# A Study of Lead-Free Solder Alloys

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**ABSTRACT**:
With the ongoing concern regarding environmental pollutants, lead is being targeted in the electronic assembly arena. This paper highlights lead-free solders and the different combinations of elemental makeups.

**INTRODUCTION**:
The study of lead-free solder has become a hot subject over the past few years. Government regulations are becoming more strict, and handling of waste materials are becoming more regulated. Now is the time to take a serious look at alternative materials for making electrical interconnections. The history of government regulation suggests that targeted materials often become the subject of a ban within a certain timeframe; lead in paint, lead in plumbing, and lead in gasoline have all been eliminated thus far. There is no reason to believe that lead in solder will not meet the same fate.

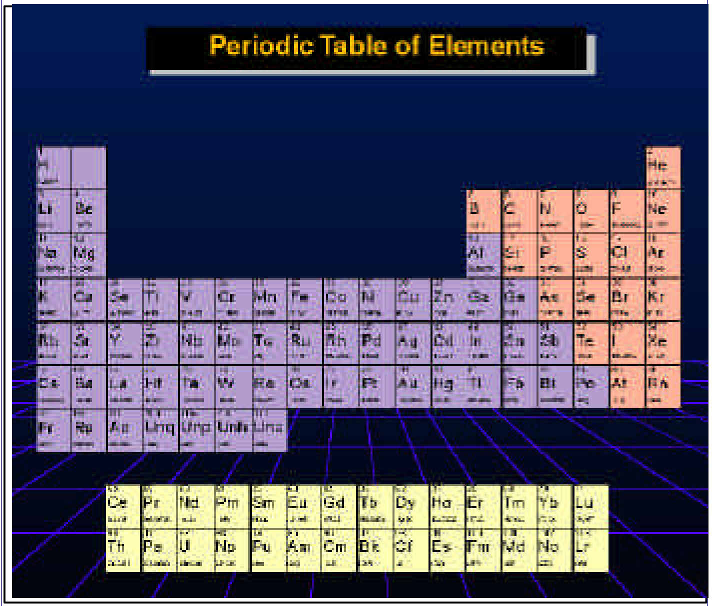
**Why Lead Free?**

1. ***Pending Legislation***
   - WEEE Directive
   - Lead Tax
   - Bill HR-2479
2. ***Liability Risk***
   - Worker Exposure
   - End Product Disposal
3. ***Manufacturing Waste***
   - Wave Soldering
   - Surface Mount
   - Hot Air Solder Coat
4. ***Water Treatment***
   - OA Process Water
   - General Process Water

*(Figure 1).*

Due to potential litigation, liability risk is the primary reason for economic concern. If a worker is not properly monitored and is exposed to an elevated lead level, the lead could be carried home on his clothing, leading to contamination in the home, which is an area of concern and is a potential problem.

The next concern is waste treatment in manufacturing. There are all types of wastes generated from a soldering operation: solder, solder dross, wipes and packaging containers. Some have a recycling value and others have to be disposed of as hazardous waste. On the process side, there are effluent wastes during cleaning, where solder balls and some heavy metal salts are washed off. In general, electronic manufacturing is a clean and safe environment to work in; however, governments still are targeting the removal of lead from solder, due to lead pollutants generated in other industries. The reason for the recent concern is that a great number of products are being disposed of in landfills, products such as televisions, radios, games and other products available to the consumer, and potential solder from these products is leaching into municipal water supplies. In response to the new wave of regulations, the following list of desirable attributes has been compiled for lead-free solder.



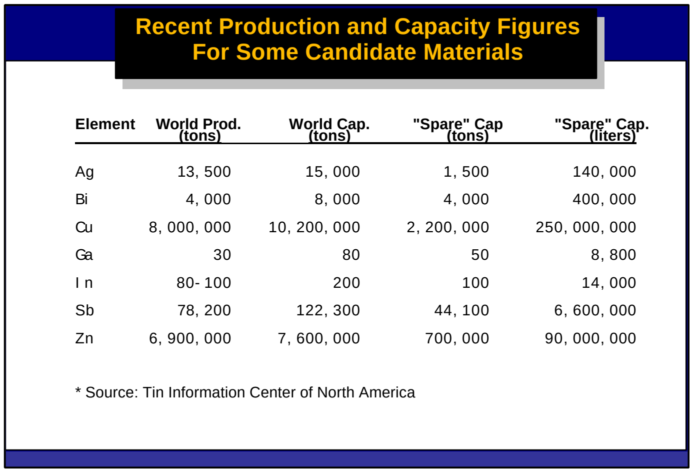
*(Figure 2)*

1. The selected element will have no negative environmental impact now or in the future.
2. Sufficient quantities of base materials must be available now and in the future.
3. Melting temperatures similar to 63/37 tin/lead, preferably below 200°C.
4. Equal or similar thermal and electrical conductivity.
5. Adequate joint strength and thermal fatigue resistance.
6. Easy repairability.
7. Low cost.
8. Compatibility with existing processes.

**EXPERIMENT:**

Starting with the above list, we began to search for the best alloy. Looking at the periodic table of elements, the choices of acceptable elements dwindles rapidly (*see figures 3 & 3A*).

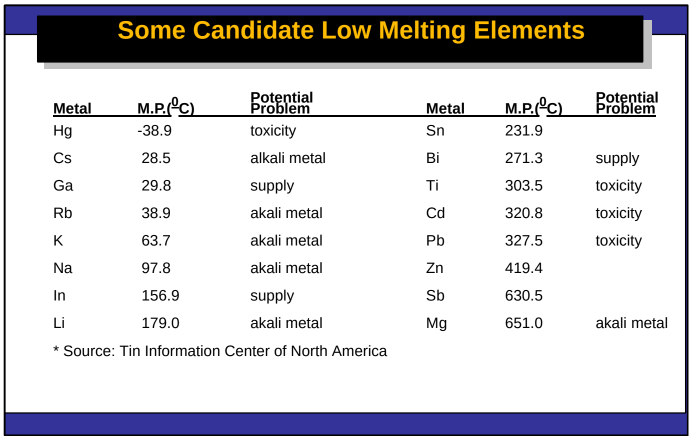
Silver is in adequate supply but has a cost disadvantage. Bismuth poses a potential supply problem since it is a by-product of lead mining, and also has embrittlement problems. Bismuth is also a poor conductor, both thermally and electrically. Concerning cadmium, toxicity is the leading reason not to use this element.


**Recent Production and Capacity Figures For Some Candidate Materials**

| Element | World Prod. (tons) | World Cap. (tons) | "Spare" Cap (tons) | "Spare" Cap. (liters) |
|---|---|---|---|---|
| Ag | 13, 500 | 15, 000 | 1, 500 | 140, 000 |
| Bi | 4, 000 | 8, 000 | 4, 000 | 400, 000 |
| Cu | 8, 000, 000 | 10, 200, 000 | 2, 200, 000 | 250, 000, 000 |
| Ga | 30 | 80 | 50 | 8, 800 |
| I n | 80- 100 | 200 | 100 | 14, 000 |
| Sb | 78, 200 | 122, 300 | 44, 100 | 6, 600, 000 |
| Zn | 6, 900, 000 | 7, 600, 000 | 700, 000 | 90, 000, 000 |

* Source: Tin Information Center of North America

*(Fgure 3)*

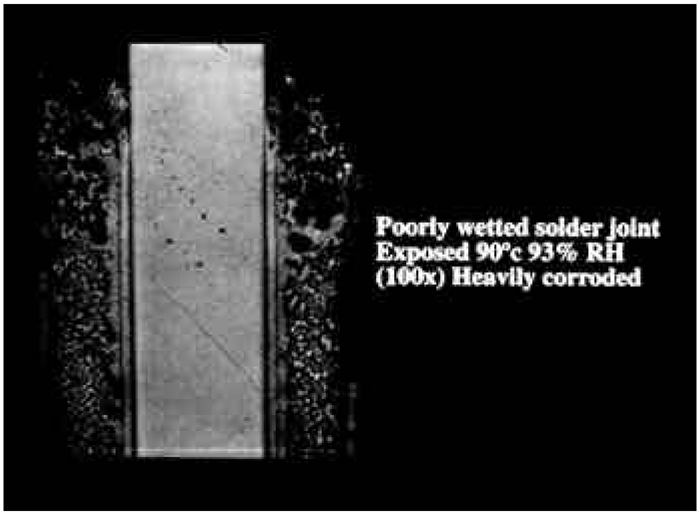

**Some Candidate Low Melting Elements**

| Metal | M.P.($^0$C) | Potential Problem | Metal | M.P.($^0$C) | Potential Problem |
|---|---|---|---|---|---|
| Hg | -38.9 | toxicity | Sn | 231.9 | |
| Cs | 28.5 | alkali metal | Bi | 271.3 | supply |
| Ga | 29.8 | supply | Ti | 303.5 | toxicity |
| Rb | 38.9 | akali metal | Cd | 320.8 | toxicity |
| K | 63.7 | akali metal | Pb | 327.5 | toxicity |
| Na | 97.8 | akali metal | Zn | 419.4 | |
| In | 156.9 | supply | Sb | 630.5 | |
| Li | 179.0 | akali metal | Mg | 651.0 | akali metal |

* Source: Tin Information Center of North America

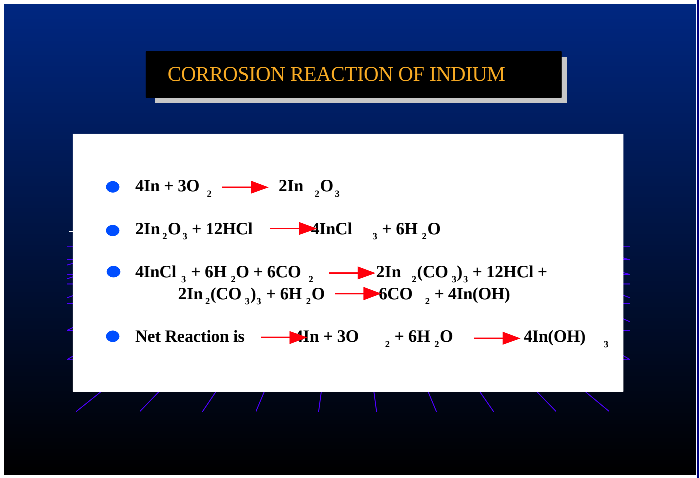
*(Figure 3A)*

With copper, there is plenty of supply, and it is soluble in tin. In low percentages, copper works well. There is a long history of tin alloys containing copper. Gallium supply and costs are the main reason not to use it, as well as its brittleness. The cost, inadequate supply, poor resistance to corrosion and rapid oxide formation during melting all eliminate the element indium.



*(Figure 4A)*

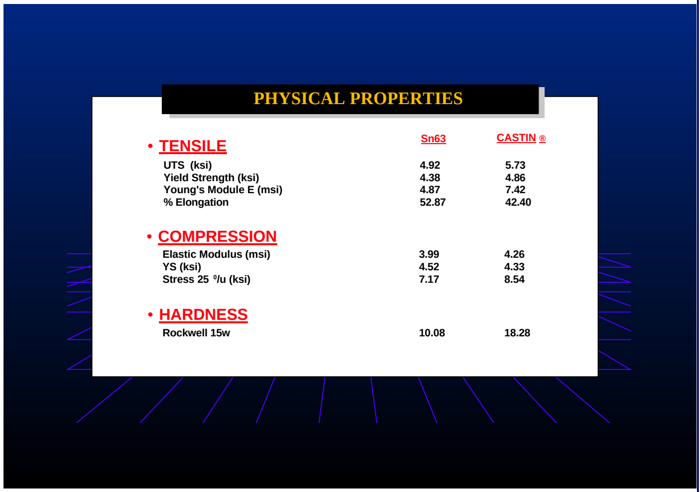
*Figure 4A* shows a solder fillet formed with an indium eutectic, aged at 90°C and 93% relative humidity. The corrosion of indium can be seen as the dark areas on the solder joint. The remaining area is the tin. The reaction that has occurred is seen in *figure 4B*. For the most part, indium is safe if kept in low humidity conditions, or if it is conformally coated. Antimony has an adequate history and supply to be a viable solder additive. Tin is the base of solders, toxicity is low and supply is adequate. Zinc is in adequate supply, but has oxidation problems and also causes solder to become brittle. This oxidation problem creates an issue with existing automatic soldering equipment.


CORROSION REACTION OF INDIUM

- $4In + 3O_2 \longrightarrow 2In_2O_3$
- $2In_2O_3 + 12HCl \longrightarrow 4InCl_3 + 6H_2O$
- $4InCl_3 + 6H_2O + 6CO_2 \longrightarrow 2In_2(CO_3)_3 + 12HCl +$
  $2In_2(CO_3)_3 + 6H_2O \longrightarrow 6CO_2 + 4In(OH)$
- Net Reaction is $\longrightarrow 4In + 3O_2 + 6H_2O \longrightarrow 4In(OH)_3$

*(Figure 4B)*

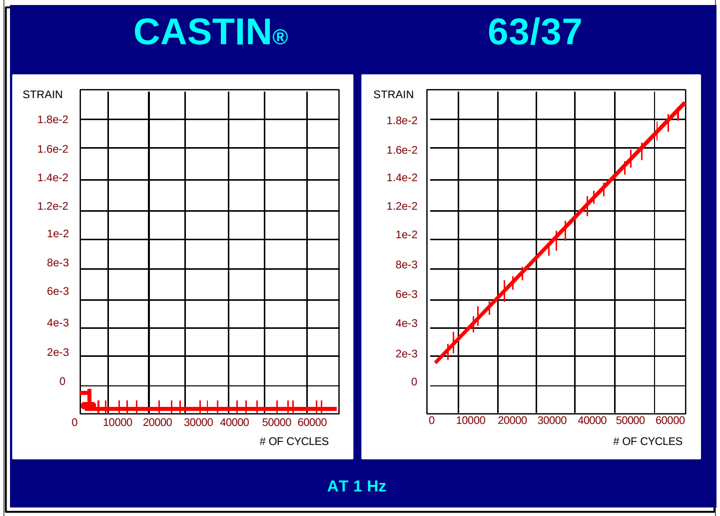
After review of acceptable elements, and a good deal of testing, the CASTIN alloy was developed. CASTIN is a combination of copper, antimony, silver and tin. The nominal composition is 96.2% tin, 2.5% silver, .8% copper and .5% antimony. The grain structure is much coarser than the existing 63/37 alloy. This would lead one to believe that the alloy would be more brittle; however, this is not the case. The melting point of CASTIN is 216°C. The alloy was tested to compare with the eutectic 63/37. The initial test showed that CASTIN was superior to the 63/37 (*figure 5*).


PHYSICAL PROPERTIES

| | Sn63 | CASTIN ® |
|---|---|---|
| • **TENSILE** | | |
| UTS (ksi) | 4.92 | 5.73 |
| Yield Strength (ksi) | 4.38 | 4.86 |
| Young's Module E (msi) | 4.87 | 7.42 |
| % Elongation | 52.87 | 42.40 |
| • **COMPRESSION** | | |
| Elastic Modulus (msi) | 3.99 | 4.26 |
| YS (ksi) | 4.52 | 4.33 |
| Stress 25 $^0$/u (ksi) | 7.17 | 8.54 |
| • **HARDNESS** | | |
| Rockwell 15w | 10.08 | 18.28 |

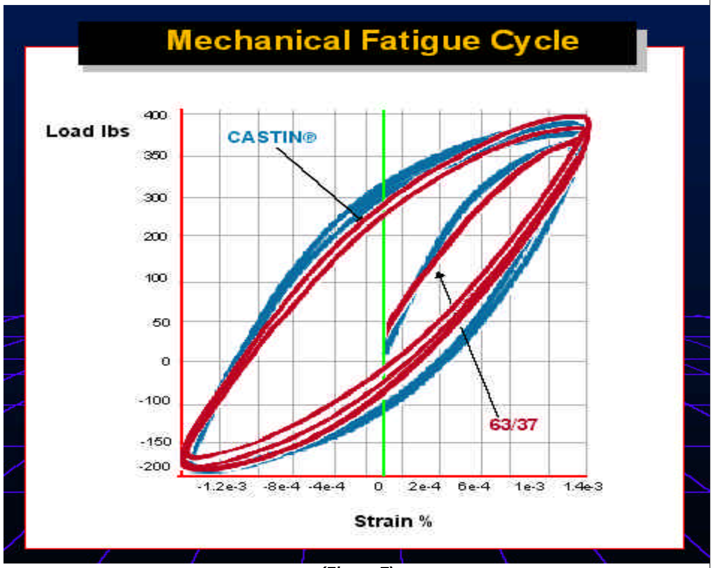
*(Figure 5)*

The test was then changed to mimic thermal stresses. This showed more compatible results that led to the assumption that CASTIN would be more adaptable to a wide range of stresses than 63/37 (*figure 6*).



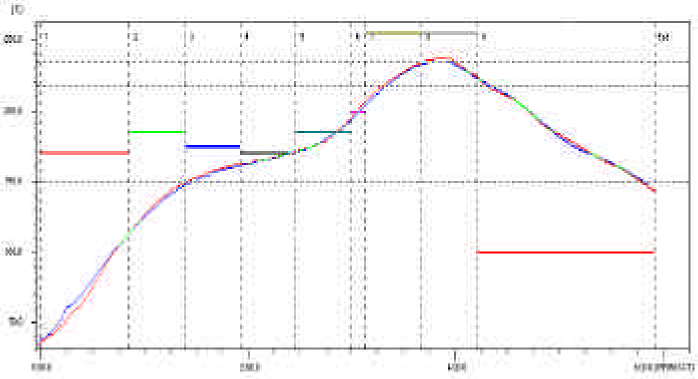
***(Figure 6)***

When the curves of the mild stresses are overlaid, they are almost identical (*figure 7*).



***(Figure 7)***

CASTIN is almost a drop-in substitution for 63/37 in most soldering applications. When used in a wave soldering process, the identical 250°C-260°C pot temperature is used. When implemented in surface mount, reflow profiles need to be slightly hotter; a spike of 235°C is recommended (*figure 8*), with a time above 216°C 30-45 seconds. When soldering on a high-density board, nitrogen is recommended to retard thermal problems with the flux and board materials. When hand soldering, the iron should be set at 750°F.



The process of solder coating of circuit boards with CASTIN has shown some promise. The early indications show that this alloy has flatter pads and a more uniform coating ability. Not all joints are going to appear bright and shiny, since the alloy has a coarser grain structure than tin/lead. CASTIN exhibits a whiter, slightly frostier joint, dependent on cooling rates. The faster the cooldown, the shinier the joint. PCBs surface coated with CASTIN have storage and wetting characteristics similar to 63/37 HASL coating. The solder coating machine used in one test was a horizontal leveler made by Teledyne Halco. Pot temperature had to be increased to 530°F. The fillet formation and wetting angle was similar to 63/37. Based on this test, CASTIN meets all the requirements of a lead-free alloy for use in electronic assembly.

## CONCLUSION:

Eventually, there will be an overall movement to eliminate lead from all aspects of soldering, board coating, and component terminations. As with any new manufacturing product or process, certain criteria have to be changed in order to facilitate proper inspection of this alloy for reasons of quality control.

CASTIN is the best trade-off in terms of temperature, physical properties and ease of application. The combination of tin, silver, copper, and antimony is processable. Component tinning, bare board coating, surface mount assembly, and wave soldering are all achievable with CASTIN.

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