AN INVESTIGATION INTO THE USE OF LEAD-FREE SOLDERS IN THE ELECTRONICS INDUSTRY

by

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A dissertation submitted in part fulfilment of the HETAC requirements for the award of M.Sc. in Environmental Protection.

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September, 2002

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ABSTRACT

Tin-lead solder is the most common material used to join conductors in electronic assembly and has been used in electronics assemblies since the earliest days of radio. After many decades, highly engineered systems have developed. The mechanical, electrical and thermal properties of tin/lead solder, combined with its low material cost, have made it the material of choice for joining active and passive components. However, well publicised environmental and toxicity concerns have led to increased controls and legislation which aim to eliminate the use of lead. The major continuing use of lead is in automobile batteries. Lead used in electronic solder represents only 0.6% of the total use.

In Europe, the EU Waste Electrical and Electronic Equipment (WEEE) Directive will eliminate or severely restrict the use of lead in electronic manufacturing.

The environmental concerns and the new legal restrictions relating to the use of lead have initiated the search for acceptable alternate joining materials for electronics assembly. This dissertation reviews the physical, mechanical and potentially hazardous properties of lead-free solders compared with tin/lead solders. The performance of lead-free solders in electronics assembly is assessed and compared to common tin/lead solders. Fatigue testing results are reported for thermal cycling electronics assemblies soldered with lead-free compositions. The dissertation also includes a discussion on substitution availability and supply.

Acknowledgements

I would like to acknowledge the help and support afforded to me during the research and experimentation carried out in the course of this work. In particular I would like to thank my project supervisor Mr. Noel Connaughton, Work colleagues at Pulse Engineering, family and friends without whose support this work would not have been possible.

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1.0 Introduction

Leaded solders have been used in electronic applications for more than fifty years. Leaded solders have predominated because they are inexpensive relative to other alloys and perform reliably under a variety of operating conditions. They also possess unique characteristics (e.g., low melting point, high strength ductility and fatigue resistance, and high thermal cycling, electrical conductivity and joint integrity) that are well-suited for electronic applications. Finally, leaded solders predominate in the electronics industry because of the large instilled manufacturing base that supports their use.

Soldering is a way of making a long-lasting joint between two metal surfaces, and is an important technique in many industries, particularly electronics, plumbing and general engineering.
Joining of conductors by soldering is one of the basic technologies in the assembly of electronic circuits. Solder provides mechanical strength, electrical continuity, and protection from the environment. . In electronics, the solder joint has the purpose of not only bonding two surfaces, but of providing an electrically conductive path, and it is crucial to the overall reliability of the assembly. In soldering, more accurately “soft” soldering, the melting temperature of the alloy is normally much lower than that of the metals being joined, i.e. below 450 degrees C, and usually between 200-300 degrees C. (Above 450 degrees C, the process is defined as “hard” soldering or brazing).
For soldering to take place, the alloy has to “wet” the surfaces to be joined. “Wetting” means that the solder metallurgically interacts with the substrates, thus forming a strong bond on solidifying. Fluxes are an important part of the whole process, since they ensure that all the surfaces are clean and oxide-free, thus promoting good wetting.

The most commonly used solder alloy for joining electronic components is 60 weight percent Sn and 40 weight percent Pb, or the eutectic 63Sn/37Pb. The soldering systems based on these alloys have been highly developed and refined with decades of experience; much has been learned about the metallurgy, mechanical properties, flux chemistries, manufacturing protocols and reliability. In electronic equipment assembly, soldering processes have been engineered to produce, at competitive costs, very small geometry joints approaching 75 microns in size.
Leaded solders perform three basic functions in the electronic interconnection industry:

1. provide the final surface finish for printed circuit boards,
2. applied to component leads to achieve a compatible solderable surface, and
3. used to attach electronic components to printed circuit boards.

Although many circuit board manufacturers have succeeded in eliminating lead from the surface finish step of printed circuit board, leaded solder continues to be the predominant component lead finish and choice for assembly soldering.

As lead is an environmental pollutant of concern, the pressure to reduce the industry's use of lead is growing. Studies have shown that small quantities of lead can cause brain, nervous system, liver and kidney damage, WHO (2000). Lead exposure to workers in the electronics industry has been measured and appears to be well-controlled, in terms of actual exposures to the process used.

Despite the long term acceptance of lead by human society, lead poisoning is now well recognized as a health threat. The common clinical types of lead poisoning may be classified according to their clinical picture as (a) alimentary; (b) neuromotor and (c) encephalic Sax (1984). Lead poisoning commonly occurs following prolonged exposure to lead or lead compounds. The damage often is induced slowly, but definitely and irreversibly.

With the profound evidence in toxicity, use of lead chemicals in paint and petroleum applications has been prohibited for several years. The storage batteries, due to the required recycling practice, do not contribute to the pollution or contamination and pose no immediate issue. On the other hand, although solder is only a small percentage by weight of electronic products (TVs, refrigerators, PCs, phones etc.), this equipment often end up in landfill after being disposed, and the lead could be leached out into the water supply.

A major force pointing towards alternative materials is the possibility of legislation or regulations restricting or eliminating the use of lead. Assembly-related forces are the need for lower temperature solders to avoid thermal damage to sensitive components.

Government regulations are becoming stricter, and handling of waste materials is becoming more regulated. With regard to waste generation 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 are still targeting the removal of lead from solder, primarily due to experiences gained from lead pollutants generated in other industries.

Article 1 of the European Union *Proposal for a Directive on Waste from Electrical and Electronic Equipment* states its objectives as follows:

> *This Directive sets out measures that aim firstly, at the prevention of waste from electrical and electronic equipment, secondly at the re-use, recycling and other forms of recovery of such wastes, and thirdly at minimising the risks and impacts to the environment associated with the treatment and disposal of end-of-life electrical and electronic equipment. It is also the aim of this Directive to harmonise national measures concerning end-of-life electrical and electronic equipment in order to ensure the functioning of the internal market and to avoid obstacles to trade and distortion of competition within the Community. (Proposal for a Directive on Waste from Electrical and Electronic Equipment* (2001)).

The European parliament voted on Tuesday, 15 May 2001 to adopt the proposed EU directives on waste electrical and electronic equipment (WEEE). The next stage is consideration by the Member States. While the adoption date of 2006 has not changed, the scope of the Directive has changed tremendously.

Individuals and groups have been arguing for years that lead in solder is neither truly replaceable nor any more dangerous than the lead-free substitutes.

The most dramatic amendment, however, is a list of items currently exempt from the Directive has increased. This implies a possible exemption for lead in solder used in components and assembly for all computer and communications equipment.

2.0 Objectives of Dissertation

The objectives of this dissertation were to assess environmental, economic, legislative and technical issues surrounding the continued use of leaded solders in electronic applications and possible replacement technologies. The specific areas addressed were:

- An explanation of the term “solder” and why it is so important to the electronics industry.
- The reasons behind the pending removal of lead from electronic assemblies, with particular reference to environmental and legislative factors.
- The environmental impacts and toxicity of leaded solders versus the known environmental impacts of the alternative lead-free solders.
- Investigation of the commercially available substitutes and determination of the most appropriate choices in industry today.
- Investigation of the extra process parameters required and problems encountered to process lead-free as distinct from leaded solder assembly processes.
- Identification and selection of a set of lead-free pastes to run sample assembly experiments.
- Through experiment and theory, define a generic process flow for the practical introduction of lead-free solders.
- Perform a preliminary investigation into the long-term reliability of lead-free solders through a combination of environmental exposure experiments.
- Make recommendations on the most appropriate strategies to be taken by the industry in the future taking environmental, economic, legislative and technical factors into account.

3.0 Methodology:

3.1 Introduction

The methodology employed falls into two main categories:

- Assessment of current legislation and technologies
- Experimental Methodology

3.2 Assessment of current legislation and technologies

The assessment of current legislation and technologies involved investigating the reasons behind the pending removal of lead from electronic assemblies, with particular reference to environmental and legislative factors. The environmental impacts and toxicity of leaded solders versus the known environmental impacts of the alternative lead-free solder materials were investigated. The commercially available substitutes were also identified and a determination made of the most appropriate choices in industry today.

The primary method of research was through the Internet sites of the EU Commission, various lead-free dedicated sites, solder suppliers' sites and EPA and USEPA web sites. Phone calls and email contact was made with top electronics companies with known solutions already in place. The main contributors were 3COM, Ericsson, Nokia, Alcatel, Bosch and Nortel.

Although some technical white papers are available on individual aspects of lead-free soldering, no books were identified dealing with this specific issue.

3.3 Experimental Methodology

To meet the objective of the identification and selection of a set of lead-free pastes to run sample assembly experiments, the author of this dissertation conducted experiments in the following areas; Material Selection, Defining a Process and Reliability Testing.

Material Selection

The first selection made by the author was that of the alloy. There are numerous lead-free alloys available today including a number of patents. The following input criteria were used to select the most appropriate Alloy:

- Research by Universities and Consortia. Very useful information can be found in research work available on the Internet and in papers, e.g.: IPC Roadmap (A Guide for Assembly of Lead-Free Electronics) - http://www.leadfree.org.
- The DTI report "Lead-free soldering" and the "Update 2000" http://www.npl.co.uk/npl/ei/news/pbfree.html.
- Improved Design Life and Environmentally Aware Manufacturing of Electronics Assemblies by Lead-Free Soldering: "IDEALS" by Marconi Materials Technology Ltd,
- Philips CFT, Siemens AG, Multicore Solders Ltd, Witmetaal BV and NMRC.
- Road Map 2000 for Commercialization of Lead-free Solder-ver.1.2 by Japan Electronic Industry Development Association.
- Experiences from other companies already producing lead-free products.

Since the wetting characteristic of lead-free alloys is not as good as SnPb at lower temperatures, the author found that a good flux was very important to the process. Temperatures in lead-free processing have increased, whereas the fluxes that are used today for lead-free soldering are the same as used for Tin/Lead.

Flux's main job (flux/vehicle in solder paste also) is to remove and prevent oxidation. For both wave and reflow processes, activation temperature and activation time during heating and soldering need to be reformulated for use with lead-free alloys.
The requirements which the author set regarding flux was that the selected flux must meet the following criteria:

a. Must comply with appropriate legislation and be environmentally friendly;

b. Must enhance solderability and be compatible with all materials used in the lead-free process.

c. Must have an acceptable cost.

Once all selections for the lead-free materials were made, the author reviewed the selected items and compared them with current legislation. All the materials compatible with the higher soldering temperatures were compatible with current legislation.

Defining And Developing An Efficient Method

The author had to develop an effective method for process development to determine correct process settings. Lead-free soldering is not merely a matter of replacing one alloy with another, there is no "drop-in" replacement. Introduction of a new material affects the entire process; therefore, all machine settings had to be reviewed.

In reflow soldering, the authors goal was to meet or reproduce the correct profile for the solder paste, and to stay within the specification for the components and board materials. The challenge was to do this with those machines that are currently in production, and without decreasing throughput.

Reliability

From the literature review, the author found that the question of what happens to a lead-free solder joint if it becomes contaminated with lead is important, because it can lead to eventual joint failure under operating conditions. During the transition to lead-free soldering it is very likely that tin/lead parts will still be used in a great deal of production. Exposure to lead *from* boards, components and repair operations could occur for years to come.

A summary of the work undertaken including the aims and outcomes of each activity is included in Technical Summary section of this report. The main body of work was inter-company reports produced by the author [and referred to in the reference section, and in the literature review.]

After defining the process flow, the author then carried out assembly experiments on five main lead-free alloys, which were obtained from solder suppliers. All assembly and basic environmental testing was conducted by the author in Pulse Ireland, and more detailed analysis such as SEM and X-ray was performed under the author's direction at the Pulse Failure Analysis laboratory in Chang An, China.

4.0 LITERATURE REVIEW

The following section details the current situation with regard to the removal of lead from solders. The research performed by the author focuses on the areas of:

- **Environmental impact and toxicity**
- **Relevant Environmental Legislation both in Europe and abroad**
- **Economic aspects associated with the introduction of lead-free products**
- **Technical aspects associated with the introduction of lead-free soldering**

4.1 Impacts and Toxicity

Investigations of the various lead-free solder alloy candidates have been in progress for the past few years. Researchers have been determining the solder alloys' physical and mechanical properties, environmental impacts and occupational toxicity in comparison with conventional leaded solders.

4.1.1 Environmental Impacts and Toxicity of Leaded versus Lead-Free Solders

Smith (1999) in his paper seeks to continue the research into the environmental impacts of lead free alloys. Comparisons are made between seven lead-free solder alloys:

Tin/Silver/Copper, Tin/Silver, Tin/Copper, Tin/Antimony, Tin/Indium, Tin/Silver/Bismuth and Tin/Bismuth. These alloys were tested in the various physical forms most likely to occur in Printed Circuit Board (PCB) fabrication, assembly and finished product disposal to determine the environmental impact from each alloy. The goal of the research is to assist the industry in selecting the best alloy from the many available alternatives.

4.1.2 Waste Regulation Worldwide

Management of waste in industrialised countries ranges from highly regulated, specific government controlled operations to practical non-existence. Within this range falls most industrialised countries which significantly regulate industrial /commercial hazardous waste, with or without also regulating household hazardous waste disposal.

When waste is disposed in a landfill, it is weathered by rainfall and reactions with other wastes, which allows metal elements and their salts to be leached from the metal surfaces of the waste. If the metal-bearing leachate is allowed to contact stormwater, groundwater or to migrate into groundwater, local drinking water supplies are threatened with contamination (Surface Mount Technology, 1998).

4.1.3 Deionised Water Leach Methods

Many members of the European Union, including France and Germany, as well as Japan utilise deionised (demineralised) water leaching tests. A draft European Union test method also specifies deionised water leaching. The State of Texas also publishes a seven day deionised water leach method. These methods are used to demonstrate the contamination potential to drinking water and groundwater from a waste that comes into contact with drinkable water. A portion of the material under study is mixed with some multiple of its weight in deionised water, shaken or tumbled for a specified time, then allowed to leach while being shaken, tumbled or undisturbed (Smith *et al.*, 1998).

4.1.4 Aggressive Leach Methods

Aside from the deionised water leaching methods, there are methods which utilise leaching fluids containing various acids. These methods are used both to simulate acid rain and to simulate improper waste disposal; mixing household waste with industrial waste in the same disposal unit. The Synthetic Precipitation Leaching Procedure (SPLP) developed by the United States Environmental Protection Agency (USEPA) is one such test. The leaching fluid in this test contains nitric and sulfuric acids, diluted to a pH of 5.0. Some European environmental authorities use a similar leaching fluid. These fluids contain either sulfuric acid or sodium nitrate. The Toxicity Characteristic Leaching Procedure (TCLP) was developed by the USEPA for determining whether a waste was hazardous by virtue of its toxicity. TCLP fluid contains dilute (pH 5.0) acetic acid, which mimics the organic acids typically found in landfill leachate where household waste is disposed in the landfill. Consumers typically dispose of their used electronic products by “throwing them in the trash”, so this scenario of electronics being disposed with food and other household waste is highly plausible. The State of California promotes a Soluble Threshold Leaching Concentration (STLC) test, which also utilises citric acid to mimic the landfill disposal scenario and its effects on waste leaching (USEPA, 1986).

4.1.5 Metal Toxicity

There are existing environmental and toxicological regulations on both lead and lead-free solder alloying elements. Among these are the following:

Silver and silver compounds can cause biological effects such as digestive tract irritation and agryria, which is characterised by a permanent blue-grey pigmentation of the skin, eyes and mucous membranes. Ecotoxicity reproductive effects and mutagenicity have been observed in laboratory studies; however, toxicological data has not been fully investigated.

Antimony and antimony compounds can cause biological effects such as severe digestive tract irritation with abdominal pain, nausea, vomiting and diarrhoea. Toxicological data has not been fully investigated; however, antimony carries one of the lowest allowable concentration limits in drinking water.

Copper and copper compounds can cause biological effects such as severe digestive tract irritation with abdominal pain, nausea, vomiting and diarrhoea. Ecotoxicity has been observed in laboratory studies; however, toxicological data has not been fully investigated.

Indium and indium compounds have shown developmental toxicity in rats and mice. Particular symptoms of this developmental toxicity include fetal mortality, foetal malformation, reduced foetal weight, and malformations in the tail, ribs, digits and kidneys. Ecotoxicity and mutagenicity have been observed in laboratory studies; however, more toxicological studies are needed.

There are regulatory concerns for the lead replacement metals regarding environmental impact and use in the workplace. PCB manufacturers and printed circuit board assembly (PCBA) assemblers moving to lead-free solder materials will need to evaluate these new materials in the workplace for environmental permitting, management and industrial hygiene issues (Smith, 1999).

4.1.6 Surface Mount Council Toxicity Data

The Surface Mount Council (SMC) in its report gives a table showing the relative toxicity of the various lead-free soldering elements. The table is reproduced here:

TABLE 1: Relative Toxicity of the Various Lead-Free Soldering Elements

Metal Element	OSHA PEL or ACGIH TLV (mg/m^3)
Bismuth	None
Zinc Oxide Fume	5
Tin (inorganic)	2
Tin (organic)	0.1
Antimony	0.5
Copper (dust)	1
Copper (fume)	0.1
Indium	0.1
Silver (metal dust and fume)	0.1 [a]
Silver (and soluble compounds)	0.01 [b]
Lead (inorganic)	0.05 [c]

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[a] OSHA PEL [b] ACGIH TLV [c] ACGIH TLV is 0.15 mg/m^3

Based on this data and other data cited in its report, the Surface Mount Council assigns this toxicity ranking to the common lead-free solder alloying elements:
Bi < Zn < In < Sn < Cu < Sb < Ag < Pb (Allenby *et al.*, 1999).

The issue of the toxicity of antimony has been raised as the search for viable lead-free alloys continues. The paper, *"A Study of Antimony in Solder"* AIM (2001), details third party and governmental studies and legislation concerning antimony and its "toxicity", and compares this data to that which concerns "safe" metals such as silver, copper, tin, and zinc, as well as lead.

4.1.7 CERCLA Priority List of Hazardous Substances

In the United States, the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) requires the USEPA and the Agency for Toxic Substances and Disease Registry (ATSDR) to prepare a list, in order of priority, of substances "which are deemed to pose the most significant potential threat to human health due to their known or suspected toxicity and potential for human exposure". Substances considered to be the most hazardous are listed in order from 1 to 275.
ATSDR/USEPA also publish a "Top 20 Hazardous Substances" list, which are simply the first 20 of the 275 elements that are listed on the CERCLA Priority List of

Hazardous Substances. The rankings of the metals of interest are:

TABLE 2: Metal Toxicity Ranking (in order of priority). USEPA (2001)

Metal	Ranking
Lead	6
Zinc	7
Bismuth	8
Copper	9
Silver	10
Antimony	11

4.1.8 OSHA Limits for Air Contaminants

The Occupational Safety & Health Administration (OSHA) of the U.S. Department of Labor, under Code of Federal Regulations (CFR), Title 29, has regulated the maximum level of air contaminants of certain elements to which workers are allowed to be exposed over the course of eight hours. These limits for air contaminants are intended to protect workers from the harmful effects of certain elements, and are listed under Table Z-1 of that document.

4.1.9 USEPA/IRIS Elemental Summaries

The Integrated Risk Information System (IRIS) is a division of the USEPA that has compiled summaries of various elements. These reports are quite detailed, with the most important aspect of these to note being that all of the elements summarised have shown some undesirable effects when in certain forms and/or when these are exposed to humans at levels deemed to be excessive. Of additional interest is the fact that of all of the aforementioned metals, only lead has officially been classified as carcinogenic.

4.1.10 WEEE Targeted Substances.

The proposed EU WEEE Directive (2001) describes the major sources of lead intake for humans as food, soil and dust. Food receives lead mainly by atmospheric deposition of lead on plants, but to a minor extent also by plant absorption of lead from the soil. Soil will naturally contain low levels of lead, but lead emissions of many years have added to the levels observed.

Lead may enter the environment during its mining, ore processing, smelting, refining, use, recycling or disposal. Generally, the initial means of entry is via the atmosphere. Lead may also enter the atmosphere from the weathering of soil and volcanoes, but these sources are minor compared with anthropogenic ones. The form of lead that enters the atmosphere is not determined; however metallic lead may be released from smelting and refining plants. If released or deposited on soil, lead will be retained in the upper 2-5 cm of soil, especially soils with at least 5% organic matter or a pH of 5 or above. Leaching is not important under normal conditions although there is some evidence to suggest that lead is taken up by some plants. Generally, the uptake of lead from soil into plants is not significant. It is expected to slowly undergo speciation to the more insoluble sulphate, sulphide, oxide, and phosphate salts.

Lead enters water from atmospheric fallout, runoff or wastewater; little is transferred from natural ores. Lead is a stable metal and adherent films of protective insoluble salts form that protect the metal from further corrosion.

In its recent opinion, the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) notes that the progressive ban on the use of lead in petrol has reduced airborne lead and is considered to be a primary reason for the lowering in lead blood levels in children and adults.

Under EU Council Directive 67/548/EEC (1967) on the classification and labeling of dangerous substances, as amended, lead compounds are classified as:

R20/22 - Harmful by inhalation and if swallowed

R33- Danger of cumulative effects.

R 61- May cause harm to the unborn child

R 62- Possible risk of impaired fertility

Toxic to reproduction, category 1 under Council Directive 67/548/EEC (Annex6)

Lead is a cumulative general poison with pregnant women, the foetus, infants, and children up to 6 years of age being the most susceptible subgroups to adverse health effects *(WHO 1995, WHO 1996)*. Lead can cause damage to both the central and peripheral nervous systems of humans. Effects on the endocrine system have also been observed. Lead can have negative effects on several systems in the human body. Furthermore, lead is a probable human carcinogen as there is sufficient evidence from experiments on animals. In addition, lead can adversely affect the cardiovascular system and the kidneys. Lead accumulates in the environment and has high acute and chronic toxic effects on plants, animals and micro-organisms.

In 1986, the World Health Organisation (WHO), established a "*Provisional tolerable weekly intake*" (PTWI) for children of 25 μg/kg body weight. Children having a lead intake exceeding this value are therefore exposed to a concentration likely to cause health injuries. The PTWI for adults was reduced in 1992 by the WHO from 50 μg/kg body weight to 25 μg/kg body weight (as for children) based on the objective of protecting children at the embryonic stage.

As stated in the opinion of the CSTEE relating to the "lead Danish notification", there is inadequate scientific data to demonstrate conclusively the safe level of lead in blood. Young children are considered at particular risk and subtle effects have been reported below 100 μg/l blood.

In the general non-smoking adult population and older children, the major source of lead is food, with an estimated intake of around 10 μg/day (WHO, 1995). In Denmark, the estimated average dietary intake for adults (1988-1992) was 27 μg/day with the 95 percentile being 46μg/day (LST, 1995). The dietary intake decreased during the 5-year period (1993-1997) (VFD unpublished results) but it can not be excluded that certain groups stay at risk.

The CSTEE notes that recent blood lead level measurements in children in the Netherlands indicate that for approximately 3.3% of children between 1 and 12 years, the 100 μg/l value is exceeded. In addition, the CSTEE has stated that there is epidemiological data on health effects of lead in children indicating that even below a blood lead level of 100 μg/l, adverse effects might occur. The CSTEE will review in the future the appropriateness of the existing WHO value.

In the EU, between 1.5 % and 2.5 % of all lead applications are used in electrical and electronic equipment (EEE). Other main uses are batteries (63%), extruded products such as pipes or construction products (9%), gasoline additives (2%), pigments, stabilisers in PVC and others (WEEE, 2000).

The main applications of lead in EEE include soldering of printed circuit boards, glass of cathode ray tubes, soldering and glass of light bulbs and fluorescent tube.

The cathode ray tubes of a personal computer contain about 0.4 kg lead in glass, a TV set about 2 kg lead. The lead oxide in these tubes constitutes the largest share of lead in WEEE. In cathode ray tubes, lead is present in the form of silicates. A light bulb contains between 0.3 and 1 g of lead in lead-tin solder and 0.5 to 1 g of lead silicates in the glass (on average 1.5 g lead in solder and glass). In Sweden, this application amounts to the use of about 100T of lead annually. Solders in printed board assemblies contain about 50 g/m^2.

The incineration of WEEE makes a large contribution to the total lead emissions from incinerators. Lead from WEEE represents about 50% of the lead input to incinerators. After incineration, 65% of the lead is found in the slags, 35% in the residues and 1% in the air (WEEE, 2000).

Due to the heavy metal content of WEEE, significant amounts of slag have to be classified as hazardous. Consequently, the slag has to be landfilled in hazardous waste landfills. The CSTEE notes that the lead contaminated slag and bottom ash may be required to be landfilled. This creates the potential for slow leaching. Although impacts are likely to be small, they can influence attainment of sustainability goals.

Leachate collection and treatment of controlled landfills respecting environmentally sound technical standards, such as those set out in EU Directive 99/31/EC (1999) does not completely eliminate exposure nor does it solve all the problems either. High standard landfills dispose of leachate collection and bottom sealing systems. In these cases, the leachate is collected and sent to treatment plants on site or to municipal sewage treatment plants. In the worst case, the heavy metals may disturb the treatment process, but in any case they will mainly end up in the sewage sludge and in smaller but uncontrollable amounts in surface waters. The sewage sludge will either be used on agricultural land (if, among other conditions, the limit values of the EC Sewage Sludge Directive - Council Directive 86/278/EEC (1986) are not exceeded) or go to landfill or incineration. As regards the landfilled sewage sludge, similar problems regarding the emissions of landfill will occur since exposure from landfills can not be completely eliminated.

In the case of uncontrolled landfills, contaminated leachate goes directly to the soil, groundwater and surface water. Leachate containing the above pollutants from uncontrolled landfills might contaminate water to an extent that its use as drinking water is impossible on the basis of the limits set out in Council Directive 80/778/EEC (1980) relating to the quality of water intended for human consumption.

4.1.11 International Proposals to Ban Lead Usage

The USEPA has taken regulatory action to remove lead from common consumer products such as gasoline, plumbing and paint products and to impose strict management requirements on lead-acid batteries to prevent disposal in the solid waste stream. These actions have successfully resulted in the average recorded blood lead levels of persons in the U.S. falling, and as a result, lead exposure is no longer a major public health threat in the U.S. USEPA (2001).

4.1.12 The debate on the Scientific Foundation for Lead Ban Proposals

According to the International Packaging Consortium (IPC), the European lead ban/restriction proposals are not based on sound science. The European proposals are largely based on the theory that certain lead uses pose an unmanageable environmental and public health risk when lead-containing products are discarded; however, many studies have demonstrated that this theory is untrue.

The U.S. Department of Health and Human Services, in its Toxicological Profile for Lead (1993) concluded that lead tends to be immobilized by the organic and clay components of soil and remains bound in the soil. These studies also found that lead concerns are minimal for properly managed landfills.

U.S. public-health officials have classified lead as the number one environmental threat to children (Waldman, 1991). It was this claim that lead-poising is responsible for damaging the intelligence of children, which prompted US environmental and health officials to tighten the guidelines on acceptable level of lead (Putka, 1992).

Lead Industry Association Inc. (LIA) reported that all current uses of lead combined have an insignificant health effect on the most sensitive population (young children) as concluded in a recent study by Environ Corporation (Hwang, 1999).

It is evident that findings have provided the basis for formation of two opposite positions regarding the hazards and regulation of lead.

Vianco (1993) reporting on the "Environmental Concerns of Lead" indicated that lead waste derived from the use of electronic solders has two primary sources: (1) the disposal of electronic assemblies (Radios, TV's etc) and (2) waste generated by the assembly of circuit boards. In relation to point (1), scientific data is not readily available which describes technical scenarios or has provided conclusive evidence of the leaching and movement of lead from tin/lead solder joints on discarded electronic chassis in landfills.

Lead bearing waste from circuit board assembly processes is generally in the form of solder dross. Dross is 96% to 98% tin and lead and it is readily recycled to retrieve the elemental metals for re-use (Swanson, 1991).

The exposure of factory workers to lead such as in the form of dust particles generated by dross or the melting of solders during processing is strictly controlled by OSHA procedures for air quality and contamination monitoring. Maximum airborne concentration (TWA) is 0.05mg/m^3 (Metals Handbook, 9th ed., 1981).

An action level of 0.03mg/m^3 was established which when exceeded, requires certain procedures be instituted by the company management to minimise further exposure to workers. Airborne lead concentrations for several soldering operations from studies conducted over a five year period (sampling sensitivity – 0.002 to 0.005 mg/m^3) exhibited levels well below the TWA limit as well as the action level. All values were below the 25 micrograms/deciliter limit.

In summary, lead exposure to workers appears to be well controlled both in terms of the actual processes used in manufacturing as well as guidelines set by OSHA. However, a lack of scientific evidence exists with respect to the hazard posed by tin/lead solder joints in electronic assemblies which are disposed in municipal landfills.

Allenby et al. (1999) in the section of their report entitled "*Lead in the Environment and in Industry*" specifically dealt with the "*Adverse Health Effects of Lead*". Lead bio-accumulates in the body; that is, it is retained over time and can have adverse health impacts when a sufficient accumulation has occurred. Once in the body, the lead binds strongly to proteins and inhibits normal synthesis and function. Effects include nervous and reproductive system disorders, delays in neurological and physical development, cognitive and behavioral changes, reduced production of hemoglobin with resulting anemia and hypertension (Putman, 1986).

Occupational exposure to inorganic lead occurs primarily by inhalation, and possibly by ingestion. Dermal absorption is typically not a contributory factor, especially under conditions of good industrial hygiene. Exposure to lead is customarily determined by measuring lead levels in the blood, an approach that also reflects contributions from non-occupational exposure such as lead in drinking water, inhalation of contaminated dusts and soils, leachate from pottery, and inhaled or ingested lead from paint flakes.

OSHA regulates the permissible workplace exposure limit for inorganic lead at 50 micrograms/m^3. This exposure limit is related to maintaining blood lead levels at or below 40 micrograms/deciliter, believed to prevent adverse health effects from exposure to lead throughout a working lifetime. For workers planning to have children, OSHA recommends maintaining blood lead levels below 30 micrograms/ deciliter.

A potential source of worker exposure in electronics is the soldering process, especially the wave solder operation. Observations near hand soldering and tinning operations indicate that there is little danger of airborne lead exposure. Personal hygiene was the primary controlling factor in lead exposure. Part of this is due to the relative non-volatility of lead at normal soldering temperatures (Sax, 1984 and Forsythe, 1956).

In the ambient environment, as opposed to the workplace, the potential for exposure to mobilised lead is at least as important as the presence of lead. The degree of mobilisation differs greatly among the reservoirs in which lead is contained. The USEPA regards the three major sources of lead in blood as lead-based paint, urban soil and dust, and lead in drinking water. Other sources include smelters and municipal waste and sewage sludge incinerators. The use of lead in products is thought by USEPA to be of much less concern.

There is a small natural background concentration of lead in the physical and biological environment due to its mobilisation and dissemination from these deposits and from other sources. These natural emissions of lead to the atmosphere are about 13000 tonnes per year. None of the natural sources are very significant, but the more important are windblown soil and volcanoes (Nriagu, 1989).

There have been various attempts to estimate the concentrations that result from these emissions, by both theoretical extrapolation and the measurement of lead in remote parts of the Earth and in the remains of ancient man. These estimates suggest that the natural lead concentration in air was some 3-5 orders of magnitude less than current levels, and in water about 2-3 orders of magnitude less. Analyses of lead in the teeth and bones of ancient Nubians buried in the Sudanese desert, some as ancient as 3300 - 2800 BC, give concentrations of about 10-100 times less than in modern specimens. While it is still possible to measure in certain remote areas environmental levels of lead as low as those attributable to natural emissions, it is clear that man-made mobilisation has increasingly contaminated all phases of the physical and biological environment.

The mining of galena and other lead ores adds a small amount of lead to the atmosphere as a consequence of windblown dust dispersion. (Nriagu and Pacyna, 1988).

The dominant emitter to the atmosphere was from leaded petroleum fuels used in transportation. Since the 1920s, a major use of lead has been as an antiknock additive in petroleum. This use is now gone in North America and in Europe, but remains highly significant in much of the rest of the world.

A large proportion of the lead used in products is recycled, mostly from automobile storage batteries. The difference between the amount of lead added to products each year and the amounts removed by recycling and disposal represents the increase in the embedded lead contained in products (Nriagu and Pacyna, 1988).

The fluxes of lead to water and soils have also been estimated. For aquatic ecosystems, the dominant source by far is fallout from the atmosphere. In the case of soils, three sources are significant; coal ashes, discarded manufactured products and atmospheric fallout. The estimate for manufactured products includes only discarded batteries and cable sheathing. Typical airborne and waterborne concentrations of lead are given, where blood lead levels and standards are also presented. The background concentrations are well below urban concentrations for both air and water, and those in turn are well below the regulatory standards. The ranges in blood lead are much smaller than the environmental ranges, reflecting a moderately long cycling time for lead in the body.

4.1.13 Lead in Air, Water and Blood

TABLE 6: Concentration of Lead in Air, Water and Blood.

	Locale or Limit Concentration in air (µg/m^3)	**Concentration in water (µg/m^3)**	**Concentration in blood (µg/m^3)**
"Background"	0.0002	1	10
	Ng, Patterson (1981)	Tsuchiya (1979)	Ratcliffe (1981)
Urban	2	5 - 15	15 - 20
	Ng, Patterson (1981)	Carson *et al.* (1986)	Ratcliffe (1981)
Regulatory Limit	50 (workplace)	50 (drinking water)	40 (OSHA)
	Tsuchiya (1979)	Tsuchiya (1979)	Tsuchiya (1979)

It is inevitable that requirements to recycle lead will increase, and that use of recycled lead will increase. Some recycled lead may not be suitable in electronic assemblies however, since it emits alpha particles. Much freshly mined lead contains traces of uranium and radium which gives 210 Pb as a decay product, with a 22 year half-life. If the uranium and radium are removed by refining, then well-aged lead will have low radioactivity and be most suitable for electronic applications. Recycled lead however, may contain material originating from multiple sources, including some that is recently mined or some which contains traces of uranium. If used for electronic applications therefore, the properties of recycled lead need to be carefully screened (Allenby *et al.*, 1999).

Considerations of substitutes for lead solder should not be made without simultaneous consideration of other environmental issues associated with manufactured products. An approach to thinking about manufacturing in concert with its surrounding systems, termed "industrial ecology", is a subject discussed by Jelinski *et al.* (1991). It seeks to optimise the total materials cycle from virgin material, to finished material, to component, to product, to waste product, and to ultimate disposal or recycling. The selection of materials for joining in electronic assembly is therefore an activity embedded within a large process; that of thinking through each step of manufacturing and use for each material and optimising the ensemble of materials and constituents.

From this broader perspective, the choice of a joining process is but one of a series of decisions in the industrial ecology analysis of manufactured products.

4.1.14 Tin in Electronics.

Referring to tin and its properties in relation to the environment, the International Tin Research Institute (ITRI) state that tin can be found almost everywhere in nature. Small amounts are found in soil and rocks as well as plants and in water. There is approximately 0.35g contained in humans and this figure does not tend to increase with age.

More than 300 million tinplate cans of food are eaten daily. This is a powerful confirmation that tin is an essentially safe material. For more than a hundred years, canned food has been a significant part of the diet of much of the human race.

Regulatory authorities find there is no requirement to list tin as a substance of concern in drinking water.

The WHO has reported that inhalation of elemental tin does not produce any effects in man. About a third of all tin produced today goes to make tinplated steel (tinplate) for food and beverage cans and other packaging.

Recyclability is one of tinplate's great merits. More and more tinplate cans are recovered from municipal waste using magnetic extraction, or they are collected in 'can banks'. Some cans go to specialist detinners where the tin is chemically removed and made into new ingots for new applications.

Tin Technology has been active in research and development of lead-free soldering for over a decade and is a pioneer of the technology, with a global network in both research and industry. This activity was consolidated in 1999 with the launch of SOLDERTEC, the Soldering Technology Centre, as a centre of excellence in the field.

The SOLDERTEC website at *http://www.lead-free.org* is a world-leading resource for the lead-free soldering community, with detailed information on legislation, research, industry activities, databases etc.

The largest single use for tin is in solder alloys, which consume about 31 percent of world tin production (ITRI, 2001 [Online] Available: http://www.ITRI.co.uk).

Jorgensen (1999) in his article at the IPC Works conference in 1999, detailed the National Center for Manufacturing Services (NCMS) Lead-Free Solder Project, which looked at properties, toxicology, manufacturing feasibility, performance reliability, availability and economics. Joe Felty of Raytheon, who presented the NCMS results, says the three alloys settled on were Sn-58Bi, Sn-3.5Ag-4.8Bi, and Sn-3.5Ag.

Saying that research has focused on the problems with lead without taking into consideration the environmental effects of its substitutes, Smith and Swanger studied Sn-3.2Ag-0.5Cu, Sn-3.5Ag, Sn-2Ag, Sn-0.7Cu, and Sn-5Sb when leached using USEPA methods (designed to simulate waste disposal and groundwater contact). (Unlike NCMS, they omitted bismuth, because it is a byproduct of lead smelting. Indium was excluded because of the lack of worldwide availability.)

Of the alloys studied, antimony and lead-free silver was found to have the least environmental impact on a relative ranking basis. Their experiments show that lead-free solders leach at levels that would cause them to be classified as a hazardous waste.

Seeling (1997) reporting on the alternatives to lead-free solders, discusses the issue of the toxicity of antimony. As with most metals, salts, oxides and organo-metallic compounds of antimony are typically the most toxic forms of the element. However, they do not form in standard soldering processes. Antimony has been approved for use in potable water systems as well as in food containers. In pewter tableware, which is commonly used in the preparation of food, antimony is often found at levels of 7 to 9 percent, and copper at levels of 1 to 3 percent. Furthermore, the antimony-doped alloy has been environmentally tested to confirm that it will not leach silver or copper into ground water. The accepted reason is that the two elements tied in the tin and antimony reduce their solubility.

In the paper "Lead-Free Soldering - Where the World is Going" Lee (1999) makes reference to the long-term acceptance of lead by human society, and the fact that lead poisoning is now well recognized as a health threat.

The common clinical types of lead poisoning may be classified according to their clinical picture as (a) alimentary; (b) neuromotor; and (c) encephalic (Sax, 1984).

The lead poisoning commonly occurs following prolonged exposure to lead or lead compounds. The damage often is induced slowly, but definitely. In Japan, the lead pollution environmental standard in landfills is set at 0.3 mg/1. In the toxic materials detection tests recently performed by the Japanese Environmental Agency, it was confirmed that the amount of lead leaching from the pulverised remains of TV tubes and printed substrates for PCs far exceeds the environmental standard (JEIDA, 1998).

4.2 Legislation affecting the use of lead in the electronics industry

The European parliament voted on Tuesday, 15 May 2001 to adopt the proposed EU Directives on waste electrical and electronic equipment (WEEE). The next stage is consideration by the Member States. This now compels companies in the electronics industry to comply with the Directive in their manufacturing procedures; there are also similar proposals of legislation from major consumer countries such as Japan, with which the international electronics industry must comply.

The "Proposal for a Directive on Waste from Electrical and Electronic Equipment" (WEEE) includes the following objectives:
"*This Directive sets out measures that aim firstly, at the prevention of waste from electrical and electronic equipment, secondly at the re-use, recycling and other forms of recovery of such wastes, and thirdly at minimising the risks and impacts to the environment associated with the treatment and disposal of end-of-life electrical and electronic equipment. It is also the aim of this Directive to harmonise national measures concerning end-of-life electrical and electronic equipment in order to ensure the functioning of the internal market and to avoid obstacles to trade and distortion of competition within the Community.*"

For the purpose of the Directive, the following definitions were created:
"Electrical and Electronic Equipment" shall mean equipment which is dependent on electric currents or electromagnetic fields in order to work properly and equipment for the generation, transfer and measurement of such currents and fields falling under the categories set out in Annex I A and designed for use with a voltage rating not exceeding 1000 Volt for alternating current and 1500 Volt for direct current. Electrical and Electronic Equipment includes all components and sub-assemblies

which are part of the product as well as consumables which are referred to in Annex II.

"End of life Electrical and Electronic Equipment" is electrical or electronic equipment which is a waste within the meaning of Article 1(a) of Directive 75/442/EEC (1975).

"Prevention" shall mean measures aiming at the reduction of the quantity and the harmfulness for the environment of end of life electrical and electronic equipment, their materials and substances.

"Producer" shall mean manufacturer of electrical and electronic equipment or professional importer of electrical and electronic equipment into a Member State.

"Dangerous substance or preparation" shall mean any substance or preparation which has to be considered dangerous under Directive 67/548/EEC (1967).

The Scope of the Directive beings as follows:

"*This Directive shall cover the categories of electrical and electronic equipment falling under the categories set out in Annex I A, regardless of the date when this equipment was put on the market.*"

Whilst the adoption date of 2006 has not changed, the scope of the Directive has changed tremendously. The Directive keeps getting more and more open to challenge and the exemptions continue to increase.

The draft Directive was amended to state that: *"Exemptions from the substitution requirement should be permitted if (it is) not possible from (the) scientific and technical point of view........or where scientific evidence demonstrates that their use does not result in any significant risk to health or the environment."*

Individuals and groups have been arguing for years that lead in solder is neither truly replaceable nor any more dangerous than the lead-free substitutes.

The most dramatic amendment, however, is that the list of items currently exempt from the Directive has increased to include the following:

- Lead contained in high melting temperature type solder
- Lead in glass in electronic components
- Lead in piezoelectric devices

- Lead in servers, storage and storage array systems, voice and data transmission and networking equipment

This implies a possible exemption for lead in solder used in components and assembly for all computer and communications equipment. This changes matters, as companies that assemble the above have been some of the most active in the issue.

The third draft of the WEEE Directive was issued after the 1999 United Kingdom Department of Trade and Industry (DTI) report (Richards *et al.*,1999) described two drivers for a change to lead-free soldering; the direct threat of EC legislation and the actions being taken on a more voluntary basis by Japanese companies.
In Japan, the roadmap of the Environmentally Conscious Engineering in Electronics Committee suggests that component compatibility should be achieved to a large extent during 2001 and that the use of lead-free solder should become standard in new products by 2003. Current knowledge of that region suggests that these targets are likely to be met or exceeded.

Lee (1999) describes a global history of lead-free legislation. In 1994, Denmark, Sweden, Norway, Finland and Iceland signed a statement to phase out lead in the long run. On June 16, 1997, a press release from the Swedish Government identified lead as one of the elements which will be eliminated from products over the next 10 years. The Sweden Environmental Quality Objectives direct that any new products, including batteries, introduced in Sweden should be largely free from lead by 2020. Swedish manufacturers are also under a voluntary ban effective from 2000 (HDP User Group International Inc., 1999).

At about the same time frame, recycling laws were proposed in various Asian countries. In October 1996, Discard Processing/Resource Reclamation Committee of the Industrial Structure Council in the Japanese Ministry of International Trade and Industry (MITI) announced goals for recycling discarded automobiles. Also in 1996, Japanese Automobile Industrial Association set up a self-managed environmental program. The lead used in new automobiles is cut in half by 2000 (versus 1996) (excluding lead used in batteries), and is proposed to be cut to one third by 2005 (versus 1996). At present, most of the lead usage in Japanese vehicles is in the paint and the radiators.

There are impending producer responsibility laws for electronic and electrical equipment for a number of European countries. Laws have been passed in Holland and Switzerland before 1999 involving producer responsibility. Norway followed in 1999 and Sweden in 2000. In some cases producer responsibility may involve the manufacturer, importer or reseller taking responsibility for the take-back of products and proper end-of-life treatment. A threshold limit for recycling of specified material types may be included also.

The move toward lead-free raised the attention of some major manufacturers. Nortel Network is one of the lead-free pioneers in Europe. They initiated lead-free programs in 1991, selected Sn99.3/Cu0.7 in 1994, built 500 lead-free phones in 1998 and targeted meeting the WEEE Directive in 2001 (Gibbs, 1999).

In Asia, since 1998, recycling laws are being enacted in various countries including Japan and Taiwan. In Japan, the recycling law applies only to TVs, refrigerators and similar items. On January 30th, 1998, JEIDA (Japanese Electronic Industry Development Association) & JIEP (Japanese Institute of Electronics Packaging) presented a lead-free roadmap. Some major Japanese OEMs began to jointly develop recycling processes for electronic products.

NEMI called for a "Lead Free Initiative Meeting" in February, 1999 at Anaheim, CA to review the situation, and since then rolled out a series of action items to establish a lead-free direction for the U.S. electronics industry. The second NEMI meeting was held in May 1999 at Northbrook, IL. This meeting effectively motivated many manufacturers to get involved in lead-free development. Then IPC announced their new stance that IPC is not lobbying against lead-restrictions, but feel they can better serve the industry by helping with lead-free. The IPC statement probably fairly truly reflects the opinion of most of U.S. industry; "Lead in electronics is not perceived as a health issue, but government and commercial drivers will push for its adoption anyway. Thus IPC will facilitate activities to enable it to happen" (Buetow,1999).

4.3 Economic aspects of lead-free products

From an economic perspective, the cost of solder bar is dictated by the raw materials cost. However, for fabricated products such as solder pastes, the processing cost of manufacturing this material can become a dominant factor, and the difference between tin/lead and lead-free materials becomes very small (Handworker, 1999).

The first mass-produced lead-free unit was released in October 1998. This lead-free labelled Panasonic MiniDisc MJ30 player reportedly experienced a large increase in market share over standard product and encouraged further releases by that company. At the time of writing, four Panasonic MD players, a stereo headphone and a video recorder are now available that use lead-free solder. Hitachi have also utilised lead-free soldering for a camcorder and for a PC audio board. Many other products are scheduled for release, both by these and other companies. Some lead-free units made in Japan can already be found for sale in Europe.

Companies within Europe continue to investigate the possibilities for lead-free soldering but as yet have not announced the release of product. In the USA, the IPC "Get the Lead Out" conference in October 1999 re-focused attention on the lead-free issue in that region. The roadmap prepared by IPC, collating contributions from participants at the conference, suggested that US based companies should prepare for lead-free soldering with "a view" to the release of product by 2004. The change to lead-free soldering has now been initiated on a global scale. The drive forward is now so strong that further delays or alterations to the WEEE proposals are unlikely to affect adoption of the new technology although they may influence the rate of take-up. Motorola, for example, are actively seeking to remove lead regardless of legislative policies.

Industry sectors such as automotive have also started moving towards lead-free processing although they are not directly affected by proposed legislation. This is also driven in part by the potential high temperature performance improvements from lead-free alloys.

The most significant incentive for European and US manufacturers to develop lead-free soldering technology now appears to be a need to compete with environmental and market led actions of Japanese OEMs.

The proposed WEEE Directive, while still very significant, now appears to be a secondary incentive to adoption of lead-free technology (NPL, National Physical Laboratory U.K. (2001), IPC (2001), DTI UK (2000).

Jorgensen (2000*a*) highlights the fact that pressure coming from the pending Waste Electrical and Electronic Equipment (WEEE) Directive is calling for U.S. companies with European customers to be lead-free by 2004. Some companies are calling for their suppliers to be ready as early as 2003. He believes that the passing of the WEEE Directive will lead to the placing of trade embargoes on outside manufacturers supplying leaded product to Europe.

The same is happening in Japan. Japanese OEMs were presented with proposed take-back legislation, basically calling for the OEMs to pay for the reclamation of their product in landfills. Seeing this as an unnecessary cost, and possibly using good foresight based on the WEEE Directive, several of these OEMs set stepped-up deadlines for lead elimination (Jorgensen, 2000*b*).

The Japanese Ministry of International Trade and Industry (MITI) has proposed take-back legislation in Japan. This draft proposal requires consumer and business users to return end-of-life (EOL) equipment to retailers for recycling. According to this Directive, the manufacturer or importer is responsible for the cost of recycling. In response to this and other similar proposed legislation, several major Japanese electronic manufacturers have initiated their own roadmaps and publicly announced accelerated plans to completely eliminate lead solder by 2001. These "green" companies include Matsushita Panasonic, Sony, Toshiba, and Hitachi, with others likely to follow. The following are some interesting dates and facts released by these companies.

Sony: All lead will be eliminated except for high-density electronics packaging by 2001.

Toshiba: Lead will be eliminated from mobile phones by 2002.

Hitachi: Will reduce its lead usage in 1999 by half that of 1997. All products were to be lead-free by 2001.

Panasonic: Have come forward to say that by 2001, all lead will be eliminated from major electronics products. Panasonic has also taken the lead elimination issue one step further by marketing its products as new, lead-free, environmentally friendly electronics. In October of 2001, Panasonic released the first lead-free mini-disc player and marketed it in that manner by putting a green leaf logo on the box with the slogan; "Produced for the Environment". Upon its release, the mini-disc player gained an eleven percent share of the market. Panasonic plans on marketing its other lead-free consumer electronics in the same manner.

Sweden has issued a proposal that would recommend (i.e. not require) that all uses of lead be phased out by the year 2020. Denmark has proposed banning the import, sale, and production of certain lead compounds or products containing lead compounds or metallic lead (the use of lead in electronic applications would be excluded). The EU has proposed banning the use of lead in automotive vehicles unless those uses can be easily separated from the vehicle prior to shredding at the end of the vehicles useful life (printed wiring boards are specifically excluded from the ban). The EU has also proposed that all uses of lead in electronic and electrical products sold on the European market be banned by the year 2004 (IPC, 2001).

4.4 Technical aspects of introducing Lead-Free Solder

The acknowledged lack of an obvious drop-in replacement for tin/lead solder means that there is a great deal of uncertainty regarding choice of alloy type. However, there has been significant progress towards agreement for using one family of alloys, at least for many applications.

The European IDEALS programme (1995-1999) concentrated on a SnAgCu alloy for its trials (The final public domain report of the Brite-Euram IDEALS project is available on Caswell Technology's website

(*http://www.caswelltechnology.co.uk/tech/emtec.htm*)).

A need was seen for clear guidance in this area and prompted SOLDERTEC / ITRI to recommend a SnAgCu alloy range for most processes. Importantly, agreement was also achieved between a number of major solder suppliers as to the viability of this option. Subsequently, NEMI (National Electronics Manufacturing Initiative) in the US have also chosen an alloy from within this range for further evaluation and recommendation for reflow soldering (U.K. DTI, 2000).

NEMI announced the alloy its Lead-Free Assembly Project is recommending for use by industry as a "standardised" lead-free solder alternative.

For reflow applications (which represent at least 70% of all board assembly production), the NEMI group is recommending use of Sn3.9Ag0.6Cu - a predominantly tin-rich alloy with 3.9% silver and 0.6% copper. For wave solder production (which requires larger amounts of solder), the group is recommending Sn0.7Cu, a less expensive tin/copper alloy (0.7% copper), or (as an alternative) Sn3.5Ag (tin with 3.5% silver).

Based on findings of its 1998 roadmap, NEMI organised an industry task force in early 1999 to investigate process and material considerations of lead-free electronics assemblies . The task force investigated past efforts and developed a program plan to address lead-free electronics manufacturing solutions. The first step of this plan, which is being implemented by NEMI's Lead-Free Assembly Project, was to evaluate, select and recommend a single lead-free solder alloy to pursue as an industry standard.

The Lead-Free Assembly Project found no drop-in replacement for tin/lead solder. The group compiled a worldwide patent database of candidate alloys and collected all available material properties. In addition to information compiled or generated by the group, data was obtained from two industry reports; the final report of the NCMS Lead-Free Solder Project, a $10.3M in-kind program performed in the US between 1993 and 1997 (*http://www.ncms.org/3portfolio/1ProjectPortfolio/pubs.htm*) and a report on lead-free soldering from the U.K. Department of Trade and Industry (DTI) (*http://www.dti.gov.uk*) (Richards *et al.*,1999).

Based on thorough analysis of the data collected, the most promising solutions for the types of high-reliability products made by the majority of North American electronics manufacturers were combinations of tin, copper and/or silver. After consideration of the data on available alloys, the particular combination of Sn3.9Ag0.6Cu was chosen as it could be readily supplied by four different solder manufacturers (NEMI, 2000).

The SOLDERTEC choice was based on a comparison of solder properties and indicated that SnAgCu could be adopted as a general-purpose standard alloy. However, it was also noted that SnAgBi type alloys are likely to be used for surface mount consumer products and that SnCu solders may be developed for use in wave soldering situations where the cost of the alloy is a particularly significant consideration.

The reliability of SnAgCu solders has been shown to be functionally equivalent to that of SnPb solder in some fatigue tests. The performance of SnAgBi alloys has also been shown to be good up to certain maximum test temperatures but dependant on any lead contamination in the joint.

Investigations continue on zinc-containing alloys to deal with their poor oxidation and corrosion characteristics, and short paste storage times. If these problems can be overcome, they remain an attractive proposition due to the closeness of their melting temperatures to that of SnPb.

While some lead-free alloys and coatings are covered in international and national standards, this is by no means sufficient for future needs. Work has been initiated to update some of the most important standards to provide guidelines for impurity levels etc, but this will inevitably lag behind technological progress. Informal or in-company specifications are likely to be produced and used well in advance of international standards. Lead levels in "lead-free" electronic solders are expected to be defined in the region of 0.1 - 0.2% in the same way as in plumbing solders (NEMI, 2000).

Many of the major U.S. electronics manufacturers have been concerned that their ability to produce durable, reliable, safe, and affordable electronic products might be compromised with alternative solders or other interconnection materials.

In the last seven years, our knowledge of the manufacturing, product performance, and reliability of lead-free solders has increased to the point where we now understand the major roadblocks in the conversion to lead-free interconnections and can formulate plans to address them. These roadblocks can be easily understood in the context of the definition of a "drop-in" replacement for eutectic tin-lead solders.

Such an alloy would exhibit the following attributes:

1. **Toxicity**: Lower toxicity than lead.
2. **Cost and availability**: Equal to or better than eutectic Sn/Pb.
3. **Manufacturing requirements**: Melting behavior the same as Sn/Pb; wetting behavior equal to or better than Sn/Pb.

This includes:

- A liquidus temperature very near 183°C to maintain the fluxes, temperature profiles, and assembly processes used for eutectic Sn/Pb. (The liquidus temperature is the temperature above which the alloy is completely liquid.)
- A pasty range close to 0°C (Since eutectic Sn/Pb changes from a liquid to a solid at a single temperature, 183°C, its pasty range is zero. Alloys that are not eutectic have a non-zero pasty range).
- Wettability comparable to eutectic Sn/Pb on a variety of surface finishes with various fluxes.

4. **Reliability**: Performance at least as good as eutectic Sn/Pb in thermal cycling and end-use environments (consumer electronics, telecommunications, military, aerospace, and automotive) for all component types. The three storage and operating temperature ranges of general interest are:

- –55° to +125°C for military electronics
- –55° to +100°C for consumer electronics and telecommunications
- –55° to +180°C for aerospace and automotive electronics.

Tin/lead solder is the most widely utilised soldering alloy. The popularity of this alloy is due to its relatively low melting temperature, aggressive bonding characteristics, good wicking tendencies, good electrical continuity and low cost. The low melting point of tin/lead solders is often preferred because of the reduced probability of thermal shock to soldered assemblies during high speed soldering operations.

Tin/lead solder electroplate will also protect copper circuit boards from oxidising, allowing them to be stored for long periods of time.

Although many solder alloys have been formulated for special applications, there has been relatively little effort to develop electronic alloys specifically to be lead-free.

The desired solution would be a lead-free alloy which can be substituted directly for Sn/Pb solder with minimal changes to the rest of the system.

An alloy originally invented by Engelhard as a lead-free plumbing solder and called Silvabrite 100 has the composition 95.5Sn/4Cu/0.5Ag. According to a member of the Kester research organisation, the best lead-free candidate to date is an alloy sold under the name of Kester Aquabond. Its composition is 97Sn/2Cu/0.8Sb/0.2Ag. Its performance mimics that of Sn/Pb in many ways, but its melting point is about 20-40 °C higher than that of Sn/Pb.

The cost of materials should not be the dominant consideration in selecting candidate materials. It is the total cost of the assembly that must be held within competitive limits. Many factors must be considered to form a total picture of the cost impact including; repairability, process rate (joints/hour), cost of capital, cost of equipment, floor space, process yield, material waste, disposal of waste, material/process consistency, ease of process control, and the window of acceptable process parameters. The discussion addresses only the materials costs, and leaves a quantitative discussion of lifecycle costs to future work (Allenby *et al.*, 1992).

Seeling and Suraski (2001) take an in-depth view of Sn/Ag, Sn/Ag/Cu and Sn/Cu alloys and compare the reliability testing results and process considerations for these. Many of the systems are based on adding small quantity of third or fourth elements to binary alloy systems in order to lower the melting point and increase the wetting and reliability.

It is reported that with increasing amount of additive elements, (1) the melting point of the system decreases, (2) the bond strength first rapidly decreases, then almost levels off, then decreases again, and (3) the wettability increases rapidly first, reaching the maximum at composition corresponding to mid point of plateau of bond strength, then decreases (Furusawa *et al.*, 1997).

A paper from the Surface Mount Council (SMC) entitled, "Examining the Environmental Impact of Lead-Free Soldering Alternatives." argues that lead-free products are not really any more environmentally-friendly than the electronic products today soldered with tin-lead. The SMC feels that the focus of future regulation should be on recovery and recycling of the metals at the end of the products life, as required in the European Union Waste Electrical and Electronic Equipment (WEEE) Directive, rather than the outright elimination of lead-based solder.

TABLE 7: Research on Metal Alloys by Organisation Investigated
(Kester, 2001)

ORGANIZATION	ALLOY
NEMI	SnCu0.7, SnAg3.5, SnAgCu
NCMS	SnAg3.5, SnBi58, SnAg3.2Bi2.0 CASTIN, SnAg3.4Bi4.8 SnIn20Ag2.8 (Indalloy) SnAg3.5Cu0.5Zn1.0
ITRI	SnAgCu, SnAg2.5Cu0.8Sb0.5 SnCu0.7, SnAg3.5 SnBiAg, SnBiZn

TABLE 8: Alloy Material Cost compared to Eutectic Tin-Lead Solder
(Kester, 2001)

ALLOY	PRICE MULTIPLIER REFERENCED TO TIN-LEAD*	USE
SnAgCu	2.2 to 2.7	Considered a benchmark
SnCu	1.5	Low-cost alternative for wave soldering
SnAgBi	2.2 to 2.7	Possible Pb replacement (especially for SMT). Bi concern for SnPb finish boards. Avoid any Pb!
SnZn	2.2 to 2.7	Concerns with corrosion resistance. Requires special fluxes. No long-term reliability data available.
SnAg	2.2 to 2.7	Extensive data

*NOTE: Price is compared to SnPb at current (2001) metals market price.

4.5 Board Level Reliability of Lead-Free Packages

Providing a package that can meet stringent reflow and pre-conditioning requirements while still maintaining acceptable package level reliability is not enough, as the impact to board level reliability is also a primary concern. The actual impact of these different lead-free replacement alloy systems on the board level reliability is not well understood, especially across the different package types.

Swaminath et al. (2001) highlights the fact that most lead-free replacement alloys place higher demands on package material sets due to the required higher reflow temperatures. This condition results in different material sets, assembly processes and pre-conditioning requirements for packages.
Saminwath's study focused on the board level reliability of lead-free replacements for all significant package families; Ball Grid Array's (BGAs), Chip Scale Packages (CSPs) and leaded packages. In order to execute this study, a partnership was formed between industry leaders in package assembly, board fabrication/assembly, solder alloy supplier and an OEM. Through this partnership, the mounting of the lead-free components was analysed and the board level reliability assessment was begun to match end user requirements.

Hernandez and Vianco (1998) detail Sandia National Laboratories development of alternative solder materials to replace traditional lead-containing alloys. The alloys are based on the Sn-Ag, Sn-Ag-Bi and Sn-Ag-Bi-Au systems. Prototype hybrid microcircuit (HMC) test vehicles have been developed to evaluate these lead-free solders using Au-Pt-Pd thick film metallisation. Populated test vehicles with surface mount devices have been designed and fabricated to evaluate the reliability of surface mount solder joints. The test components consist of a variety of dummy chip capacitors and leadless ceramic chip carriers (LCCC's). Inter Metallic Compound (IMC) layer reaction products that form at the solder/substrate interface have been characterised and their respective growth kinetics quantified. Thicker IMC layers pose a potential reliability problem with solder joint integrity. Since the IMC layer is brittle, the likelihood of mechanical failure of a joint in service is increased. The effect of microstructure and the response of these different materials to wetting, aging and mechanical testing was also investigated.

4.6 Authors Experiments

The Author whilst working for PULSE Engineering, a U.S. based multinational electronics company, also directly conducted experiments in the following areas:

- Material Selection

As there is no alternative alloy to SnPb having the same melting point, reliability and process-friendly characteristic, whichever alternative lead-free alloy is chosen, its implementation will affect the entire product and process

In the process of lead elimination, the author found that there were distinct areas of attention:

Selection of lead-free solder paste (reflow) and alloy (wave). The materials and technologies to utilize them are available currently, and that a components lead-free finish material is dictated by the lead-free solder alloy/paste materials selection.

Final recommendations made by the author for alloy selection are as follows:

The author found that two alloys were suitable for reflow and wave soldering: SnAg3,5 and SnAgCu (Ag>3.5 %). For consumer electronics SnAgBi is a good alternative. SnCu0.7 can be used in wave soldering if cost is a main player and the used materials are compatible with higher temperatures.

The requirements which the author set regarding flux was that the selected flux must meet the following criteria:

a. Must comply with appropriate legislation and be environmentally friendly;

b. Must enhance solderability and be compatible with all materials used in the lead-free process.

c. Must have an acceptable cost.

- Defining a process

The author had to develop an effective method for process development to determine correct process settings. Introduction of a new material affects the entire process; therefore, all machine settings had to be reviewed.

In reflow soldering, the authors goal was to meet or reproduce the correct profile for the solder paste, and to stay within the specification for the components and board materials. The challenge was to do this with those machines that are currently in production, and without decreasing throughput.

The author found that for the wave soldering process, switching to lead-free will also effect most machine parameters.

- Reliability testing

Lead-free alloys can suffer decreased reliability when contaminated with lead. To avoid problems related to this, the most prudent course of action is to reduce the lead-free transition period to as short as possible.

The author ran a series of tests on PCB's which had come through the new process, and subjected them to environmental stress testing in the authors lab, incorporating tests such as thermal shock, high temperature and temperature humidity testing. Further testing was then carried out on the boards in the main production facility in China under the supervision of the author these tests included cross sectioning, an X-ray and SEM (Scanning Electron Microscope) investigation of the parts.

5.0 ENVIRONMENTAL IMPACTS AND TOXICITY OF LEAD FREE SOLDER

5.1 Overview of current materials and processes

A very wide range of solder alloys are available to suit the various requirements for metal joining, but most are based on tin and lead. In the electronics industry, a sharp melting point at not too high a temperature is desirable, in order to avoid thermal damage to components.

An alloy of 62 percent tin and 38 percent lead has a sharp melting point at the lowest possible temperature for these two metals (183 degrees C), and this alloy, or compositions quite near it (e.g. 60 percent tin - 40 percent lead) are the most common ones used in electronics soldering. Other alloy compositions are also used for specialised applications such as:

- High-melting 95 percent tin - 5 percent antimony
- 96.5 percent tin - 3.5 percent silver for service at elevated temperatures
- Low-melting 42 percent tin - 58 percent bismuth for soldering components particularly susceptible to thermal damage.

Solders are produced in various physical forms, depending on the way it is to be used.

These include:

- Cast ingots or bars
- Sticks
- Wire
- Small shapes or "preforms"
- Pastes

Cast ingots are used for making up solder baths, which are required for various mass production techniques such as "wave soldering". Sticks are often employed in engineering or plumbing, while solder wire is commonly used for "hand soldering" in electronics, using a soldering iron. Preforms are special shapes such as rings or mesh which are designed to be placed in a particular location, such as around protruding leads, and which are then subsequently heated to form the joint.

Solder pastes comprise a very fine alloy powder dispersed in a viscous flux medium. A common type of flux is based on natural pine rosin, which acts as a very weak acid when heated, but a number of other compounds are used as well. Their function is to aid in the wetting of the PCB substrate and allow the solder flow more freely at the solders appropriate melting point. Electronics fluxes must not be too corrosive to avoid damaging the circuitry and are available in water soluble or low residue forms.

Pastes can be deposited in virtually any required shape or thickness by a number of methods, and they are subsequently heated or “reflowed” to make the joint.

The fluxes required for the soldering process may be applied in a separate stage, but they are often intimately mixed with the solder itself. For example, solder wire is available with a core of flux running through it, preforms are made coated with flux powder.

5.1.1 Soldering techniques

The simplest soldering method is “*hand soldering*”. Here, a flux-cored solder wire is placed next to the surfaces to be joined (often a component lead and its appropriate pad) and a heated soldering iron is then placed in contact with the joint area. The solder melts, wets the metal surfaces, and the iron is removed, leaving the solder to solidify into the joint. Hand soldering is used in some aspects of electronics production, particularly the repair of faulty circuit boards.

For maximum output and efficiency, various mass soldering techniques have been devised that are able to produce a large number of soldered joints in a short time. One of the earliest of these processes is called “*wave soldering*”, since it employs a continuously-generated wave of molten solder to form the joints. A printed circuit board with all its components in position is placed on a gently inclined conveyor, which carries it through each of the soldering stages. The first stage is fluxing, where the underside of the circuit board (i.e. where the intended joints are located) passes over a fluxing device, usually a foamed wave of flux. The board then passes over heating panels that evaporate the flux solvent on the board, activate the flux itself, and preheat the board to minimise thermal shock. The circuit board finally passes over the solder wave, which contacts the whole underside and forms all the desired joints. Modern wave soldering machines have become very sophisticated, with computer control of all the production variables, and, in some cases, complex solder wave forms and inert atmospheres to achieve specific production objectives.

In wave soldering, the molten solder provides both the alloy and the heat required for the joint-forming operation.

In the other main technique called “*reflow soldering”*, the solid solder is placed in its correct position first, and then heat is subsequently applied by some means to melt it and form the joints.

The solder can be in the form of preforms or, more commonly, paste. Solder paste can be applied to a circuit board by syringe, stenciling, or screen printing, and these techniques are capable of very great accuracy. This is increasingly important with the rapidly growing use of "Surface Mount Technology" (SMT), where components are mounted directly onto the surface of a board, instead of their leads being inserted through drilled holes. Surface mounting enables components to be packed more closely together, and thus accurate printing of solder paste is essential.

There are various ways to apply heat in a reflow process. These include convection (hot gas), infra-red and vapour phase. Heating by means of a hot belt is suitable for smaller circuits, while a more recent technique for specialised applications uses a laser beam to heat each joint in turn.

Electronics is playing an increasingly important role in our lives, and many everyday items now depend on it. For example, motor cars, washing machines, cameras, radios, telephones, computers, etc., all depend on reliable electronics, and this has been achieved by the continuous evolution of soldering with tin-lead alloys. Evolution of this technology is continually occurring.

It is clear that lead-free soldering is a foregone conclusion. There are several alternatives under investigation, some of which are already in use. These investigations of the various lead-free solder alloy candidates have been in progress for the past few years. Researchers have been determining the solder alloy's physical and mechanical properties, environmental impacts and occupational toxicity.

Environmental regulators worldwide propose to limit the use of lead in manufactured products. In response to these actions, the electronic manufacturing community has developed several lead-free solder blends. The Printed Circuit Board (PCB) fabrication industry has also moved towards tin, silver, nickel and gold plating of surface mount pads and through holes. While there has been research with regard to the electrical and mechanical properties of lead-free solders, there has been little published research on the environmental effects of the available lead-free formulations.

5.2 Environmental Concerns of Lead

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 small as 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 minimise 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 very much reduced.

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, the electronics industry has demonstrated that the use of lead in the workplace is relatively safe.

The primary concern comes from the proper disposal of lead-containing materials. The issue arises due to the possibility that lead, from the materials that have been disposed of in landfills, might be leached out into the groundwater, and subsequently find its way into the drinking water.

The technical debate on this issue centers on the probability of leaching and determination of an acceptable level of lead in drinking water. The global electronics industry uses about 20,000 tons of lead each year, less than half of one percent of the world's total annual lead production. However, because lead is an environmental pollutant of concern, the pressure to reduce the industry's use of lead is growing.

Lead has been used for applications in glass, glazes and enamels since ancient times, The oldest artifacts that were made of lead reportedly dated back to 1600 - 2000 BC (Nordyne,1991).

Today the largest use of lead is in the manufacture of storage batteries, which accounts for 81% of all lead products. Other major uses of lead include ammunition, paints, cable sheathing, sheet lead and solders.

The United States is the world's leading producer of primary lead. Australia, Canada, Peru, Mexico, and Yugoslavia follow, in descending order. The U.S. primary lead production, which constitutes about 20% of world production, exhibited a trend of decline during the period of 1980 - 2001 (US Bureau of Mines, 2001).

Lead waste derived from the use of electronic solders has two primary sources:

1. The disposal of electronic assemblies (Radios TV's etc) and
2. Waste generated by the assembly of circuit boards.

In regards to point (1), scientific data is not readily available which describes technical scenarios or has provided conclusive evidence of the leaching and movement of lead from tin lead solder joints on discarded electronic chassis in landfills.

Lead bearing waste from circuit board assembly processes is generally in the form of solder dross. Dross is 96% to 98% tin and lead and it is readily recycled to retrieve the elemental metals for re-use. The exposure of factory workers to lead such as in the form of dust particles generated by dross or the melting of solders during processing is strictly controlled by Occupational Health and Safety Authority (OSHA) procedures for air quality and contamination monitoring. Maximum airborne concentration (TWA) is 0.05mg/m^3. An action level of 0.03mg/m^3 was established which when exceeded, requires certain procedures be instituted by the company management to minimise further exposure to worker.

The following table presents the airborne lead concentrations for several soldering operations from studies conducted over a five year period (sampling sensitivity –0.002 to 0.005 mg/m^3). Soldering processes used in the assembly of electronics (wave soldering, manual etc) exhibited levels well below the TWA limit as well as the action level .

Table 9. Lead Particle Concentrations from the Air Monitoring of Several Soldering Processes. (Vianco, 1993)

Type of Soldering	Typical Airborne lead Concentrations (Mean) mg/m^3
Automatic wave	
Electronics assembly	0.010
Manual gun and Iron	
Electronics and Electromechanical	0.010
Radiator manufacture Repair	0.028
Open dip pot tinning	
Electronics, Assembly, tool and die	0.004
Radiator manufacture	0.046
Open Flame joining	
Arts and crafts	0.015
Radiator Manufacture	0.038

The blood lead levels of eight individuals (from a test group of 37) who performed the accompanying job description, are detailed in the following table. All values were below the 25 micrograms/deciliter limit.

In summary, lead exposure to workers appears to be well controlled both in terms of the actual processes used in manufacturing as well as guidelines set by OSHA. However a lack of scientific evidence exists with respect to the hazard posed by tin-lead solder joints in electronic assemblies which are disposed in municipal landfills.

Table 10: Blood Lead Levels of Workers Performing Soldering Operations. (Vianco, 1993)

Employee	Blood Lead Level µg/100mL	Job Description
1	15	Mass Soldering
2	14	Hand Iron soldering
3	14	Hand Iron soldering
4	14	Hand Iron soldering
5	13	Occasional Hand
6	11	Iron soldering Layout

Note: Mean blood level for 37 employees, 11.7µg/100mL.
Values cited are typical for all 37 employees.

5.3 Lead in the Environment and in Industry

5.3.1 Adverse Health Effects of Lead

Lead bio-accumulates in the body; that is, it is retained over time and can have adverse health impacts when a sufficient accumulation has occurred. Once in the body, the lead binds strongly to proteins and inhibits normal synthesis and function. Effects include nervous and reproductive system disorders, delays in neurological and physical development, cognitive and behavioral changes, reduced production of hemoglobin with resulting anemia, and hypertension (Putman, 1986).

Occupational exposure to inorganic lead occurs primarily by inhalation, and possibly by ingestion. Dermal absorption is typically not a contributory factor, especially under conditions of good industrial hygiene.

Exposure to lead is customarily determined by measuring lead levels in the blood, an approach that also reflects contributions from non-occupational exposure such as lead in drinking water, inhalation of contaminated dusts and soils, leachate from pottery, and inhaled or ingested lead from paint flakes.

OSHA regulates the permissible workplace exposure limit for inorganic lead at 50 micrograms/m^3 This exposure limit is related to maintaining blood lead levels at or below 40 micrograms/deciliter, believed to prevent adverse health effects from exposure to lead throughout a working lifetime.

For workers planning to have children, OSHA recommends maintaining blood lead levels below 30 micrograms/deciliter.

A potential source of worker exposure in electronics is the soldering process, especially the wave solder operation. Observations near hand soldering and tinning operations (Monsalve, 1984) indicate that there is little danger of airborne lead exposure. Personal hygiene was the primary controlling factor in lead exposure. Part of this is due to lead relative non-volatility at normal soldering temperatures (Sax, 1984, Forsythe, 1956).

In the ambient environment, as opposed to the workplace, the potential for exposure to mobilised lead is at least as important as the presence of lead. The degree of mobilisation differs greatly among the reservoirs in which lead is contained. The USEPA regards the three major sources of lead in blood as lead-based paint, urban soil and dust, and lead in drinking water. Other sources include smelters and municipal waste and sewage sludge incinerators. The use of lead in products is thought by USEPA to be of much less concern.

5.3.2 Lead in the Environment

Lead is the most abundant of the heavy metals in Earth's crust, occurring principally as the sulfide ore galena. The ores also tend to contain silver, and the demand for the ores is thus based to some extent on the uses of silver. Natural emissions of lead to the atmosphere are about 13,000 tonnes per year. None of the natural sources is very significant, but the more important are windblown soil and volcanoes (Nriagu, 1989).

There have been various attempts to estimate the concentrations that result from these emissions, by both theoretical extrapolation and the measurement of lead in remote parts of Earth and in the remains of ancient man. These estimates suggest that the natural lead concentration in air is some 3-5 orders of magnitude less than current levels, and in water about 2-3 orders of magnitude less. While it is still possible to measure in certain remote areas environmental levels of lead as low as those attributable to natural emissions, it is clear that man-made mobilisation has increasingly contaminated all phases of the physical and biological environment.

The mining of galena and other lead ores adds a small amount of lead to the atmosphere as a consequence of windblown dust dispersion. Of much more consequence is the smelting of lead from its ore, which is responsible for about 15% of the emissions (Figure 1) (Nriagu and Pacyna, 1988).

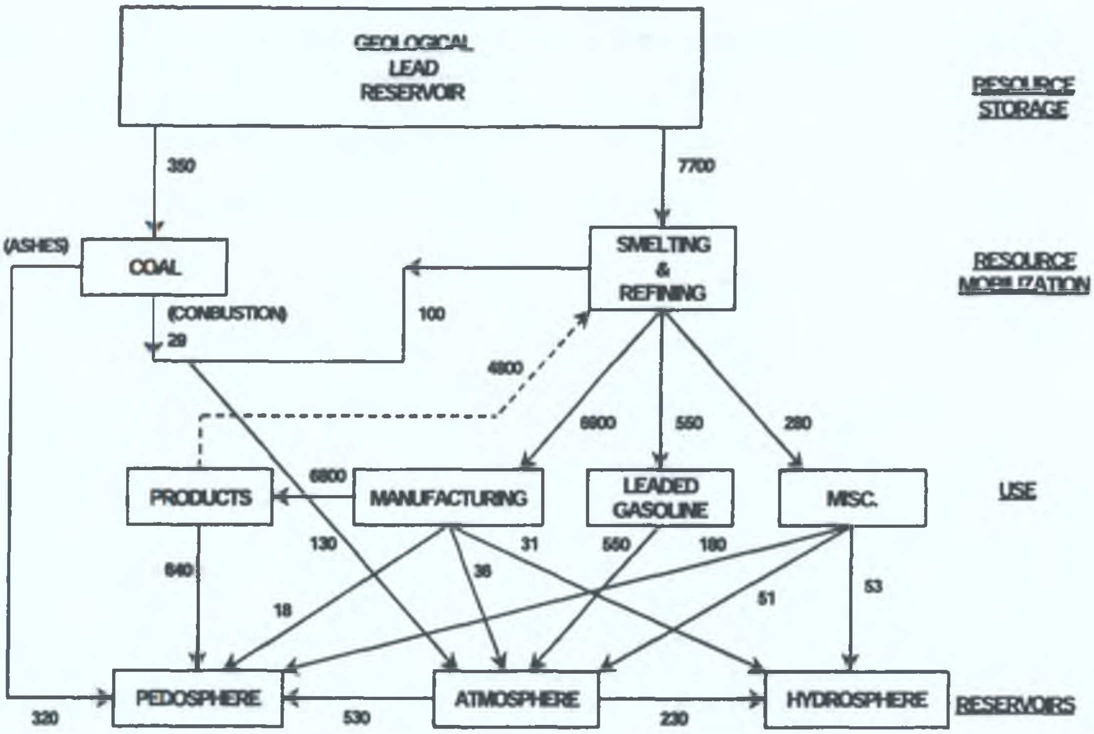

Figure 1: The cycling of lead through the world environment

Flows (in million pounds per year) are indicated in the above figure with an accuracy of about 25% with attention to the contributions of manufacturing activities. A large proportion of the lead used in products is recycled, mostly from automobile storage batteries. The difference between the amount of lead added to products each year and the amounts removed by recycling and disposal represents the increase in the embedded lead contained in products (Nriagu and Pacyna, 1988), (Allenby *et al.*, 1999).

The fluxes of lead to water and soils have also been estimated. For aquatic ecosystems, the dominant source by far is fallout from the atmosphere. In the case of soils, three sources are significant: coal ashes, discarded manufactured products, and atmospheric fallout. The estimate for manufactured products includes only discarded batteries and cable sheathing.

5.3.3 Industrial Uses

Lead has been used in industry for decades, and in some applications for centuries. The amount used in electronic solder is relatively minor.

The use of lead in electrical and electronic equipment was reviewed in 1986 (Key and Schlabach, 1986).
Their results show the dramatic decrease in lead use for cable sheathing with the substitution of polyethylene in the 1950s. Battery use has held fairly constant over the last decade for which information is available. No estimate is currently available for the quantity of lead used through out the industry as a stabiliser in plastic cable.

5.4 Legislation of Lead as a Toxic Substance.

Management of waste in industrialised countries ranges from highly regulated, specific, government controlled operations to practical non-existence. Within this range falls most industrialised countries which significantly regulate industrial/commercial hazardous waste, with or without also regulating household hazardous waste disposal.

When waste is disposed in an open landfill it is weathered by rainfall and reactions with other wastes, which allows metal elements and their salts to be leached from the metal surfaces of the waste. If the metal bearing leachate is allowed to contact stormwater, groundwater, or to migrate into groundwater, local drinking water supplies are threatened with contamination. The USEPA interest in lead-free solders derives from this concept, as well as lead's toxicity when absorbed into the skin or ingested. As these exposures are difficult to imagine from electronic products (few people eat printed circuit boards), the disposal/leachate problem becomes the USEPA primary focus for lead regulation.

The EU proposes to ban all lead in electronic products by the year 2004 (WEEE, 2000). Japan is also taking a similar regulatory stance (JEIDA, 1998). While the toxic effects of lead are well known, a literature search revealed no evidence that there has been research into the environmental effects of lead-free solders.

Hazardous waste is defined as any waste that may "pose a substantial present or potential threat to human health and the environment when improperly treated, stored, transported, or otherwise managed."
The USEPA identified four characteristics of hazardous waste:

- toxicity
- corrosivity
- reactivity
- ignitability.

USEPA also developed standardised procedures and criteria for determining whether a waste exhibits one of these characteristics.

5.5 Toxicity Characteristic Leaching Procedure

The Toxicity Characteristic Leaching Procedure (TCLP) was developed by USEPA for determining whether a waste was hazardous by virtue of its toxicity. The law defines a hazardous waste as a waste that presents a threat to human health and the environment when “improperly managed,” thus the USEPA has developed a set of assumptions that describe possible ways in which a waste can be disposed improperly. The USEPA intended this so called “mismanagement scenario” to simulate a “plausible worst case” of mismanagement. Under this worst case scenario, USEPA assumes that potentially hazardous wastes would be co-disposed with municipal solid waste in a landfill with actively decomposing material overlying a groundwater aquifer.

5.5.1 Development of the Extraction Procedure

The TCLP itself was developed specifically based on these assumptions regarding waste mismanagement.

Assuming that potentially hazardous waste could be disposed in a landfill containing actively decomposing municipal waste, the USEPA reasons that the most likely pathway for human exposure to toxic constituents would be through drinking water contaminated by leachate from the landfill. Thus, the TCLP defines the toxicity of a waste by measuring the potential for the toxic constituents present in the waste to leach out and contaminate groundwater and surface water (and by extension, drinking water sources) at levels of health or environmental concern. Electronic devices containing tin/lead solders are disposed in municipal landfills. These landfills allow lead to leach from the disposed items.

Specifically, the TCLP requires analyzing a liquid waste or liquid waste extract to determine whether it contains unacceptably high concentrations of any of eight toxic metal constituents identified in the U.S. National Interim Primary Drinking Water Standards. These are: Arsenic, Barium, Cadmium, Chromium, Lead, Mercury, Selenium, Silver. Some U.S. States have added copper, nickel, and zinc to this list.

Consistent with the mismanagement scenario, the liquid extract is obtained from solid waste by exposing the waste to organic acids (the acids likely to be found in a landfill containing decomposing municipal wastes). Full details of the various leach methods can be found in Appendix 3.

5.6 Surface Mount Council Toxicity Data

The Surface Mount Council in its report gives a table showing the relative toxicity of the various lead free soldering elements. The table is reproduced here.

Table 11: Surface Mount Council Toxicity Data

Metal Element	**OSHA PEL or ACGIH TLV (mg/m^3)**
Bismuth	None
Zinc Oxide Fume	5
Tin (inorganic)	2
Tin (organic)	0.1
Antimony	0.5
Copper (dust)	1
Copper (fume)	0.1
Indium	0.1
Silver (metal dust and fume)	0.1*a*
Silver (and soluble compounds)	0.01*b*
Lead (inorganic)	0.05*c*

a: OSHA PEL *b*: ACGIH TLV *c*: ACGIH TLV is 0.15 mg/M^3

Based on this data and other data cited in its report, the Surface Mount Council assigns this toxicity ranking to the common lead free solder alloying elements:

Bi < Zn < In < Sn < Cu < Sb < Ag < Pb

Lead and its compounds have been rated as one of the top 17 chemicals that impose the greatest threat to human health (USEPA, 2001).

Public-health officials have classified lead as the number one environmental threat to children. The U.S. Center for Disease Control has lowered the threshold definition of dangerous levels of lead in the blood stream by 60%, from 25 microgram per deciliter to 10 microgram per deciliter.

5.7 The Alternative Metals

5.7.1 Antimony

Antimony (Sb) has several forms, the most common of which is a hard, silver-white crystalline solid. Antimony has an atomic weight of 121.75, a melting point of 630.5°C, and a boiling point of 1635°C.

Antimony has been used in a variety of applications for 2,000 years, and today is most commonly found alloyed with other elements. Antimony is used to harden lead for batteries and in cable sheaths. Antimony also has been used to manufacture semiconductors.

Antimony is one of the main ingredients in food-grade pewter, and is found in most lead-free plumbing solders.

5.7.1.1 Advantages of Antimony in Solder Alloys

Antimony has demonstrated several advantages when used as a doping agent in solder alloys. When used in tin-lead solders in the 0.3% - 0.5 % range, the alloys exhibit better thermal fatigue resistance than alloys that do not contain antimony. When added to tin based solders, antimony forms intermetallic structures with other materials, such as silver and copper, which adds to the strength of the alloy.

In Ames Research Laboratory's patent on an SnAgCu alloy, it is stated that, "In another embodiment of the invention, the solder may include at least one alloy component selected from the group consisting essentially of Si, Sb, Zn, Mg, Ca, a rare earth element, and such metals in a collective amount not exceeding about 1% weight for example, to improve wettability, enhance fatigue strength, and/or refine solder joint grain size".

5.7.1.2 The Toxicity of Antimony

According to the USEPA, antimony is ranked below zinc, bismuth, copper, and silver (all of which are constituents of lead-free alloys), as well as lead, in terms of its potential threat to human health.

5.8 The Properties of Tin

Tin is an important commodity in international trade, but it does not occur naturally as a metal. By far the most important tin mineral is cassiterite, a naturally occurring oxide of tin with the chemical formula SnO_2.

Pure tin is a silvery white metal which is soft, ductile and malleable. In its purest form, cassiterite contains 78.6 percent tin. The cassiterite occurs either in rocks, often very irregular veins or lodes, or in debris which has built up from the gradual wearing down of tin-bearing rocks to form alluvial deposits which are found in river beds and valleys or on the ocean floor close inshore. Tin mining is very much a global industry with tin mining operations located worldwide.

Tin is a member of Group IV of the Periodic Table, along with carbon, silicon, germanium and lead. In compounds, it can appear in two oxidation states, either +2 (stannous form) or +4 (stannic form), and it forms various industrially-important compounds of each type.

The chemical symbol for tin is Sn and it has an Atomic number of 50. Tin's atomic mass is 118.69 and the metal has a density of $7.28 g/cm^3$ and melts at 232 degrees C.

Tin is valued for its non-toxicity, resistance to corrosion and attractive appearance. In density, tin could be described as a medium weight metal - heavier than aluminium, and zinc, but light in comparison with copper, silver, lead, mercury and gold.

Tin readily forms alloys with other metals to create useful materials such as solders, bronzes, pewter, bearing alloys and fusible alloys.

5.8.1 Tin and the Environment.

Tin can be found almost everywhere in nature. Small amounts are found in soil and rocks as well as plants and in water. There is approximately 0.35g contained in humans and this figure does not tend to increase with age.

5.8.2 Tin in General Electronics

Aside from its important use as a constituent of solder alloys to form joints between metals, tin has a number of other applications in the general electrical/electronics field. A major use is the application of a coating of either pure tin or a tin alloy (usually 60 percent tin - 40 percent lead) to preserve the solderability of a surface.

When a surface has poor solderability, molten solder finds it difficult to adhere properly, and thus a faulty joint may be subsequently formed. This will can cause failures on any electronics assembly, since only one poor joint will cause a malfunction.

The deposition of either tin or tin-lead alloy on a clean surface (often copper or nickel-iron in electronics) prevents oxidation or other tarnishing of the surface, and thus preserves its solderability. Such coatings (usually 5 - 8 micrometres thick) are applied to the leads or pads of electronic components, and also to the tracks of printed circuit boards; the application may be by electroplating (for example "barrel plating" of small components) or dipping into a bath of the molten alloy.

The electroplating of tin-lead plays an important role in the production of printed circuit boards. It preserves the solderability of the final tracks and pads and it is also required in the most common circuit board processes to produce the complex pattern of tracks on the board.

Here, the tin-lead electroplated coating acts as an "etch resist" on the board, so that when the PCB is treated with an etching solution, all the unwanted copper surfaces are dissolved away, leaving the desired copper track pattern under the tin-lead coating.

In modern circuit board production, the plating stages of PCBs take place in large tanks, and the whole process is monitored and controlled by computer; the thickness of tin-lead alloy required is about ten micrometres.

Another production process uses a technique known as "hot air levelling" to leave a bright uniform coating of tin-lead on the final circuit board; here, the board is briefly immersed in the molten alloy, and excess is efficiently removed by applying jets of hot air.

5.8.3 Tin in Solder

The largest single use for tin is in solder alloys, which consume about 31 percent of world tin production. Tin is an important constituent of the majority of solders because of its ability to bond with a large number of metals.

6.0 EXPERIMENTAL DATA AND DISCUSSION

6.1 Introduction

There is no alternative alloy to tin-lead which has the same melting point, reliability and process-friendly characteristic. Consequently, whichever alternative lead-free alloy is chosen, its implementation will affect the entire product and process, including the selection of new fluxes, board finishes and components.

As each manufacturing process is unique, it was essential that testing be performed on products currently manufactured by the authors employer Pulse Engineering. Whereas previous research as presented in the literature review provided a good starting point, it is not the case that one may simply imitate what has been done previously, as there are different factors relating to each individual manufacturing process that will yield different results. Factors such as the materials used, reflow temperatures and other process specific factors account for these differences, and no two assembly processes are identical.

A full account of all of the tests performed and the data gathered are presented in Appendix 4, (Experimental Results) which details specifically what work was done and includes data on the author's tests, which validates the author's conclusions.

The author directly conducted experiments in the following areas:

- Material Selection

Whereby a set of Solder pastes, Flux and lead finishes were determined for the purpose of the experiment

- Defined a Process

Whereby the author set the assembly process conditions and designed the experiment, and selected the appropriate equipment and process flow to complete the experiment.

- Reliability Testing

Whereby the author ran a series of environmental stress tests on the assembled prototype products, including thermal shock and lead-pull tests, to determine the products expected reliability under field operating conditions.

This chapter presents an account of the work carried out by the author, and the rationale for the various tests. A discussion on all tests is then presented. The specific resulting data on the various tests are contained in Appendix 4.

To assess the practical aspects of eliminating lead from a process at a production facility where the author worked, it was found that there were a number of critical issues that needed to be focused on:

- Selection of lead-free solder paste (reflow) and alloy (wave)
- Availability of materials and technologies
- Components lead-free finish material
- Heat resistance of plastics and other component materials

These issues are individually discussed in detail below.

6.2 Alloy selection

The first selection made by the author was that of the alloy. There are numerous lead-free alloys available today including a number of patented alloys. The following input criteria were used to select the most appropriate alloy:

- Research by Universities and consortia. Very useful information can be found in research work available on the Internet and in papers, e.g.: IPC Roadmap (A Guide for Assembly of Lead-Free Electronics) - http://www.leadfree.org.

- The UK DTI report "Lead-free soldering" and the "Update 2000" Available online at http://www.npl.co.uk/npl/ei/news/pbfree.html.

- The report entitled “Improved Design Life and Environmentally Aware Manufacturing of Electronics Assemblies by Lead-Free Soldering” (IDEALS) by Marconi Materials Technology Ltd, Philips CFT, Siemens AG, Multicore Solders Ltd, Witmetaal BV and NMRC.

- Road Map 2000 for Commercialisation of Lead-free Solder-ver.1.2 by Japan Electronic Industry Development Association.

- Experiences from other companies already producing lead-free products.

Although most companies are hesitant to provide information on defect numbers, Pulse customers such as 3COM and Nortel provided a great deal of information to the author about solder contamination, process adjustments, solder temperatures, parts wear and flux residues and their subsequent contamination factor.

The author found that the availability of elements like indium and gold is limited; therefore, costs are high (> $150 per kg). Price and availability issues reduce the field of candidate elements to Sn, Ag, Zn, Sb, Cu, Bi and Cd. Cadmium is toxic and is therefore also banned from the list. Antimony is also toxic, but only at temperatures above 630 degrees C (Antimony's melting point), when toxic fumes are emitted. Bismuth has recycling and fillet lifting issues.

Tin is most suitable, exhibiting low cost and excellent physical, electrical and thermal properties. Other elements need to be added in order to drop the melting point to an acceptable level.

Having considered all of the above factors, a commercially available solder was chosen. This is marketed by the trade name “CASTIN”, from “AIM Solder”. This is specially formulated Tin, Silver, Copper formulation which has the lowest melting point and lowest cost of the commercially available SnAgCu family. It was tested alongside a SnPb solder so that comparisons could be made. Various lead finishes on the IC leads were also investigated to determine if any significant issues arose. The lead finishes chosen were SnPb, NiPd, and NiPdAu.

The author used wetting balance tests to indicate the solderability of available alloys. Wettability in soldering is a function of solder temperature, contact time, flux, and reflow/wave configuration. Relevant results of the wetting balance tests performed are presented in Appendix 4.

Melting point was also one criterion for alloy selection, since the process temperatures, peak and time above liquidus for reflow and solderpot temperature and contact time for soldering will very much depend on melting temperature. The lower the melting point, the wider the process window, which makes it easier to design an effective assembly process.

Thermal properties of the alloy are critical. Automotive requirements range from -40 to +150 degrees C in the motor compartments, where some consumer requirements only have to deal with ambient temperatures of minimum 0 and maximum 60 degrees C. This allows some consumer electronic suppliers to use small amounts of bismuth in order to reduce melting temperatures. Again results relating to the thermal properties of the chosen alloys are contained in Appendix 4.

Final recommendations made by the author for alloy selection are as follows:
The author found that the alloy SnAgCu was suitable for reflow and wave soldering.

For consumer electronics, SnAgBi would be a good alternative. SnCu0.7 can be used in wave soldering if cost is a critical issue and the used materials are compatible with higher temperatures, since the solder temperature will need to be at or above 270 degrees C.
Again the above statements are the result of the cost analysis of the individual alloys as presented in the literature review, and the results obtained from the prototype assembly experiments as are detailed in Appendix 4.

6.2.1 Flux selection

Since the wetting characteristic of lead-free alloys is not as good as tin-lead at lower temperatures, the use of a good flux is very important to the process. Temperatures in lead-free processing have increased, whereas the fluxes that are used today for lead-free soldering are the same as used for tin-lead.
The main function of flux (and flux/vehicle in solder paste) is to remove and prevent oxidation. For both wave and reflow processes, activation temperature and activation time during heating and soldering need to be reformulated for use with lead-free alloys. For the reflow process, this means that the flux should be able to withstand the higher peak temperatures (up to 250 degrees C) at the same time above liquidus. For wave soldering, the flux must be capable of withstanding 130 degrees C preheat and 280 degrees C solder liquidous temperatures for approximately 3 seconds contact time as is evident by the solder profiles used in the authors experiment to reflow the chosen lead-free pastes.

VOC-free water based fluxes, and RMA Flux from the same solder supplier as the CASTIN paste "AIM" were used by the author as they represent the cleanest technology currently available. New technologies such as dissolving rosin in VOC-free water based fluxes are being investigated right now by manufacturers such as AIM, but were not available at the time the experiments were run.

The requirements which the author set regarding flux was that the selected flux must meet the following criteria:

a) Must comply with appropriate legislation and be environmentally friendly
b) Must enhance solderability and be compatible with all materials used in the lead-free process

Must have an acceptable cost

The fluxes chosen as mentioned above were obtained from AIM to ensure as close a chemical match as possible and to eliminate possible process incompatibility issues which would detract from the main focus of the experriment.

6.2.2 Board material and finish

For lead-free soldering processes, the author focused on FR-4 halogen-free material. Halogen-free boards are desirable because the proposed WEEE directive proposes to phase out halogenated flame retardants by 2004. The new materials had to be able to withstand the requisite higher temperatures. They did not exhibit warpage or delamination of the layers at these higher temperatures. Halogen-free boards were already available for 1.3 times the price of conventional FR-4.

The majority of printed circuit boards in today's soldering processes have a tin-lead coating on the pads, as well as in the through-holes. This coating is applied using HASL (Hot Air Solder Levelled).

Organic Solderability Protectants (OSP) is an alternative finish which the author investigated, and was available for a price in the same range as HASL. OSP was easily processed, and was relatively free of ionic contamination.

6.2.3 Component material and finishes.

The author found that a number of electronic components were already available with lead-free finishes. Alternatives are pure tin or tin-copper. In general, the changeover to lead-free finishes for components is expected to be the last part of the total lead-free process conversion and certainly the most difficult step of lead-free implementation. Component manufacturers do have concerns about going lead-free with respect to reliability, as well as higher process temperatures.

Current technology for certain components, such as BGAs and relays, is not so advanced that all of these components can meet the new requirements for heat resistance of 260 degrees C for 10 seconds. New moulded components with solutions to popcorning and delamination need to be designed and approved by end customers. Compounds used for these components should also be halogen-free. Higher temperatures can cause warpage with connectors and BGAs. The author found that most companies complain that lead-free components are not available for the market, as component manufacturers appear to want to produce lead-free products for higher volume demand.

6.2.4 Selection compatibility with legislation.

Once all selections for the lead-free materials were made, the author reviewed the selected items and compared them with current legislation. All the materials compatible with the higher soldering temperatures were compatible with current legislation.

6.3 Defining and Developing an Efficient Assembly Method

The author had to develop an effective method for process development to determine correct process settings. Lead-free soldering is not merely a matter of replacing one alloy with another. Introduction of a new material affects the entire process; therefore, all machine settings had to be reviewed.

In reflow soldering, the author's goal was to meet or reproduce the correct profile for the solder paste, and to stay within the specification for the components and board materials. The challenge was to do this with the machines that are currently in production, and without affecting (decreasing) throughput.

The prototype tests found that for the wave soldering process, switching to lead-free also affects most machine parameters. For these processes, as it was also the goal to implement lead-free alloys in combination with VOC-free water based fluxes without decreasing productivity or throughput.

An experiment had to be designed in order to find out if the intended production machines were capable of doing this.

The author found in the Design of Experiments, and more in the Taguchi approach, a very effective method of ascertaining equipment capability. By applying this technique, it was possible to significantly reduce the time required for experimental investigations.

The use of Taguchi experiments optimised the product/process design to make the performance minimally sensitive to the various causes of variation. which reduces the number of experimental runs.

6.4 Discussion and Conclusions based on the Experimental Tests

On evaluating the results, the author found that the solder temperature of 265 degree C is preferred. The use of nitrogen for SnAgCu reduces dross formation, and also reduces solder failures. The best results were found with longer contact times, resulting in better hole filling and eliminating bridges.

This experiment proved that preheat temperature is of minor importance as long as one stays within the specification. This is an advantage, because this meant that a larger temperature difference over the board did not impact soldering significantly.

6.5 Cost Evaluation

The author found that lead-free soldering will impact on several cost aspects in the assembly process. The costs can be analysed under the following three headings:

Material Costs:

These are costs of the materials used in the assembly itself :

- solder
- board material
- components
- flux
- nitrogen
- cleaning chemistries

Operational Costs:

The operational costs include:

- Maintenance
- Through-put
- Repair costs due to solder defects

For some processes, operational costs decreased. Due to the new materials that were used, the defect level and maintenance times were reduced.

Energy costs:

In the wave soldering process, there was a significant increase in preheat temperatures. This resulted in a maximum 25 % more heat required for the board. The solder temperature increased by a maximum 3 %. The indication here being that the lead-free process is less energy efficient due to the extra power requirement to reach the raised melting temperatures of lead-free solders.

6.6 Reliability

6.6.1 Lead-Contamination in Lead-Free Electronics Assembly

From the literature review, the author found that the question of what happens to a lead-free solder joint if it becomes contaminated with lead is important because during the transition to lead-free soldering, it is very likely that tin-lead parts will still be used in a great deal of production. In other words, just because one implements a lead-free solder alloy does not mean that tin/lead coated components and boards will

Unfortunately, in the past the presence of lead in lead-free alloys has been presumed to be acceptable. The logic behind this was that tin and lead are soluble in a lead-free system. However, what has been overlooked is that the intermetallic crystalline structures in lead-free systems are not soluble and will precipitate at lead boundaries. Thus, when using a lead-free alloy to solder to tin-lead coated component leads, lead can actually create voids in the solder joint that can result in joint failure.

One of the most pressing questions in lead-free soldering pertains to the lead-contamination of lead-free solders and its effects. In additional work carried out by the author and also presented in the literature review and references, lead-free alloys can suffer decreased reliability when contaminated with lead. To avoid problems related to this, the most prudent course of action is to reduce the lead-free transition period. In other words, when a company implements a lead-free solder alloy, it should also implement lead-free component terminations and circuit board coatings.

The author ran a series of tests on PCBs which had come through the new process, and subjected them to environmental stress testing in the Pulse Ireland laboratory. The tests included thermal shock, high temperature and temperature humidity testing. Further testing was then carried out on the boards in the main production facility in China under the supervision of the author. These tests included cross sectioning, an X-ray and SEM (Scanning Electron Microscope) investigation of the parts.
Work on reliability of lead-free assemblies has shown it to be equivalent to tin-lead in terms of cycles to failure in thermo-mechanical fatigue tests. Specific conclusions from the reliability work were that tin-lead solder consistently yielded the best wetting and joint formation; the other lead-free solders offer potential for component attachment in surface mount technology. The joint strengths of the lead-free alloys are very comparable to those of tin-lead solder. The results of the tests are presented in Appendix 4.

6.7 Discussion of results of experimental tests

As can be corroborated in Appendix 4, (Experimental Results), all the components assembled had electrical continuity.

Existing equipment sets in the production facility were capable of processing lead-free assemblies reliably.

For the tested components, no failures were observed.

The results suggested no difference in the reliability among the various lead-free solder joints tested.

The contact angle data for Ni/Pd and Ni/Pd/Au finish components was higher than for Sn/Pb components for all types of solder pastes evaluated. Differences in contact angle proved to be a cosmetic issue only and did not correlate to any difference in reliability or mechanical strength of the joints.

The lead-pull data was lower for Sn/Pb finish components compared to Ni/Pd and Ni/Pd/Au for all types of solder pastes evaluated. Data was essentially equivalent for Ni/Pd and Ni/Pd/Au finished components.

The lead-pull failure mode analysis showed the Sn/Pb components failed within the solder. In most cases with Ni/Pd and Ni/Pd/Au components, the solder was pulled completely from the pad.

Temperature cycle testing of the 3 different lead finish components with each solder paste showed no failures out to 3000 cycles. The temperature cycle range was -65 deg C to +150deg C.

Cross-sections of temp cycled units showed no cracks in the solder joints out to 250 temperature cycles.

Wetting balance test results showed that the Sn/Pb components took longer to pass the T_0 line than the Ni/Pd or the Ni/Pd/Au finished components in reference to the Wetting balance graphs contained in Appendix 4.. The gold flash on the Ni/Pd/Au components improved wetting performance as measured by time to pass T_0.

The process window for lead-free wave soldering is within the established region for tin-lead soldering, albeit at the top end in terms of soldering time and temperature.

The process window for lead-free reflow soldering is compatible with the majority of current component demands, but the minimum soldering temperature of 225 - 230°C is a cause for concern for some IC packages, capacitors and connectors. This is clearly an impediment to the rapid adoption of lead-free solders unless the reflow temperature can be reduced.

Full Scale production of PCB's using the experimental technology was not possible due to economic constraints, however, the author would recommend the running of full scale production to ensure the repeatbility of the process, and to determine if such a process would be robust enough, to survive the many variables experienced in production. In effect the experiment performed was under very controlled circumstances and may not be fully representative of full scale production.
The author would also recommend a continued life cycle assessment of the lead-free manufactured samples to get a more accurate representation of the MTBF (Mean Time Between Failures) and FIT (Failure in Time) characteristics of the products.

7.0 DISCUSSION AND CONCLUSIONS

The proposed WEEE Directive is a very important piece of legislation for the electronics industry that cannot be ignored – it was initially one of the main drivers for the introduction of lead-free solders, it has since been somewhat diluted due to continued debate. Economics, cost reduction opportunities, competitive action and free-trade issues are now likely to be the key drivers for change.

The WEEE lead ban/restriction proposals are largely based on the theory that certain lead uses pose an unmanageable environmental and public health risk when lead-containing products are discarded; however, many studies mentioned in the literature review have demonstrated that this theory is largely untrue.

All of the studies that have been conducted to assess lead-free solders have concluded that there is currently no drop-in replacement for tin-lead solder in all electronic applications. Possible alternatives include lead-free metallic solders and conductive polymers.

A project, funded jointly by Environment Canada, the U.S. Environmental Protection Agency, and the International Lead-Zinc Research Organization, found that properly designed and operated municipal incinerators efficiently captured lead and did not violate air quality standards even when the quantity of lead in the feed stream was increased six-fold.

The data from impact and toxicity experiments referred to previously shows that most lead free solders leach at levels that would cause them to be classified as a hazardous waste, failing both silver and antimony levels. If lead free solders containing silver or antimony are improperly disposed and contact groundwater, the solders could render that groundwater unsafe to drink. Solder dross from these alloys carries the same risks, as the dross behaved similarly to the parent alloys in these experiments. Bismuth and indium are not currently regulated and their toxicity has not been widely studied, thus they pose unknown challenges for adopters of lead free solders.

As the benefits of lead-free solders are recognised, the author believes that the applications that commercially justify their adoption will be clarified. The justification will result from the industries ability to market the perceived benefits of the change.

The lead-free soldering option will be more expensive due to the higher cost of the solder alloys, lead being relatively cheap, and also due to the higher processing temperatures involved; there will also be a significant one-off cost in implementing the process. However, for industrial soldering processes, the material costs are a minor proportion of the total processing costs and the use of lead-free solders in itself is not expected to place a noticeable cost premium on the final product. Panasonic's experience of lead-free implementation as mentioned in the literature review has been cost-neutral because the reduction in bridging defects offset the additional consumables costs. However, the prospect of incurring knock-on costs, such as the use of more temperature resistant packaging for components or connectors, must be accounted for.

The adoption of lead-free soldering will have an impact on several industrial sectors. For the solder, component and circuit board manufacturers, it will entail new products and major modifications to existing product lines with appropriate standards needing to be devised. Electronics manufacturers will have to implement changes to their processing conditions and the different characteristics of the soldered joints.

In summary, the lead-free issue is here to stay, as market pressures will continue to drive the issue and many electronic devices are still covered under the WEEE directive.
The scope of the issue and those affected, however, has definitely changed and some companies may take a step back from their current activities to review their situation.
Lead-free soldering technology has been demonstrated to be viable. In addition it is attractive from an environmental point of view.

The focus has changed over the past few years from compliance with legislation to reaction to market requirements. In these days of environmentally aware consumers the real driving force both now and into the future is the end consumer. It is generally accepted that there is an increasing feeling of moral responsibility towards the environment which is expected to continue.

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Appendix 1.

PROPOSAL FOR A DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL ON WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT.

THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE EUROPEAN UNION,
Having regard to the Treaty establishing the European Community, and in particular Article 175 thereof, Having regard to the proposal from the Commission, Having regard to the opinion of the Economic and Social Committee, Having regard to the opinion of the Committee of Regions, Acting in accordance with the procedure laid down in Article 251 of the Treaty,
Whereas:

(1) The objectives of the Community's environment policy, as set out in Article 174 (1) and (2) of the EC Treaty, aim in particular at preserving, protecting and improving the quality of the environment, protecting human health and utilising national resources prudently and rationally. Whereas this policy is based on the principles that preventive action should be taken, that environmental damage should as a priority be rectified at source and that the polluter should pay;

(2) The Community programme of policy and action in relation to the environment and sustainable development ("Fifth Environmental Action Programme") states that the achievement of sustainable development calls for significant changes in current patterns of development, production, consumption and behaviour and advocates, inter alia, the reduction of wasteful consumption of natural resources and the prevention of pollution; whereas this programme mentions Waste Electrical and Electronic Equipment (WEEE) as one of the target areas to be regulated, in view of the application of the principles of prevention, recovery and safe disposal of waste.

(3) The Review of the Community Waste Strategy states that where the generation of waste cannot be avoided, it should be reused or recovered for its material or energy.

(4) The Council, in its Resolution of 24 February 1997 on the Community strategy for waste management, invited the Commission to develop, as soon as possible, an appropriate follow-up to the projects of the priority waste streams programme, including WEEE.

(5) The European Parliament, in its Resolution of 14 November 1996 asked the Commission to present proposals for Directives on a number of priority waste streams, including electrical and electronic waste, and to base such proposals on the principle of producer responsibility. The

European Parliament, in the same Resolution, requests the Council and the Commission to put forward proposals for cutting the volume of waste.

(6) Article 2(2) of Council Directive 75/442/EEC of 15 July 1975 on waste, as last amended by Commission Decision 96/350/EC, provides that specific rules for particular instances or supplementing those of the said Directive on the management of particular categories of waste may be laid down by means of individual Directives.

(7) The amount of WEEE generated in the European Union is growing rapidly, the content of hazardous components in electrical and electronic equipment is a major concern during the waste management phase and recycling of WEEE is not undertaken to a sufficient extent.

(8) The objective of improving the management of WEEE cannot be achieved effectively by Member States acting individually. In particular, different national applications of the producer responsibility principle lead to substantial disparities in the financial burden on economic operators. Having different national policies on the management of WEEE hampers the effectiveness of national recycling policies.

(9) The provisions of this Directive should apply to products and producers irrespective of the selling technique, including distance and electronic selling.

(10) The scope of the legislation should cover all electrical and electronic equipment used by consumers and electrical and electronic equipment intended for professional use which are likely to end up in the municipal waste stream.

(11) It is necessary to draw up as quickly as possible the legislation which is lacking concerning the design and manufacture of electrical and electronic equipment to minimise their impact on the environment during their life cycle. In the interest of overall consistency between Directives relevant to electrical and electronic equipment, this legislation should be developed in accordance with the principles set out in the Council Resolution of 7 May 1985 on a new approach to technical harmonisation and standards.

(12) Separate collection is the precondition to ensure specific treatment and recycling of WEEE and is necessary to achieve the chosen level of protection of human and animal health and the environment in the Community. Consumers have to actively contribute to the success of such collection and should be encouraged to return WEEE. For this purpose, convenient facilities for the return of WEEE, including public collection points, where private households should be able to return their waste free of charge, have to be set up.

(13) A collection target for WEEE used by private households should be aimed at in order to attain the chosen level of protection and harmonised environmental objectives of the Community and more specifically to ensure that Member States strive to set up efficient collection schemes.

(14) Specific treatment for WEEE is indispensable in order to avoid the dispersion of pollutants into the recycled material or into the waste stream and is the most effective means of ensuring compliance with the chosen level of protection of the environment of the Community. Recycling facilities have to comply with certain minimum standards to prevent negative environmental impacts associated with the treatment of WEEE.

(15) A high level of recovery, in particular re-use or recycling, should be achieved and producers encouraged to integrate recycled material in new equipment.

(16) Basic principles with regard to the financing of WEEE management have to be set at Community level and financing schemes have to contribute to high collection rates as well as to the implementation of the principle of producer responsibility; to achieve the benefits of the producer responsibility concept most efficiently, producers should be encouraged to fulfil their responsibility individually provided they contribute to the financing of waste from products put on the market before entry into force of the financing obligation introduced by this Directive.

(17) Users of electrical and electronic equipment from private households should have the possibility of returning WEEE free of charge. Producers shall therefore finance the treatment, recovery and disposal of WEEE. In order to reduce costs for producers resulting from the management of waste from products put on the market before entry into force (historical waste) of this legislation, a transition period of five years after entry into force of the Directive is granted. The responsibility for the financing of the management of historical waste should be shared by all existing producers and fulfilled through either individual or collective systems. Collective systems should not have the effect of excluding niche and low volume producers, importers and new entrants.

(18) Information to users about the collection systems and their role in the management of WEEE is indispensable for the success of WEEE collection. Such information implies the proper marking of electrical and electronic equipment which could end up in rubbish bins or similar means of municipal waste collection.

(19) Information for treatment facilities provided by producers is important to facilitate the

management, in particular the treatment, of WEEE.

(20) Information about the numbers and weight of items of electrical and electronic equipment put on the market in the European Union and the rates of collection and recycling of WEEE is necessary to monitor the success of collection schemes.

(21) Since the measures necessary for the implementation of this Directive are measures of general scope within the meaning of Article 2 of Council Decision 1999/468/EC of 28 June 1999 laying down the procedures for the exercise of implementing powers conferred on the Commission80, they should be adopted by use of the regulatory procedure provided for in Article 5 of that Decision.

HAVE ADOPTED THIS DIRECTIVE:

Article 1

Objectives

This Directive lays down measures which aim, as a first priority, at the prevention of waste electrical and electronic equipment, and in addition, at the reuse, recycling and other forms of recovery of such wastes so as to reduce the disposal of waste. It also seeks to improve the environmental performance of all economic operators involved in the life cycle of electrical and electronic equipment and in particular operators directly involved in the treatment of waste electrical and electronic equipment.

Article 2

Definitions

For the purposes of this Directive:

1. “electrical and electronic equipment” means equipment which is dependent on electric currents or electromagnetic fields in order to work properly and equipment for the generation, transfer and measurement of such currents and fields falling under the categories set out in Annex I A and designed for use with a voltage rating not exceeding 1000 Volt for alternating current and 1500 Volt for direct current.

2. “waste electrical and electronic equipment” means electrical or electronic equipment which is a waste within the meaning of Article 1(a) of Directive 75/442/EEC; waste electrical and electronic equipment includes all components, sub-assemblies and consumables, which are part of the product at the time of discarding;

3. “prevention” means measures aimed at reducing the quantity and the harmfulness to the

environment of waste electrical and electronic equipment, their materials and substances;

4. “re-use” means any operation by which waste electrical and electronic equipment or its components are used for the same purpose for which they were conceived. “Re-use” includes the continued use of waste electrical and electronic equipment which is returned to collection points, distributors, recyclers or manufacturers;

5. “recycling” means the reprocessing in a production process of the waste materials for the original purpose or for other purposes, but excluding energy recovery;

6. "energy recovery" means the use of combustible waste as a means of generating energy through direct incineration with or without other waste but with recovery of the heat;

7. “recovery” means any of the applicable operations provided for in Annex II.B to Directive 75/442/EEC;

8. “disposal” means any of the applicable operations provided for in Annex II.A to Directive 75/442/EEC;

9. “treatment” means any activity after the waste electrical and electronic equipment has been handed over to a facility for depollution, disassembly, shredding, recovery or disposal and any other operation carried out for the recovery and/or the disposal of the waste electrical or electronic equipment and its components;

10. “producer” means anyone who manufactures and sells electrical and electronic equipment under his own brand, who resells under his own brand equipment produced by other suppliers or who imports that equipment on a professional basis into a Member State; the provisions of this Directive should apply to products and producers irrespective of the selling technique, including distance and electronic selling;

11. “distributor” means anyone who provides a product on a commercial basis to the party who is going to use that product;

12. “waste electrical and electronic equipment from private households” means waste electrical and electronic equipment from private households, as well as commercial, industrial, institutional and other waste electrical and electronic equipment which, because of its nature and quantity, is similar to waste electrical and electronic equipment from private households;

13. “dangerous substance or preparation” means any substance or preparation which has to be considered dangerous under Directive 67/548/EEC or Directive 88/379/EEC.

Article 3

Scope

1. This Directive shall cover electrical and electronic equipment falling under the categories set out in Annex I A. Articles 4 (with the exception of paragraph 2), 7 and 9 are not applicable to electrical and electronic equipment falling under the categories 8, 9 and 10 of Annex I A.

2. This Directive shall apply without prejudice to other Community legislation, in particular as regards safety and health requirements as well as requirements set out in specific Community waste management legislation, such as Directive 91/157/EEC on batteries and accumulators containing certain dangerous substances.

Article 4

Separate Collection

1. Member States shall take the necessary measures to ensure that systems are set up so that final holders and distributors can return waste electrical and electronic equipment from private households free of charge. To meet this obligation, Member States shall ensure the availability and accessibility of the necessary collection facilities, taking into account the population density.

2. Member States shall ensure that distributors, when supplying a new product, offer to take back free of charge similar waste electrical and electronic equipment from private households provided that the equipment is contaminant free (including radioactive and biological).

3. Member States shall take the necessary measures to ensure that producers provide for the collection of waste electrical and electronic equipment from holders other than private households. They shall be allowed on a voluntary and individual basis to set up and operate take-back systems for waste electrical and electronic equipment from private households.

4. Member States shall take the necessary measures to ensure that all waste electrical and electronic equipment collected in accordance with this Article is transferred to authorised treatment facilities. Member States shall take the necessary measures to ensure that the collection and transportation of separately collected waste electrical and electronic equipment is carried out in a way which ensures the suitability for re-use and recycling of those components or whole appliances which might be re-used and/or recycled.

5. Member States shall endeavour to achieve no later than 1 January 2006 a minimum rate of separate collection of four kilograms on average per inhabitant per year of waste electrical and

electronic equipment from private households. Once the information required under Article 11 enables the Commission to formulate a collection target of waste electrical and electronic equipment from private households as a percentage of the amount of electrical and electronic equipment sold to private households, the Commission will propose that the Council and the Parliament establish such compulsory targets. Technical and economic experiences gained in the Member States shall be taken into account when the collection targets for waste electrical and electronic equipment are formulated.

Article 5

Treatment

1. Without prejudice to Article 7(2), Member States shall take the necessary measures to ensure that producers set up systems to provide for the treatment of waste electrical and electronic equipment. For the purposes of Article 4 of Directive 75/442/EEC, this treatment shall, as a minimum, include the removal of all fluids and a selective treatment in accordance with Annex II provided that this treatment does not hinder the re-use and recycling of components or whole appliances.

2. Member States shall ensure that any establishment or undertaking carrying out treatment operations obtains a permit from the competent authorities, in compliance with Articles 9, 10 and 11 of Directive 75/442/EEC. The derogation from the permit requirement referred to in Article 11(1)(b) of Directive 75/442/EEC may apply to recovery operations concerning waste electrical and electronic equipment if there is an inspection by the competent authorities before the registration. This inspection shall verify:

(a) the type and quantities of waste to be treated;

(b) the general technical requirements to be complied with;

(c) the safety precautions to be taken,

in order to achieve the objectives referred to in Article 4 of Directive 75/442/EEC. This inspection shall take place once a year. Member States using the derogation shall send the results to the Commission.

3. Member States shall ensure that any establishment or undertaking carrying out treatment operations shall store and treat waste electrical and electronic equipment in compliance with the technical requirements set out in Annex III.

4. Member States shall take the necessary measures to ensure that the permit referred to in

paragraph 2 includes all conditions necessary for compliance with the requirements of paragraphs 1 and 3 as well as Article 6.

5. The treatment operation may also be undertaken outside the respective Member State or the EU provided that the shipment of waste electrical and electronic equipment is in compliance with Regulation (EEC) 259/93.

Article 6

Recovery

1. Without prejudice to Article 7(2), Member States shall take the necessary measures to ensure that producers set up systems to provide for the recovery of separately collected waste electrical and electronic equipment in order to meet the objectives laid down in this Directive.

2. Member States shall take the necessary measures to ensure that no later than 1 January 2006 the following targets are met by producers:

a) For all separately collected waste electrical and electronic equipment falling under category 1 (large household appliances) of Annex I A the rate of recovery shall be increased to a minimum of 80 % by an average weight per appliance. Within the same time limit the component, material and substance re-use and recycling shall be increased to a minimum of 75 % by an average weight per appliance .

b) For all separately collected waste electrical and electronic equipment falling under the categories 2, 4, 6 and 7 of Annex I A, with the exception of equipment that contain Cathode Ray Tubes, the rate of recovery shall be increased to a minimum of 60 % by weight of the appliances. Within the same time limit the component, material and substance re-use and recycling shall be increased to a minimum of 50 % by weight of the appliances.

c) For all separately collected waste electrical and electronic equipment falling under category 3 of Annex I A, with the exception of equipment that contains cathode ray tubes, the rate of recovery shall be increased to a minimum of 75% by weight of the appliances. Within the same time limit the component, material and substance re-use and recycling shall be increased to a minimum of 65% by weight of the appliances.

d) For all separately collected waste gas discharge lamps the rate of component, material and substance re-use and recycling shall reach a minimum of 80% by weight of the lamps.

e) For all separately collected waste electrical and electronic equipment containing a Cathode Ray Tube the rate of recovery shall be increased to a minimum of 75 % by an average weight per appliance. Within the same time limit the component, material and substance re-use and recycling shall be increased to a minimum of 70 % by an average weight per appliance.

3. The Commission shall, in accordance with the procedure laid down in Article 14, establish the detailed rules necessary to monitor compliance by Member States with the targets set out in this Article. The Commission shall take this measure no later than 1 January 2005.

4. On the basis of a proposal from the Commission, the European Parliament and the Council shall establish targets for recovery, re-use and recycling for the years beyond 2008.

Article 7

Financing of WEEE from private households

1. Member States shall take the necessary measures to ensure that holders of waste electrical and electronic equipment from private households can return such waste free of charge in accordance with Article 4.

2. Member States shall take the necessary measures to ensure that, producers provide for the financing of the collection of waste electrical and electronic equipment from private households deposited at collection facilities, set up under Article 4(1), as well as for the treatment, recovery and environmentally sound disposal of waste electrical and electronic equipment.

3. The obligation under Article 7(2) shall enter into force with a delay of five years starting from entry into force of the Directive. Member States shall ensure that producers may comply with this Article by means of collective or individual systems. No discrimination should occur between producers who comply with this Article by means of collective systems or individual systems.

The responsibility for the financing of the management of waste from products put on the market before entry into force of the financing obligation (historical waste) shall be shared by all existing producers. Where a producer, opting for an individual system, cannot prove to be discharging his responsibility with respect to a fair share of the historical waste, he shall contribute to the financing of an alternative system.

Article 8

Financing of WEEE from users other than private households

Member States shall take the necessary measures to ensure that the financing of the costs for the collection, treatment, recovery and environmentally sound disposal of waste electrical and electronic equipment from users other than private households is covered by agreements between the producer and the user of the respective equipment at the time of purchase.

Article 9

Information for users

1. Member States shall take the necessary measures to ensure that users of electrical and electronic equipment in private households are given the necessary information about:

– the return and collection systems available to them,

– their role in contributing to re-use, recycling and other forms of recovery of waste electrical and electronic equipment,

– the meaning of the symbol shown in Annex IV.

2. Member States shall take the necessary measures to encourage consumers to contribute to collection, treatment and recovery of WEEE.

3. With a view to achieving a high rate of collection Member States shall take the necessary measures to ensure that producers appropriately mark electrical and electronic equipment which might normally be disposed of in rubbish bins or similar means of municipal waste collection with the symbol shown in Annex IV. If - in exceptional cases - necessary because of the size or the function of the product, the symbol shall be printed on the packaging of the electrical and electronic equipment.

Article 10

Information for treatment facilities

Member States shall ensure that producers provide, as far as it is needed by treatment facilities, appropriate information to identify the different electrical and electronic equipment components and materials, and the location of dangerous substances and preparations in the electrical and electronic equipment.

Article 11

Information requirements

1. Member States shall provide information on an annual basis on the quantities and categories of electrical and electronic equipment put on the market, collected and recycled within the Member States, both by numbers and by weight.

2. Member States shall ensure that the information required under this Article is transmitted to the Commission by 1 January 2007 and on a three-yearly basis thereafter. The information shall

be provided in a format, which shall be adopted by the Commission within one year of the entry into force of this Directive in accordance with the procedure laid down in Article 18 of Directive 75/442/EEC.

Article 12

Obligation to report

Without prejudice to the requirements of Article 11, Member States shall send a report to the Commission on the implementation of this Directive at three-year intervals. The report shall be drawn up on the basis of a questionnaire or outline drafted by the Commission in accordance with the procedure laid down in Article 6 of Directive 91/692/EEC with a view to establishing databases on waste electrical and electronic equipment and their treatment. The questionnaire or outline shall be sent to the Member States six months before the start of the period covered by the report. The report shall be made available to the Commission within nine months of the end of the three-year period covered by it.

The first report shall cover a period of three years from 1 January 2006.

The Commission shall publish a report on the implementation of this Directive within nine months of receiving the reports from the Member States.

Article 13

Implementation in national law

1. Member States shall bring into force the law, regulations and administrative provisions necessary to comply with this Directive within 18 months of the adoption of this Directive. They shall immediately inform the Commission thereof.
2. When Member States adopt these provisions, these shall contain a reference to this Directive or shall be accompanied by such reference at the time of their official publication. The procedure for such reference shall be adopted by Member States.
3. Member States shall communicate to the Commission all existing laws, regulations and administrative provisions adopted within the scope of this Directive.

Article 14

Committee procedure

1. The Commission shall be assisted by the committee instituted by Article 18 of Directive 75/442/EEC and in accordance with the procedure laid down in the following paragraphs, in order to adapt the Annexes II, III and IV to this Directive to scientific and technical progress.

2. Where reference is made to this paragraph, the regulatory procedure laid down in Article 5 of Decision 1999/468/EC shall apply, in compliance with Article 7 (3) and Article 8 thereof.

3. The period provided for in Article 5(6) of Decision 1999/468/EC shall be [No more than three months].

Article 15

Entry into force

This Directive shall enter into force on the twentieth day following that of its publication in the *Official Journal of the European Communities.*

Article 16

Addressees

This Directive is addressed to the Member States.

Done at Brussels,

For the European Parliament For the Council The President The President

ANNEX I A

CATEGORIES OF ELECTRICAL AND ELECTRONIC EQUIPMENT COVERED BY THIS DIRECTIVE

(1) Large household appliances

(2) Small household appliances

(3) IT & Telecommunication equipment

(4) Consumer equipment

(5) Lighting equipment

(6) Electrical and electronic tools

(7) Toys

(8) Medical equipment systems (with the exception of all implanted and infected products)

(9) Monitoring and control instruments

(10) Automatic dispensers

ANNEX I B

INDICATIVE LIST OF PRODUCTS WHICH FALL UNDER THE CATEGORIES OF

ANNEX I A

1. **Large household appliances**
Large cooling appliances
Refrigerators
Freezers
Washing machines
Clothes dryers
Dish-washing machines
Cooking
Electric stoves
Electric hot plates
Microwaves
Heating appliances
Electric heaters
Electric fans
Air conditioners

2. **Small household appliances**
Vacuum cleaners
Carpet sweepers
Irons
Toasters
Fryers
Coffee grinders
Electric knives
Coffee machines
Hair dryers
Tooth brushes
Shavers
Clocks
Scales

3. **IT & Telecommunication equipment**

Centralized data processing:

Mainframes

Minicomputers

Printer units

Personal computing:

Personal computers (CPU, mouse, screen and keyboard included)

Lap-top computers (CPU, mouse, screen and keyboard included)

Note-book computers

Note-pad computers

Printers

Copying equipment

Electrical and electronic typewriters

Pocket and desk calculators

User terminals and systems

Facsimile

Telex

Telephones

Pay telephones

Cordless telephones

Cellular telephones

Answering systems

4. **Consumer equipment**

Radio sets (clock radios, radio-recorders)

Television sets

Videocameras

Video recorders

Hi-fi recorders

Audio amplifiers

Musical instruments

5. **Lighting equipment**

Luminaires

Straight fluorescent lamps
Compact fluorescent lamps
High intensity discharge lamps, including high pressure sodium lamps and metal halide lamps
Low pressure sodium lamps
Other lighting equipment
6. **Electrical and electronic tools**
Drills
Saws
Sewing machines
7. **Toys**
Electric trains or car racing sets
Hand-held video game consoles
Video games
8. **Medical equipment systems (with the exception of all implanted and infected products)**
Radiotherapy equipment
Cardiology
Dialysis
Pulmonary ventilators
Nuclear medicine
Laboratory equipment for in-vitro diagnosis
Analysers
Freezers
9. **Monitoring and control instruments**
Smoke detector
Heating regulators
Thermostat
10. **Automatic dispensers**
Automatic dispensers for hot drinks
Automatic dispensers for hot or cold bottles or cans
Automatic dispensers for solid products

Appendix 2:

Summary of the WEEE Directive and it's requirements.

Contents of the Proposal for a Directive on Waste Electrical and Electronic Equipment

Article 1 sets out the objective of the Directive.

Article 2 contains the definitions for the purposes of this Directive.

The definition of electrical and electronic equipment (**Article 2.1**) comprises all appliances run by electricity and included in the categories set out in Annex I A of the Proposal. The purpose of the indicated voltage limits is to ensure that large industrial equipment, which might be construed as falling under one of the categories of Annex I A, is not covered by the Proposal. The voltage limits are the upper limits set out in Article 1 of Council Directive 73/23/EEC of 19 February 1973 on the harmonisation of the laws of Member States relating to electrical equipment designed for use within certain voltage limits **(OJ L 77, 26.03.1973, p. 29.)** Voltage ratings refer to the voltage of the electrical input or output, not to voltages, which may appear inside the equipment.

Components are parts of electrical and electronic equipment, such as housings, screens, keyboards, electric motors, circuit boards, capacitors, rectifiers, transistors, tubes, etc. Subassemblies are parts of the equipment - not necessarily parts of the electricity flow – without which the original piece of equipment could not operate as intended by the manufacturer.

Examples of sub-assemblies are shelves in a refrigerator. Consumables are short-term replaceable/disposable parts of the equipment, such as toner cartridges or batteries. The provisions regarding waste electrical and electronic equipment apply only to components, subassemblies and consumables when these materials are part of the product at the time of discarding.

Article 2.10: With a view to avoiding discrimination against EU manufacturers, the provisions of this Directive should apply to products and producers irrespective of the selling technique, including distance and electronic selling; Producers for the purposes of this Directive are not suppliers or manufacturers of individual components, subassemblies or consumables. Where companies market products under their own brand which were originally manufactured by other companies, the definition of producer applies to the companies marketing the products rather than to the original manufacturers.

According to the definition of waste electrical and electronic equipment from private households

(**Article 2.11**), special equipment, such as radio therapy equipment, would – due to its nature - not fall under the requirements of the Proposal applying to equipment from private households. Computer systems of a kind, however, which would be suitable for use by private households as well as small companies e.g. a law firm, would fall under the definition of WEEE from private households. If the law firm used several computers which clearly exceeded the number usually found in private households, the end-of-life computers would – in view of the number concerned - not fall under the definition of WEEE from private households.

Article 3 sets out the scope of the proposed Directive. The proposed Directive applies to all categories of electrical and electronic equipment listed in Annex I A. This list is exhaustive.

Examples of equipment falling under each of these categories are given in Annex I B. In view of the rapidly changing market in electrical and electronic equipment, it was considered useful to avoid an exhaustive list of equipment. It follows clearly from national experience that an exhaustive product list would be subject to permanent updating.

Due to the specific distribution of products, such as medical equipment systems, monitoring and control equipment and automatic distributors, it was not considered necessary to apply the same collection, financing and user-information provisions to these products as to equipment mainly or exclusively used by consumers.

As regards medical equipment systems, implants are not covered by the scope of the proposed Directive.

Article 4 provides for the separate collection of WEEE. One of the main problems regarding current waste management practice with WEEE is the lack of collection which would enable recyclers to obtain sufficient material for large-scale production. (AEA Technology, Recovery of WEEE: Economic and Environmental Impacts, June 1997, p. 84.) This is in particular true for electrical and electronic equipment used in private households. As a consequence, Member States have to ensure that collection systems are set up.

The main challenge to create efficient collection systems is to motivate consumers to participate. However, in view of the principle of subsidiarity, only general requirements for collection systems could be set in the proposed Directive. Measures ensuring an efficient collection system may vary according to the different product groups of this waste stream and the specific features of the different regions within the EU and should therefore be taken at national or regional level.(These measures include financial encouragement to return equipment, such as deposits, information of the consumers, including public awareness campaigns, and a consumer friendly orientation of collection facilities, including convenient opening hours, accessibility of the facilities and efficient service provided at the collection points.)

The main principles set out in the present Proposal include the requirement of setting up collection points, which are easily accessible for consumers, the possibility for consumers to return their equipment free of charge and the involvement of distributors in the collection system.

In order to avoid substantial disparities in the financial burden due to WEEE management, a harmonised standard needs to be established for collection to be a success. However, at this stage it is not possible to give a legally binding collection target in view of the absence of precise data on the annual arisings of WEEE from private households. Therefore, a "soft" collection target has been given as a guide for the Member States. The indicated amount of 4kg of WEEE per inhabitant is an average amount which should be achieved per inhabitant. It represents a typical average collection yield that has been achieved by several countries of the European Union in the course of pilot collection schemes (Collection targets for waste from electrical and electronic equipment (Germany 1998), European Commission DG XI, p. 13.) and corresponds to the collection achieved in practice under the Dutch WEEE legislation. At a later stage, after experience has been gathered during the implementation of the WEEE Directive, compulsory targets will be formulated.

Article 5.1 in connection with Annex II specifies the necessary treatment measures. These include the removal of substances which cause the main difficulties at the various stages of the management of WEEE. (Detailed explanations and descriptions of the background to the required measures are found in the study "Pilotsammlung von Elektroaltgeräten in Bregenz – Wissenschaftliche Begleitstudie" (Bregenz/Österreich 1996), Bundesministerium für Umwelt, Jugend und Familie.)

In any case, the possibilities of re-use and recycling are to be considered when these treatment operations take place. In the context of setting up the list of Annex II extensive discussions on the inclusion of Liquid Crystal Displays (LCDs) in this list took place. Research shows that LCDs contain a number of substances, some of which are suspected to be cancerogenic. In addition, it was shown that the thermal treatment of LCDs might lead to the formation of toxic compounds. While some large manufacturers of liquid crystals made considerable efforts to prove that the waste management of their LCDs does not lead to risks for health or the environment, doubts remain regarding the composition of certain imported LCDs.

The Proposal introduces a permit requirement for establishments or undertakings carrying out treatment operations. This permit includes the treatment requirements and the requirements with regard to the treatment site. In addition, compliance with the re-use and recycling targets set out in **Article 6** is part of the permit.

Producers should have the possibility to set up centralised large-scale treatment plants in order to make recycling economically viable. As a consequence, **Article 5.5** stresses the possibility of undertaking treatment operation outside the Member State where the WEEE is generated.

Article 6 sets a standard for the recycling of WEEE. In general, recycling targets are considered necessary to avoid the limitation of recovery to incineration or the removal of a few valuable materials only, with the rest going to disposal operations. All targets foreseen in Article 6 reflect the state of the art of recyclers. This has been proven in a large pilot test (Apparetour Back to the beginning – National pilot project, for collecting, recycling and repairing electrical and electronic equipment in the district of Eindhoven (Eindhoven 1997), p. 52.)

and was confirmed by specialised recyclers. In the course of the above mentioned pilot project, specific consideration was given to the assessment of the cost implications of achieving the recycling targets. For all concerned categories of WEEE, the respective costs corresponded to the average recycling costs generated in the other European Pilot Projects. This indicates that the achievement of the recycling targets does not involve specific extra costs.

The recycling targets of Article 6 merely refer to waste equipment which has been separately collected according to Article 4 of the Proposal. The re-use of components, not the re-use of whole appliances, contributes to the achievement of these targets.

In line with the principle of producer responsibility, producers of electrical and electronic equipment have the obligation to recycle as well as to dispose of the non-recoverable fractions. Producers could discharge their respective responsibility by leaving the actual work to third parties, which might be local municipalities or private enterprises.

Article 7 establishes the financing system for the management of WEEE. One aim of the financing system is to encourage consumers to return their equipment to collection points, rather than disposing of it through the ordinary municipal waste collection or other channels resulting in inappropriate treatment. It is clear from the pilot projects on WEEE that charging consumers with disposal costs at the point of return would have negative repercussions on the collection results.(Experience from all Austrian and German pilot projects ("Collection targets for waste from electrical and electronic equipment", European Commission 1998, p. 10.) Therefore, and in line with the principle of producer responsibility, producers have to finance the treatment, recovery and environmentally sound disposal of waste electrical and electronic equipment from private households. Their responsibility should start from designated collection points onwards.

In order to reduce costs for producers resulting from the management of waste from products put on the market before entry into force (historical waste) of this legislation, a transition period of five years after entry into force of the Directive is granted.

Important benefits might arise from financing systems, set up by companies individually for their products. However, it needs to be ensured that producers, engaged in individual systems, share the responsibility for the financing of the management of waste from products put on the market before entry into force of the financing obligation (historical waste). Therefore, it will be necessary that those producers, which are opting for an individual system, contribute a fair share to the financing of the management of historical waste in general.

Article 8: As regards electrical and electronic equipment not used by private households, the financing of the waste management needs to be agreed between the producer and the user of the equipment at the time of purchase.

Article 9 provides for information to be given to consumers, whose participation is of paramount importance for the functioning of collection schemes. A specific means of information is the marking of certain items of small electrical and electronic equipment to avoid disposal via the ordinary rubbish bin or a similar means of municipal waste collection.

Article 10 ensures that producers provide treatment facilities with information on the content of electrical and electronic equipment in order to facilitate the recycling of these appliances and to prevent negative impacts on the health of workers or the environment due to hazardous substances contained in electrical and electronic equipment. The information needed by treatment facilities should be provided on request of the recycler and might take the form of databases, manuals or information on the internet.

Article 11 stipulates that Member States have to provide the information needed to assess the success of this legislation and to estimate future arisings of WEEE.

Annex IA contains an exhaustive list of the categories of electrical and electronic equipment which are covered by the present Proposal.

Annex IB contains a list illustrating, for each of the categories, examples of products covered by the respective category.

Annex II lists the substances or preparations which have to be removed from separately collected WEEE for environmental reasons.

Annex III lays down certain minimum requirements as regards the conditions of WEEE storage and treatment sites.

Annex IV provides for the mark to be put on equipment which fits into dustbins or similar means of household waste collection.

Contents of the Proposal for a Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment

Article 1 sets out the objective of the Directive.

Article 2 contains the definitions for the purposes of this Directive. The definition for electrical and electronic equipment is identical to the respective definition of the Directive on Waste Electrical and Electronic Equipment (WEEE). Also the definition of producer follows the concept of the above-mentioned Directive although it was adapted to the purposes of the term producer as used in Article 4.

Article 3 sets out the scope of the present Directive. This scope corresponds to the scope defined by Article 3 of the WEEE Directive.

Article 4 lays down the requirement to substitute the heavy metals – lead, mercury, cadmium and hexavalent chromium – as well as the brominated substances – PBDE (polybrominated diphenyl ethers), including in particular 5-BDE, 8-BDE and 10-BDE, and PBB (polybrominated biphenyls), as these substances cause significant environmental problems during the waste management phase. Exemptions for applications of these substances are granted in those cases where substitution is not feasible or the potential negative environmental and/or health impacts caused by substitution outweigh the environmental benefits of the substitution. The exemptions from the substance phase-out are listed in the Annex to the Directive. The inserts included in this Annex should be modified by the Commission, assisted by the Article 18 Committee of Directive 75/442/EEC, according to technical progress and new scientific evidence. The Commission is to consult producers of electrical and electronic equipment before taking decisions on amendments of the Annex.

The Annex contains the list of applications, which are exempted from the substitution requirement in Article 4 of the Directive. The list needs to be regularly updated according to technical progress and new scientific evidence.

Appendix 3. Metals Leach Methods.

Details of the various leaching methods employed in the U.S.

Seven-Day Distilled Water Leachate Test - State of Texas (USA) Method

This test is intended only for dry, solid wastes, i.e., waste materials without any free liquids.

1. Place a 250 gm. (dry weight) representative sample of the waste material in a 1,500 ml. Erlenmayer flask.
2. Add one liter of distilled water into the flask and mechanically stir the material at a low speed for five minutes.
3. Stopper the flask and allow to stand for seven days.
4. At the end of seven days, filter the supernatant solution through a 0.45-micron filter, collecting the supernatant into a separate flask.
5. Subject the filtered leachate to the appropriate analysis.

TCLP - Toxicity Characteristic Leaching Procedure – United States EPA Method

This analysis determines the soluble portion of the analytes. This is a Federal guideline and differs from the State of Texas method in several ways. The alkalinity of the sample must first be determined in order to know which of two different extraction fluids should be used. Samples with a low alkalinity use extraction fluid #1 which is a sodium acetate solution with a pH of 4.93. Samples with a high alkalinity use extraction fluid #2 which is a dilute acetic acid solution with a pH of 2.8. The sample is then tumbled in the appropriate extraction fluid for 18 hours. However the choice of extraction fluids does not apply to volatiles. When analyzing for volatiles, fluid #1 is always used and a Zero Headspace Extraction (ZHE) apparatus is required. Results from this leachate are compared against TCLP regulatory limits for the analyte.

California Waste Analysis Methods

TTLC and STLC are used when determining the hazardous waste characterization under California State regulations as outlined in Title 26 of the California Code of Regulations (CCR).

TTLC - Total Threshold Limit Concentration

This analysis determines the total concentration of each target analyte in a sample. Samples are analyzed using published USEPA methods. When any target analyte exceeds the TTLC limits the waste is classified as hazardous and its waste code is determined by the compound(s) that failed TTLC. The results of this analysis can be used to determine if analysis for STLC level is necessary by comparing 10 times the STLC limit to the TTLC results. A factorof ten is necessary to compensate for a 1:10 dilution factor that is present in one analysis but not the other. If the TTLC results do not exceed 10 times the STLC limit then normally no further analysis is required.

STLC - Soluble Threshold Limit Concentration

This analysis determines the amount of each analyte that is soluble in the "Waste Extraction Test", (W.E.T.) leachate. This W.E.T. leachate procedure is used for solid samples or for samples containing > 0.5% solids. The sample is tumbled in 10 times its weight of a 0.2% sodium citrate buffer for 48 hours. This leachate is then analyzed to determine the soluble concentrations.

The concentration of analyte in the leachate is compared against the STLC and TTLC regulatory values.

Appendix 4. Experimental Results

Lead-Free Solder Joint Evaluation

Mechanical tests performed included contact angle measurements and lead pull. Temperature cycle testing was performed to evaluate the package integrity after cycling through temperature extremes. The wetting balance test was used as a tool to determine the solder wetting time for the individual IC components.

The results show that contact angles do increase with Ni/Pd and Ni/Pd/Au finishes. However, Ni/Pd and Ni/Pd/Au finishes achieve equivalent or better lead pull and temperature cycle testing results versus Sn/Pb. This indicates that any difference in performance of the three different lead finishes is visual only.

Experimental Design

This evaluation was performed using the test matrix outlined below.

TABLE 1: Designed Experiment

Run	Lead Finish	Solder Paste
1	Sn/Pb	Sn/Pb RMA
2	Sn/Pb	Sn/Pb WS
3	Sn/Pb	Castin Pb-Free WS
4	Ni/Pd	Sn/Pb RMA
5	Ni/Pd	Sn/Pb WS
6	Ni/Pd	Castin Pb-Free WS
7	Ni/Pd/Au	Sn/Pb RMA
8	Ni/Pd/Au	Sn/Pb WS
9	Ni/Pd/Au	Castin Pb-Free WS

The IC test vehicle used for this evaluation was a Small Outline Integrated Circuit (SOIC). Components were built using three different leadframe finishes.

The solder pastes included in the study were a widely used 63/37 RMA paste and a widely used 63/37 water soluble paste. The printed circuit boards Cu surfaces were protected with ENTEK® PLUS CU-106A. This coating is an organic material (substituted benzimidazole) used to preserve the solderability of Cu through multiple soldering operations. During SMT reflow, most of the organic solderability protector (OSP) is displaced by the wetted solder and becomes a negligible constituent of the solder paste residue. Some of the OSP (<25%) volatilises at reflow temperatures.

Performance Measures and Results

In this study the author used visual, mechanical, and reliability test methods to classify the performance of the various solder joints. The various methods used and results obtained are shown below.

Contact Angle

The definition of contact angle used herein is the angle formed by the tangent to the backside of the lead and the tangent to the solder fillet at the point of contact of the lead with the fillet. Contact angle is measured by performing a cross-section on the lead of interest. Once the cross-section is available, the contact angle measurement can be taken.

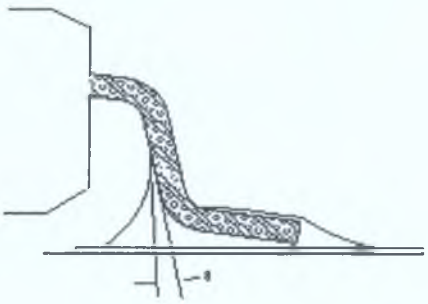


Figure 1: Contact Angle to Back Side of Lead

In general, lower contact angles are considered to indicate a soldering condition that has produced good results and higher contact angles indicate either a situation where the wetting rate has been decreased or where the equilibrium wetting point has changed. Contact angle can also be affected by the geometries of the soldered surfaces (relative to the surface tension of the solder) and by the volume of solder present.

For this experiment, board mounted IC units from each of the 9 groups were cross-sectioned and the contact angle was measured and recorded. Table 2 presents the contact angle data for each of the experimental groups.

TABLE 2: Contact Angle to Back Side of Lead

Run	Lead Finish	Solder Paste	Avg	Std dev
1	1 – Sn/Pb	1-Sn/Pb RMA	0	0
2	1 – Sn/Pb	2-Sn/Pb WS	0	0
3	1 – Sn/Pb	3-Castin Pb-Free WS	1.6	3.6
4	2 - Ni/Pd	1-Sn/Pb RMA	12.6	2.3
5	2 - Ni/Pd	2-Sn/Pb WS	16.0	2.2
6	2 - Ni/Pd	3-Castin Pb-Free WS	24.6	4.4
7	3 - Ni/Pd/Au	1-Sn/Pb RMA	11	2.2
8	3 - Ni/Pd/Au	2-Sn/Pb WS	13.8	1.9
9	3 - Ni/Pd/Au	3-Castin Pb-Free WS	32.8	4.4

The contact angle data is presented graphically below.

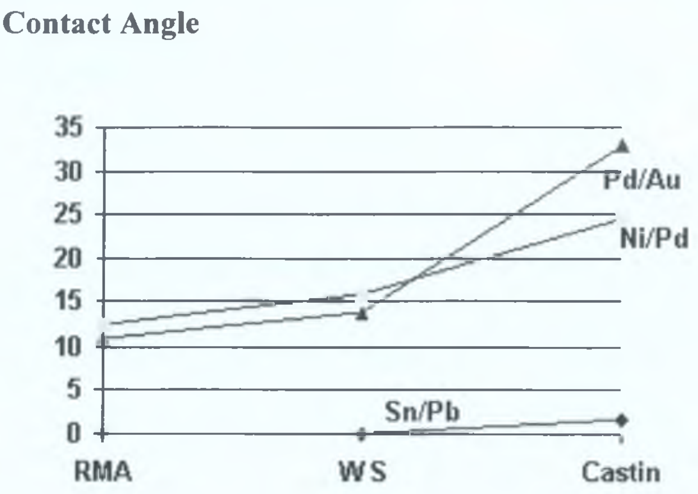


Figure 2: **Contact Angle Measurements**

The matrix design of this experiment allows for calculation of an Analysis of Variance (ANOVA) table for the 2 factors evaluated. The ANOVA table calculations compute the variance in the contact angle data observed between the 3 different lead finishes and the 3 different solder pastes. From this information we can assign percent contributions of each factor to that variance. Results of the ANOVA calculations are presented below.

TABLE 3: **ANOVA Table for Contact Angle Response % of Variance Attributable to each Factor**

Source	df	SS	% Contribution
Lead Finish	2	646.4	64.25
Solder Paste	2	238.3	23.69
LF x SP interaction	2	47.5	4.72
Residual	2	73.8	7.34
Total	8	1006.0	100.00

The ANOVA calculations indicate that the lead finish has the strongest impact on contact angle. The solder paste had a lesser impact on contact angle variance with the interaction of the 2 factors being nearly negligible. The highest contact angle measured was 40 degrees, thus all of the groups exhibited wetting angles considered to be acceptable. This difference in contact angle between the lead finishes and solder pastes has previously been shown to be a visual issue only and does not negatively impact on the mechanical strength of the solder joint. X-Ray Photographs of cross-sectioned units for the 3 different lead finishes mounted with the Castin Pb-free solder paste are presented below.

PLATE 1: Sn/Pb finish component with Castin Lead-free solder paste.

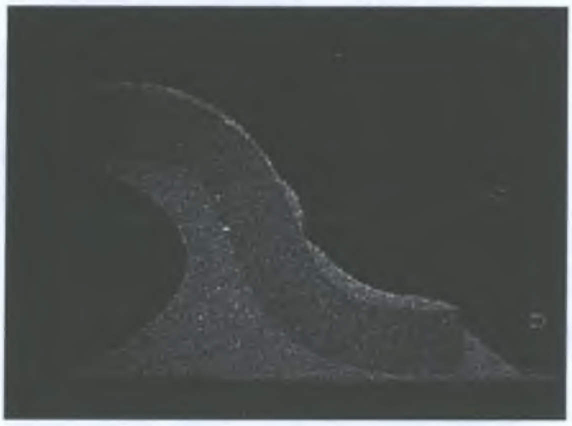


PLATE 2: Ni/Pd finish component with Castin Lead-free solder paste.

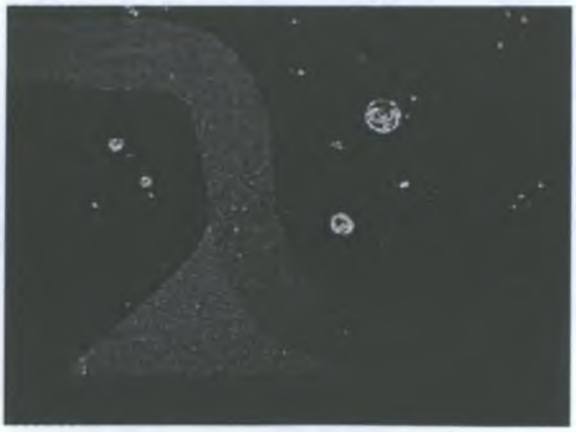
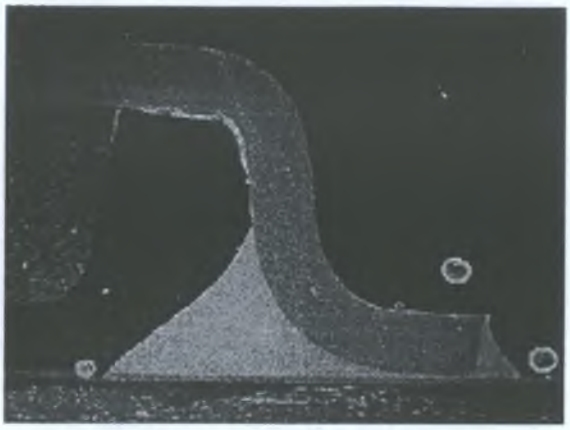


PLATE 3: **Ni/Pd/Au finish component with Castin Lead-free solder paste.**



Lead Pull

Lead pull testing was performed to determine the mechanical force needed to pull an individual IC lead from the PCB land pattern after soldering. First, in order to allow for access to an individual lead on the PCB, the leads are cut near to the package body. Next, with the leads separated from the package body, the PCB is fastened in a test fixture. Then the lead is pulled until it separates from the PCB. The force needed to pull the lead from the PCB is measured and recorded.

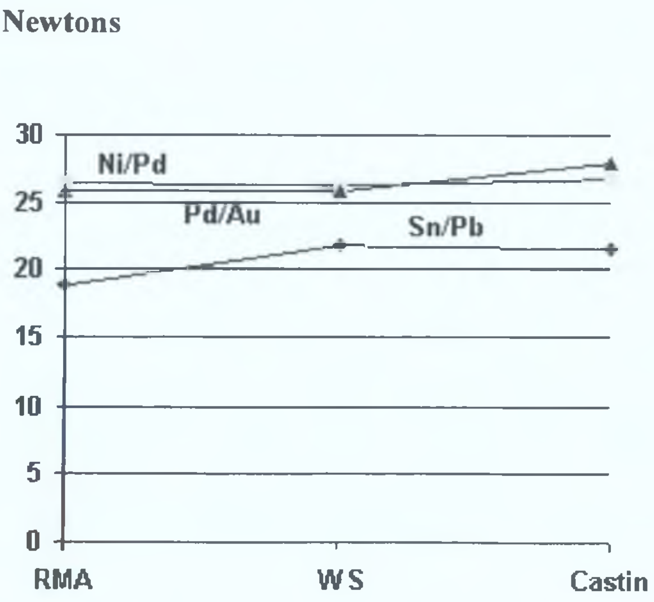


Figure 3: **Lead Pull Results**

The lead pull data shows that the mechanical strength of the solder joint is equivalent, and independent of the solder paste selection for both Ni/Pd and Ni/Pd/Au finishes. The lead pull test data indicates that mechanical strength of the joints is worse for the Sn/Pb finish components versus the Ni/Pd and Ni/Pd/Au finishes. In all cases, the mechanical strength of the solder joints made with the Castin lead-free solder paste was equivalent or better than that of the joints made with the conventional RMA and water-soluble pastes.

Lead Pull Failure Modes

After the leads were pulled from the PCBs on the various groups above, the components and PCBs were inspected to determine where the failure actually occurred. Each unit was categorised into one of two different failure modes. Category 1 was indicated when the solder was pulled completely from the pad. This mode of failure would indicate the wetting to the lead to be stronger than the wetting to the pad. Category 2 was used when solder was left on both the lead and the pad. This failure mode would indicate that the yielding occurred within the solder itself. Results are presented in Table 4 below.

TABLE 4: Failure Modes for Lead Pull

Run	IC Finish	Solder Paste	Mode 1 solder pulled completely from pad.	Mode 2 solder left on both the lead and the pad.
1	1-Sn/Pb	1 - Sn/Pb RMA	3	39
2	1-Sn/Pb	2 - Sn/Pb WS	2	40
3	1-Sn/Pb	3 - Castin Pb-Free WS	0	42
4	2-Ni/Pd	1 - Sn/Pb RMA	30	12
5	2-Ni/Pd	2 - Sn/Pb WS	40	2

6	2-Ni/Pd	3 - Castin Pb-Free WS	39	3
7	3-Ni/Pd/Au	1 - Sn/Pb RMA	39	3
8	3-Ni/Pd/Au	2 - Sn/Pb WS	39	3
9	3-Ni/Pd/Au	3 - Castin Pb-Free WS	41	1

The data indicates that for the Sn/Pb components, the predominant failure mode was within the solder itself with solder being left on both the lead and the pad. For the Ni/Pd and Ni/Pd/Au finish components, the solder was pulled completely from the pad.

Temperature Cycle Testing

Temperature cycle testing of IC components is a reliability test performed to determine the package integrity after repeated exposure to temperature extremes. These temperature ranges are intended to simulate worst case operating duty cycles. For this experiment, 10 board-mounted units from each group were exposed to a temp cycle range of -65 deg C to +150 deg C for 3000 cycles. The units were removed from the temp cycle chamber at various read points and tested electrically. The results in Table 5 show that all of the lead finish and solder paste combinations passed electrical test out to 3000 cycles.

TABLE 5: Temp Cycle Results (Sample Size/# Fails)

Cycles	0	100	150	250	500	1000	2000	3000
1	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0
2	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0
3	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0
4	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0

5	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0
6	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0
7	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0
8	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0
9	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0

Additional units from each group were exposed to the temperature cycle testing above for mechanical cross-sections. One unit from each of the nine variations was removed from the chamber after 50, 100, and 250 cycles. Each unit was cross-sectioned and 10 leads were inspected looking for cracks in the solder joint. Fresh board mounted units (no temp cycle exposure) were also sectioned and inspected to provide a baseline comparison. Cross-section results are presented in Table 6 below.

TABLE 6: Cross-section results for Temp Cycle Units

Cycles	0	50	100	250
1	10/0	10/0	10/0	10/0
2	10/0	10/0	10/0	10/0
3	10/0	10/0	10/0	10/0
4	10/0	10/0	10/0	10/0
5	10/0	10/0	10/0	10/0
6	10/0	10/0	10/0	10/0
7	10/0	10/0	10/0	10/0
8	10/0	10/0	10/0	10/0
9	10/0	10/0	10/0	10/0

The cross-section results show that there were no cracks noted in any of the joints after temperature cycling out to 250 cycles.

Wetting Balance Test Results

The wetting balance test (sometimes called a meniscograph) is a method used by some to test wettability of IC leads. The wetting balance test is classified in ANSI/J-STD-002 as a "Test without established Accept/Reject Criterion". This test method is recommended for engineering evaluations only and not as a production pass/fail monitor.

The wetting balance test measures the forces imposed by the molten solder upon the test specimen as the specimen is dipped into and held in the solder bath. This wetting force is measured as a function of time and plotted. A typical wetting balance curve is shown below. Initially, the force is negative, indicating that the solder has not yet begun to wet to the specimen and, in fact, shows a bouyancy effect. The force exerted by the solder approaches zero as the solder begins to wet to the specimen. One commonly used performance measure is the time to cross the zero axis of wetting force. This point indicates the transition from non-wetting (F<0) to wetting (F>0)

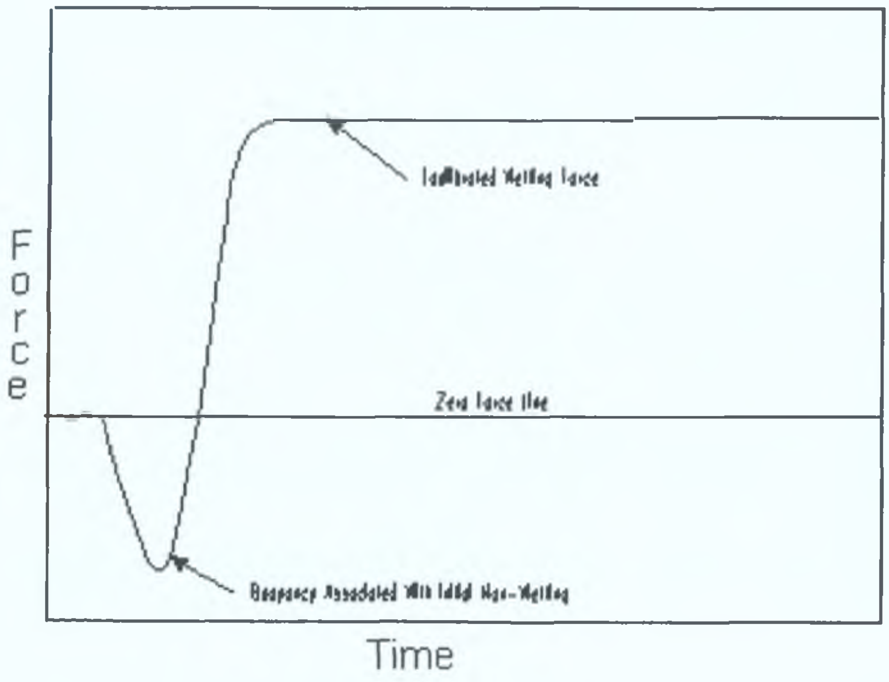
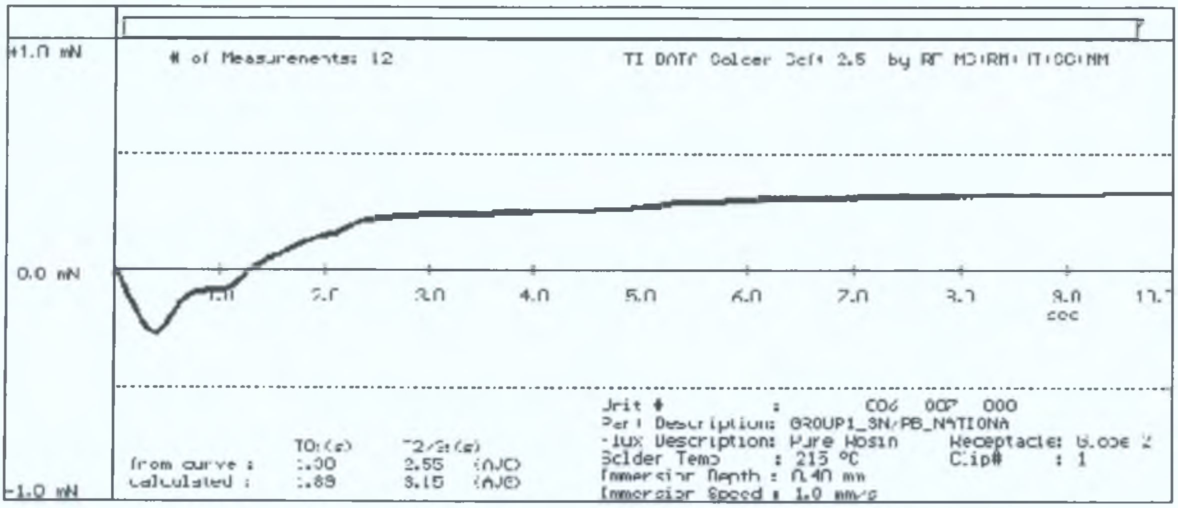


Figure 4: **Typical Wetting Balance Curve**

The wetting balance test was used to compare wetting performance of 3 different lead finishes used in this experiment. Samples of each lead finish were tested and the wetting balance curve for the combined readings was plotted. Figures 5-7 present the curves for Sn/Pb, Ni/Pd, and Ni/Pd/Au respectively. For this test, eutectic 60/40 Sn/Pb solder was used. The flux used was RMA.

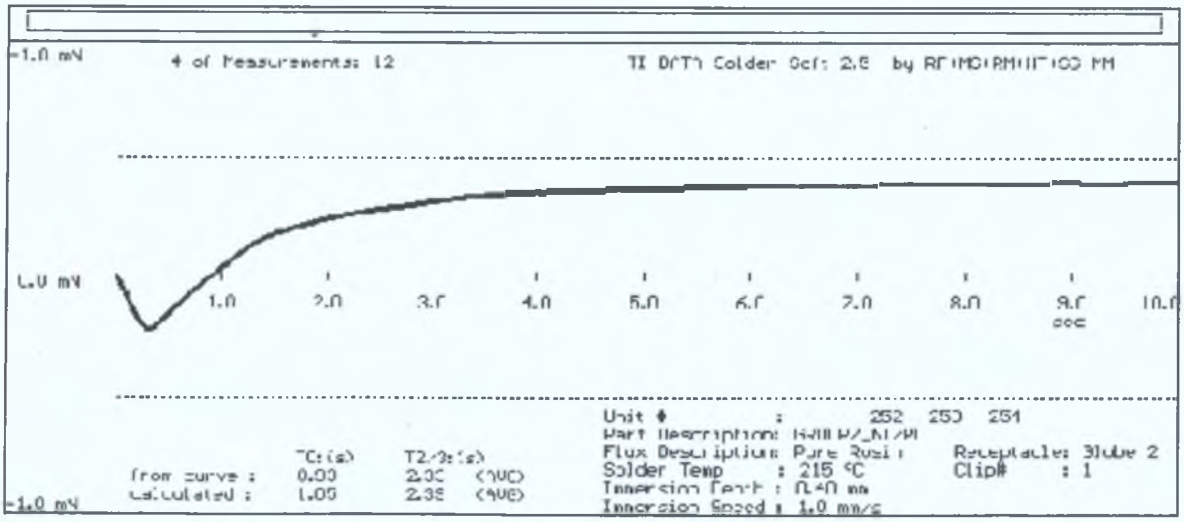
Figure 5: Wetting balance curve for Sn/Pb finish ICs



	T0:(s)	T2/3:(s)	
from curve :	1.00	2.55	(AVG)
calculated :	1.89	3.15	(AVG)

Unit # : C06 007 000
Part Description: GROUP1_SN/PB_NATIONA
Flux Description: Pure Rosin Receptacle: Globe 2
Solder Temp : 215 °C Clip# : 1
Immersion Depth : 0.40 mm
Immersion Speed : 1.0 mm/s

Figure 6: Wetting balance curve for Ni/Pd finish ICs



	T0:(s)	T2/3:(s)	
from curve :	0.00	2.00	(AVG)
calculated :	1.05	2.35	(AVG)

Unit # : 252 253 254
Part Description: [illegible]
Flux Description: Pure Rosin Receptacle: Globe 2
Solder Temp : 215 °C Clip# : 1
Immersion Depth : 0.40 mm
Immersion Speed : 1.0 mm/s

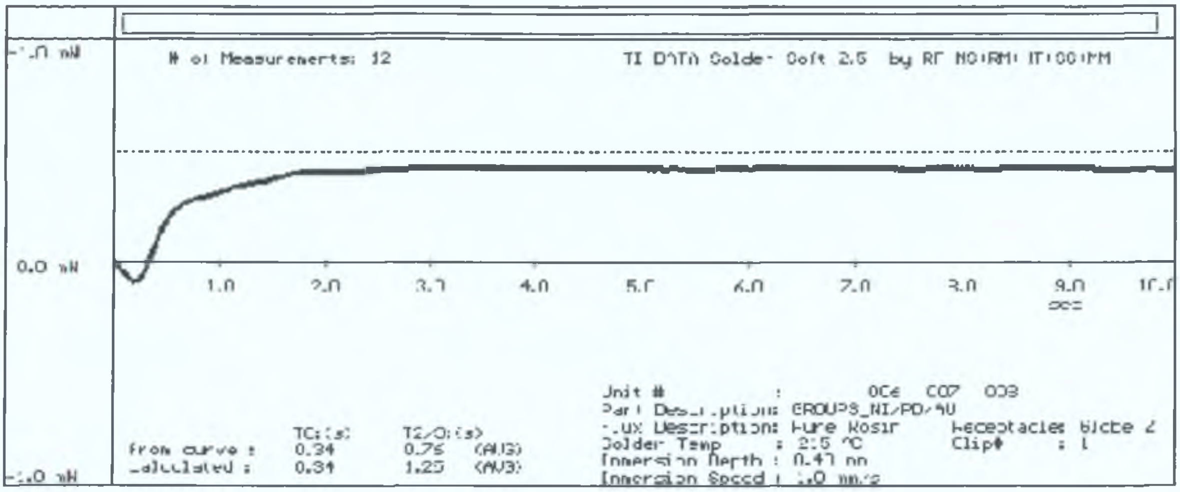


Figure 7: **Wetting balance curve for Ni/Pd/Au finish ICs**

Average time to cross the Zero axis was calculated and recorded for each lead finish. Results are presented in Table 7 below.

TABLE 7: Average wetting balance Time-to-Zero

Group	Lead Finish	T_0 (seconds)
1	Sn/Pb	1.30
2	Ni/Pd	0.93
3	Ni/Pd/Au	0.34

From the wetting balance results, it can be seen that the Ni/Pd and the Ni/Pd/Au finishes both crossed the Zero axis more quickly than the Sn/Pb with the Ni/Pd/Au giving the fastest time to cross Zero. This result would be expected in the wetting balance test as the additional gold on the surface of the Pd wets very quickly.

Results Summary

Contact angle data for Ni/Pd and Ni/Pd/Au finish components was higher than for Sn/Pb components for all types of solder pastes evaluated. Differences in contact angle proved to be a cosmetic issue only and did not correlate to any difference in reliability or mechanical strength of the joints.

Lead pull data was lower for Sn/Pb finish components compared to Ni/Pd and Ni/Pd/Au for all types of solder pastes evaluated. Data was essentially equivalent for Ni/Pd and Ni/Pd/Au finished components.

Lead pull failure mode analysis showed the Sn/Pb components failed within the solder. In most cases with Ni/Pd and Ni/Pd/Au components, the solder was pulled completely from the pad.

Temperature cycle testing of the 3 different lead finish components with each solder paste showed no failures out to 3000 cycles. The temperature cycle range was -65 deg C to +150deg C.

Cross-sections of temp cycled units showed no cracks in the solder joints out to 250 temperature cycles.

Wetting balance test results showed that the Sn/Pb components took longer to pass the T_0 line that the Ni/Pd or the Ni/Pd/Au finished components. The gold flash on the Ni/Pd/Au components improved wetting performance as measured by time to cross zero.