schematic illustration of the process.

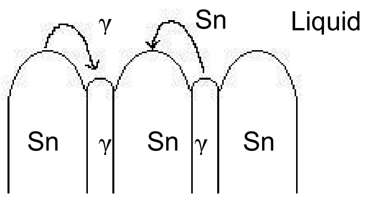


Figure 10 – Illustration of Sn/Ag eutectic solidification.

The (Sn) phase in the eutectic composition 96.5 Sn/3.5 Ag predominates over the γ phase; the (Ag) solute is dissolved in the (Sn) phase due to the longer distance to the γ phase. The (Ag) enrichment in the liquid (the ones that do not incorporate the γ phase) may cause constitutive super-cooling and lead to the formation to dendrites, with γ phase growing between the dendrite arms.

Another important eutectic formation for the solder alloys is the tin/copper eutectic. This eutectic is located at 99.3 wt% (Sn) and 0.7 wt% (Cu) with a melting point of 227ºC (Fig. 11). As previously discussed, this alloy also has a eutectic transformation similar to the Sn/Ag eutectic.

$$L(99\%Sn) \xrightarrow{227^{\circ}C} \beta - Sn(100\%Sn) + \eta(60.9\%Sn) \qquad (5)$$

The η corresponds to the Cu_6Sn_5 phase at 45.45 at% (Sn).

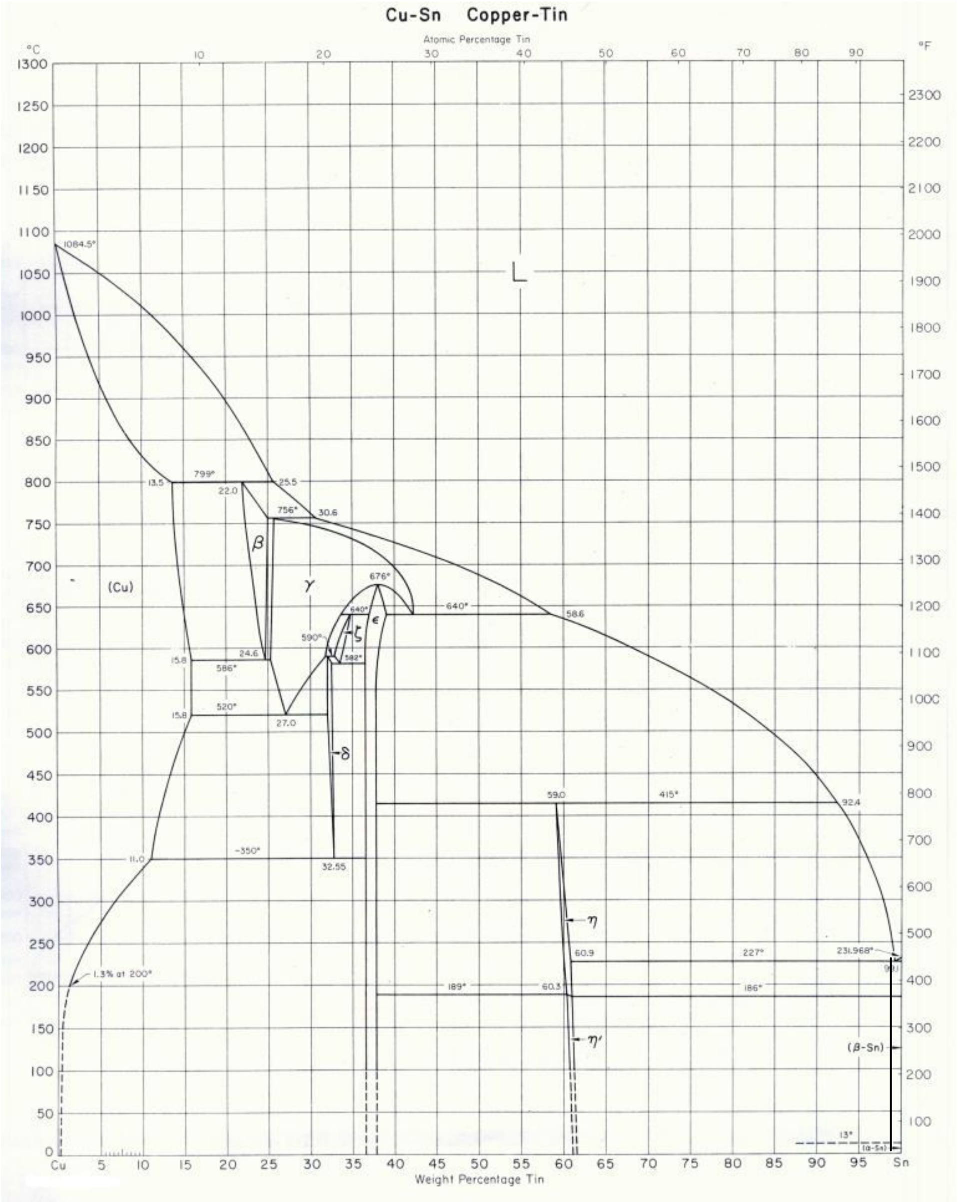


Figure 11 – Tin/copper binary phase diagram **[19]**.

In accordance with the binary phase diagrams, there are two possible binary eutectic reactions in the Sn-rich region of the ternary system Sn/Ag/Cu. These reactions are shown in the circle on the ternary phase diagram of figure 12. Copper reacts with (Sn) to form a eutectic structure of Sn-matrix phase and η intermetallic compound phase (Cu_6Sn_5) at 227ºC. A reaction between (Ag) and (Sn) forms a eutectic structure of Sn-matrix phase and γ intermetallic phase (Ag_3Sn) at 221ºC. Finally, (Sn) solidifies in the end leading to the ternary invariant eutectic point U_7. (Ag) also reacts with (Cu) to form a eutectic structure of Ag-rich α phase and Cu-rich α phase at 779ºC. However, this transformation is not detected in the solidification, is thermodynamically favourable for (Ag) or (Cu) to react with (Sn) to form the presented intermetallic compounds. The ternary solder alloy Sn/Ag/Cu consists of a Sn-matrix phase, γ intermetallic phase (Ag_3Sn) and η intermetallic compound phase (Cu_6Sn_5) **[11]**.

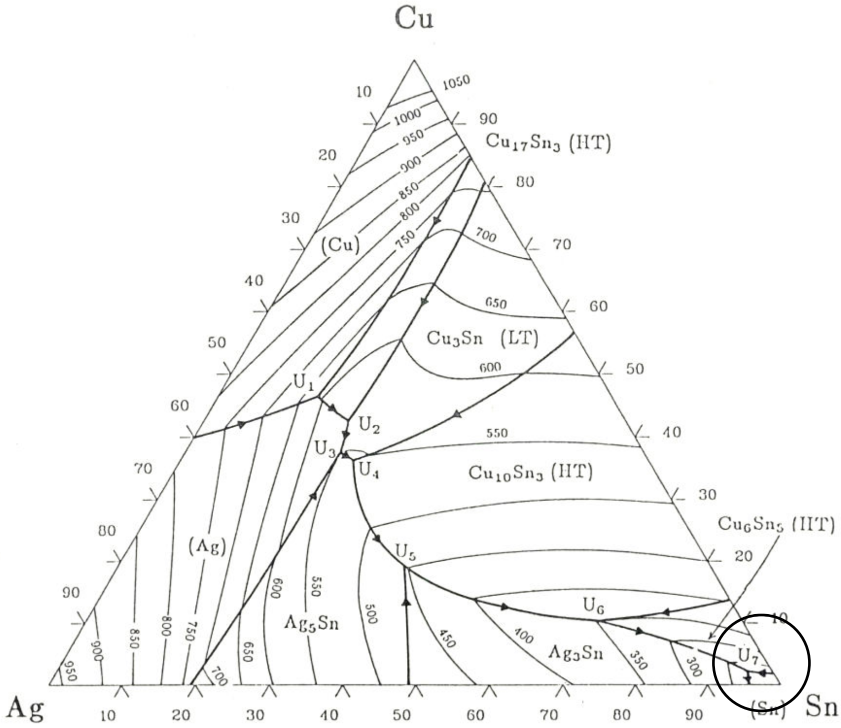


Figure 12 – Tin/silver/copper ternary phase diagram **[21]**.

In terms of mechanical behaviour, in the Sn/Ag/Cu solders the thermomechanical strains will concentrate near the pad interfaces creating regions of high plastic deformation. In these regions the (Sn) phase will recrystallise above room temperature, producing fine grains that are more susceptible to creep deformation (grain boundary sliding or cracking) than the initial microstructure. Thus, providing an easy path for crack propagation during thermo cycles and decreasing the thermal fatigue life. In the Sn/Pb solders the fractures appear on the same locations but due to the microstructural coarsening of the (Sn) and (Pb) phases near the interface, leading to a local softening and to fatigue crack propagation **[18]**.

3.3.3 Intermetallics

In the soldering process there are interfacial reactions between two different materials. When the solder touches the pad, two reactions take place at the interface solder/base material (joint):

- Dissolution of the base material into the molten solder;
- Formation of an interfacial reaction product, consisting of one or more elements from each of the solder and base material compositions.

Liquid dissolution interfacial reactions stop upon solidification of the solder but can continue to develop in the solid state, through solid-state diffusion, at a slower rate. From these solid-state reactions, intermetallic compound layers result at the interface.

An intermetallic compound is one type of intermediate phase that is a solid solution with intermediate ranges of composition. Intermetallic compounds may form when two metal elements have a limited mutual solubility. These compounds possess new compositions of a certain stoichiometric ratio of the two component elements for a binary system. The new phases have different crystal structures from those of their elemental components. The properties of the resulting intermetallic compound generally differ from those of the component metal, exhibiting fewer metallic characteristics, such as reduced ductility, reduced density and reduced conductivity **[11]**. Figure 13 shows an optical micrograph of the solder/pad interconnection. It can be seen the formation of Cu_6Sn_5 in the copper interface, followed by the formation of acicular Ag_3Sn plates.

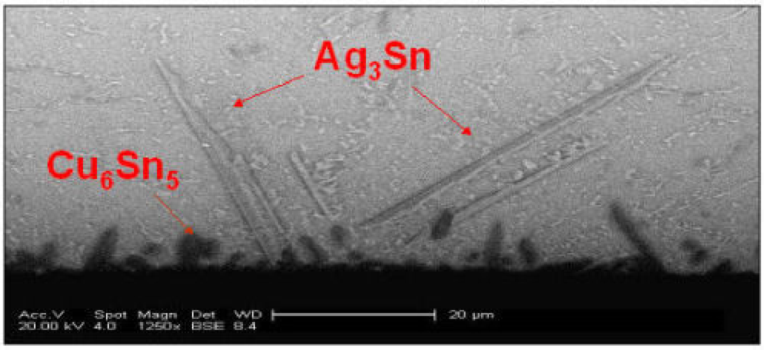


Figure 13 – Solder/pad interconnection. Intermetallic formation **[22]**.

The relatively hard Ag_3Sn and Cu_6Sn_5 particles in the Sn-matrix of Sn/Ag/Cu alloys can strengthen the alloy through the building of long-range internal stress. These hard particles can also serve as the most effective blocks for fatigue crack propagation. The formation of these particles can lead to finer grains, the finer the intermetallic particles are, the finer the microstructure will be. This facilitates the grain boundary gliding mechanisms leading to extended fatigue lifetime under elevated temperatures. The thin intermetallic layers provide the necessary permanent bond with the substrate, acting as “fixation phase”. However, if the intermetallic layers become thicker the mechanical properties of the solder joint will weaken, due to the brittle nature of the compounds and to the difference of the thermal expansion between the intermetallics and the bulk solder. This can lead to internal stress development, resulting in crack formation along the solder/substrate interface. Optimum thickness is expected to be in the range of 1 to 5 micron. **[11]**

A nickel barrier can be applied over the copper substrate to control the (Cu) dissolution and intermetallic compound growth. This will lead to different reactions. If the (Cu) pads are protected with an OSP coating, this one will vaporize on reflow allowing the solder to touch the bare (Cu) and form the intermetallics described above. When the pads are protected with an ENIG (electroless nickel/immersion gold) finish, the (Au) gold dissolves and migrates into the solder promoting the intermetallic layer formation between (Sn) and (Ni) – Ni_3Sn_4 or ternaries $(Cu, Ni)_3Sn$, $(Cu, Ni)_6Sn_5$. Literature presents the following relationships **[23]**:

- Hardness ($HV_{0.2}$: GPa) - $(Cu, Ni)_3Sn$ (5.5) > $(Cu, Ni)_6Sn_5$ (4.9) > Cu_6Sn_5 (4.6) > Ni_3Sn_4 (4.3) > Ag_3Sn (1.4).
- Poisson ratio - Ag_3Sn (0.35) > Cu_6Sn_5 (0.32) > $(Cu, Ni)_6Sn_5$ (0.30) > $(Cu, Ni)_3Sn$ (0.27) > Ni_3Sn_4 (0.27).
- Young’s Modulus (GPa) - $(Cu, Ni)_3Sn$ (152) > $(Cu, Ni)_6Sn_5$ (100)> Ni_3Sn_4 (58)> Cu_6Sn_5 (57)> Ag_3Sn (55).

The Hardness and Young’s Modulus for the Sn/Ag/Cu solder are 0.16 GPa and 50GPa, respectively.

Ternary intermetallic compounds like $(Cu, Ni)_3Sn$ and $(Cu, Ni)_6Sn_5$ are hard and brittle but appear only on second reflows and are not usually observed. The Ag_3Sn, Cu_6Sn_5 and Ni_3Sn_4 (with (Ni) barrier present) are more common. From the relationships above, in comparison with the solder properties these intermetallics present harder and more brittle properties, which represent weaker zones in the structure. Due to its elongated plate-like shape, the A_3Sn presents more damage in case of excess. This intermetallic nucleates in front of the Cu_6Sn_5 layer and can grow rapidly during cooling. The structural differences between the (Sn) and Ag_3Sn will induce a strain at the boundary between them, leading to a preferential crack-propagation path, especially when the Ag_3Sn plates are aligned in the direction of the crack propagation **[24, 25]**.

3.4 Electronic components

Electronic components are basic electronic elements usually packaged in a discrete form with two or more connecting leads or metallic pads. Components are connected together by being mounted on a PCB. The simplest components can be divided in passive and active components. Of the passive components some of the most used are:

Capacitor or condenser

A capacitor is an electrical device that can store energy in the electric field between a pair of closely spaced conductors called plates. When current is applied to the capacitor, electric charges of equal magnitude, but opposite polarity, build up on each plate **[26, 27]**.

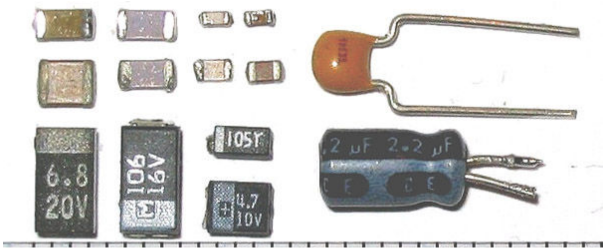


Figure 14 – Capacitors components. At top left: SMD ceramic; at bottom left: SMD tantalum; at top right: through-hole tantalum and at bottom right: through-hole electrolytic **[26].**

Resistor

It is a two-terminal electronic component that resists an electric current by producing a voltage drop between its terminals. The electrical resistance is equal to the voltage drop across the resistor divided by the current through the resistor, according to the Ohm’s law (R = V/I) **[26, 27]**.

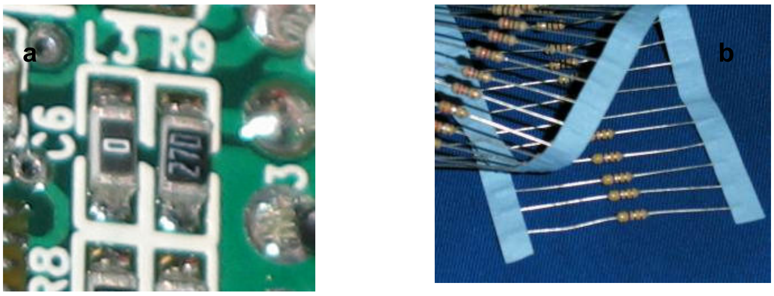


Figure 15 – Resistor components. a) surface mount resistors. b) through-hole resistors **[26]**.

In the active components parts the integrated circuit is the most commonly used, but others also exist:

Diode

It allows an electric current to flow in one direction, but blocks it in the opposite direction. Circuits that require current flow in only one direction typically include one or more diodes in the circuit design **[28, 29]**.

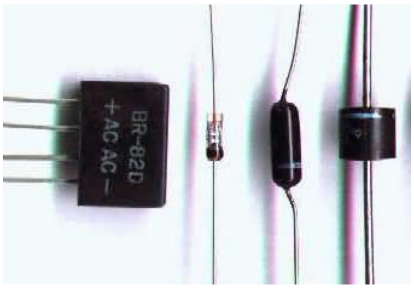


Figure 16 – Different types of Diodes **[26]**.

Transistor

A transistor is a semiconductor device, normally used as an amplifier or an electrically controlled switch. The transistor is the fundamental for the operation of computers, cellular phones, and all other modern electronics **[28, 29]**.

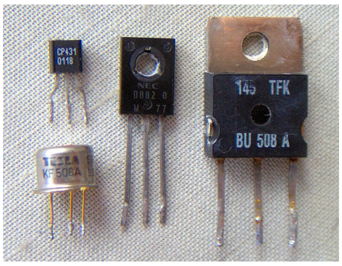


Figure 17 – Types of transistors **[26]**.

Integrated circuit (IC)

It is a miniaturized electronic circuit consisting mainly of semiconductor devices and passive components. Integrated circuits are often classified according to the number of transistors and other electronic components they contain **[26, 27]**.

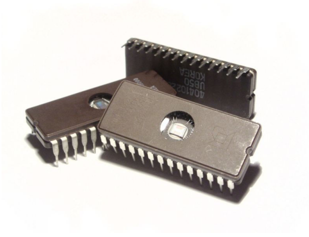


Figure 18 – Example of Integrated Circuits **[26]**.

3.5 Industrial soldering processes

There are at least two steps that a board must undergo before the soldering stage: printing and component placement. Figure 19 shows an integrated manufacture line for electronic boards.

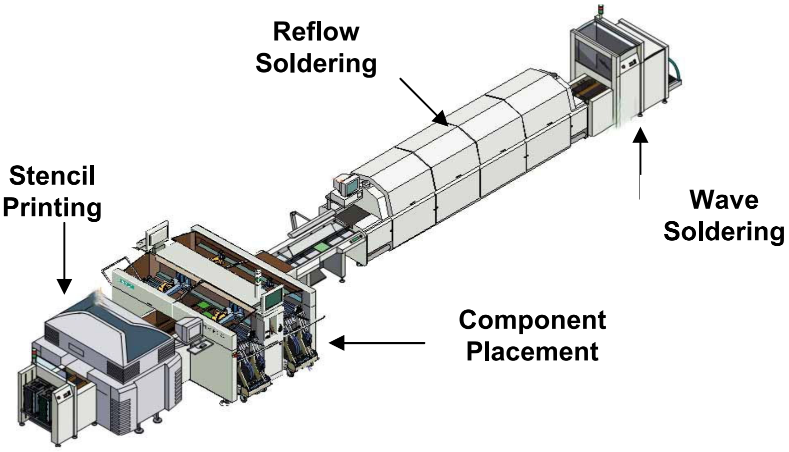


Figure 19 – Illustration a PCB manufacture line **[6]**.

Printing

The board is placed under a stencil that has small apertures that match the pads on the board. The solder paste is applied on the top of the stencil and a squeegee blade spreads it over the stencil, the paste enters the small apertures and is deposited on the specified pads. The paste is made from small solder particles that when they are exposed to a solder profile will heat up, melt, coalesce and form the final joint after cooling. The paste provides some adhesive qualities (tackiness) during transportation of the board before soldering to prevent component loss or dislocation. A fluxing agent is incorporated into the paste, in order to clean the lead, pad and the solder particles.

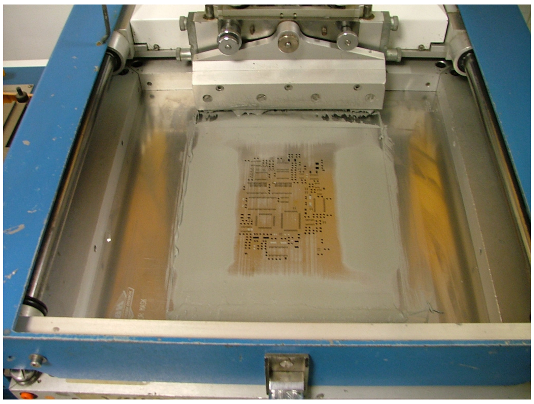


Figure 20 – Stencil printing machine **[6]**.

Component placement

In the component placement stage, robotic machines (pick-and-place machines) are used to place surface mount devices (SMDs) in the pads of the PCB that already have solder paste. These machines are used for high speed, high precision placement of a whole range of electronic components, like capacitors, resistors, integrated circuits.

Figure 21 – Component placement machine **[6]**.

Soldering processes can be divided in the methods that involve application of solder and heat simultaneously to the parts to be soldered like wave soldering, and the reflow method in which the solder and the heat are applied separately. In the reflow method the heat can be local (LASER, hot gas, hand soldering) or can be general (hot air convection, infra-red radiation, a combination of both, vapour phase) **[8]**.

3.5.1 Reflow soldering

After the component placement on the pads (with the paste) the boards will move in a conveyor to the reflow machine (oven). The ovens produce heat by radiation through ceramic infra-red heaters, it may also have fans to force heated air to the assembly which is called infra-red convention ovens. Normally, the reflow ovens are divided in the following zones: pre-heat, soak, reflow and cooling, following the same stages of a temperature profile. Reflow ovens from 4 to 12 zones are available on the market.

Pre-heat

During the pre-heat the volatile material in the paste will evaporate as well as starting the initial cleaning action of the flux that is in the paste. It prepares the board to have the minimal temperature differential on the board surface before going into soak zone, because when a PCB with components enters the reflow oven it is at ambient temperature, around 18-20ºC, and some components have a 3-4 ºC/s rise temperature limit. The temperature in pre-heat zone should be between 80-150ºC.

Soak

This zone should be considered as a continuation of the pre-heat zone. During the pre-heat some areas on the surface of the board will heat up faster than others, due to materials thermal conductivities and geometry/size, it can be seen differences of 10-15ºC under some components. The soak zone allows an even distribution of temperatures on the surface of the board.

Reflow

The reflow zone is where the temperature rises over the liquidus temperature of the solder paste, normally 217-221ºC for lead-free alloys. To avoid excessive heat on the board and degrade the components, the aim is to reflow in the shortest time possible, within 30 second, and still produce reliable joints.

Cooling

When all the joints have soldered, the board moves out of the heating zones, begins to cool naturally and the solder will solidify. The solder should not be in the liquid state when the board exits the oven, because that can cause component displacement. Some blowers/fans are used to blow ambient air to speed up the cooling. Nitrogen and refrigeration systems may be also used to reduce the oxygen content inside the oven, leading thus to less oxidation, and to increase the rate of cooling. Faster cooling rates after reflow can reduce the intermetallic layer at the joint interface. The thicker the intermetallic layer the weaker this joint is proven to be **[8, 9]**.

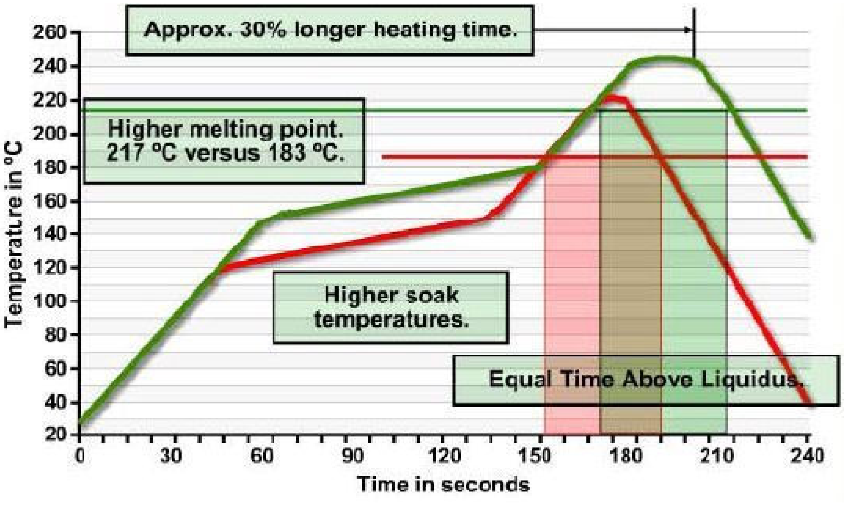


Figure 22 – Reflow time temperature profile. Comparison between Sn/Pb (red) and Sn/Ag/Cu (green) **[17]**.

The reflow ovens also have fume extraction. During reflow fumes can evaporate from the paste, the printed board substrate and the masking on the surface of the board. The extraction ports are positioned in the pre-heating and reflow zones.

3.5.2 Wave soldering

Wave soldering uses a pot with molten solder, the components are placed on the PCB and pass through a wave of solder, which is pumped from the pot. Wave soldering is used for both through-hole and surface mount printed circuit assemblies. For through-hole, the PCB touches the “cascade” of molten solder and by capillarity the solder rises through the holes and will form the joints (Fig. 23). In the case of SMDs, the components are placed with adhesives on the PCB surface before being run through the molten solder wave.

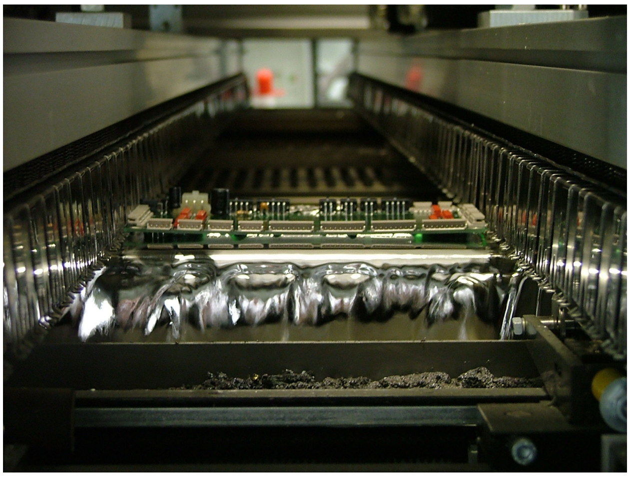


Figure 23 – Wave soldering. A board passing through the molten wave of solder **[6]**.

A standard wave solder machine consists of three zones: the fluxing zone, the pre-heating zone and the soldering zone. An additional zone, cleaning, can be used depending on the type of flux used.

Fluxing

The flux can be applied by foam or spray. Correct application in terms of quantity and dispersion is very important for the wave soldering process.

Pre-heating

To avoid thermal shock on the board due to the differences between the room temperature and the molten solder temperature, a zone of infra-red heaters are introduce prior to soldering. The top of the board should reach a minimum of 100ºC before passing over the solder wave.

Wave soldering

A good support on the board is necessary to prevent sagging. For lead-free the solder temperature should be within the range of 260-270ºC. There are several types and shapes of waves that can be used for single and double waves. In the double waves we have T-waves, extended waves (lambda waves…), this is all related to the form of the wave. A double wave should be used when SMDs are to be soldered in the bottom of the board. Hot air knife can be added to the double wave machines. This apparatus consists in projecting a stream of hot air to the board after the wave. In this way bridges and spikes are removed **[8]**.

3.5.3 Hand soldering

The hand soldering of through-hole component termination is still very common for small volume PCB assemblies and for components that cannot go through reflow or wave soldering. It is also used in rework of the PCB to substitute damaged components **[9]**. A soldering iron is used to melt the solder that comes in a wire. This wire may or not have a flux core. The component is placed on the pad and then the soldering iron melts the cored wire to wet the joint. Then, the tip is wiped clean on a moist sponge and tinned with cored solder wire to improve heat transfer and prevent corrosion. The same process can be used for desoldering but instead of using a cored wire, a copper solder wick is used. This process is illustrated below.

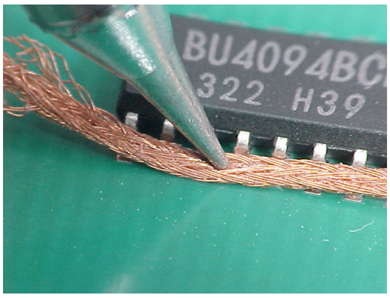


Figure 24 – Desoldering using a copper solder wick/braid **[6]**.

With the transition to lead-free solders the temperature on the tip has increased and is normally 315 – 426 ºC. Due to the poor heat transfer the temperature of the soldering iron has to be 40ºC above the melting point of the solder, but the higher the temperature the faster the oxide formation on the tip and the dewetting of the tip. Therefore, the temperature should be the lowest possible.

One of the problems in lead-free hand soldering is the deterioration of soldering iron tip (vd. Fig. 25). This is caused by the high tin content of the solders, the molten tin reacts with almost every metal, so the soldering iron have a big probability to be eroded after two or three months in permanent use. In order to increase lifetime, soldering irons tips have to be coated with special materials (iron, nickel and chrome coatings are used) **[8, 9]**.

Figure 25 – Erosion of a soldering iron tip due to high contents of tin **[26]**.

3.5.4 Other soldering processes

Some of the “alternative” soldering methods are now briefly described:

Vapour phase reflow

This machine uses the high heat transfer rate from the vapour of a fluid to reflow the solder. The board enters in a chamber with the vapour which condensates on the board and transfer the heat to it, the fluid acts together with flux and improves the wettability. The vapour phase soldering has a uniform type of heating in an inert atmosphere and is most suited for complicated products, e.g. with a mix of large and small components. Some defects like component lifting and displacement may arise because as the vapour condenses on the surface of the board and turns to liquid, component movement can occur **[8]**.

Selective soldering

This process has the same principle as the wave soldering process. It incorporates a table that can move in all directions (x-y-z), which manipulates the PCB over a focused flux spray and a pin-point solder fountain (Fig. 26). The system can contain several solder fountains, located according to the x-y positions of the pins to be soldered. These systems offer flexibility and the ability to expose only desired regions of the board to flux, solder and heat **[6]**.

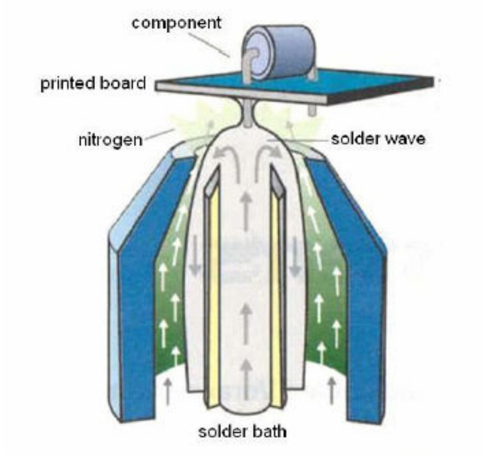


Figure 26 – Illustration of the solder fountain functionality in selective soldering **[6]**.

3.6 Solder joints

3.6.1 Joint defects

In this sub-section some of the most common "defects" that can be found in lead and lead-free assembly processes will be presented, as well as some possible reasons and action to take, in order to mitigate them. Some of the examples that will be presented are not considered as defects by IPC-610-D Standard, but for simplifications purposes it shall be include this "abnormalities" in the defect section. The IPC-A-610-D standard presents acceptance requirements for the manufacture of electronic assemblies. It is a manual that includes detailed information, pictures and illustrations portraying what is or not expected to encounter on an electronic product. This standard specifies 3 classes of acceptance criteria **[28]**:

- Class 1 – General electronic products. Includes products suitable for applications where the major requirement is function of the complete assembly;
- Class 2 – Dedicated service electronic products. Includes products where continued performance and extended life is required, and for which uninterrupted service is desired but not critical. Typically the end-use environment would not cause failures;
- Class 3 – High performance electronic products. Includes products where continued high performance or performance on demand is critical, equipment downtime cannot be tolerated, end-use environment may be uncommonly harsh, and the equipment must function when required, such as life support or other critical systems.

The most common defects that can be found are described bellow:

Solder shorts

The boards and components are getting smaller, and with this also is the distance between components and terminations. This effect appears mostly in wave processes in which the solder does not separate from two or more leads before the solder solidifies creating a short. An example of this defect can be found in figure 34 b). Increasing the flux quantity, optimise pre-heat, adjust process (speed) can help to mitigate this problem **[29]**.

Solder balls

Solder balls on the topside of the board after reflow processes can be caused by the incompatibility between the solder resist and solder paste. Solder resist affects the mobility of the paste in the liquid state during reflow, as the paste reflows and coalesces, some small parts of the solder do not flow back to the joint (Fig. 27). It also can be due to poor flux pre-heating **[29]**.

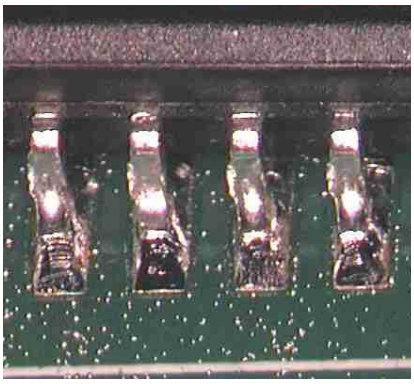


Figure 27 – Solder balls defect. **[28]**

Voids

Most of the voids are caused by moisture that becomes water vapour during the soldering process and expands, sometimes voids can come out of solder while the solder is in the liquid state, producing blow holes or non metallic material that is trapped in the printed board and it is not displaced during the soldering. Voids can be seen mostly on the base of the board because the solder solidifies firstly on the top and entraps them there. It reduces the joint strength but it is not necessarily a reliability issue, if not in excess. A good humidity storage control and baking the boards before soldering can eliminate the moisture **[29]**.

Figure 28 shows an X-ray image of SOT23 (Small Outline Transistor) solder joints after reflow on a lead-free production line, where it can be seen the voids in the solder.

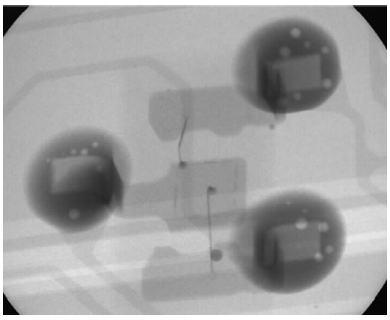


Figure 28 – X-Ray image of a SOT23 presenting voiding on all the joints **[29]**.

Poor or incomplete filling

The hole is poorly filled or is not filled completely, the IPC standard states that 75% of the hole must be filled (Fig. 29). There are some possible reasons for this but the most common are fluxing and heating issues **[29]**.

Figure 29 – Examples of poor wetting defects. a) poor wetting. b) Incomplete fill. **[28]**

Secondary reflow

This defect may appear in lead-free processes if tin/lead is used on the PCB or on the components. This composition does not dissolve easily into the lead-free solder, so the layer at the interface will have a significant amount of tin/lead. Separation occurs when the previously reflowed board is exposed to a temperature of 180ºC or a second reflow, not high enough to reflow the lead-free solder joints but sufficient for the tin/lead interface. The X-ray image shows separation of J lead terminations with lead-free solder. This type of failure mode can be caused by lead contamination from the PCB or termination plating **[29]**.

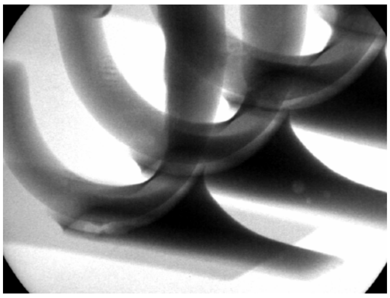


Figure 30 – X-ray image of second reflow on J-lead component. **[6]**

3.6.2 Inspection and characterisation techniques

The inspection and characterisation can be made through optical and/or electronic microscopy. The optical inspection is done through an optical microscope following the requisites of the standard IPC A-610-D class 3 and aims to determine the quality of the joints with respect to visual defects. The characterisation of solder joints implies the preparation of the samples for inspection. That process includes the micro-sectioning of the components, mounting in resin, grinding and polishing. Only then the sample is ready to be observed in the SEM (Scanning Electron Microscope). This equipment allows seeing all the internal and metallurgical defects present on the solder joint.

In SEM the surface of the specimen is examined with an electron beam and the back scattered electrons are collected and used to generate a sign that will display an image on a monitor, through the cathode ray tube. The specimens have to be electrically conductive. If it is not the case a thin gold surface coating must be applied on the samples. Besides the high magnification range (up to 5nm) it also allows qualitative and semi-quantitative analysis of the elemental composition of localised regions **[12, 13]**.

Another method of assessing the defects in a continuous and easier way is the procedure for monitoring the PPM (parts per million) defect levels in the four assembly stages. Assemblers take sample boards after each of the assembly stages and inspect them accordingly with the requirements of IPC-A-610-D class 3.

The minimum of 5000 opportunities in each of the following processes have to be taken, which may require additional boards or panels to be inspected if the minimum number of opportunities is not achieved. Number of opportunities means the number of possible failures in each process.

Solder paste printing

In this case, the opportunities for error to be determined are based on the number of stencil apertures printed in the samples.

$$\frac{Number\ of\ defective\ print\ deposits}{Total\ number\ of\ printed\ apertures} \times 1{,}000.000 = PPM\ Level \qquad (6)$$

Component placement

The opportunities for error to be determined are based on the number of components placed on the printed board samples.

$$\frac{Number\ of\ placement\ defects}{Total\ number\ of\ components\ placed} \times 1{,}000.000 = PPM\ Level \qquad (7)$$

The defects considered after placement are not limited to misalignment they may include missing, reversed or damaged components. Reference should be made to the relevant sections of IPC-A-610.

Reflow soldering

The opportunities for error to be determined are based on the number of reflowed solder joints produced in the sample.

$$\frac{Number\ of\ defective\ solder\ joints}{Total\ number\ of\ reflowed\ joints} \times 1{,}000.000 = PPM\ Level \qquad (8)$$

The defects considered after reflow are not limited to solder shorts or opens, they may include insufficient paste, solder balls, damaged components etc. Reference should be made to the relevant sections of IPC-A-610.

Wave soldering

The opportunities for error to be determined are based on the joints that are wave soldered in the sample.

$$\frac{Number\ of\ defective\ solder\ joints}{Total\ number\ of\ wave\ soldered\ joints} \times 1{,}000.000 = PPM\ Level \qquad (9)$$

The defects considered after wave soldering are not limited to insufficient solder penetration and solder shorts, they may include lifted parts, solder balls and solder skips. Reference should be made to the relevant sections of IPC-A-610 **[28]**.

3.7 Reliability Testing

Reliability is stated as the characteristic expressed by the probability that the part will perform its intended function for a specific period of time under defined usage conditions **[30]**. A product has two principal failure modes (Fig. 31), early failures – failures that occur in the early time of operation and wear out failure – failure that occurs in the end of life of the product. Between these two stages there is a small but finite probability that a failure can occur, but it is the early failures that are more important and are due to reliability factors. It is on this stage that manufacture errors are more prone to emerge. The wear out failure is due to simple ageing and use of the product.

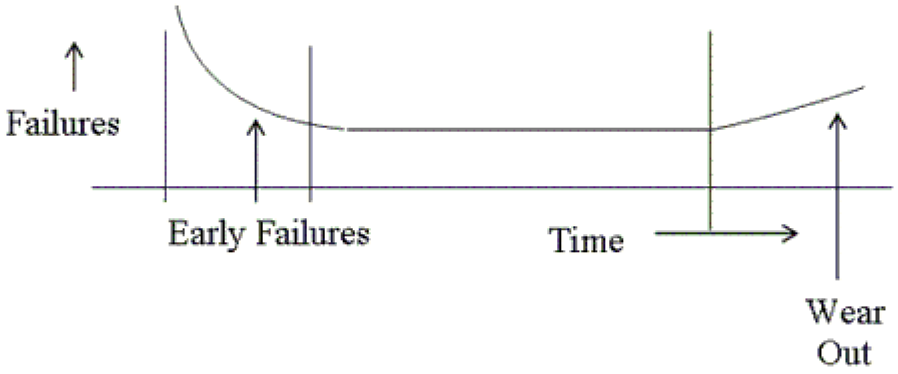


Figure 31 – Graphic showing the evolution of failures in time **[30]**.

In the case of lead-free solders, one of the most important questions is the behaviour of these materials under conditions of thermomechanical fatigue (TMF). This phenomenon is well known in the tin/lead solders but in the case of the lead-free ones the reality changes. It was found that TMF vary with component type and thermal cycling conditions for these alloys. The basic reliability concern in surface mount technology is the reliance on the solder joints to provide both mechanical and electrical interconnection of components to the substrate under conditions of cycle fatigue. Under cyclic thermomechanical strains and stresses the joints develop fatigue cracks that eventually may lead to failure. One of the principal causes of failure is the fatigue damage accumulation in the solder from cyclic thermal expansion and contraction, due to the differences in the coefficient of thermal expansion of the parts **[11]**.

CHAPTER FOUR

Lead-free process validation of commercial solders in industrial boards

4.1 Introduction

In this chapter information is presented about the boards that were studied as well as all the results extracted from the assembly process, visual inspection, reliability tests, optical and electronic microscopy of the sectioned samples. Due to confidentiality reasons some information about the boards is not presented. All the boards previously described were inspected and tested. The most relevant data is now present in the following sub-chapters.

4.2 Soldering of industrial boards

Several companies contributed to the study with their own products. Images of the boards are presented in Annex I. Information about the boards used in the present work will be presented in the next paragraphs:

Board A

This product, part of a video monitor unit, is a single sided through-hole circuit board, with both leaded and surface mount components. Surface mount components were placed on the board using reflow cured adhesive and then soldered along with the leaded components by wave soldering. Table 3 presents the soldering data of board A.

Table 3 – Summary of the board A soldering trials data.

Tin/Lead				
Process	***Alloy***	***Flux***	***Process Data***	***Board***
Wave	63Sn/37Pb	No clean, rosin free Alpha Metals E191/1	250°C	OSP coated
Lead - Free				
Wave	SN100C Sn/Cu/Ni	Water-based, VOC free, spray DKL Metals E-Qual 355 flux	266°C (two waves)	OSP coated

Board B

This product, part of an intercom system used in theatres, is a single sided through-hole circuit board, with leaded components only. Table 4 presents the soldering data of board B.

Table 4 – Summary of the board B soldering trials data.

Tin/Lead				
Process	***Alloy***	***Flux***	***Process Data***	***Board***
Hand	60Sn/40Pb	No-clean, rosin free, Interflux IF14 fluxed solder wire	350°C (iron tip)	Sn/Pb HASL
Lead - Free				
Wave	SN100C Sn/Cu/Ni	Water-based, VOC free, spray DKL Metals E-Qual flux	255°C (single wave)	Lead-free HASL

Board C

This product is an assembly that is used in door lock mechanisms in hotels. It has a reflow soldered, surface mount circuit board, with surface mount devices only. Table 5 presents the soldering data of board C.

Table 5 – Summary of the board C soldering trials data.

Tin/Lead				
Process	***Alloy***	***Flux***	***Process Data***	***Board***
Reflow	62Sn/36Pb/2Ag	ROL0 no-clean Koki SE48-M955	-	Sn/Pb HASL
Lead - Free				
Reflow	96.5Sn/3.0Ag/0.5Cu	Koki Eco Plus S3X58-M406	-	Sn finish

Board D

This product is used in telephone systems as part of a call charging unit. The assembly has a double sided, plated through-hole, mixed technology circuit board, with both leaded and surface mount components on the top side only. Surface mount components were reflow soldered to the board, followed by wave soldering of the through-hole components. Table 6 presents the soldering data of board D.

Table 6 – Summary of the board D soldering trials data.

<table>
<tr><th colspan="5">Tin/Lead</th></tr>
<tr><th><i>Process</i></th><th><i>Alloy</i></th><th><i>Flux</i></th><th><i>Process Data</i></th><th><i>Board</i></th></tr>
<tr><td>Reflow</td><td>62Sn/36Pb/2Ag</td><td>No-clean, Alpha Metals UP78-T</td><td>-</td><td>Au/Ni plated</td></tr>
<tr><td>Wave</td><td>60Sn/40Pb</td><td>No-clean, alcohol based flux; Multicore X33 12i</td><td>250°C</td><td>Au/Ni plated</td></tr>
<tr><th colspan="5">Lead - Free</th></tr>
<tr><td>Reflow</td><td>95.5Sn/3.8Ag/0.7Cu (4 boards)
96.5Sn/3.0Ag/0.5Cu (4 boards)
95.5Sn/3.8Ag/0.7Cu (8 boards)</td><td>Multicore LF310
Alpha metals OM338
Multicore LF318</td><td>-</td><td>Au/Ni plated</td></tr>
<tr><td>Wave</td><td>SN100C
Sn/Cu/Ni</td><td>Hand–sprayed, no clean, alcohol based flux; Multicore X33 12i</td><td>270ºC</td><td>Au/Ni plated</td></tr>
</table>

Board E

This product is part of a Taxicab display sign. It has a double sided, plated through-hole circuit board, with both leaded and surface mount components. The through-hole components and surface mount chip resistors were assembled by wave soldering, the connector was hand soldered to the board. Table 7 presents the soldering data of board E.

Table 7 – Summary of the board E soldering trials data.

<table>
<tr><th colspan="5">Tin/Lead</th></tr>
<tr><th><i>Process</i></th><th><i>Alloy</i></th><th><i>Flux</i></th><th><i>Process Data</i></th><th><i>Board</i></th></tr>
<tr><td>Wave</td><td>63Sn/37Pb</td><td>No-clean, rosin-free foam Kester 950E flux</td><td>250°C</td><td>Sn/Pb HASL</td></tr>
<tr><th colspan="5">Lead - Free</th></tr>
<tr><td>Wave</td><td>96.5Sn/3.0Ag/0.5Cu</td><td>No-clean, rosin-free, water based spray Warton Ecowave 45 flux</td><td>260°C</td><td>Lead-free HASL</td></tr>
</table>

Board F

This is a product used in digital display devices such as LCD monitors to improve the image quality. The assembly has a double sided, plated through-hole, mixed technology circuit board, with both leaded and surface mount components on the top side only. Surface mount components were reflow soldered to the board, followed by wave soldering of the through-hole components. The tin/lead through-hole components were attached using the lead-free process. Table 8 presents the soldering data of board F.

Table 8 – Summary of the board F soldering trials data.

Tin/Lead				
Process	***Alloy***	***Flux***	***Process Data***	***Board***
Reflow	63Sn/37Pb	No-clean, ROL0, Indium Corporation NC-SMQ-92J	-	ENIG
Lead - Free				
Reflow	96.5Sn/3.0Ag/0.5Cu	No-clean, Alpha Metals OM-338	-	ENIG
Wave	SACX Sn/Ag/Cu/Bi	No-clean, rosin based, sprayed Alpha Metals EF-6000 flux	260ºC	ENIG

4.3 Reliability tests

The objective of the reliability trials is to determine if there are significant differences in the performance between the conventional tin/lead and lead-free solder joints in the real products provided by the industrial assemblers. For this purpose some tests have been selected according to each product requirements, in order to accelerate the stresses that solder joints will suffer in service. The assemblies were sent to the assemblers for electrical functional test before and after the reliability tests, the tests were selected in a way that may give information about the joints and their failure, and to avoid tests that can lead to failure in different parts of the assemblies. The maximum temperature of 100ºC has been considered compatible with all the devices and board materials.

Several boards from each assembler were selected and submitted to various reliability tests, in table 9 it is showed the distribution of boards to each test. Meaning of the abbreviations in table 9: TL - tin/lead; LF – lead-free; R – reserve board; L – low temperature storage; H1 – high temperature storage (7 days); H2 – high temperature storage (28 days); TC1 – thermal cycling (3000 h); TC2 – thermal cycling (6000 h); TS – thermal shock; V – vibration. Further details will be given later on.

Table 9 – Allocation of boards on each reliability test.

Board	Solder	R	L	H1	H2	TC1	TC2	TS	V
A	TL	1	1	1	1	4	4	0	0
	LF	1	1	0	1	2	2	0	0
B	TL	1	1	1	2	2	4	2	5
	LF	1	1	1	1	2	4	2	3
C	TL	1	1	1	2	6	7	2	0
	LF	1	1	1	2	6	7	2	0
D	TL	1	1	0	2	8	0	1	2
	LF	1	1	0	1	8	0	1	2
E	TL	1	1	0	2	4	2	2	1
	LF	1	1	0	2	4	2	2	1
F	TL	1	1	0	2	3	2	1	0
	LF	1	1	0	2	6	3	2	0

A brief description of each reliability test selected for the assembler boards is presented below.

Reserve boards (R)

One board of each type was marked as “reserve” in its as-received state for comparison testing. This may provide a baseline for comparing the possible degradation during the reliability tests.

Low temperature storage – steady state (L)

The solder joints were exposed to extreme temperature likely to be encountered by such assemblies. One board from each assembler was submitted to this test. The test was carried out at (-40ºC) with a storage period of 72 hours (Fig. 32). Testing follows the method of EN 60068-2-1 for non-heat dissipating specimens with gradual change of temperature.

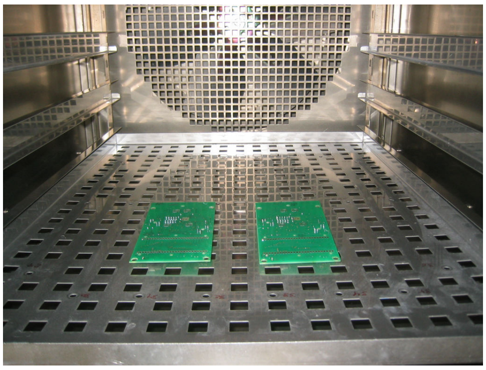


Figure 32 – Boards D ready for the low temperature storage test.

High temperature storage – dry heat - steady state (H1 and H2)

The product in service will not suffer very high temperatures, so the temperature was limited to 100°C. The effects of ageing are expected to be gradual but it will be useful to determine an evolution if visible, therefore this test was divided in two groups, one with periods of 7 days (H1) and the other with 28 days (H2) of storage. Testing follows the method of EN 60068-2-2 for non-heat dissipating specimens with gradual change of temperature.

Thermal Cycling (TC1 and TC2)

This test was carried out in the power-off state so no self-heating effects will be considered. Following the recommendations of IPC-9701 for product categories 1, 2 and 3, the test conditions will be: 0 to 100°C with number of thermal cycles NTC-E (6000 cycles). An intermediate test was performed to assess any early failure, so the test was divided in two groups with periods of 3000 (TC1) and 6000 (TC2) cycles. Thermal cycling applied a long period of artificial ageing, it is expected that this test may induce a significant degradation in the solder joint but without leading to a loss of electrical contact. Therefore a mechanical shock was done to discover possible weakened joints after the thermal cycling but before the electrical testing. The level of shock was done according to the standards for the end-use of the assembly. The test is a simple free fall drop test (method of EN 60068-2-32).

Thermal Shock – rapid change of temperature (TS)

This test provides some insight into performance under conditions of cyclic high stress/strain and low temperature (-40 to 100°C). The method follows the standard EN 60068-2-14.

Vibration test (Group V)

This test was performed with random vibration according to the standard EN 60068-2-64. Random excitation attempts to apply all frequencies within a specified frequency range to ensure some level of continuous resonance response throughout the test duration, at an intensity that is freely developed by the specimen. The test conditions were as follows:

- Test frequency range: $f1 = 5Hz$, $f2 = 1000$ Hz.
- Acceleration spectral density: 10.0 (m/s^2) 2/Hz.
- Duration of exposure: 30 minutes in the three axis.
- Vibration axis: Three periods of vibration to be applied to each board, one each in the X, Y and Z directions (relative to the edges of the board).

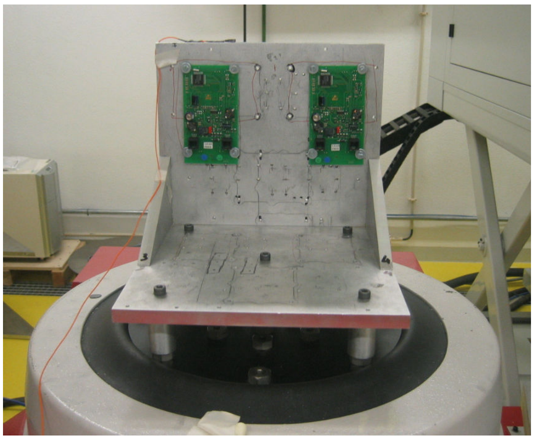


Figure 33 – Vibration test on the boards D under the yy axis.

Component attachment strength test

It was performed a limited number of joint strength tests on the simpler geometry SMDs using a side shearing test method similar to that described in EN 60068-2-21. This test was performed on appropriate boards that have undergone both their full test regime and electrical function check.

Table 10 - Summary of test standards and test methods

Test	Standard	Conditions
Visual inspection	Standard IPC-A-610-D	-
Low temperature storage	EN 60068-2-1Section 2. Test Ab	Conditions Temperature (-40°C) Duration 72 h
High temperature storage	EN 60068-2-2 Section 2. Test Bb	Temperature +100°C Duration 168 h or 672 h
Thermal cycling	IPC 9701 Cats 1,2 & 3 Test Condition 1 NTC level E	0°C to 100°C 3000 cycles or 6000 cycles
Mechanical shock	EN 60068-2-32 Part 2.1 Test Ed: Free Fall	1000 mm vertical drop steel surface. Number of falls 2
Thermal shock	Standard EN 60068-2-14 Part 2 Test Na (or Nb)	Conditions air to air temperature range (-40°C) to +100°C. 5 cycles, 3h/ 25 s/3h
Vibration	EN 60068-2-64	Random excitation: f1 =5Hz, f2 =1000 Hz Duration of exposure: 30 minutes Vibration axis: one each in the X, Y and Z directions
Component attachment strength	EN 60068-2-21 Test Ue3 Shear Test. Test Method 8.5.3.2	10N for 10s. Then destructive at 0.2mm/s

4.4 Characterisation of the tested boards

All boards were visually inspected after the soldering trials, before and after the reliability tests. The visual inspection of the boards was carried out following the standard IPC-A-610D class 3.

4.4.1 Results before reliability testing

Before the reliability tests the following anomalies were found:

Board A

Some bridging, misaligned components, solder balling and solder residues were found in both types of solder and boards. Rework was carried out on most of the tin/lead and in all the lead-free assemblies. The following defects were present:

- One open joint in the tin/lead and lead-free boards;
- Two components placed with inversed polarity.

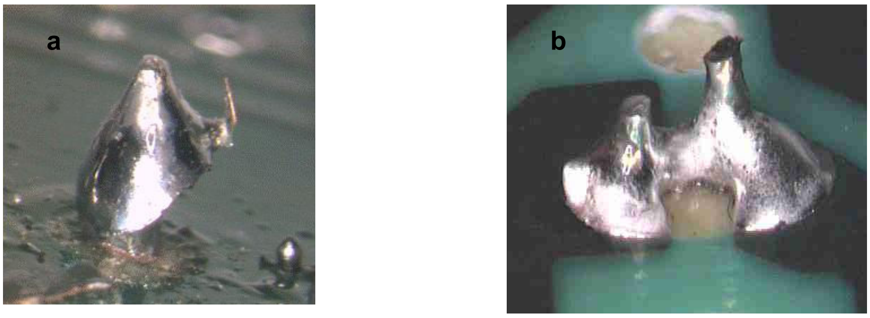


Figure 34 – Examples of defects found: a) open joint. b) Solder short between leads.

Board B

In visual inspection no major defects were identified, although most lead-free boards showed occasional solder balling or solder splashes. No rework was carried out on any of the boards.

Board C

No defects were observed during visual inspection and no rework was carried out on any of the boards.

Board D

Barrel fill was not complete on some leads of the heavier leaded components, although for most components, a good topside fillet was formed. The tin/lead boards showed less problems and only insufficient barrel fill and solder splash was found. The lead-free boards present more problems related to poor wetting, flux residues, defects like a blow-hole, solder spikes and blistering of a component were also found.

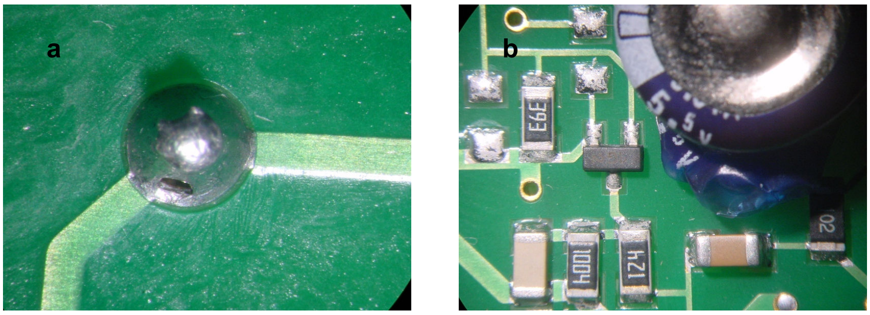


Figure 35 – Examples of defects found: a) blow hole. b) Blistering of the plastic coating.

Board E

Visual inspection has not identified major soldering defects.

Board F

No rework or defects were reported.

4.4.2 Results after reliability testing

After the reliability testing the boards were submitted to functionality tests and visual inspection. The main issues reported are described in the following points:

Low temperature storage test

All the boards submitted to the low temperature storage test presented no visual change or damage. All the boards passed the functionality tests except the tin/lead versions of boards D and E. The origin of the faults was not identified. No solder joint damaged was visually evident.

High temperature storage test

No significant changes were noted in the boards, apart from some change in the appearance of the flux residue and slight discoloration.

- Board A: both tin/lead and lead-free failed the functional tests. No visually damage was found. Possibly component failure led to the fault.
- Board B: both solders failed in the electrical functional test due to one component distortion during the high temperature test.
- Board C: No visible changes found. All boards passed the functional tests.
- Board D: No other changes except some change in appearance of residues on board were found on the boards. Only the tin/lead board has failed the functional test due to component failure.
- Board E: One tin/lead board has failed the functional test, but no visible solder joint damage was located.
- Board F: No visible changes. All boards passed the functional tests.

Thermal cycling test

This test was very severe for all the boards. About 54% of the boards failed to function.

- Board A: Both solders failed the functional tests. Some joints showed signs of severe degradation but failure could be due to component failure. Some components are susceptible to failure when temperatures reach 100ºC.
- Board B: All boards passed the electrical tests at 3000 cycles except for one lead-free board that had a component failure. On the 6000 cycles only one tin/lead board survived, the remaining boards presented open joints and severe degradation.
- Board C: All boards passed the electrical tests. No significant changes apart from discoloration and joint degradation were observed.
- Board D: All boards have failed on the functionality tests. Cracks on the joints near the lead and the pad (Fig. 36 a), damaged electrolytic capacitors (Fig. 36 b) and fillet tearing was observed (Fig. 36 c). The failures come from the two electrolytic capacitors, after replacing those components the boards became functional. There is a doubt if the failure is due to component or joint failure, because in most of the boards swelling and sometimes burst of these components was verified.
- Board E: Only two tin/lead boards have failed the electrical tests. These boards showed severe degradation of the tin/lead through-hole joints. Solder joint failure was likely to be the route cause of this result.
- Board F: All boards failed the electrical tests. The joints presented severe degradation and cracks near the leads.

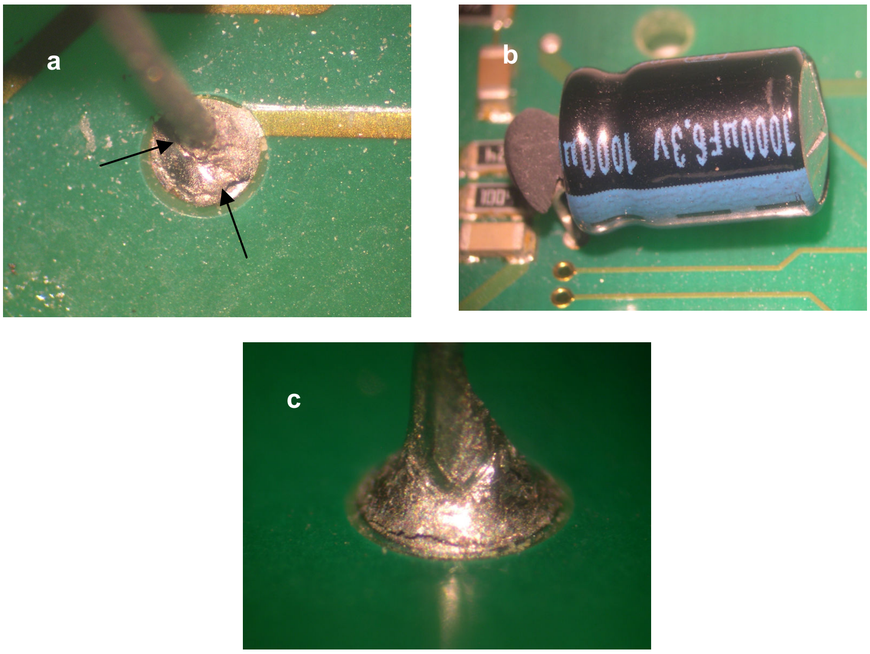


Figure 36 – Defects found on board D. a) Cracks near the lead and pad. b) Damaged electrolytic capacitor. c) Fillet tearing.

Thermal shock test

The thermal shock test showed no significant change in the visual inspection and only one lead-free component from board B has failed in the electrical functional test due to component internal damage.

Vibration test

No significant change in the visual inspection was found in all the boards and all have passed in the electrical functional test.

Component attachment strength test

All the boards showed good component strength, maintaining their initial values after testing (comparing with the non tested sample). The tin/lead boards that were submitted to the thermal cycling test have shown a decrease in the component strength. Lead-free ones presented equal performance comparing with the reserve boards and some showed slightly higher component strength after reliability testing.

4.5 Characterisation of solder joints by microscopy techniques

Visual inspection was carried out on all the products before and after the reliability tests. This inspection identified process defects and defects that could develop during the reliability testing. Inspection was carried out according to IPC-A-610D **[26]**.

After the reliability tests some of the products were selected to be sectioned and inspected by optical and electronic microscopy. The preparation of these samples involved cutting out the area of interest, mounting in resin, grinding and finally polishing the joint sections. Characterisations of the joints were done according to a specific plan that had the objective of capturing the most relevant joints and components in each assembler's boards. Figures 37 and 38 show examples of the joint sectioning details of one of the several boards in study.

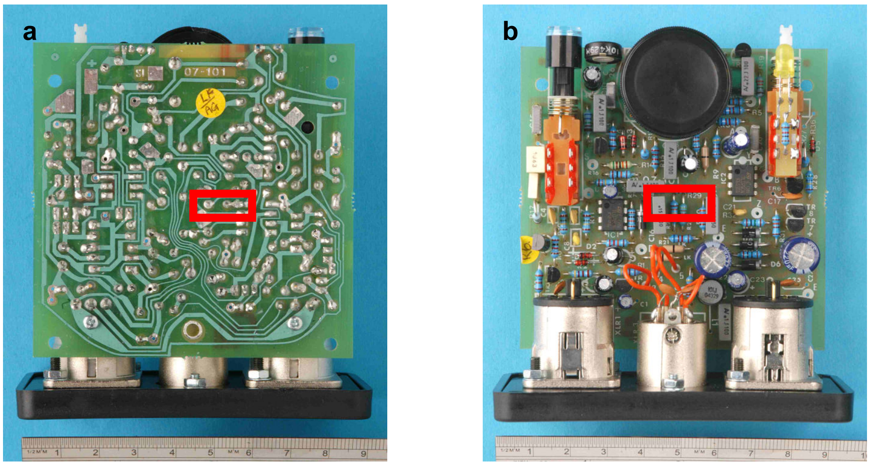


Figure 37 – Joints sectioned. a) Bottom side. b) Top side.

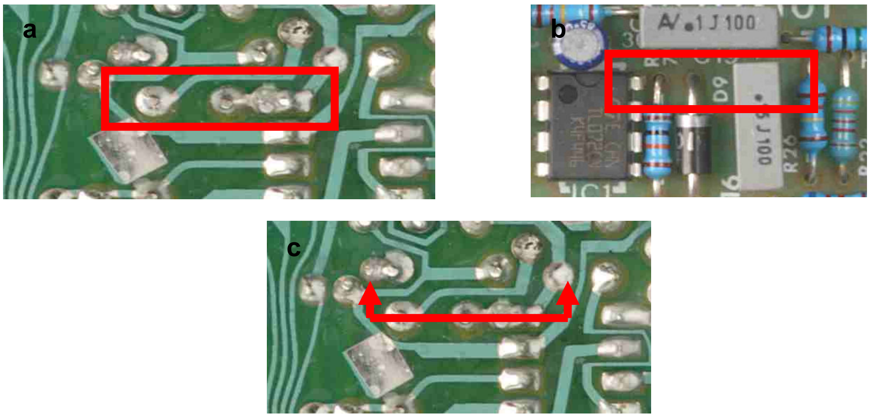


Figure 38 - Close-up view of area of interest. a) Bottom side. b) Top side. c) Plane of section.

Joints from five of the products in the study were prepared in order to examine the solder microstructure, intermetallic layers and wetting to the component and PCB. This corresponds to more than 74 joint sections that were inspected.

4.5.1 Optical microscopy

The boards presented in these sub-chapters were submitted to reliability tests and compared with non tested ones.

Board A

The tin/lead SMD's presented good joint appearance, the lead-free samples presented some voiding as can be seen in the MELF's (Metal Electrode Leadless Face) on figure 39.

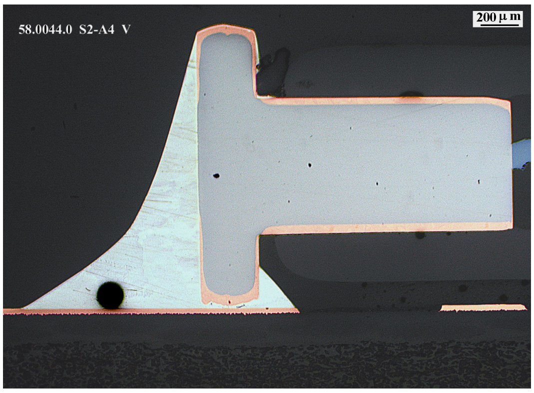


Figure 39 – Optical micrograph of sample board A: Sn/Cu/Ni; reserve (40X). Void on the solder joint of a MELF component.

Board B

All the samples from board B showed good wettability. Both tin/lead and lead-free reserve samples (non-tested) showed good joints. The tin/lead samples did not have defects in any of them, the lead-free samples had voids in all the samples and cracks in the thermal cycling one. The difference between the two solders after thermal cycling can be seen in the following figures.

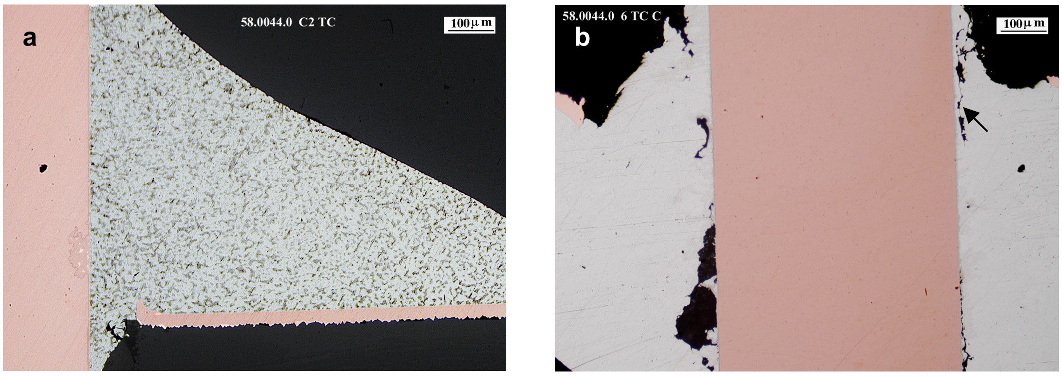


Figure 40 – Differences between lead and lead-free solders after thermal cycling. a) optical micrograph of sample board B: 60Sn/40Pb; thermal cycling (3000 cycles; 0ºC to 100ºC) (100X). No degradation. b) optical micrograph of sample board B: Sn/Cu/Ni; thermal cycling (3000 cycles; 0ºC to 100ºC) (100X). Crack propagation near the lead (arrow).

Board C

In Board C the tin/lead reserve sample presented solder wicking (see arrow in Fig. 41). The solder wicking defect is characterised by the solder paste tending to wet the component termination rather than the pad and lead. This is due to the slow wetting of the pad and faster wetting of the termination, tin/lead terminations in lead-free alloys can produce this effect, because the tin/lead coating wets very fast and drags the solder up, can be caused by the profile or the soldering process. Pad solderability can be tested to compare different boards or process parameters. It can be seen that the solder is on both sides of the termination, nevertheless this joint is considered satisfactory.

The tin/lead and lead-free samples did not have any degradation due to testing, except for the lead-free submitted to thermal cycling that had a small crack. All the lead-free samples had voids and cracks on the thermal cycled samples (see arrows in Fig. 42).

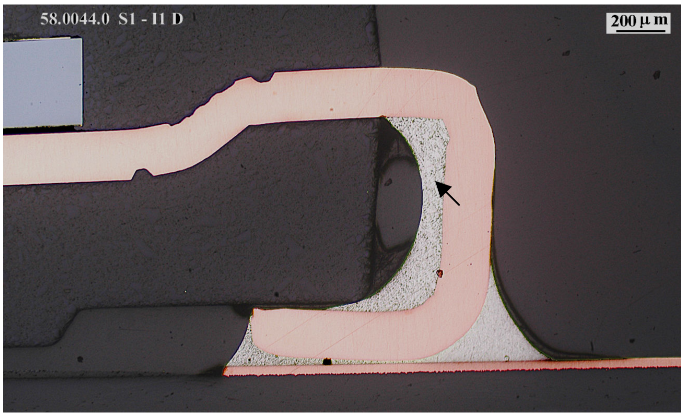


Figure 41 – Optical micrograph of sample board C: 62Sn/36Pb/2Ag; reserve (40X). Presents solder wicking (arrow).

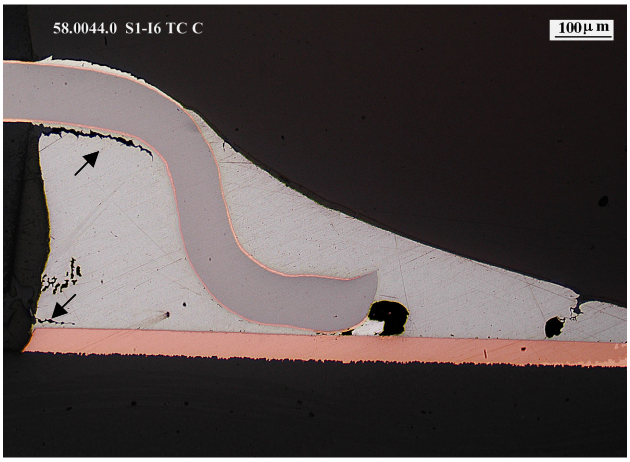


Figure 42 – Optical micrograph of sample board C: 96.5Sn/3.0Ag/0.5Cu; thermal cycling (3000 cycles; 0ºC to 100ºC) (100X). Crack propagation near the lead and pad (arrows).

Board D

These boards presented poor wetting, insufficient fill on the through-hole joints (less than 75% fill on the barrel), some cracks on the through-hole joints that suffered the thermal cycling test. The following image shows the good connection on the lead-free joint between component/solder/pad, with the formation of a visible intermetallic layer. The formation of Cu_6Sn_5 in the copper interface, followed by the formation of acicular Ag_3Sn plates can be clearly observed in figure 43.

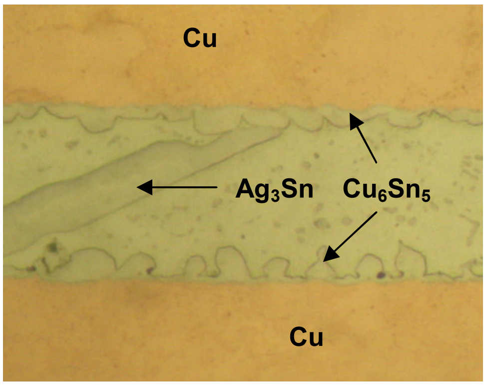


Figure 43 – Board D, component/solder/pad interconnection.

Board E

The tin/lead reserve sample presented good joints. In the lead-free solder joints some voiding is present. High temperature storage and thermal shock sample from both solders did not have any visible problems. For thermal cycling the tin/lead samples showed crack and the lead-free sample had little cracks (figure 44 a and b). One of the tin/lead samples that was subjected to thermal cycling had an intergranular crack propagation near the interface between the solder and the lead (Fig. 45).

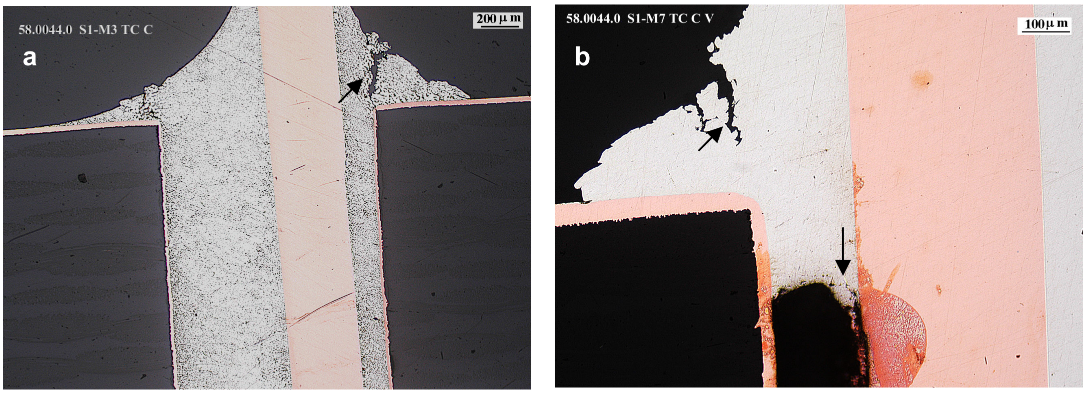


Figure 44 – Optical micrographs of samples from board E. It shows the differences between lead and lead-free solders after thermal cycling. a) 63Sn/37Pb; thermal cycling (3000 cycles; 0ºC to 100ºC) (40X). Crack propagation from the surface (arrow). b) 96.5Sn/3.0Ag/0.5Cu; thermal cycling (3000 cycles; 0ºC to 100ºC) (100X). Void and crack initiation (arrows).

Figure 45 – Optical micrograph of sample from board E: 63Sn/37Pb; thermal cycling (3000 cycles; 0ºC to 100ºC) (100X). Intergranular crack propagation near the lead (arrow).

Board F

All through-hole components of the board F samples presented complete fill and good wettability (Fig. 46). The lead-free through-hole joints submitted to the thermal cycling test presented cracks near the pad (Fig. 46 a); pad lifting appeared in almost every component (Fig. 46 b). The SMD joints showed good quality after testing and the tin-lead joints were in good conditions with only some voiding present.

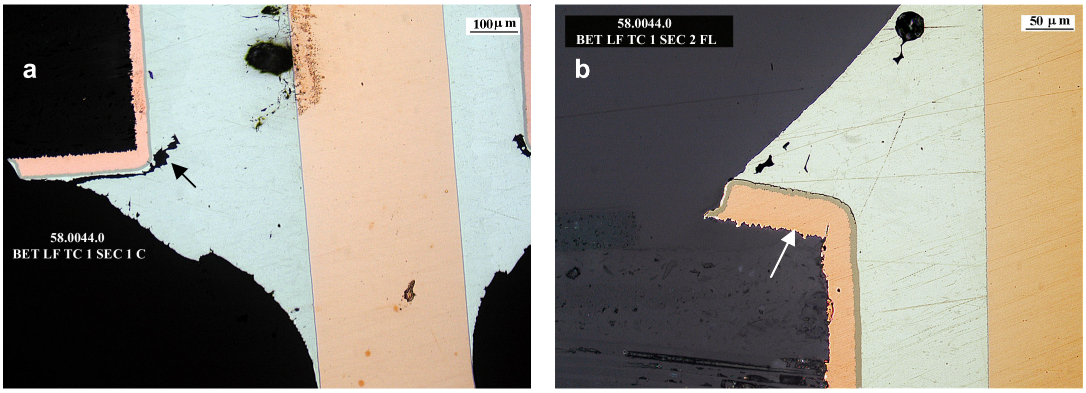


Figure 46 – Optical micrographs of samples from board F. a) 96Sn/3.0Ag/0.7Cu; thermal cycling (3000 cycles; 0ºC to 100ºC) (100X). Crack propagation near the pad (arrow). b) 96Sn/3.0Ag/0.7Cu; thermal cycling (3000 cycles; 0ºC to 100ºC) (200X). Pad lifting (arrow).

4.5.2 Scanning electron microscopy

Some samples were also analysed by scanning electron microscopy (SEM) with attached energy dispersive spectroscopy (EDS) microprobe. Images and EDS composition maps of the detected elements (Sn, Ag, Cu, Pb, Ni) were obtained in several areas of the samples.

Figure 47 shows, as an example, the reaction that takes place at the solder/pad interface. The micrograph was taken in a tin/lead joint of board F. It is observed that the entire intermetallic layer is composed of two sub-layers: the Cu_6Sn_5 near to the solder and the Cu_3Sn next to the copper substrate. It is normal to observe only the Cu_6Sn_5, because the overall layer development is not very extensive on service conditions.

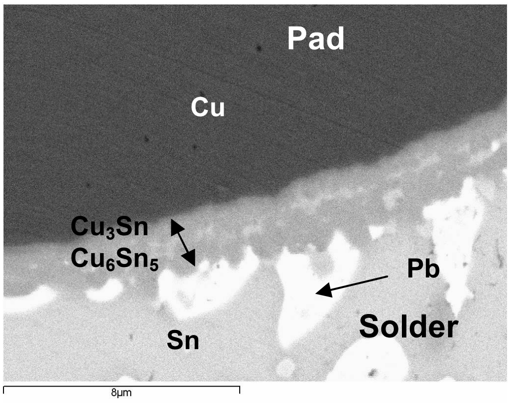


Figure 47 – Scanning electron micrograph of board F: 63Sn/37Pb microstructure near the copper pad.

The accumulation of (Pb) in front of the intermetallic interface is a consequence of the Sn-rich phase being consumed by the formation of the compound layer. The (Pb) does not participate in the formation of the Cu_6Sn_5 and Cu_3Sn intermetallics, this element simply accumulates at the interface between the Cu_6Sn_5 and the solder. The (Pb) element also has very low miscibility in (Sn), as can be seen in the tin/lead equilibrium phase diagram (Fig. 7), leading to two distinct phases in the microstructure. Another example can be seen in the micrograph and composition maps shown in figures 48 and 49.

On figure 48 and respective X-Ray mapping images of (Sn), (Ag), (Cu), (Pb) and (Ni) (Fig. 49 a, b, c, d and e) the following evidences can be observed: Sn-matrix with (Ag) small particles (Fig. 48), the (Ag) particles are not visible in the micrograph; (Pb) in large bright islands (Fig. 49 d); copper in the matrix comes from the components and solidifies in front of the (Ni) barrier. (Ni) finish coating (Fig. 49 e). No degradation of the microstructure is visible after the thermal cycling test.

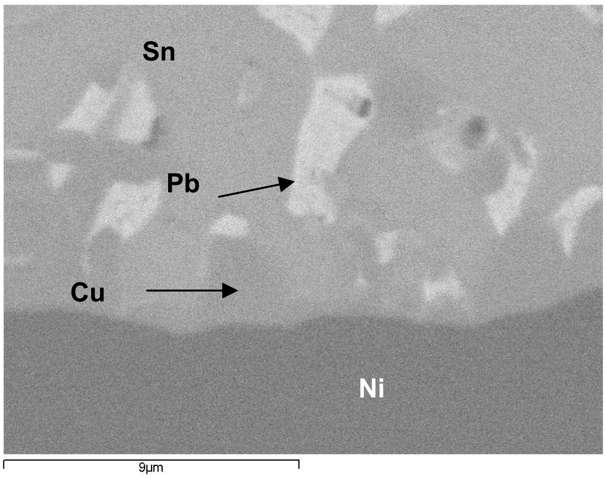
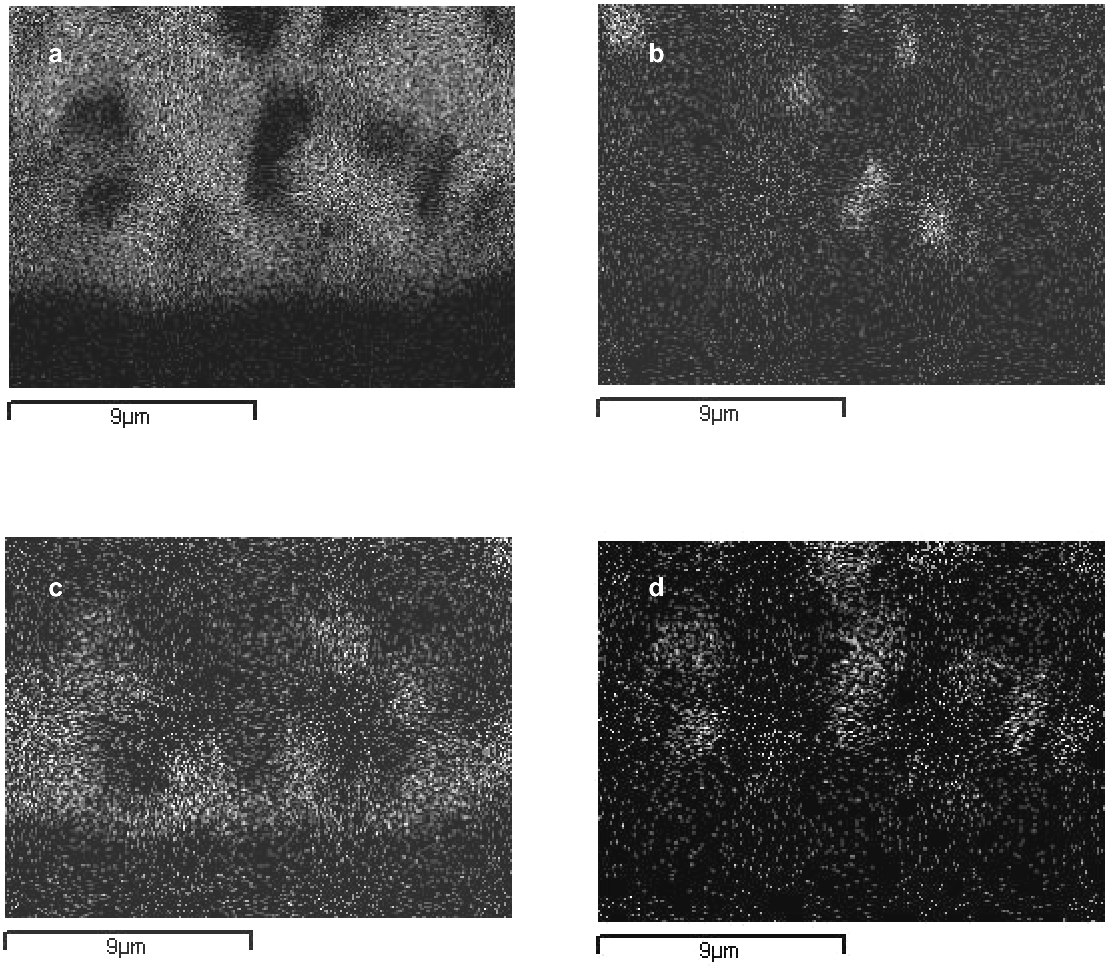


Figure 48 – Scanning electron micrograph of board F: 63Sn/37Pb; thermal cycling (3000 cycles; 0ºC to 100ºC). Microstructure near the lead.



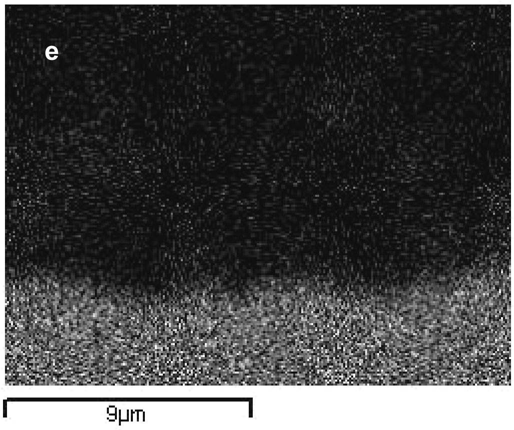


Figure 49 – Corresponding X-ray EDS maps of Sn (a); Ag (b); Cu (c); Pb (d) and Ni (e).

Figure 50 shows an interface between solder and lead. In the EDS images more can be seen. (Cu) precipitates in front of the (Ni) barrier (Fig. 51 c), low contents of (Ag) in the Sn matrix (Fig. 51 a and b) (not visible in the micrograph) and no (Pb) present (Fig. 51 d).

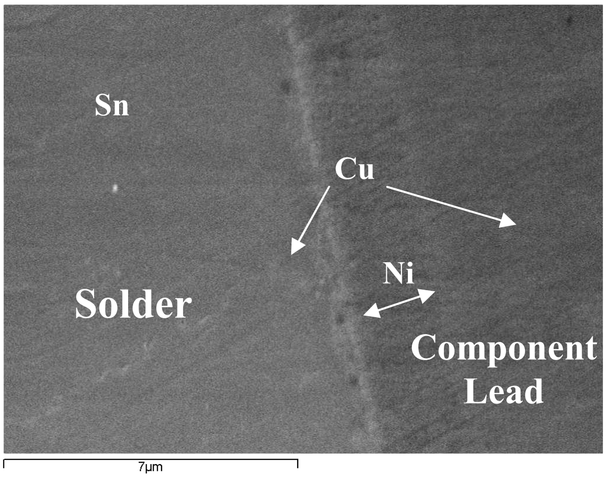
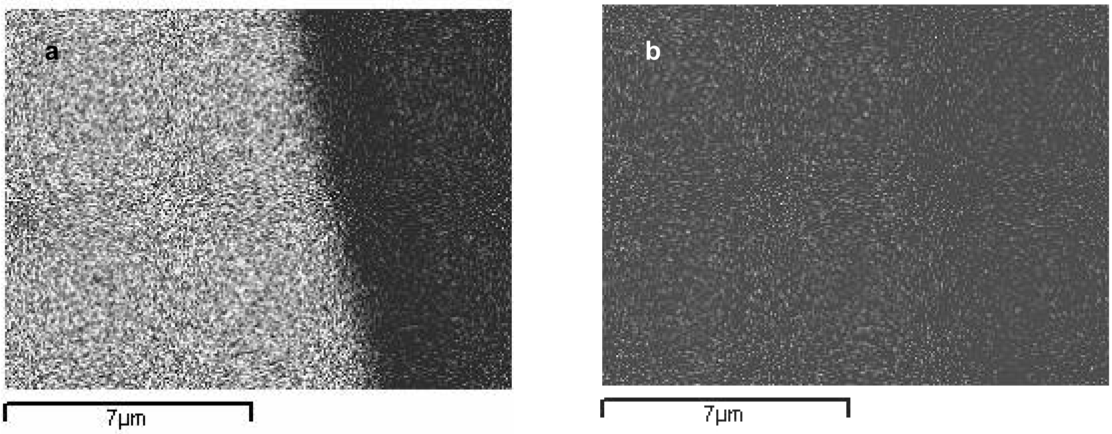


Figure 50 – Scanning electron micrograph of board F: Sn/Ag/Cu/Bi; thermal cycling (3000 cycles; 0ºC to 100ºC). Solder/lead interface.



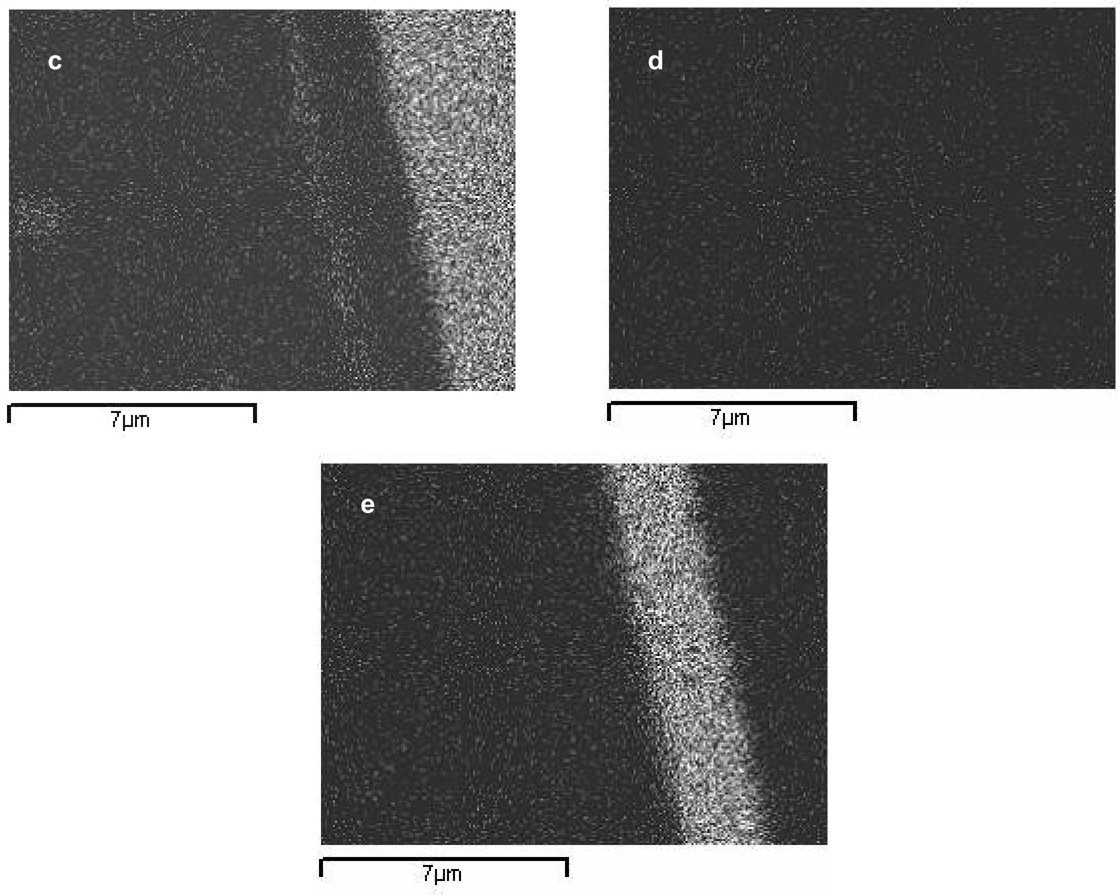


Figure 51 – Corresponding X-ray EDS maps of Sn (a); Ag (b); Cu (c); Pb (d) and Ni (e).

The copper in front of the nickel barrier does not come from the pad, there is no dissolution from the pad. The copper comes from the solder or the lead of the components that are cut-off. On solidification the copper that has the same crystal structure as nickel, face-centered cubic (FCC), is the first to nucleate on such interface. On the board D the characterisation by SEM showed a well defined eutectic microstructure, figure 52. The figure on the right presents the nucleation of (Cu) on the pad in the form of Cu_6Sn_5 followed by the growth of large plates of Ag_3Sn.

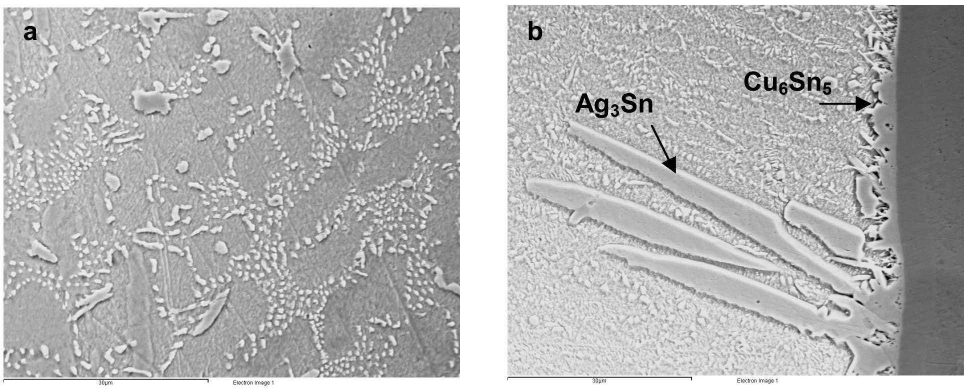


Figure 52 - Scanning electron micrograph of board D. a) Sn/Ag/Cu eutectic microstructure; b) intermetallics at the solder/pad interface.

In this characterisation it was also found a very well known defect: pad lifting. Figure 53 shows a detail of pad lifting effect and the consequent crack on the board.

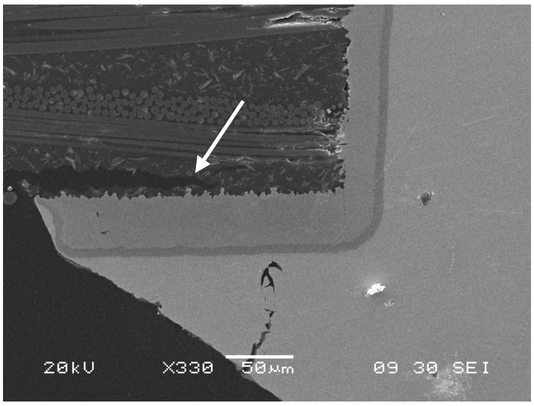


Figure 53 – Scanning electron micrograph of board F: Sn/Ag/Cu/Bi; Thermal cycling (3000 cycles; 0ºC to 100ºC). Evident pad lifting (arrow).

The pad lifting phenomenon is due to the mismatch between the coefficients of thermal expansion (CTE) of the components during the manufacturing, as previously mentioned in sub-chapter 3.1.1. In table 11 it is shown the CTE's of the main constitutive elements of the board's components. In this case, the solder is mainly constituted by tin that has a higher CTE ($23.5x10^{-6}$/K) than the board ($17x10^{-6}$/K). The board expands during soldering, when the solder solidifies and the board cools down then the solder contracts more than the board, the pad edges contracts and can be lifted from the surface of the laminate.

Table 11 – Coefficients of Thermal Expansion of the different joint materials **[8, 23]**.

Material	**CTE ($x10^{-6}$/K)**
Sn	23.5
Ag	18.9
Cu	17
Ni	13
Pb	29
Cu_3Sn	18.4
Cu_6Sn_5	20
Laminate	17

4.6 Conclusions

In soldering trials carried out at the assembler's industrial facilities no major difficulties in the lead-free soldering process were reported. Especially reflow soldering process has been carried out with very few problems. Some soldering defects were experienced with the lead-free soldered products; namely bridging, solder balls, incomplete barrel filling. Blistering of some components in board D was also found. These defects and issues found during the soldering trials were standard problems, often seen in the lead processes. Most of them can be attributed to pre-heat and soldering temperatures in the process. The blistering found on some components of the board D is due to the incapability of some components to withstand the higher lead-free temperatures and/or to the presence of moisture and consequent poor storage of components.

After the reliability tests, most of the boards passed the electrical functionality tests, except for the thermal cycled ones. In general the lead-free joints showed good performance on the reliability tests carried out. The SMD (Surface Mount Devices) are less degraded than the through-hole joints for majority of the tests, this can be due to assembly process conditions and to expected performance of the through-hole joints under testing. The through-hole joints showed more defects than the other regular solders, like pad lifting, and crack propagation near the pads in almost all joints after the thermal cycling test. The board D samples that were submitted to thermal cycling have all failed the functionality tests. Although some cracks were found on the joints of the electrolytic capacitors it was not concluded that the faults come from these cracks, because these components do not stand the high temperatures imposed by the thermal cycle test. The lead-free through-hole joints of the board F samples showed poor performance, presenting more degradation on the lead-free joints, especially under the thermal cycling test. This can be related to the new lead-free wave solder alloy with corrosion inhibitors used by that company to replace the tin/lead alloy in the wave solder process.

From the reliability tests and after the characterisation can be concluded that the lead-free boards showed a good performance under testing, being equivalent or better than the tin/lead ones. The defects or anomalies found in most of the joints result from the manufacture process (voiding and pad lifting). For the through-hole joints the cracks that can be seen in some of the samples are always away from the interface and follow an intergranular fracture mode. The cracks did not propagate very far in the joint neither through the intermetallic layer, thus, indicating a good connection between materials, strong intermetallics, in both tin/lead and lead-free solders, and it should not compromise the integrity and functionality of the product.

A continuous work was done together with the industrial partners in order to assess the difficulties and problems that are raised in the everyday work in the manufacture of electronic products. The industrial partners named some difficulties with change over to lead-free:

- Lack of components in the market with a lead-free termination finishes, especially true for through-hole components;
- Some components in market are stated as RoHS compliant but can not stand high temperature, particularly plastic parts;
- Lead-free HASL (hot air solder levelled) boards are not easy to find;
- Because some clients still ask for tin/lead soldered products, the search for both lead and lead-free components raised some difficulties;
- The cost associated with lead-free has been high;
- Rework of soldered joints takes longer and is more difficult.

Some industrial partners also claimed to have an increase of defect occurrences, especially blow-holes and incomplete filling in wave soldering. Others said that their infra-red reflow oven was not appropriate for lead-free assembly. On the other hand, positive feedback was also noticed:

- No clients have seen a reduction in reliability of their products so far;
- There are no new defects found;
- The levels of defects are similar to those on the tin/lead process.

CHAPTER FIVE

General overview – environmental and economical impacts

5.1 Environmental impact and main relevant factors of lead-free soldering

To producers and manufacturers, waste reduction, recovery and recycling should be and will inevitably be treated as a long-term goal with an ongoing effort. A product should be designed for minimal environmental impact with its full lifecycle in mind. Lifecycle assessment includes all the energy and resource inputs to a product, the associated wastes, and the resulting health and ecological burdens. The goal is to reduce environmental impacts from cradle to grave.

Lead is considered to be a cumulative poison; significant amounts can bring discomfort and disability. Some specific potential health problems include disorder of the nervous and reproductive systems, reduced production of haemoglobin, anaemia and hypertension. The main concerns related to the use of lead in the industry are:

- Landfill contamination;
- Effluent discharge from the production process;
- Worker's exposure through fume, dust inhalation and direct ingestion **[11].**

The environmental issues bring new concerns to the produces and manufactures that have to cope with these new changes. It is this side of the business that has to study and balance the alternatives in terms of cost and benefit.

Fumes emissions, leaching tests and occupational health

In terms of environmental studies several tests were carried out in some of the assembler's facilities. The objective was to investigate the environmental impact associated with the lead-free process and waste treatment in manufacturing, through the evaluation of pollution level involved by the use of lead-free solder during the assembly processes. Therefore, three main tests have been carried out in order to compare the results between the lead and lead-free solders:

- Sampling and analysis of fume emissions;
- Occupational exposure measurements;
- Leaching tests of soldered printed circuits and dross of the wave processes.

Samples from the reflow, wave and hand soldering processes, with different solder alloys, have been collected and analysed. In the environmental measurements carried out at the companies participating in the project it was observed that all emission results using lead-free solder pastes were lower than the obtained with lead containing alloys. For boards containing lead solders, the lead content values implies that should be considered as hazardous waste acceptable only at landfills for hazardous waste. For boards containing lead-free solders, the values were below the detection limits and can be considered as inert waste. In the occupational health measurements, these were under the limit values for organic compounds and metals in both types of solders.

5.2 Industrial guidelines for lead-free implementation

5.2.1 Economical study

In terms of economics the lead-free changeover brings big impacts to the assemblers and manufactures. The RoHS directive affects areas like: manufacturing, quality, design, purchasing, marketing, sales, finance and management. The first question that emerges from this directive is: what do I need to change/invest to cope with the new demands?

Each producer has to know their own process and some questions have to be answered:

- Is the present equipment is capable of lead-free manufacturing, in terms of temperature, process control, material)?
- Are the current facilities are capable? (separate manufacturing lines, stocks handling)
- Is new equipment is needed? (Soldering irons, wave soldering…)
- Is personnel training is needed? (purchasing, technical staff, engineers, designers)

Regarding equipment issues the wave process is the one that presents more difficulties due to the bath temperature increase, increased pre-heat temperatures, flux changes, longer wave contact time and high contents of tin in the solders. The following image shows the corrosion of a pot with lead-free solders where the assembler just removed the old bath and introduced the lead-free one on the same pot. The pots have to be prepared to the high contents of tin, new pots and coatings are available in the market and suitable for lead-free solders.

Figure 54 – Tin corrosion on a wave soldering machine pot **[17]**.

The cost of producing is not a simple and straightforward issue. Many factors contribute for the overall cost:

- Solder product cost;
- Operational cost;
- PCB and component cost;
- Equipment cost;
- System cost.

The solder product cost includes metal elemental price, alloy compositional cost and production. Metal prices fluctuate with the market demand and the higher the content of an expensive metal in the alloy the higher the price of the solder. Production like ingots, powder, adding flux in the solder and others, bring indirect costs to the final price of the solder. The operational costs are different for reflow and wave. In reflow process using solder paste the main factors are:

- Electrical consumption for oven operation;
- Reflow oven maintenance;
- PCB change (if applicable);
- Component change (if applicable);
- Machine modification (if applicable);
- Nitrogen usage (if applicable);

In a wave soldering process:

- Solder replenishment required due to dross;
- Solder replenishment required due to compositional stability;
- Pot stability;
- Electrical consumption;
- PCB change (if applicable);
- Component change (if applicable);
- Machine modification (if applicable);
- Nitrogen usage (if applicable);
- Wave machine maintenance.

PCB and component cost are related mainly to the higher process temperature required. A change to a different PCB or component delivering a higher temperature tolerance may involve additional costs.

Regarding equipment most of the companies did not have any problems in adapting their reflow ovens to the lead-free processes, with a good profiling and optimisation the existing ovens can still be used. In the wave process the companies found more difficulties due to the higher process temperatures and two approaches were observed: some adapt their wave machines for lead-free (e.g. new pots and other parts), which represent a relatively low investment; and others calculated the estimated time for failure (corrosion in the pot, etc), ran the lead-free process in their old machines and bought a new wave machine at the end of the calculated lifetime.

The system costs involve the overall assessment of costs: solder material; process operational cost; component and PCB cost; equipment cost and amortisation; defects; product performance and reliability. The defects and reliability of the product are the most important factors of the system costs. A product failure is very expensive **[31]**. Most of the costs related with lead-free are coming from new equipments; energy consumption, due to higher temperatures and re-training the staff.

5.2.2 Project Benchmarking

The number PPM levels were recorded and compiled every month. Here are some results obtained during the project:

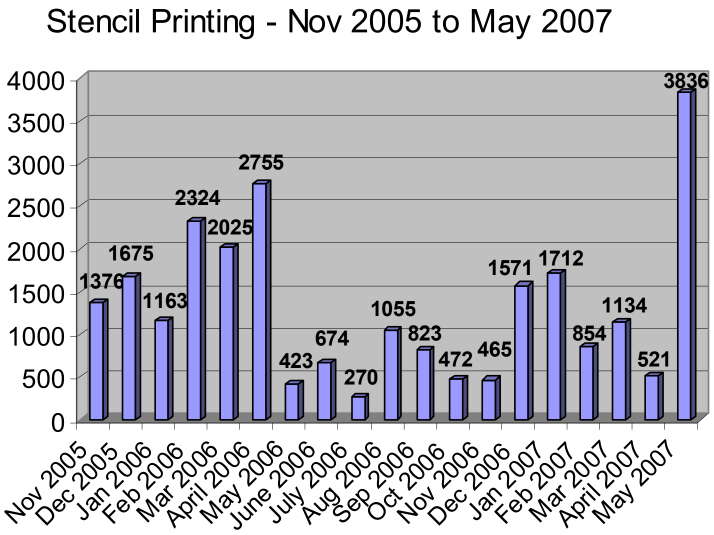


Figure 55 – Stencil printing average PPM defect levels from both lead and lead-free companies.

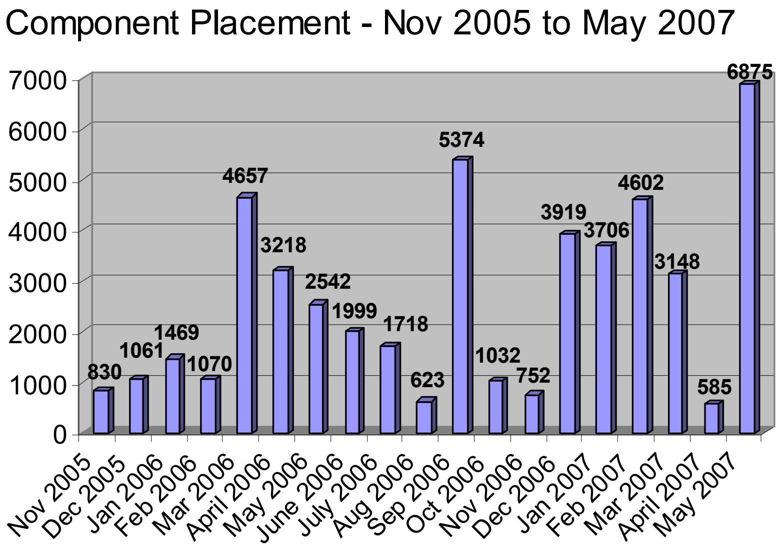


Figure 56 – Component placement average PPM defect levels from both lead and lead-free companies.

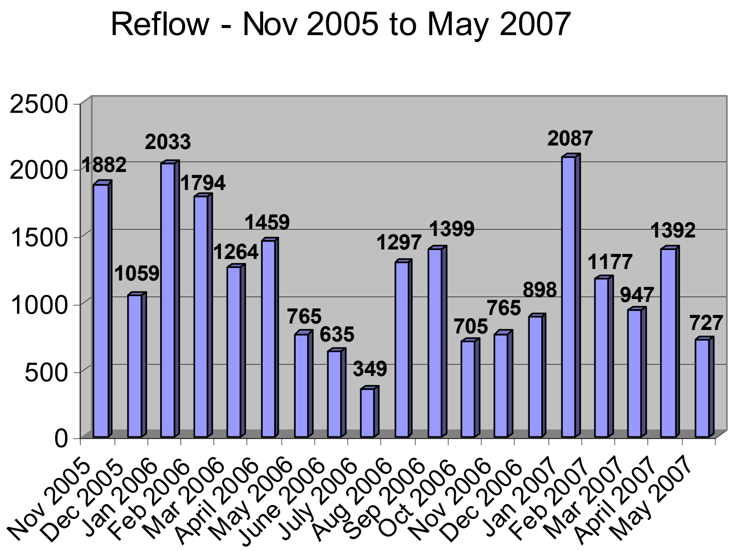


Figure 57 – Reflow average PPM defect levels from both lead and lead-free companies.

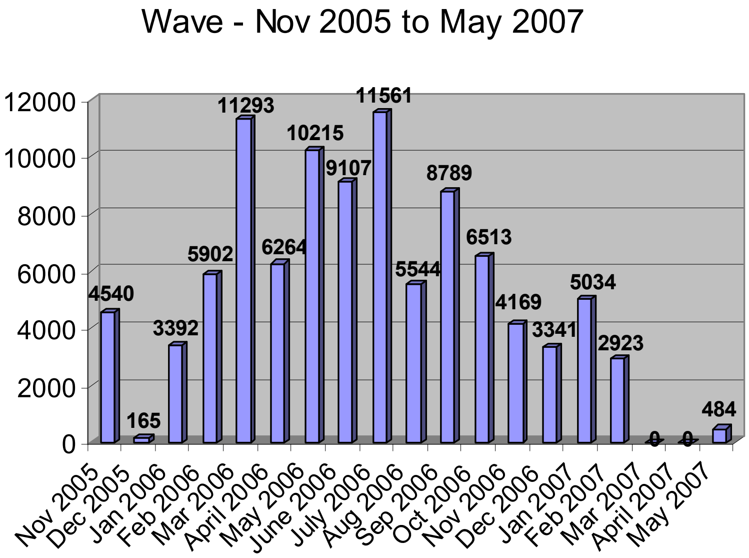


Figure 58 – Wave average PPM defect levels from both lead and lead-free companies.

Some companies did not supply data continuously during the project, which explains the absence of data in some parts and some abnormal values. In all the graphs some results can be seen that differ from the normal trend. This can be due to some product changes in production and the lack of participants on some months. The companies with lead-free data were introduced here only from May 2006 forward.

Until May 2006 very slight changes in the defect results are observed. Wave soldering is the step of the process that presents more defects. After May 2006 the lead-free assemblers or assemblers that have done the transition to lead-free started to contribute for the PPM project. The majority of the lead participating companies have made the transition for lead-free. The wave soldering continues to be the most problematic process. In most of the processes, defects have decreased or maintain after June 2006 (lead-free implementation) except for wave soldering process, showing once more the difficulties of the transition for this process.

After the implementation of lead-free assembly there was not any significant modification in the results in the reflow process for all companies during the study. The wave soldering process showed more defects in the time of transition but on the other hand a trend of decreasing the level of defects can be seen along the following months. Maybe there was a continuous effort on the optimising of the wave process.

It is interesting to note that the lead-free soldering, including reflow process, shows less or equal number of defects compared to the tin/lead results, except for wave soldering that present more defects. This shows that the main difficulty in the lead-free transition appears in the wave soldering process. An increase of the defect levels was expected with the implementation of the lead-free process due to changes in fluxes, temperatures, profiles and others. Although that was not observed, especially on the surface mount process that decreased or maintained the level of defects. This shows that the companies made an effort to cope with the new changes in the process.

CHAPTER SIX

Final conclusions and future work

6.1 Final conclusions

This thesis presents a brief introduction to the area of soldering in electronics where a great evolution and effort in research and development of new solders and equipments can be seen. The lead-free “obligation” brought a new boost in this area, leading engineers to discover new solder alloys with the addition of elements, changing properties and characteristics, optimising processes.

From the practical part of this work it can be concluded that the SMEs were prepared for transition and are engaged in taking this opportunity to reach a higher level. Some of the companies embraced this “forced” transition to upgrade and improve their facilities, bringing better capabilities and opportunities in their businesses. In the Economical chapter (5.2.1) some factors that should be taken into consideration when implementing the lead-free process are mentioned. It is natural that an SME prefers not to invest in new equipment but the companies present in this study showed that the purchase of new equipment that is suited and prepared to run lead-free brought less defects, easier transition, higher production levels; and on the other hand the companies that have chosen to adapt their process showed higher defect levels and more time consumed in tuning up the process. These factors also bring costs that sometimes are not visible, it should be the companies’ choice to calculate and decide whether or not to invest in new equipment. The main issue found in manufacturing and in reliability of the products is a component problem, an effort has to be made in order to fit the components in the lead-free processes and increase their availability on the market. Components should not only be RoHS compliant but they have to be able to withstand the temperatures imposed by the lead-free process.

The defects or anomalies found in most of the assemblers samples result from the manufacturing process (voiding and pad lifting). This shows the need for process optimisation (temperature profiles, fluxing, pre-heating…) in the manufacturing stage. The wave soldering is by far the most problematic process. The decrease of the level of defects presented in this study shows that the companies are aware of this problem and started immediately to implement corrective measures.

From the reliability tests it can be concluded that most of the faults found were due to component failures and not from the joint integrity. The degradation of both types of solders is similar, but the operators should be trained to identify the differences between the lead and lead-free solders. The inferior wettability and dull aspect of the lead-free alloys should be taken in account when doing visual inspection, non trained operators can be misled to classify those products as defective.

Comparing to the lead process the lead-free soldering process presented equal or better performance. The problems found in the new lead-free solders and processes it should not constitute a major problem in the reliability of the products. This shows that the lead-free soldering is ready to be implemented in the small to medium size enterprises, despite the issues that may be encountered on the way. These issues can be easily overcome with continuously process monitoring and tuning up. It is important to keep in mind that in order to reduce the cost of the soldering process and increase the reliability of the solder joints, companies should monitor or continue to monitor their processes and defects.

This work also allows to conclude that the partnership between universities, research and development centres and industry is a must for the evolution and improvement of the companies processes and products. A lot of work was done that brought great benefits to this sector.

6.2 Future Work

Following the trend of the electric and electronic industry and the ELFNET Roadmap **[32]**, some recommendations for the future work should be approached:

- Thermally compatible components;
- Design for reliability – new tools and processes for high reliability products;
- High reliability solders – modifications of alloys (adding ternary elements, nano particles to improve properties);
- New materials to CTE matching – decrease the CTE’s differences in a board;
- Improvement in the soldering and de-soldering processes including rework and repair – new heat management to mitigate collateral damage (laser soldering, low temperature soldering, vapour phase soldering, optimised selective soldering);
- Harmonised reliability standards and data for the lead-free soldering;
- New technologies for inspection and testing of components and joints;
- Use of refurbishment material for low cost reliable reusable components.

REFERENCES

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Annex I

Board A

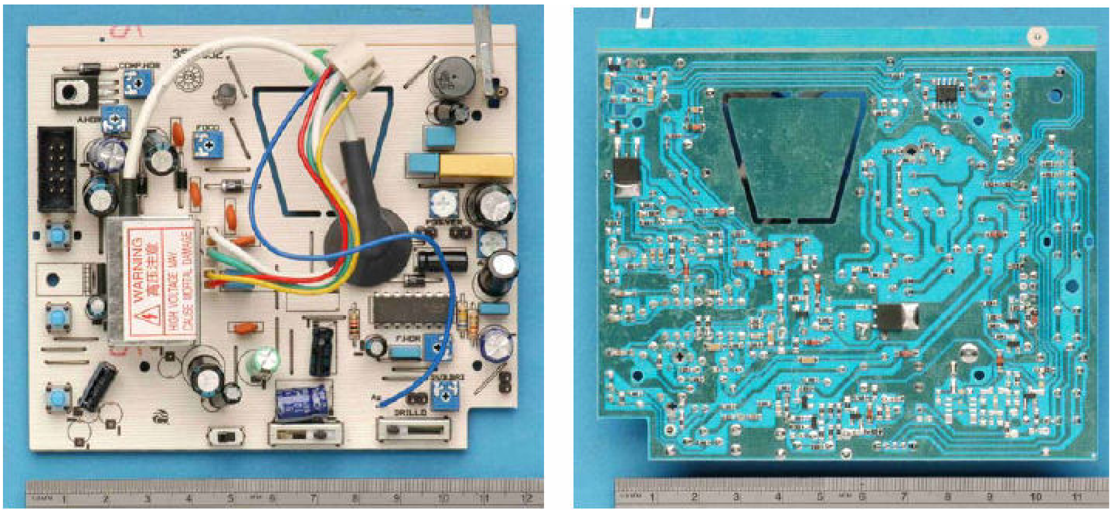

Fig I-1 – Board A supplied by one of the assemblers partner

Board B

Fig I-2 – Board B supplied by one of the assemblers partner

Board C

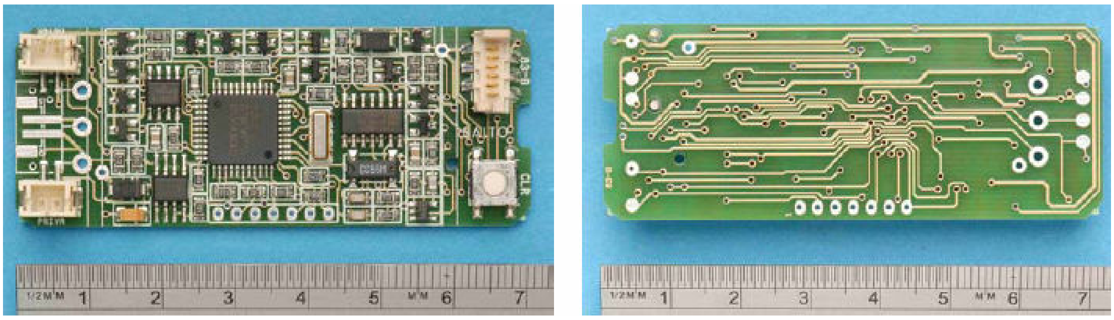

Fig I-3 – Board C supplied by one of the assemblers partner

Board D

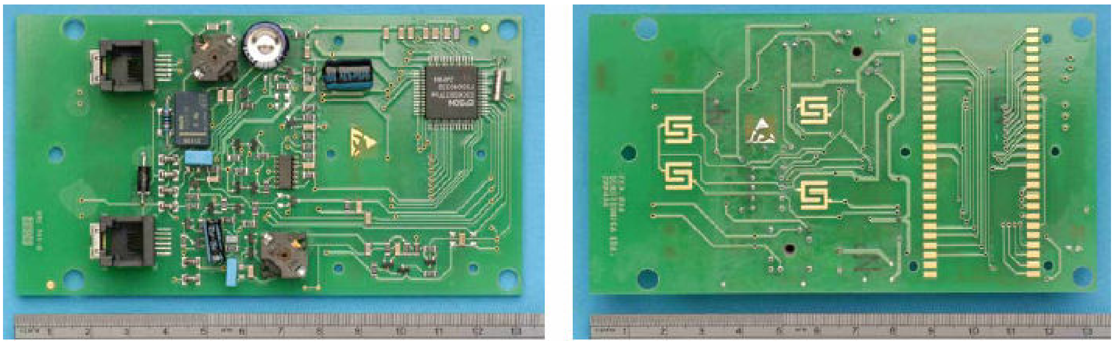

Fig I-4 – Board D supplied by one of the assemblers partner

Board E

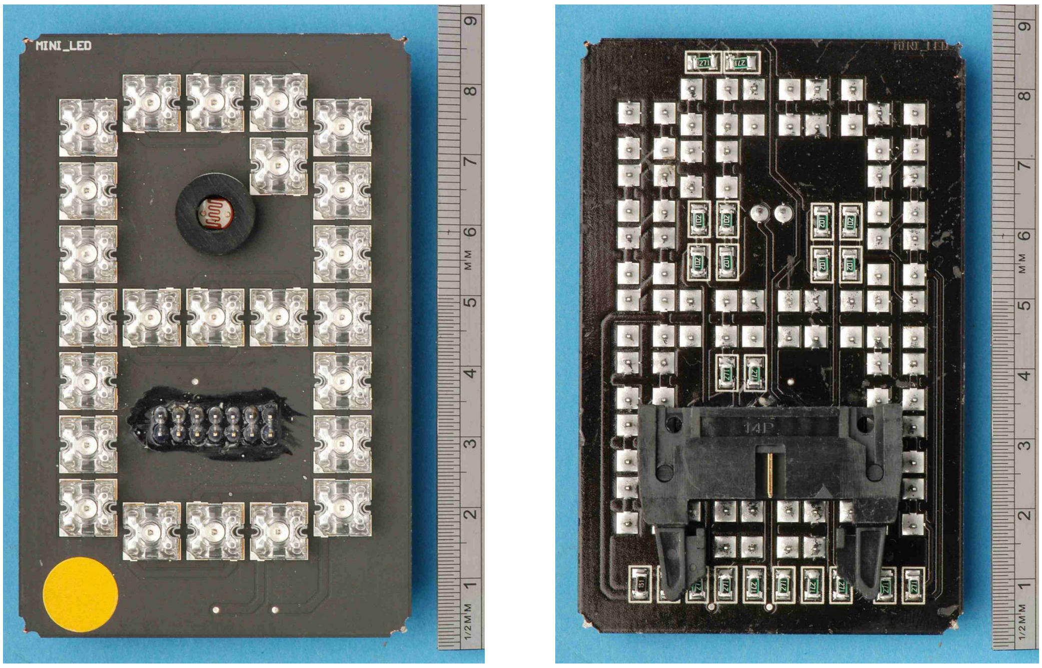

Fig I-5 – Board E supplied by one of the assemblers partner

Board F

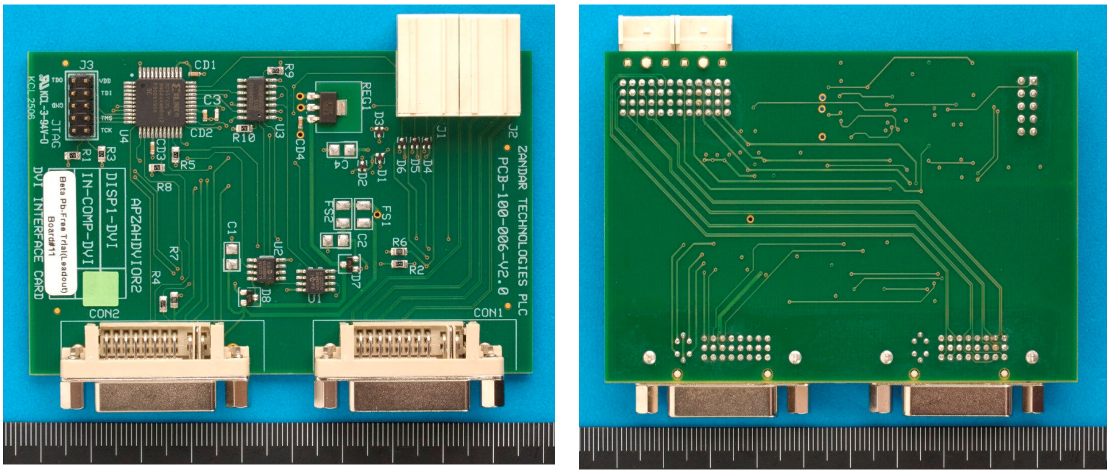

Fig I-6 – Board F supplied by one of the assemblers partner