

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

1-31-94

PROTOTYPING LEAD-FREE SOLDERS ON HAND-SOLDERED, THROUGH-HOLE CIRCUIT BOARDS¹

Paul T. Vianco

CONF-940658--2

Center for Solder Science and Technology
Sandia National Laboratories
Albuquerque, NM

and

Patrick M. Mizik

AlliedSignal Aerospace Company
Kansas City Division
Kansas City, MO

ABSTRACT

The lead-free solders 96.5Sn-3.5Ag (wt.%), 95.5Sn-4.0Cu-0.5Ag, 91.84Sn-3.33Ag-4.83Bi were used in the assembly of a through-hole circuit board to determine the feasibility of their suitability in hand soldering processes. Prototypes assembled with 63Sn-37Pb solder were manufactured to serve as control units. Implementation of the lead-free alloys was performed with a rosin-based, mildly activated (RMA) flux and a 700°F soldering tip. A procedure was developed to remove the tin-lead finish from the leaded components and replace it with a 100Sn hot dipped coating. Assembly feasibility was demonstrated for all three lead-free solders. Defect counts were greater than observed with the tin-lead control alloy; however, the number of defects diminished with experience gained by the operator. Visual examination of the solder joints indicated satisfactory wetting of both the device leads and circuit board land with no apparent damage to the underlying laminate nor to the device packages. Cross sections of the lead-free solder joints showed that they were more susceptible to void formation within the holes than was the case with the tin-lead solder. Some cracking was observed at the interface between the Sn-Ag-Bi solder and the copper lands; the relatively high strength of this solder and the fast cooling rate of the hand assembly process was believed responsible for this defect.

KEY WORDS: Manufacturing/Fabrication/Processing, Joining

MASTER

1. INTRODUCTION

Electronic products have depended upon soldering technologies to assemble devices, circuit boards, and entire product systems. The continued success of soldering in electronics manufacturing arises from this technology meeting the specific challenges of the electronics revolution: they are: (1) miniaturization, (2) increased device functionality, and (3) cost-effective manufacturing. Applications that include interconnects between device packages and the circuit boards, as well as connectors and

¹This work was performed at Sandia National Laboratories, which is supported by the U.S. Dept. of Energy under contract number DE-AC04-94AL85000.

872

backplane attachments, have used the eutectic 63Sn-37Pb (wt.%) and near-eutectic 60Sn-40Pb solders. These alloys have reflow temperatures, mechanical strengths, and electrical properties that make them suitable for a wide range of service conditions as well as for the large scale assembly processes used to manufacture the particular product. The higher lead containing solders such as the 90Pb-10Sn and 95Pb-5Sn have important applications in die-attach processes such as the controlled collapse chip component (or C4) technology used in computer systems[1]. The indium-lead solders, 60Pb-40In and 50In-50Pb, have been used extensively for soldering to precious metal based substrates and thick film networks such as found in hybrid microcircuit systems. Because the tin component of traditional tin-lead solders reacts very quickly with the precious metals (e.g., gold and silver) causing rapid dissolution of the precious metal substrates or thick films[2], the substitution of indium for tin is the preferred approach to limit solder/substrate interactions which may jeopardize the integrity of the solder joints.

Although lead-bearing solders have clearly been a contributing factor to the progress of the electronics industry in this country (and the ensuing economic impact), it has also been documented that lead is extremely toxic to humans and animal life when ingested in large doses. The use of tin-lead solders in the manufacture of electronic products generates lead waste by two methodologies: (1) solder usage during assembly processes and (2) the disposal of discarded electronic (solid) waste[3]. Lead-bearing waste from assembly processes is in the form of solder dross. However, because dross is nearly 96-98% metal, it can be readily refined into their elemental form (e.g., tin and lead) although its handling is strictly regulated. The second source of lead waste, the disposal of used electronic hardware, has a less defined scenario with respect to contamination of the environment. The potential of such a hazard would depend upon the amount of the solder alloy being disposed of at the site (solder is not a large percentage of the circuit board mass); the method by which the lead is leached from the solder joints; and lastly, the mechanism responsible for the transport of lead into the ground water and/or food chain. Clearly, an absence of scientific knowledge on any one of these sub-processes makes the development of even a qualitative scenario for contamination and human toxicity, at best, difficult. Nevertheless, lead is being closely scrutinized by environmental and legislative groups in order to reduce its use in all manufactured products (including electronic solders). Incentives to reduce lead use can be in the form of restrictive laws and regulations (at the federal, state, and local levels of government) or by means of heavy usage taxes.

The identification of one or more suitable non-lead containing solder replacements is hardly a simple task. After all, soldering technology encompasses more than simply the selection of an alloy with a suitable melting temperature. Consideration must also be given to the substrate materials, the role and type of flux used in the process, the process(es) by which heat is delivered to the joint area, and finally the requirement for post-assembly cleaning procedures that will ensure reliable operation of the product while in service. In fact, the success of tin-lead solder technology in the electronics arena is based upon the integration of an extensive data background on materials properties, design specifications, and process engineering knowledge so as to produce a reliable product that is cost effective to manufacture.

The nearly exclusive use of tin-lead solders for printed wiring board assemblies has left a gap, not only in the background data of properties for alternative solders, but also with respect to the logistics required to qualify the manufacturability of those alternative solders in assembly processes. For example, the development engineer must take advantage of relatively inexpensive, albeit "sterile" laboratory testing in order to initially screen potential candidate solders. Such tests would include wetting experiments, short term intermetallic compound growth measurements, and some mechanical properties evaluations. Relative comparisons with control alloys such as the tin-lead solders would provide an adequate, initial evaluation. Next, the selected solders would be used to build prototype assemblies. The test vehicles should be of the appropriate technology (surface mount, through-hole, or mixed) with a variety of packages that represent the particular

product. The type of defects must be "realistically" defined and a quantitative evaluation scheme established for the test vehicles. Proper defect analysis will not only allow for the distinction of performance differences between the various solders, but also identifying material related defects as opposed to those caused by the manufacturing process. This latter task necessarily requires the use of metallurgical analysis of the solder joints in order to detect those defects or microstructures not visible to the unaided eye.

This report describes the evaluation of three lead-free solders for use on a through-hole circuit board assembly. Wettability was considered to be an important property of the solders for adequate manufacturability. Therefore, laboratory studies were performed which used the meniscometer/wetting balance technique to determine the wetting performance of the candidate solders on copper surfaces. The meniscometer/wetting balance procedure comprises the immersion of a substrate plate into a bath of solder (Fig. 1). The equilibrium geometry of the meniscus formed on the plate is determined by the balance of the interfacial tensions as expressed by Young's equation shown at the bottom of the diagram. The solder-flux interfacial tension, γ_{LF} , represents the solder surface tension as modified by the flux coating. The contact angle, θ_c , provides a generalized, quantitative parameter from which wetting was assessed because it takes into account the effect of all of the interfacial tensions. *The smaller the contact angle, better the wettability.* The two experimentally measured parameters are (1) the meniscus height, H, determined by the meniscometer and (2) the meniscus weight, W, which is measured by the wetting balance apparatus. Values of the contact angle and the solder-flux interfacial tension, respectively, are calculated from the following equations:

$$\theta_c = \sin^{-1} \left\{ \frac{[4W^2 - (\rho g P H^2)^2]}{[4W^2 + (\rho g P H^2)^2]} \right\} \quad (1)$$

$$\gamma_{LF} = (\rho g / 4) [4W^2 / (\rho g P H^2)^2 + H^2] \quad (2)$$

where ρ is the solder density, g is the acceleration due to gravity, and P is the sample perimeter. These measurements provide an initial screening as to the potential use of the lead-free solders in the construction of the prototype circuit boards.

2. EXPERIMENTAL PROCEDURES.

A primary objective of this study was the development of suitable processes for the hand assembly of through-hole circuit boards with the alternative solders. Therefore, the experimental procedures section will be extended in order to detail those procedures.

2.1 Solder Alloys

The lead-free solders (wt.%) used in this study and their melting points (T_l , liquidus temperature and T_s , solidus temperature) were as follows: 96.5Sn-3.5Ag ($T_l=T_s=221^\circ\text{C}$); 95.5Sn-4.0Cu-0.5Ag ($T_l=222^\circ\text{C}$, $T_s=216^\circ\text{C}$); 91.84Sn-3.33Ag-4.83Bi ($T_l=T_s=212^\circ\text{C}$); and 63Sn-37Pb ($T_l=T_s=183^\circ\text{C}$) which served as the control alloy. The working temperatures of the solders for the meniscometer/wetting balance tests were 260°C , 267°C , 260°C , and 260°C , respectively. The hand assembly trials with the prototype test vehicles were performed with the solder in wire form. The wire diameters for the 63Sn-37Pb, 96.5Sn-3.5Ag, and 95.5Sn-4.0Cu-0.5Ag solders were 0.51 mm, 0.51mm, and 1.6 mm. Wire of the experimental solder, 91.84Sn-3.33Ag-4.83Bi, was formed from cast

round stock drawn into a quartz tube of inner diameter of 2.36 mm. Then, the wire was further reduced by rolling into a rectangular cross section of 0.86 x 1.17 mm. The 77% reduction accompanying the rolling process did not cause cracking in the wire except for small, isolated cracks on the corners. None of the wires were cored with flux so that flux was applied manually to the joints.

2.2 Meniscometer/Wetting Balance Measurements

The test substrates were oxygen-free, high conductivity (OFHC) copper measuring 2.54 x 2.54 x 0.0254 cm. The samples were solvent degreased, etched in a 1:1 bath of HCl and deionized water, and then rinsed in water and alcohol. A rosin-based, mildly activated (RMA) flux was coated on the samples prior to immersion into the solder bath. Five (5) samples were evaluated in the meniscometer to determine the meniscus height, H, and five (5) substrates were tested in the wetting balance apparatus which measured the meniscus weight, W. The data output from the wetting balance provided the meniscus weight as a function of time, thereby allowing for an initial comparison to be made of the wetting kinetics. The rate at which the solder wets the substrates is an important factor in hand soldering operations in order to minimize heat damage to the device and circuit board laminate arising from the contact of these features with the soldering iron tip.

2.3 Prototype Test Vehicles and Components

A photograph of the through-hole test vehicle circuit board appears in Fig. 2. The laminate was polyimide quartz (1.57 mm thick) with "1 oz." copper pads and traces on the front surface and a "1 oz." copper ground plane on the back surface. There were no internal layers. All of the holes were copper plated. The hole diameters ranged from 0.91 mm to 1.47 mm. One set of circuit boards had the copper features electroplated with 100Sn which was then fused. X-ray fluorescence was used to determine the thickness of the tin layer. Two circuit boards were examined on both the component side and the non-component (or ground plane) side. The tin thicknesses on the front surfaces were 16 ± 5 μm and 14 ± 5 μm and on the back surfaces, 6.2 ± 0.9 μm and 6.0 ± 0.5 μm .

A second group of test vehicles from the vendor was specified to have bare copper features. This latter group of circuit boards was next coated with an immersion tin finish (1-2 μm thick), using a commercially available chemistry. The coating process was performed at AT&T/Engineering Research Center in Princeton, NJ. The x-ray fluorescence technique was used again to determine the thickness of the tin coating. The thicknesses was identical on both sides of the tested boards and measured at 1.9 ± 0.3 μm , well within the range expected from the process.

The circuit boards were populated with the following discrete leaded devices (the lead diameter and corresponding circuit board hole diameter, respectively, appear in parenthesis): RN70 resistors (0.81 mm, 1.12 mm), RN55 resistors (0.64 mm, 0.89 mm), RW80 resistors (0.51 mm, 0.89 mm), CK05 capacitors (0.64 mm, 0.89 mm), CK06 capacitors (0.64 mm, 0.89 mm), and DO91 diodes (0.81 mm, 1.12 mm). Each of the ratios of plated-through hole diameter-to-lead diameter conform with recommendation Level A, IPC-D-275, "Design Standard for Rigid Printed Boards and Rigid Printed Board Assemblies." The device packages were received with 63Sn-37Pb finish on the leads. Lead contamination in the joints would significantly affect the melting properties of the solders by the introduction of lower melting temperature phases in the solder[4]. Moreover, the mechanical properties of the joints would also be affected.

Therefore, a procedure was developed to remove the tin-lead finish from the leads and replace it with a 100Sn hot dipped coating. The hot dipping procedure was preferred because it permitted the removal of the tin-lead finish without the need for chemical stripping, cleaning, and re-plating procedures. The 100Sn coating was applied at the

same time. Moreover, the hot dipped 100Sn finish was preferred to an electroplated coating in order to reduce the likelihood of tin whisker formation[5]. The development of the process was based upon maintaining a lead contamination level of less than 0.1 wt% on the leads. A double immersion procedure was used. In a series of steps, the leads were coated with a diluted solution of rosin-based, mildly activated (RMA) flux and isopropyl alcohol (1:1). Next, the leads were immersed into the first bath of molten tin (100Sn) at 270°C for 5 s with slight agitation. The tin coating was allowed to cool; the leads were re-coated with flux and then immersed into a second bath of molten tin (also at 270°C) for 5 s. The leads were cleaned of flux residues. Observations were made of the condition of the device packages. A small amount of cracking was observed on the resistor body in the immediate vicinity of the lead juncture where the device body came in closest proximity to the molten solder. Nevertheless, the devices were generally able to withstand the hot dipping process without significant deterioration to the device body.

Sample leads were cross sectioned and examined by scanning electron microscopy (SEM) to determine the coating thickness and uniformity. The minimum thickness was determined to be 5 μm . This value satisfies the specifications set by MIL-STD-1276D for hot dipped coatings. In addition, energy dispersive x-ray analysis (EDXA) was performed on selected regions of the cross sections in order to check for the presence of any lead contamination. No trace of lead was detected in the tin coatings. Calculations were performed to determine when the contamination of the second bath reached 0.1 wt% at which point, that bath was used for the initial immersion and a new tin bath was set up for the second dip.

2.4 Prototype Test Vehicle Assembly

The prototype units were assembled in three stages. Each stage utilized information gained from the previous effort. Stage I included the assembly of two (2) test vehicles per solder alloy. The test vehicle finishes were electroplated-and-fused 100Sn. The solder joints on the test vehicles formed with the baseline 63Sn-37Pb solder were done so with a 315°C (600°F) soldering tip. The lead-free solder prototypes included 8-10 joints made with the 315°C tip and the remainder fabricated with a 371°C (700°F) soldering tip. The second board assembled with the 96.5Sn-3.5Ag solder was done entirely with the 371°C tip.

The assembly procedure (which was similar for each of the three stages) was comprised of the following steps: (1) The device leads were inserted into the appropriate holes. The leads were then clipped to allow an extension of 0.76-1.8 mm below the bottom surface of the circuit board. (2) The leads and hole area were coated with RMA flux (which had been diluted 1:1 with isopropyl alcohol). (3) The solder wire and iron were introduced into the joint area and the solder reflowed (from the single side) by the traditional techniques. Initial observations by the operator indicated that for the higher melting, lead-free solders, the melting time of the solders was considerably reduced from 6-9 s to 4-7 s when switching from the 315°C tip to the 371°C tip, respectively. In both instances, flow of the solder into the joint (after melting) was 2-3 s. Although time of contact between the iron and the joint is critical in hand soldering due to the relatively high temperature of the tip, in neither case of a 315°C or 371°C iron tip was damage to the circuit board laminate observed. (4) After the circuit boards were fully populated, the flux residues were removed with a d-Limonene spray followed by a final spray rinse in isopropyl alcohol. This procedure was selected as an alternative to solvent-based flux removal processes. (5) Finally, the circuit boards were visually inspected for solder joint defects by certified personnel (details provided in the following section) after which the prototypes were subjected to ionic cleanliness testing. No rework was performed on the solder joints which exhibited defects.

The second stage (Stage II) of the assembly trials involved the building of two (2) circuit boards per solder alloy. The circuit boards had the electroplated/fused 100Sn coatings.

The units fabricated with the tin-lead alloy were done so with the 315°C soldering iron tip while all of the lead-free prototypes were constructed with the 371°C tip. The same operator who assembled the Stage I units, also soldered the Stage II test vehicles.

The Stage III prototypes were built with the circuit boards that had received the immersion tin coating. One (1) circuit board was assembled per solder. As in Stage II, the units assembled with the 63Sn-37Pb alloy had solder joints formed with the 315°C soldering iron tip; all of the lead-free prototypes were manufactured with the 371°C tip.

2.5 Prototype Test Vehicle Inspection

All of the prototype units were examined for defects by certified inspectors. The analysis was performed on both the component (top) and non-component (bottom) surfaces of the circuit boards. The defects included: (1) insufficient or excessive solder, (2) voids, (3) poor wetting or dewetting, (4) incomplete filling of the hole (to the bottom side), and (5) cold joints. The number of joints with one or more defects were represented as a percentage of the total number of joints. The defective joints were categorized according to the temperature of the soldering iron tip where appropriate (Stage I). The qualitative appearance of the joints was evaluated also by the authors.

As noted, the defects were categorized according to component (top) and non-component (bottom) sides of the test vehicles. Qualitatively, a beginning determination of the root cause of a defect would begin with the location of the particular defect. Defects located on the top surface would likely be due to wetting properties of the pad and leads as well as general workmanship by the operator. On the other hand, because soldering was performed from one side only, defects on the bottom side reflected the wetting/capillary flow of the solder through the hole.

The circuit boards from the Stage I were cut up into two segments. The solder joints from one segment were cross sectioned and prepared for metallographic examination of the microstructure. The second segment was intended for mechanical test evaluation.

3. RESULTS AND DISCUSSION

3.1 Meniscometer/wetting balance data

The meniscometer/wetting balance data on the four solder alloys appear in Table 1. The 63Sn-37Pb demonstrated exceptional wetting with the lowest contact angle of 17°. As anticipated, the wettability of the lead-free solders was not as good as that of the tin-lead alloy; however, their wetting performance, as indicated by the contact angles, was considered "very good" (96.5Sn-3.5Ag and 91.8Sn-3.4Ag-4.8B) to "good" (95.5Sn-4.0Cu-0.5Ag). These results indicated that the solders were viable candidates for prototype feasibility studies.

The excellent wetting of the tin-lead solder is due in part to a particular attribute of lead; that is, it lowers the surface tension of the alloy. This point is clearly evident from a comparison of the interfacial tensions values (γ_{LF}). The fact that bismuth has the same effect as lead on the solder surface tension is also apparent in the data in Table 1. A lower surface tension can assist the capillary flow of solder within confined geometries such as holes and gaps, given adequate solderability of the hole surfaces, themselves. This property is particularly important for through hole soldering because of the requirement that the solder flow from one side of the circuit board to the other.

The time-dependent parameters of W (wetting rate) and t_w (wetting time) provide an initial estimate of the speed with which wetting takes place. The time required for wetting to take place is an important factor in through hole hand assembly; this time period must be minimized in order to limit heat damage to the circuit board structure.

The data in Table 1 serve to form a relative comparison between the lead-free solders and the 63Sn-37Pb baseline alloy. The wetting rates of the 96.5Sn-3.5Ag, 95.5Sn-4.0Cu-0.5Ag, and 91.8Sn-3.4Ag-4.8Bi solders were all quicker than that of the tin-lead solder. Likewise, the wetting time values were lower for the lead-free solders than 63Sn-37Pb. The 91.8Sn-3.4Ag-4.8Bi showed the lowest wetting time at 1.2 s. Therefore, the data in Table 1 suggests that while the presence of lead improves the equilibrium wettability of the solder, its absence results in faster rate kinetics for the wetting process. However, it must be noted that the time to form the solder joint is also dependent upon the time to heat the joint region (lead and pad area) as well as the time needed to melt the solder. As a consequence, these factors, rather than the fundamental kinetics of wetting, may be equally as important to the time period required to complete the soldering process as the fundamental kinetics.

In summary, the meniscometer/wetting balance test results indicated that the selected lead-free solders had sufficient wettability on copper to be viable candidates for prototype assembly. The wetting kinetics were comparable to those of the traditional tin-lead solders so that soldering time differences would be largely a function of the heating rate of the joint and solder wire by the particular iron tip, rather than a function of the fundamental kinetics representing the solder/copper interaction. The relatively high surface tensions of the non-lead containing solders (particularly the 96.5Sn-3.5Ag and 95.5Sn-4.0Cu-0.5Ag alloys) could adversely affect the ability of the molten alloys to fill holes, given adequate wettability of the hole (and land) surfaces.

3.2 Stage I Prototypes

First, observations were made of the circuit boards and device packages. No damage was observed on either the device bodies or the circuit board laminate. Flux residues were likewise absent, demonstrating the efficiency of the cleaning process. The ionic cleanliness test data for the two prototype units per solder alloy were as follows (and expressed in μg equivalent NaCl per unit surface area of the devices and board): (1) 63Sn-37Pb, 0.0 and 5.4; (2) 96.5Sn-3.5Ag, 0.0 and 3.7; (3) 95.5Sn-4.0Cu-0.5Ag, 0.0 and 0.0; and (4) 91.8Sn-3.4Ag-4.8Bi, 0.0 and 0.0. These levels were well below the internally prescribed limit of 10 μg NaCl.

The appearance of the solder in the fillet was a primary concern for inspection of the solder joints. When compared to the shiny, smooth fillet surfaces formed with lead-containing solders (e.g., 63Sn-37Pb), the solder fillets of the no-lead solders had a grainy or frosty appearance. This surface morphology is due to the microstructure of the solders. Although the lead-free solders have a multiphase structure similar to the tin-lead alloys, the phases tend to be relatively larger so as to give the solder surface considerable relief. This surface relief makes the inspection for cold joints or disturbed joints (i.e., joints in which lead movement had taken place during the solidification process) overly conservative.

The predominant type of defect noted from the prototype units assembled with the non-lead containing solders was incomplete wetting of the back side lands due in large part to insufficient filling of the holes. It appeared that the higher melting temperature of the lead-free solders and premature release of the soldering iron by the operator did not allow the solder to remain molten long enough so as to permit it to flow completely through the hole. Also, the quality of the holes was found to be only satisfactory. Shown in Fig. 3 is an optical micrograph of the typical hole barrel. The rough surface (as further exemplified by the contour of the copper plating layer) caused the hole wall to be particularly susceptible to incomplete coverage by the copper and 100Sn layers. Poor solderability of the copper layer could result from an intermittent absence of tin coating. Moreover, the concentric striations comprising the rough morphology (and likely caused by the drilling procedure) are particularly effective at restricting the flow of molten metal through the hole. The relatively high surface tensions of the lead-free solders (as

compared to that of the 63Sn-37Pb alloy) could provide a secondary contribution to the larger percentage of defects.

Wetting of the lead and pads on the top side (where the soldering operation took place) was, in general, very good. Excessive solder was the most frequently observed defect. It was likely that the molten solder accumulated at the top surface due to restricted flow into the hole area.

A third defect that was frequently observed in joints located on either the top or bottom surfaces as well as within the joint itself (through metallographic examination) were voids. Voids within the solder joints is exemplified by the optical micrograph in Fig. 4. The most likely source of the voids was a consequence of poor wetting (and hence flow) of the solder in the hole. However, the quality of the hole walls could also have been a factor. A rough barrel surface increases the likelihood that the deposited copper plating would not completely cover the hole walls. Consequently, the temperatures accompanying the soldering process cause the immediate vaporization of absorbed water vapor and entrapped organic solvents which displace the molten solder. It appeared unlikely that the voids would have jeopardized the mechanical or electrical integrity of the joints.

Microsections of the lead-free solder joints showed that intermetallic compound layer formation at the solder/copper interface was not significantly different than that observed with the 63Sn-37Pb solder. The higher working temperatures of the no-lead solders caused an increase of copper dissolved into the solder fillet, as was evidenced by the number of Cu_6Sn_5 particles observed in the solder volume.

Shown in Table 2 is a summary of the defects observed on the Stage I prototypes. The defect count is represented as a percentage of the joints with one or more defects. The data is categorized for both the component (top) and non-component (bottom) side of each test vehicle, since a defect on either side would constitute an unsatisfactory joint. The results are shown for each of the two soldering temperatures; the data from the two circuit boards have been combined together. The furthest right column ("Total Defects") combines the results of the both boards, the two soldering temperatures, and both sides of each test vehicle.

As expected, the 63Sn-37Pb solder exhibited the least number of defects. Microsections of the solder joints exhibited an unusually large amount of void formation (Fig. 4), given the extensive use of this solder. This observation suggests that, as noted earlier, the voids were likely a consequence of the rough morphology of the hole walls.

The 95.5Sn-4.0Cu-0.5Ag alloy performed the best of the lead-free solders with a total defect count of 7% of the joints. The defect count was only slightly lower with the higher temperature soldering iron tip. Also, the percentage of joints with defects were the same on both sides. This trend indicates that the bottom surface was not prone to a greater number of defects due to poor flow of the solder through the hole. Examination of the solder joint microstructure by metallographic cross section showed that the 95.5Sn-4.0Cu-0.5Ag solder joints had the least amount of void formation of the lead-free solder candidates. Although a defect rate of 7% is excessively high for even limited production environments, it was encouraging, considering the differences in materials performance of this solder compared with that of the traditional tin-lead solder(s).

Although the higher surface tension of the 95.5Sn-4.0Cu-0.5Ag solder (and the other lead-free alloys) may have contributed to the greater number of defects as compared with the tin-lead solder, it is clear that the differences between the lead-free solders reflected by the data in Table 1, may not significantly affect the performances of the candidate solders. Other contributing factors were more significant to the observed performance (defects).

The second best performing alloy was the 96.5Sn-3.5Ag solder at a total defect rate of 16%. The number of defects on the component side were higher with the lower soldering iron temperature; however, the opposite trend was observed on the non-component side albeit to a much smaller degree. This trend on the non-component side may reflect a combination of low sampling count of joints made with the 315°C iron tip temperature (N=8 as opposed to 16 and 20 for the Sn-Ag-Bi and Sn-Cu-Ag solders, respectively). Sensitivity of the wettability of the circuit board holes cannot be discounted. The joints fabricated with the 96.5Sn-3.5 Ag solder were more susceptible to void formation within the barrel as observed from microsections of the test vehicle.

The 91.8Sn-3.4Ag-4.8Bi exhibited the largest percentage of joints with defects. Excess solder and the appearance of cold joints were the predominant items on the component side of the circuit board. Further observations indicate that cold joints may have, indeed, been a mis-interpretation of the frosty appearance of these solder joints. However, it should be pointed out that these joints had a more consistently frost appearance than did the other lead-free solders. Wetting on the component side of the circuit boards was excellent. Defects on the non-component side were largely unfilled holes. The propensity for void formation within the joint was comparable to the level observed with the 95.5Sn-4.0Cu-0.5Ag solder.

A significant defect observed in these solder joints was cracking at the interface between the solder and the copper features of the circuit board (Fig. 5). Cracks were not observed at the solder/lead interface. Observations of the cracked regions made at higher magnification showed the fracture path to have formed at the interface between the intermetallic compound layer formed during the solder operation and the bulk solder. This failure mode is typical of the lead-free solder joints which have been overloaded, particularly at relatively high rates of load application[6]. Microhardness data on the 91.8Sn-3.4Ag-4.8Bi solder are much higher than those of the 96.5Sn-3.5Ag solder (32.5 ± 2.6 Knoop versus 17.4 ± 1.6 Knoop, respectively), suggesting a superior strength to the tin-silver-bismuth solder. However, this exceptional strength may prove to be a detriment. Hand soldered joints are characterized by rapid solidification and cooling of the solder joint. Therefore, the interface between the intermetallic compound layer and the 91.8Sn-3.4Ag-4.8Bi solder was not capable of withstanding the "impact loading" caused by the ensuing thermal contraction of the solder, hence cracking took place at the interface. Preliminary electron microprobe studies of the interfacial region of thermally aged solder/copper diffusion couples have not revealed compositional variations of the interface chemistry, as compared to that characterizing the 96.5Sn-3.5Ag/copper interface, that would suggest that the chemical composition of the region had weakened the solder/intermetallic compound layer interface.

Aside from the cracking phenomena apparently inherent with the 91.8Sn-3.4Ag-4.8Bi solder, there were no characteristics inherent in the physical metallurgy of the other lead-free solders that would jeopardize the manufacturability of the test vehicle.

3.3 Stage II Prototypes

The quantitative defect analysis data appears in Table 3. The defects associated with the 63Sn-37Pb baseline solder were primarily insufficient solder on the non-component side of the board. The likely cause was poor flow of the solder through the circuit board holes. Generally, the Stage II prototypes built with the lead-free solders exhibited an overall improvement in the defect rate and a greater consistency to the quality of the solder joints. The number of "cold joints" caused by inadequate heat supply to the joint was reduced. This trend was attributed to increased experience by the operator with the melting and flow properties of these solders. As in the Stage I prototypes, defects were predominantly inadequate wetting of the non-component side lands caused by poor solder flow through the holes. The 95.5Sn-4.0Cu-0.5Ag solder showed an increase in the total number of defects, due largely to the formation of voids in the non-component side solder fillets.

The ionic cleanliness test data for the two prototype units per solder alloy were as follows (μg equivalent NaCl): (1) 63Sn-37Pb, 0.0 and 5.4; (2) 96.5Sn-3.5Ag, 0.0 and 0.0; (3) 95.5Sn-4.0Cu-0.5Ag, 0.0 and 0.0; and (4) 91.8Sn-3.4Ag-4.8Bi, 0.0 and 0.0. As with the Stage I prototypes, these residue levels were well below the maximum specification.

Metallographic cross sections confirmed the improved quality of the joints. The propensity for void formation was reduced with the 96.5Sn-3.5Ag and 91.8Sn-3.4Ag-4.8Bi solders. When adequate solder was present, wetting of the lands and barrels was excellent. Joints made with the 91.8Sn-3.4Ag-4.8Bi solder continued to show cracking at the intermetallic compound layer/solder interface.

The results of the Stage II build, combined with those from the Stage I prototypes, clearly demonstrated that successful implementation of lead-free solders in hand assembly processes will depend upon adequate training of the operator in the use of these new alloys. The quality of the holes in these particular test vehicles may have accentuated the number of defects, causing the results to be somewhat conservative.

3.4 Stage III Prototypes

As noted above, the Stage III prototypes were fabricated with circuit boards coated with an immersion tin protective finish on the copper features. The ionic cleanliness test data for each prototype unit per solder alloy were as follows (μg equivalent NaCl): (1) 63Sn-37Pb, 1.3; (2) 96.5Sn-3.5Ag, 1.9; (3) 95.5Sn-4.0Cu-0.5Ag, 1.9; and 91.8Sn-3.4Ag-4.8Bi, 1.9. These levels were well below the internally prescribed limit of 10 μg NaCl, yet higher than those observed with the 100Sn fused coatings. The slight increase in ionic residues may have arisen from plating chemicals entrapped in the immersion tin finish or within the laminate.

The defect analysis is shown in Table 4. The number of defects increased as compared to the performance of the prototypes built with the electroplated 100Sn finish. Interestingly enough, the 91.8Sn-3.4Ag-4.8Bi solder showed the best performance of the lead-free solders. Because the test vehicle assembled with the 63Sn-37Pb solder also showed a dramatic increase in the number of defects, it would appear that the immersion tin finish on the circuit boards was responsible for the poor performance of the Stage III units. Analysis of the inspector's report showed that defects on the component (top) side were largely "excessive solder" and an overly grainy appearance; the latter being likely a consequence of the excessive solder content of the joints. Discoloration of the joint area (primarily the immersion tin coating on the lands), was also noted. The non-component side (bottom) was characterized by voids, incompletely filled holes, and poor wetting of the circuit board lands. Incomplete wetting through the holes would have contributed to the excessive solder on the component side. An overly grainy appearance to the solder fillets, was also recorded.

The data and observations cited above suggest that the immersion tin coating increased the number of defects by reducing the wettability of the solder joints. Specifically, defects on both the component and non-component sides of the test vehicles were caused by poor wettability of the holes. It was noted earlier that the surface morphology of the hole wall surfaces was rough (Fig. 3). This property would have been especially detrimental to the protective function of the thin (2-3 μm) immersion tin coating. Exposed copper left unprotected by the tin coating would be readily oxidized, giving rise to the poor wettability of the holes by the molten solder.

4. CONCLUSIONS

1. Prototype through-hole circuit boards were hand soldered with three lead-free alloys. An initial evaluation of the solderability of the 96.5Sn-3.5Ag, 95.5Sn-4.0Cu-0.5Ag, and 91.8Sn-3.4Ag-4.8Bi solders was based upon contact angle measurements made by the meniscometer/wetting balance technique. Wetting rate and wetting time data further substantiated the suitability of these alloys for hand assembly.
2. The circuit board finishes were electroplated 100Sn and immersion tin. A procedure was developed for the removal of the tin-lead finish from the leads of the devices, and replacing it with a hot dipped, 100Sn coating.
3. Defects on the solder joints of the Stage I and Stage II prototypes (i.e., those circuit boards with the electroplated 100Sn finish) were caused largely by insufficient flow of lead-free solders through the holes. Hole walls with less than satisfactory wettability and operator inexperience with these higher melting temperature solders were the primary sources of the defects. Overall, the percentage of defective joints on prototypes assembled with the lead-free solders diminished between the Stage I and Stage II test vehicles, due largely to the improved techniques of the operator.
4. The use of the immersion tin surface finish on the circuit boards significantly deteriorated the performance of the lead-free solders as well as that of the baseline 63Sn-37Pb alloy. The thin tin coating may have been insufficient to cover the roughened surface of the holes, causing poor wettability, thereby inhibiting flow of the solder to the non-component side of the circuit boards.
5. Aside from materials issues that appear readily solvable, proper operator training together with revised inspection criteria should permit the successful implementation the lead-free solders in hand assembly processes. The physical metallurgy of the candidate lead-free solders did not present any particular barriers to the successful manufacture of these test vehicles.

5. REFERENCES

- [1] V. Marcotte in M. Cieslak, et al, ed., The Metal Science of Joining, TMS, Warrendale, PA, 1992, p. 315.
- [2] F. Yost, F. Ganyard, and M. Karnowsky, Met. Trans. A, **7A**, 1141 (1976).
- [3] P. Vianco and D. Frear, Jour. of Metals, **45**, (7), 14 (1993).
- [4] P. Vianco and J. Dal Porto in B. Livesay and M. Nagarkar, ed., New Technology in Electronic Packaging, ASM, Inter., Materials Park, OH, 1990, p. 25.
- [5] H. Manko, Soldering Handbook for Printed Circuits and Surface Mounting, Van Nostrand Reinhold , New York, NY 1986, p. 286.
- [6] D. Frear and P. Vianco, "Intermetallic Growth and Mechanical Behavior of Low and High Melting Temperature Solder Alloys", to be published, Metall. Trans. A (1994).

6. ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of personnel at AS/KCD: Bettye Walker and Margaret Conrad, circuit board assembly; Cheryl Woodward, visual inspection; and William Gross, cleanliness testing and those at SNL: Jerome Rejent, solder coating process development and Charles Carter, metallography towards the success of this study.

Figures

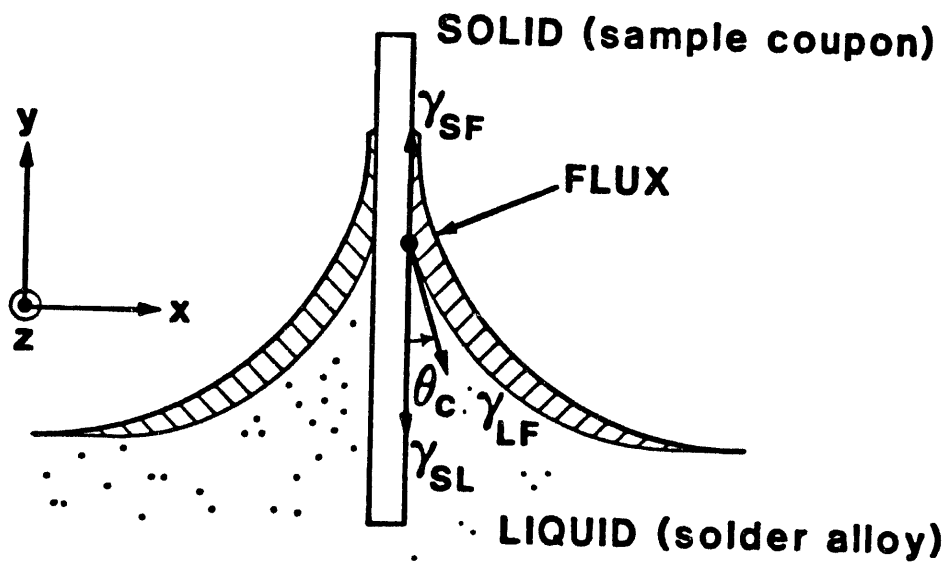
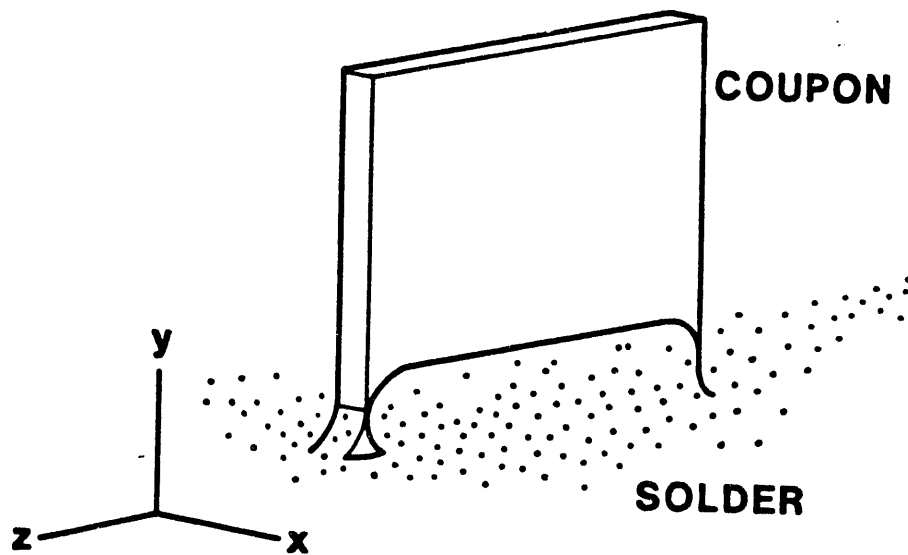
Fig. 1 Test configuration and measured parameters for the meniscometer/wetting balance technique.

Fig. 2 Photograph of the through-hole test vehicle for prototype tasks.

Fig. 3 Optical micrograph of the hole barrel.

Fig. 4 Optical micrograph of 63Sn-37Pb solder joint showing typical void formation within the hole.

Fig. 5 Optical micrograph of a crack at the land/knee hole location in a 91.8Sn-3.4Ag-4.8Bi solder joint.



$$\gamma_{SF} - \gamma_{SL} = \gamma_{LF} \cos \theta_c$$

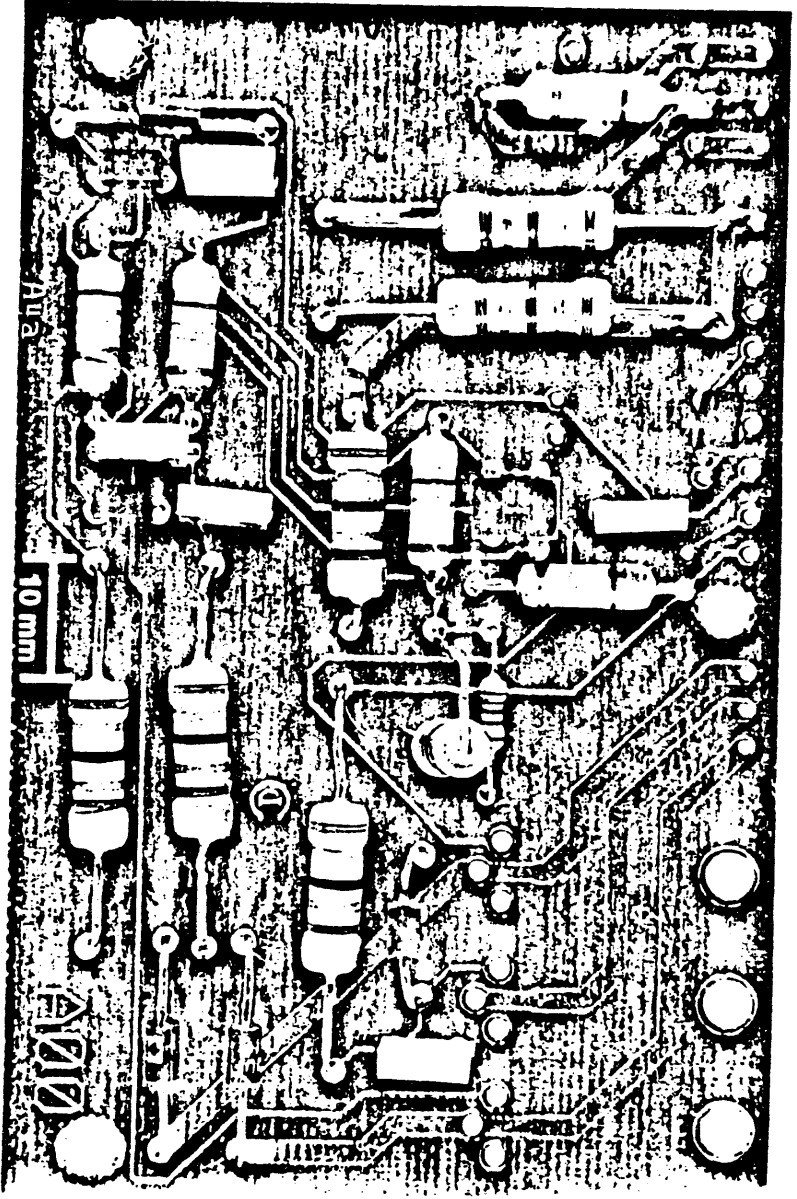


FIG. 2

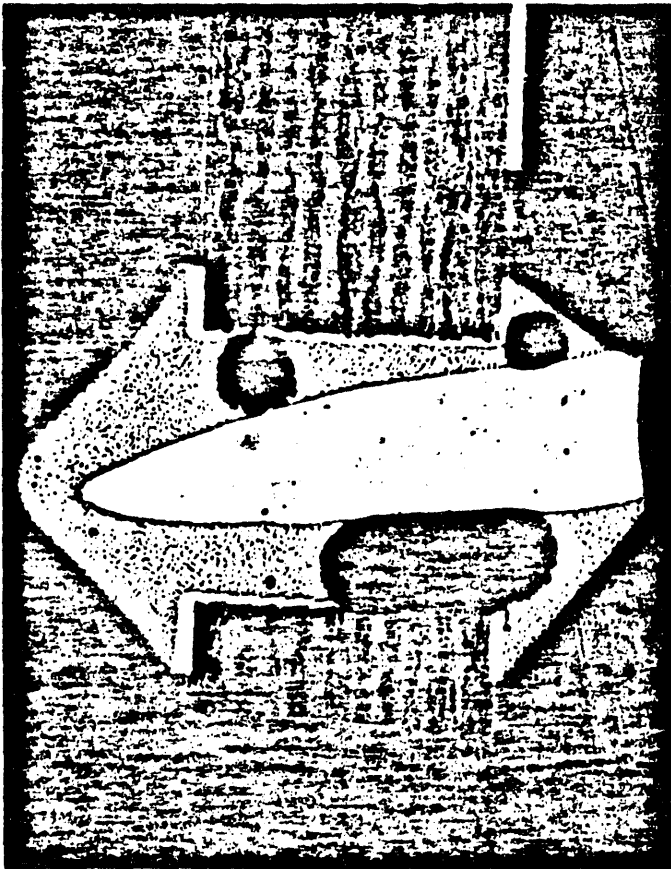


FIG. 4

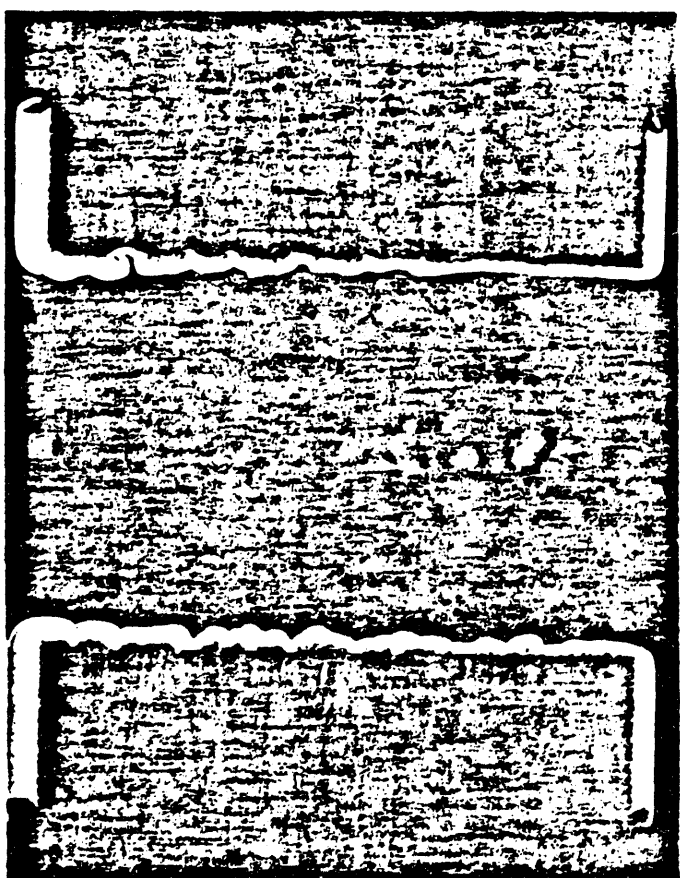


FIG. 3

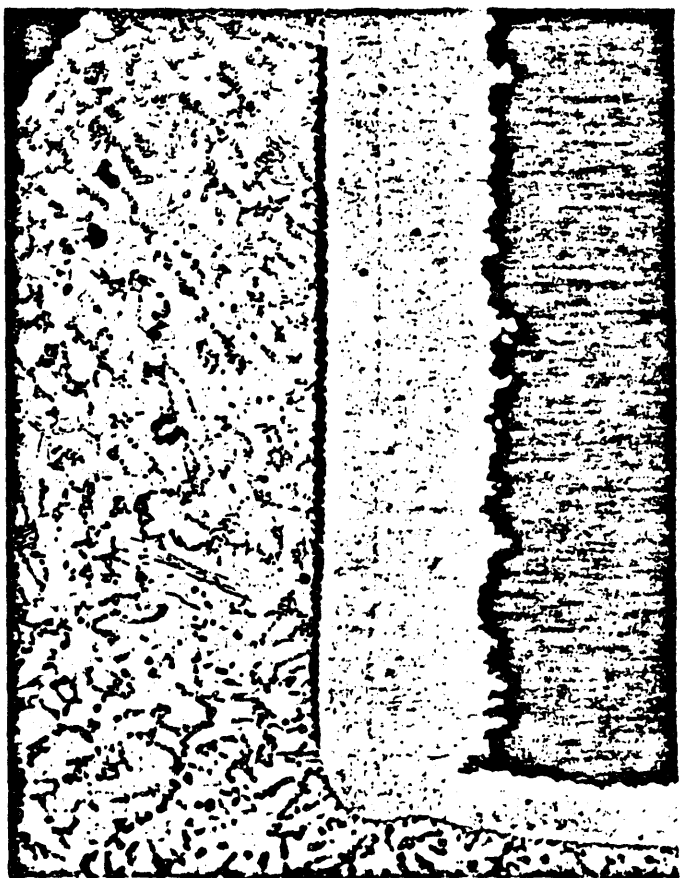


FIG. 5

Solder/Temp. (C)	Contact Angle (deg)	γ_{LF} (dyne/cm)	\dot{w} (dyne/s)	t_w (s)
63Sn-37Pb/260	17 ± 4	380 ± 10	2030 ± 250	3.8 ± 0.8
96.5Sn-3.5Ag/260	36 ± 3	460 ± 30	3500 ± 360	2.0 ± 0.2
95.5Sn-4.0Cu-0.5Ag/267	41 ± 4	500 ± 50	2110 ± 250	3.3 ± 0.1
91.8Sn-3.4Ag-4.8Bi/260	31 ± 2	410 ± 20	3460 ± 400	1.2 ± 0.1

Solder	Percent Defects (%)				
	Component Side		Non-Component Side		Total
	315C	371C	315C	371C	
63Sn-37Pb	0.0	***	2.0	***	0.5
96.5Sn-3.5Ag	32	11	13	18	16
95.5Sn-4.0Cu-0.5Ag	10	7.0	10	8.0	7.0
91.8Sn-3.4Ag-4.8Bi	44	13	44	24	22

Sampe_1

Table 2

Solder	Percent Defects (%)				
	Component Side		Non-Component Side		Total
	315C	371C	315C	371C	
63Sn-37Pb	0.0	***	12	***	6.0
96.5Sn-3.5Ag	***	5.0	***	16	10
95.5Sn-4.0Cu-0.5Ag	***	7.0	***	15	11
91.8Sn-3.4Ag-4.8Bi	***	9.0	***	15	12

Sampe_2

Table 3

Solder	Percent Defects (%)				
	Component Side		Non-Component Side		Total
	315C	371C	315C	371C	
63Sn-37Pb	15	***	54	***	34
96.5Sn-3.5Ag	***	69	***	81	75
95.5Sn-4.0Cu-0.5Ag	***	74	***	46	60
91.8Sn-3.4Ag-4.8Bi	***	56	***	30	43

Sampe_4
Table 4

Tables

Table 1. Meniscometer/wetting balance data for the solder alloys.

Table 2 Percent of joints with defects in Stage I prototypes.

Table 3 Percent of joints with defects in Stage II prototypes.

Table 4 Percent of joints with defects in Stage III prototypes.

DATE

FILMED

5/9/94

END

