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Survey on Lead Free Solder Systems

Results of a Danish R&D project on the environmental and technical impacts of substituting lead containing solders by lead free solder systems

Poul Juul
HYTEK

Kim Zachariassen
DELTA

Turi Roslund and Svend Aage Hansen
Bang & Olufsen A/S

Lars Ebdrup
Grundfos Elektronics A/S

Brian Sloth Bentzen
Simrad Shipmate A/S

Ivan Ring Nielsen
TechnoData A/S

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1 Foreword

This report covers an overview of the results achieved within the national Danish Lead Free Soldering project. The project has had the aim of comparing electronics joining technologies based on lead free alloys with traditional SnPb-solders. The report describes the environmental aspects of introducing lead free solder systems in electronics manufacture compared with lead containing solder. It also contains a technical assessment of two promising lead free solder systems (Sn-4.0Ag-0.5Cu and Sn-3.5Ag). Experiments have been carried out on FR4 PCBs using both reflow soldering and wave soldering techniques.

The project aims to describe the environmental aspects of the electronics industry's transition from traditional lead-rich solder to lead-free solders for bonding components to printed circuit boards. The project is funded by a grant from the Danish Environmental Protection Agency, from which Henri Heron was supervising the project.

Party to the project are Technoconsult (project leader), DELTA Danish Electronics, Light and Acoustics, Grundfos, HYTEK, SIMRAD and Bang & Olufsen. The Danish Toxicology Centre was subcontracted to make the toxicological evaluation of the solders and fluxes.

The project partners want to thank Teleinstrument (Alpha-Fry Technologies) and CYNCRONA (Multicore) for providing the solders used in the project. Furthermore we appreciate the cooperation with another Danish project organised under the auspices of SPM with whom we shared the test printed circuit boards.

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Poul Juul, HYTEK
Kim Zachariassen, DELTA
Turi Roslund, Bang & Olufsen A/S
Svend Aage Hansen, Bang & Olufsen A/S
Lars Ebdrup, Grundfos Electronics A/S
Brian Sloth Bentzen, SIMRAD AS
Ivan Ring Nielsen, TechnoData A/S

2 Background

The electronics and electrical industries are facing increasing pressure from legislation to remove lead from its products. This is because of the hazards to health during manufacture of the materials and environmental damage and human exposure caused by their end of life disposal. The second draft of a proposal for a directive on Waste from Electrical and Electronic Equipment was drafted in the middle of 1998. The proposal should become an EU directive for enforcement in all member States by July 2006. More information is available on the below web address:
http://www.lead-free.org/download/files/pdf/Directive_Section_WEEE_Final_Proposal.pdf.

When the European Commission ratifies the legislation, there will be a major impact on all industries using electronic and electrical components.

For producers using/producing solder systems, electronic components and printed circuit boards (PCB's), this legislation is likely to result in the following changes in their production/assembly systems:

- Switch from the traditional tin/lead solder to a lead free solder or
- Switch from the traditional tin/lead solder to conductive adhesives
- Switch from tin/lead plating on PCBs to a lead free plating
- Switch from tin/lead plated components to lead free plated components
- Modification of the soldering process (temperature, fluxes, etc.)

This project included a survey on commercially available lead-free alloys for both reflow soldering and wave soldering. An environmental pre-screening of solder alloys and fluxes was carried out in order to identify technical and environmentally promising systems. Two systems were identified to have technical and environmental characteristics that suited the applications concerned, namely Sn-4.0Ag-0.5Cu and Sn-3.5Ag. A traditional tin-lead solder paste (Multicore CR39) was used for reference. The lead free solder pastes were provided by Alpha-Fry Technologies via the Danish representative, Teleinstrument A/S and the reference Multicore solders were supplied by CYNCRONA A/S. Wave soldering was performed with a Boliden Bergsøe Sn-3.8Ag-0.7Cu system while the flux used was from Alpha Metal (RF 800).

The incentive to design lead-free solder assemblies lies in the fact that there is no recycling capability for the lead content of solder and that the current fluxing technology is based on VOC (volatile organic compounds) carriers and solvents, which are vented to the atmosphere during soldering. The development of a complete environmentally acceptable soldering technology is thus of vital importance to industry.

A double-sided plated-through-hole FR4 glass-epoxy type test board was supplied in two different board finshes, immersion gold and OSP. Selected components, 25 types are all supplied from the Bang & Olufsen stockage, and 20% were found to have lead free component finish.

Three experimental cases were included in the project:

1. Double reflow soldering followed by hand soldering (at Bang & Olufsen)
2. A combination of reflow (at Bang & Olufsen) and wave soldering (at HYTEK)

3. Finally a production case including reflow, wave and hand soldering was carried out jointly by SIMRAD, Grundfos and HYTEK.

The first two cases were based on a double-sided plated-through-hole FR4 test board while the production case used a multilayer FR4 with two different board finish variants (SnPb HASL and immersion tin solder).

Design and assembly of test boards was performed by Bang & Olufsen and DELTA in collaboration. Automatic assembly including screen printing of solder paste, component pick & placement, and lead free reflow soldering was successfully realised at a maximum temperature of 240°C, and a soldering time of 60 seconds at >217°C using the present manufacturing equipment. Lead free hand soldering of leaded components was found to require much heat and full wetting of the plated-through-holes was problematic. Special solder iron set-up is required compared to tin-lead soldering and further work is required in order to reach consistent hand soldered joints.

Robustness to solder heat is a key issue, and component selection/specification have to match the resistance to the solder heat guideline of 260°C, and soldering time of 60 seconds at >217°C.

OSP board finish is found to result in incomplete wetting of the solder lands, which is the case for both of the lead free solders, and in that respect the immersion gold board finish is preferred.

Qualification testing has been performed by high temperature ageing, temperature cycling and damp heat testing, and the properties of lead free joints compared to similar tin-lead joints have been evaluated by visual examination, X-ray examination, component shear testing, microsectioning and optical microscopy. Temperature cycling testing is found to be the major accelerating factor in joint degradation and results from destructive physical analysis show that the degradation takes place in the solder bulk material of the lead free joints.

In general, the performance and reliability of the lead free reflow soldered joints is found to match standard tin-lead soldered joints, and both of the lead free solders tested are found to show very similar performance.

A considerable R&D effort is currently under way in different parts of the world in a bid to find suitable alternatives to lead containing solders. The major alternatives for the volume production seem to be based on lead free solders and conductive adhesives. Some of the ongoing research activities in lead free solder development are listed below:

a. National Centre for Manufacturing Science (NCMS), Michigan, USA. A consortium based research programme evaluating lead free solders for electronics manufacturing. www.ncms.org. The programme was carried out by a consortium of AT&T, Lucent Technologies, EMPF, Ford Motor Company, GM-Delco Electronics, GM-Hughes Aircraft, NIST, Renssekaer Polytechnic Institute, Rockwell International Corp, Sandia National Laboratories, TI and Hamilton Standard. The goal of the project was to determine whether safe, reliable, non-toxic and cost effective substitutes existed for lead-bearing solders in electronics manufacturing.
b. A research consortium funded by the Department of Trade and Industry (DTI) in which Multicore, the Tin Research Institute and GEC Marconi among others are the participating partners. www.itri.co.uk. The consortium selected alloys with two criteria in mind: suitability for electronic assembly and supply potential. Thus the following alloys were short-listed for trials: Bi-42Sn: Eliminated due to poor mechanical properties and low melting point. Sn-

9Zn: Eliminated due to corrosion of the zinc phase. Sn-5Sb: Eliminated due to the melting temperature being too high. Sn-3.5Ag and Sn-0.7Cu was found to have adequate properties.

c. TWI, UK runs a project on the characterisation of lead free solders. www.twi.co.uk.
d. BRITE/EURAM project on "Improved Design Life and Environmentally Aware Manufacture of Electronics Assemblies by Lead Free Soldering". BRPR960140 headed by GEC Marconi, UK. www.cordis.lu. Conclusions are that optimum solders are based on Sn-Ag-Cu. The Sn-3.8Ag-0.7Cu alloy was recommended for general purpose use, possibly with the addition of antimony. Sn-3.8Ag-0.7Cu-0.5Sb was recommended for wave soldering. Sn-Bi-Ag could be used for single sided wave soldering.
e. BRITE/EURAM project on "Development of Adaptive Solder Technology for Reliability and environment Compatibility of electronic assemblies. BRPR980683 headed by Thomson CSF, France. www.cordis.lu.
f. IVF programme on "Integrity of Lead Free Solders - Manufacturability, failure mechanism, etc." www.ivf.se.
g. Norther Telecom, Canada: Development of novel lead free alloy for mobile telephones.
h. Nokia with Multicore is doing research to replace lead containing solder in cellular phones.
i. Loughborough University, UK investigates fundamental characterisation of lead free systems using DSC, TGA, etc.
j. Japan Institute of Electronics Packaging: Consortium work finished in 1996 i9ncluded: Senju Metals, Harima Chemicals, Alpha Metals Japan, Nihon Handa, Ishikawa Metals, Uchibashi Estec, Speria Japan Solder Coat, Univ. of Tokyo, Osaka Univ., ICS, SC Lab, Tokyo Electric Univ., Tabai Espec, Mitsui Mining, Nippon Mining & metals, Nippaku, Ishihara Chemicals, Tanaka Electronics Industry, Furukawa Electric Industry, TDK, Murata, Rubicom, Sony, Fujitsu, NEC, Hitachi, Toshiba, Panasonic, Fuji Electric and Omron
k. Japanese Universities: Many universities are involved with the research and development of lead-free solders/soldering such as University of Tokyo, Osaka University, Yokohama National University, Shibaura Institute of Technology, Kohnan University and National defence Academy.

Many more national projects than listed here are going on.

2.1 Legislation

There is a continual world-wide environmental movement away from the use of lead towards ‘non-toxic’ products. Various alternatives have replaced the traditional use of lead in wine bottle capsules, fishing weights, casting alloys for toys, as well as solders for certain plumbing applications. Once considered a joke, lead-free ammunition (bullets and shot) is now available and experiencing a significant growth in demand, particularly in the USA where the possibility of litigation against environmental contamination or employee exposure to hazardous materials is high.

Added to this, there are now a series of initiatives worldwide that outline targets for electronic equipment re-use and recycling. In such initiatives, the use of hazardous materials such as lead is often limited in order to improve the ease of recycling.

Legislation directly affecting the solder and electronic assembly industries has been agreed by the EU system outlining targets for electronic equipment re-use and recycling (Directive on Waste of Electronic and Electrical Equipment, WEEE). At the same time agreement was reached to limit the use of hazardous materials (Directive on Reduction of Hazardous Substances, RoHS) to improve the ease of recycling and to limit the hazards of certain substances including lead. The RoHS directive temporarily exempts lead in solders. These two directives, entering into force by 1 July 2006, will impact not just on solder alloys but component finishes and temperature ratings, board finishes and flame retardancy issues.

The European Commission has also passed a Directive on End-of-Life Vehicles which again is aimed towards recycling and re-use targets and prohibiting the use of certain hazardous materials. Lead in solders for automotive applications have a temporary exemption from the lead ban. This Directive enters into force 1 July 2003.

The Danish Environment Agency has also taken action against products containing lead compounds and metallic lead in a number of product areas.

The Japanese Ministry of Trade (MITI) has drafted a recycling law for electrical appliances with a 2001 deadline. This does not yet include lead phase-out but it is expected to come.
Although there is no federal legislation yet in the US, there are a number of State electronics recycling initiatives to consider. In addition, the EPA has recently proposed a crack-down on lead emissions from plants that may impact the soldering industry.

A permitted residual lead content in “lead-free” solders has yet to be defined. The US EPA defines lead-free plumbing solders as those containing less than 0.2% Pb although this may be reduced to 0.1% in the future. It is this level of impurity limit that may also be expected in “lead-free” solders for electronics.

IPC – Association Connecting Electronics Industries Environmental Health and Safety (EHS) Committee has announced the Environmental Protection Agency's (EPA) finalization of a lead reporting rule could impact U.S. PWB and EMS companies. The final legislation changes the Toxics Release Inventory reporting threshold for lead and lead compounds from 11,000 kg per year to 50 kg per year.

This new legislation is retroactive to January 1, 2001, requiring companies to begin tracking and reporting all lead and lead components used during the 2001 calendar year. EPA calculates the rule will cost the industry $80 million for the first year, and $40 million per year in subsequent years. The electronics industry alone is expected to submit more than 3,500 reports at a cost of more than $25,000 per company for the first year, and more than $12,000 per company each year following.

Companies with 10 or more employees that use or process 100 pounds of lead, or more than 350 pounds of eutectic tin-lead solder per year, will be effected the most. IPC is currently pursuing all available avenues in it continued efforts to halt the implementation of this rule. However, facilities are advised to begin immediately tracking their lead use for the record-keeping process. The full text of EPA's final rule can be found on the EPA's Web site at www.epa.gov/tri.

3 Lead free soldering

A survey was carried out to identify the currently available lead free soldering systems on the Danish market (all provided by international vendors). Most of the systems provided are based on variations to the below generic alloy-families:

a. 96.5% Sn / 3.5% Ag
b. 99.3% Sn / 0.7% Cu
c. 42% Sn / 58% Bi
d. 48% Sn / 52% In
e. 91% Sn / 9% Zn
f. 93.6% Sn / 4.7% Ag / 1.7% Cu

The most convenient way to separate the available lead-free alloys is first to consider their melting temperature. Most fit into one of the following categories; low melting temperature (below 180C), mid-range melting temperature (200-230C), and the high-temperature alloys (230-350C). Various lead replacement alloys are shown in the below figure:

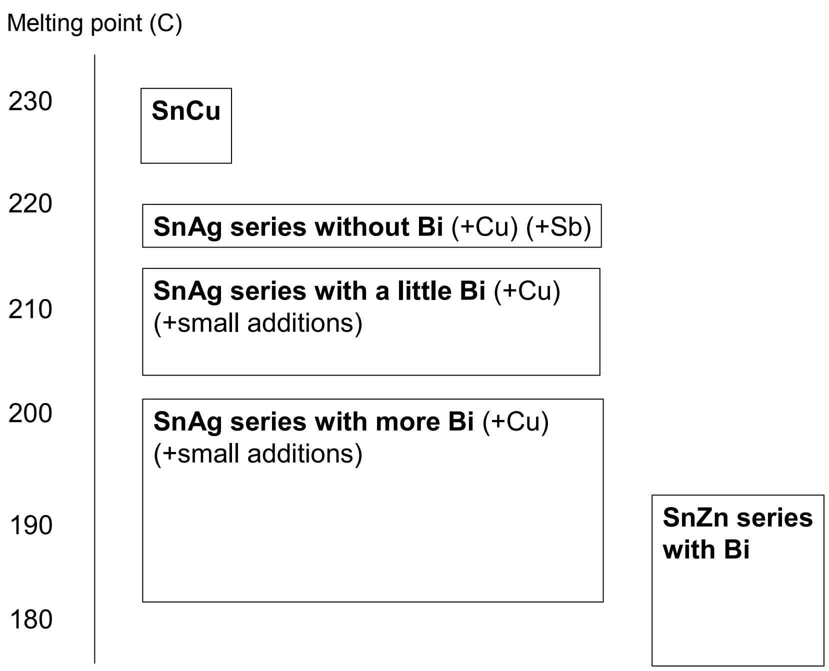


Figure 1: Lead free alloys categorised by melting temperature

These families are developed in order to suit various applications parameters like low melting point, fatigue properties, corrosion, good strength, etc. Another problem with these systems may be that the substances are only available in rather limited quantities (Bi, Ag and in particular In).

3.1 Test set up

The test boards were designed and ordered as double-sided plated-through-hole FR4 epoxy-type printed circuit boards in two different board finish variants:

- Immersion gold
- OSP

The layout of the test board is designed to accept the full range of selected SMD and leaded in-hole mounted components included in both of the Danish lead free projects and are shown in the below figures.

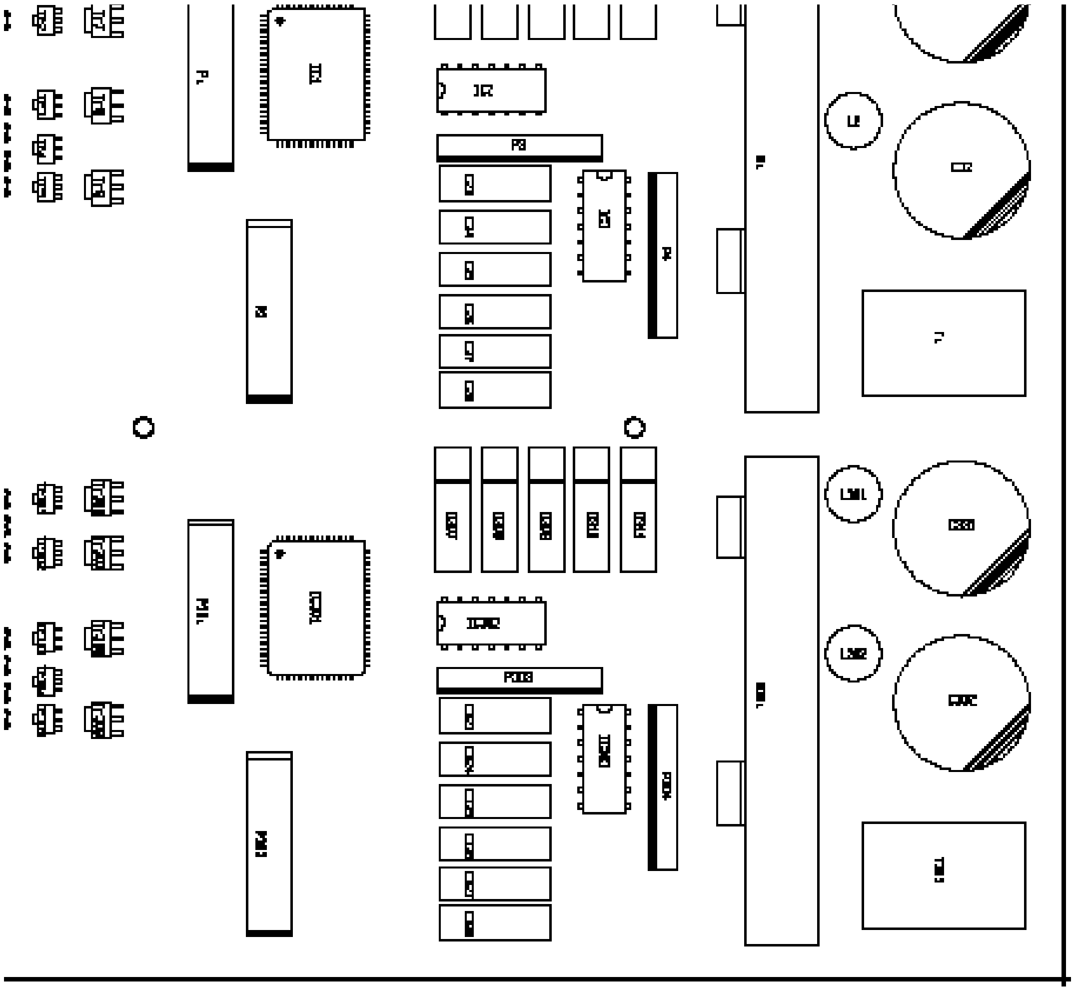


Figure 2: Primary side of the test board

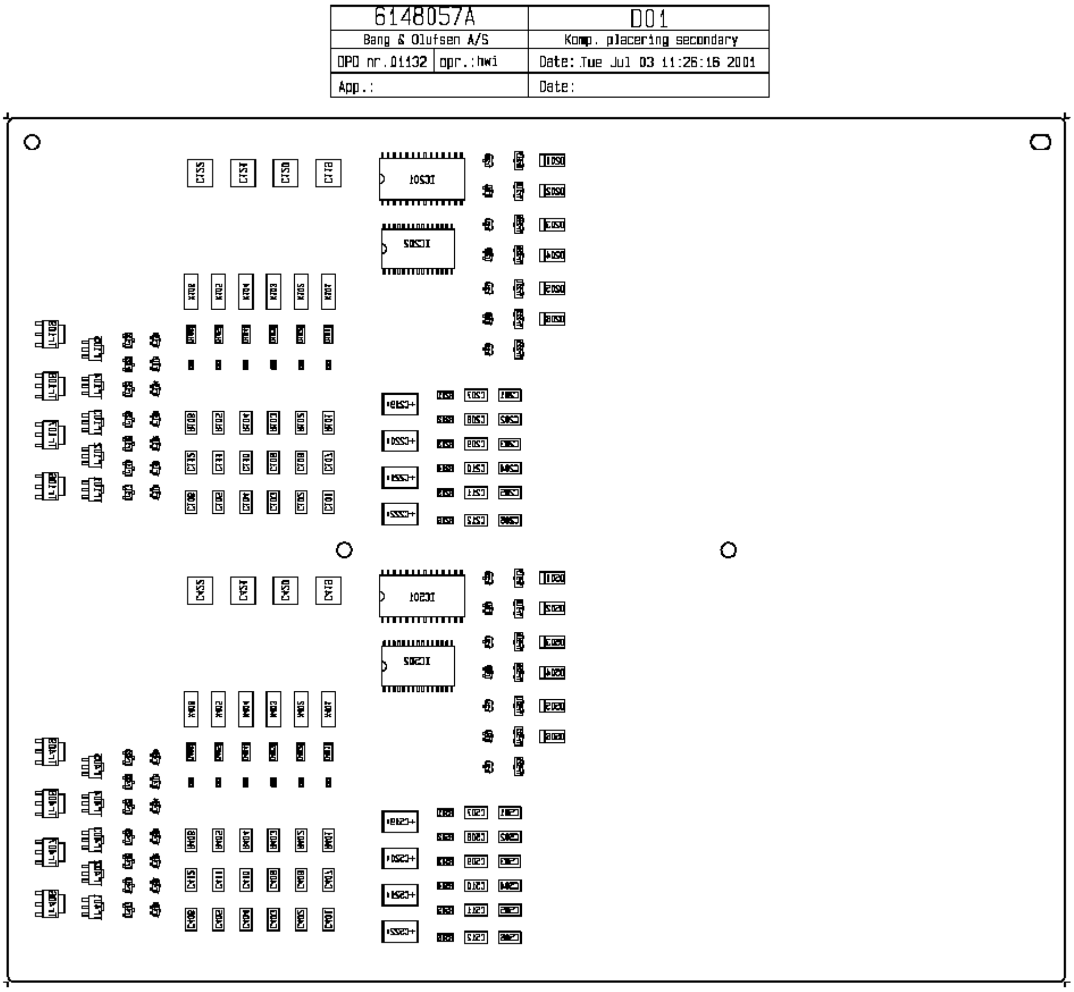


Figure 3: Secondary side of the test board

A range of typical components was specified and sourced at the same time from the Bang & Olufsen storage. In general, few components in today's component technology are expected to be lead free due to the widely usage of lead in the tin-lead component finish. Based on the present situation components with standard finish were accepted in this study, and the component finish was characterised by SEM/EDX:

Component	***Type & size***	***Termination finish (analysed, EDX)***
Ceramic multilayer capacitor	GRM series, 0402	SnPb
Ceramic multilayer capacitor	NPO, 1206	Sn
Metallised film capacitor	Polyester, 2220	Sn
Chip resistor	Thick film, 1206	SnPb
High speed diode	Glass sealed, SOD80	SnPb
Ceramic resonator	Melf	Ag
Transistor	-323	SnPb
Transistor	-23	SnPb
Transistor	SOT 89	SnPb
Transistor	SOT 223	SnPb
Integrated circuit	PQFP 44	SnPb
Connector	Smd type	SnPb
Power diode	Leaded	SnPb
Trafo	Leaded	Sn
Tantalum chip capacitor	Case D size	Sn/Pb
Metallised film capacitor	Leaded	Sn/Pb
Aluminium electrolytic capacitor	Leaded	Sn/Pb
Chip resistor	Thick film, 2012	Sn/Pb
Coil	Leaded	Sn/Pb
Power transistor	Leaded, TO-220	Sn/Pb
Integrated circuit	Leaded, DIP-14	Sn/Pb
Integrated circuit	Smd, SO28	Sn/Pb
Integrated circuit	Smd, SO30	Sn/Pb
Connector	Leaded, 12-way	Sn/Pb
Heat sink support	Leaded	Al

20% of the components were found to have lead free component finish.

All 120 test boards were reflow soldered in a convection oven (Heller 1800) under nitrogen atmosphere. The reflow profile for the lead free and the reference solder is shown in the below figure.

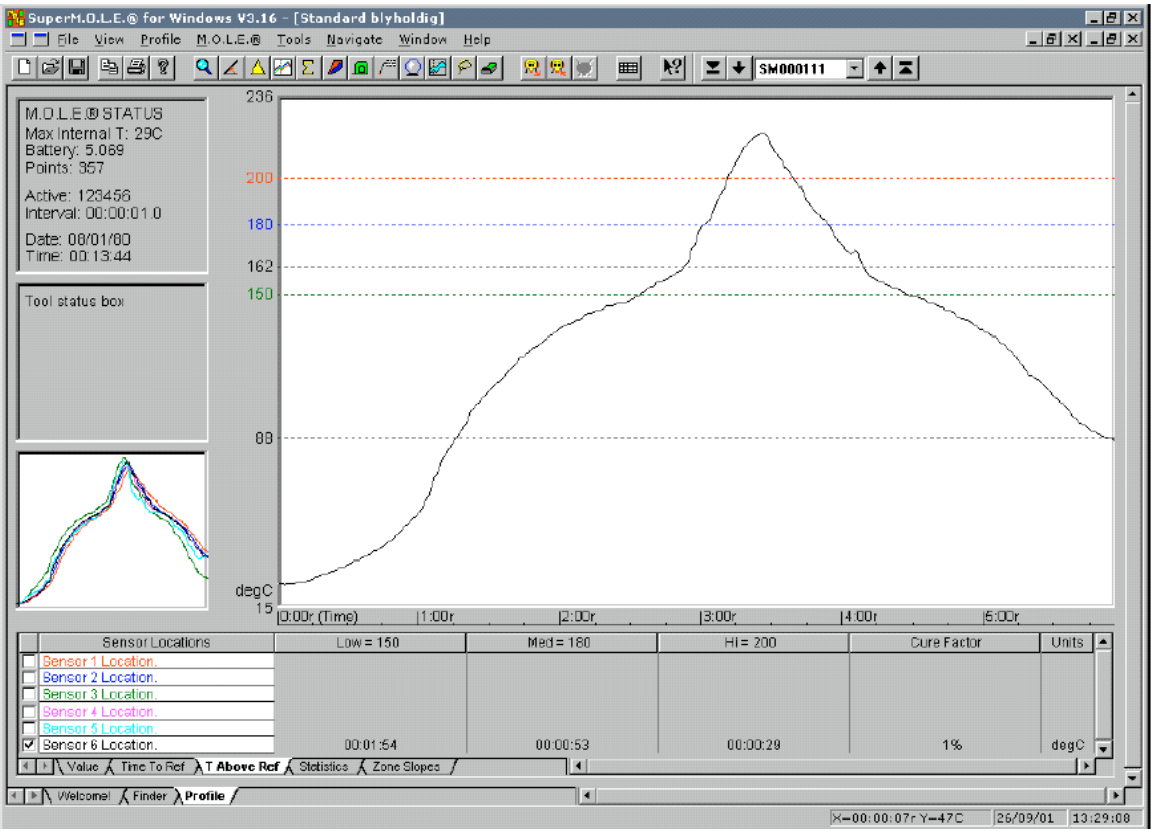


Figure 4: Reflow profiles for lead free solder paste and the reference paste

Following 60 test boards were wave soldered using a SEHO 8000 machine (double wave). The temperature profile was established according to the flux and solder specification (see below figure).

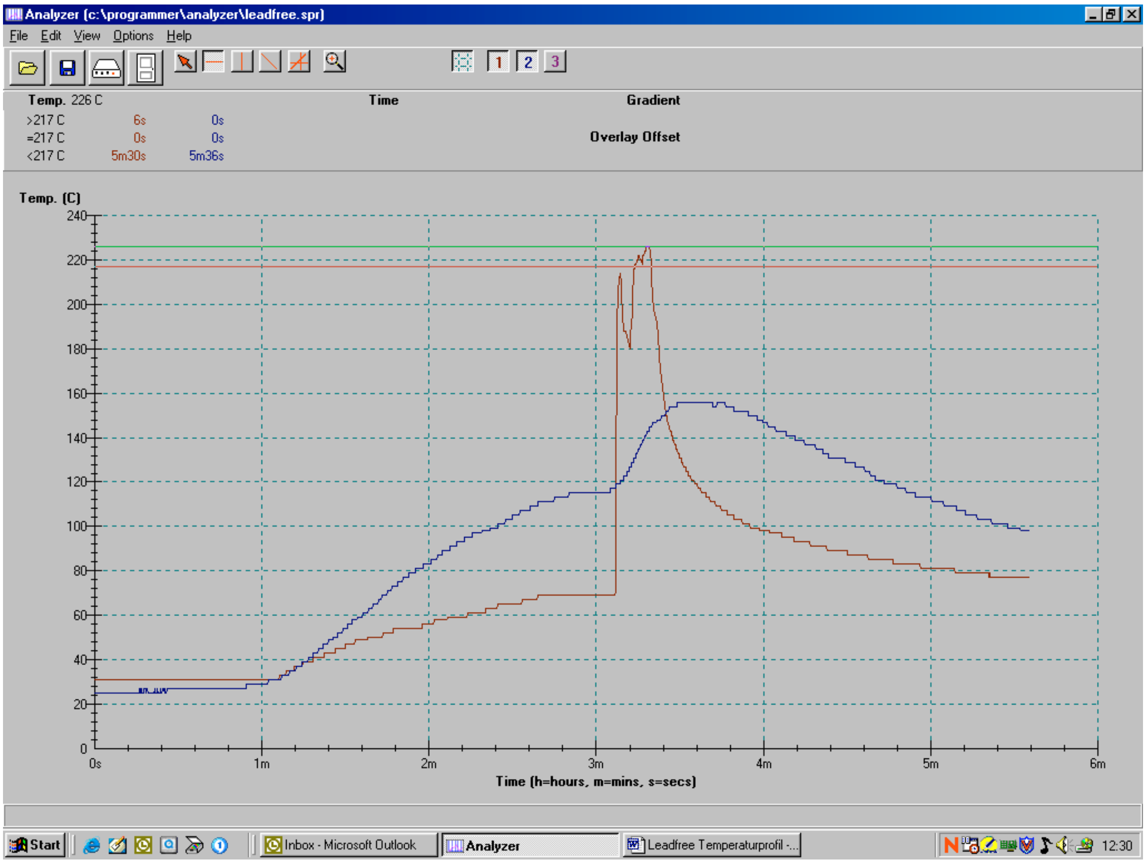


Figure 5: Wave soldering profile for lead-free alloys. Temperature profile #1 measured in solder joint on power transistor (C). Temperature profile #2 measured on PCB topside according to flux specifications.

3.2 Test plan

A test plan to be used in two different projects was developed by DELTA. The test flow used in the present project is shown in the white boxes in the below figure:

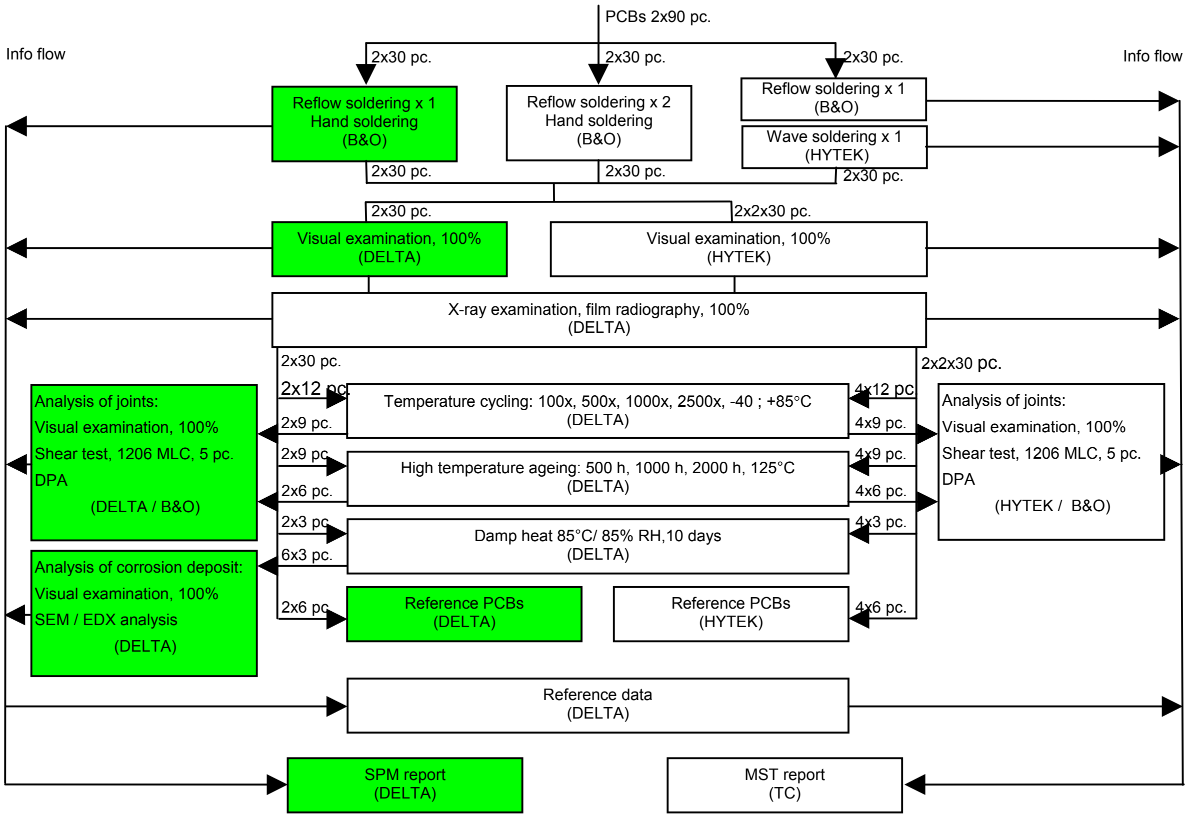


Figure 6: Test plan (white boxes apply to the present project)

3.3 Contamination and SIR Tests

SIR test is a methodology used to characterise electronics assembly residues and their impact on reliability. It is usually performed on industry standard test board coupons containing test patterns. The insulation resistance of a test pattern is monitored at various intervals as temperature and humidity are varied.

The SIR tests were performed using the IPC-B-24 test board for as well reflow soldering as wave soldering. Each measurement represents the average of 12 test patterns. The test results are shown in the below figures:

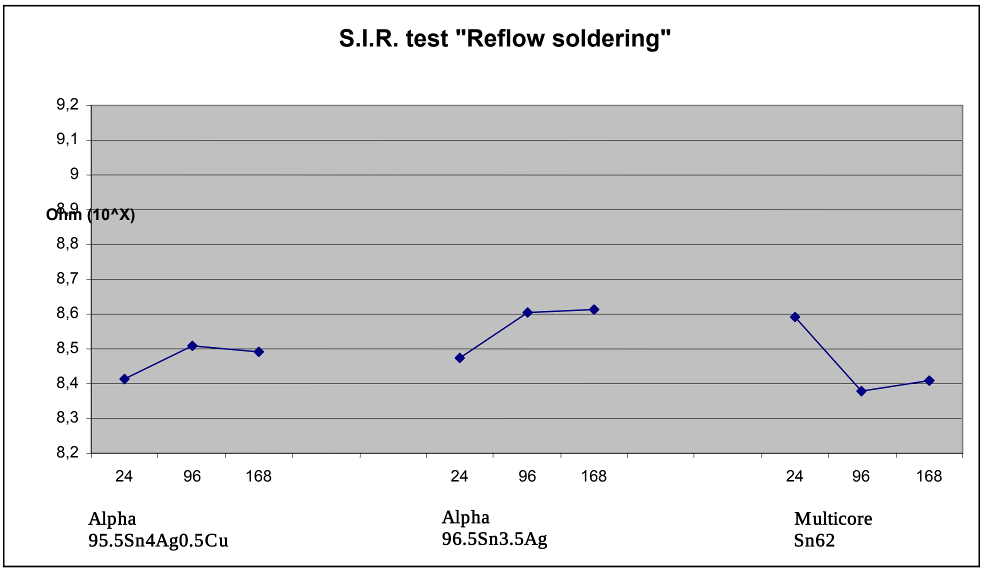


Figure 7: SIR test results for reflow soldering

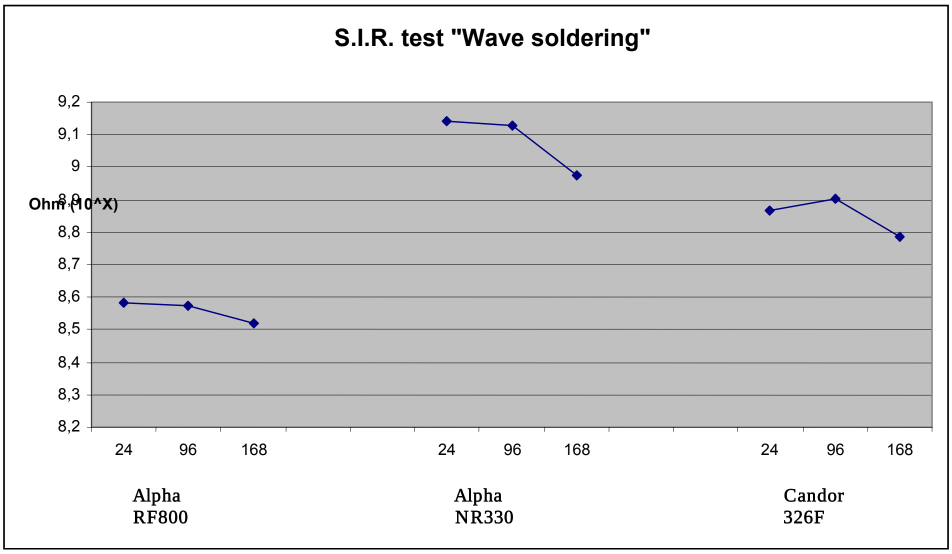


Figure 8: SIR test results for wave soldering

As can be seen from the above figures there is no significant difference between the two lead free solders and the lead containing reference solder.

The results of the contamination test using Alpha Ionograph 500M test equipment is shown in the below figure:

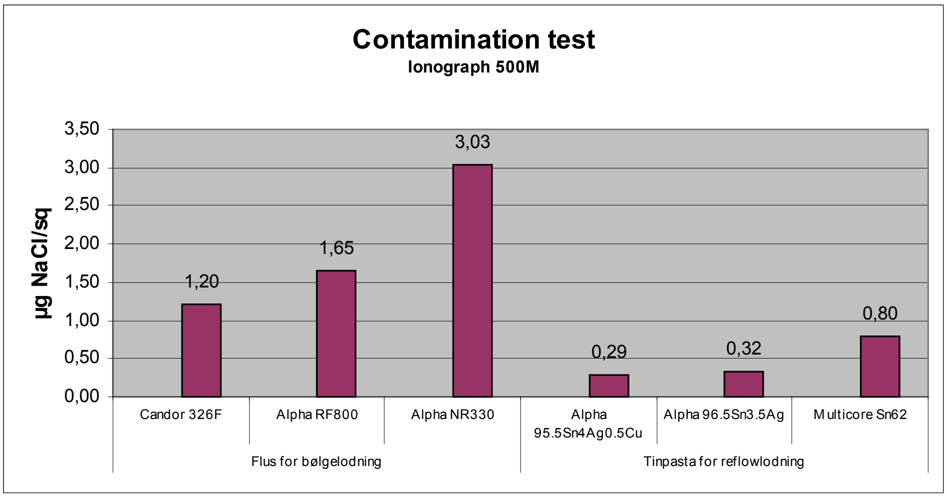


Figure 9: Contamination test results for wave soldering (left part) and reflow soldering (right part)

The contamination test shows acceptable levels compared to the applied standards on PCB type IPC-B-24.

After wave soldering the Candor 326F shows the best results followed by Alpha Metals RF800 (left part of figure 7). After reflow soldering Alpha Metals PNC0106A 88-3-MXX 95.5Sn/4Ag/0.5Cu shows the best result followed sharply by Alpha Metals PNC 0121E 88% type3 SnAg.96.5,3.5 (right part of figure 7).

3.4 Inspection of lead-free PCBs using the Omron VT-WIN

Six test boards went through a standard programme on the Omron VT-WIN Automatic Optical Inspection System. Since the test boards are fairly simple, the programme only took a couple of hours to create and fine-tune. The programme was created using the standard library in the Omron VT-WIN.

After a little fine-tuning on the lead containing board, all three types passed through inspection mode, without any need for special adjustments to cope with the lead free boards. The lead free boards, however, exhibited more white when viewed with Colour Highlight (due to the fact that they are less reflective).

Even with the current software and standard library it did not cause any problems to test the boards. However, Omron is preparing an additional library for lead free soldered components, which better handles the less reflective lead free solders.

3.5 Double reflow soldering

60 test boards were reflow soldered on two sides at Bang & Olufsen and following analysed at DELTA.

Component shear testing was performed using a Dage 22 Micro Pull Tester equipped with a 10 kg load cell. Shear test results were recorded vs. temperature cycling testing and vs. high temperature ageing for a ceramic multilayer capacitor (NPO 1206 size) and a glass sealed diode (SOD 80). The test results obtained on OSP and NiAu surface finish are shown in figures 8 and 9:

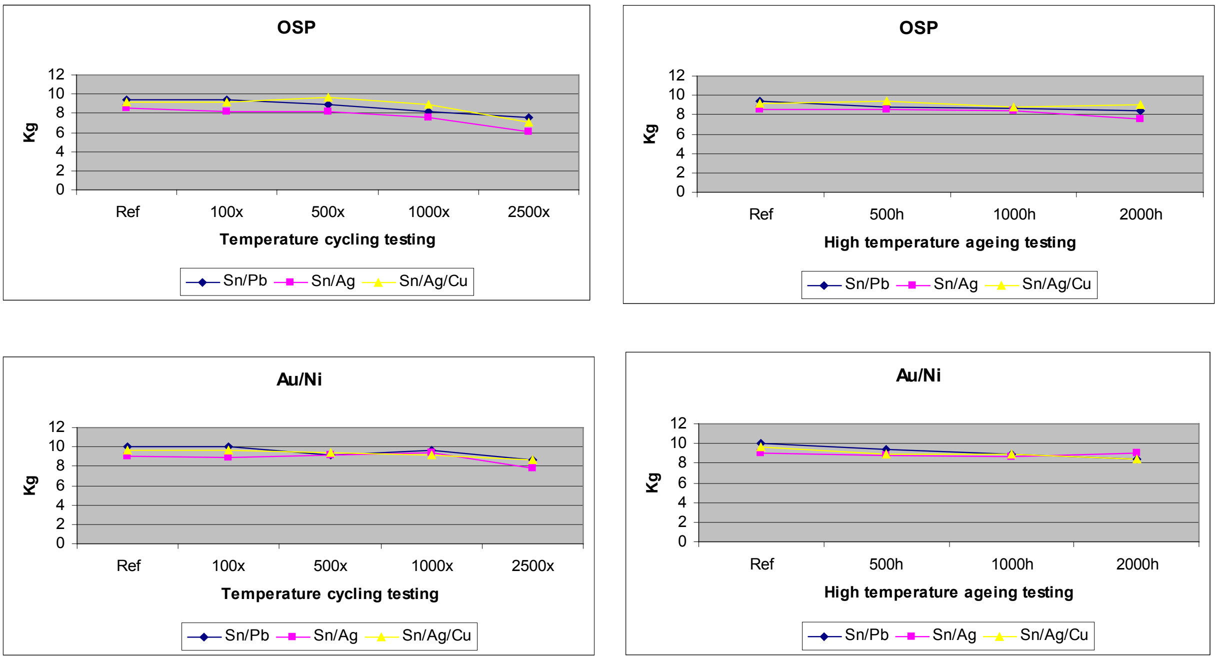


Figure 10: Die shear results, NPO 1206 ceramic multilayer capacitor

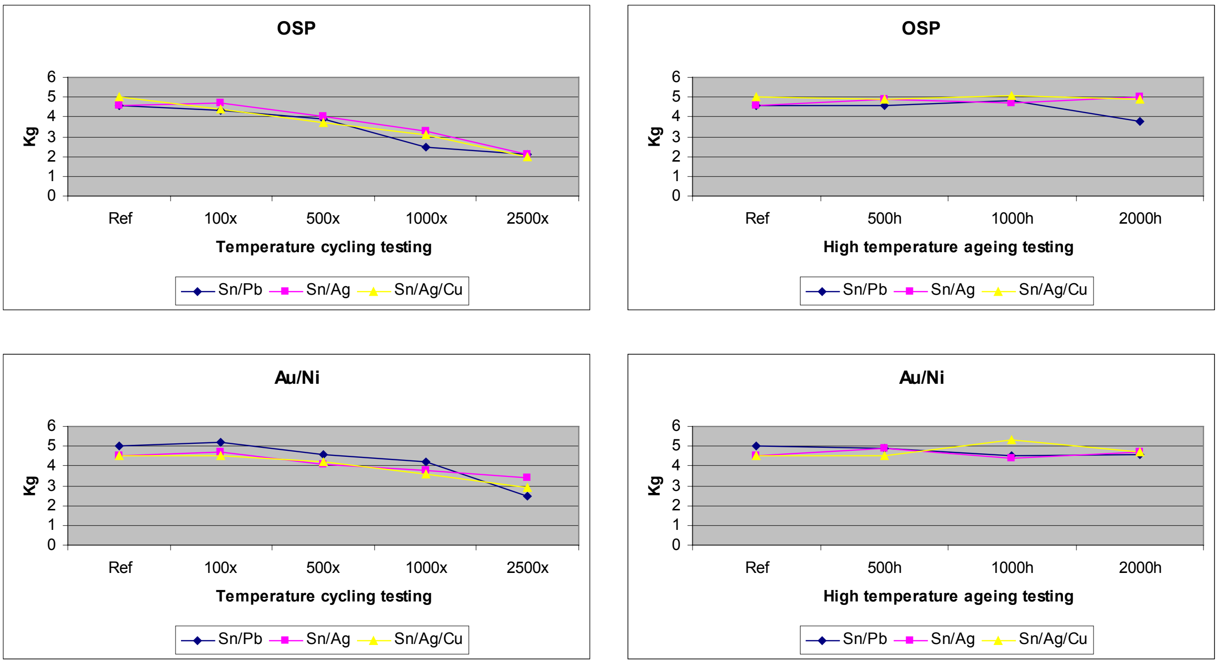


Figure 11: Die shear results, SOD 80 diode

The shear test of the wave soldered SMD components did not give usefull test results since the variation indicated that other parameters that the solder joint (mounting glue) influenced the strength. A following microscopy survey revealed that the variation was caused by the production process, where different amounts of glue and solder obviously influenced the strength of the joint.

3.6 Combined reflow and wave soldering

60 test boards were reflow soldered on one side at Bang & Olufsen and the wave soldered at HYTEK. The following analyse was carried out at HYTEK.

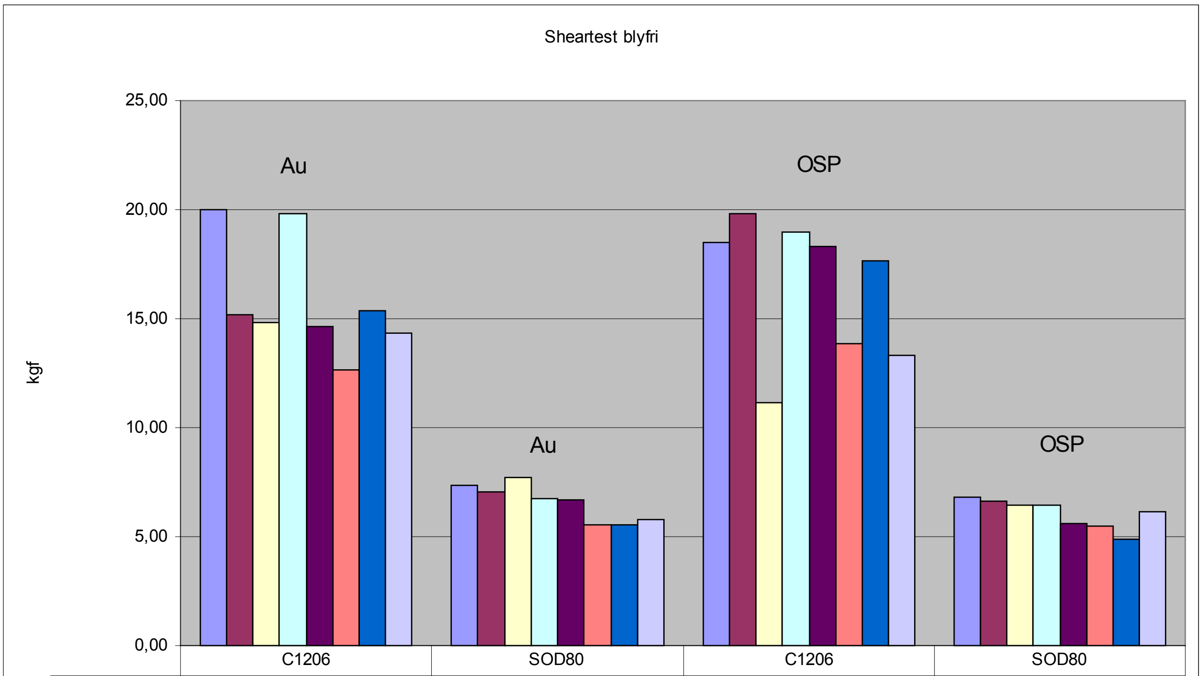
All test boards have been subject to X-ray examination in order to check the integrity of the solder joints by examining the collected X-ray films at low magnification using stereo microscopy.

The lead free through hole mounted components showed stress lines at 100x thermal cycling. No stress lines were observed on the components mounted with lead containing solders. The lead containing solder joints showed stress lines at 500x thermal cycling.

Microscopy of the solder finishes of SMD components showed no tendency to stress lines at 1000x thermal cycling, independent from the type of solder.

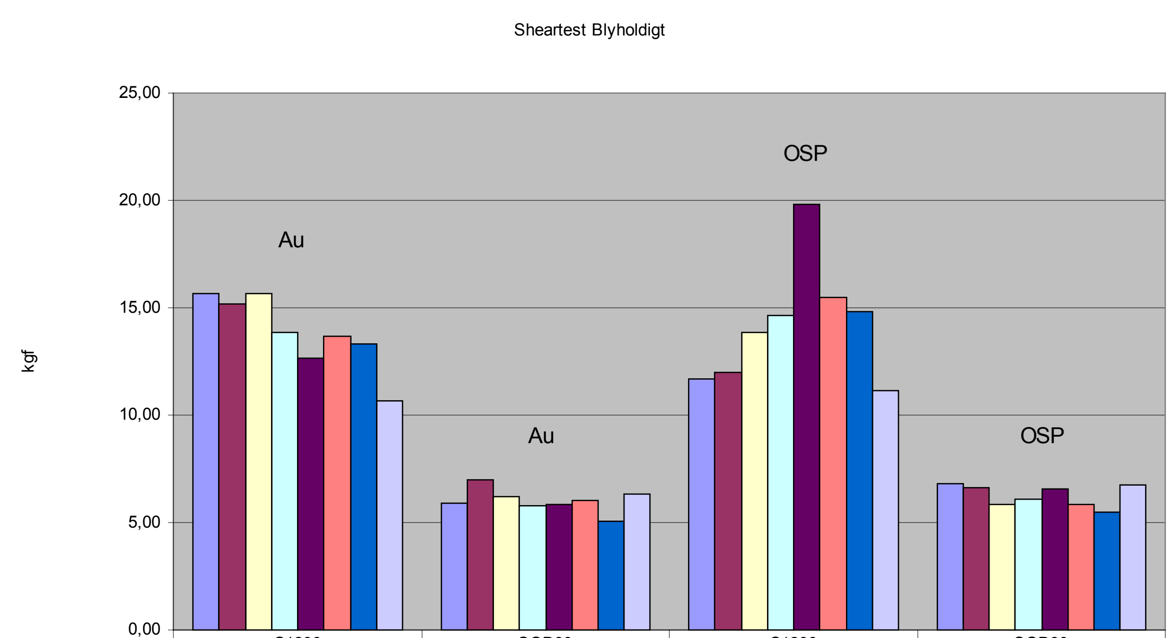
The microscopy showed no visible difference whether the soldering was made on OSP or NiAu board surface finish.

The shear test gave a rather big spreading in data indicating that other parameters than the solder joint itself affected the results. A following microscopy of the broken solder joints confirmed that the amount of SMD adhesive and the adhesive strength together with a variation in the amount of solder from the wave soldering process could have affected the test. The major results of the C1206 and SOD80 SMD components mounted on board having NiAu and OSP finish is shown in the below figures:



	C1206	SOD80	C1206	SOD80
Ref. PCB	20,00	7,35	18,50	6,78
X100 cyklus	15,17	7,07	19,83	6,60
X500 cyklus	14,83	7,72	11,17	6,45
X1000 cyklus	19,83	6,73	19,00	6,42
X2500 cyklus	14,67	6,70	18,33	5,62
Ageing 500h	12,67	5,53	13,83	5,47
Ageing 1000h	15,33	5,53	17,67	4,85
85/85	14,33	5,80	13,33	6,17

Figure 12: Shear test results of lead free joints



	C1206	SOD80	C1206	SOD80
Ref. PCB	15,67	5,93	11,67	6,80
X100 cyklus	15,17	7,02	12,00	6,60
X500 cyklus	15,67	6,22	13,83	5,85
X1000 cyklus	13,83	5,78	14,67	6,07
X2500 cyklus	12,67	5,85	19,83	6,58
Ageing 500h	13,67	6,00	15,50	5,82
Ageing 1000h	13,33	5,07	14,83	5,50
85/85	10,67	6,33	11,17	6,73

Figure 13: Shear test results of lead containing joints

3.7 Hand soldering

Hand soldering using lead-free solder wire requires a slightly different approach. A higher temperature of the soldering iron tip is required as well as a longer pre-heat (3-5 seconds) of the solder pad and component lead before applying the solder wire. Therefore lead free hand soldering requires much heat (pre-heat may be required) and full wetting of the plated-through-holes is problematic. A solder iron set-up suitable for lead free soldering is required compared to traditional tin-lead soldering.

3.8 Production case

This lead-free production case was initiated to investigate and compare on a well known product the reliability of lead-free solder joints vs. lead-containing joints for the three soldering methods: reflow soldering, wave soldering and hand soldering. The case should also verify whether or not immersion tin solder pad finish was a usable alternative to SnPb HASL, when changing to lead-free soldering processes.

The PCB selected for the production case was an existing Power Supply Unit produced by SIMRAD since 2000. The PCB was a multi layer (4 layers) FR4 with SMD and through-hole components on topside. The SMD components were reflow soldered and nearly all through-hole components were wave soldered. Only two leaded power transistors were finally hand-soldered. A total of 36 boards were manufactured divided in three batchs. Please consult Appendix 1 for more details about the case.

After manufacturing the product went through visual inspection, temperature cycling and shear force test. None of these tests indicated any SMD solder joint reliability difference between the 3 batches. Also with the hand soldered through-hole component joints no clear differences were found, although one of the lead-free joints had indication of crack formation after 500 temperature cycles. However, on the wave soldered joints small cracks were seen on the lead-free process, in the micro sectioning performed immediately after the wave soldering; although they did not cause any circuit failures even after 500 temperature cycles. The lead-free solder joints seem harder and more brittle than the lead-containing joints. This indicates that stress relieve clinching on the component leads might become necessary to minimize coefficient of expansion of the different materials.

To verify the strength of the SMD solder joints in each batch, and the effect of the temperature cycling a number of 1206 capacitors were shear force tested. The average results for each batch are shown in the below figure:

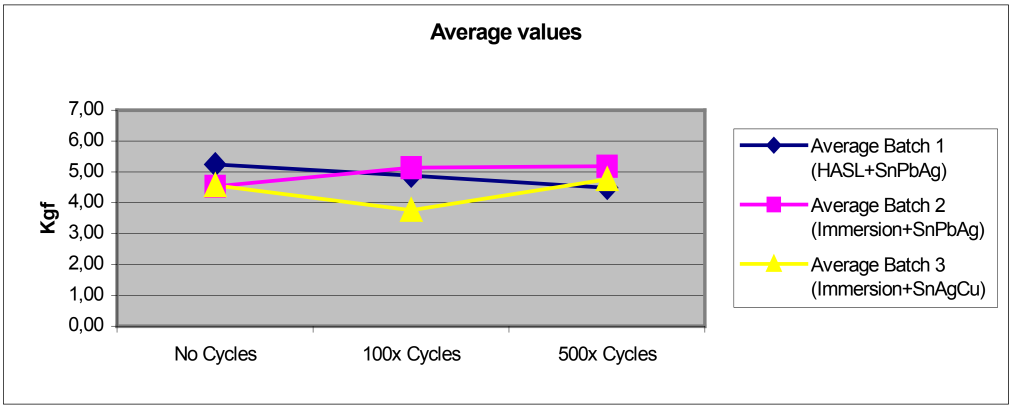


Figure 14: Average shear force results for 1206 capacitors

Also for the objective Immersion Tin as HASL alternative, none of the 3 tests indicated that immersion tin could not be used as an alternative to HASL, both in lead-free and lead-containing applications. Compared with HASL solder pads the immersion tin solder pads showed equal solder ability - both in the lead-containing and in the lead-free soldering processes. The top fillets generally seemed to float out equally on the pad on all 3 batches. The only difference noticed was, that at some through-hole top side solder fillets, a clear border line was seen between the solder fillet and the solder pad. Since the tin surface of the pad is very thin and chemically applied, the border line must be a natural consequence and must be purely depended on the flux application and spreading at the PCB top side solder pads. It must however be stressed, that the PCBs with immersion tin surfaces were only 1 – 2 weeks old at the production time and the impact of a long-term storage was not investigated in this production case.

4 Health and environmental issues

International projects have mainly focused on the technical properties of lead-free solders. The aim of most projects has been to find and investigate ways of lead substitution and not to assess whether the alternatives are recommendable from a health and environmental point of view.

However, some projects have included toxic aspects, see e.g. proceedings from IPCworks'99 (IPC, 1999). Most of these investigations have focused on the inherent toxicity of lead and alternative metals. The investigations have typically been superfluous and often based on non-validated databases as e.g. RTECS. In a recent Danish project (SPM, 1999), the Danish Toxicology Centre made a more in depth assessment of the inherent toxicity of most of the metals used in lead-free and lead containing alloys. It was seen (not surprisingly!) that lead is to be viewed as very toxic but at the same time that several of the other metals have suspicious toxicological and environmental effects as well. However, for most metals relatively few toxicological data are available, whereas a substance as silver is several orders of magnitude more eco-toxic than lead.

The second discussion in relation to actual risk is 'what is the exposure level when using lead solders?' A main topic at the IPCWorks'99 conference was that so far no studies have shown that workers in electronics mounting facilities have a higher blood lead level as a result of their occupation and that the likeliness that leaching of lead after end-of-life disposal directly to landfills is very limited as lead will form stable compounds and bind tightly in the soil environment. The latter statement was partly supported as part of the Danish Kamille-project /18/. The leaching from landfills of residues from waste incineration is different, as incineration makes lead very mobile. Again very few data exist for the leaching of alternative metals.

Toxicological profiles for silver, copper, antimony, bismuth, indium, zinc, tin and lead can be obtained from the SPM Report SPM-151. The SPM report generally concluded that lead poses high human toxicity and moderate toxicity towards aquatic organisms. Thus, substitution to lead free solder seems justified with regard to human toxicity.

However, the future general-purpose lead-free solder implies the use of silver, which has low human toxicity but is much more toxic to aquatic organisms than lead. The other metals are low to moderate toxic to humans and of moderate aquatic toxicity. One has to bear in mind that a toxic hazard, e.g. as described in the toxicological profiles not necessarily implies a toxicological risk. The toxic substance, metal or formed compound, e.g. oxide, must be present in (bio)available forms and in sufficiently high concentrations to result in toxic doses in humans or other organisms.

In summary:

- the focus in most international projects has not been on health and environmental issues
- the human health effect of substituting lead is positive
- the ecotoxicological effect of substituting lead is questionable
- the basic data set in order to assess several of the alternative metals is relatively weak.

Clarification of these issues (i.e. data generation) will require substantial research effort. As a consequence of the above summary, the health and environmental aspects of the current project are not intended to be carrying out actual risk assessment on lead and alternative metals to assess whether traditional lead solder is better or worse than the new alternatives.

The idea in the current project is to avoid that substitution of lead will cause new foreseeable problems. The selection made is therefore based on existing knowledge from the SPM project (SPM, 1999) and

Kamille-project /18/ by also including amounts in the different solders and application of a ranking system. Furthermore, the project has focused on the toxicity of new auxilliary materials (e.g. cleaning agents and fluxes), which have to be introduced in connection with the application of the new solders at different processing conditions as compared to traditional solders.

The use of modern technology, where the solder process takes place in full containment will reduce or eliminate the exposure of workers to solder vapors and fumes to negligible, regardless of the solders used (lead-containing or lead-free). In spite of this there will always be a risk of occupational exposure in connection with maintenance, repair, cleaning, etc., which still makes it justifiable from a human toxicological point of view to avoid lead in solders.

Due to higher processing temperatures, the tendency of chemicals and materials to become airborne increases during lead-free processes compared to lead-containing processes. The uses of the lead-free solders will possible result in an increased evaporation from the solder metals and fluxes as compared to the use of the traditional lead-containing solders.

Furthermore, the concentration of activators (in general irritating and some even allergenic) in the fluxes, seems to be higher (at least the double) in fluxes used in connection with lead-free solders as compared to the fluxes in lead-containing solders. Experience from the practical testing program in this project indicates that the flux of the lead-free solders is more corrosive to the materials. Combined with the fact that the lead free soldering temperature is higher, developing more fumes and vapors this may indicate that the lead-free solder processes may develop more acrid, irritating and in some cases allergenic fumes and vapors than the traditional lead-containing solder processes. From a human working environment point of view it still seems justified to avoid lead in solders, but the risk of exposure is low.

From a wiev of risks to humans from substances spread in the environment this risk is lowered by substitution.

From an ecotoxicological point of view substitution to lead-free solders is more uncertain as emission and environmental fate are uncertain; exposure is therefore uncertain. In a life cycle perspective, the main environmental load will not be during the production/solder process, provided the production is optimized (e.g. with minimal losses during manufacturing), but after end of use.

The figures from Odense Renovationsselsskab A/S (13) show that it is possible to avoid direct depositing electronic waste. The use of incineration as a method of disposal involves certain risks of emission of metals and metal oxides, which are removed on filters. But the residue has to be landfilled giving rise to leaching at a later date. High degree of recycling is considered to be the most appropriate method in order to avoid undesirable environmental effects in accordance with the “Affald 21” (11), which is the Danish national action plan (until 2004) on waste handling. The goal is to:

- Increase recycling of resources from EE-products, e.g. PCB´s shall be recycled or processed with at least 80% reuse of each of the metals: copper, nickel, platinum, palladium, lead, gold and silver
- Limitate the incineration of EE-products
- Dispose the EE-products in an environmental-friendly way

The pros and cons regarding ecotoxicology between solder containing lead or silver may be partly resolved by recycling electronics to avoid emissions.

5 Conclusion

5.1 Lead free printed circuit board assembly

- Test boards have been realised by lead free reflow soldering at a peak temperature of 240°C and soldering time of 60 s at >217°C.
- Lead free hand soldering requires much heat (pre-heat may be required) and full wetting of the plated-through-holes is problematic. Special solder iron set-up is required compared to traditional tin-lead soldering.
- Integrity of realised lead free reflow soldered joints is found to be acceptable, even if some tendency of solder void formation is observed most pronounced for the OSP board finish test variants.
- OSP board finish is found to result in incomplete wetting of solder lands in the case of both of the lead free solders tested due to somehow poorer wetting properties compared to tin-lead soldering.
- Resistance to solder heat was found to be critical in the case of the metallised polyester film capacitor due to a specification/performance mismatch by lead free soldering condition. Robustness to solder heat is a key issue in component selection/specification in lead free soldering.

5.2 Reliability of lead free solder joints

- Damp heat testing confirmed the flux from both of the lead free solder pastes to be acceptably low activated, no corrosion observed.
- Component shear testing vs. high temperature ageing testing did not indicate any critical solder joint degradation up to 2000 h at 125°C.
- Similar component shear testing vs. temperature cycling is found to result in gradual degradation in the solder joints, but still typical lead free solder joints are expected to pass 1000x, -40°C; +85°C without open circuit failures.
- Results from component shear testing indicate OSP board finish to offer a somehow lower performance relative to gold-nickel board finish, probably due to the difference in wetting properties.
- Destructive physical analysis of reliability tested parts confirmed the performance of the tested lead free solders to be very similar. In all cases of solder joint degradation the degradation is found to be in the "bulk" solder material of the joints.
- In general, the results indicate the reliability of tin-silver-copper and tin-silver lead free reflow soldered joints to be somehow comparable/similar to the reliability of traditional tin-lead reflow soldered joints.

5.3 Environmental impact

- Lead is very toxic to humans and may cause serious deleterious chronic effects. The other metals (tin, silver and copper) have significantly weaker toxicological effects on humans than lead.
- From a human toxicological point of view it may seem justified to avoid lead in solders, as there is a risk of exposure. The use of modern technology, where the solder process takes place in full containment will reduce or eliminate the exposure of workers to solder vapors and fumes to nothing, regardless of the solders used (lead-containing or lead-free).

- There will though always be a risk of occupational exposure in connection with maintenance, repair, etc., which from a human toxicological point of view may still justify avoidance of lead in solders.
- There is a risk of human exposure from residues from incineration of waste containg lead solder.
- From an ecotoxicological point of view substitution to lead-free solders is more uncertain as emission and environmental fate are uncertain; exposure is therefore uncertain. In a life cycle perspective, the main environmental load will not be during the production/solder process, provided the production is optimized (e.g. with minimal losses during manufacturing), but after end of use. The future general-purpose lead-free solder implies the use of silver, which is much more toxic to aquatic organisms than lead.

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7 Appendix 1: Pb-free production case

Brian Sloth Bentzen – Simrad Støvring AS / SMT in FOCUS
Lars Ebdrup – Grundfos Electronics A/S
Poul Juul – Hytek
Maks Rasmussen - Hytek

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7.1 Introduction

As well known, we are moving towards a European ban on the metal, lead. A draft proposal in the Restrictions on the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) directive, associated with the European Waste from Electrical and Electronic Equipment directive (WEEE), bans lead from electronic products. The date for this ban is somewhat unclear but should be January 1st 2006 or 2007. However, the Japanese electronic industry is leading and forcing this process of removing lead from electronic products. Some of the major Japanese manufacturers already has lead-free soldered products in the stores. So, besides the driving force from a future ban on lead, it could very well end up as a competition and sales parameter.

The Danish project "Lead-free Soldering Materials" was initiated to investigate the process and environmental issues involved in changing to lead-free production of electronics. The project partners were Bang & Olufsen, Grundfos Electronics, Simrad Støvring, Hytek, Delta, DTC and Technoconsult.
The Pb-free production case described in this paper was a part of the Danish project.

7.2 Case objectives

This lead-free production case was initiated to investigate and compare the "lead-free" solder joint reliability against lead-containing joints for the three soldering methods: reflow soldering, wave soldering and hand soldering, on a well-known product.
The case should also verify whether or not immersion tin solder pad finish was a usable alternative to SnPb HASL, when changing to lead-free soldering processes.

7.3 Case set-up

The PCB selected for the production case was a well-known and reliable PSU unit produced since 2000. The PCB was a multi layer (4 layers) FR4 with SMD and through-hole components on topside. The SMD components were reflow soldered and nearly all through-hole components were wave soldered. Only two leaded power transistors were finally handsoldered. See Fig. 1.

None of the SMD or leaded components were qualified for the higher temperature lead-free soldering process or checked for lead on the component terminals.

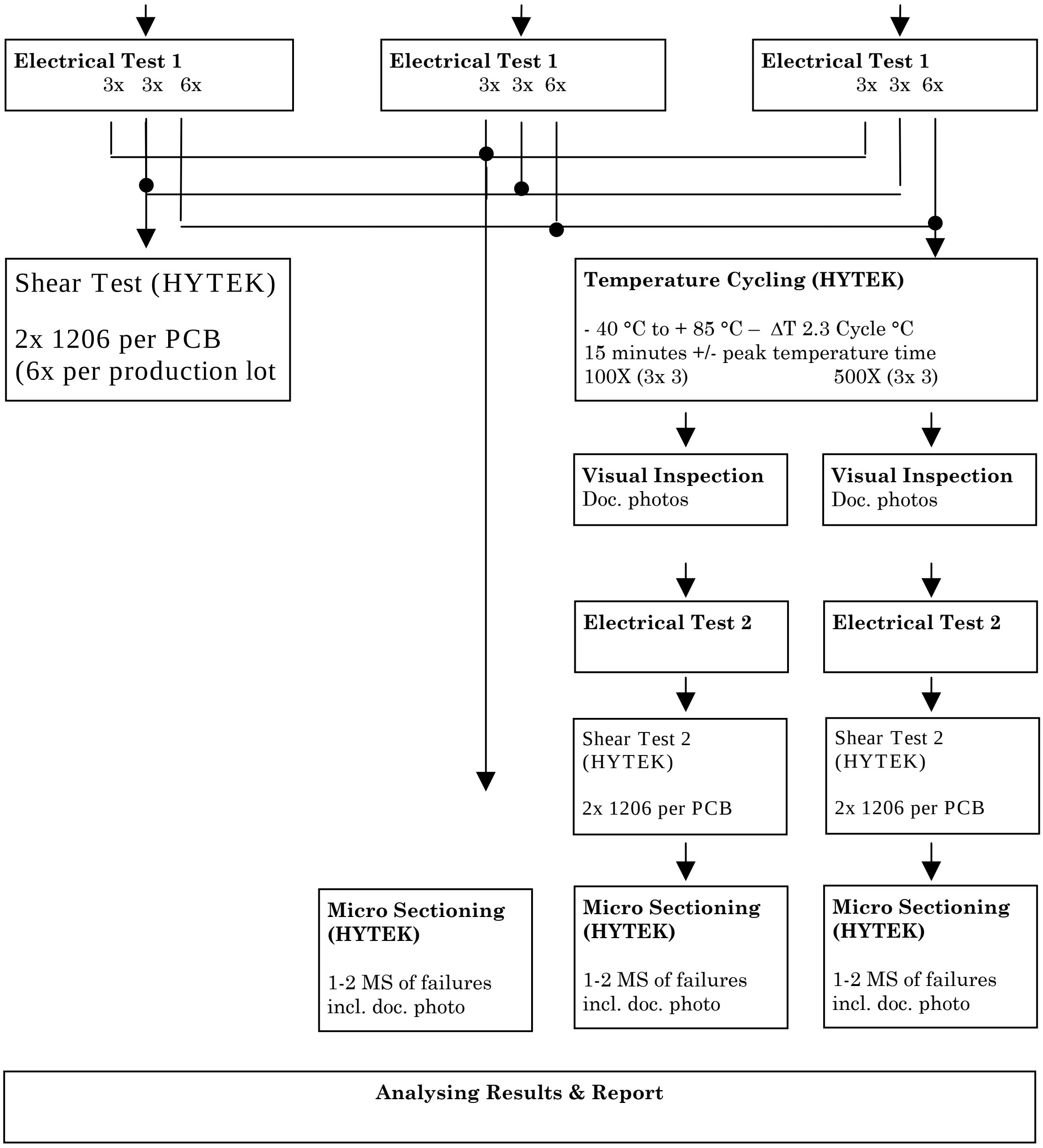
Three batches of 12 PCBs were separately produced. Batch 1 (control batch): Pb-containing on HASL PCB, batch 2: Pb-containing on immersion tin PCBs and batch 3: "Pb-free" on immersion tin PCBs.
Batch 2 was included in the case set-up to ensure, that poor solderability due to the immersion tin coated solder pads were not mistaken to relate to the lead-free process.

To verify the completed specimens against the case objectives, they were inspected visually, electrical tested, run through temperature cycling and shear force tested according to the schedule shown on the next page.

Fig. 1. PSU unit

7.4 Test schedule

SMD Production PCB: HASL SnPb Paste: Sn62Pb36Ag2 Reflow O_2 Level: < 500 ppm **Batch 1** (PCB no. 1-12)	**SMD Production** PCB: Immersion Sn Paste: Sn62Pb36Ag2 Reflow O_2 Level: < 500 ppm **Batch 2** (PCB no. 13-24)	**SMD Production** PCB: Immersion Sn Paste: Sn95.75Ag3.5Cu0.75 Reflow O_2 Level: < 500 ppm **Batch 3** (PCB no. 25-36)
↓	↓	↓
Manual Leaded Mounting	Manual Leaded Mounting	Manual Leaded Mounting
↓	↓	↓
Wave Soldering Alloy: Sn63Pb37 Flux: Rosin 10% solid content Wave O_2 Level: Ambient air	**Wave Soldering** Alloy: Sn63Pb37 Flux: Rosin 10% solid content Wave O_2 Level: Ambient air	**Wave Soldering (HYTEK)** Alloy: Sn95.5Ag3.8Cu0.7 Flux: Rosin 10% solid content Wave O_2 Level: Ambient air
↓	↓	↓
Hand Mountig & Soldering Wire: Sn60Pb40	**Hand Mounting & Soldering** Wire: Sn60Pb40	**Hand Mounting & Soldering** Wire: Sn95.8Ag3.5Cu0.7
↓	↓	↓
Visual Inspection Documentation photos	**Visual Inspection** Documentation photos	**Visual Inspection** Documentation photos



7.5 Screen printing

The screen printing of all 36 PCBs (18 panels) were performed on an off-line semi-automatic screen printer equipped with a manual vision system. A standard 150 µm (0.006”) thick laser cut stainless steel stencil was used. All apertures were reduced by 20% in length and width.

7.6 SMD placement

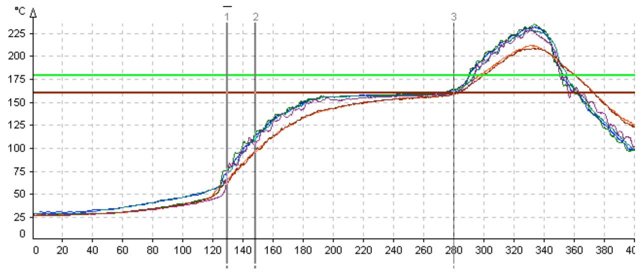
All PCBs were processed on fully automated SMD placement equipment.

7.7 Reflow soldering

All 36 PCBs (18 panels) were reflow soldered in a medium size forced convection oven under nitrogen atmosphere. The rest oxygen level was < 500 ppm.

The two lead-containing product batches (1 and 2) were reflow soldered with the profile shown in Fig. 2 below. And the "lead-free" product batch (3) was reflow soldered using the profile pictured in Fig. 4.
The thermocouples were attached to 3 components on each PCB in the panel. See Fig. 3. The large coil L16 was the PCB's cold spot which resulted in a fairly high peak ΔT. The solder paste alloy used was respectively Sn62Pb36Ag2 and Sn95.75Ag3.5Cu0.75.

Fig. 2. Reflow profile for solder paste Sn62Pb36Ag2:



Preheat ΔT: ~ 2 – 3 °C
Peak temperature: 208.8 – 234.8 °C (ΔT 26.0 °C)
Time above melting point 179 °C: 56.9 – 65 seconds
O_2 < 500 PPM

Fig. 3. PCB used in Reflow profiling

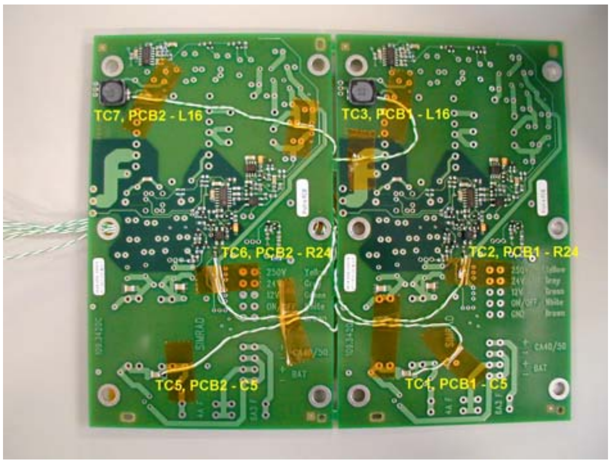
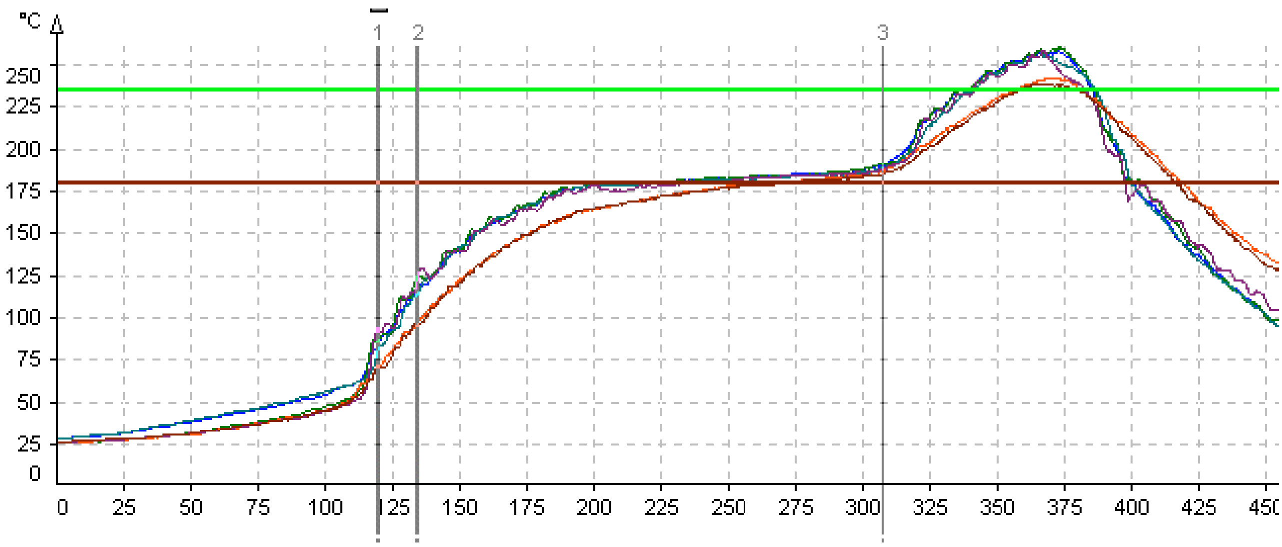


Fig. 4. Reflow profile for lead-free solder paste Sn95.75Ag3.5Cu0.75



Preheat ΔT: ~ 2 – 3 °C
Time above melting point 217 °C: 54.8 – 66.5 seconds
Peak temperature: 238.8 – 259.9 °C (ΔT 21.1 °C)
Time above 235 °C: 20.6 – 46.5 seconds
O_2 < 500 PPM

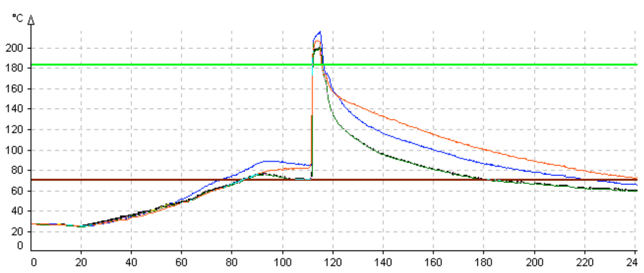
7.8 Through-hole component mounting

All through-hole components were hand mounted by operator.

7.9 Wave soldering

In the lead-containing process, the flux was applied using a foam-fluxing unit. The wave-soldering machine, used in the lead-free soldering process, did not have a foam-fluxing system. The flux was therefor applied by dipping the populated PCB into a flux bath. The excess flux was removed with a paint roller. Earlier tests in the project indicated that synthetic and low solid content fluxes could not clean the solder lands etc. sufficient enough. So, an older 10% rosin flux was chosen for this production case. The solder alloy used was respectively Sn63Pb37 and Sn95.5Ag3.8Cu0.7.

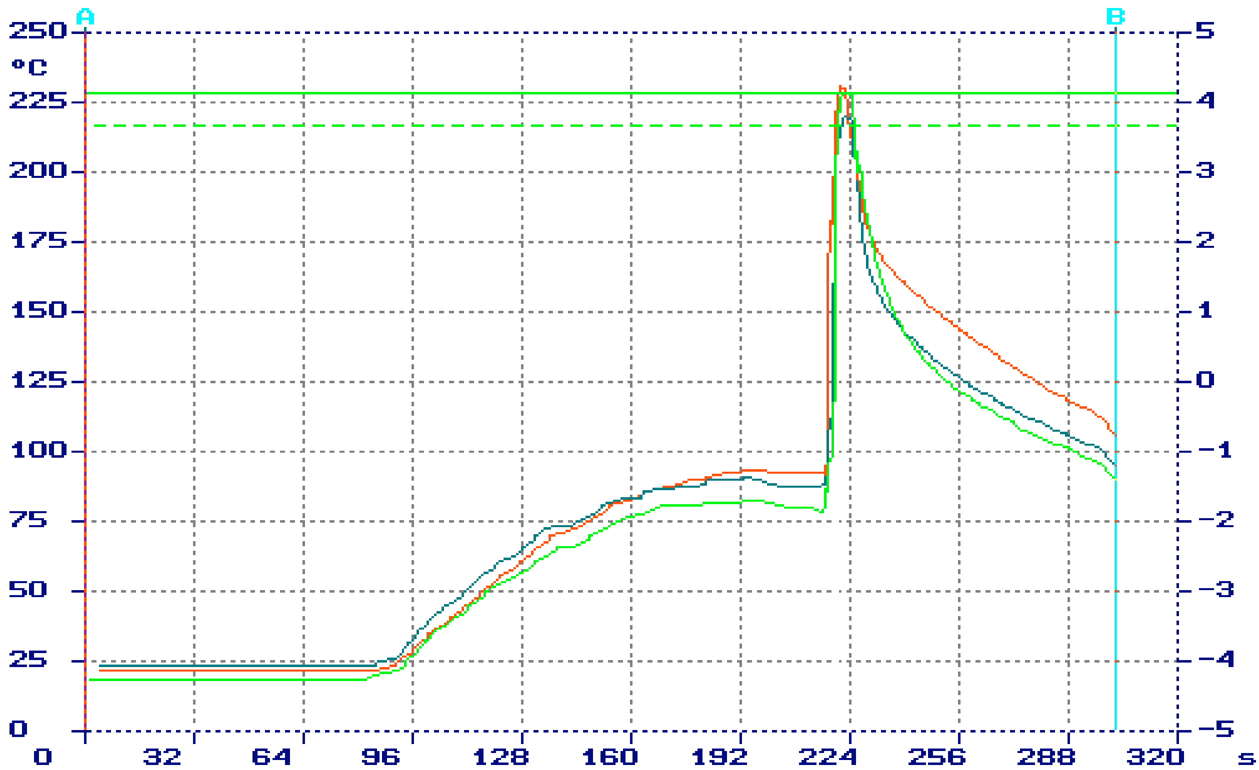
Fig. 5. Wave soldering profile for Sn63Pb37 alloy



Solder pot temperature: ~ 250 °C
Peak temperature: 204.8 – 215.6 °C
Time above 183 °C: 3.7 – 4.5 seconds
Conveyor angle: 7 °
Air environment

Fig. 6. PCB used in Wave profiling

Fig. 7. Wave soldering profile for lead-free alloy Sn95.5Ag3.8Cu0.7



Solder pot temperature: ~ 270 °C
Time above 217 °C: 3.0 – 4.9 seconds
Peak temperature: 220 – 231 °C
Conveyor angle: 6.5 º
Air environment

7.10 Hand soldering set-up

A standard thermostat controlled soldering iron, set to 400 °C, was used to solder lead-containing solder wire. For the lead-free hand soldering a soldering iron with self-regulating soldering tip (400 °C) was used. And the solder wire used was respectively Sn60Pb40 and Sn95.8Ag3.5Cu0.7.

7.11 Results and observations

All PCBs were visually inspected after reflow soldering, wave soldering and hand soldering. There was a clear difference in the appearance of the solder joints. The joints soldered with the lead-free alloys were generally more dull and gray. But on this batch (3) there was also a huge difference found in the appearance, probably depending on the component terminal alloy or lead contamination (not verified). Compare photographs of Q13 and IC4 in Table 1.

Table 1. Visual comparison of SMD solder joints

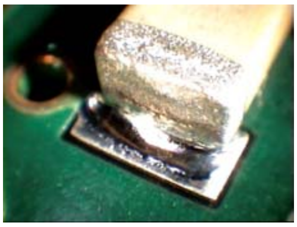
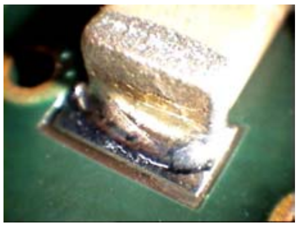
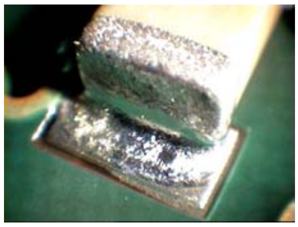
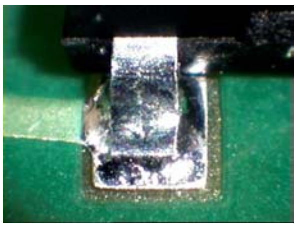
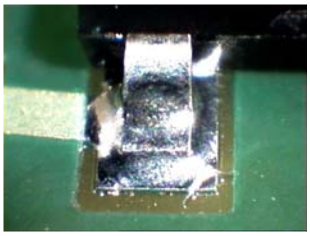
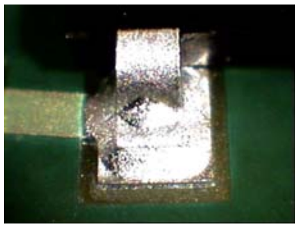
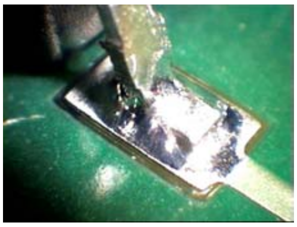
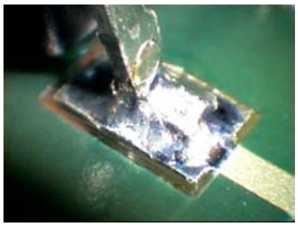
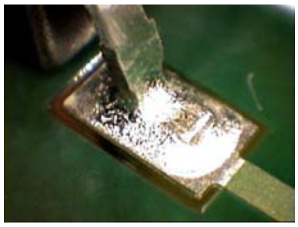
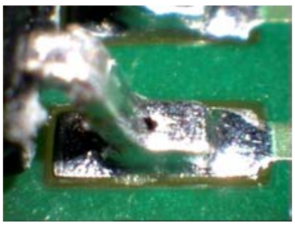
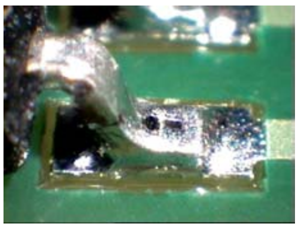
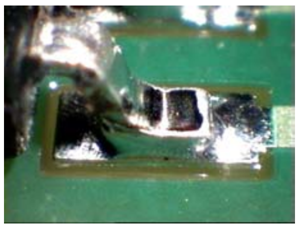
	Batch 1	Batch 2	Batch 3
	PCB: HASL SnPb Paste: Sn62Pb36Ag2	PCB: Immersion Sn Paste: Sn62Pb36Ag2	PCB: Immersion Sn Paste: Sn95.75Ag3.5Cu0.75
C13, 1206			
Q13, SOT23			
IC1 pin 1, Optocoupler			
IC4 pin1, SO8			

Table 2. Visual comparison of wave soldered through-hole solder joints

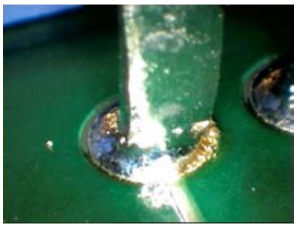
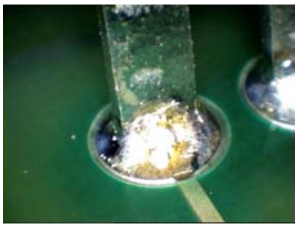
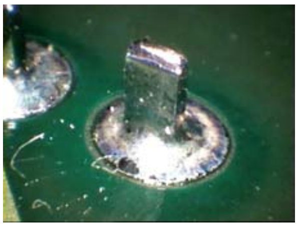
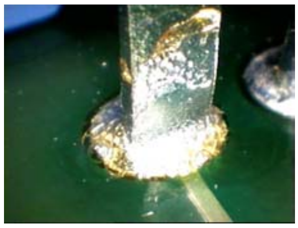
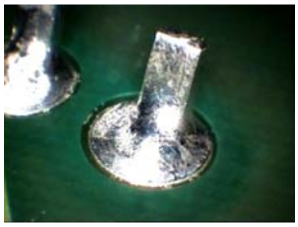
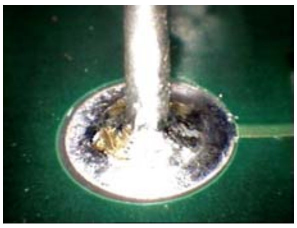
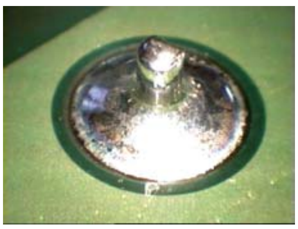
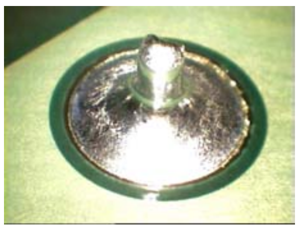
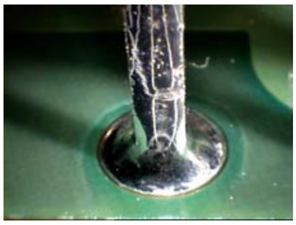
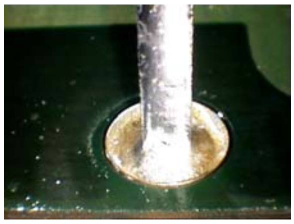
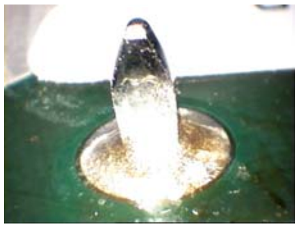
	Batch 1	Batch 2	Batch 3
	PCB: HASL SnPb Alloy: Sn63Pb37 Flux: Rosin 10%	PCB: Immersion Sn Alloy: Sn63Pb37 Flux: Rosin 10%	PCB: Immersion Sn Alloy: Sn95.5Ag3.8Cu0.7 Flux: Rosin 10%
Q4 pin 1, TO-220 Top & bottom	 	 	 
R7 Top & bottom	 	 	 

Table 3. Visual comparison of hand soldered through-hole solder joints

	Batch 1	Batch 2	Batch 3
	PCB: HASL SnPb Alloy: Wire: Sn60Pb40	PCB: Immersion Sn Wire: Sn60Pb40	PCB: Immersion Sn Wire: Sn95.8Ag3.5Cu0.7
Q14 pin3, TO-247 Top & bottom	 	 	 

The 36 completed PCBs were electrical function tested. As seen below, two PCBs from the “lead-free” batch 3, failed due to tombstoning and one missing component. These PCBs were repaired and re-tested with positive results. 2x 9 PCBs were tested again respectively after 100 and 500 temperature cycles with no additional failures detected.

Table 4. Result of electrical tests

	Batch 1	Batch 2	Batch 3
	PCB: HASL SnPb Paste: Sn62Pb36Ag2 Alloy: Sn63Pb37 Flux: Rosin 10% Wire: Sn60Pb40	PCB: Immersion Sn Paste: Sn62Pb36Ag2 Alloy: Sn63Pb37 Flux: Rosin 10% Wire: Sn60Pb40	PCB: Immersion Sn Paste: Sn95.75Ag3.5Cu0.75 Alloy: Sn95.5Ag3.8Cu0.7 Flux: Rosin 10% Wire: Sn95.8Ag3.5Cu0.7
Electrical test 1 Before Temp. Cycle Test	PCB failed = 0 Yield = 100% (12 PCBs)	PCB failed = 0 Yield = 100% (12 PCBs)	PCB failed = 2 (*) Yield = 80% (12 PCBs)
Electrical test 2 After 100x Temp. Cycles	PCB failed = 0 Yield = 100% (3 PCBs)	PCB failed = 0 Yield = 100% (3 PCBs)	PCB failed = 0 Yield = 100% (3 PCBs)
Electrical test 2 After 500x Temp. Cycles	PCB failed = 0 Yield = 100% (3 PCBs)	PCB failed = 0 Yield = 100% (3 PCBs)	PCB failed = 0 Yield = 100% (3 PCBs)

(*) PCB no. 27 failed due to R31 tombstoning. Repaired. Re-test was OK.
PCB no. 31 failed due to a missing component (D1). Repaired. Re-test was OK.

To test the solder joint reliability of the 3 batches, 2x 9 PCBs were exposed to a temperature cycle test; respectively 100x and 500x at 33 rH. See specification in Fig. 8. Earlier test performed, indicated a difference in joint reliability between lead-containing and “lead-free” joints after 500x temperature cycles. It was therefor decided not to continue the temperature cycling beyond 500 cycles.

Visual inspection of the 9 PCBs exposed to 100 temperature cycles initially showed no evidence of beginning joint degrading or cracking. However, even though the PCBs did not fail in the electrical function test after 500 temperature cycles, there was now clear evidence of crack formation on the wave soldered through-hole components. And the crack formations were seen on all 3 test batches. On the SMCs there were no indication of solder joint cracks whatsoever.

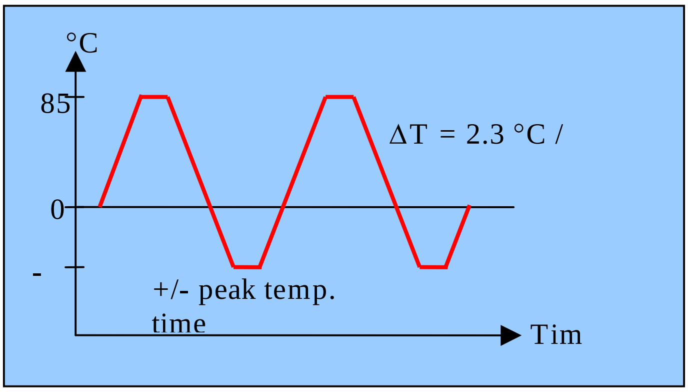


Fig. 8. Temperature cycle profile

9x micro sectioning was done on 0805R (R21) and 1206C (C20), in the same cut; and 9x on a through- hole diode (D11). The micro sectioning revealed, that after 500 temperature cycles some SMD solder joints started to show some initial crack formations. See Fig. 9. These were seen randomly on the 3 batches. The micro sectioning also showed, as the visual inspections did, that all three batches had crack formations in the through-hole solder joints. It was also revealed, that minor cracks were already seen on batch 3 (lead-free process) at the D11 diode, immediately after wave soldering. See Fig. 10.

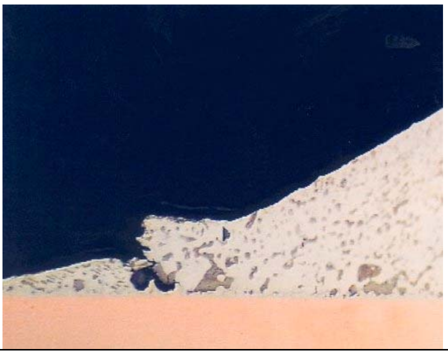


Fig. 9. Crack in SMD joint - 500x temp. cycles immediately after wave soldering	Fig. 10. Crack in “lead-free” through-hole joint

To verify the strength of the SMD solder joints in each batch, and the effect of the temperature cycling, 18 (totally 54) 1206 capacitors were shear force tested.

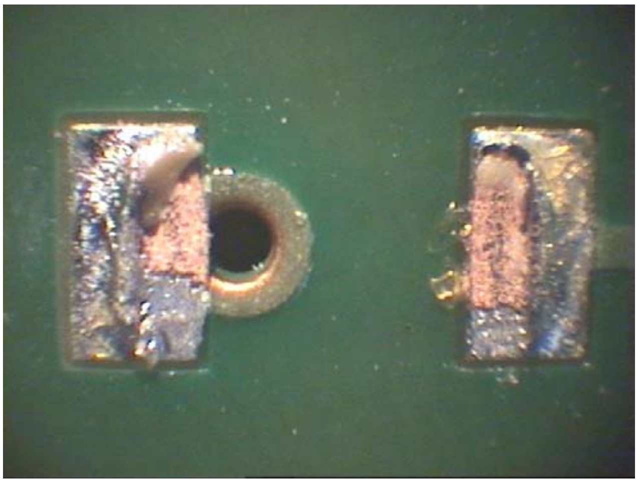
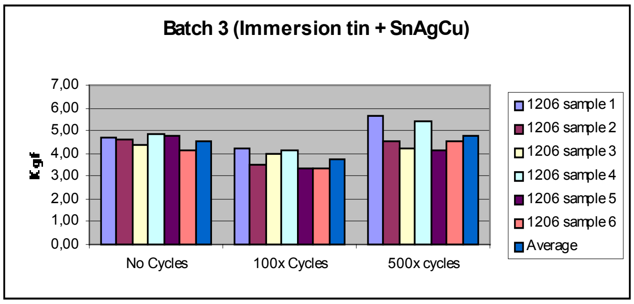
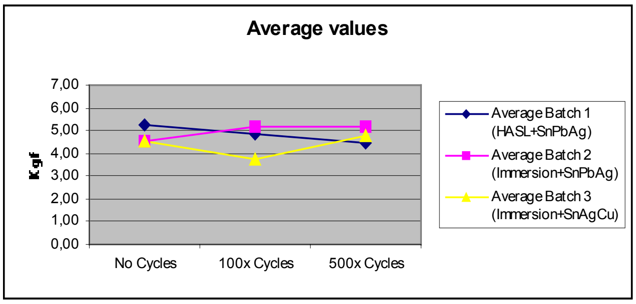


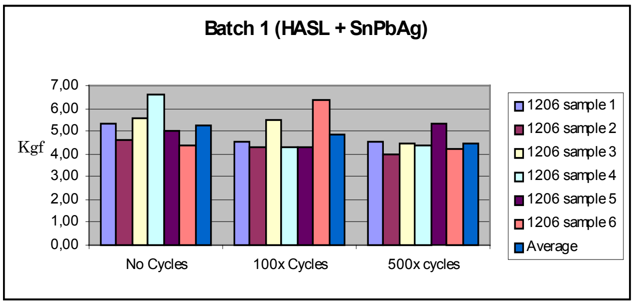
Fig.11: 1206C solder joints after the shear force test

Fig. 11 shows the typical solder joint remains after the shear force test. It clearly indicates, that the separation is mainly seen between the com-ponent body and the terminal, although there also appear to be some separation between the solder fillet and the terminal.





The results of the tests are shown in the Fig. 12 diagrams. The 4th diagram shows the calculated average of each temperature cycling group of all 3 batches.



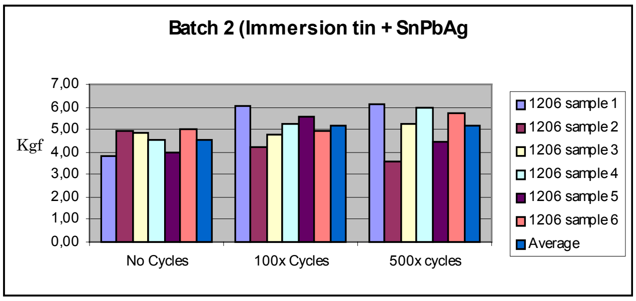


Fig. 12. Shear force test results

As seen in the Fig. 12 diagrams, there was no clear evidence that one batch performed better or worse than the others. The deviation seen on the average calculation must be caused by the difference in the amount of solder alloy, the solderability of the component terminals and test variations.

7.12 Conclusion

On the objective "Solder Joint Reliability", none of the 3 tests i.e. visual inspection, temperature cycling and shear force test indicated any SMD solder joint reliability difference between the 3 batches.

Also with the hand soldered through-hole component joints no clear differences were found, although one of the "lead-free" joints had indication of crack formation after 500 temperature cycles.

However, on the wave soldered joints small cracks were seen on batch 3 (lead-free process), in the micro sectioning performed immediately after the wave soldering; although they did not cause any circuit failures even after 500 temperature cycles. The lead-free solder joints seem harder and more brittle than the lead-containing joints. This indicates that stress relieve clinching on the component leads might become necessary to minimize coefficient of expansion of the different materials.

On the objective "Immersion Tin as HASL Alternative", none of the 3 tests i.e. visual inspection, temperature cycling and shear force test indicated that immersion tin could not be used as an alternative to HASL, both in lead-free and lead-containing applications.

Compared with HASL solder pads the immersion tin solder pads showed equal solder ability - both in the lead-containing and in the lead-free soldering processes. The top fillets generally seemed to float out equally on the pad on all 3 batches. The only difference noticed was, that at some through-hole top side solder fillets, a clear border line was seen between the solder fillet and the solder pad. Since the tin surface of the pad is very thin and chemically applied, the border line must be a natural consequence and must be purely depended on the flux application and spreading at the PCB top side solder pads.

It must however be stressed, that the PCBs with immersion tin surfaces were only 1 – 2 weeks old at the production time and the impact of a long-term storage was not investigated in this production case.

7.13 Hints

Screen printing of lead-free solder paste and SMD component placement on the lead-free deposits showed no complications whatsoever and no change in the processes were necessary.

For reflow soldering, a standard medium size forced convection oven was able to cope with the higher peak temperature, although it was necessary to reduce the soldering speed from 0.55 m/min to 0.45 m/min to reduce the peak ΔT. Depending on the mix of components on the PCBs, changing to lead-free soldering, longer and more powerful ovens may become necessary as might individual PCB profiling to minimize the peak ΔT due to the narrow peak temperature window. Vapor phase soldering could also be an option.

In the wave soldering process, individual temperature profiling will also become necessary. Selecting an appropriate flux showed to be the most important task. It seemed, that an older rosin flux gave a better result than a newer low solid content flux. However, wave soldering in a low oxygen (nitrogen) atmos-phere might help increase the process window and the usable flux selection.

Hand soldering using lead-free solder wire requires a slightly different approach. A higher temperature of the soldering iron tip is required as well as a longer pre-heat (3-5 seconds) of the solder pad and component lead before applying the solder wire.

The appearance of the “lead-free” solder joint might depend on the amount of lead contamination.

7.14 Contact information:

Brian Sloth Bentzen
Simrad Støvring AS
Østre Allé 6
DK-9530 Støvring
Phone: +45 99865152
E-mail: brian.bentzen@simrad.com
Web-site: www.simrad.com

or

Brian Sloth Bentzen
SMT in FOCUS
Birkagervænget 10, Godthåb
DK-9230 Svenstrup
Phone: +45 99865152
E-mail: brian.bentzen@smtinfocus.com
Web-site: www.smtinfocus.com

Lars Ebdrup
Grundfos Electronics A/S
Birkevænget 2-10
DK-8850 Bjerringbro
Phone: +45 87505513
E-mail: lebdrup@grundfos.com
Web-site: www.grundfos.com

Poul Juul
Maks Rasmussen
Hytek
Dannebrogsgade 58
P.O. Box 519
DK-9100 Aalborg
Phone: +45 98117003
E-mail: hytek@hytekaalborg.dk
Web-site: www.hytekaalborg.dk

Appendix 2: Toxicological evaluation of solders and fluxes

8 The toxicology of metals

Lead (Pb)

The absorption of lead by adults is relatively poorly from the gastro-intestinal tract (10 %), whereas children absorb 40-50 %. No data were available about uptake through the skin. Inhaled lead particles may be swallowed and subsequently absorbed from the gastro-intestinal tract. The percentage of particles retained in the lung increases with reduction in particle size. About 90 % of lead particles in ambient air that are deposited in lungs are small enough (less than 0.5 μm) to be retained in the alveols. Absorption of retained lead through alveoli is relatively efficient and complete (9). Lead occurs in blood rich soft tissue (blood, lungs, spleen, kidneys, liver and bone marrow) and skeleton. The half-life time of lead concentration in soft tissue is approximately 40 days, whereas the lead bound in the skeleton is halved in approximately 20 years. Lead ions is excreted in the faeces via the bile and the urine (14).

Acute lead poisoning is relatively infrequent and occurs from ingestion of acid soluble lead compounds or inhalation of lead vapours (14). Lead causes depression of the central nervous system with symptoms like headache, restlessness, changed behaviour, and decreased memory functions. The peripheral nervous system is also affected, the symptoms being numbness of fingers and toes, and weakness of wrists and ankles. Lead inhibits the haeme synthesis, ***i.e.*** the production of haemoglobin and may cause anaemia. Humans exposed to lead have shown chromosomal aberrations in a number of cytogenetic studies, but not in other studies. The evidence for lead being carcinogenic is ambiguous. Lead impairs reproductive ability in both women and men. Lead also may cause preterm delivery of babies and minor malformations.

The aquatoxicity of lead depends on the water hardness. The biocompatibility of lead is smaller in hard water than in soft water. Lead is toxic to aquatic organisms. The bioaccumulation is low.

Tin (Sn)

Tin is poorly absorbed into the body from the gastro-intestinal tract. No data were available about uptake through the skin or by inhalation. The highest tissue concentrations in humans were found in the gastro-intestinal tract, bones, kidneys and the liver. Minor concentrations were found in the lungs and adrenal glands. Tin ions is primarily excreted in the urine and to a lesser extent in the faeces via the bile.

The acute toxicity of tin is low. Rare cases of tin allergy have been seen. Long-term inhalation of tin and insoluble tin compounds may cause tin dust lungs (stannosis). Intake of tin has caused vomiting, diarrhoea, and depression of the central nervous system with symptoms like fatigue, headache and ataxia. Long-term intake of soluble tin salts has caused liver and kidney toxicity. Tin is not toxic to reproduction, mutagenic or carcinogenic.

Silver (Ag)

Silver may be taken up from the gastro-intestinal tract and the lungs. Some silver compounds may be absorbed through the skin. Silver binds to plasma proteins in the blood. Silver is primarily accumulated in the pancreas, liver and spleen, and to a lesser extent in other tissues. Silver is mainly excreted in the faeces via the bile. Urinary may take place, when the blood level of silver is above a certain concentration.

Metallic silver is highly inert and is generally considered of low toxicity to mammalian species including man. However, death has been observed in rats following ingestion of large doses colloidal silver (15). In rare cases, silver has resulted in skin allergy. Inhalation of high concentrations of silver fume resulted in headache and dyspnoea, and later reduced oxygen pressure in capillary blood. For many years, it was believed that the only effect from silver was argyria. Argyria results after long-term exposure and is a cosmetic illness. Recent studies show, that silver may be toxic to the kidneys. In animal studies, silver was able to pass the blood-brain barrier and accumulate in certain areas of the brain. Such animals were less active than unexposed animals, which may indicate that silver may have a harmful effects on the central nervous system. Silver is not mutagenic or carcinogenic. There is some evidence that silver may cause minor developmental anomalies in the foetus.

Silver ions are lethal to bacteria, and are very toxic aquatic organisms. Algae, daphnia, fresh water mussels, and fathead minnows were all found capable of accumulating silver; but the food chain was not an important route of silver accumulation for animals at higher tropic levels, suggesting no food chain magnification.

Copper (Cu)

Copper is an essential metal in humans, animals and plants. Copper is taken up from the gastro-intestinal tract and the lungs, and is primarily accumulated (stored) in the liver and to some extent in the kidneys. Copper is excreted in the faeces via the bile. To a some extent, the body is capable of regulating the copper accumulation in the liver.

Copper is a rare skin sensitiser. Acute copper poisoning by ingestion causes gastro-intestinal symptoms like gastric pain, nausea, vomiting and diarrhoea. Severe poisoning may cause kidney and liver failure, and possibly haemolytic anaemia.

Chronic copper poisoning in humans is not known except in Wilson’s disease. Patients with this disease suffer from disorders in the copper metabolism and have an abnormal accumulation of copper in the liver (30 times over normal level) and the brain, possibly resulting in cellular necrosis and liver cirrhosis, and neurological symptoms. In normal persons, ingested copper is mainly accumulated in the liver and only reaching ***e.g***. the brain in low doses. This is confirmed by animal studies.

Copper is not affecting reproduction. Copper is not carcinogenic, but is mutagenic in some bacterial strains.

Copper is toxic to aquatic organisms, bacteria, and algae. The toxicity to fish is comparable to that of lead.

Summary - toxicology

Toxicological profiles for lead, tin, silver and copper was compiled to give basis for comparing the toxicities of these metals to humans and environment. The table below shows a brief conclusion of the profiles.

	Pb	Sn	Ag	Cu
Acute (mg/kg)	>4,800	-	10,000	-
Irritation	-	-	-	-
Corrosion	-		[+]	-
Sensibilisation	-	-	([+])	(+)
Neurotoxicity	++	[+]	(+)	-
Mutagenicity	[+]	-	-	(+)
Carcinogenicity	[+]	-	-	(+)
Reproduction	+++	-	(+)	-
Liver toxicity	-	[+]	-	(+)
Kidney toxicity	-	[+]	-	(+)
Blood toxicity	++	-	-	(+)
OEL (DK)	0.05	2	0.01	0.1
$LC_{50, trout}$ (mg/l)	0.22	0.42	0.03	0.25
$EC_{50, daphnia}$ (mg/l)	3.6	1.5	0.005	0.09

[ ] = effects caused by compounds other than metal itself
( ) = effects are weak or uncertain
+ = strength of effects

Lead poses high human toxicity and moderate toxicity towards aquatic organisms. Tin has low human toxicity and the aquatoxicity of inorganic tin compounds is comparable to that of lead. Silver has low human toxicity but is much more toxic to aquatic organisms than lead. Silver has the lowest Occupational Exposure Level (OEL)compared to lead, tin and copper due to it´s ability to cause argyria. Copper has low human toxicity and is moderate toxic to aquatic organisms.

Summary conclusion of the toxicity of the metals:

	Human toxicological effects	Environmental effects
Lead	+++	++
Tin	+	++
Silver	+	+++
Copper	+	++

9 The toxicology of fluxes

The fluxes assessed in this project are composed by the following main groups of ingredients:

1. Rosins and modified rosins
2. Solvents
3. Waxes
4. Antoxidants
5. Activators

Some of the ingredients are multifunctional, but for simplicity they are placed in one of the main groups.

Rosins and modified rosins

Inhalation exposure to rosin based solder-flux fume is likely to have low systemic toxicity following single exposure (12). Inhalation exposure to rosin based solder-flux fume can lead to occupational asthma or worsen existing asthmatic conditions. Components of the fume may also give rise to allergic dermatitis (8).

The available data indicate that both rosin fume and rosin itself are of low toxicity to animals. The fume is also irritating to the eyes and upper respiratory tract and on contact with the skin. Several resin acids present in solder fume from rosin flux have allergenic potential on application on the skin. There are several case reports of skin reactions being triggered in solderers following dermal exposure to solder fume, liquid fluxes or flux residues. However mode of induction of the sensitized condition is unclear (12).

No toxicokinetic studies on rosin-based solder flux fume are available. Nevertheless, some conclusions can be reached from other studies in which rosin alone or resin acids were employed. Resin acids and other small molecules present in the particulate fraction of solder fume, when inhaled, are probably absorbed via the lungs and distributed throughout the body. Uptake of components via dermal and oral routes is also possible. Resin acids ar unlikely to accumulate in body tissues. Elimination of resin acids following absorption may occur via the bile (into faeces) or the urine.

The environmental effects of rosins and modified rosins during the solder process or disposal of PCB´s is estimated not to have any significant environmental effects.

Solvents

Solvents are irritating to the respiratory tract by inhalation and are toxic to the nervous system. Inhalation of high concentrations of solvent vapors may cause acute narcotic effects, and some industrial solvents have a history of use as general anesthetics. Vapors are also irritating to eyes.

Dermatological problems are well known to result from skin contact with solvents. Solvents are inrritating to the skin, mucosae and the eyes and defats the skin. Prolonged or repeated exposure to solvents may cause dermatitis.

Solvents may enter the body by inhalation, intake or via the skin. Solvents may have toxic effects on the blood and cause damage to liver and kidneys.

Most solvents will evaporate in the production phase of the electronic equipment. It is evaluated that solvents used during the production may cause irritation to eyes and respiratory tract, whereas neurotoxic effects are unlikely to occur due to fairly low exposure concentrations.

The environmental effects of the use of solvents in the fluxes are during the solder process the production of VOC´s. By the disposal of PCB´s the solvents will not have any significant environmental effects.

Waxes

Waxes are generally regarded as harmless, but they may contain PAH´s if they are not well refined. PAH are suspected to be carcinogenic. Especially during heating, PAH´s may become airborne. In general the small PAH´s (Mw$\leq$202) hace low or no mutagenic effects, whereas the big PAH´s (Mw $\geq$202) is highly mutagenic (17).

The environmental effects of waxes during the solder process or disposal of PCB´s is estimated not to have any significant environmental effects.

Antioxidants

The antioxidants used in the products tested in this project are very different in their chemical composition. In general they are all more or less irritants. By heating they will become airborne forming vapors that may be irritating or even toxic.

The environmental effects of the antioxidants are negligible due to very low concentrations on the final PCB.

Activators

As for antioxidants the activators are of different chemical composition. They are though divided in to two main categories: organic acids, salts and halogen compounds. They are all strong irritants and may cause skin- and respiratory allergy.

The environmental effects of the activators are negligible due to very low concentrations on the final PCB.

Summary - toxicology

Each of the functional groups (e.g. solvents and activators) embraces a variety of different chemical substances, with a variety of toxicological effects. In general though the following human toxicological effects have been registered during the toxicological evaluation:

Substance	Toxicology
Rosins and modified rosins	Irritation
Solvents	Irritation and effects on the nervous system
Waxes	Carcinogenic if they contains PAH

Antoxidants	Irritation
Activators	Irritation, and dermal and respiratory allergy

It will not be relevant or possible at this stage to generalize on environmental effects of the fluxes, as the effects are estimated to be negligible compared to the environmental effects of the metals in the solders.

10 Toxicological evaluation of solders and fluxes

In this chapter the products used in the project are presented one by one. A toxicological evaluation has been made of each substance in each product. The ingredients of the products are all assigned an identification code in order to be able to identify each single substance in the Annex 1: ***Toxicological Profiles***.

By the end of each subchapter there is a comparative toxicological summary evaluation of the products in each type of soldering process (reflow, wave and hand soldering).

The identity and precise amount of ingredients/components in the products is confidential and only known to DTC.

Reflow soldering (Pastes)

The solders used in connection with reflow soldering in this project are all solder pastes. Solder paste, also sometimes called solder cream, consists mainly of solder particles and flux. Solder paste is a rather complicated concoction of these elements and is distinguished according to :

- Metal content
- Alloy
- Solder particle size
- Form of solder particles
- Activity level of flux (6).

The toxicological evaluation is focusing on the metals and the fluxes. The metal content of the three evaluated pastes are:

- ➢ 62Sn36Pb2Ag
- ➢ 96.5Sn3.5Ag
- ➢ 95.5Sn4Ag0.5Cu

Fluxes are included in the pastes, one for the lead-containing paste and another for the lead-free pastes.

62Sn36Pb2Ag and flux

In the following tables the ingredients are presented in weight-% of the entire product:

Metal part:

Component	Identification	CAS-no.	w/w-%
Component 1	Tin	7440-31-5	30-60
Component 2	Lead	7439-92-1	30-60
Component 3	Silver	7440-22-4	1-5

Flux:

Component	Identification	CAS-no.	w/w-%
Component 4	Rosin, Modified Rosin	Confidential.	1-5

	(MF 1)	Known to DTC	
Component 5	Rosin, Modified Rosin (MF 2)	Confidential. Known to DTC	1-5
Component 6	Solvent (S1)	Confidential. Known to DTC	1-5
Component 7	Solvent (S2)	Confidential. Known to DTC	0-1
Component 8	Activator (AC1)	Confidential. Known to DTC	0-1
Component 9	Activator (AC2)	Confidential. Known to DTC	0-1
Component 10	Antioxidant (AO1)	Confidential. Known to DTC	0-1
Component 11	Antioxidant (AO2)	Confidential. Known to DTC	0-1
Component 12	Wax (W1)	Confidential. Known to DTC	0-1
Component 13	Wax (W2)	Confidential. Known to DTC	0-1

According to the Danish regulation the product should not be classified as there is no content of lead compounds, only metallic lead. The classification of the flux, would be: Xi (Irritant): R36/38 Irritating to eyes and skin (1,2).

Lead poses high human toxicity and moderate toxicity towards aquatic organisms. Silver has low human toxicity but is much more toxic to aquatic organisms than lead. Tin has low human toxicity and the aquatoxicity of inorganic tin compounds is comparable to that of lead.

The flux is irritating to the skin and eyes on direct contact.

At room temperature (20 °C) lead, tin and silver will remain, as metals and the flux is not volatile at this temperature.

The range of the soldering temperature is 235 °C – 250 °C. When tin, lead, and silver is heated in air to temperatures in this range they may be oxidized to tin-, lead-, and silver oxides and to a little extent become airborne.

In products, if lead oxides are included as an ingredient with equal or more than 5 weight-% the product would be classified as: T (Toxic), N (Dangerous for the environment): R61 May cause harm to the unborn child, R62 Possible risk of impaired fertility, R20/22 Harmful by inhalation and if swallowed, R33 Danger of cumulative effects, R 50/53 Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment (1,2).

The chemical composition of the flux fumes at soldering temperature has not been determined by the producer. The flux is a non-corrosive flux, based on rosins. By heating the flux to soldering temperatures (235 °C – 250 °C), it is likely that the rosin derivatives will form fumes containing a complex mixture of resin acids, aldehydes and carbon oxides. Furthermore, by heating the flux there is a small risk of evaporation of small amounts of nitrogen oxides, ammonia, bromides and fluorides. Chemical reactions between one or more of the components are likely to take place, but these have not been established.

Inhalation of the airborne metals (especially lead) and the flux fumes is of relevance for the working environment. Inhalation of the airborne metals, may cause metal dust lungs, and lead may affect the central and the peripheral nervous systems and the haeme synthesis, ***i.e.*** the product ion of haemoglobin and may cause anaemia. Furthermore exposure to lead may cause chromosomal aberrations, impair the fertility and cause preterm delivery of babies and minor malformations. The evidence for lead being carcinogenic is ambiguous.

The flux fumes given off at soldering are irritating to the nose, throat and respiratory organs. Prolonged or repeated exposure to the fumes may cause sensitization and occupational asthma.

The emission to the air from the solder process to the environment may contain metal oxides of tin, lead and silver. Furthermore small amounts of e.g. COx, NOx, resin acids, aldehydes, ammonia and fluorides may occur.

In case of the product entering the aquatic environment, e.g. by rinsing the circuit boards the product should be considered as toxic to the aquatic environment. Lead is toxic to aquatic organisms, the toxicity though, depends on the water hardness. Lead is more toxic in soft water than in hard water. Silver ions are lethal to bacteria, and is very toxic aquatic organisms. The aquatoxicity of inorganic tin compounds is comparable to that of lead.

The biocompatibility of lead is smaller in hard water than in soft water. The bioaccumulation is low.

96.5Sn3.5Ag and flux

In the following tables the ingredients are presented in weight-% of the entire product:

Metal part:

Component	Identification	CAS-no.	w/w-%
Component 1	Tin	7440-31-5	60-100
Component 2	Silver	7440-22-4	1-5

Flux:

Component	Identification	CAS-no.	w/w-%
Component 3	Rosin, Modified rosin (MF3)		1-5
Component 4	Solvent (S1)		1-5
Component 5	Solvent (S7)		0-1
Component 6	Activator (AC8)		1-5
Component 7	Activator (AC7)		0-1
Component 8	Antioxidant (AO3)		0-1
Component 9	Antioxidant (AO6)		0-1
Component 10	Wax (W4)		0-1
Component 11	Wax (W1)		0-1
Component 12	Wax (W5)		1-5

The classification of the product, according to the producer is:
Xi, Irritant; R43 May cause sensitization by skin contact (1,2).

The paste has low acute toxicity, is irritating to the skin and the eye and may cause severe damage on the eye in case of contact. Prolonged or repeated contact with skin may cause itching and soreness and possible sensitization. Furthermore the product may de-fat the skin and lead to irritation and dermatitis. Exposure to dust may cause gastrointestinal irritation.

A small part of the product is soluble in water. The product is slowly biodegradable and it has a tendency to bioaccumulate. It is rated as hazardous to aquatic organisms.

Silver has low human toxicity but is much more toxic to aquatic organisms than lead. Tin has low human toxicity and the aquatoxicity of inorganic tin compounds is comparable to that of lead.

At room temperature (20 °C) or, when not in use (not heated), the product contains only substances with low volatility. During soldering the range of the temperature are 260 °C – 270 °C. The producer has not determined the chemical composition of the flux fumes at soldering temperature. By heating the product (metals plus flux) there is a small risk for evaporation of tin- and silver oxides from the metals, and a complex mixture of resin acids, aldehydes and carbon oxides from the rosin, which is the main ingredient in the flux. There will also be a small risk for formation of e.g. nitrogen oxides, phosphin, phosphide and phosphorous oxides. Most likely, chemical reactions between two or more components will take place, but these have not been established.

Inhalation of the airborne metal fumes (metals/metaloxides) and the flux fumes is of relevance for the working environment. The metal fumes given off at soldering may cause metal dust lungs. The flux fumes are irritating to the nose, throat and respiratory organs. Prolonged or repeated exposure to the fumes may cause pulmonary sensitization and asthma. Exposure to processing fumes may cause gastrointestinal irritation.

The emission to the air from the solder process to the environment may contain metal oxides of tin and silver. Furthermore small amounts of e.g. carbon oxides, nitrogen oxides, resin acids, aldehydes, phosphin, phosphide and phosphorous oxides may occur.

In case of the product entering the aquatic environment, e.g. by rinsing the circuit boards the paste should be considered as toxic to the aquatic environment. Inorganic tin compounds are toxic to aquatic organisms. The bioaccumulation is low. Silver ions are lethal to bacteria, and is very toxic to aquatic organisms.

A small part of the product is soluble in water. According to the producer the paste is slowly biodegradable and it has a tendency to bioaccumulate.

95.5Sn4Ag0.5Cu and flux

In the following tables the ingredients are presented in weight-% of the entire product:

Metal part:

Component	Identification	CAS-no.	w/w-%
Component 1	Tin	7440-31-5	60-100
Component 2	Silver	7440-22-4	1-5
Component 3	Copper	7440-50-8	0-1

Flux:

Component	Identification	CAS-no.	w/w-%
Component 4	Rosin, Modified rosin (MF3)		1-5
Component 5	Solvent (S1)		1-5
Component 6	Solvent (S7)		0-1
Component 7	Activator (AC7)		1-5
Component 8	Activator (AC8)		0-1

Component 9	Antioxidant (AO3)		0-1
Component 10	Antioxidant (AO6)		0-1
Component 11	Wax (W4)		0-1
Component 12	Wax (W1)		0-1
Component 13	Wax (W5)		1-5

The classification of the paste according to the producer is: Xi (Irritant): R43 May cause sensitization by skin contact (1,2).

The product has low acute toxicity, is irritating to the skin and the eye and may cause severe damage on the eye in case of contact. Prolonged or repeated contact with skin may cause itching and soreness and possible sensitization. Furthermore the product may de-fat the skin and lead to irritation and dermatitis. Exposure to dust may cause gastrointestinal irritation.

The paste has low volatility and a small part of the product is soluble in water. The product is slowly biodegradable and it has a tendency to bioaccumulate. It is not rated as hazardous to aquatic organisms.

Silver has low human toxicity but is much more toxic to aquatic organisms than lead. Tin has low human toxicity and the aquatoxicity of inorganic tin compunds is comparable to that of lead. Organic tin compounds are toxic to the aquatic ecosystems. Copper has low human toxicity and is moderate toxic to aquatic organisms.

At room temperature (20 °C) when not in use (not heated) the product is not volatile.

The range of the soldering temperature is 260°C - 270°C. The chemical composition of the flux fumes at soldering temperature has not been determined by the producer. By heating the product (metals as well as the flux) there is a risk for evaporation of tin-, silver- and copper oxides from the paste. As the flux is identical with that for the flux used in connection with paste: 96.5Sn3.5Ag (4.1.2) and the range of soldering temperature is the same, the evaporation from this flux will also be the same: a complex mixture of resin acids, aldehydes and carbon oxides from the rosin, which is the main ingredient in the flux. There will also be a small risk for formation of e.g. nitrogen oxides, phosphin, phosphide and phosphorous oxides. Most likely, chemical reactions between two or more components will take place, but these have not been established.

Inhalation of the airborne metals (metals/metal oxides) and the flux fumes is of relevance for the working environment. The metal fumes given off at soldering may cause metal dust lungs. The flux fumes are irritating to the nose, throat and respiratory organs. Prolonged or repeated exposure to the fumes may cause pulmonary sensitization and asthma. Exposure to processing fumes may cause gastrointestinal irritation.

The emission to the air from the solder process to the environment may contain metal oxides of tin, silver and copper. Furthermore small amounts of e.g. carbon oxides, nitrogen oxides, resin acids, aldehydes, phosphin, phosphide and phosphorous oxides may occur.

In case of the product entering the aquatic environment, e.g. by rinsing the circuit boards with water, the product should be considered as toxic to the aquatic environment. Inorganic tin compounds are toxic to aquatic organisms. Silver ions are lethal to bacteria, and are very toxic to aquatic organisms. Copper is cytotoxic, and inhibits algal growth.

A small part of the product is soluble in water. According to the producer, the paste is slowly biodegradable and it has a tendency to bioaccumulate.

Evaluation

The following table gives a summary overview of the possible exposure of workers and the environment to the products used in the reflow process.

Exposure

	62Sn36Pb2Ag and flux	96.5Sn3.5Ag and flux	95.5Sn4Ag0.5Cu and flux
Process temperature:	235 °C – 250 °C	260 °C – 270 °C	260 °C – 270 °C
Workers:			
Inhalation	***No-heating:*** No vapors or fume ***Heating:*** Vapors, fume, smoke: Metal oxides (tin, lead and silver), resin acids, aldehydes, COx, NOx, ammonia and fluorides.	***No-heating:*** No vapors or fume ***Heating:*** Vapors, fume, smoke: Metal oxides (tin and silver), resin acids, aldehydes, COx, NOx, phosphin, phosphide and POx.	***No-heating:*** No vapors or fume ***Heating:*** Vapors, fume, smoke: Metal oxides (tin, silver and copper), resin acids, aldehydes, COx, NOx, phosphin, phosphide and POx.
Skin	Flux, vapors or fume.	Flux, vapors or fume.	Flux, vapors or fume.
Environment:			
Drost	Metal oxides (tin, lead and silver)	Metal oxides (tin and silver)	Metal oxides (tin, silver and copper)
Exhaust	Vapors or fume: Metal oxides (tin, lead and silver), resin acids, aldehydes, COx, NOx, ammonia and fluorides.	Vapors or fume: Metal oxides (tin and silver), resin acids, aldehydes, COx, NOx, phosphin, phosphide and POx.	Vapors or fume: Metal oxides (tin, silver and copper), resin acids, aldehydes, COx, NOx, phosphin, phosphide and POx.
Waste	Metals on PCB	Metals on PCB	Metals on PCB

The process temperature is higher using the lead-free solders compared to the use of lead-containing solder. The tendency of chemicals to become airborne increases by increasing temperature. As a consequence the use of the lead-free solders in this project will possibly lead to an increase in the evaporation from the solders and fluxes compared to the use of the traditional lead-containing solder. Even though the process temperatures are relatively low, there will be a certain degree of thermic decomposition of the organic substances. The main fraction will consist of metal oxides and to a lesser extent resin acids, aldehydes, COx and NOx. By using the lead-containing solder: 62Sn36Pb2Ag and flux, substances like ammonia and fluorides may be formed in very small concentrations. Whereas, the use of lead-free alternatives may result in the formation of very small concentrations of phosphin, phosphide and POx. These emissions will all enter the workplace or the environment unless necessary precautions are taken with containment, filters etc.

The composition of the drost from the production or the waste differs mainly due to the content of the metals.

The following table gives an overview of the main effects of the referred exposures of workers and the environment to the solders.

Effects of the metal parts of the alloys as metal compounds in vapor, fumes, waste water, etc.

	62Sn36Pb2Ag	96.5Sn3.5Ag	95.5Sn4Ag0.5Cu
Human(occup)			
Irritation	-	-	-
Corrosion	-	-	-
Sensibilisation	(+)	(+)	(+)
Neurotoxicity	++	(+)	(+)
Mutagenicity	++	(+)	+
Carcinogenicity	+ (IARC: 2B)	-	(+)
Reproduction	+++	(+)	(+)
Liver toxicity	(+)	(+)	(+)
Kidney toxicity	[+]	[+]	(+)
Blood toxicity	++	-	(+)
Accumulation	+++	+	+
Environmental			
Bioaccumulation	+	+	+
Toxic to aquatic org.	+	+	+
Toxic to bacteria	+	+	+
Toxic to algae	+	-	+

[ ] = effects caused by compounds other than metal itself
( ) = effects are weak or uncertain
\- = No
\+ = Yes

Lead is very toxic to humans. The other metals in the solder are little to moderate toxic to humans. During the solder process fumes of metal and metal oxides may be formed and emitted to the air in the working environment, and inhaled by the workers. Especially lead may cause severe systemic effects.

Lead is moderate toxic to the environment. Silver appears to be much more toxic to aquatic organisms than the other metals in the solder, whereas the aquatoxicity of copper is moderate (in the order of lead). The lead-free solder contains more tin, silver and copper instead of lead.

Below is an overview of the toxicological effects of the fluxes used in the solder process.

Effects of the flux part of the alloy

	Flux to 62Sn36Pb2Ag	Flux to 96.5Sn3.5Ag	Flux to 95.5Sn4Ag0.5Cu
Classification	Flux: Xi R 36/38	Flux: Xi R43	Flux: Xi R43
Human(occup)			
Irritation	+	+	+
Corrosion	-	-	-
Sensibilisation	(+)	++	++

Neurotoxicity	-	-	-
Mutagenicity	-	-	-
Carcinogenicity	-	-	-
Reproduction	-	-	-
Liver toxicity	-	-	-
Kidney toxicity	-	-	-
Blood toxicity	-	-	-
Astma	+	+	+

( ) = effects are weak or uncertain
- = No
+ = Yes

Exposure to the fluxes, when not in use may cause irritation by skin contact. When heating the fluxes acrid vapors and fumes are formed, that are very irritating to the eyes and the respiratory system. Prolonged or repeated inhalation may cause asthma. Vapors and fumes may also irritate the skin. The fluxes in the lead-free solder pastes may cause skin and respiratory allergy.

The environmental effects of the fluxes is considered negligible compared to the environmental effects of the metals in the solders.

Wave-soldering (Alloys)

During wave soldering the assembled circuit boards, which have been pre-treated with solution of flux, are mechanically fed over a 'standing wave' of molten solder. This method is used in automated large batch production and is usually enclosed (3).

The solders used in connection with wave soldering in this project consist of metal bars and fluxes that are separated. The fluxes are added separately during the solder process.

The toxicological evaluation is focusing on the metals and the fluxes. The metal content of the to evaluated alloys are:

- 63Sn37Pb
- 95.5Sn3.8Ag0.7Cu

The fluxes used with the alloys are different for the two alloys (the same flux could also have been applied).

63Sn37Pb Alloy and Flux

In the following tables the ingredients are presented in weight-% of the entire product:

Metal part:

Component	Identification	CAS-no.	w/w-%
Component 1	Tin	7440-31-5	63
Component 2	Lead	7439-92-1	37

Flux:

Component	Identification	CAS-no.	w/w-%
Component 1	Rosin, Modified rosin (MF3)		5-10
Component 2	Rosin, Modified Rosin (MF1)		1-5
Component 3	Solvent (S3)		60-100
Component 4	Solvent (S4)		1-5
Component 5	Activator (AC4)		1-5

Component 6	Activator (AC3)		0-1

According to the Danish regulation the product should not be classified. Partly as the alloy is regarded as a material and because there is no content of lead compounds, only metallic lead.

The classification of the flux is: Xi (Irritant): R11 Highly flammable, R36 Irritating to the eyes, R43 May cause sensitization by skin contact (1,2).

It is possible though, that according to the Danish regulation the flux should be classified as a possible carcinogen (1,2). The content of benzene of one of the ingredients decides the classification with regard to the carcinogenicity.

Lead poses high human toxicity and moderate toxicity towards aquatic organisms. Tin has low human toxicity and the aquatoxicity of inorganic tin compounds is comparable to that of lead. Organic tin compounds are toxic to the aquatic ecosystems.

The flux contains high amounts of a solvent with high volatility. The solvent which has an ability to de-fat the skin, irritate the eyes, the skin and the respiratory tract. By inhalation of high concentrations it may cause headache, nausea and malaise. Prolonged or repeated exposure may affect the central nervous system, and cause sensitization to the skin.

The producer has informed that the flux is totally soluble in water, easily biodegradable and is not meant to be bioaccumulated. Furthermore the flux is evaluated to be non-toxic to water living organisms.

The range of the soldering temperature is 200 °C – 210 °C. As tin and lead is heated in air to temperatures in this range they may be oxidized to tin- and lead oxides and to a reduced extent become airborne.

In products, if lead oxides were included as an ingredient with equal or more than 5 weight-% the product would be classified as: T (Toxic), N (Dangerous for the environment): R61 May cause harm to the unborn child, R62 Possible risk of impaired fertility, R20/22 Harmful by inhalation and if swallowed, R33 Danger of cumulative effects, R 50/53 Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment (1,2).

The producer has not determined the chemical composition of the flux fumes at soldering temperature. By heating the flux, VOC´s will be emitted and there is a small risk for evaporation of a complex mixture of resin acids, aldehydes, carboxylic acid and carbon oxides. There will also be a small risk for formation of e.g. bromides. Most likely, chemical reactions between two or more components will take place, but these have not been established.

Inhalation of the airborne metals (especially lead) and the flux fumes is of relevance for the working environment. Inhalation of the airborne metals, may cause metal dust lungs, and affect the central and the peripheral nervous system and the haeme synthesis, ***i.e.*** the product ion of haemoglobin and may cause anaemia. Furthermore exposure may cause chromosomal aberrations, impair the fertility and cause preterm delivery of babies and minor malformations. The evidence for lead being carcinogenic is ambiguous. The flux fumes given off at soldering are irritating to the nose, throat and respiratory organs. Prolonged or repeated exposure to the fumes may cause sensitization and occupational asthma. High concentration of vapor may have narcotic effects.

The emission to the air from the solder process to the environment may contain metal oxides of tin and lead and VOC. Furthermore small amounts of e.g. carbon oxides, resin acids, aldehydes, carboxylic acid and bromides may occur.

In case of the product entering the aquatic environment, e.g. by rinsing the circuit boards the aquatoxicity of lead depends on the water hardness. The biocompatibility of lead is smaller in hard water than in soft water. Lead is toxic to aquatic organisms. The aquatoxicity of inorganic tin compounds is comparable to that of lead. The bioaccumulation is low.

95.5Sn3.8Ag0.7Cu Alloy and Flux

In the following tables the ingredients are presented in weight-% of the entire product:

Metal part:

Component	Identification	CAS-no.	w/w-%
Component 1	Tin	7440-31-5	95.5
Component 2	Silver	7440-22-4	3.8
Component 3	Copper	7440-50-8	0.7

Flux:

Component	Identification	CAS-no.	w/w-%
Component 1	Rosin, Modified rosin (MF3)		1-5
Component 2	Rosin, Modified Rosin (MF1)		1-5
Component 3	Solvent (S3)		30-60
Component 4	Solvent (S4)		30-60
Component 5	Activator (AC4)		5-15
Component 6	Activator (AC3)		1-5

According to the Danish regulation the metal alloy should not be classified (1,2).

According to the producer the flux is classified as: F (Highly flammable), Xi (Harmful): R11 Highly flammable, R36 Irritating to the eyes, R43 May cause sensitization by skin contact.

It is possible though, that according to the Danish regulation the flux should be classified as a possible carcinogen (1,2). The content of benzene of one of the ingredients decides the classification with regard to the carcinogenicity.

The flux contains high amounts of a solvent, which has an ability to de-fat the skin, irritate the eyes, the skin and the respiratory tract. By inhalation of high concentrations it may cause headache, nausea and malaise.

Prolonged or repeated exposure may affect the central nervous system, and sensitization of the skin.

The producer informs that the main part of the flux almost immediately mixes with water, is easily biodegradable and is meant not to be bioaccumulating. Furthermore the flux is evaluated to be mildly toxic to aquatic organisms.

Silver has low human toxicity but is much more toxic to aquatic organisms than lead. Tin has low human toxicity and the aquatoxicity of inorganic tin compounds is comparable to that of lead. Copper has low human toxicity and is moderate toxic to aquatic organisms.

The range of the soldering temperature is 235 °C – 250 °C. As tin, silver and copper is heated in air to temperatures in this range they may be oxidized to tin-, silver- and copper oxides and to a reduced extent become airborne. The producer has not determined the chemical composition of the flux fumes at the soldering temperature. By heating flux, VOC´s will be emitted and there is a small risk for evaporation of a complex mixture of resin acids, aldehydes, carboxylic acid, carbon oxides and for formation of e.g. bromides. Most likely, chemical reactions between two or more components will take place, but these have not been established.

Inhalation of the airborne metals/metal oxides and the flux fumes is of relevance for the working environment. The metal fumes given off at soldering may cause metal dust lungs. Prolonged or repeated exposure to the fumes may cause dermal and respiratory sensitization and occupational asthma. High concentration of vapor may have narcotic effects, and affect the central nervous system.

The emission to the air from the solder process to the environment may contain metal oxides of tin and lead and VOC. Furthermore small amounts of e.g. carbon oxides, resin acids, aldehydes, carboxylic acid and bromides may occur.

In case of the product entering the aquatic environment, e.g. by rinsing the circuit boards the product should be considered as toxic to the aquatic environment. The aquatoxicity of silver is high. Silver ions are lethal to bacteria, and are very toxic to aquatic organisms. Inorganic tin compounds are toxic to aquatic organisms. The aquatoxicity of inorganic tin compounds is comparable to that of lead. Copper is cytotoxic, and inhibits algal growth.

The metals in the alloy has a tendency to bioaccumulate.

Evaluation

The following table gives a summary overview of the possible exposure of workers and the environment to the products used in the wave soldering process.

Exposure

	63Sn37Pb and Flux	95.5Sn3.8Ag0.7Cu and Flux
Temperature:	235 °C – 250 °C	260 °C – 270 °C
Workers:		
Inhalation	***No-heating:*** Solvent vapors ***Heating:*** Vapors or fume: Metal oxides (tin and lead), resin acids, aldehydes, carboxylic acid, COx and bromides.	***No-heating:*** Solvent vapors ***Heating:*** Vapors or fume: Metal oxides (tin, silver and copper), resin acids, aldehydes, carboxylic acid, COx and bromides.
Skin	Flux liquid, Solvent vapors or fume.	Flux liquid, Solvent vapors or fume.
Environment:		
Drost	Metal oxides (tin and lead), bromides.	Metal oxides (tin, silver and copper), bromides.

Exhaust	Vapors or fume: Metal oxides (tin and lead), resin acids, aldehydes, carboxylic acid, COx and bromides.	Vapors or fume: Metal oxides (tin, silver and copper), resin acids, aldehydes, carboxylic acid, COx and bromides.
Waste	Metals on PCB, bromides	Metals on PCB, bromides

In the wave soldering process the use of lead-free solders requires higher process temperature than by the use of lead-containing solder. As a consequence the use of the lead-free solder will possibly lead to an increase in the evaporation from the solders and fluxes compared to the use of the traditional lead-containing solder. Even though the process temperatures are relatively low, there will be a certain degree of thermic decomposition of the organic substances. The main fraction will consist of metal oxides and to a lesser extent resin acids, aldehydes, carboxylic acids and COx. Bromides may be formed in very small concentrations. These emissions will all enter the workplace or the environment unless necessary precautions are taken with containments, filters etc.

The composition of the drost from the production or the waste differs mainly due to the content of the metals.

The following table gives an overview of the main effects of the referred exposures of workers and the environment to the solders.

Effects of the metal part of the alloys as metal compounds in vapor, fumes, smoke, waste water, etc.

	63Sn37Pb	95.5Sn3.8Ag0.7Cu
Human(occup)		
Irritation	-	-
Corrosion	-	-
Sensibilisation	(+)	(+)
Neurotoxicity	++	(+)
Mutagenicity	++	+
Carcinogenicity	+ (IARC: 2B)	(+)
Reproduction	++	(+)
Liver toxicity	[+]	(+)
Kidney toxicity	[+]	(+)
Blood toxicity	++	(+)
Accumulation	+++	+
Environmental		
Bioaccumulation	+	+
Toxic to aquatic org.	+	+
Toxic to bacteria	-	+
Toxic to algaes	+	+

[ ] = effects caused by compounds other than metal itself
( ) = effects are weak or uncertain
- = No
+ = Yes

Lead is very toxic to humans. The other metals in the solder are little to moderate toxic to humans. During the solder process fumes of metal and metal oxides may be formed and emitted to the air in the working environment, and inhaled by the workers. Especially lead may cause severe systemic effects.

Lead is moderate toxic to the environment. Silver appears to be much more toxic to aquatic organisms than the other metals in the solder, whereas the aquatoxicity of copper is moderate (in the order of lead). The lead-free solder contains more tin, silver and copper instead of lead.

Below is an overview of the toxicological effects of the fluxes used in the solder process.

Effects of the fluxes

	The flux to 63Sn37Pb	The flux to 95.5Sn3.8Ag0.7Cu
Classification	Flux: F, Xi: R11-36-43	Flux: F, Xi: R11-36-43 The Danish classification may be: F,Xn: R11-45-48/20-36-43-65
Human(occup)		
Irritation	+	+
Corrosion	-	-
Sensibilisation	++	++
Neurotoxicity	+	+
Mutagenicity	-	-
Carcinogenicity	-	(+)*
Reproduction	-	-
Liver toxicity	-	-
Kidney toxicity	-	-
Blood toxicity	-	-
Astma	+	+

( ) = effects are weak or uncertain
\- = No
\+ = Yes
* Depends on the content of benzene

Due to the high content of low-boiling solvents in both fluxes, they are very volatile also when the flux is not heated in soldering process. The solvents have an ability to de-fat the skin, irritate the eyes, the skin and the respiratory tract. By inhalation of high concentrations it may cause headache, nausea and malaise. Prolonged or repeated exposure may affect the central nervous system, and sensitization of the skin. The flux used in connection with the lead-containing solder is more volatile than the lead-free solder flux.

When heating the fluxes acrid vapors and fumes are formed, that are very irritating to eyes and the respiratory system. Prolonged or repeated inhalation may cause asthma. Vapors and fumes may also irritate the skin.

The environmental effect of the fluxes is considered negligible compared to the environmental effects of the metals in the solders.

Hand-soldering (Wires)

Hand soldering involves the use of a soldering iron. The iron is purely a means of applying heat to the solder so that it melts and forms the required joint (4). The solder used during the hand soldering process is solder wires with "built-in" flux.

The toxicological evaluation is focusing on the metals and the fluxes. The metal content of the to evaluated wires are:

- 60Sn40Pb
- 96.5Sn3.5Ag

The two wires have different “built-in” fluxes.

60Sn40Pb and Flux

In the following tables the ingredients are presented in weight-% of the entire product:

Metal part of wire:

Component	Identification	CAS-no.	w/w-%
Component 1	Tin	7440-31-5	30-60
Component 2	Lead	7439-92-1	30-60

Flux part of wire:

Component	Identification	CAS-no.	w/w-%
Component 3	Rosin, Modified rosin (MF3)		1-5
Component 4	Activator (AC6)		0-1
Component 5	Antioxidant (AO5)		0-1

According to the Danish regulation the product should not be classified partly as the wire is regarded as a material and partly because there is no content of lead compounds, only metallic lead.

The classification of the flux, isolated from the metals would be: Xi (Irritant): R36 Irritating to the eyes, R43 May cause sensitization by skin contact (1,2).

Lead poses high human toxicity and moderate toxicity towards aquatic organisms. Tin has low human toxicity and the aquatoxicity of inorganic tin compunds is comparable to that of lead.

The flux is based on rosin and has low acute toxicity. The flux is irritating to the skin. Prolonged or repeated contact with skin may cause itching and soreness and possible sensitization.

The material in the wire has low volatility. The flux is totally soluble in water. The flux is easily biodegradable and it has no tendency to bioaccumulate. The flux is regarded as non-toxic to aquatic organisms.

At room temperature (20 °C) the product contains only substances with low volatility.

During soldering the range of the soldering temperature are 200 °C – 210 °C. The chemical composition of the flux fumes at soldering temperature has not been determined by the producer. By heating the product (metals as well as the flux) there is a small risk of evaporation of tin- and lead oxides from the metals, and a complex mixture of resin acids, aldehydes, ammonia, amines, carbon oxides, nitrogen oxides and chlorides from the flux. Most likely, chemical reactions between two or more components will take place, but these have not been established.

In products, if lead oxides were included as an ingredient with equal to or more than 5 weight-% the product would be classified as: T (Toxic), N (Dangerous for the environment): R61 May cause harm to the unborn child, R62 Possible risk of impaired fertility, R20/22 Harmful by inhalation and if swallowed, R33 Danger of cumulative effects, R 50/53 Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment (1,2).

Inhalation of the airborne metals (especially lead) and the flux fumes is of relevance for the working environment. Inhalation of the airborne metals, may cause metal dust lungs, and affect the central and the peripheral nervous system and the haeme synthesis, ***i.e.*** the product ion of haemoglobin and may cause anaemia. Furthermore exposure may cause chromosomal aberrations, impair the fertility and cause preterm delivery of babies and minor malformations. The evidence for lead being carcinogenic is ambiguous.

The flux fumes given off at soldering are irritating to the nose, throat and respiratory organs. Prolonged or repeated exposure to the fumes may cause pulmonary sensitization and asthma. Exposure to dust or processing fumes may cause gastrointestinal irritation via swallowing of inhaled dust/fumes.

The emission to the air from the solder process to the environment may contain small amounts of metal oxides of lead and silver. Furthermore small amounts of e.g. resin acids, aldehydes, ammonia, amines, carbon oxides, nitrogen oxides and chlorides may occur.

In case of the product entering the aquatic environment, e.g. by rinsing the circuit boards the flux is totally soluble in water. The flux is easily biodegradable and it has no tendency to bioaccumulate. It is not rated as hazardous to aquatic organisms. The metals should be considered as toxic to the aquatic environment. Lead is toxic to aquatic organisms, the toxicity though, depends on the water hardness. Lead is more toxic in soft water than in hard water. The aquatoxicity of inorganic tin compounds is comparable to that of lead.

The biocompatibility of lead is smaller in hard water than in soft water. The bioaccumulation is low.

96.5Sn3.5Ag and Flux

In the following tables the ingredients are presented in weight-% of the entire product:

Metal part of wire:

Component	Identification	CAS-no.	w/w-%
Component 1	Tin		60-100
Component 2	Silver		1-5

Flux part of wire:

Component	Identification	CAS-no.	w/w-%
Component 3	Solvent (S6)		0-1
Component 4	Solvent (S5)		0-1
Component 6	Activator (AC5)		0-1
Component 7	Antioxidant (AO3)		0-1
Component 8	Antioxidant (AO4)		0-1
Component 9	Wax (W3)		1-5

According to the Danish regulation the product should not be classified.

Tin has low human toxicity and the aquatoxicity of inorganic tin compunds is comparable to that of lead.

The flux is based on wax and has low acute toxicity. There is lack of data on some of the ingredients of the flux, which, makes the evaluation of the toxicity of the flux incomplete. Prolonged or repeated contact with skin may cause irritation.

The flux has low volatility and is practically insoluble in water. The flux is slowly biodegradable and it has a tendency to bioaccumulate. The flux is regarded as non-toxic to aquatic organisms.

Silver has low human toxicity but is much more toxic to aquatic organisms than lead. Tin has low human toxicity and the aquatoxicity of inorganic tin compounds is comparable to that of lead. Organic tin compounds are toxic to the aquatic ecosystems.

At room temperature (20 °C) the product contains only substances with low volatility.

During soldering the range of the soldering temperature is 235 °C – 250 °C. The producer has not determined the chemical composition of the flux fumes at soldering temperature. By heating the product (metals as well as the flux) there is a small risk for evaporation of tin- and silver oxides from the metals, and a complex mixture of ammonia, amines, carbon oxides and nitrogen oxides. There will also be a small risk for formation of e.g. chlorides. Most likely, chemical reactions between two or more components will take place, but these have not been established.

Inhalation of the airborne metals (especially lead) and the flux fumes is of relevance for the working environment. Inhalation of the airborne metals may cause metal dust lungs. The flux fumes given off at soldering are irritating to the nose, throat and respiratory organs. Prolonged or repeated exposure to the fumes may cause asthma.

The emission to the air from the solder process to the environment may contain metal oxides of tin and silver. Furthermore small amounts of e.g. ammonia, amines, carbon oxides and nitrogen oxides may occur. There will also be a small risk for formation of e.g. chlorides

In case of the product entering the aquatic environment, e.g. by rinsing the circuit boards the flux is practically insoluble in water. The flux is slowly biodegradable and it has a tendency to bioaccumulate. It is not rated as hazardous to aquatic organisms. Silver ions are lethal to bacteria, and are very toxic to aquatic organisms. Tin is moderate toxic towards aquatic organisms.

Evaluation

The following table gives a summary overview of the possible exposure of workers and the environment to the products used in the hand soldering process.

Exposure

	60Sn40Pb and flux	96.5Sn3.5Ag and flux
Temperature:	~350 °C	~400 °C
Workers:		
Inhalation	***No-heating:*** No vapors or fume ***Heating:*** Vapors or fume: Metal oxides (tin and lead), resin acids, aldehydes, ammonia, amines, COx, NOx and chlorides.	***No-heating:*** No vapors or fume ***Heating*** Vapors or fume: Metal oxides (tin and silver), ammonia, amines, COx, NOx and chlorides.
Skin	Flux in wire, vapors or fume.	Solvent vapors or fume.
Environment:		

Drost	Metal oxides (tin and lead), chlorides.	Metal oxides (tin and silver), chlorides.
Exhaust	Vapors or fume: Metal oxides (tin and lead), resin acids, aldehydes, ammonia, amines, COx, NOx and chlorides.	Vapors or fume: Metal oxides (tin and silver), ammonia, amines, COx, NOx and chlorides.
Waste	Metals on PCB, chlorides	Metals on PCB, chlorides

The process temperature is higher using the lead-free solders compared to the use of lead-containing solder. The tendency of chemicals to become airborne increases by increasing temperature. As a consequence the use of the lead-free solders in this project will possibly lead to an increase in the evaporation from the solders and fluxes compared to the use of the traditional lead-containing solder. Even though the process temperatures are relatively low, there will be a certain degree of thermic decomposition of the organic substances. The main fraction will consist of metal oxides and to a lesser extent resin acids, aldehydes, COx and NOx. There is furthermore a small risk for formation of chlorides.

These emissions will all enter the workplace or the environment unless necessary precautions are taken with encapsulation, filters etc. There will be special requirements on the exhaust/ventilation as the wires are used in hand soldering processes.

The composition of the drost from the production or the waste differs mainly due to the content of the metals.

The following table gives an overview of the main effects of the referred exposures of workers and the environment to the solders.

Effects of the metal pars of the alloys as metal compounds in vapor, fumes, smoke, waste water, etc.

	60Sn40Pb	96.5Sn3.5Ag
Human(occup)		
Irritation	-	-
Corrosion	-	-
Sensibilisation	-	([+])
Neurotoxicity	++	(+)
Mutagenicity	[+]	-
Carcinogenicity	+ (IARC: 2B)	-
Reproduction	+++	(+)
Liver toxicity	[+]	[+]
Kidney toxicity	[+]	[+]
Blood toxicity	++	-
Accumulation	+++	+
Environmental		
Bioaccumulation	+	+
Toxic to aquatic org.	+	+
Toxic to bacteria	-	+
Toxic to algaes	+	-

[ ] = effects caused by compounds other than metal itself
( ) = effects are weak or uncertain
- = No
+ = Yes

Lead is very toxic to humans. The other metals in the solder are low to moderate toxic to humans. During the solder process fumes of metal and metal oxides may be formed and emitted to the air in the working environment, and inhaled by the workers. Especially lead may cause severe systemic effects.

Lead is moderate toxic to the environment. Silver appears to be much more toxic to aquatic organisms than the other metals in the solder. The lead-free solder contains silver and more tin instead of lead.

Below is an overview of the toxicological effects of the fluxes used in the solder process.

Effects of the fluxes

	Flux to 60Sn40Pb	Flux to 96.5Sn3.5Ag
Classification	Flux: Xi R 36-43	None
Human(occup)		
Irritation	+	(+)
Corrosion	-	-
Sensibilisation	++	-
Neurotoxicity	-	-
Mutagenicity	-	-
Carcinogenicity	-	-
Reproduction	-	-
Liver toxicity	-	-
Kidney toxicity	-	-
Blood toxicity	-	-
Astma	+	+

( ) = effects are weak or uncertain
- = No
+ = Yes

When not heated, both fluxes are of low volatility. The flux in the lead-containing wire is allergenic.

When heating the fluxes acrid vapors and fumes may be formed, that is very irritating to eyes and the respiratory system, and the flux in the lead-containing wire is allergenic. Prolonged or repeated inhalation may cause asthma. Vapors and fumes may also irritate the skin.

The environmental effect of the fluxes is considered negligible compared to the environmental effects of the metals in the solders.

Summary of toxicology

Occupational considerations

During the solder process fumes of metals and metal oxides may be formed. The fumes may be emitted to the working environment and be inhaled. Especially lead may cause systemic effects, and vapors and gasses may irritate the mucosae of eyes and respiratory tract, and possibly cause respiratory diseases with symptoms like asthma and respiratory allergy. Skin contact during handling flux and solder materials may irritate the skin and in some cases cause development of skin allergy.

As the lead-free processes requires higher processing temperatures, the tendency of chemicals to become airborne increases. As a consequence the use of the lead-free solders will possible lead to an increase in the evaporation from the solder metals and fluxes compared to the use of the traditional lead-containing solders.

In general, regarding the fluxes, the concentration of activators seems to be higher (at least the double) in fluxes used in connection with lead-free solders as compared to the fluxes used in lead-containing solders (see figure below).

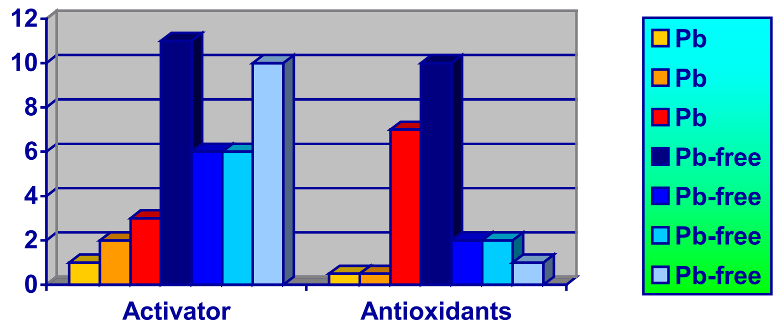


Fig. Content of activators and antioxidants in the fluxes used in connection with resp. lead-containing and lead-free solders in w/w-%.

Furthermore, experience from the practical testing program in this project indicates that the flux of the lead-free solders is more corrosive to the materials. Combined with the fact that the lead-free soldering temperature is higher, developing more fumes and vapors this may indicate that the lead-free solder processes may develop more acrid, irritating and in some cases allergenic fumes and vapors than the traditional lead-containing solder processes.

From a working environmental point of view though, it seems justifiable to substitute the lead-containing solders by lead-free materials, as lead poses high human toxicity compared to tin, silver and copper. That is assuming humans are exposed. Whereas, if containment of the processes are very efficient, there will be no occupational exposure of solderers. There will though always be a risk of exposure, e.g. during maintenance, cleaning and reparation, which still may justify the substitution of lead-containing solders to lead-free.

Consumer considerations

Data indicates that neither of the solder technologies (lead-containing or lead-free) poses any nuisance to the consumer.

Environmental considerations

From a human toxicological point of view lead-free solder are to be preferred compared to lead-containing solders. Lead is moderately toxic to the environment, but it is uncertain whether lead metal, ***e.g.*** in solder, will be bioavailable from electronic equipment dumped in waste sites. If incinerated, lead will be present in smoke to some extent as lead metal and oxides.

The general-purpose lead-free solder contains in addition to tin silver and copper instead of lead, but in much lower contents, ***e.g.*** Sn95/Ag4/Cu1. Silver and copper are less toxic to humans than lead. Copper is an essential element. Silver appears to be much more toxic to aquatic organisms than the other metals in solder, whereas the aquatoxicity of copper is moderate (in the order of that of lead). However, as for lead, it is uncertain whether silver and copper metals will be bioavailable from electronic equipment dumped in waste sites.

If incinerated, these metals may be present to some extent in smoke as oxides and possibly also as metals. The content of copper in the incinerated metals may have a catalytic effect on the formation of dioxins (10).

In case electronic equipment is deposited there will be a risk for the metals and chemicals to leach into the environment. Some chemicals may also evaporate. Odense Renovationsselsskab A/S receives and treats electronic waste from the public and companies in Odense city. The waste is separated in fractions of materials and components. In 2001 84% were recycled, 10% incinerated and nothing was deposited (13). There is no information of the last fraction (6%). The numbers illustrate that it might be possible in the future to avoid depositing the electronic equipment, thus eliminating this disposal way as a source of emission.

The overall disposal of EE-products (except for refrigerators and deep freezers) in 1997 was 103.000 tons in Denmark. About 60.000 tons of these were electrical products and about 43.000 tons were electronic products.
The amount of electronic waste is expected to increase (10). Part of these are consumer electronics. The Danish Trade Organization for Consumer Electronics has estimated that the amount of disposed consumer electronics is expected to increase by 36% from 1997 to 2001 (total amount 14.000 tons). In 1994, 60% of the electronics was discarded. This amount was estimated to be 89% in the year 2001 (10). Unfortunately new figures are not yet available but are expected in a short period of time.

The European recycling industry for electrical and electronic products is expected to increase their turnover from 144 mio. USD in 1995 to 419 mio. USD in 2002 (12), which seems to be an essential increase. Question is weather it is possible to keep step with the increasing amount of electronic waste.

Conclusion and recommendations

In summary, lead poses high human toxicity and moderate toxicity towards aquatic organisms. Thus, substitution to lead-free solder seems justified with regard to human toxicity. However, the future general-purpose lead-free solder implies the use of silver, which has low human toxicity but is much more toxic to aquatic organisms than lead. The other metals (tin and copper) are little to moderately toxic to humans and of moderate aquatic toxicity. One has to bear in mind that a toxic hazard, ***e.g.*** as described in the toxicological profiles not necessarily implies a health risk. The toxic metal or formed compounds, ***e.g.*** oxide, must be present in (bio)available forms and in sufficiently high concentrations to result in toxic doses in humans or other organisms.

Lead is very toxic to humans and may cause serious chronic effects. The other metals (tin, silver and copper) have significantly weaker toxicological effects on humans than lead. From a human toxicological point of view it may seem justified to avoid lead in solders, if there is a risk of exposure. The use of modern technology, where the solder process takes place in full containment will reduce or eliminate the exposure of workers to solder vapors and fumes to nothing, regardless of the solders used (lead-containing or lead-free). There will though always be a risk of occupational exposure in connection with maintenance, reparation, etc., which still makes it justifiable from a human toxicological point of view to avoid lead in solders.

From an ecotoxicological point of view substitution to lead-free solders is more uncertain as emission and environmental fate are uncertain; exposure is therefore uncertain. In a life cycle perspective, the main environmental load will not be during the production/solder process, provided the production is optimized (e.g. with minimal losses during manufacturing), but after end of use.

The figures from Odense Renovationsselsskab A/S (13) show that it is possible to avoid depositing electronic waste. The use of incineration as a method of disposal involves certain risks of emission of metals and metal oxides, which are removed on filters. High degree if recycling is considered to be the most appropriate method in order to avoid undesirable environmental effects in accordance with the "Affald 21" (11), which is the Danish national action plan (until 2004) on handling waste. The goal is to:

- Increase recycling of resources from EE-products, e.g. PCB´s shall be recycled or processed with at least 80% reuse of each of the metals: copper, nickel, platinum, palladium, lead, gold and silver.
- Limitate the incineration of EE-products.
- Dispose the EE-products in an environmental-friendly way.

The controversy between solder containing human toxic lead or aquatoxic silver may be resolved by recycling electronics to avoid emissions.

Summary recommendations:

Occupational Health:	• Proper protective measures (enclosure/containment, efficient exhaust, etc.) • No manual handling
Environmental Health:	1. Reduce losses during manufacturing 2. Proper treatment of hazardous waste 3. High recovery for the metals during recycling