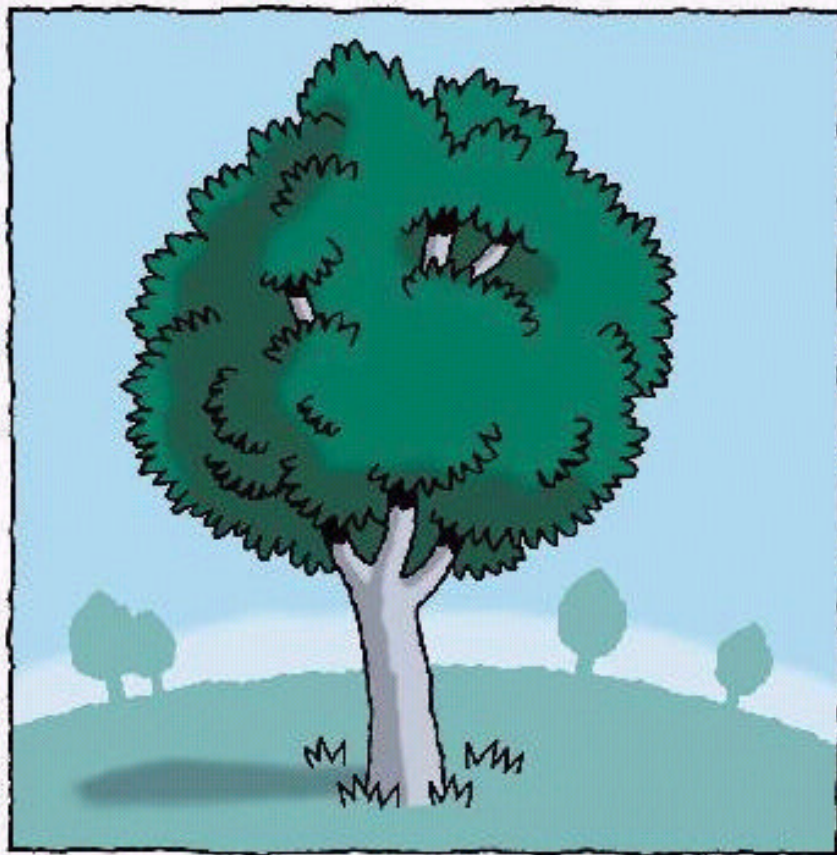


LEAD-FREE



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1. INTRODUCTION : LEGISLATION & MARKETING

LEAD SUBSTITUTION : Voluntary moves should set the pace

Lead substitution is not really ecology driven : less than 1% of lead is used in electronic manufacturing and recycling will be imposed by the new WEEE Directive in a few years. Furthermore a ban is not the best management approach to environment protection and RESPONSIBLE USE OF ANY SUBSTANCE (including its recycling/disposal) is still a more efficient way to a better future.

But the move towards lead-free processes is clearly underway for both political and marketing reasons :

- Anticipation of possible regulations given the high “visibility” of lead substitution which happened in “consumer products” (paintings, gasoline, etc...)
- Consumer preference for “green” products if price remains the same.
- Voluntary commitments by many Japanese, European and American OEMs to eliminate uses for some applications as early as 2001/2002.

All these drivers lead to progressive substitution especially in soldering ; components and cathode ray tubes will be the most difficult applications to substitute(not before 8/10 years).

The EU WEEE (Waste of Electrical and Electronic Equipments) directive draft has been significantly modified by the Commission to meet all services views and respond to some industry’s concerns:

- Two directives have been proposed: WEEE on recycling and ROS(Reduction of dangerous substances);WEEE is based on article 175 of the EU Treaty and ROS on article 95 of the EU Treaty; in the second case there is NO possible strengthening of the regulation at the national level

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- Lead ban (and other so called “dangerous substances”) is postponed from 2004 to 2008.
- Quantitative targets for recycling are still too ambitious.
- A third directive (EEE) based on article 95 is under drafting by DG enterprise to develop more environmentally friendly products through normalisation; industry should have an active and leading role in this drafting.
- Financing of recycling is born by producers after the equipment have been collected in a dedicated centre by retailers and local authorities.
- Visible fee is not clearly established for historical waste and retroactivity of the directive could be legally questioned.

This shows, if necessary, the usefulness of a precise, dynamic and technical lobbying by industry. These proposals are now official; they still have to be discussed and probably amended by the EU Council and EU Parliament: this process should still take 15 to 18 months. Industry should follow these evolutions carefully.

Moreover many issues remain to be settled : efficiency of import controls, trade disparities, SME’s difficulties, standardisation of new alloys really more environmentally friendly, including recyclability...

So we should have a final picture of the regulatory framework in Europe by the end of 2001...

In the meantime, companies should go forward and substitute lead in all soldering applications wherever it is technically and economically feasible. Promosol will stand by your side to accompany you in this wide challenge.



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2. PROMOSOL's OFFER

**ECOREL FREE range,
SOLDEREL FREE range**

Promosol has developed in its research laboratories in Paris and Kuala Lumpur, lead-free solder paste by taking into consideration the various technical requirements.

Development has been focussed on :

- Choice of alloys

- Non toxic
- Solidus temperature near to temperature of Sn Pb and Sn Pb Ag
- Eutectic properties
- Good mechanical and electrical properties
- Good wetting ability
- Cost-availability
- **SOLDEREL FREE / ECOREL FREE** selected alloys :
 - . Sn Ag 4 Cu 0.5
 - . Sn 96 Ag
 - . Sn 93.5/Ag 3.5/Bi 3.0 for particular SMT purpose

- Formulation of organic part

- Improve wettability
- Avoid reactivity powder/organic part
- Increase stability due to higher temperature, more robust activators

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3. PROMOSOL RESEARCH PROGRAMS

Promosol is actively participating to two research projects on lead-free.

A) IVF-integrity of lead-free solders

The IVF Research Program deals about integrity of lead-free solders. It's a fundamental research program tackling manufacturability, failure mechanisms and mechanical reliability.

Members of this program are PROMOSOL, IVF, ERICSSON and VOLVO.

A huge number of tests are realised to better understand failure mechanisms (for example with larger solidification range and with new types of intermetallic growth).

The aim is to generate long term reliability data testing with low cycle mechanical fatigue test and thermal life tests in humid and controlled atmosphere.

This program was completed in July 2000.

The table below is a summary of the different alloys studied during IVF research program in comparison with the standard soldering alloy, Sn₆₃Pb₃₇ :

Sn	96.5	93.5	96.3	95.5
Ag	3.5	3.5	3.2	4
Bi		3		
Cu			0.5	0.5

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The mechanical strength were evaluated using three reliability tests:

- Environment test : repeated thermal cycle test (between - 40 and 100°C with thermal stage of 30 min)
- Low cycle fatigue test performed by repeated stress and strain loadings (+/-20 µm with 0.2 Hz frequency).
- Thermal aging performed at constant temperature at 25°C, 100°C and 150°C.

A1 . Environment test

After component assembly on 2 types of PCB finishes Sn Pb and Ni Au with 2 different reflow profiles (version 1 and version 2), the quality of the solder has been evaluated before and after 1 000 cycles – 40°C + 100°C.

The difference in the two reflow profiles are :

- Preheat : version 1 → 250 min, version 2 → 350 min
- Time over liquidus : version 1 → 80 sec ; version 2 → 45 sec
- Cooling rate : version 2 faster than version 1

The mechanical strengths of the soldering joints were achieved by a shear test using a shear tester Dage BT 22. The solder leads were put away from the pads and the strengths were recorded.

Average shear strength of soldering joints.

Solder Alloy		Sn96.5-Ag3.5		Sn93.5-Ag3.5-Bi3.0		Sn96.3-Ag3.2-Cu0.5		Sn Pb
Reflow Condition		Version 1	Version 2	Version 1	Version 2	Version 1	Version 2	
Strength (Kg)	As assembled	3.33	4.68	4.12	4.61	4.38	4.23	3.67
	After 1000 temp.cycles	3.78	3.81	4.17	4.20	4.48	4.66	2.96

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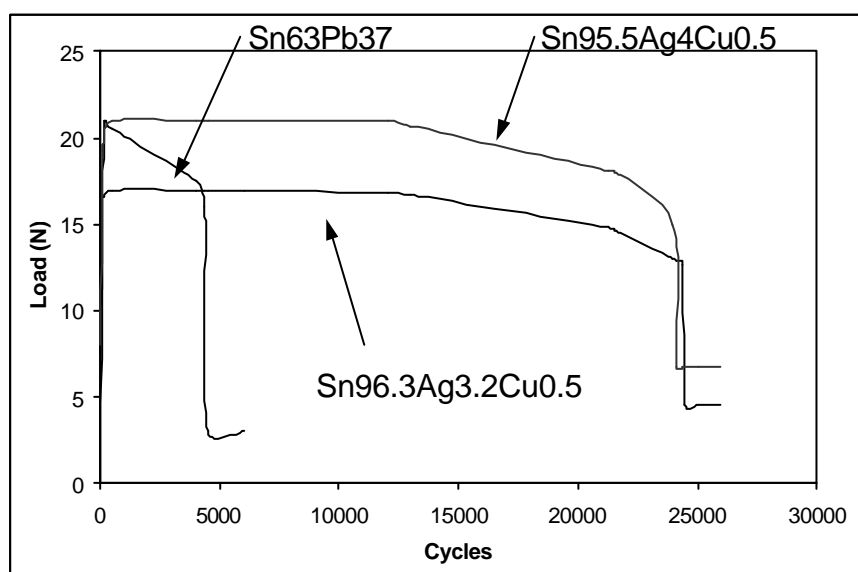
Analysis of results shows :

- The shear strength of the lead free joints is higher than that using eutectic alloy Sn Pb.
- Shear strength of lead free joints processed by reflow profile version 2 is usually higher than that by version 1. This result can be expected because the rapid cooling rate can result in a fine granular structure, thus increase the mechanical strength.
- No evidence indicates a degradation of joining strength after temperature cycling testing.

A2. Low cycle fatigue test (0.2 Hz)

Low cycle fatigue test shows that Sn Ag Cu solders are more resistant than Sn Pb (see figure below).

4400 fatigue cycles are needed to reach joint failure with SnPb, but two different composition of SnAgCu joints (96.3/3.2/0.5 et 95.5/4/0.5) can support more than 24000 fatigue cycles. This could be attributed to the formation of η intermetallic compound of Cu_6Sn_5 in the joint structure.



Results from low cycle fatigue testing of different solder joints on Au metallization

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A3. Mechanical strength of lead free joints

A special test board was designed to test the shear strength after ageing at 25°C , 100°C, 150°C during 200, 500 and 1 000 hours.

The shear strength was measured with a Dage Microtesteur BT22 and each of the solderjoints and fracture surfaces were studied with SEM and EDS.

It was shown that out of the two metalization tested, the Sn Pb metallization consistently yield a higher shear strength than the Ni Au metallization.

This is most likely due to the gold diffusion from Ni Au metallization of pads, resulting in brittle Sn Au intermetallic (Au Sn₄, Au Sn₂ and Au Sn) formation within the solder.

Expect those differences in strength, the solders generally behave the same way on both metallization.

Concentrating on the Ni/Au metallization, it was found that out the solder, the Bismuth containing solder Sn₉₀ Ag₂ Bi_{7.5} Cu_{0.5} and in particular Sn_{93.5} – Ag_{3.5} – Bi₃, have the highest shear at room temperature.

During temperature ageing, in addition to intermetallic formation, the microstructural evolutions of the alloys play also an important role.

During thermal cycle tests, microstructure of SnPb solder becomes coarse and is responsible of the significant decrease of the mechanical resistance. The coarsening mechanisms are due to the relatively high solid solubility of Pb in Sn and vice versa, although the SnAg system has limited solubility, making it more resistant to the phase coarsening.

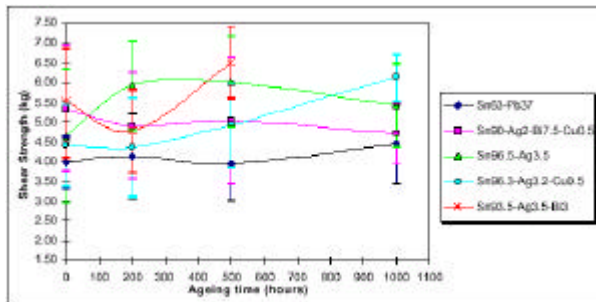
Moreover after aging at 150°C, the strength of the bismuth containing solders decrease drastically and becomes much weaker than the SnPb (see figures below). When bismuth concentration is 7.5%, large bismuth grains and low melting phases(SnAgBi and SnBi eutectics respectively with melting points at 136.6°C and 138°C) are formed making the solder weaker. With 3% of bismuth strength decrease is predominantly due to considerable grain coarsening and not directly due to the presence of bismuth. These low melting point phases are not

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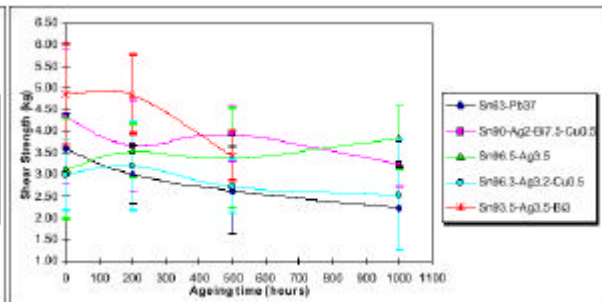


formed at 100°C, so the shear strength remains high during ageing at 100°C (see curves below).

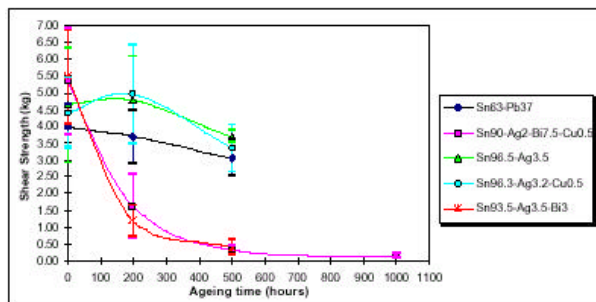
Lead-free solders without bismuth SnAg and SnAg Cu are much more stable when exposed to thermal test. This could be attributed to small grains remaining in the microstructure after aging, acting as locks to the motion of dislocations. In comparison, SnPb gradually becomes much weaker.



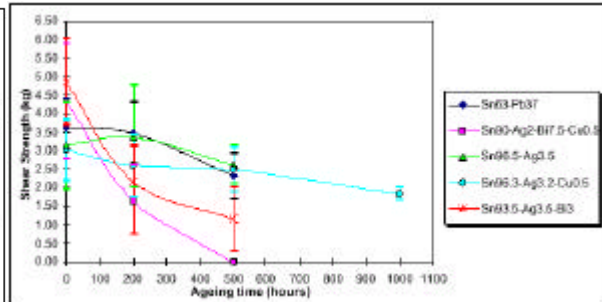
Shear strength vs aging time at 100°C on the SnPb metallization



Shear strength vs aging time at 100°C on the NiAu metallization



Shear strength vs aging time at 150°C on the SnPb metallization



Shear strength vs aging time at 150°C on the NiAu metallization

Finally, it appears that the lead-free with bismuth is more adapted to printed circuits not working under high temperature conditions. If the solder is required to work at high temperatures, e.g. in automobile, SnAg or SnAgCu system solders is the good choice.

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B) CEPIA compatibility study :

The CEPIA research program contains a complete application research. Members of this program are PROMOSOL, VALEO (Automotive), ALCATEL (Telecom), SCHLUMBERGER (Oil Industry), ST MICROELECTRONICS (SO, QFP, BGA manufacturer), TRONICO and BORDEAUX UNIVERSITY. The aim is to select solder paste compatible with high volume, high speed and high density processes and to choose solder alloys compatible with new components finishes including μ BGA's.

The completion of this study is scheduled for end 2001.

Members of the IVF project meeting in PARIS



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4. TECHNICAL REQUIREMENTS AND CONSEQUENCES OF A LEAD FREE ALTERNATIVE

4.1 TECHNICAL REQUIREMENTS

The industry of Electronic assembly has various technical requirements for lead-free solder paste. Some of these requirements can be fulfilled, others are still under Research & Development.

- Adequate Electrical conductivity
- Eutectic (small pasty range)
- Good thermal conductivity
- Good solderability
 - Alloy oxydation
 - Organic part adaptation
 - Solderpaste process window has to be adapted
- Good physical properties : fine microstructure, mechanical resistance, elongation, fatigue, minimal thermal expansion
- Consistency in manufacturing for a consistency in melting point alloy (Problem with quaternary alloys)
- Compatibility with finishes and components - Incomplete knowledge of intermetallics if pollutions by oxydes or elements such as Au, Ag, Pb traces...
- Minimization of intermetallic phases :
Due to increased temperature, intermetallic phases are favorised in lead-free alloys and even grow when the joint is solid.
- Alloy standardization for repair must be developed.

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4.2 TECHNICAL CONSEQUENCES

Increased temperature of alloys (Sn Pb – 183°C, Sn Ag 4 Cu 0,5 – 217°C) leads to :

- Higher reflow temperature
- More robust organic part
- Increase of intermetallics due to higher temperature (Ag 3 Sn, Cu 6 Sn 5 and Cu 3 Sn)
- Coarser microstructure ; to avoid a coarse cristallization in liquid phase a fast cooling is preferred
- Components adaptation
- Finishes adaptation

Bismuth containing alloys can create in presence of lead low temperature intermetallics (90°C) generating fillet-lifting.

During a second reflow or wave soldering process, this phenomena can be enhanced.

4.3 SOME SOLDERING PROCESS RECOMMANDATIONS

Printing Process

It is well known that 80 % of solder defects can be attributed to bad printing results.

Lead free powder reacts differently with organic part than standard powder. This reaction can lead to shorter stencil life.

Promosol development of new organic part dedicated and compatible with lead free powders, allows to conserve printing parameters and stencil life identical to standard solder pastes containing SnPb.

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Reflow Process

During the reflow, critical points must be considered. First, as most of lead-free solders have higher liquidus temperature, from 30 to 40°C, than standard SnPb. As for standard SnPb solderpastes, the minimum reflow peak temperature must be high enough to have a fluid alloy and a correct wettability, for example for SnAg4Cu0.5, 240°C can be considered as a minimum.

But it becomes also more and more important to control the temperature variation over PCB's. When large temperature variation takes place over printed board during reflow process, the maximum temperature can easily reached more than 250°C inducing concerns with the components. This issue is more crucial on the larger PCB's, which require some accommodation .

A solution is the use of dual source reflow oven, combining both the hot air convection and Infrared (IR) technology coupled with thermal masking materials to evenly distribute the heat. Moreover, the use of a design of experiments method should help greatly for quick optimisation of temperature variation over boards.

Thermal resistance of component must also be considered for the assembly. The aluminium electrolytic capacitors currently in use accept maximum temperature of 230 to 240°C. But now some component manufacturers develop new higher temperature resistant Al capacitors. For the assembly, a good selection of adapted components will be necessary.

The second major component concern is the mechanical joint strength reliability, especially with the QFP components. Some works have highlighted the influence of the component finishing on the strength. Thus, SnPb solder and SnAgBi solder form weaker joints on SnPb plated electrodes than on NiPd finishes. The high dissolution rate of Sn into molten solder compared to Pd dissolution (respectively 100 and 0.02 µm/sec at 230°C) leads to very high wetting. The solders go up very high along the lead, leaving a weaker foundation for the solder joint.

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Wave soldering process

The concerns change a few with the selected alloys for the wave soldering.

If SnCu is chosen, the Cu contamination of the solder bath from the PCB finishing will influence considerably the melting temperature. So the liquidus temperature increases from 230°C for Sn-0.7Cu to 300°C for Sn-2.0Cu. For this reason it is imperative to control the Cu concentration of SnCu solder bath and add pur tin periodically to keep stable Cu concentration along process.

Also the crossing rate with SnCu wave bath can be as high as 1.5 times the standard SnPb baths. In adding alloying element in trace amounts, this crossing rate can be reduced to equivalent rates as SnPb baths. Moreover, this addition also helps control whisker formation.

With SnAgBi baths, the major concern of bath life is impurity level of Pb. Addition of only 0.2% of Pb as contaminant in the bath, could reduced joint pull strengths up to 5% of the original strength, at 0.5% Pb contamination the pull strengths decrease up to 40%. In the last case, the fracture points are observed at the solder to land interface. It is easily understandable the use of standard HASL printed circuit boards does not suit at all in the presence of Bi containing solder baths, unless changing bath solder very frequently, which higher greatly the process cost.

Finally, the fillet lifting phenomena observed with Bi family of alloys makes them really poor candidates for a SnPb substitute specially in wave application.

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5. CHOICE OF SOLDER ALLOYS

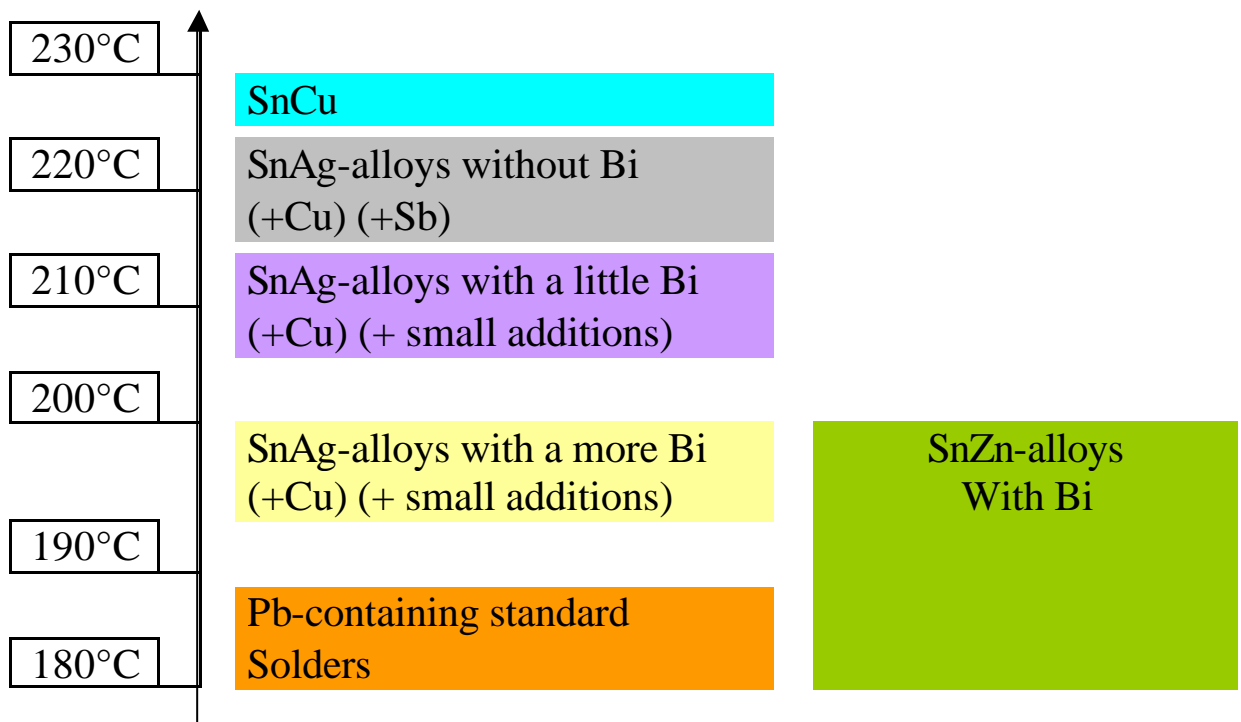
During the last years, significant research has been done for a drop-in replacement for eutectic tin-lead solder with a melting point near 183°C. The solution has to be non-toxic with comparable cost and equal or superior mechanical properties as well as plenty supply.

One application parameter is operating temperature range. Telecommunications and consumer electronics have an operating range from -55° to 100°C, while under the hood and on engine automotive electronics must be reliable from -55°C to 165°C or more.

So for consumer and telecommunication applications, alloys with a melting point below 183°C should be acceptable, but for some automotive applications alloys with melting point higher than 183°C will be needed.

Quarternary alloys might present real difficulties in terms of consistent powder's manufacturing especially for very fine ones.

Let us have a look at the different candidates :



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We have listed the pro's and con's of six different alloys :

96.0 Sn/4Ag 221°C

- Adequate wetting behaviour and strength
- Is already used in Electronics ; so a good knowledge is available in various applications
- Good thermal fatigue properties compared to Sn/Pb
- Forms an uniform microstructure and exhibits good microstructural stability, when soldered to copper base metal
- Limited solubility of Ag in Sn brings a better resistance
- Alloy already used for specific application (eg. Automotive)

Sn/Cu 0.7 227°C

- for high temperature applications required by automotive industry
- low cost
- specific for wave soldering

95.5 Sn/4.0 Ag/0.5 Cu 217-219°C

- Ideal for high operating temperatures up to 175°C
- Wetting is reduced on Cu when using traditional fluxes . flux adaptation
- Soldering under nitrogen improves wettability
- Addition of copper reduces the copper dissolution rate and accordingly the intermetallic growth rate (Cu₆Sn₅) at the interfaces as compared with SnAg or SnAgBi alloys ; it also lowers the melting point compared to Sn/Ag

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91 Sn/9Zn

- Fast oxidation and corrosion due to zinc
- Storage problem
- Poor wettability

The reaction of zinc with organic part in solder paste makes it a poor candidate with the present state of art but studies are actively going on especially in Japan.

91.8 Sn/3.4 Ag/4.8 Bi 200-216°C

- Bismuth alloys decreases solidus temperature
- Good wetting
- Bismuth increases joint strength, better fatigue resistance
- NCMS (National Center for Manufacturing Sciences) Lead-free Solder Project reported very good thermal fatigue resistance on OSP printed circuit boards
- Cost and relative scarcity of bismuth might be a problem
- In presence of lead, fragile intermetallic (melting point : 96°C) will develop; so lead finish components cannot be used with this alloy.
- Bismuth toxicity is still discussed, although it is thought to be lower than Ag or Cu.

90 Sn/2.0 Ag/7.5 Bi/0.5 Cu 198-212°C

- > 5% Bi leads to small DSC (Differential Scanning Calorimetry, method to determinate the melting and solidification temperature) peak near 138°C :
 - binary eutectic Sn/Bi at 138°C
 - ternary eutectic Sn/Ag/Bi at 136,6°C
 - same remarks as above

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PROMOSOL CONCLUSION

- Sn/Ag4/Cu0,5 is a serious candidate ; this alloy is a good compromise and it is patent free.
- But the problem of higher temperature compared to traditional alloys has to be considered as well as compatibility with PCBs and components.
- Research has to be continued on thermal stress of components, reliability of solder joint and about intermetallic formation on the different PCB finishes : Au, Ni, etc.
- Other alloys based on bismuth, antimony, might appear interesting in the coming year for specific applications.

OTHER ASSOCIATIONS RECOMMANDATION :

Several organisations are giving recommendations for lead-free alloys :

- NEMI, US
Solder recommendation for reflow : Sn 3.9% Ag 0.6%Cu (also recommendation of ZVEI, German Electronic Association).
Solder recommendation for wave : Sn - 0.7Cu for wave
No bismuth
- ITRI/SOLDERTEC
General purpose solder suitable for SMT, wave and hand soldering
Sn (3.4 - 4.1)% Ag (0.45 - 0.9)%Cu
additionnally
Solder recommendation for reflow : Sn Ag Bi types
Solder recommendation for wave : Sn Cu based alloys
- IPC
Solder recommendation for reflow :
 - SnAgCu (Exact composition to be determined in the next 2 years)
 - SnAgBi for specific SMT applications, for both alloys work underway to compile additional reliability data (to be completed in 2002)Solder recommendation for wave :
 - SnCu 0.7

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6. PATENTS

A huge number of patents especially for Sn Ag Cu :

- Senju/Matsushita (Sn Ag 3-5 Cu0.5-3)
JP 50 50 289, March 1993,
only for Japan, high temperature solder
Seems to precede the one below
- Iowa/Ames laboratory (Sn Ag 3.5-7.7 Cu 1.0-4.0)
US 5 527 628 July 1993, only for US,
Licence to several solder suppliers, Sn Ag Cu ternary eutectic solder
- Publication Gebhardt 1959 (Sn Ag 4 Cu 0.5)
Believed to be patent free
- Several other patents on Bi and Zn containing alloys

**CHECK WITH YOUR OWN LEGAL COUNCIL
especially for patent concerning the USE...**

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7. POSITION ON LEAD-FREE OF DIFFERENT ASSOCIATIONS

- Orgalime
- IPC
- ITRI / Soldertec

Promosol actively participates to Orgalime's working groups.
Promosol is an active member of IPC and ITRI.

7.1 ORGALIME

- Orgalime is a federation of European engineering industries : electrical, ELECTRONIC, mechanical, metal working, etc.
- Founded in 1954
- 25 national trade federations or associations
- 100 000 COMPANIES / 6.5 million people employed
- 850 BILLION €/ 35 % of EU manufactured EXPORT

ORGALIME'S GENERAL VIEWS ON THE WEEE DIRECTIVE

- It should FOCUS on RECYCLING
- It should be PRACTICAL TO IMPLEMENT
- The SCOPE should be LIMITED :
 - Exclude professional equipment (not present in municipal waste)
 - Focus on large household appliances, IT products, TV's
- It should MINIMIZE COST with market driven instruments

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- FINANCING for equipment from private last owners/ users
 - COLLECTION COST = PUBLIC AUTHORITIES
 - PICK UP COST of sorted products = PRODUCERS
- FINANCING for equipment from non private last owners COST TO BE AGREED by business partners involved
- VISIBLE FEE to handle historical waste

ORGALIME'S VIEWS ON THE PROPOSED LEAD BAN

- LEAD RECYCLING is FEASIBLE
- RISK ASSESSMENT should always be conducted before banning a substance
- TECHNICAL PROBLEMS to be solved before deciding on any dates :
 - Reliability / Compatibility issues
 - Standardisation process
 - SME's adaptation
 - Lead free only one of many technological issues
- The longer the TRANSITION PERIOD, the lower the COST (500/600 M€/year) ;trade issues are also tackled in a better way
- VOLUNTARY industry initiatives should be recognized and encouraged

FOR MORE INFORMATION (POSITION PAPER, TECHNICAL FICHES ON SUBSTITUTION, etc.) GO TO :

www.orgalime.org

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7.2 IPC POSITION ON LEAD-FREE

7.2.1 IPC

IPC is an association which group the electronics industries (designers, board manufacturers, assembly companies, suppliers and EOM) since over 40 years.

IPC technical programs provide you following information :

- Standards to facilitate communication between suppliers and customers
- Guidelines with current industry position on a wide range of subjects
- Research to solve industry problems
- Correlation of industry test methods
- New developments in interconnection technology

The association develops and approves standards and specifications.

7.2.2 Position on Lead-Free Electronics, adopted by the IPC board of directors, April 1999 :

“The US electronics interconnection industry, represented by the IPC, uses less than 2% of the world’s annual lead consumption. Furthermore, all available scientific evidence and US government reports indicate that the lead used in US printed wiring board (PWB) manufacturing and electronic assembly produces no significant environmental or health hazards.

Nonetheless, in the opinion of IPC, the pressure to eliminate lead in electronic interconnections will continue in the future from both the legislative and competitive sides. IPC encourages and supports research and development of lead-free materials and technologies. These new technologies should provide product integrity, performance and reliability equivalent to lead-containing products without introducing new environmental risks or health hazards. IPC prefers global rather than regional solutions to this issue, and is encouraging a coordinated approach to the voluntary reduction or elimination of lead by the electronics interconnection industry”.

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7.2.3 Specific work of IPC :

To develop a roadmap to lead-free through limited choice of alloys, compatibility study with PCB and components finishes, standardisation efforts (to be completed in 2004), components adaptation (260°C), etc. : see alloy recommendation page 11.

FOR MORE INFORMATION (especially the lead-free forum) GO TO :

www.ipc.org
www.leadfree.org

7.3 ITRI / SOLDERTEC

ITRI (The International Tin Research Institute) was founded in 1932 and spent much of that time working in soldering technology. Lead-free solders research has been active since around 1990.

SOLDERTEC represents the recent consolidation of lead-free activities and is being launched as a new centre of excellence by ITRI in response to the needs of the electronic industry.

Objectives :

- Pioneer research progress especially on mechanical reliability
- Evaluate new alloys and materials : see alloys recommendation page 11
- Standardise lead-free environmentally friendly assembly

FOR MORE INFORMATION GO TO :

www.itri.co.uk
www.lead-free.org