

A Benchmark Process For the Lead-Free Assembly of Mixed Technology PCB's

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Over the past five years, the electronic assembly industry has been examining a variety of alloy systems as lead-free alternatives for the conventional 63Sn/37Pb eutectic system. Many of the proposed systems are quite interesting from a technical standpoint, but fall short when considering practical issues such as cost, availability, and repeatability of manufacture. The intent of this paper is to provide the industry with a practical, and technically feasible, lead-free process that can be implemented or used as a baseline to compare other more complex systems. The benchmark process consists of: 1) PCB's with a very thin metallized silver coating on the pads (rather than the Sn/Pb hot air solder leveled pads-HASL, 2) 96.5Sn/3.5Ag and 95.5Sn/4.0Ag/0.5Cu eutectic and near eutectic alloy systems for solder paste applications; 3) 99.3Sn/0.7Cu eutectic alloy system for wave soldering applications; and 4) 99.3Sn/0.7Cu alloy for hand soldering applications. Although this approach represents a practical, feasible process, there are a few significant issues associated with implementation of a lead-free process. The costs of the materials are still higher than the standard Sn/Pb process, there are increased limits on the degree of wetting, the process requires an inert atmosphere in the wave soldering process (nitrogen at the wave is sufficient), and it pushes the reflow temperature to practical limits of 235-245°C (which increases the thermal demands on the components).

BACKGROUND

Why Are Companies Looking For Lead-Free Alternatives? Is Lead Unsafe to Use? ¹

When considering issues with health and safety, two terms are commonly used - hazard and risk. Hazard refers to the inherent toxic nature of a material and its effect if ingested, inhaled, or absorbed into the body. Risk relates more to the safety of a material when used with the proper precautions, or the probability that the hazard will occur.

Lead is a hazardous material; it is known to be toxic. High absorption of lead into the body leads to lead poisoning which is a well-known and serious problem. Low levels of lead absorption may affect cognitive powers, the nervous system, and the reproductive system.

When assessing the risk of lead, one examines the chance of ingesting it by eating, drinking, or inhaling. In the electronics industry, lead does not, under normal conditions in typical applications, approach a temperature which would create lead fumes; therefore, this risk is not measurable and can be confirmed by lead monitoring. Other simple precautions such as wearing some type of a face mask during maintenance and dross removal at the wave solder pot, as well as prohibiting smoking in areas with lead, further minimize the risk of lead ingestion in the workplace. As long as those coming in contact with solder paste, bar solder, solder wire, etc. clean their hands before eating, drinking, and smoking, this risk is also eliminated.

Generally, ingestion represents a higher source of risk of lead absorption than inhalation. Stressing the importance of proper hygiene, with a ban on eating, drinking, and smoking in areas with lead exposure, will minimize risk. Given the proper precautions, our industry has demonstrated that the use of lead in our workplace is relatively safe.

If the risk of using lead in the electronics industry is so low, why is the elimination of lead even being considered? The primary concern comes from the proper disposal of lead-containing materials, such as PWB's. The issue arises due to the possibility that lead, from the PWB's that have been disposed of in landfills, might be leached out from the PWB into the groundwater, and subsequently find its way into the drinking water.

The technical debate on this issue centers around the probability of leaching and determination of an acceptable level of lead (if there is one) in the drinking water.

Is Lead-Free Legislation Imminent?

The legislative process is a political one, and hence, very unpredictable. At this time, there is not a strong legislative effort to restrict lead use in electronics in the USA. Since the electronics industry represents a very small percentage of the overall lead usage, but a significant and growing percentage of the GNP, restrictions on lead use in electronics will meet strong opposition.

Europe is taking a more aggressive position toward lead-free legislation. The European Union is scheduled to vote on the WEEE (Waste from Electrical and Electronic Equipment) Directive with a new commission in late 1999 or early 2000. This draft directive calls for a ban on lead in all electronics except automotive and certain other categories by January 2004. Laws on electrical and electronic waste are already in effect in Holland and Switzerland. The probability that this directive will pass into law with the current draft implementation dates is unknown.

Recycling statements involving electrical and electronic waste have been enacted in Asia (including Japan and Taiwan). JEIDA (Japanese Electronic Industry Development Association) and JIEP (Japanese Institute of Electronics Packaging) developed a lead free road map in January 1998. A number of OEMs have developed recycling processes and several including Sony, Toshiba, Matsushita, Hitachi, and NEC have committed to implement lead free electronics in selected portions of their product offerings during 2001 in compliance with Japanese legislation.

Is the Electronics Industry Implementing Lead-Free Processes?

Many multinational electronics companies have initiated technical programs to evaluate lead-free alternatives so that they could be prepared to implement lead-free systems in the event that final restrictive legislation is instituted.

A handful of companies are implementing lead-free processes as a marketing strategy. These companies are test marketing their electronics as lead-free, environmentally friendly products.

SELECTING A SYSTEM OF LEAD-FREE MATERIALS

What Are the General Requirements of A Lead-Free Alternative to the Sn/Pb Eutectic in the Assembly Process?

A set of requirements that is universally agreed upon for a lead-free alternative does not exist. Based upon numerous discussions with many professionals involved with the assembly process, the following list of technical and practical requirements has been developed:

1. **Metal Price** - Many assemblers have required that the price of the lead-free alloy be no more than the price of 63Sn/37Pb. Unfortunately, no lead-free alternative exists which is even within 35% of the cost of 63Sn/37Pb. Given that the price of the lead-free alternative will be higher, the industry would certainly like to minimize the price differential.

When selecting an alloy for bar solder and for wire solder, the metal cost requirement is particularly important. Since high volumes of poundage are used and the metal cost accounts for a large percentage of the total product cost, bar solder and wire solder are particularly sensitive to the metal cost. When selecting a lead-free bar solder and wire solder, metal cost is one of the most important factors. Metal cost is a relatively small percentage of the overall manufacturing cost of making solder paste.

2. **Melting Point** - Most assemblers, but not all, require a minimum solidus temperature of 150°C in order to meet the operating temperature requirements of the electronic device. The maximum liquidus temperature is application dependent:

Bar Solder For Wave Soldering: Liquidus temperature low enough to permit successful wave soldering at pot temperatures of 500°F (260°C).

Wire Solder for Hand/Robotic Soldering: Liquidus temperature low enough to allow operating tip temperatures of 650°F (345°C).

Solder Paste: Liquidus temperature low enough to allow reflow temperatures of less than 250°C (482°F). This temperature represents the maximum practical limit of many existing reflow ovens. Many engineers require maximum reflow temperatures of less than 225-230°C; however, no practical solution now exists for this requirement. Just about everyone agrees that the closer an alloy gets to a reflow temperature of 220°C, the better. It is desirable to avoid the higher reflow temperatures to minimize component damage (minimize requirements for special components), minimize board discoloration and warpage, and avoid excessive oxidation to pads and leads.

3. **Adequate Electrical Conductivity** - A basic requirement of an electrical connection.
4. **Adequate Thermal Conductivity** - The alloy must be able to transfer heat rapidly to dissipate the thermal energy as needed.
5. **Small Mushy Range** - Non-eutectic alloys freeze over a range (range of liquidus to solidus temperatures). Most metallurgists suggest a mushy range of less than 10°C to achieve proper solder joint formation and low defects. A broad freezing range in an alloy can result in hot tearing and cracking of the solder joint, leading to premature failure.
6. **Low Toxicity** - The alloy, and its component elements, must be non-toxic. This requirement rules out consideration of cadmium, thallium, and mercury. Some people also require that the element can't be the by-product of a refining process of a toxic material. This requirement could rule out consideration of bismuth since the primary source of bismuth is a by-product of lead refining.
7. **Acceptable Solderability (solders with existing equipment and no-clean flux systems)** The alloy should provide sufficient wettability to work with conventional no-clean flux systems. The need for an inert atmosphere in the wave soldering machine is acceptable since inerting the wave is not too costly. However, for SMT reflow it is desirable for the alloy to be

air reflowable, due to the high cost of inerting the reflow oven.

8. **Acceptable Physical Properties (strength, elongation, fatigue, etc.)** - The alloy must be capable of providing the mechanical strength and reliability that we have come to expect from 63Sn/37Pb without exhibiting fillet lift on through hole devices (especially with broad pasty range alloys).
9. **Repeatability Of Manufacture / Consistency In Melting Point** - The electronic assembly process is a high volume manufacturing process where repeatability and consistency are required to achieve low defect levels. Alloys whose compositions can not be repeated lot after lot, or whose melting point varies greatly from lot-to-lot due to compositional shifts, are not acceptable candidates. Alloys with more than 3 elements are prone to macrosegregation and other compositional variations which can result in variable melting points. The more complicated the alloy, the more sensitive the alloy will be to variability.
10. **Solder Joint Cosmetics** - The appearance of the solder joint should be very similar to that of Sn/Pb. This is not a technical requirement, but is more of a practical requirement for ease of acceptance and implementation.
11. **Availability** - When attempting to find a solution for the industry, it is critical to select an alloy system whose components are sufficiently available. From a technical curiosity standpoint, indium is quite unique. However, when reviewing the worldwide availability of indium, it is quickly eliminated from consideration.

Additionally, the industry would prefer a standard alloy system over a patented system. A standard alloy would be broadly available and would allow for competitive pricing. A patented alloy could be limited in supply and could increase the price of the material considerably.

12. **Compatibility with Lead** - The transition to a total lead-free system will not occur immediately. Lead may still be present on some component terminations or on some PCB pads. Some alloy combinations with lead result in extremely low melt temperature phases. These low temperature phases degrade the strength of the connection. When bismuth, tin, and lead come together and form an alloy, a low melt point phase at 96°C forms which significantly reduces joint strength.^{2,3,4}

Which Elements and Alloy Systems Are Considered when Reviewing Lead-Free Alternatives?

Tin is the base metal used for every candidate lead-free alloy. Tin is always selected as the base metal due to the fact that it is relatively inexpensive, sufficiently available, has desirable physical, electrical/thermal conductivity, and wetting properties, and is the base metal for the familiar 63Sn/37Pb alloy. The other elements which are commonly used as companion elements with tin include: 1) silver (Ag), 2) indium (In), 3) zinc (Zn), 4) antimony (Sb), 5) copper (Cu), 6) bismuth (Bi).

These elements are selected because they tend to reduce the melting point when alloyed with tin and possess desirable mechanical, electrical, and thermal properties. Table II provides the metal cost per pound, density, spare annual capacity, and relative availability for each of the candidate elements. When considering the relative availabilities of each element, it is helpful to consider a couple of use estimates. Approximately 100 million pounds of 63Sn/37Pb are consumed each year in the electronics industry. Of the 100 million pounds used worldwide,

about 35 million pounds are used in North America. As an example, if only 3% of the North American assembly industry adopted a tin/indium lead-free alloy using 20% indium, the worldwide spare capacity of indium would be consumed.

$$(35 \text{ million lb})(3\%)(20\%) = 0.21 \text{ million lb compared to spare indium capacity of } 0.20 \text{ million lb/yr}$$

Element	Metal Cost Per Pound* (as of 2/3/99)	Density at 25 °C (lbs/in³)	Spare Annual Capacity (millions of pounds)**	Availability
Lead	\$0.45	0.41	----	----
Zinc	\$0.50	0.258	1560	Available
Copper	\$0.65	0.324	4900	Available
Antimony	\$0.80	0.239	100	Available
Bismuth	\$3.40	0.354	9	Limited
Tin	\$3.50	0.264	180	Available
Silver	\$84.20	0.379	3.5	Limited
Indium	\$125.00	0.264	0.2	Scarce

* metal cost only - does not include fabrication costs, margins, development, support, etc.
 ** as defined by the US Bureau of Mines

Over the past five years or so, a variety of alloy systems have been proposed and evaluated as lead-free alternatives. The entire list of options would certainly exceed 75. However, the primary options can be summarized in a list of less than 15. Table III provides a summary of the significant lead-free alternatives and shows the cost per pound, cost per unit volume (cost per unit volume is a more meaningful measurement of cost for solder paste), and the patent status for each alloy. The alloys are listed in order of increasing liquidus temperature

Alloy	Melting Range (C)	Metal Cost/Lb (as of 2/3/99)	Density at 25C (lbs/cubic in)	Metal Cost per in³	Patent (Yes/No)
63Sn / 37Pb	183	\$2.37	0.318	\$0.75	No
42Sn / 58Bi	139	\$3.44	0.316	\$1.09	No
77.2Sn / 20In / 2.8Ag	179-189	\$30.06	0.267	\$8.02	Yes
91Sn / 9Zn	199	\$3.23	0.263	\$0.85	No
91.8Sn / 3.4Ag / 4.8Bi	208-215	\$6.24	0.272	\$1.70	Yes
90Sn / 7.5Bi / 2Ag / 0.5Cu	186-212	\$5.09	0.273	\$1.39	No
96.2Sn / 2.5Ag / 0.8Cu / 0.5Sb	213-219	\$5.48	0.267	\$1.46	Yes
95.5Sn / 4Ag / 0.5Cu*	217-218	\$6.55	0.269	\$1.76	No*
95Sn / 3.5Ag / 1.5In	218	\$8.15	0.268	\$2.18	No
93.5Sn / 3.5Ag / 3Bi	216-220	\$5.92	0.269	\$1.59	No
96.5Sn / 3.5Ag	221	\$6.32	0.368	\$2.33	No
99.3Sn / 0.7Cu	227	\$3.48	0.264	\$0.92	No
95Sn / 5Sb	232-240	\$3.37	0.263	\$0.88	No

* Some Sn/Ag/Cu alloy compositions are covered by patents; however, this composition can generally be considered free and clear.

With All Of These Candidate Alloys, How Do You Narrow The Field To A Couple Of Logical Choices?

A number of techniques can be used to reduce the options to a manageable number. In this discussion, successive screening based upon known facts, coupled with some practical constraints, will be used to narrow the options.

Indium - Indium is probably the most effective element for reducing the melt point in tin alloys. It also has exceptional physical properties and wetting properties. However, indium is much too scarce and it is much too expensive to be considered for broad application. For these reasons, alloys containing indium will be excluded from further consideration. Indium alloys may be the perfect choice for selective applications, but are not appropriate as an industry-wide solution. Additionally, differential-scanning calorimetry testing also indicates that a low melt point phase exists at 114°C (237°F) with the 77.2Sn/20In/2.8Ag alloy which may make the alloy unsuitable for some applications.

Zinc - Zinc is very inexpensive (the price of zinc is as low as that of lead), is readily available, and is extremely effective in reducing the melt point in tin alloys. Zinc's challenges are more associated with its rapid reactivity with oxygen. It quickly forms a stable oxide. The effect of this reactivity is excessive drossing during wave soldering, and more problematic is the very poor wetting properties due to the stable oxide formation. Perhaps these technical problems can be overcome with the use of inerting and special flux formulations, however, at this time, a workable system with zinc requires broader demonstration. For these reasons, zinc alloys will be excluded from further consideration.

Bismuth - Bismuth is effective in reducing the solidus temperature of tin alloys, but bismuth is not as effective at reducing the liquidus temperature, which results in a broader mushy or freezing range. A broader freezing range is not desirable and can cause fillet lifting. Bismuth also demonstrates very good wetting properties and has good physical properties. One of the major concerns about bismuth is the low melt point phase which is formed when tin/bismuth alloys are used in the presence of lead. When lead, perhaps present in component terminations or on PCB pads, is present in the soldering system with tin and bismuth, a low melt point phase of Sn/Pb/Bi forms at 96°C which can lead to joint fracture^{2,3,4}. An additional concern is the fact that bismuth availability could be limited by restrictions on lead. At this time, the primary source of bismuth is a by-product of lead refining. By restricting lead use, much less bismuth will be available from this source. Bismuth reserves that are directly mined are available, but at a higher cost. For these reasons, bismuth alloys will be excluded from further consideration.

Four And Five Part Alloys - Four and five part alloys provide an exciting array of various alloy and compositional combinations. The opportunities for experimentation are endless. Most four and five part alloys are effective in reducing the solidus temperature over most binary alloy systems; however, most are not very effective at all in reducing the liquidus temperature. This is due to the fact that most four and five part alloys are not eutectic compositions. This means that different alloy phases or compositions melt at different temperatures in the freezing range, and some of the phases melt at the binary alloy liquidus temperature. The net effect of this is that the reflow temperature can not be significantly reduced from that needed for the simple binary alloy system.

An additional consideration is the variability in composition, and hence, in the melting temperature, that should be expected from a four or five-part alloy. Achieving "within lot" and "lot-to-lot" compositional consistency in powder for solder paste is a challenge for more than three-part alloys. The complexity involved with achieving this same level of consistency with four and five-part alloys is much greater.

Complex alloys were excluded from further consideration. If there were an identified complex alloy composition which delivered significant benefits to binary systems, then it would be left in the final options. However, no known four or five part alloy, with significant advantages (cost or performance) over binary or ternary alternatives, has yet been introduced to the industry.

What's Left? - After excluding the alloys defined above, the following list of candidate alloys are provided in Table IV. The remaining alloys are: 1) 95.5Sn/4.0Ag/0.5Cu (melting range = 217-218°C); 2) 96.5Sn/3.5Ag (melting point = 221°C); 3) 99.3Sn/0.7Cu (melting point = 227°C); and 4) 95Sn/5Sb (melting range = 232-240°C). Based upon the specific requirements of each soldering application, the appropriate alloy can now be selected.

Excluded Alloys	Remaining Alloys	Melting Range (°C)	Metal Cost Per Pound (2/3/99)	Reasons for Exclusion
63Sn/37Pb (standard)		183	\$2.37	Lead content.
42Sn/58Bi		138	\$3.44	Bismuth content. Melting point too low for some applications
77.2Sn/20In/2.8Ag		179 - 189	\$30.06	Indium content (cost and availability)
91Sn/9Zn		199	\$3.23	Zinc content (poor wetting).
90Sn/7.5Bi/2Ag/0.5Cu		186 - 212	\$5.09	Bismuth content. Four part alloy. Broad freezing range.
	95.5Sn/4.0Ag/0.5Cu	217 - 218	\$6.55	----
95Sn/3.5Ag/1.5In		218	\$8.15	Indium content.
96.2Sn/2.5Ag/0.8Cu/0.5Sb		213-218	\$5.48	4 part alloy. No major benefits over binary alloys. Lower Ag content potential appeal for wave soldering.
	96.5Sn/3.5Ag	221	\$6.32	----
93.5Sn/3.5Ag/3Bi		216 - 220	\$5.92	Bismuth Content. Low melt point phase with Pb contamination.
	99.3Sn/0.7Cu	227	\$3.48	----
	95Sn/5Sb	232 - 240	\$3.80	-----

Which Alloys Should Be Considered For Bar Solder (Wave Soldering) And Wire Solder (Hand/Robotic Soldering)?

The application specific requirements for selecting an alloy for bar solder or for wave soldering include:

1. Solder successfully with a maximum solder pot temperature of 500°F (260°C).
2. Provide low levels of defects (skips, bridges, etc.).
3. Lowest cost possible.
4. Does not generate excessive dross.

All of the final alloy selections could probably meet the requirements for wave soldering, but the 99.3Sn/0.7Cu and 95Sn/5Sb alloys provide considerable cost savings over the other alternatives. The 99.3Sn/0.7Cu alloy provides a 13°C advantage in liquidus temperature over the Sn/Sb alloy; thereby, making it the best candidate for wave soldering.

The application specific requirements for wire solder for hand soldering are very similar to those outlined for bar solder. Cost considerations remain a high priority, as well as the ability to provide good wetting and soldering. The alloy for wire solder must be capable of easily being extruded and drawn into wire. The alloy must be able to solder at tip temperatures of 650-700°F (345-370°C). The 99.3Sn/0.7Cu alloy meets these requirements.

Which Alloys Should Be Considered For Solder Paste (Print & Reflow)?^{2,5,6,7}

Alloy cost is less of a consideration with solder paste than it is with bar solder or wire solder, since the metal cost is a smaller percentage of the overall manufacturing cost with solder

paste. The major objective with alloy selection for solder paste is to minimize the required reflow temperature. When reviewing the final list of alloys, the two alloys with the lowest liquidus temperatures are 95.5Sn/4.0Ag/0.5Cu (melting range = 217-218°C) and 96.5Sn/3.5Ag (melting point = 221°C).

Either of these alloys would be an appropriate choice; strong arguments could be made for either one. The Sn/Ag/Cu alloy has the lower liquidus temperature. The Sn/Ag alloy represents a consistent, repeatable binary alloy which has been used for years in the electronics industry, and has a good history of reliability. The Sn/Ag eutectic has been selected as an alloy of choice by a few of the major multinational companies evaluating lead-free alternatives while Sn/Ag/Cu is under earlier advanced testing by the greatest number of major multinational companies.

Have These Recommended Lead-Free Systems Been Evaluated On Commercial Equipment? If They Have, What Was Learned?

Wave Soldering Evaluation - A standard Electrovert Econopak Plus wave soldering machine was filled with 99.3Sn/0.7Cu alloy. The wave soldering machine was equipped with a USI ultrasonic spray fluxer, Vectaheat convection preheat, and CoN₂tour boundary inert system with an "A" wave. Two types of lead-free PCB board finishes were evaluated: 1) bare copper with an OSP coating; and 2) bare copper with an immersion silver (Alpha Level) finish. All boards were soldered with a 2% solids, VOC-Free, no-clean flux (NR300A2). The same design of boards were also soldered on the same equipment, using the same conditions, with the standard 63Sn/37Pb alloy.

The following conclusions were made:

- Inerting the wave solder machine appears to be a requirement to insure adequate wetting while using the 99.3Sn/0.7Cu alloy. A fully inerted machine or tunnel is not required. The inert boundary soldering system provided by the CoN₂tour is sufficient.
- The joint appearance of boards soldered with 99.3Sn/0.7Cu was indistinguishable from boards soldered with 63Sn/37Pb. Shininess of solder joint, solder joint formation, pad wetting, and topside hole-fill were examined with little or no difference in the two alloys.
- The Sn/Cu alloy did not have a higher tendency to bridge compared to Sn/Pb. This conclusion is based upon limited data and requires more exhaustive study.
- Successful soldering with the 99.3Sn/0.7Cu alloy can be achieved with a solder pot temperature of 500°F (260°C). Limited trials at 475°F (245°C) were also successful.
- The copper content did not drift during the several weeks that the Sn/Cu alloy was used. This was a concern since the solubility of copper in the tin is quite limited and is very temperature dependent. In a high volume operation, the typical copper pick-up from the board is expected to be the same rate as with Sn/Pb.

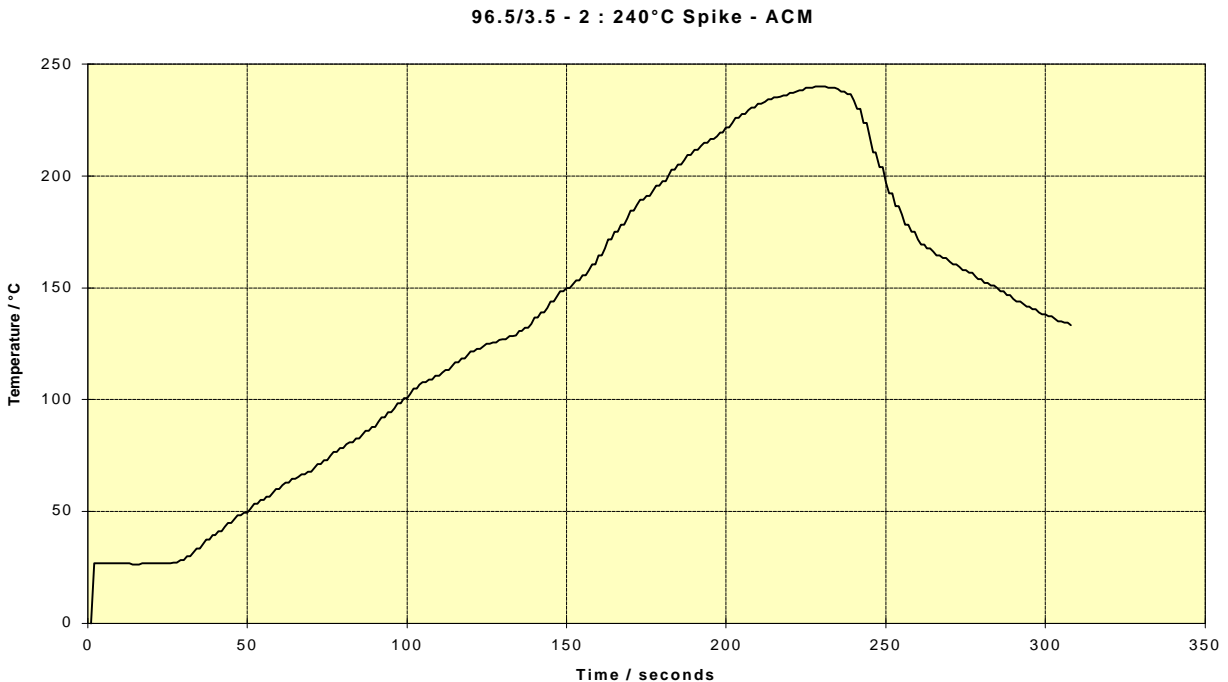
Print & Reflow Evaluation - Flux system modifications were employed for the Sn/Ag Sn/Ag/Cu and alloy systems. This modification was needed to deliver good wetting under conditions of the higher reflow profile. The higher reflow profile (approximately 20°C higher than the conventional reflow) requires an activator system with high thermal stability.

Additionally, the higher temperature reflow, when performed in air, tends to noticeably discolor conventional no-clean flux systems. This flux system is extremely tolerant to the higher reflow temperatures and does not turn brown or amber when exposed to 240°C in air UP-Series Solder Paste was evaluated in the 95.5Sn/4.0Ag/0.5Cu alloy.

The UP-Series Solder Paste performed extremely well in the print evaluation. An MPM UP2000 printing machine was used for this study. The solder paste was printed at a speed of 1 inch/second through a 6 mil thick laser-cut stencil using a pitch range of 16 - 50 mil. Zero snap-off contact printing was used. The print definition was excellent and solder paste exhibited good release properties from the stencil. The solder paste demonstrated excellent response to pause as no kneading was required to prepare the paste for the initial print after a number of extended pauses (60 minutes or more). The stencil life exceeded eight hours.

The solder paste demonstrated a tack life of over eight hours. The reflow evaluation was performed in an Electrovert Omniflo seven-zone oven with forced convection heating in an air environment. The reflow profile was a straight ramp up to 240°C over a 200 second period. The time above liquidus temperature (221°C) was 45 seconds.

Figure 2



The following conclusions were made:

- The UP-Series Solder Paste 95.5Sn/4.0Ag/0.5Cu 88-3-M13 solder paste demonstrated acceptable printing characteristics.
- The lead-free solder paste provided acceptable tack and tack life properties.
- For the board designs evaluated, a maximum reflow temperature of 240°C was acceptable for the 95.5Sn/4.0Ag/0.5Cu alloy.
- Nitrogen was not required to achieve acceptable wetting in a single reflow operation.

- The shininess of the solder joints was very good and comparable to the standard Sn/Pb alloy.
- The residue appearance of the lead-free solder paste was far superior (clear and colorless) as compared to the standard flux residues obtained with conventional flux systems with the Sn/Pb alloy after a standard air reflow (45 seconds above 183°C, peak temperature of 220°C).
- Wetting and spread characteristics were comparable to the Sn/Pb standard.
- Boards processed with no solder mask, only bare FR-4, exhibited severe discoloration (darkening) when subjected to the higher temperature reflow profile. Light green solder masks displayed some very slight discoloration in the higher temperature reflow. Medium-to-dark green solder masks showed no noticeable darkening in the reflow.
- Some components showed signs of discoloration and oxidation in the higher temperature reflow. When using this lead-free system with boards which have surface mount devices on both sides, it is recommended to place the bottomside SMD's (to be wave soldered) on after reflow, to avoid excessive thermal exposure and to maintain solderability.
- Also performed using UP-Series 96.5Sn/3.5Ag alloy. Results were identical. Reflow temperatures increased by 3-5°C.

How About The Mechanical Properties, Solder Joint Reliability, Electrical Reliability Testing, Thermal And Electrical Conductivities, and Wetting Tests? Have These Tests Been Performed On The 96.5Sn/3.5Ag And 99.3Sn/0.7Cu Alloys?^{2,5,6,7}

The 96.5Sn/3.5Ag alloy has been used for years in certain electronics applications. It is a known entity. The 95.5Sn/4.0Ag/0.5Cu is currently undergoing the same rigorous examination and is demonstrating very similar performance with possible advantages in certain areas. Ford Motor Company has completed a thorough thermal fatigue testing study of the Sn/Ag alloy with test boards and with actual electronic modules, using thermal cycles of -40°C to 140°C ⁶. Additionally, they have placed the lead-free modules in actual vehicles. The reported results of Ford's testing indicate that the Sn/Ag alloy offers reliability equivalent to, or better than, the Sn/Pb alloy. Motorola has also completed thermal cycling and vibration studies of the Sn/Ag and Sn/Pb alloys⁷, and also conclude that the Sn/Ag alloy provides passing results. Other OEMs have achieved similar results in studies of Sn/Ag and Sn/Ag/Cu alloys.

TABLE V PROPERTY COMPARISON OF SN/AG AND SN/PB⁶

Composition	Melting Point (°C)	Density (kg/m ³)	Coefficient of Thermal Expansion (ppm/°C)	Electrical Conductivity (% IACS)	Electrical Resistivity (μΩ cm)	Surface Tension (N/m)	Thermal Conductivity (W/[mK])
63Sn/37Pb	183	8400	21.4 @ 25°C	11.5	14.99	0.49	57.9 @ 32.6°C
96.5Sn/3.5Ag	221	7290	22 @ 20°C	14	12.31	0.48	55.3 @ 23.9°C

The electrical conductivity, surface tension, thermal conductivity, and coefficient of thermal expansion of Sn/Ag and Sn/Pb are all reported as comparable⁶. See Table V above for the exact values.

CONCLUSIONS

A practical, technically feasible, benchmark lead-free soldering process has been described. An overview of the process includes:

1. The use of the 95.5Sn/4.0Ag/0.5Cu or 96.5Sn/3.5Ag alloy with the UP-Series flux system for solder paste applications.
2. The use of the 99.3Sn/0.7Cu alloy for bar solder for wave soldering.
3. The use of the 99.3Sn/0.7Cu alloy for wire solder for hand/robotic soldering.

This system does not achieve every objective established by all engineers for a lead-free alternative, but it does deliver on a large number of them. The most obvious limitation of this system is the 240°C reflow temperature required for the 96.5Sn/3.5Ag alloy (which is 20-30°C higher than is used for Sn/Pb), and the increased demand which this reflow places on the components. A close partnership and cooperation with the component suppliers could potentially resolve many of the obstacles with the higher reflow profile.

As new technologies are developed and more favorable alternatives are introduced, this system will undoubtedly become obsolete. However, the single biggest value that this system provides is a baseline or a benchmark with which other more sophisticated systems can be compared. Before examining a more complex system, ask a few questions which can be answered in a quantifiable way:

Solder Paste

1. How much will the new alloy system reduce the required reflow temperature compared to Sn/Ag which is 240°C min (235°C min for 95.5Sn/4.0Ag/0.5Cu)?
2. How does the cost of the metal and of the solder paste compare to Sn/Ag or Sn/Ag/Cu alloy?
3. What are the specification limits on the individual elements in the alloy and how much do the solidus and liquidus temperatures vary as the individual elements vary over the specification limits?

Bar Solder

1. What is the cost of the alloy and how does it compare to Sn/Cu alloy?
2. What benefits will the alloy provide that the Sn/Cu alloy does not?

FUTURE WORK

The emphasis of future work will be to facilitate the evaluation of the benchmark process by:

- having samples of lead-free bar solder, wire solder, and solder paste readily available for customers to evaluate;
- offer the opportunity for customers to visit Alpha's Labs which will have a wave solder machine filled with Sn/Cu solder;
- demonstrate the benchmark process Productronica 1999 on a fully functional mixed technology line.

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