IMPLEMENTING LEAD FREE SOLDERING – EUROPEAN CONSORTIUM RESEARCH

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INTRODUCTION

Lead is one of those materials that man has used throughout history because it is easily extracted and refined with relatively low energy costs and it has a range of useful properties. The significant problem with the material however is its mammalian toxicity and this has driven its elimination from applications where there is an effective substitute. It has been removed from food and water contact applications, such as potable water distribution systems and food cans, and it has been largely eliminated from automotive fuel and paint formulations. In some countries, it has been replaced in PVC stabilisers, ammunition and fishing weights. Of course there are still very large applications for lead, particularly in the ubiquitous accumulator in every automobile and many stationary back-up power systems. However, this is not an acceptable justification for the continued use of the element in smaller applications if there is an alternative. Consequently, the relatively small use of lead in soldering in the electrical and electronics industry started to receive attention from environmentalists and legislators about ten years ago. The toxicity of lead towards its immediate users was not the main driver for elimination from soldering. However, the redistribution of the material into the environment via the landfill of "spent" electronic equipment was seen to present a long-term problem for groundwater purity. The table below gives some indication of the relative risks of lead ingestion by different routes.

Over the last ten years, there have been a large number of publications describing work into lead free electronics soldering. They have come from all regions of the world and from academic organisations, individual companies and consortia. Although a number of these studies have culminated in "production trials", these have invariably been on a limited scale and they were essentially a demonstration, rather than the first step to implementation. This situation has changed significantly since the 4th quarter of 1998. In quick succession, the second draft of a proposed European Directive[1] was published and major players in the Japanese electronics industry voiced their intent to eliminate lead in the next few years. More to the point, products actually went on sale that had been assembled by a lead free process. Although the draft European Directive may undergo changes before it is issued and it may take some time to pass into law in the member states of the EU, the effect was to signal to the market that we were now talking about "when" not "if" for lead elimination. There is now a clear indication that many manufacturers will be running lead free assembly processes in at least part of their production. The roll out of lead free soldering will then depend on technical roadblocks and commercial pressures. It is quite possible that there will be rapid adoption in some sectors, while others remain wedded to lead solders. One factor that may change the picture is the advance of contract manufacture. This may be a powerful driver for harmonisation, not just in moving to lead free soldering, but in the selection of a limited number of general-purpose alloys.

This paper describes the essential findings from a major collaborative programme of work carried out in Europe with funding from the European Community via the BRITE EURAM programme. The results collected by all the partners have been freely exchanged and their permission to report them here is warmly acknowledged.

THE PROGRAMME

The consortium gathered informally to discuss the possibility of applying for funding support in late 1994. Some of the partners had been involved in an earlier project funded within the UK that had identified the basic materials and process options for lead free soldering[2]. However, it was recognised that many unknowns remained to be explored and, despite a growing literature base[3], nobody seemed to be planning to run lead free processes on a scale sufficient to understand the implications for yield and to identify second order technical effects.

Consortium

The consortium was well balanced, both in terms of integrating the supply chain in the electronics assembly industry, in terms of process and product type, and finally in terms of geographical distribution. The work started in April 1996 under the acronym "IDEALS", tortuously created from the project title "Improved Design Life and

Environmentally Aware Manufacturing of Electronic Assemblies by Lead-free Soldering"[4]

The consumable suppliers were Multicore Solders Ltd. (UK) and Witmetaal (NL). And the users were Philips (NL), Siemens (Germany) and GEC (UK) and the team was well supported by the laboratory and analytical skills of the NMRC (Eire). Everyone would have preferred to include a major component manufacturer because it was recognised that the availability of suitable components with appropriate solderable coatings could be a major roadblock. However, no partner could be found, although both Siemens and Philips have component manufacturing arms. At the beginning of the project, GEC was able to contribute electroplating facilities that were to be used to explore the options for PCB finishes. In the event, this avenue was not followed after preliminary experiments showed the difficulty in electroplating controlled deposits of SnAg3.5

Objectives

The overriding objective of the programme was to demonstrate the viability of lead free wave soldering and reflow assembly processes and the associated repair and rework of lead free devices. The team intended to define the process window in each case and to provide a broad spectrum of reliability data supported by analytical studies. At the end of the programme both wave and reflow assembly processes were running with lead free consumables at some of the users' facilities.

As part of the process developments, alloy and flux options were explored, including the use of VOC free fluxes for the wave soldering process. The earlier work meant that there was already a clear list of alloys to be used. The developments were largely restricted to the investigation of subtle composition changes for alloys melting in the range 190-220°C. The decision was made to concentrate on the alloy options with melting temperatures above the current alloys although it was recognised that the tin-bismuth eutectic alloy (SnBi58) is a contender for some applications. Other alloys probably have niche markets but this programme was firmly targeted at the mainstream electronics assembly industry.

Having selected alloys with higher melting temperatures than Sn62 and Sn63, there was some hope that there might be improved reliability performance in adverse environments and this objective was considered in the testing of soldered joints and assemblies.

EXPERIMENTAL

The following is only a summary of the full programme. Each of the partners carried out a significant number of sub-tasks that contributed to the overall picture that this paper is summarising.

Materials

A variety of alloys were studied in detail at different times during the project and the main materials may be summarised in the following four groups:-

1. SnAg3.8Cu0.7
2. SnAg3.8Cu0.7 with various additions of antimony.
3. SnAg3.8Cu0.7 with various additions of bismuth.
4. SnBi5Ag1+ where the "+" was added as a grain refiner. One of the partners has requested that this remain confidential at this time.

In addition, data were collected for SnCu0.7 and SnAg3.5 with various additions of antimony to provide an insight into the performance of the main selected alloys. The benchmark alloys were Sn62 for the reflow process and SnPb36Bi2 for the wave soldering process. This latter material has long been a standard alloy at Philips.

A variety of boards were used as the test vehicles and they were supplied with several finishes. These included:-

a) Organic solderability preservative (OSP)
b) Gold over nickel
c) Immersion tin
d) Silver immersion finish
e) HASL using SnCu0.7
f) Tin lead solder

In addition, component lead finishes included:-

g) Electroplated pure tin
h) SnPb5-50
i) Ni/Pd
j) Ag/Pd fired inks
k) Ag/Pd with Ni/Sn solderable finish

The wave soldering fluxes were all low solids No Clean formulations, including formulations containing <1.0% volatile organic compounds (VOC). The fluxes for reflow soldering were also No Clean types with a variety of stencil printing characteristics and residue properties. Repair and rework was carried out with No Clean flux cored wires or solid wire and liquid fluxes.

Wetting tests

These were conducted using a wetting balance (Multicore MUST II and GEC Meniscograph Mk 6B) under a variety of conditions, depending on the objective of the experiments. Benchmarking of the various alloys was normally achieved with a standard rosin test flux applied to copper coupons or a suitable coated substrate or component lead.

Temperature selection for the tests was a key consideration. The benchmarking was achieved by comparing wetting performance at the same temperature and at fixed superheats above the liquidus temperatures of the various alloys.

Measurements to support process investigations made use of the fluxes, solder contact times, and test temperatures to be used in the process.

Process tests

The programme was based on industrial scale wave and reflow soldering process equipment and in both cases, nitrogen and air atmospheres were available. The reflow oven was a high specification convection system (Seho FDS 6440 3.6) and the wave soldering machine was equipped with radiation and forced air convection preheaters and a dual wave (Vitronics-Soltec Deltawave 6622 S&V). Conventional rework techniques were employed on boards that had been assembled in the wave and reflow lead free processes. A PACE MBT250 rework station fitted with either hot gas tools or iron plated soldering iron tips was used together with a Finetech hot gas rework station.

Boards were built for inspection and reliability testing using the production equipment described above. The process window was defined by varying the conditions for soldering and looking for an impact on the quality of the product. As the project progressed, a number of the production facilities of the partner companies started their own parallel investigations so that a number of real products had been assembled with lead free consumables under different conditions.

Inspection and analysis

Current soldering processes still rely on inspection that operates on the simple, but true, statement "if it looks good, then it is good". The team set out to review the visual quality of the solder joints against accepted existing standards. It was decided to use the same criteria adopted by Philips (UN-D1291) in their own production facilities as an example of internationally acceptable standards. In the case of reflow soldering, the Siemens internal standard (F1412) was also used.

Conventional optical and scanning electron microscopy was routinely carried out on all the combinations of solder alloy, solderable finish, process conditions, and ageing conditions. In addition, selected X-ray laminography of soldered joints and X-ray analysis of materials was carried out as appropriate.

Reliability tests

A range of test conditions was selected to give an overview of the likely reliability of lead free soldered joints. They were based on established procedures for conventional SnPb assemblies and the team recognised the dangers inherent in this approach. There is a great deal of debate about the interpretation of reliability test data, but there is sufficient experience with SnPb joints to show that the correct failure mechanisms are accelerated and so extrapolation of the results is feasible. It was possible that using the same methods for lead free soldered joints would fail to accelerate the real-life failure mode and thereby give misleading reliability data. In the event, consideration of the whole body of evidence showed that the accelerated tests were appropriate. However, it also showed the dangers in making uncritical comparisons between results collected under apparently identical conditions. Subtle changes in laminate construction and the quality of board finishes had a measurable effect on joint performance.

The principle tests employed were as follows:-

a) Measurement of joint strength for a variety of components (passive components, miniMELF, SO14, PLCC, QFP) after ageing in thermal cycling (-20°C/+100°C in 30/10/30 minute dwells) for different cycle counts.
b) As (a) except –40°C/+125°C.
c) Thermal shock tests were conducted over the transition –65°C/+125°C with a 3 minute dwell and a cycle time of 10 minutes.
d) Power cycling test using a specially designed vehicle. The cycle was 30 minutes long with the power on for 15 minutes. The joints on resistors (1206) reached a peak temperature of 100°C in about 5 minutes and returned to room temperature within 19-20 minutes after the cycle started. The leads on a metal quad flat pack reached 100°C (20 lead side) and 110°C (30 lead side) after about 4.5 minutes and also returned to room temperature 19-20 minutes into the cycle.
e) Random vibration testing was carried out with a frequency range of 50-2000Hz and a maximum acceleration of 30G for up to 8 hours per axis.
f) Combination of (e) and thermal shock between –40°C and +125°C with 10 minutes dwell and 25 minutes total cycle time.

In addition, the mechanical properties, and some physical properties, of the selected lead free alloys were also characterised by standard testing techniques.

RESULTS

Alloy properties

The melting characteristics of the alloys closely considered in this programme are summarised in the table below. In looking at the data, it is important to recognise that alloys may show different behaviour when subjected to directional non-equilibrium cooling in real soldered joints.

On solidification under conditions similar to those found with real electronics assembly joints, the alloys gave eutectic-like microstructures with a tin matrix containing distributed dispersed particles of Ag_3Sn and or Cu_6Sn_5, depending on the alloy and whether it melted in contact with a copper substrate. In contrast with SnPb alloys where the lead rich phase coarsens on ageing, the dispersed phase in the alloys studied tended to refine and spheroidise on ageing. The microhardness of the SnPb, SnAg and SnAgCu alloys (with or without 0.5% Sb) were in the range $H_{v10}=17\pm2$ compare with SnCu at $H_{v10}=13\pm2$. All of the alloys soften by about 20% on ageing at 125°C for 1,000 hours.

Some of the basic physical property data for the lead free alloys was collected but in other cases, it was inferred from the values for pure tin. As an illustration, some data are summarised in the following table for SnAg3.8Cu0.7alloy.

While the mechanical properties of solder alloys are only indirectly linked to the behaviour of solder joints made from them, some measurements of the bulk materials were made to provide a basis for comparisons and analysis of other results. The series of graphs below illustrate the differences that were seen between the candidate alloys, but it is fair to say that they were not large under the particular conditions of test.

The Young's modulus results for the lead free alloy showed the effect of having a higher melting temperature compared with SnPb40. The yield stress data suggest that the lead free alloys will be superior to SnPb40 at elevated temperatures.

Creep experiments run on the alloys showed that significantly more creep deformation occurs with SnPb40 than in the lead free alloys

Wetting behaviour

The surface tension of the lead free alloys is significantly higher than SnPb40. This can be inferred from the wetting balance measurements but a more direct indication is given in the table below where the contact angle for pre-alloyed pellets melted onto various surfaces is shown. Repeating the same measurements with solder pastes based on the alloys masks the effect to some extent. However, contact angles of 4-6° for SnPb37 and SnPg36Ag2 on a variety of surfaces increased to values of 6-14° for alloys of tin, silver and/or copper. In all cases, repeating the experiments in nitrogen reduced the contact angle by 1-3°.

The consolidated wetting balance data in Graph 3 show that, given an appropriate test temperature, the maximum wetting force registered was largely independent of the solder alloy composition.

The same general picture is given in Graph 4, which shows a measure of the speed of wetting as a function of superheat above the liquidus temperatures of the alloys. While the results fall in the same general range, it is arguable that the alloys based on the SnCu0.7 system showed more sluggish wetting. This is clearer in Graph 5 where the superheat temperature has been replaced by the actual temperature. This shows that SnPb40 wets more quickly than the other alloys at any given temperature and that the alloys containing silver show better performance than those that do not.

Despite the apparently poorer performance of the lead free alloys, it is important to note that the wetting times are still short and within reach of the normal process window for mass soldering processes. However, they imply that process temperatures/times would have to rise in proportion with the increased liquidus temperature of the alloys. Real process work was to show that this was true, but not to the extent at first anticipated.

The same general results were obtained throughout the programme and whatever the combination of substrates and fluxes. One particular area of interest was the addition of antimony to the various alloys. It was felt that specific advantages would be gained to offset the additional complication of controlling more elements in the solder alloy and the concerns expressed by some over the toxicity of antimony. The data below show that a small addition of antimony has no apparent effect on wetting performance while larger additions seem to retard wetting. This reflects the known effect of antimony on the wetting performance of SnPb37.

Wave soldering

Wave soldering processes are particularly sensitive to the cost of metal, even though the contribution to the cost of a finished assembly is small. The project team was therefore conscious of the need to reduce alloy costs to a minimum while trying to minimise the melting temperature and sacrificing no process yields or reliability in the finished assembly. With this in mind, the first series of experiments evaluated SnCu0.7, SnBi5Ag1, SnBi5Ag1+, at solder bath temperatures of 250-275°C in air and nitrogen (for SnCu0.7). Both single sided and double sided boards were assembled, mostly on OSP finish although HASL and electroplated SnPb were used.

The results with SnCu0.7 were generally unacceptable, showing poor joint fillet shape and the high temperatures/times needed to effect soldering caused deterioration of the board materials. SnBi5Ag1 gave similar results and the microstructure of the solidified alloy was coarse. The addition of "+" as a grain refiner solved this and gave the best fatigue behaviour of soldered joints in preliminary thermal cycling tests (-20°C/100°C). All of the alloys except SnCu0.7 were superior to the benchmark solder alloy (SnPb36Bi2) but the team focussed on SnBi5Ag1+ for further trials. However, further study showed that this alloy produced characteristic defects (see below) on double sided pth boards and its application was eventually restricted to single side assemblies.

The process window for single sided boards using SnBi5Ag1+ is shown in Table 5. Although these minimum values are more aggressive than current wave soldering processes, they fall inside the upper range limit for lead-bearing solders in a comparable application.

Once the problems associated with double-sided boards had been recognised, and the underlying mechanism understood, the wave soldering team extended their study to the SnAg3.8Cu0.7Sb0.25 alloy. This was not susceptible to the problem but of course carried the cost penalty of a higher silver content. Double-sided boards also presented the additional problem of pth filling where the thermal demands of the operation stretched the process window to higher temperatures. Table 6 summarises the results for double-sided pth boards using this alloy. Single sided boards were built under the same conditions as for the SnBi5Ag1+ alloy.

The extended assembly trials used components with SnPb finishes; chip capacitors, resistors, miniMELF, SOT-23 with electroplated tin coatings; connectors, transformers, and QFP with leads dip-coated with the assembly solder alloy; wire tags with electroplated silver leads; and chip capacitors with AgPd thick film metallisation. A number of current production boards were assembled and the defect rates compared with current production. In one case the defect rate was higher while in another, it was lower. An added complication was the failure to fully evaporate the VOC flux during preheating with the result that microballing was apparent on some boards. This was not a direct consequence of the use of lead free solder alloys but a consequence of the high latent heat of evaporation of water in the flux. It was concluded that nitrogen inerting of the process was advisable to reducing losses by alloy drossing. The layout rules for wave soldering do not appear to require changing but the rules for connecting copper in double-sided pth and multilayer boards have to be strictly obeyed. Failure to follow the rules may result in excessive thermal demand and badly oriented components.

During the course of the work, one wave soldering line implemented the switch to SnBi5Ag1+ solder alloy and the change has been reported to be cost-neutral.

Reflow soldering

The alloy materials costs for solder pastes are a relatively small part of the cost of solder paste, which is in turn a small part of the finished electronic product cost. The exposure of boards and components to elevated temperature in the reflow process is much greater than in the wave soldering process and so there is a premium in reducing the peak temperature required. While the use of a lower melting alloy, such as SnBi58 is a possible route, the low melting temperature also calls into question the reliability of soldered assemblies under adverse conditions. There is a number of complex alloys with melting temperatures close to Sn/Pb that could be considered, but they each have constraints in terms of performance or availability of the component metals, e.g. In alloys. The team therefore concentrated efforts on defining the process window for the simplest alloy with the lowest melting temperature in the SnAgCu system, that is the ternary eutectic SnAg3.8Cu0.7. The value of adding Bi to this system was also investigated to see if the peak reflow temperature could be reduced without an impact on solder joint integrity.

Solder paste flux was found to have an effect on the process window and on the quality of the joints (see below) but desirable results were obtained using materials within the normal design scope of No Clean solder paste formulations. The full evaluation of the reflow process window was conducted using boards with OSP, immersion silver, immersion tin, or gold over nickel finishes. The majority of the passive components had a pure tin metallisation whereas the QFP leads generally had a SnPb15 finish. Some of the QFP were given a lead-free finish by dipping the leads in pure molten tin prior to assembly onto the boards. Three fluxes for the solder pastes were used in this part of the trial although a large number of formulations were evaluated throughout the course of the programme.

The laboratory-based process widow definition was carried out on the test vehicle shown in Photograph 1. Reflow process temperature profiles were logged using a Multicore Soldapro via thermocouples attached to either a passive device or the leg of a QFP. In view of the critical nature of the temperature measurements, they were calibrated against “indicator solder pastes” run through the reflow oven. By using a series of formulations based on different eutectic alloys, it was possible to see direct evidence of the peak reflow temperature that had been reached and to correlate this with the thermocouple readings on the logging device. The oven was set up to produce preheats and peak temperatures at three levels (**H**igh, **M**edium, **L**ow) and the resulting profiles were labeled LL, LM, MH, HH etc. A linear temperature profile up to the peak temperature was also evaluated. The recorded profiles are reproduced in Graphs 7 and 8. Both air and nitrogen reflow atmospheres were used. Of course the main focus of the exercise was on the lower preheat and reflow temperatures and some example data derived from the profiles are shown in Table 7.

It was shown that reliable soldered joints passing visual inspection criteria could be produced with a peak reflow temperature of 225°C and a time over 217° of 10 seconds. Clearly a superheat above liquidus of only 8°C might be difficult to control and a practical minimum for the coolest part of a board might therefore be 230°C.

A number of production plant demonstrations of lead free assembly were run at two sites within GEC and at a Siemens facility. One of the sites, a Marconi Communications factory within GEC has been running one production line using solder paste made from the ternary tin silver copper alloy since 2 Q 1999. A contributing factor in the decision to move to a lead free alloy was that a solder joint reliability issue on a particular connector was resolved by the lead free alloy. In all of the evaluations, tin lead coated components were used and this widens the reflow process window considerably. The early melting of the tin/lead coatings initiated reflow of the solder paste by dissolving the higher melting temperature alloy. The resulting alloy of course shows a solidus temperature of 179°C. A number of production site trials of lead free soldering where tin/lead coated components were used have been carried out using the same reflow profile as used for the existing Sn62 or Sn63 solder pastes. This observation prompted a short series of experiments in which Bi was added to SnAg3.8Cu0.7 to measure the effect on minimum reflow conditions. Pastes were made by mixing powders of SnAg3.8Cu0.7 with SnBi58 to give final compositions that contained 2.5% and 5% bismuth. Pre-alloyed powder was also used and the effect on reflow behaviour is summarised in Table 8.

The influence of both lead and bismuth on peak reflow temperature is clear. Bismuth at 5% offered a peak temperature reduction of about 8°C for soldering to a lead free surface, which is significant since the work showed that reflow and good joint formation of the SnAg3.8Cu0.7 alloy could be achieved with a superheat of only 8°C. A smaller addition of bismuth gave a proportionate reduction but the effects of lead and bismuth were not additive, within the limits of the experiments. This result indicates that there are apparent opportunities to use alloys that contain bismuth, but other factors (see below) suggest caution in using the element.

Repair and rework

The team studying rework capability used conventional process equipment and techniques to remove components from assemblies produced in the mass soldering trials and to replace them using either solder paste or flux-cored solder wires. The resulting assemblies then went through the same reliability tests as the original boards.

Most of the repair work concentrated on re-soldering QFP legs using SnAg3.8Cu0.7 or SnAg3.5 flux cored solder wire for all the board finishes in the programme. It was found in most cases that there was already sufficient copper dissolved in the residual solder from the original joint to make the use of the ternary alloy unnecessary. In fact, if SnAg3.8Cu0.7 cored wire was used, some of the joints appeared “gritty” due to the precipitation of excessive amounts of copper/tin intermetallic compound particles.

Rework of the lead free soldered joints presented no particular problems. It was necessary to use peak heat source temperatures above 360°C and there was a tendency for flux splashing to occur. Wetting was limited and the spread of solder was less than for Sn/Pb, as expected from the contact angle experiments. Nitrogen inerting was preferred in the hot gas repair work. Some joints were repaired up to 12 times and individual QFP lead pull strengths were measured. There was no statistically significant change in either the average recorded pull strength or in the scatter of results when OSP boards and Sn/Ag coated QFP leads were put through this programme.

Separate experiments showed that Sn/Pb soldered joints could also be repaired by normal techniques using the lead free cored solder wire.

Inspection and analysis

Solder joints made with the lead free alloys tended to be duller than the equivalent Sn/Pb joints. Mention has already been made of the tendency for wave soldered boards to carry “fatter” joints and to show limited pth fill. Solder spread in reflow was usually seen to be restricted but detecting the edge of the solder fillet on pads was not always easy. In the case of OSP finish boards, this could result in a halo of copper being visible at the perimeter of the pads. In some visual inspection standards, this would be considered unacceptable even though it is fundamentally a cosmetic defect. There was a detectable difference between the soldered joints produced with different paste formulations. Some pastes required nitrogen to give the biggest reflow process window when they would have performed adequately in air with Sn/Pb solder. However, this problem was easily overcome by the correct selection of No Clean flux chemistry.

Apart from double-sided pth boards made with SnBi5Ag1 or SnBi5Ag1+ alloys in a wave process, the overwhelming opinion of all the partners inspecting soldered joints made under the recommended process conditions was that they met the existing visual inspection criteria for Sn/Pb soldered joints. This was reinforced at each of the production trials although operators could tell the difference between the lead and the lead-free soldered joints in some cases because of subtle changes in their appearance.

The joints made with SnBi5Ag1 or SnBi5Ag1+ showed a characteristic defect known as pad lifting which is best described in Schematic 1. The combined effect of the direction of heat flow from the joint as it exits the wave and the presence of a small amount of low melting temperature material in the alloy result in final solidification of the solder taking place after it has contracted away from the PCB pad. In fact, this phenomenon has been reported before and it may result either from the presence of bismuth and/or lead in a tin-rich solder alloy. Both elements produce low melting temperature phases that can be concentrated at an interface as cooling and solidification proceeds through the solder fillet. There was no evidence in this programme that the solder joints made with SnAg3.8Cu0.7 on double sided-pth boards or any of the alloys used for reflowed boards showed the same defect, even when lead was present. However, other studies carried out by the authors suggest that wave soldered boards with Sn/Pb coatings are inherently susceptible to the problem. Furthermore, there is some evidence that when using lead free solders containing bismuth in a reflow process on boards that have a Sn/Pb finish there are cooling conditions that reproduce on surface mount components the same defect as seen for pth components.

The microstructures of the lead free solder joints were entirely as expected, as was the interface with the substrate materials. There was a fine dispersion of tin/silver and/or tin/copper intermetallic particles in a tin matrix, as appropriate for the alloy composition. Where contact with Sn/Pb alloys was made, the microstructure showed an additional fine dispersion of lead particles.

The dissolution rate of copper into the wave solder pot was found to be about 5µm compared with 2.5µm for Sn/Pb alloys and silver was removed from Ag/Pd metallisation at an unacceptable rate. The use of passive components with this type of metallisation but without a barrier layer of nickel and a solderable finish is not recommended in wave soldering applications.

The intermetallic compound layers produced during soldering and subsequent ageing were the same as those present at equivalent Sn/Pb substrate interfaces. Of course, the lead free materials did not have the lead-rich region between the solder and the intermetallic layer that is typical of lead containing alloy solder joints after ageing. Intermetallic compound growth rates were not statistically different to those for Sn/Pb solders as is confirmed by the results in Table 9.

The reflowed solder joints were submitted to detailed X-Ray inspection once it was realised that they appeared to have a higher incidence of voids than those made with Sn/Pb. It was confirmed that these were omni-present on the boards made with the solder paste fluxes initially selected. The lead-containing solder joints were not free from voids, but they were fewer in number and generally smaller. The lead-free joints to chip capacitors and resistors may have been worse than those to leaded devices and there was clear evidence of voids present in the solder fillets remote from the component. Sectioning confirmed that the voids were spherical and usually “attached” to one of the surfaces present. A typical distribution of voids is shown in Photograph 2.

A full matrix of trials was carried out with model flux formulations in which resins, flux solids contents, activators and solvents were systematically varied so that the incidence of voids could be reduced.

The initial solder paste formulations produced 14% void area with SnAg3.8Cu0.7 compared with 1% for the SnPb36Ag2 control using the same flux. As can be seen in Photograph 3, voids were not completely eliminated, but they were reduced to the same level as was found on the boards soldered with the control Sn62 paste formulation. There was no correlation between the appearance of voids and the reflow profile used for the process for any of the fluxes. The substrate finish appeared to have no influence, providing solderability was not compromised, and the same results were obtained in both air and nitrogen reflow.

Reliability

No relatively short programme of work is going to match the many years of accumulated experience in testing Sn/Pb soldered assemblies for reliability. However, testing in this programme was carried out in several laboratories and to a number of protocols and the results were remarkably consistent. During the programme, evidence appeared that seemed to support preliminary conclusions about the benefits, or otherwise, of particular alloys and substrate finishes but as more data were collected, it was found that other factors had affected the results. In particular, the quality of substrate finishes affected some results and the orientation of components on the test boards also had an effect. It was concluded that it would be dangerous to read too much into individual pieces of data that showed relatively small changes in performance. In the light of this finding, the reader is advised to view the following information only as broadly representative of a very large collection of measurements made with different combinations of materials. The exception to this of course is the joints made to double-sided pth boards with SnBi5Ag1 and SnBi5Ag1+ solders described above.

Graph 9 shows a representative lead free alloy in comparison with conventional alloys in joints made to OSP copper. The resistance of the joints to degradation in thermal shock is the same within experimental uncertainty.

The same tests reported in Graph 9 were repeated for solder joints produced under different conditions of reflow and this demonstrated that there was no significant effect of changing the preheat or the peak temperature. Linking the results in Graph 10 with the visual inspection data provided evidence that solder joints that looked acceptable after reflow also performed reliably. There was no significant influence of the substrate finish on these results but there was a very weak correlation with the extent of solder joint voiding. However, the level of voiding was related to the flux composition and it is possible that the correlation was actually due to small changes in the extent of wetting of the solder on the substrate. This could change the area of contact and fillet shape producing small changes in the measured strength.

The data shown in Graph 11 imply that joints soldered with lead free alloys to resistors and subjected to power cycling consistently perform less well than those made with Sn62. However, the reverse effect is seen with QFP leads under the same conditions and Graph 12 puts the change in context by comparing the effect of device lead material. The lower strength of joints made directly to Kovar is well known with Sn/Pb alloys and that is reproduced here for the lead-free solders.

Thermal cycling tests initially produced no consistent differences between the lead free alloys and Sn/Pb soldered joints. There was evidence that solder joint strength fell faster as the number of cycles increased although the failure rate of the joints was comparable. The vibration testing was not sufficiently severe to produce failures and so no conclusions could be drawn from them.

Direct comparison of the SnAg3.8Cu0.7 alloy with and without additions of 0.25% and 0.5% Sb in joints produced by reflow soldering produced no consistent benefit in terms of reliability. In the case of wave soldering, the SnAg3.8Cu0.7Sb0.25 alloy was considered to offer the same reliability performance as the benchmark SnPb36Bi2 material. However, wave soldered joints made with SnBi5Ag1+ alloy did produce improved thermomechanical fatigue life for both surface mount devices and leaded components, despite the phenomenon of pad lifting in the double-sided boards. The effect of pad lifting in improving reliability has been reported previously and may result from increased compliance introduced into the soldered joints. However, the difficulty in defining criteria by which this defective joint could be accepted during visual inspection mean that it is not possible to capitalise on the improvement.

There was some evidence that the addition of 2.5% or 5% bismuth to SnAg3.8Cu0.7 alloys used in reflow soldering to immersion tin or OSP copper produced improvements in the mean pull strength of joints after thermomechanical fatigue. However, the standard deviation of the results with bismuth additions and the detection of some joints with low pull strength after ageing suggest that further testing is required before recommending these alloys. The use of bismuth additions where Sn/Pb finishes are present would not be recommended where soldered joints are likely to be stressed.

The failure of the soldered joints in reliability testing was in line with the observed structural changes that were followed by exhaustive metallographic studies. The most important finding of these observations was that the failure mechanism closely followed that expected for conventional Sn/Pb solder alloys. Crack propagation in the solder joints followed the same pattern even though the surface of the lead-free joints was already rough in the as-soldered condition. Voids were evident at the fracture surface in reflowed solder joints that were strength tested but they appeared to play no direct role in the progress of the deterioration of the joints during ageing.

DISCUSSION

Inevitably this paper has made generalisations in trying to pull together the results from such a comprehensive programme of work. Further studies are needed to explore the applicability of the results to a wider range of production situations and these will follow as more electronics assembly processes are investigated. However, this study has shown that lead-free soldering is a practicable proposition for at least some types of electronics assemblies.

The work has shown that the eutectic SnAg3.8Cu0.7 alloy can be used for wave, reflow and rework/repair soldering processes. Although 0.25%Sb was added for the wave soldering process, there is no clear evidence that it improves either the wetting behaviour of the alloy or the overall reliability of the soldered joints. Where cost considerations are important, an alloy with a significant bismuth content (SnBi5Ag1) may be used but only in single-sided wave soldering processes. Although it appears not to have an impact on reliability, the use of such high levels of bismuth creates visually defective joints when double-sided pth boards are used. The use of a grain refiner in the initial alloy selected for wave soldering appeared to improve joint reliability compared with the standard wave soldering process but did not eliminate the visual inspection failures on double-sided boards.

The use of an alloy containing some bismuth was briefly evaluated in reflow soldering processes and it may offer advantages if the assembly is entirely lead-free. It allows a reduction in peak reflow temperature and it may enhance thermomechanical fatigue performance. However, it may be necessary to restrict the level of bismuth to values less than 5%. Vianco[5] has shown that 5% bismuth is the maximum solubility level in tin to avoid forming the Bi-Sn(Ag) eutectic with a melting point of 137°C. In fact, this may be an overestimate because of the low solubility of bismuth (about 2.5%) in tin at room temperature. In alloys with more than 2.5%Bi, it is possible that the bismuth could precipitate as a grain boundary film after prolonged exposure to low temperatures. Once there, sudden heating to 138°C could be disastrous. If lead is present in the system, then the scenario is potentially worse because the low melting phase would be liquid at 96°C. These effect of lead and bismuth on the melting temperature of various alloys is shown in Table 10.

The effects of contamination of lead free solder joints by lead from board and component lead finishes appear to be minimal for reflow soldering, providing the alloy does not contain bismuth, but to have an impact on wave soldering. While a number of cost-competitive lead-free board finishes are available, the same is not true for all component types. Any introduction of a lead-free soldering process is likely to have to deal with lead contamination from the components for some time into the future and this should be taken into account when selecting the solder alloy.

The process windows for wave and reflow soldering were not moved to temperatures as high as might have been expected. The wave soldering process was definitely longer and hotter and there was still some concern that defect levels might still be higher. Nitrogen was generally recommended to reduce drossing and the overall costs of the process were seen to be higher than for a conventional process.

Reflow soldering could be carried out effectively at remarkably low alloy liquidus superheats. While reaching 225°C for 10 seconds was sufficient to produce good joints that behaved reliably, most users would probably increase the temperature somewhat to guarantee good results. Obviously the temperature differential across the board is a significant factor in identifying the impact of higher temperatures on process yields. If this can be maintained at low values, then the impact on component integrity would be small. However, a large ΔT on the board would subject some components to unacceptable conditions. Solder paste flux selection was found to be important in the reflow process. Spread by the lead free alloys is intrinsically less than with Sn/Pb alloys and flux formulation can improve this slightly. Correct selection of the flux can also eliminate the need for a nitrogen reflow atmosphere and it can reduce the incidence of voids in the solder joints. These voids were not found to have a significant effect on joint strength or reliability but reducing them would be considered desirable by most users. The origin of the voids is thought to be the entrapment of flux volatiles by the molten solder. The higher reflow temperature and higher alloy solidification temperature may mean that more volatiles are still being lost from the flux as the solder cools and solidifies than is the case for Sn/Pb solder. The higher surface tension of the solder means that the over-pressure inside the flux bubble required to cause it to grow and rupture is significantly greater than in systems where lead is present. This higher surface tension, and consequently higher contact angle with the substrates also encourages the flux bubble to remain anchored to surfaces, rather than float out of the solder. Whatever the reason the bubbles of flux remain in the solder joint, reducing the volatility of the flux has been found to eliminate most voids in lead free solder joints.

Although the minimum temperature for solder joint rework was increased, the process was found to be well within the capability of modern equipment and should present no particular problems. The complete compatibility issues between different solder alloys were not examined in much detail, but the evidence suggests that there would be no significant problems.

CONCLUSIONS

The results reported here reinforce the growing opinion in the industry that the eutectic SnAg3.8Cu0.7 alloy is the best all-round solution for lead free soldering. The cost of metal could be reduced by using SnBi5Ag1+ alloy for single-sided wave soldering but not for double-sided boards with pth. The temperature sensitivity of components may be a barrier to using lead-free solder alloys in some applications, despite the surprisingly low temperatures that may be used. The poor availability of lead free component lead finishes prevents many assemblies from being called "lead-free" even if they are soldered with lead-free alloys. It may also present reliability concerns for double-sided pth boards although there appears to be no impact on reflow soldered boards in the absence of bismuth. In fact, the tolerance of reflow soldering to the presence of lead, and the reduction in peak reflow temperature that may result, provides a potentially "softer" introduction of lead-free soldering than might be the case for the wave process. The downside is that it restricts the use of alloys containing bismuth that might, at low levels in the tin/silver/copper system enhance performance in thermomechanical tests.

[1] Second Draft of EC Directive on "Recycling of Waste Electrical and Electronic Equipment"; July 1998.
"Lead-free Soldering – An Analysis of the Current Status of Lead-free Soldering" DTI Publication No DTI/Pub/4066 10k/4/99/NP.

[2] "Alternative Solders for Electronic Assemblies"; DTI Sponsored Project 1991-1993 undertaken by GEC-Marconi, ITRI, BNR Europe, Multicore Solders Ltd. Final Report MS/20073, issued 26/10/93.

[3] "Lead free Solder Alternatives"; Report on four-year collaborative project by the National Center for Manufacturing Sciences (NCMS), January 1998.
"Lead free Solders Research"; Multi-client programme, Swedish Institute for Production engineering Research ((IVF) 1997-1999.
"Alternative Solders for Electronic Assemblies"; P. G. Harris & M. A. Whitmore, Circuit World, 1993, 29(2), 25-27.

[4] IDEALS – Project Funded by the European Community under the BRITE/EURAM Programme. Project No BE95-1994, Contract Number BRPR-CT96-0140

[5] J. Elec. Mats, 1994, 23(8), 757-764, Artaki, Jackson, & Vianco.

TABLE 1: LEAD INGESTION ROUTES

ROUTE OF EXPOSURE	TOXIC RISK	COMMENTS
ABSORPTION	LOW	INORGANIC Pb NOT ABSORBABLE THROUGH SKIN, ONLY CERTAIN ORGANIC Pb COMPOUNDS ABSORBABLE
INGESTION	MODERATE	10% OF INGESTED Pb ABSORBED IN GASTRO-INTESTINAL TRACT
INHALATION	HIGH	30%±10% Pb FUMES AND DUST RETAINED BY LUNGS

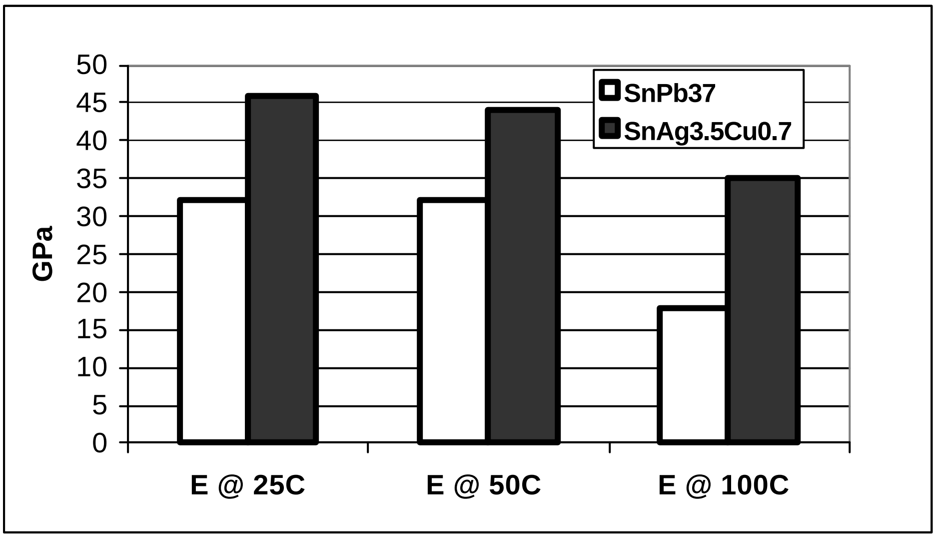
TABLE 2: CANDIDATE ALLOY MELTING TEMPERATURES

ALLOY COMPOSITION, wt%	MELTING TEMPERATURE OR RANGE, °C
Sn100	**232**
SnCu0.7	**227**
SnAg3.5	**221**
SnAg3.8Cu0.7	**217**
SnAg3.8Cu0.7Sb0.25	**217**
SnAg2.5Cu0.8Sb0.5	**210-216**
SnBi5Ag1	**203-211**
SnBi5Ag1+	**209-217**

TABLE 3: COMPARISON OF SOME ALLOY PROPERTIES

Property	Units	Sn60Pb40	SnAg3.8Cu0.7
Density	g/mm3	8.5	7.5
Melting point	deg C	183	217
CTE	$x10^{-6}$	23.9	Similar (23.5*)
Vol change on freezing	%	2.4	Larger (2.7*)
Specific heat	$J\ Kg^{-1}K^{-1}$	150	Higher (226*)
Latent heat	$KJ\ Kg^{-1}$	37	Higher (59.5*)
Thermal Conductivity	$W\ m^{-1}\ K^{-1}$	50	Higher (73.2*)
Electrical Conductivity	%IACS	11.5	Higher (15.6*)
Resistivity	micro Ohm cm	15	Lower (11*)
Surface Tension @ 260 C	mNm^{-1}	481	Higher (548*)
Surface Tension @ 500 C	mNm^{-1}	472	Higher (529*)
			*data for pure tin

GRAPH 1: YOUNG'S MODULUS OF SELECTED ALLOYS



GRAPH 2: TEMPERATURE DEPENDENCE OF YIELD STRESS FOR VARIOUS ALLOYS

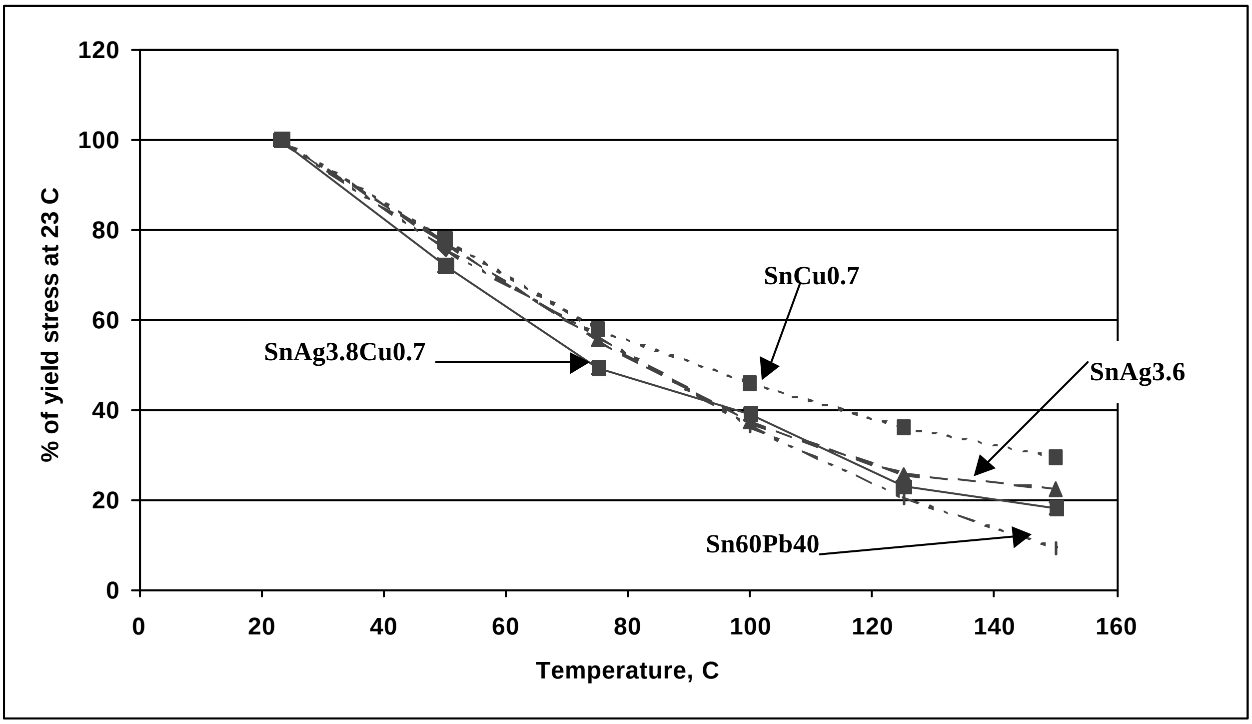
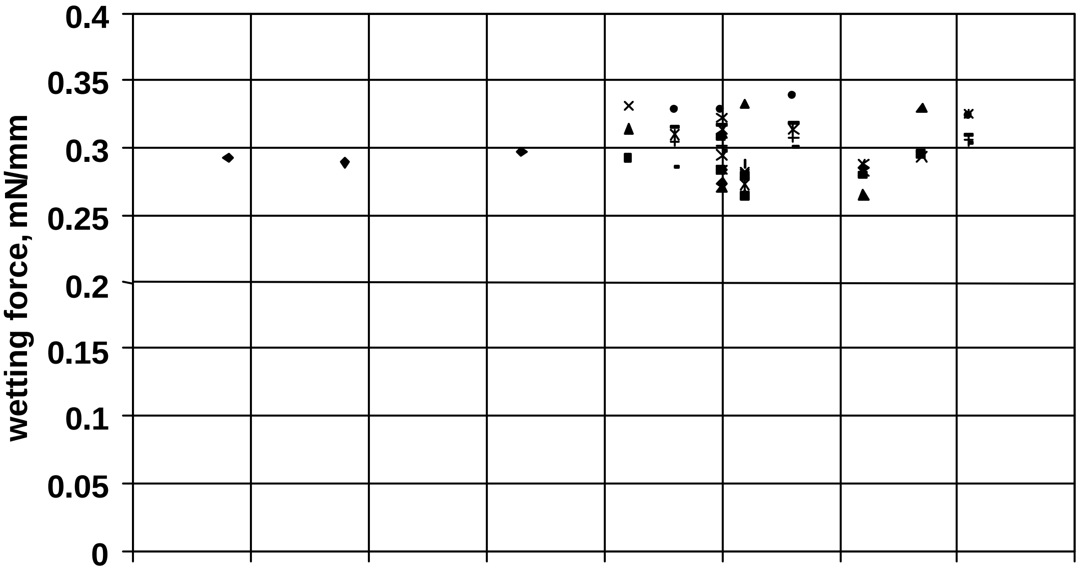


TABLE 4: CONTACT ANGLES OF THE ALLOYS VS FINISHES

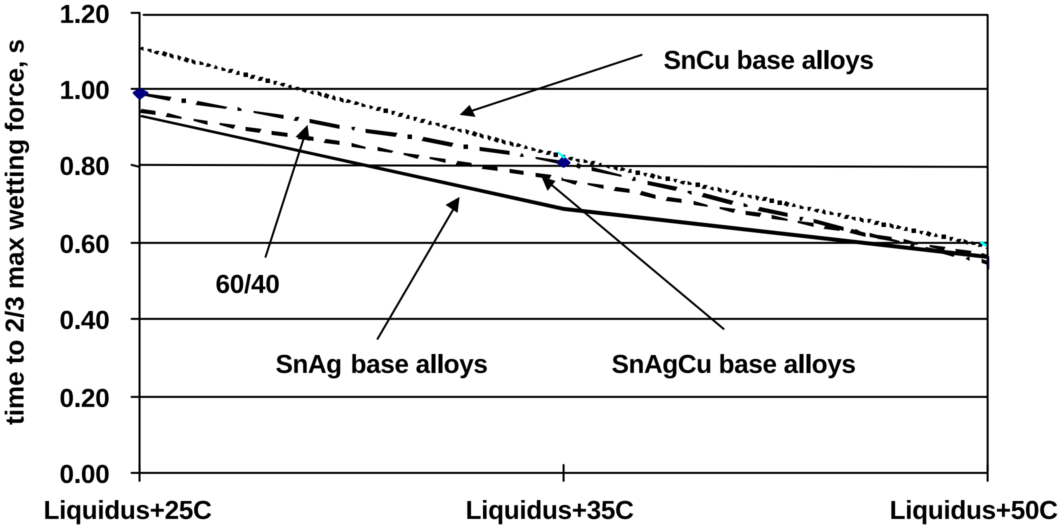
SUBSTRATE	REFLOWED ALLOY PELLET (Sn +)					
	0.5Cu	3.5Ag	3.8Ag0.7Cu	3.5Ag0.5Sb	3.8Ag0.7Cu0.5Sb	37Pb
Cu	42	43	43	41	43	12
Ag	19	26	24	30	33	13
Sn37Pb	19	19	22	20	22	5
Sn0.7Cu	15	11	18	11	10	17
Au over Ni	9	6	10	14	5	4

GRAPH 3: CONSOLIDATED MAXIMUM WETTING FORCE DATA

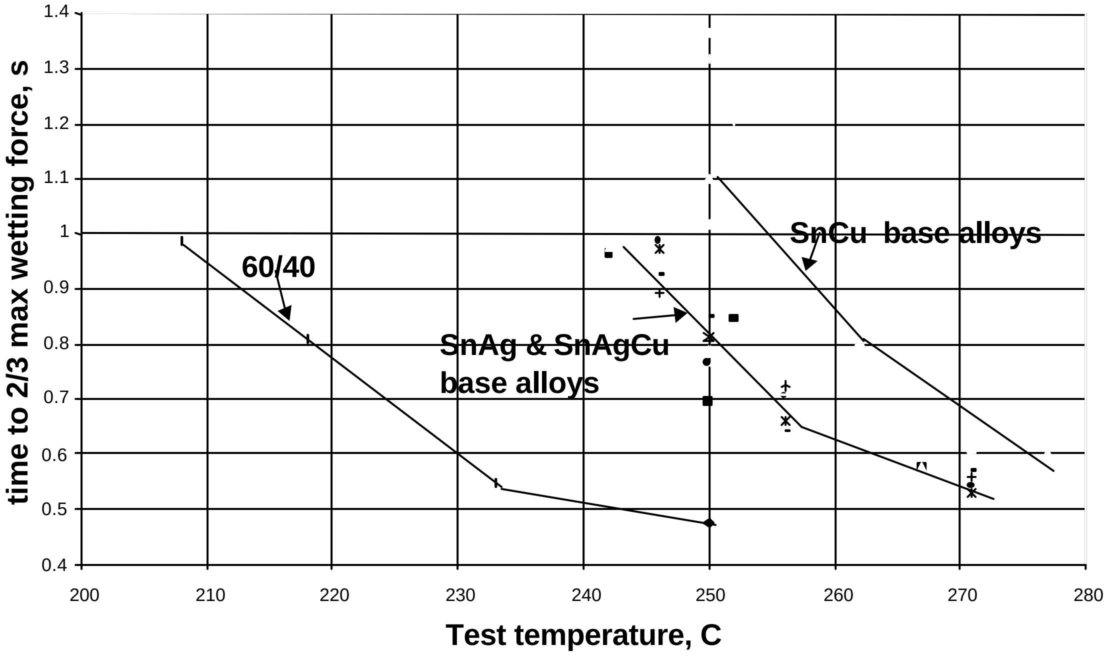
SnPb40, SnAg3.5(Sb0-0.5%), SnAg5, SnCu0.7(Sb0-0.5%), SnAg3.8Cu0.7(Sb0-0.5%)
Halide Activated Rosin Flux on copper substrates



GRAPH 4: CONSOLIDATED WETING TIME DATA
Same families of alloys flux and substrates shown in Graph 3

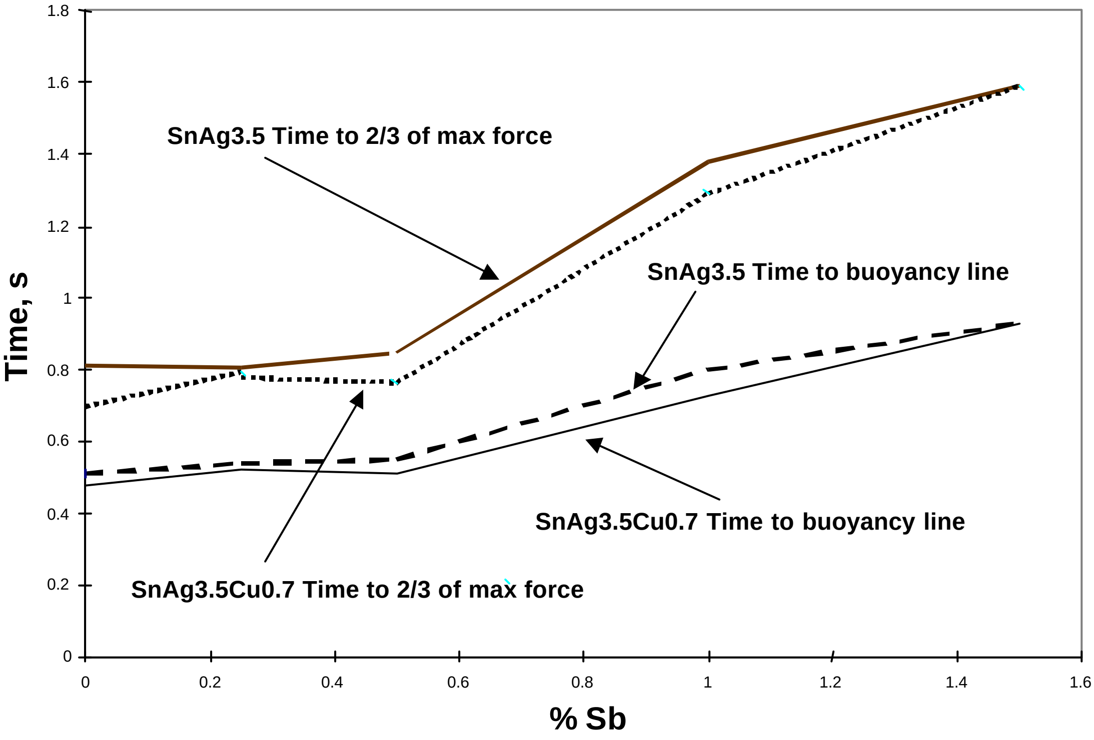


GRAPH 5: CONSOLIDATED WETTING SPEEDS VERSUS TEMPERATURE
Same families of alloys flux and substrates shown in Graph 3



GRAPH 6: EFFECT OF Sb ON WETTING TIMES

Rosin flux on Cu substrate at



250°C

TABLE 5: SINGLE SIDE WAVE SOLDERING PROCESS WINDOW (VOC FREE FLUX AND SnBi5Ag1+)

PARAMETER	VALUE	
SOLDER TEMPERATURE, °C	250	260
SOLDERING TIME (total for two waves), s	≥3.0	≥2.5
PREHEAT TEMPERATURE, °C	≥100	

TABLE 6: SINGLE SIDE WAVE SOLDERING PROCESS WINDOW (VOC FREE FLUX AND SnAg3.8Cu0.7Sb0.25)

PARAMETER	VALUE		
SOLDER TEMPERATURE, °C	250	260	265
SOLDERING TIME (total for two waves), s	≥3.5	≥3.0	≥2.5
PREHEAT TEMPERATURE, °C	≥100		

PHOTOGRAPH 1: LABORATORY TEST BOARD FOR REFLOW PROCESS WINDOW DEFINITION

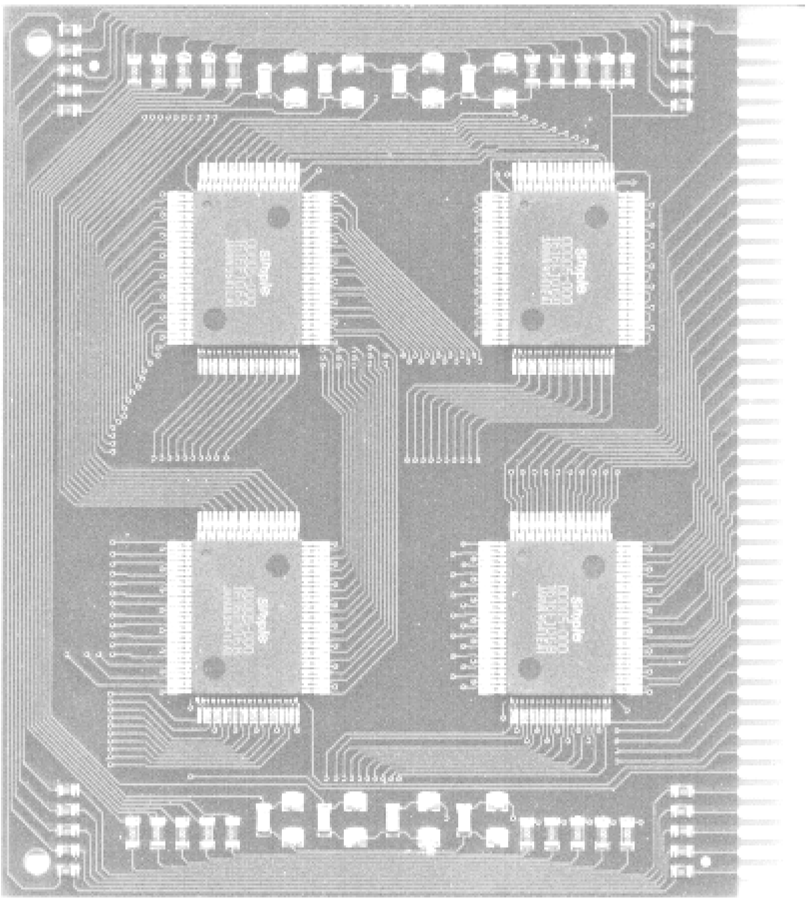
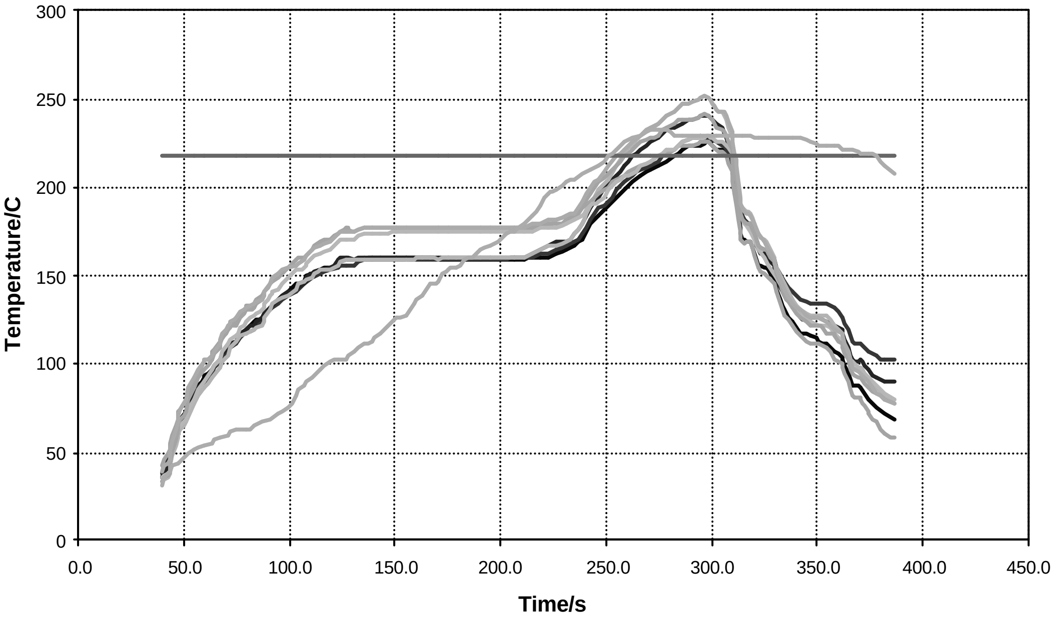


TABLE 7: REFLOW PROFILE CHARACTERISTICS

Profile Description	Peak Temperature, °C	Mean Preheat Ramp Rate, °C/s	Preheat Temperature, °C	Mean Reflow Ramp Rate, °C/s	Time above Liquidus, s
QFP Lead data					
L/M	233	1.3	158	0.9 – 1.0	41
H/M	236	1.5 – 1.6	175	0.9 – 1.0	47
Linear preheat	225	0.8	-	-	123
Pad data					
L/M	240	1.3	160	0.9 – 1.0	47
H/M	238	1.5 – 1.6	177	0.9 – 1.0	52
Linear preheat	232	0.8	-	-	130

GRAPH 7: TEST REFLOW PROFILE PAD TEMPERATURES



GRAPH 8: TEST REFLOW PROFILE QFP LEAD TEMPERATURES

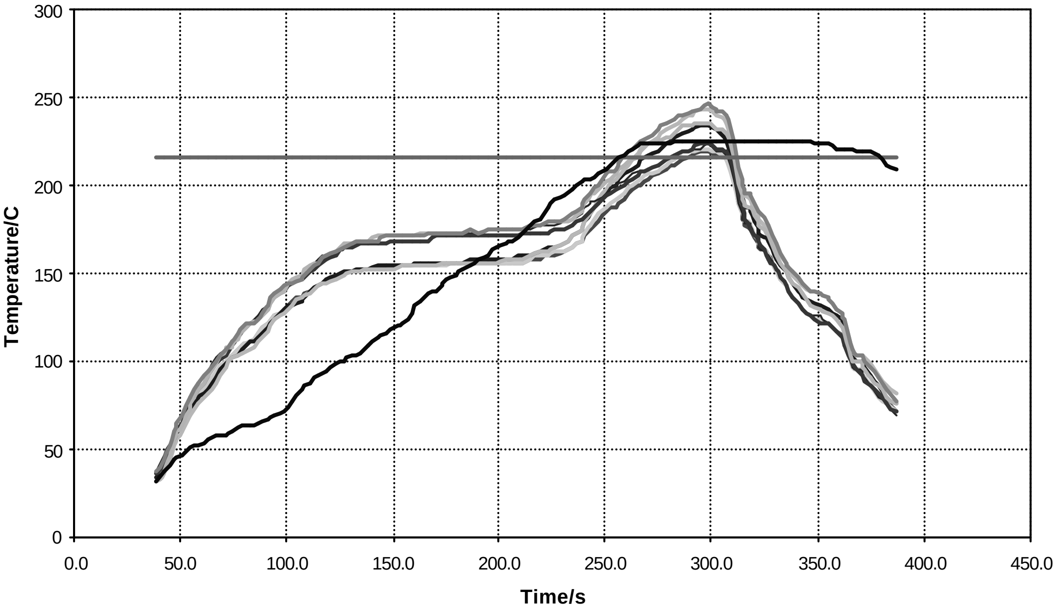


TABLE 8: ONSET OF REFLOW FOR ALLOY AND SUBSTRATE FINISH COMBINATIONS

Solder Alloy	Substrate Finish	Peak solder joint temperature, °C			
		207-210	211-214	215-217	219-222
SnAg3.8 Cu0.7 + 5Bi	Sn	X	✓	✓	✓
	Sn-Pb	X	✓	✓	✓
SnAg3.8 Cu0.7	Sn	X	X	X	✓
	Sn-Pb	X	✓	✓	✓

SCHEMATIC 1: ORIGIN OF PAD LIFTING WITH SnBi5Ag1 AND SnBi5Ag1+ ALLOYS ON DOUBLE-SIDED PTH BOARDS

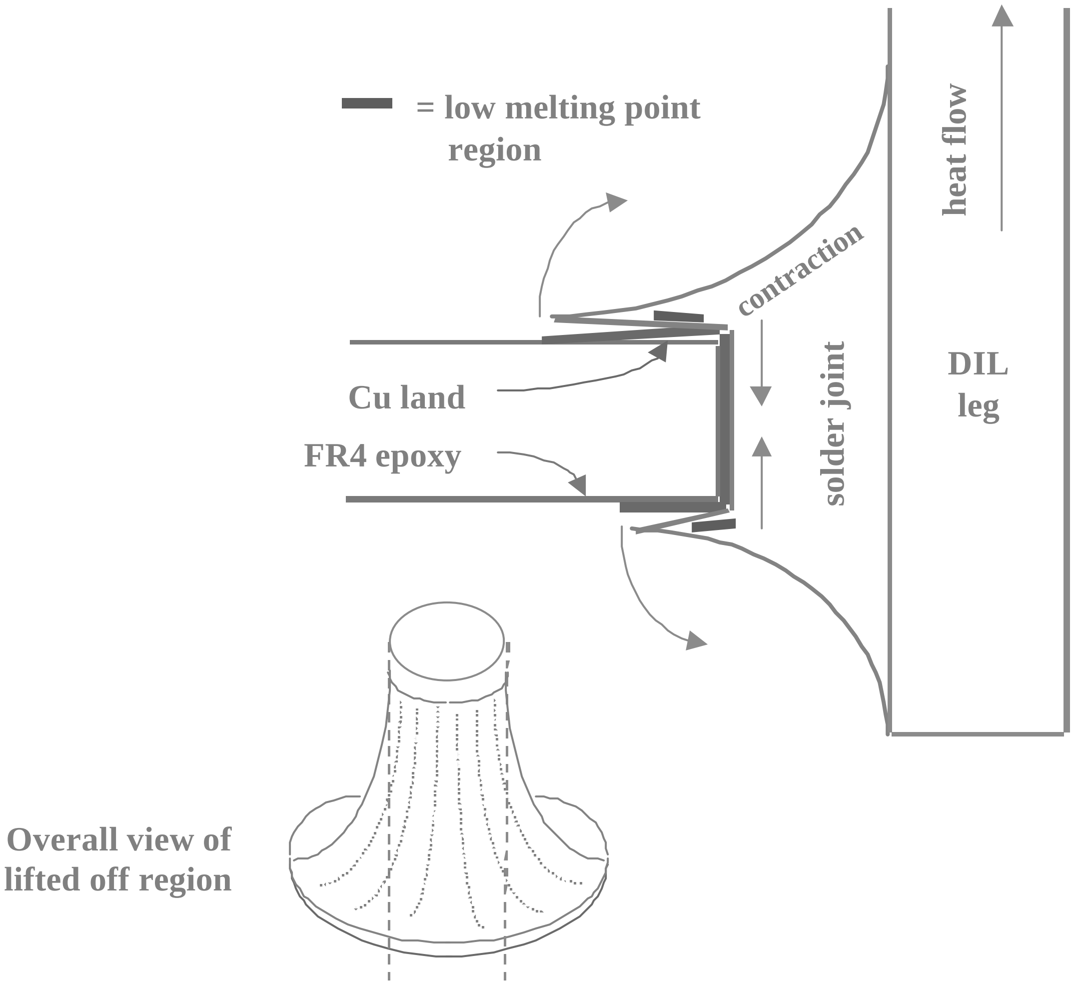
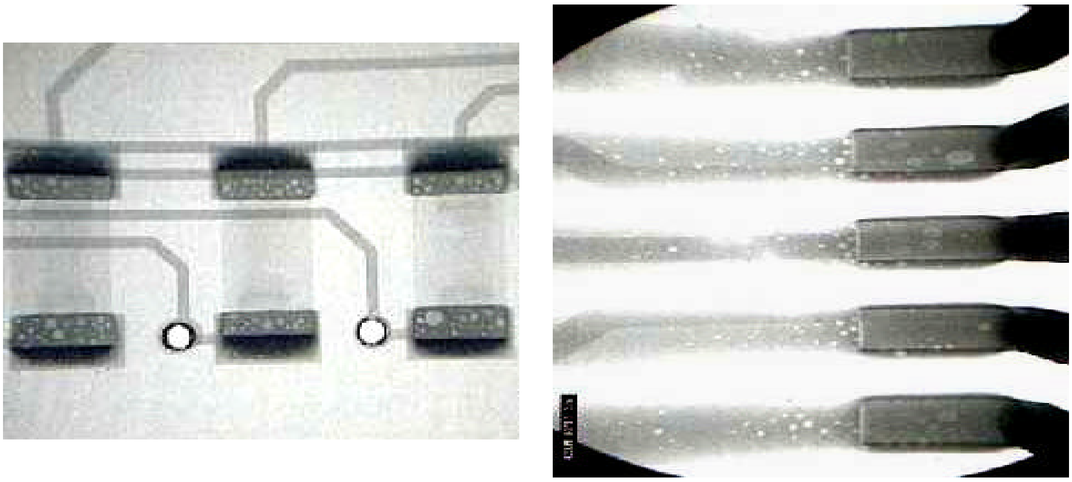


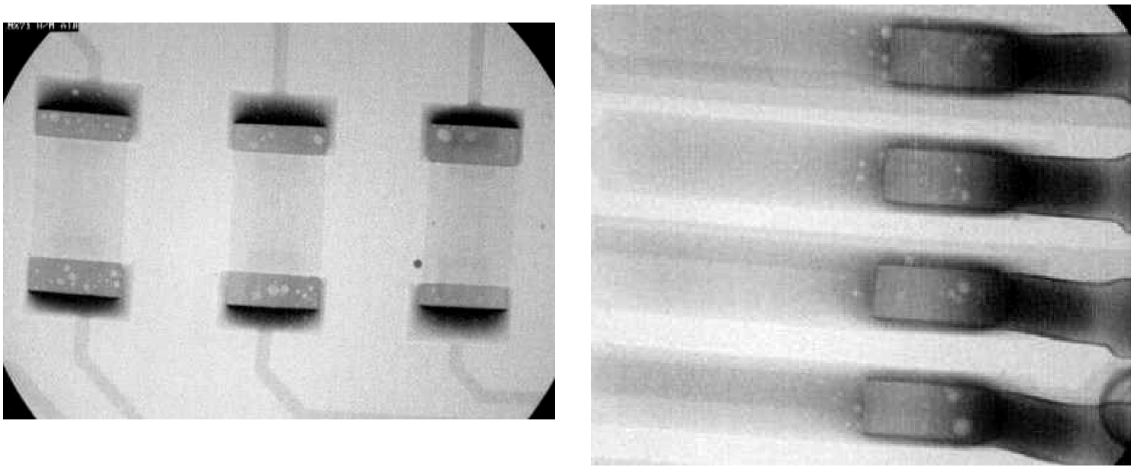
TABLE 9; INTERMETALLIC COMPOUND LAYER THICKNESS

Solder		SnCu0.7 Paste		SnAg3.5 Paste		SnAg3.8Cu0.7 Paste		SnPb37 Paste	
Surface	Ageing	Cu_6Sn_5	Cu_3Sn	Cu_6Sn_5	Cu_3Sn	Cu_6Sn_5	Cu_3Sn	Cu_6Sn_5	Cu_3Sn
Cu	As melted	1	0	2	0	3	1	1	0.5
	125°C, 1000h	2	1	2.5	1	4	1	3.5	0.5
Alpha level	As melted	1.5	0	2	0	3	0	1	0.5
	125°C, 1000h	2.5	1	2.5	1	4	1	3.5	0.5
Sn/Pb	As melted	3	0.5	3	0.5	3	0.5	2	0.5
	125°C, 1000h	3	1	3	1.5	3	1.5	3.5	0.5
SnCu0.7	As melted	2	0.5	2	0.5	3	0.5	1.5	0.5
	125°C, 1000h	2.5	1.5	2.5	1.5	3	1.5	3.5	0.5
Ni/Au Ni_3Sn_4	As melted	1.5		2		2.5		1	
	125°C, 1000h	2.5		2.5		3		1.5	

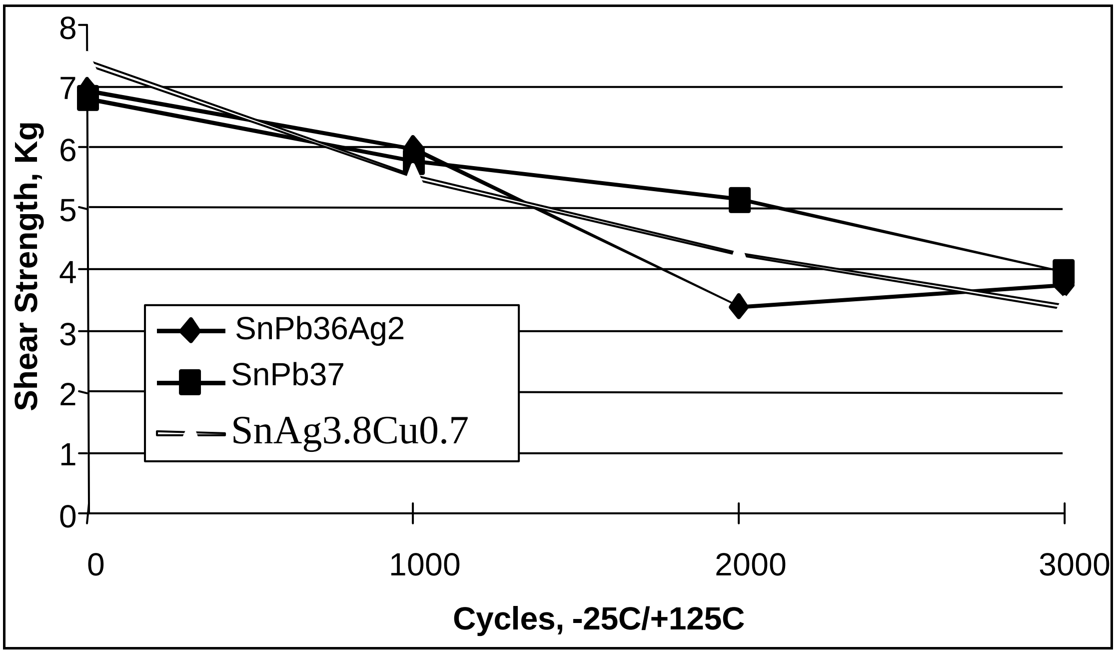
PHOTOGRAPH 2: X-RAY IMAGE OF REFLOW SOLDERED JOINTS MADE WITH ORIGINAL NO CLEAN FLUX TYPE



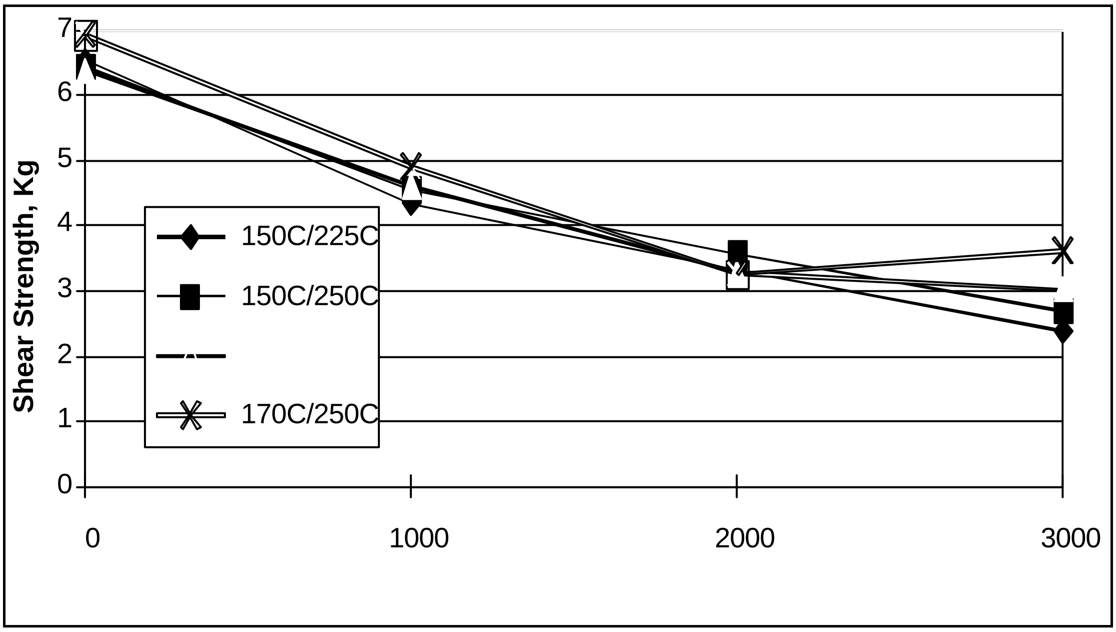
PHOTOGRAPH 3: X-RAY IMAGE OF SOLDER JOINTS MADE WITH IMPROVED LEAD-FREE SOLDER PASTE



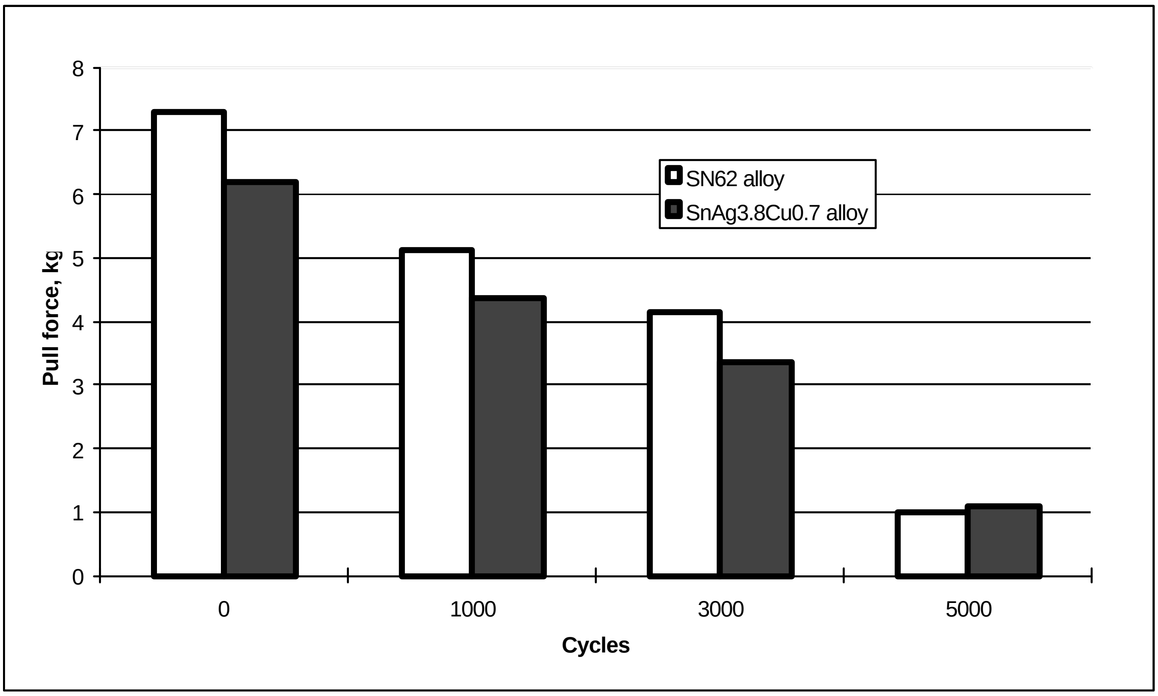
GRAPH 9: PUSH OFF STRENGTH OF 1206 RESISTORS SOLDERED TO OSP Cu FINISH AFTER THERMAL SHOCK CYCLING



GRAPH 10: THE INFLUENCE OF REFLOW PROFILE (Preheat/Peak) ON SnAg3.8Cu0.7 JOINTS MADE TO 1206 RESISTORS ON OSP Cu AFTER THERMAL SHOCK CYCLING



GRAPH 11: PUSH OFF STRENGTH OF 1206 RESISTORS SOLDERED TO OSP Cu AFTER POWER



GRAPH 12: PULL STRENGTH OF QFP LEADS SOLDERED TO OSP Cu AFTER POWER CYCLING

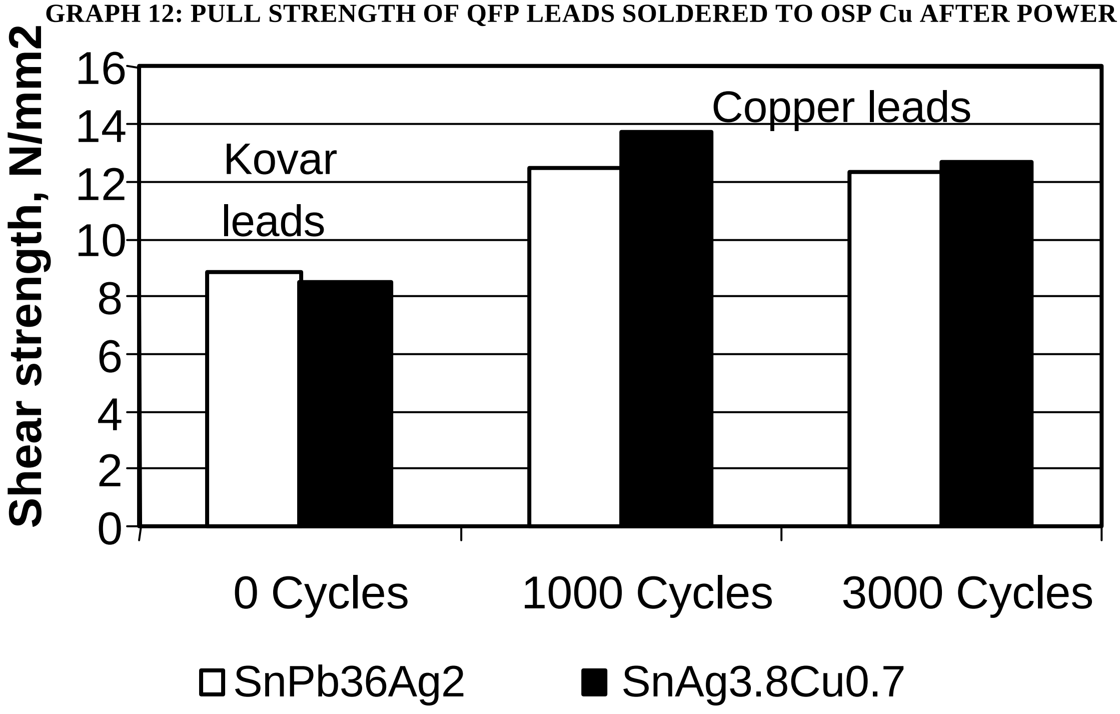


TABLE 10: EFFECT OF LEAD AND BISMUTH IMPURITIES ON THE MELTING BEHAVIOUR OF LEAD-FREE ALLOYS

Liquidus Temperature °C	Eutectic Alloy	Solidus Temperature °C with -		
		Pb	Bi	Pb + Bi
227	Sn Cu	183	138	96
221	Sn Ag	179	137	96
217	Sn Ag Cu	179	137	96