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# The Importance of Lead-Free Electronics Processes

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# The Importance of Lead-Free Electronics Processes

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## Summary

Our proposed study will identify methods for eliminating lead-bearing materials in the set of operations, namely electronic assembly, responsible for much of the lead waste generation at many DOE sites. Regulatory and social drivers for lead elimination will be analyzed, and the economic payback period and return on investment estimated. At Lawrence Livermore National Laboratory (LLNL), the payback period for implementing lead-free processes is about two years.

## Final Abstract

The Environmental Protection Agency (EPA) is placing increased importance on reducing lead-bearing wastes. Toward this end, the EPA has proposed that reporting thresholds for the Toxic Release Inventory (TRI) be lowered to ten pounds of lead content per year. The U.S. electronics industry is also placing a high priority on lead reduction or elimination. The Association of Connecting Electronics Industries, which is the major trade association for electronics packaging, including printed circuit (PC) board manufacturers, has launched a lead-free initiative that seeks to eliminate lead in solder, in PC board etch resists and finish coats, and as "tinning" for component leads. Europe and Japan are also considering various regulations that will phase out lead in the next few years.

In response to EPA and electronics industry priorities, the DOE complex will soon need to address lead phase-out issues. LLNL is now developing approaches for eliminating lead from PC board etch-resist operations. LLNL is seeking funding to continue this work and to eliminate other major uses of lead in electronics operations—particularly in hot-air solder leveling as a PC board finish, and tin–lead solder for component assembly operations. LLNL seeks to take a proactive leadership role in the DOE complex with respect to the elimination of lead.

The envisioned lead-elimination project will be approximately two years in length. During the first year, lead-free etch resists and finish coats will be analyzed, and the best ones identified for electronics assembly and PC board fabrication. During the second year, lead-free solders will be examined and tested for compatibility with alternative PC board finish coats.

Cost avoidance opportunities resulting from lead elimination include avoided TRI reporting expenses and reduction in PC board fabrication-related wastes through implementation of more efficient fabrication processes. Integrated Safety Management considerations are also relevant. Handling lead-bearing alloys poses safety issues to employees as well as possible environmental impacts. This is especially true during high-temperature, molten solder operations in which fumes may be inhaled, or during wave solder equipment-cleaning operations, in which lead-bearing dust may be generated. The elimination of lead makes the operations considerably safer.

## Keywords

lead, Pb, toxicity, Toxic Release Inventory (TRI)

## Main Text

## Hazards of Using Lead

The hazards of human exposure to lead have been well known for many years. Chronic lead exposure can result in neurological damage, irreversible renal damage, and adverse reproductive effects.[1] Lead is toxic to most living things.[2] Several lead compounds, including lead acetate, lead chromate, lead phosphate, and lead subacetate, are possible carcinogens.[3] Volatile organic lead compounds may generate vapors that are toxic when inhaled.

Lead is a teratogen that can cause fetal malformation, a mutagen that can affect both sperm and eggs, and a reproductive toxin that can impair fertility. Acute, high-level poisoning with lead can result in encephalopathy with seizures, coma, and, in severe cases, death. In many cases, the effects of lead poisoning are irreversible, or only partially reversible, and can lead to permanent impairment of the function of the brain, kidney, nervous system, or reproductive system.

Despite the risks, lead remains a commonly used industrial metal, especially in the electronics sector. It is a major component of most of the solder used for electrical interconnections. Most of the printed circuit (PC) boards manufactured in the world use lead-bearing finish coats. It is also still commonly employed as an etch resist, to protect copper circuitry during PC board etching operations.

Lead employed in electronics fabrication presents significant occupational and environmental risks. Lead fumes from soldering operations, hot-air solder leveling (HASL) procedures for PC board finishing, and other processes can result in inhalation exposures to workers. Operations that generate lead dust pose the greatest risks of worker exposure. Lead dust is often generated during cleaning and maintenance operations of a wave soldering machine. For example, brushing or scraping away solder "dross" that builds up on equipment surfaces generates lead-bearing dust and can expose personnel in the area, especially if they are not wearing proper protective equipment.

Most electronic devices are ultimately disposed of in municipal landfills as nonhazardous solid waste. Much of this equipment, such as computers, has usable lifetimes of only several years. Once in a landfill, there is an undetermined risk of lead leaching out and entering ground and surface water supplies. Much controversy exists regarding the real dangers posed by such discarded equipment. Lead users often claim that typical lead compounds that would be found in landfills have extremely low solubilities, and thus do not present significant risks to groundwater supplies through leaching processes. Whether true or not, government and market pressures are starting to change the ways that electronics equipment is being made. Many millions of dollars

[1] U.S. EPA, *Lead Health and Environmental Effects,* Report No. 121, 1980.
[2] Klaassen, C. D., *Casarett and Doull's Toxicology, the Science of Poisons,* Fifth Edition, McGraw-Hill, 1996, p. 703.
[3] LLNL's Health & Safety Manual, Section 21.20, "Safe Handling of Lead and Lead Compounds in General Industry and Construction Operations," 1999.

are currently being spent in Europe and Japan, and more recently in the U.S., on lead-free manufacturing techniques for electronics components.

## Regulatory and Market Drivers for Finding Alternatives to Lead

For several years, Europe and Japan have recognized the need to reduce environmental exposures to lead. The European Commission has proposed a directive that would phase out the use of lead and other highly toxic industrial metals by 2004 in electronic and other applications. The European Commission is also examining a directive aimed at the electronics industry entitled the Waste in Electronic and Electrical Equipment Directive. Denmark in particular is accelerating this process and has proposed actions against lead for 1999. The industrial community is leading phase-out efforts in Japan. Nortel, for instance, produced the first lead-free telephone in 1997. Panasonic developed a lead-free soldering line for its MiniDisc player in 1998.

The U.S. Environmental Protection Agency (EPA) has recently stated that lead and lead compounds present major environmental risks. Because lead does not biodegrade, it remains available in the environment as a hazard. Data show that lead concentrates in aquatic organisms and humans, according to Maria Doa, chief of the EPA TRI branch.[4] Even small amounts can bioaccumulate and result in adverse effects. The Centers for Disease Control and Prevention estimates that almost one million children still suffer from elevated blood levels of lead largely from exposure to lead-contaminated dirt, despite actions taken in the 1970s and 1980s to limit lead releases. According to 1997 TRI data, 58 million pounds of lead were released to land, either on industrial sites or in offsite waste disposal areas.[5] Although most of the contaminated soil would not come into contact with children, the perception of the EPA is apparently that if this much lead waste is transported and eventually disposed of in the ground, then risks of human exposure are unacceptably high. Land that is now an industrial site, brownfield, or disposal area may one day be a residential area or school site.

To reduce such risks, the EPA is proposing that thresholds for TRI reporting of lead wastes be radically lowered. Currently, only facilities manufacturing or processing more than 25,000 pounds of lead, or using more than 10,000 pounds of lead and lead compounds annually, are required to report their releases to air, water, and land. In August 1999, the EPA proposed to lower that threshold to 10 pounds per year.[6] Under the new reporting threshold, the EPA estimates that 15,000 additional TRI reports will need to be developed, with a total price for increased reporting of $116 million for the first year and $60 million annually thereafter. [7]

U.S. industry, especially the electronics industry, is taking lead issues seriously. Even though the U.S. electronics industry questions whether the lead it uses poses a significant health hazard, the Association of Connecting Electronics Industries (the IPC), which is the major trade association for electronic packaging (including PC board manufacturers), has stated the opinion that “the pressure to eliminate lead in electronics interconnections will continue in the future from both the legislative and competitive sides.” As a result, the “IPC encourages and supports research

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[4] *Environmental Science and Technology* staff, "EPA Watch," 33(19), October 1, 1999, pp. 407a–408a.
[5] *Environmental Science and Technology* staff, "EPA Watch," 33(19), October 1, 1999, p. 408a.
[6] *Federal Register*, 1999, 64(148), 42,221–42,243.
[7] *Environmental Science and Technology* staff, "EPA Watch," 33(19), October 1, 1999, p. 408a.

and development of lead-free materials and technologies. The new technologies would provide product integrity, performance, and reliability equivalent to that of lead-containing products without introducing new environmental risks or health hazards."[8] Toward this end, the IPC has launched a lead-free initiative and convened a lead-free summit meeting for sharing information regarding lead-free technologies. Many U.S. companies have already made major efforts to identify and test alternatives to lead-bearing solder and HASL PC board finishes.

## How Should the DOE Respond?

It is clear that efforts to remove lead from electronics manufacturing are growing. If the EPA is successful in lowering the TRI reporting threshold, the costs for tracking and documenting lead use and waste generation are expected to rise significantly at all DOE laboratories and in industry. Increased costs can be avoided, however, if the use of lead in DOE laboratory operations is eliminated. Our proposed study will identify methods for eliminating lead in the set of operations that is responsible for much, or most, of the lead waste generation at many DOE sites, namely, electronics assembly.

Electronics assembly includes various processes that use lead. At LLNL, this class of operations includes PC board fabrication and finishing, soldering of components to the PC board, and assembly and maintenance of electronics equipment. Opportunities for eliminating lead in each of these processes are discussed below.

## Approaches for Getting the Lead Out

Manufacturing a PC board consists of a series of steps that render a composite board sheathed in copper foil into an intricate array of circuitry, plated-through holes, and areas onto which electronic components are to be soldered. Figure 1 shows a typical series of steps. In etching out the circuitry, etch-resistant layers of metal are deposited onto areas of the copper that are to be kept, while the remainder is dissolved. The etch-resistant layers are typically composed of either tin or tin–lead, although nickel and other metals are sometimes used. Although many tin–lead etch resists have been replaced by other, less-hazardous metals, work still needs to be done in this area to totally eliminate the need for using lead.

A major use of lead is in the finish coatings deposited onto solderable surfaces on areas of a PC board where components will be attached. The dominant board finishing method is hot-air solder leveling (HASL), in which a layer of tin–lead is applied in a molten state and leveled as much as possible. This method is problematic not only because of the lead wastes generated, but also because of quality issues. It is difficult for HASL to provide the narrower and narrower circuit lines and spaces between lines that industry requires,[9] and to offer the smooth, level surfaces needed for surface mounting of small components. Thus, there are two motivations for replacing HASL with an alternative finish surface.

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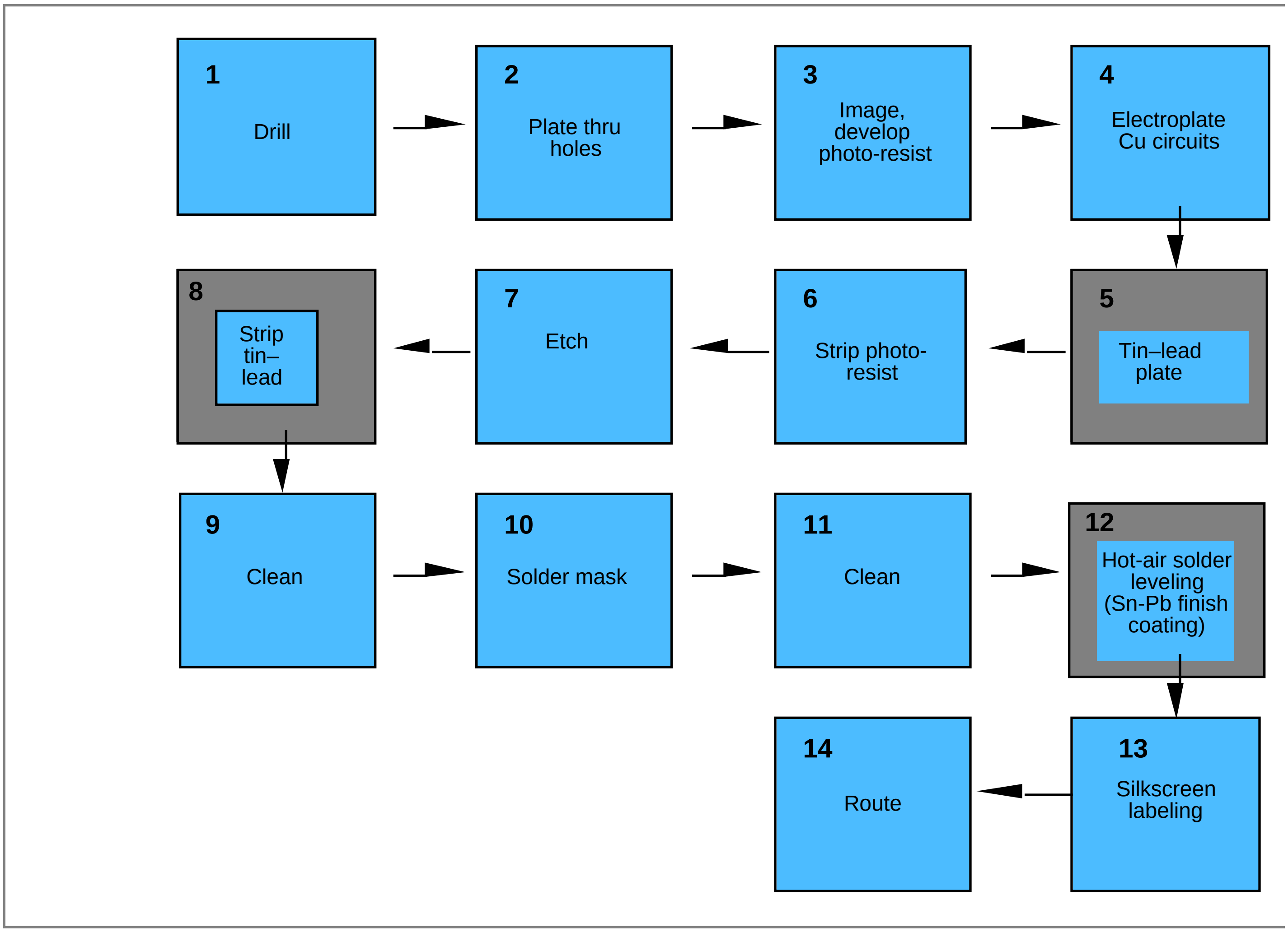
8 *IPC Review* staff, "IPC Works!" 40(6), June 1999, p. 17.

9 There is at present a need for 3-mil-wide (0.003-in.) lines and spaces; in the near future, it is predicted that 1-mil lines and spaces will be required.

**Figure 1. Typical PC board fabrication operations.**



The industry-standard solder is an alloy made of 63% tin and 37% lead. Its characteristics are well known from over a century of use. In identifying alternatives, the ability to bond both to standard HASL PC board finishes and to the new substitutes for HASL must be thoroughly examined.

## Alternative Etch Resists

Many industry shops have already eliminated lead in the etch resist operation by using a pure tin etch resist. This method is suitable for many applications and may be the best approach for DOE shops, although alternatives need to be examined as well. LLNL's PC board shop has been testing a “sacrificial plating” approach in which no etch resist is used; instead, some copper is etched off the circuit lines when the base copper is dissolved. This method is suitable for the small-volume parts runs that are done at LLNL, although the method puts more copper into the waste stream than if an etch-resistant layer were used on top of the copper traces. Problems with the copper circuit lines etching evenly may also result from the sacrificial etching method.

Another option being examined at LLNL is to use nickel as an etch resist. Nickel deposited from a sulfate bath has been shown to be quite resistant to the ammoniated copper chloride etchant that is the industry standard, although there are concerns about the brittleness of nickel and how it would stand up to thermal cycling. Thin layers of gold have also been used.

**Combining Etch Resist and Finishing Operations**. LLNL has experimented with combining the etch resist step with the finish coat. This operation could be accomplished by leaving the nickel layer on the board after etching and using it for a finish coat as well. Although preliminary work has been done on this and other approaches with limited internal funding, more extensive funding is required if alternatives are to be tested in detail.

## Alternative PC Board Finishing Materials

A PC board finish must protect solderable surfaces for up to a year, preventing them from developing oxide layers that would inhibit soldering. Because of the problems with HASL, the dominant industry method, many possible alternative finishes have been released, including deposits of gold, gold over nickel, silver, tin, palladium, and various organic coatings. The characteristics of such coatings vary widely with respect to performance and cost, and much work needs to be done to identify the best alternatives for DOE applications. For instance, gold over nickel provides a long-lasting solderable finish, but the use of too much gold drives up the price of the coating sharply and can also embrittle the solder joints that will be deposited. Tin provides a far cheaper finish, but its shelf life is thought to be shorter, perhaps only as long as three months. Organic coatings are the cheapest of all, but they have shelf life issues as well. Table 1 lists the lead-free finishes that appear to be promising candidates for alternatives to HASL, and that will be examined and compared in the proposed study.

Detailed analyses under a variety of conditions need to be performed to identify the best materials. Table 2 lists the tests that will be done on alternative coatings.

**Table 1. Lead-free PC board finishes.**

| |
|---|
| Immersion tin |
| Electroplated tin |
| Electroplated tin/bismuth |
| Castin (tin/silver/copper/antimony) |
| Immersion gold |
| Electroplated gold |
| Electroplated nickel |
| Immersion gold over electroplated nickel |
| Electroplated gold over electroplated nickel |
| Electroless gold over electroless nickel |
| Electroless palladium over electroless nickel |
| Electroplated palladium over electroplated nickel |
| Organic coatings |

**Table 2. Analyses of alternative coatings.**

| |
|---|
| Shelf-life determination |
| Effect on soldering performance |
| Thermal-cycling performance |
| Steam aging |

**Shelf-Life Determination.** After fabrication, PC boards may remain in storage for six months or a year before components are soldered to them. Some of the tin and organic finishes have been observed to deteriorate after as little as three months. Shelf-life estimates can be determined using a dry aging technique. In one variant of this test, boards are subjected to a temperature of 155°C for four hours, after which the finish is examined for signs of deterioration. There are many alternative tests, and no one test appears to have gained universal acceptance, although the 155°C test is often used. We plan to analyze the aged sample under a 500× optical microscope and by using scanning electron microscopy (SEM).

**Solderability**. Components must be solderable to a PC board after a finish coat is applied. In a solderability test, component bonding using standard tin–lead solder will be examined, and alternative solders will be analyzed later in the project. Solder bonding can be complex metallurgically. Sometimes, as in the case of HASL, the component is bonded to the finish coat itself. In other systems, the finish material vaporizes or mixes with the solder, and the bond is actually to the substrate material under the finish. Gold finishes, for instance, readily mix with tin–lead solder, resulting in the component bonding to the substrate. If too much gold penetrates the solder joint, problems can arise. It has been shown than if a tin–lead joint contains more than about 4% gold, it can embrittle. The problem may not be readily apparent, but could cause premature failure of the solder joint once the PC board has been put into use. X-ray diffraction on cross sections of PC boards will be used to determine solder joint compositions and to identify possible problems.

**Thermal Cycling**. When examining alternative finish coats, it is necessary to subject them to the extremes of temperature that electronic equipment may experience. Various thermal cycling regimens are used in industry. We will employ a method developed by Sandia Livermore to simulate the extremes that aircraft might experience, which involves cycling one hundred times between –55°C and +110°C.

**Steam Aging**. High-temperature and high-humidity tests greatly accelerate corrosion growth and are excellent indicators of problems that may arise in the finish coat over the lifetime of PC boards. We will use a testing regime involving a temperature of 93°C at 95% relative humidity for eight hours. Although there is no single industry standard, this is one of the typical analysis approaches.

## Alternative Solders

For many years, 63% tin and 37% lead solder has been the dominant material joining electronic components to PC boards. Tin–lead solder provides a fairly easy-to-apply material for forming reliable solder joints, but its lead fraction presents health and environmental risks, as discussed earlier. When choosing a lead-free alternative to 63/37 solder, the factors that need to be analyzed include:

- Impacts of different melting points. Low-melting-point solders can weaken under normal operating conditions of equipment. High-melting-point solders can require temperatures that damage board components.
- Difficulties of using noneutectic solders, in which component separation may occur.
- Strength, elongation, and other physical characteristics.
- Aging characteristics.
- Characteristics of the intermetallic compounds formed.
- Compatibility with and solderability to the PC board finish.
- Ease of application, requirements for new soldering equipment, and extent of additional personnel training.
- Possible new health or environmental consequences introduced through use of the alternative solder and how they compare to risks from tin–lead solder.

Many alternative materials have been researched including nonsolder materials, such as metallic-particle-filled adhesives, conductive adhesives, and conductive polymers. Whereas some progress has been made in this area, nonsolder materials generally do not stand up to rigorous processing, economic considerations, and functional requirements for a lead-free alternative, especially for surface-mount and fine-pitch circuitry applications. Consequently, lead-free solder development has become a necessary industry effort.[10]

Of the myriad possible replacement alloys, many are eliminated because of temperature considerations. At present, the most cost-effective PC board material, a fiberglass and resin

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[10] Hwang, J. S., *Modern Solder Technology for Competitive Electronics Manufacturing,* McGraw-Hill, 1996, p. 483.

composite called FR-4, can only withstand an application temperature of up to 240°C. Considering the typical temperature variations over different parts of the board and its components under normal manufacturing conditions, the liquidus temperature of the solder alloy should generally not exceed 200°C.[11] Elements with high melting points must be excluded. Melting points cannot be low either, because the typical electronic product operates at 50° to 80°C; boards are often tested at temperatures of up to 125°C. Furthermore, unlike pure metals, the individual metals in most solder alloys melt at a range of temperatures, called the plastic range, or mush zone. Good solders are required to have a narrow plastic range.[12]

Other metals, such as mercury, thallium, and cadmium, are excluded as candidates because of their inherent toxicity. Alkali metals have low melting points, but are excluded because of their reactivity. Rare earth elements are not considered because of their limited supply. As a result of such considerations, lead-free solders generally consist of binary, ternary, quaternary, or even pentanary combinations of the metals in Table 3.

**Table 3. Candidate elements for lead-free solders.**

| |
|---|
| Indium |
| Antimony |
| Selenium |
| Silver |
| Tin |
| Copper |
| Bismuth |
| Nickel |
| Zinc |

Most of the alternate solder alloys being examined by the electronics industry have tin as one component. The reason is that tin interacts very strongly with a wide range of metals, forming good metallurgical bonds, a property that is critical for effectively joining two surfaces.[13]

It is not possible to test all combinations of the metals discussed above. Instead, the results of the National Center for Manufacturing Sciences (NCMS) down-selection process will be used. The three alloys that appeared to be most promising in the NCMS study will be examined for their applicability to LLNL electronics applications. These alloys include tin/bismuth, tin/silver/bismuth, and tin/silver. The filters used by NCMS for selecting these alloys over other candidates included considerations of toxicity, economics, availability, and various performance

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[11] Hwang, J. S., *Modern Solder Technology for Competitive Electronics Manufacturing,* McGraw-Hill, 1996, p. 488.
[12] Mahidhara, R. K., Frear, D. R., Sastry, S. M. L., Murty, K. L., Liaw, P. K., and Winterbottom, W. L., *Design & Reliability of Solders and Solder Interconnections,* The Minerals, Metals, and Materials Society, Pennsylvania, 1997, p. 65.
[13] Mahidhara, R. K., Frear, D. R., Sastry, S. M. L., Murty, K. L., Liaw, P. K., and Winterbottom, W. L., *Design & Reliability of Solders and Solder Interconnections,* The Minerals, Metals, and Materials Society, Pennsylvania, 1997, p. 65.

metrics, such as wettability, plastic range, liquidus temperature, and fatigue characteristics. Next, “manufacturability” tests were conducted that evaluated candidate alloys' performances in electronics assembly operations, followed by reliability tests that subjected the solder joints to extreme environmental conditions.[14]

To test the applicability to LLNL electronics fabrication processes of the three solder alloys down-selected by NCMS, they will first be employed to bond components to PC board test coupons, as follows.

**Solderability: Hand Soldering**. Components will be hand soldered, using typical soldering irons and other equipment, to plated-through holes in board coupons. Coupons will be finished either with HASL or with the alternative finishes that have scored highest in the previous part of this project. Each of the three candidate alternative solders will be used during the testing. A control group will also be prepared, using standard tin–lead solder. A variety of fluxes will be used on the coupons, including activated water-soluble, mildly activated, and no-clean fluxes. Holes will range from approximately 0.01 to 0.1 inch in diameter.

**Solderability: Surface Mount**. Components will be attached to pads on the coupons, using standard surface-mount equipment and an infrared oven. Coupons will be finished either with HASL, or with the alternative finishes that have scored the highest in the previous part of this project. Each of the three candidate alternative solders will be used in the testing. A control group will also be prepared, using standard tin–lead solder. A variety of fluxes will be used on the coupons, including activated water-soluble, mildly activated, and no-clean fluxes.

**Thermal Cycling**. After soldering, all coupons will be subjected to a simulation of extreme environmental conditions that might be encountered during operation of the electronic equipment. One hundred thermal cycles of temperature ranging from –55°C to +110°C will be used, then coupons will be cross sectioned and analyzed as described below.

After the environmental simulation is carried out, the integrity and quality of the solder joints will be analyzed.

**Functional Defect Analysis**. Optical microscopy will be used to note functional defects in the solder joints, such as voids, cracking, tendency for solder ball formation, and solder wetting/spreading behavior. Assessment will be based on general industry standards.

**Scanning Electron Microscopy Analysis**. SEM will be used to identify other possible problems with the soldering, in particular, evidence of component separation in the solder alloy, microcracking, voids, and delamination of the solder fillet.

**Bond Strength**. Calibrated pull tests will be conducted to determine integrity of the solder bonds.

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[14] National Center for Manufacturing Sciences, *Lead-Free Solder Project—Final Report,* NCMS Report 0401RE96, August 1997, pp. v, 2–1 through 2–14, 3–1 through 3–14, and 4–1 through 4–40.

The aim of the assessments is to find the best lead-free solder alternatives that are also compatible with the best alternative PC board finishes.

## Cost-Avoidance Opportunities

Cost-avoidance opportunities include avoided TRI reporting expenses as well as reduction in PC board fabrication-related wastes through implementation of simpler, more-efficient board fabrication processes. Preliminary estimates indicate that if lead waste can be kept below the EPA's suggested reporting threshold of 10 pounds per year, as much as $200,000 in lead tracking and documentation costs may be saved annually at LLNL. Electronics operations are one of the main sources of unrecycled lead wastes at LLNL, and elimination of lead in these processes could be key to keeping wastes below the reporting threshold.

Elimination of the HASL process and its attendant waste—mainly lead-bearing wastewaters from cleaning operations—may save another $50,000 annually. One of the final tasks of the proposed project will be to analyze in greater detail the actual cost avoidance that might be expected from removing lead in LLNL electronics operations.

## Project Schedule

Timelines are expressed in Table 4 as number of months after project kickoff. The envisioned project will be approximately two years in length.

**Table 4. Project schedule.**

| Task | Month started | Month completed |
|---|---|---|
| Etch resists: analysis of alternative technologies | 1 | 4 |
| Finishes: identification of best alternative | 1 | 12 |
| Solder: best alternative that is compatible with best finish alternatives | 13 | 20 |
| Cost-avoidance study | 16 | 20 |
| Final-report preparation | 20 | 22 |

## Conclusion

The use of lead-free processes has both human health and environmental advantages and may provide production advantages as well. The proposed project seeks to identify the best lead-free electronics fabrication methods for national laboratory operations, from the viewpoints of occupational and environmental risks, as well as overall performance. We have outlined an approach to identify the best alternatives for the three electronics fabrication operations in which lead is used: etch resist deposition, PC board finishing, and component soldering.

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