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Investigation into Lead-Free Solder in Australian Defence Force Applications

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ABSTRACT

This report outlines the findings derived from a study into the issues associated with the use of lead-free solder in electronic systems. It provides an assessment of the potential problems that might arise from the transition from the traditional tin-lead solder to alternative lead-free solder alloys. The information will enable the Australian Defence Force (ADF) to better understand the differences in alternative alloy properties and behaviour that may affect ADF systems if implemented. There is currently no single recommended lead-free solder alloy for military environments. The use of current lead-free solders brings with it the risk of reduced reliability for electronic systems and the implications for ADF systems, especially mission critical systems, need to be understood.

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Executive Summary

The aim of this report is to explore the issues of lead-free solder (and lead-free finishes) to aid in understanding the effects it will have on item performance and reliability. Organisations and research groups worldwide have studied / experimented on lead-free solders and have published experimental data and results from testing the performances of different lead-free solders. A selection of these results are also summarised to provide insight into the strengths and weaknesses of some lead-free alloys. It should be noted that most of the collated data targets commercial industries, therefore experimental conditions from which the results are based may not be sufficient to reflect the service conditions experienced in the military environment.

Products in the electronics market are mainly driven by consumer demand; the military market only makes up a small percentage of the total electronics market, therefore many commercial-off-the-shelf items will contain lead-free solder.

If lead-free solder (or finishes) becomes integrated into military applications, as is or will be inevitably the case due to commercial-off-the-shelf item acquisitions, it becomes important to identify the type of solder material in the item and understand its limitations and reliability in the application to which it will be integrated. Management processes must be in place to closely monitor, control and detect lead-free solder as commercial-off-the-shelf items are obtained.

The absence of lead in solder has introduced a range of issues which vary according to the type of solder (and board / component finish). Major issues are the formation of tin whiskers (a well-documented phenomenon, leading to short circuits) and tin pests (under cold conditions tin changes into a brittle form). Other issues addressed in this report include lead-contamination, higher melting temperatures, flux issues and board / component finishes.

For a change-over to lead-free solder to commence, equipment used for electronic maintenance may need to be revised to suit the processing requirements of lead-free solders. Specific lead-free tooling information can be sought from solder tooling manufacturers. To prevent lead contamination, lead-free tooling workstations require complete isolation from existing tin-lead (SnPb) solder tooling equipment.

A number of analytical techniques for identifying lead-free solders are explored, but the most effective method is currently XRF technology (x-ray fluorescence) which is available as a hand-held, mobile, point-and-shoot device. Sufficient training is required to minimise the potential errors associated with operating the device.

If lead-free items are to be introduced into military service, proven long-term reliability data and compatibility data (this involves flux compatibility, alloy mixing, etc) should be acquired from the suppliers / manufacturers for a given set of conditions for a particular application.

To date there are no lead-free solder alloys that are qualified for use in military environments; most of the lead-free solders possess inherent disadvantages that could compromise the reliability of the solder joint and therefore affect the overall function of the component / system on which it is used. Therefore it is recommended that, especially for items in mission and safety critical systems, current versions of lead-free solder be avoided.

Contents

1. INTRODUCTION 1

2. SELECTION CRITERIA 2
2.1 Lead-Free Solders 2
2.2 Lead-Free Finishes 4

3. ELEMENTS IN LEAD-FREE SOLDER 4

4. TYPES OF LEAD-FREE SOLDER 5

5. PROBLEMS/RISKS ASSOCIATED WITH LEAD-FREE SOLDER 5
5.1 Lead-Free Solder Issues 6
5.1.1 Tin Whiskers 6
5.1.2 Tin Pests 7
5.1.3 Lead Contamination 8
5.2 Assembly Issues 8
5.2.1 Melting Point of Solder 8
5.2.2 Coefficient of Thermal Expansion (CTE) 8
5.2.3 Flux Issues 9
5.2.4 Board Finishes and Component Finishes 10
5.2.4.1 Gold Content 11
5.2.4.2 Palladium Content 11
5.2.5 Wetting and Intermetallic Bond Formation 11
5.2.6 Reworking 11
5.3 In-Service Issues 12
5.4 Economic Issues 12
5.5 Inspection Issues 12

6. LEAD-FREE SOLDER TOOLING/WORKSTATION 13

7. ANALYTICAL TECHNIQUES 13
7.1 Handheld XRF (X-Ray Fluorescence) 14
7.2 Scanning Electron Microscope- Energy Dispersive Spectroscopy 14
7.3 Optical Emission Spectrometer 15
7.4 Swab Check 15

8. SUMMARY 15

9. REFERENCES 16

APPENDIX A: RECOMMENDATIONS 19

APPENDIX B: CURRENT LEAD-FREE SOLDER ALTERNATIVES 21

APPENDIX C: COST OF METALS AND ALLOYS 23

APPENDIX D: FLUX TYPES 25

APPENDIX E: RELIABILITY TESTS 27

APPENDIX F: COEFFICIENT OF THERMAL EXPANSION 29

APPENDIX G: AVAILABLE RESEARCH/TEST RESULTS/RECOMMENDED ALLOYS 31

- **G.1. Joint Group on Pollution Prevention/ Joint Council of Aircraft Ageing (JGPP/JCAA) Project 31**
- **G.2. NASA-DoD Lead-Free Electronics (LFE) Project 32**
- **G.3. Airworthiness Advisory 2008 ..... 32**
- **G.4. Boeing (2000) 33**
- **G.5. Boeing (2002) 34**
- **G.6. IPC SPVC- Round Robin Testing & Analysis 35**
- **G.7. NCMS (National Center for Manufacturing Sciences) Lead-Free Solder Project 35**
- **G.8. Interflux® Electronics 36**
- **G.9. Summary 36**

APPENDIX H: STANDARDS AND PUBLICATIONS 37

- **H.1. Industry Standards and Publications 37**
- **H.2. High Performance/Reliability Standards and Publications 37**

APPENDIX I: BIBLIOGRAPHY 39

1. Introduction

Lead-based solder has been widely used in military (and commercial) electronic equipment for several reasons. The most common solder is a eutectic alloy of tin and lead (SnPb) which has a defined melting point at 183°C, produces a shiny solder joint which is indicative of a good solder joint, it is readily available at low cost, exhibits good wetting ability, and good thermal cycling properties. Furthermore, tin whiskers and tin pests were never encountered as a problem with eutectic SnPb solder.

The movement towards lead-free components is already underway with legislation in the European Union and directives such as the WEEE (Waste Electrical and Electronic Equipment) and RoHS (Restrictions of use of Hazardous Substances) that became effective from July 1st 2006. These directives aim to ensure that materials containing lead (among other hazardous substances) are phased out and current electrical components containing lead are disposed of in an environmentally friendly manner. Other countries such as the US, Japan, China and Korea currently have no laws which restrict the use of lead in electrical components, but instead have implemented other initiatives to reduce its use. Australia currently has no law restricting lead in electrical components.

The legislations mainly apply to Class 1 (consumer) and Class 2 (commercial) items. Class 3 items are exempted due to the need for high reliability, which encompass those items required in the medical and military field. Current lead-free solders in the commercial industry have only been fully utilised over the last several years which means that reliability (which, for aircraft components, needs to be ensured over the life of the component) of these alternatives is still not known with certainty and mitigations to some lead-free solder problems are also yet to be fully explored.

A number of manufacturers have shifted completely to lead-free solder due to the demand for "environmentally friendly" products. Given that some military components rely on commercial-off-the-shelf (COTS) parts, lead-free components are therefore likely to be introduced into some military systems.

This report provides a selection criteria for a lead-free solder, lead-free solder issues, some alternatives to lead-free solder that have already been explored in the consumer/commercial markets, analytical techniques that can assist in detection and monitoring of lead-free solder parts lead-free solder tooling and workstation general requirements. Furthermore, information presented in this report predominantly concerns hand soldering as opposed to production soldering methods (i.e. wave soldering).

Due to a lack of data on the long-term reliability of lead-free solders in electronic systems, it is not yet possible to quantify the risk associated with their use in military systems. The report provides a current analysis of the state-of-the-art with lead-free solders and explains the range of problems that are known to be associated with their use.

2. Selection Criteria

2.1 Lead-Free Solders

Lead-free solders currently have a wide range of varying alloy compositions and therefore varying mechanical, thermal, and physical properties. Understanding the characteristics of a lead-free solder type and the requirements/demands of the conditions in that application are important in order to select and apply a solder that is compatible. This is crucial to ensuring long-term reliability. For example, will it be exposed to thermal cycling? Will it be exposed to corrosive media? Is strength an important characteristic for the application? What other properties are important for the application? Is the material widely available and in which forms? Is the selected lead-free solder susceptible to adverse effects if contaminated? Can the contamination be contained or avoided? Is the item a (or part of a) safety or mission critical item? Is the lead-free solder compatible with the component type and board finish? How does the solder alloy react to specific environmental, mechanical, chemical conditions?

Some aspects to consider when selecting lead-free solder may include:

- Melting temperature of the alloys/ thermal damage of PCB components
  The higher the melting temperature of the alloy, the more likely it is to damage nearby components or the surface to which it is applied. In addition, lead-free solder typically has a broader melting range and longer wetting time, which means a longer contact time between the solder tip and component lead.
- Availability
  The composition of the solder influences its cost. Expensive solder elements such as indium can drive up final costs.
- Cost
  See availability. Also refer to Section 5.4 and Appendix C for further cost implications.
- Solder forms
  Is the particular lead-free solder selected for the application available in wire form for hand soldering?
- Wetting ability
  The wetting ability is determined by the compatibility of the solder to the component board (i.e. the surface finish or component finish). It is also achievable with the correct flux choice. In comparison to SnPb, lead-free solders generally require longer wetting times.
- Toxicity from fluxes
  The stronger fluxes that may be required (see Section 5.2.3) may emit fumes of a higher toxicity; therefore during soldering operations it is essential to ensure continued protection from fume emissions.
- Flux compatibility
  Fluxes are chemical agents used to remove the oxide layers on the surface of the metal to be soldered in order to allow good wetting and therefore, produce a good solder joint. Fluxes can be selected based on the level of activity (high to low) or composition (rosin, resin, organic, inorganic). Furthermore, fluxes can contain halides, but the use of halides is not recommended due to their ability to corrode surfaces (see section 5.2.3 and

Appendix D). A good flux will have thermal stability at the temperature required for soldering a particular alloy. It will also have an activation[1] temperature which suits the soldering temperature (i.e. no premature or delayed activation).

- Hand soldering tooling requirements
  The tools to work with lead-free solder need to be able to cope with the changes in lead-free solder properties (see Section 6).

Properties of lead-free solder will also require consideration, including:

- Mechanical properties
  Does the lead-free solder need a particular level of hardness or strength to cope with certain levels of stresses and/or vibrations? The nature of the application will dictate the choice of the solder alloy.
- Physical appearance
  For eutectic SnPb solder, a dull solder joint was cause for rejection. Lead-free solder joints typically appear duller and grainier than a SnPb solder joint. IPC-A-610D [2] is an industry standard providing criteria for lead-free solder acceptance.
- Toxicity
  Some elements in lead-free solder are considered toxic; cadmium is a hazardous substance that should be avoided in lead-free solder, and bismuth also has some toxicity concerns [3] although bismuth-containing alloys are still available.
- Stability during storage
  The quality of solder wire/bar/paste should remain the same throughout its storage life.
- Fatigue strength
  Solder joints may be subjected to cycles of stress. The fatigue strength of the solder is its ability to withstand stress cycles without bond failure. The need for fatigue strength is application dependent.
- Effects from potential lead contamination
  Potential lead contamination can arise during the transition period, therefore procedures should be established that prevent the possibility of cross-contamination.
- Component stability from environmental factors
  Environmental factors such as heat, humidity and chemicals during operation should be accounted for and the selection of lead-free solders is chosen on these accounts accordingly.
- Coefficient of Thermal Expansion (CTE) compatibility
  A large difference in CTE between a solder joint/finish and a board substrate may produce stress due to the different expansion and contraction rates during heating/cooling periods.

Most of these characteristics will be described in more detail in upcoming sections of the report.

[1] Activation of a flux is its chemical reaction with the oxides to remove them from the surface.

2.2 Lead-Free Finishes

Although this report primarily covers lead-free solders, lead-free finishes on circuit boards and component leads should also be considered in this transition period since traditional finishes included lead and the use of surface finishes contributes to the wetting ability and integrity of the solder joint on PCBs. A successful lead-free finish will provide good solderability and wetting for the selected solder and flux. A description of some lead-free board/component finishes are provided in section 5.2.4.

3. Elements in Lead-Free Solder

Candidate elements that are usually considered as a substitute alloy to lead include bismuth, copper, indium, cadmium, silver, antimony, gold, zinc and nickel (though cadmium is not recommended due to its toxicity). The melting temperature of the element and its characteristics are summarised in the following table.

Table 1: Common alloying elements, melting temperatures and characteristics

Element	Element Melting Temperature (°C)	Comments
Tin (Sn)	*232*	*Base alloy metal. Low melting temperature and readily available. Tin whiskers and tin pests are, however, problematic.*
Bismuth (Bi)	271.5	Lowers melting temperature. Provides higher tensile strength. However, increases brittleness and prone to thermal fatigue. Expands on solidification. When contaminated with lead, bismuth-alloys become brittle. Has some toxicity concerns.
Copper (Cu)	1084	Cheap and affected the least with lead impurities. However, oxide layer is more difficult to remove.
Indium (In)	156.6	Lowers melting temperature. Very expensive and scarce. Extremely soft and lacks mechanical strength in alloys with high Indium contents. Corrosion-prone. Fast oxide formation during melting.
Zinc (Zn)	419.5	Oxidises and corrodes readily. Requires strong fluxes.
Antimony (Sb)	630.5	Increases mechanical properties. Slightly reduces thermal and electrical conductivity. Considered toxic (listed on the EACEM list of "not to be used" substances) [4]
Gold (Au)	1063	Increases melting temperature. Issues with gold embrittlement with increasing gold content. Very expensive.
Cadmium (Cd)	321.1	Cadmium and its compounds are listed in the RoHS directive [5] and are therefore considered a hazardous substance. To comply with restrictions, cadmium should not be used in alternative lead-free solder alloys.
Silver (Ag)	962	Absorbs copper, fast intermetallic growth with copper. Expensive.

4. Types of Lead-Free Solder

The types of lead-free solder available are too numerous to list. For hand-soldering, the most popular lead-free alloys used for Class 1 and Class 2 items are currently from the tin-silver-copper (SAC), tin-silver or tin-copper family. These alloys are available in wire form with no clean, water soluble or rosin fluxes. Table 2 below outlines a list of common lead-free solder alloys and their characteristics. Appendix B provides a more comprehensive list of lead-free solder alloys.

The listed lead-free alloys generally exhibit poorer wetting and a higher melting temperature than SnPb (except for Sn/57Bi/1.0Ag, though it exhibits increased brittleness and is prone to degradation when contaminated with lead) and are more costly to acquire (refer to Section 5.4 for details).

Table 2: List of elements commonly used in solder alloys for Class 1 and 2 applications, along with their characteristics

Solder Family	Solder Alloy	Melting Temp (°C)
Standard (SnPb)	*Sn63/Pb37*	*183*
SnAgCuSb	CASTIN® Sn/Ag2.5/Cu0.8/Sb0.5	217
SnAg	Sn/Ag3.5	221
	Sn/Ag5	221-240
SnCu	Sn/Cu3	227-300
	Sn/Cu0.7	227
SnSb	Sn/Sb5	232-240
SnAgBi	Sn/57Bi/1.0Ag	138
SnAgCu	Sn/Ag3/Cu0.5 (305)	217-218
	Sn/Ag3.8/Cu0.7	217-218
	Sn/Ag3.5/Cu0.7	217-218

Currently there is no MIL-STD for a lead-free solder qualified for military use.

5. Problems/Risks associated with Lead-Free Solder

Lead-free solder in electronic consumables for domestic/commercial applications have been implemented successfully because they are reliable for their expected life-span and are generally exposed to milder conditions when compared to military/aerospace conditions. The following sub-sections provide a list of issues associated with the use of lead-free solder.

5.1 Lead-Free Solder Issues

5.1.1 Tin Whiskers

Lead-free solders are prone to the formation of tin whiskers, and the likelihood of tin whisker formation increases with tin content. Tin whiskers appear as thin strands of tin caused by a spontaneous growth from the surfaces of tin alloys, believed to initiate from compressive stress and a break in the tin oxide layer. The stress can originate from events such as oxidation, thermal cycling, intermetallic layer formation, and mechanical processes. Furthermore tin-whiskers can arise from the solder alloys, surface finishes or component finishes. The formation of tin whiskers on PCBs is especially consequential in that it can form an alternative conductive path, creating short circuits and resulting in component failure.

The growth rates of tin whiskers are unpredictable, but have been known to reach lengths of up to 10 mm. There is data available, however, that suggests that certain elements alloyed to tin can either act to promote or suppress tin whisker growth under certain conditions (they cannot prevent it) [6].

Lead acts to suppress the formation of tin whiskers, hence this issue was not widely problematic before the restrictions came into action.

Research has also suggested that an increase in applied current and current density will increase the formation of tin whiskers [7]. To a certain extent increasing temperatures will also play a role in promoting tin whisker formation. Higher temperatures above the optimum range of formation will induce some form of relief and hillocks[2] form instead of long thin whiskers. These hillocks are less likely to cause short circuiting.

One of the possible mitigation strategies to the tin whisker phenomenon is the application of a conformal coating as a protection barrier to trap the growth of tin whiskers. In a study by NASA [8] a tin-plated specimen was half coated with 2 mm thick conformal Aralane 5750 and the other half without coating as a control. The item was stored in ambient conditions for 9 years. It was found that "Lifting" of the 2 mm coat by the growth of tin whiskers may be observed, but breakthroughs of the coating were minimised and the whiskers tended to buckle under the pressure. Therefore the whiskers remained entrapped under the coating. The NASA study also found that the thinner the coat (<2 mm), the more likely whiskers were to penetrate the coating.

The prevention of tin whisker penetration cannot be guaranteed, rather conformal coatings of sufficient thickness reduce the risks by reducing the number of tin-whiskers breaking through the barrier.

The disadvantage of using conformal coatings on PCBs is that it may complicate solder repair work; coatings such as epoxy and silicon make solder rework difficult, whereas acrylic coatings are easily removed for solder rework. Note that acrylic coatings appear to be the most highly susceptible to tin whisker penetration [9].

[2] Protrusions from the tin plating that are short and thick-based are referred to as hillocks.

The document, GEIA-STD-0005-2, *Standard for Mitigating the Effects of Tin Whiskers in Aerospace and High Performance Electronic Systems*, is a government standard for high reliability applications which aims to 'establish processes for documenting the mitigating steps taken to reduce the harmful effects of tin finishes in electronic systems.' The document outlines three major control levels and states procedures required to be undertaken to control the problem of tin whiskers, the control level depending on the criticality of the application.

Furthermore, JEDEC[3]/IPC[4] published a document, JP002, outlining tin whisker mitigation strategies [10] and iNEMI[5] documented recommendations on lead-free finishes for high reliability products, which also includes commonly available mitigation strategies [11]. Most of these strategies are not aimed at preventing the growth of whiskers but merely to reduce growth rate and risks. Such mitigation strategies that were commonly addressed include the use of non-tin plating, tin alloys incorporating elements which act to suppress tin whisker growth (such as bismuth), using underlay materials (to reduce compressive stress at the tin-substrate boundary) and the use of conformal coatings. In a recent study by Panashchenko [12] the use of a nickel underlayer appeared to have no noticeable effect on mitigating the growth of tin whiskers under temperature cycling and elevated temperature humidity conditions.

The full description of the potential mitigation techniques should be sought from the documents for further details but will not be reiterated here as it is more applicable to the manufacturing stage. It should be noted that these documents were produced for industry standards and therefore may not be sufficient for military standards (especially mission-critical systems).

5.1.2 Tin Pests

Tin is an allotropic material, meaning that it has more than one crystal form. The beta form is the common white and useful form of tin. The alpha form is the uncommon form of tin which manifests itself as brittle and grey. The transformation of beta-tin to alpha-tin is accompanied by an increase in volume and will occur at temperatures below 13°C.

Tin pests are regarded as a "disease" whereupon once transformation has initiated, it spreads rapidly to the remaining white tin structure.

The document GEIA-HB-0005-2 supplies a table of elements [13] that act to promote and suppress tin pests, however, the duration of the tests from which the data is achieved are not sufficient to determine long-term reliability. As derived from the table, zinc, antimony, bismuth and silver appear to be among the elements with some suppressing ability to the formation of tin pests. There is evidence that the addition of bismuth alloys can aid in the inhibition of tin pest formation, although as discussed in section 5.1.3 bismuth in tin alloys can suffer from lead contamination problems.

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[3] JEDEC is an organisation aimed at developing standards in the microelectronics industry

[4] IPC, the Association Connecting Electronics Industry, is an organisation representing companies of the electronics industry; one of its roles includes the development of industry standards.

[5] iNEMI, International Electronics Manufacturing Initiative is an organisation comprising of electronic manufacturers, suppliers, universities and other associations to allow collaboration between members to facilitate improvement in the electronic technology.

Tin pests will bring about a decrease in electrical conductivity and loss of joint integrity. Given that tin pests usually begin to emerge in colder temperatures, it is important to assess the possible temperature conditions upon which the solder will be exposed to throughout service, and conduct appropriate reliability tests using those conditions and lead-free alloys to determine potential tin-pest susceptibility.

5.1.3 Lead Contamination

Lead contamination in lead-free alloys need to be avoided. Even traces of lead contamination can cause detrimental effects on some lead-free alloys, leading to premature solder joint failure. In particular, as mentioned previously, bismuth alloys are adversely affected by lead contamination in that it increases the brittleness of the solder joint. The level of thermal cycling that can be withstood by lead-contaminated bismuth alloys drops significantly below uncontaminated bismuth-containing alloys under the same conditions.

Sources of lead contamination may arise from component finishes, board finishes, contaminated tooling and workstations.

5.2 Assembly Issues

5.2.1 Melting Point of Solder

The melting point of eutectic SnPb solder is 183°C. Most lead-free solders will have a melting point above that of SnPb solder (refer to Appendix B). If higher soldering temperatures are required, there is an increased risk of thermally degrading non-metallic components in proximity to the soldering area and also damaging the circuit board. This could be due to either the hotter solder tip or the prolonged contact of the solder tip to the substrate to compensate for lower wetting. Understanding the glass transition temperature (Tg)[6] of the circuit board material will help to ensure that the soldering temperature stays below the Tg so as to avoid affecting the circuit board stability. If the Tg is exceeded, the board may warp or be physically damaged due to the softening of the material at localised areas. Circuit boards can be preheated to avoid thermal shock.

Another issue to be wary of is that higher processing temperatures may also evaporate entrapped moisture in the board, which can consequently act to expand the circuit board, resulting in cracking. Cracking may begin internally within the board and progress by expanding to the surface. Delamination of the board is possible by similar mechanisms.

5.2.2 Coefficient of Thermal Expansion (CTE) [7]

It may be difficult to acquire a component with all materials of similar CTEs, however, it should be noted that large differences in CTEs between two materials will produce different expansion rates with equal increase in temperature. The material expansion rates become uneven upon

[6] Glass transition temperature is the temperature at which a polymer changes from a 'glassy' state to a 'rubbery' state.
[7] Coefficient of thermal expansion denotes a measure of material expansion with a change in temperature.

heating and this may sometimes induce stress and subsequent solder joint cracking. Using materials with similar CTEs can avoid this issue (though this may not be a simple option).

Indium alloys have been found to impart ductility to a solder alloy which can compensate for the mismatch in CTE by absorbing the stresses caused by the CTE difference and prevent joint cracking [14].

A list of CTE values for materials commonly used in electronic assemblies are provided in Appendix F.

5.2.3 Flux Issues

Flux used for SnPb solders may not necessarily be as effective on lead-free solders and this is related to the general decreased wetting and higher soldering temperatures. Aspects to consider include the flux activation temperature, activity level, compatibility, and reliability properties. For hand soldering, lead-free solder wire is available with compatible flux solution in the core.

The flux becomes chemically active when it reaches a certain temperature range, reacting with the oxides and displacing them to allow wetting of the surface by the solder. If there is premature activation, the reactivity of the flux will be insufficient throughout the soldering process and a good solder joint will not be achieved. Similarly, fluxes can also be consumed too quickly during processing (this may also happen if during manual soldering the wire is in direct contact with the soldering tip [15]). Therefore the activation temperature of the flux must suit the melting temperature of the lead-free solder alloy.

Another issue with flux types is that more aggressive fluxes may be required to achieve effective lead-free soldering, which is accompanied with aggressive cleaning solutions post-soldering to remove the residue. Stronger fluxing agents can also produce toxic fumes, so extraction fume cupboards must be in place and PPE be worn during soldering.

Some fluxes also contain halogens to increase the flux activity and achieve better wetting, but the presence of halogens has been found to be problematic if not completely removed post-soldering. Halides can react with the metal to form metal salts. These metal salts (lead salts generally have a lower solubility in aqueous solution than tin or copper) are hygroscopic and will absorb moisture from the atmosphere, and in the presence of a voltage will result in corrosion. It is best to use halogen free flux to prevent this problem. Alternatively ensure that the residues are completely cleaned from the component. A test for the presence of halides in flux can be performed by a simple Silver Chromate test[8].

It is recommended that if required, solder/flux manufacturers are consulted for advice on flux issues with specific lead-free solders for a particular application. For more information on flux categories, refer to Appendix D.

[8] A sample of the flux is placed on silver chromate paper. After 15 minutes the paper is rinsed with isopropyl alcohol and left to dry. If there is a change in colour from the original silver chromate, it is an indication that there are halides present in the flux.

5.2.4 Board Finishes and Component Finishes

The board finish and component finish and their interaction with solder contribute to the reliability of the solder joint. Therefore the solderability of lead-free alloys may vary according to the type of finish. Alternative board finishes and characteristics are listed in Table 3. Alternative component finishes and characteristics are listed in Table 4.

Table 3: Commonly used lead-free board finishes and their characteristics [16][17]. HASL, which contains lead and was used as a common board finish, is also included

Board Finish	**Comments**
Hot Air Solder Leveling (HASL)	*SnPb finish, excellent solderability. But to comply with current RoHS restrictions this material may no longer be used as a surface board finish.*
Organic Solderability Preservatives (OSP)	Potential concerns over solder paste wetting and compatibility with mixed metals. Solderability degradation with high temperature exposure (and multiple thermal cycles).
Electroless Nickel/Immersion Gold (ENIG)	Nickel oxidises quickly after plating hence the use of immersion gold deposits. Increased gold in solder joints may result in increased brittleness. Thin areas of gold plating may result in 'black pad' due to nickel oxidation.
Tin (Sn)	Pure tin finishes are susceptible to tin whisker phenomenon leading to potential electrical shorts.
Matte Tin	Matte tin finish has a nickel coating applied to the base before tin is applied as the top coat. Less prone to tin whiskers than pure tin finish.
Immersion Silver (Ag)	Silver migration is a potential issue.
Electroless Palladium (Pd)	High cost. Issues with potential brittleness with levels of more than 1% palladium in the solder joint [16].
Lead-Free Hot Air Solder Leveling (Pb-Free HASL)	Derived from the common HASL but in lead-free version. Has a higher melting temperature and increased cost.

Table 4: Commonly used component finishes and their characteristics

Component Finish	**Comments**
Sn	Excellent wetting. However prone to tin whiskers.
SnBi	Low melting temperature. Lead contamination is detrimental to the integrity.
Pd-containing (NiPd)	Potential solder joint embrittlement for Pd thicknesses within 0.51-0.76 microns [18].
Pd-Ag, Pd-Pt-Ag	Decreased solderability when compared to SnPb finishes.
Au-containing	Potential solder joint embrittlement for Au contents exceeding 3 wt% (caused by formation of brittle $AuSn_4$ compound) [18].

Due to the potential issues with some finishes, it is important to identify the type of finish utilised in conjunction with a given lead-free solder alloy and ensure compatibility.

5.2.4.1 Gold Content

The thickness of gold plating on the component or board in comparison to the thickness of the solder joint is an important consideration. Gold will dissolve into the solder joint and form a brittle $AuSn_4$ intermetallic phase which affects the mechanical and thermal properties of the solder joint and can lead to premature failure. Thicker gold plating will increase the possibility of gold embrittlement. Furthermore thicker gold plating can create voids in the solder joint, reducing its mechanical strength. It has been reported that an immersion gold layer of 0.05–0.2 µm thickness is adequate for solderability protection [19].

5.2.4.2 Palladium Content

Research indicates that thicker palladium layers can increase the potential for solder joint embrittlement due to the formation of $PdSn_4$ for SnPb solders, however, more research is required to determine if the thickness also affects lead-free solders [20].

5.2.5 Wetting and Intermetallic Bond Formation

Compensation for the decreased wetting ability of lead-free solders has been achieved by the following:

- using a stronger fluxing agent to promote wetting
  disadvantage – leaves behind corrosive residues and requires complete removal.
- increasing the soldering temperature
  disadvantage – decrease solder tip life, activate flux prematurely and increases the chance of damaging the PCB or nearby non-metallic components.
- prolonging the soldering time to improve formation of the intermetallic bond layer [21],
  disadvantage – increases the likelihood of PCB heat damage.

Effective lead-free soldering requires patience and trial/error to produce a consistent soldering technique with a suitable soldering temperature and wetting duration for a given lead-free alloy.

It should be noted that an insufficient level of intermetallic bonding formed within the solder connection produces a 'cold joint' which is the result of insufficient melting of the solder or movement of the component before the solder is cooled. A cold joint will not be conductive and can lose contact with the component. In contrast, if the intermetallic bond is too thick the joint may suffer from embrittlement.

5.2.6 Reworking

Reworking SnPb solder connections with lead-free alloys should be avoided due to the possibility of lead contamination which can cause incompatibilities. This also applies to reworking lead-free solder connections with SnPb alloys.

Furthermore mixing lead-free alloys is not recommended; the same lead-free alloy in the original solder connection should be used during rework/repair.

5.3 In-Service Issues

Service conditions such as moisture (humidity), temperature fluctuations, chemical contacts, vibrations, etc can affect a solder joint performance/ integrity. The types of lead-free solder that would be most suitable to the military environment are those that are able to endure its conditions without premature failure.

5.4 Economic Issues

Eutectic SnPb solder was widely available and therefore cheap to acquire, but the cost of alternative materials becomes greater depending on the type of material selected. For example, as of 2010 the cost of lead per kg was approximately USD $2.34 and the cost of copper per kg was approximately USD $7.55 [22]. The low availability of materials such as indium may also govern the choice of solder selection. A list of other metal alloys and their associated costs can be reviewed in Appendix C.

There are other economic aspects that can increase the cost of the overall transition to lead-free, and may include new soldering tips, frequent replacement of soldering tips (due to reduced tip life), reworking of lead-free soldered items or replacement if repair is not suitable (this is attributable to potential lower solder joint reliability), increased control and maintenance of lead-free products, improved fume extraction and PPE when using aggressive fluxes, and lead-free solder training.

5.5 Inspection Issues

Paragraph 40, Sect 2 Chap 7 of the AAP 7045.002-1 Soldering manual states that solder joints will be rejected on the basis of "a. dull gray, chalky, or granular appearance - evidence of a cold joint".

Lead-free solder joints do not have the same desired shiny, silver appearance as eutectic SnPb solder but most tend to produce a dull grey, grainy appearing joint. Inspections should account for the appearance of lead-free solder joints, since a dull grey, grainy lead-free solder joint will not necessarily be indicative of a poor solder quality.

The IPC standard, IPC-A-610D Acceptability of Electronic Assemblies, provides inspection criteria for the acceptance of lead-free solder joints, which has been adopted by the US Department of Defense (see Appendix H).

6. Lead-Free Solder Tooling/Workstation

Soldering equipment may need to undergo changes or replacements from the current soldering tools used with SnPb in order to accommodate the different properties that lead-free solder introduces. The major reasons for change may involve the following:

- Most lead-free solders have a higher melting temperature than SnPb solder
- The use of higher soldering iron temperatures will promote oxidation of the solder tip
- An increase in oxidation of the solder tip means a reduction in heat conductivity and solder wetting ability, and harsher flux chemicals may be required to actively promote wetting to compensate for this loss
- Using harsher flux chemicals will leave harsher chemical residue on the circuit board and therefore stronger cleaning agents will be required after soldering in order to prevent corrosion and damage to the circuit board
- The life of the soldering tip is also reduced, and will require a higher level and frequency of maintenance and care
- The possibility of lead-contamination exists if tools used for SnPb are also used with lead-free solder.

All equipment to be used for lead-free soldering in the workstation, such as solder and fluxes, microscopes, solder wick, fume extraction systems, soldering tip cleaner, cutter, pliers, scalpel and other small hand-tools need to remain in a lead-free area to avoid contamination. Furthermore no other external instruments/tools already in use with SnPb solders should be introduced into the lead-free workstation area for similar reasons [23].

An assessment of the compatibility of current equipment with the requirements of lead-free solder will need to be undertaken. Lead-free hand soldering tools should exhibit:

- Higher power/wattage and better temperature control—compensates for the decrease in wetting ability of lead-free solders and for a faster thermal recovery
- Better thermal conductivity—optimising heat transfer to compensate for higher melting temperatures of most lead-free solders
- Thicker iron plating on the solder tip—to improve the life of the soldering tip
- Selection of the correct solder iron tip size and geometry.

7. Analytical Techniques

It is imperative to maintain identification of the solder alloys which, in the event of solder joint rework, will aid in preventing the possibility of intermixing different solder alloys. In order to determine the composition of an existing solder joint, various analytical instruments are available to distinguish between metals to assist in categorising between lead-free and lead-based solders. Below is a list of such analytical instruments and a brief description of the modes of operation.

7.1 Handheld XRF (X-Ray Fluorescence)

Handheld XRF instruments function by irradiating the sample with an energy source and detecting the characteristic x-rays emitted by the sample, whereby every element has a characteristic energy due to the unique number of electrons and their positioning in the atom, allowing elemental identification. This technique provides convenient in-situ analysis. It is able to provide an identification and semi-quantification of unknown alloys by a simple point-and-shoot technique. This is probably the most effective method to use in the field to identify the alloy type in solder joints.

The NavAir "Solder Alloy Analysis, X-Ray Fluorescence Solder Alloy Identification Test Equipment Evaluation Report" [24] provides a comprehensive review of desktop and handheld versions of XRF technology. Some notable sections to mention from the report are the safety concerns involving the handheld XRF device. The x-ray source does not emit significant levels of radiation but the end-user must ensure appropriate use of the handheld device. A Class II laser beam is also used for many XRF instruments for targeting areas of analysis, and hazards from the lasers would only arise from inappropriate use of the laser (i.e. directing the laser towards the eyes).

The study also concluded that handheld versions of XRF analysers were less accurate than their desktop counterparts and this was mostly attributed to a larger sample spot size and the lack of camera imaging to view the area of interest. Larger sample spot sizes are more likely to incorporate areas outside the solder joint, leading to "contaminated" target areas and inaccurate readings. Although the purpose of a laser beam is to mark an area for analysis, the laser spot size does not necessarily equal the actual analysis spot size. Furthermore, the resolution is lower than the desktop version and discerning between lead and bismuth has proved to be difficult[9].

For simple characterisation between SnPb and lead-free solders, a handheld XRF is ideal. It is useful for obtaining a broad classification of the type of lead-free solder (i.e. SAC, SnCu, families). To achieve a higher level of accuracy for alloy percentage composition, a desktop XRF or SEM would provide a more powerful analysis.

Training is recommended to personnel using this device in order to understand aspects such as the theory behind XRF technology, troubleshooting requirements, limitations and to effectively position/ focus the spot size appropriately in order to produce results as accurately as possible.

7.2 Scanning Electron Microscope- Energy Dispersive Spectroscopy

A Scanning Electron Microscope coupled with Energy Dispersive Spectroscopy (SEM-EDS) is capable of determining metal (and non-metal) identities using an electron beam source and measuring the characteristic x-ray energies that are emitted from the sample.

Scanning Electron Microscopes are mostly available as bench-top instruments, however, there are a few portable SEMs now available on the market that can be plugged to a power socket. SEMs require that the sample be placed inside a chamber and held under vacuum during

[9] Lead and Bismuth have very close x-ray energies; percentage compositions of lead and bismuth may therefore be affected and inaccurately recorded.

analysis. Time is needed to set-up the sample and obtain the appropriate pressure in the chamber, therefore this reduces the sample turnover rate. The advantage of using the SEM is that it has a high resolution which allows the user to pinpoint specific locations on the sample for analysis, eliminating potential 'contamination' errors from the solder surroundings. The beam can be well-focused and the spot size modified if desired. It is also semi-quantitative by providing percentage compositions of the elements detected.

The disadvantages of SEMs are their high cost and the need for continuous maintenance and calibration. It is more complex to use than a handheld XRF and requires user training to understand the components, functions, limitations, and troubleshooting. This instrument would probably be unsuitable for frequent and/or rapid successive analysis for numerous components.

7.3 Optical Emission Spectrometer

An optical emission spectrometer (or atomic emission spectrometer) provides a way of looking at solid metal components by utilising a spark created between an electrode and the metal sample of interest, exciting the material and subsequently detecting the characteristic x-ray that is emitted from the material.

OES instruments are available as bench top or portable instruments[10], and can allow a generous degree of movement from a long cable between the probe and the main unit.

7.4 Swab Check

Lead Swab Checks are used to identify the presence of lead only. If the swab is rubbed over a surface containing lead, the swab will turn pink. Although it is important to categorise SnPb solders from lead-free solders, it is also as important to know what type of lead-free solders exist in the material. Further tests from the swab check will be necessary to obtain a qualitative assessment of the lead-free alloy type.

Note: Caution should be taken when using the Swab method. If dirt is also picked up in the swabbing process this may mask the indicative pink colour.

8. Summary

The movement of some industries to lead-free solder means that more COTS electronic equipment- especially from European industries- are becoming (if not already) lead-free. The chances of incorporating lead-free electronics into aircraft are therefore becoming increasingly likely. One of the main areas of concern is the integration of lead-free solder unknowingly into aircraft systems which can compromise functionality and safety if the lead-free solder joint results in incompatibility or a poor performance in the conditions it experiences during service. The risks of using lead-free solder have been outlined in this report and include such issues as the spontaneous growth of tin whiskers, tin pests, higher temperatures associated with

[10] Not handheld

processing lead-free solder which subsequently increases the chance of damaging circuit boards, lower aesthetic quality, potential compatibility issues with flux/component/board finish and alloy mixing, and generally a lower resilience under extreme service conditions. The array of issues and uncertainties associated with lead-free solder, lead-free component finishes and lead-free board finishes and lack of long-term reliability research means that it is difficult to recommend a particular solder alloy for any military application. To date there is no recommended lead-free solder for military environments.

If possible, lead-free items should be avoided, especially in mission or safety critical systems. In cases where lead-free items or units may not be avoidable, it is necessary to develop a control plan which encompasses the following practices:

- identify if the equipment is lead-free by way of appropriate analytical techniques (XRF is the most effective method of identifying lead-free solder in the field; user training is recommended to minimise errors),
- understand its risks and limitations/ ensure that the results of reliability tests for a given component at a given condition is sound in order to maintain reliability at the expected lifespan of the item,
- manage and monitor lead-free systems, for example by record keeping and appropriate labelling.

For hand soldering requirements, specific tooling for lead-free soldering should be discussed with equipment manufacturers; soldering tools with better thermal efficiency and control may be more efficient for lead-free alloys. If a lead-free workstation is required, the area and all tools used for lead-free soldering needs to be isolated from existing SnPb soldering tools and areas in order to avoid contamination issues. A suitable fume extraction system and appropriate PPE must be employed during soldering processes for protection.

Control plans are a necessity. For lead-free solders that are identified for a specific application, assess the level of inspection required to ensure reliability (i.e. creating an inspection procedure for lead-free solders). This follows in line with the Airworthiness Design Requirements Manual.

Refer to Appendix A for a list of DSTO recommendations.

9. References

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Appendix A: Recommendations

1. The use of lead-free solder in military applications is avoided where possible;
2. Lead-free solder items should not be used in applications involving mission or safety critical systems;
3. Should an item be identified as lead-free, the type of lead-free solder alloy and board/component finish (PCB) should also be identified using appropriate analytical techniques;
4. Control processes that monitor and regulate the influx of lead-free soldered items be established and soldered items should be identified and labelled as lead-free solder;
5. Reworking existing SnPb solder joints with lead-free solder joints (and vice-versa) is avoided due to the implications of lead contamination effects in some lead-free alloys;
6. Soldering tools for lead-free solder are isolated from those used for SnPb soldering such that cross-contamination is avoided;
7. Soldering/flux manufacturers are consulted for advice regarding solder/flux/finish compatibilities and reliabilities with the intended application;
8. Long-term reliability data for lead-free materials (specifically addressing the conditions to which the item will be exposed during service) should be sought from suppliers/manufacturers before integration;
9. Training is provided to relevant personnel involved with managing, acquiring or working with electronic systems or soldering processes to ensure awareness of lead-free solder and its implications in military applications;
10. Standards related to the use of lead-free electronics such as GEIA-STD-0005-01, GEIA-STD-0005-2, GEIA-HB-0005-1 and GEIA-HB-0005-2[11] be consulted for assistance in managing and understanding lead-free related issues;
11. A materials studies and failure mechanisms program be explored as part of a long-term understanding of the implications of the use of lead-free solders.

[11] GEIA, the Government Electronics and Information Technology Association, have published several relevant documents which assists aerospace, defence and other industries with the process of transitioning into lead-free electronics. Standards available from www.techstreet.com as at March 2010.

Appendix B: Current Lead-Free Solder Alternatives

A collated list of alternative lead-free alloys (some are patented solder alloys) based on tin is provided in the table below.

Table 5: List of lead-free solder alloys based on tin and their melting temperatures

Family Alloy	Solder Alloy Composition	Melting Temp (°C)
SnAgBi	Sn/3.4Ag/4.8Bi	200–216
	Sn/1.0Ag/57Bi	138
	Sn/3.5Ag/3.0Bi	206–213
	Sn/7.5Ag/2.0Bi	207–212
	Sn/2.0Ag/7.5Bi	216
	Sn/3.0Ag/3.0Bi	218
	Sn/3.0Ag/5.0Bi	216
SnAgCuBi	Sn/3.1Ag/0.5Cu/3.1Bi	209–212
	Sn/3.4Ag/1.0Cu/3.3Bi	205–214
	Sn/3.2Ag/1.1Cu/3.0Bi	240
	Sn/2.5Ag/0.5Cu/1.0Bi	217–225
	Sn/2.0Ag/0.75Cu/2.0Bi	
SnAgCu	Sn/3.9Ag/0.6Cu	216–219
	Sn/4.0Ag/0.5Cu	216–219
	Sn/4.0Ag/1.0Cu	216–219
	Sn/3.0Ag/0.5Cu	217–218
	Sn/3.8Ag/0.7Cu	217–218
	Sn/3.5Ag/0.7Cu	217–218
	Sn/4.7Ag/1.7Cu	244
SnAgCuSbBi	Sn/4.6Ag/1.6Cu/1.0Sb/1.0Bi	214–220
SnAgCuSb	Sn/2.5Ag/0.8Cu/0.5Sb	217
	Sn/0.2Ag/2.0Cu/0.8Sb	226–228
SnAgIn	Sn/3.5Ag/1.5In	218–223
	Sn/2.8Ag/20In	175–187
SnAgInBi	Sn/3.5Ag/3.0In/0.5Bi	215
	Sn/3.5Ag/4.0In/0.5Bi	210–215
	Sn/3.5Ag/8.0In/0.5Bi	197–208
SnAg	Sn/3.8Ag	221
	Sn/3.5Ag	221
	Sn/5.0Ag	221–240
	Sn/2.0Ag	221–226
	Sn/4.0Ag	221
SnCu	Sn/0.7Cu	227
	Sn/3.0Cu	227–300
SnCuNi	Sn/0.7Cu/0.05Ni	227
SnBi	Sn/58Bi	138
SnZn	Sn/9.0Zn	199

Family Alloy	Solder Alloy Composition	Melting Temp (°C)
SnSb	Sn/3.0Sb	232–240
	Sn/5.0Sb	232–240
SnAgSb	Sn/25Ag/10Sb	260–300
SnIn	Sn/52In	118
	Sn/50In	118–125
SnBiIn	Sn/20Bi/20In	143–193
SnZnBi	Sn/8.0Zn/3.0Bi	189–199
SnAu	Sn/80Au	280
	Sn/10Au	217

Table 6: List of lead-free alloys not based on tin, and their melting temperatures

Solder Alloy Composition	Melting Temperature (°C)
88Au/12Ge	356
3.0Ag/97In	143
67Bi/33In	109
97Au/3.0Si	363
82Au/18In	451–485

Note: The reported values of a collection of alternative solder melting points are derived from various sources and their accuracy cannot be guaranteed by DSTO.

For hand soldering (Class 1 and 2 applications), an example of the current choice of alloys that are available in solder wire includes:

Kester[12]:
Sn/3.5Ag
Sn/3.0Ag/0.5Cu
Sn/0.7Cu
Flux- No Clean, Water Soluble or Rosin based.

Interflux Electronics[13]:
Sn/0.7Cu
SnAgCu types
Sn/4.0Ag
Sn/42Bi (incompatible with lead)
Sn/52In (incompatible with lead)

Mektronics[14]:
Sn/3.0Ag/0.5Cu
Sn/0.7Cu

[12] Kester, Solderpaste and Flux Solutions for Lead-Free Processes <http://www.kester.com/en-US/leadfree/recommendations.aspx> (accessed Jan 2010)
[13] W.V.Riet, "Lead-Free Soldering Start-Up Guide," Presentation, Interflux Singapore Pte Ltd
[14] Mektronics Lead-Free Solder Wire <http://www.mektronics.com.au> (accessed Jan 2010)

Appendix C: Cost of Metals and Alloys

Table 7: Cost of selected metals

Metal	$USD/kg (approx)
Pb	2.34
Zn	2.38
Cu	7.55
Ag	574.86
Sn	18.30
Sb*	5.97
Bi*	26.46
In*	510.0

Note: Prices are current as of April 2010. *denotes metal prices in 2007. Values taken from the London Metal Exchange <www.metalprices.com> (accessed April 2010)

Table 8: Cost of selected metal alloys

Alloy	$/kg (approx)
Sn/37Pb	5.21
Sn/3.5Ag	13.90
Sn/0.7Cu	7.66
Sn/58Bi	7.57
Sn/5Sb	7.41
Sn/9Zn	7.11
Sn/4Ag/0.5Cu	14.41
Sn/3.4Ag/4.8Bi	13.73
Sn/3.5Ag/3Bi	13.02
Sn/2.8Ag/20In	66.13
Sn/3.5Ag/1.5In	17.93
Sn/2Ag/0.5Cu/7.5Bi	11.20
Sn/2.5Ag/0.8Cu/0.5Sb	12.06

Note: Prices are not current, but provide a comparison of the cost of various lead-free alloys against the tin-lead alloy. Table of data from "Lead-Free Alloy Trends for the Assembly of Mixed Technology PWBs," Proc. NEPCON-West 2000 (Feb. 27-Mar.2) Anaheim, CA.
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Appendix D: Flux Types

Flux systems aim to displace the oxide layers on the surface of the metal to be soldered in order to allow good wetting so the solder applied can form a sufficient intermetallic bond with the metal. There are arrays of flux types that are available on the market which serve to enhance the solderability specifically for lead-free solders. They may have enhanced thermal stability and activity to enable better wetting. Typical flux types used for SnPb solders may not be equally effective on lead-free solders. The strength of the flux, the nature of the flux, the nature of the flux residue, the cleaning solutions required for the residues, and the compatibility of the flux with the solder alloy are aspects to consider when choosing a flux system.

Flux systems are labelled according to composition, the level of activity, and the presence of halides.

Flux compositions include rosin (RO) or resin (RE), organic (OR) or inorganic (IN). Rosin/resin based flux systems can leave a sticky residue on the surface. Rosin fluxes may contain catalysts which activate upon heating and are further sub-categorised as R- Rosin (no activators), RMA- Rosin Mildly Activated and RA- Rosin activated. RA fluxes provide the highest activity level and leave the most amount of residue. Inorganic acid fluxes have a higher corrosive nature and leave residues which are also highly corrosive, which need to be completely removed after soldering. Organic acid fluxes are of organic nature (i.e. in rosin) and can leave behind residues which should also be removed. These residues are washable in water.

The activity level of the flux and its residues are indicated as high (H), medium (M) or low (L). The higher the activity level of a flux, generally the stronger the corrosive nature and amount of residue left on the surface.

The halide content of a flux will be labelled as (1) if halides are present, or (0) if there are no halides. Halides may be added to flux for higher activity levels in removing oxides and thus increase the wetting ability of the solder joint. The use of halides in flux leaves corrosive residues and must be completely removed thoroughly after soldering. Halide-free flux systems are recommended.

“No Clean” or “Low Residue” flux types are available which intend to leave little to no surface residue. If some residue remains, this residue is considered safe because it is non-degrading. However, it is recommended to remove all surface residues regardless of its nature.

Appendix E: Reliability Tests

Selected testing environments which have been used to assess lead-free solder performance and reliability for aerospace/military applications are described below:

- Thermal cycling: the application of alternating heating and cooling periods. This is usually from -55°C to +125°C for military/aerospace components to reflect the extreme temperature conditions that may be experienced in military service. An increase in temperature will promote solder joint expansion and subsequent cooling will promote solder joint contraction, and these continuous cycles induce stress on the joints. Generally lead-free solders are less likely to accommodate the stresses because most lead-free solders are less ductile.
- Vibration and shock (mechanical and thermal shock) tests: to determine a component's response to intense vibration and stresses induced through high-intensity shock.
- Humidity test: tests the solder joint in a moist and high temperature environment which simulates tropical environments. Zinc and indium alloys are especially prone to corrosion.
- Combined environments test: assessing the effects of combined thermal/shock treatments.
- Copper dissolution test: determining the rate of copper thickness loss due to lead-free solder processing under various conditions.
- Coefficient of thermal expansion test: assessing the expansion and contraction rates of different materials to determine the reliability and likely modes of failure within a component.
- Salt fog test: assesses the performance of a solder joint from the effects of salt deposits, which simulates the coastal/marine environments that may be encountered during service.

Appendix F: Coefficient of Thermal Expansion

Coefficient of Thermal Expansion values for selected materials. Where (z) is noted, this indicates the CTE along the z axis.

Table 9: Coefficient of Thermal Expansion (CTE) of selected materials. Derived from J.J. Licari and D.W. Swanson, Adhesives Technology for Electronic Applications–Materials, Processes, Reliability, *Chpt 2.4.1, pp. 76-82, Tables 2.8 & 2.9*

Material	**CTE (ppm/°C)**
Aluminium	23.5
Aluminium Nitride	3.8-4.4
Beryllia	4.7
Copper	16-17
Gold	14.1
Invar	0.64, 1.5
Kovar ®	5.1-5.5
Molybdenum	4.8
Nickel	7.8, 13.3
Palladium	11.8
Silicon	2.6-3
Silicon Carbide	2.8
Silver	19.1
Tin	20
Tin-Lead Solder (60/40)	24.6
Tungsten	4.5
Epoxy Glass Laminate	55-100 (z)
Polyimide- E Glass Laminate	45-75 (z)
PTFE- woven glass	200 (z)

Note: CTE values from the reference were collected from various sources whereby ranges of values or different values (separated by a comma) are due to differences in test methods, test conditions and purity of the sample.

Appendix G: Available Research/Test Results/Recommended Alloys

These projects are from commercial and government bodies of research. The purpose of this section is to summarise previous and current research projects on lead-free solder for reference and to provide exposure to the types of lead-free solder that, from the results of the studies, could potentially be or already are implemented (mostly applicable to Class 1 and 2 items).

G.1. Joint Group on Pollution Prevention/ Joint Council of Aircraft Ageing (JGPP/JCAA) Project

The Joint Group on Pollution Prevention (JG-PP) is comprised of members from the US Airforce, Navy, Army, Marine Corps, NASA and other defence organisations aimed at addressing and reducing or eliminating the use of hazardous substances by evaluating suitable non-hazardous alternatives.

The Joint Test Protocol, 2003[15] by the Joint Group on Pollution Prevention and the Joint Council of Aircraft Ageing (JGPP/JCAA) is aimed to specifically address lead-free solder, and lists the technical/performance requirements and test methods to be used on DoD circuit board components in order to subsequently assess their performance and reliability. The Potential Alternatives Report[16] by the JGPP/JCAA looked into a range of lead-free solders, from which a narrower selection from this list were further analysed and then recommended for use in the testing phase. Together, both reports outlined the conditions and requirements for testing the selection of lead-free solder alloys under the specified conditions, and therefore formed the base for the Joint Test Report.

The Joint Test Report[17] is only available in its draft form until testing is completed.

In particular three lead-free alloys were selected for the project; Sn/3.9Ag/0.6Cu (SAC family), Sn/3.4Ag/1.0Cu/3.3Bi (SACB) and, Sn/0.7Cu/Ni-Stabilised (SnCu). Their performance was compared against the baseline Pb/Sn system.

Test conditions included vibration, thermal shock, thermal cycling, mechanical shock, and humidity tests. The reliability of solder joints were also evaluated with lead contamination. Different circuit board components (e.g. CLCC-20s and PDIP-20s) sometimes showed different levels of lead-free solder compatibility depending on the mechanical tests performed and the type of alloy.

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[15] Joint Group on Pollution Prevention (JGPP), "Joint-Test Protocol for Validation of Alternatives to Eutectic Tin-Lead Solders used in Manufacturing and Rework of Printed Wiring Assemblies", JG-PP Joint Test Protocol, 14th Feb 2003

[16] Engineering and Technical Services for Joint Group on Pollution Prevention (JG-PP) Projects, "Potential Alternatives Report for Validation of Alternatives to Eutectic Tin-Lead Solders used in Electronics Manufacturing and Repair," Dec 2nd, 2003

[17] NASA Technology Evaluation for Environmental Risk Mitigation (TEERM) Principle Centre, "JCAA/JG-PP Lead-Free Solder Project, Joint Test Report, Executive Summary," Kennedy Space Centre, FL, July 30 2007

Some conclusions worth noting from the Joint Test Report:

- During vibration testing, the solder joint reliability varied according to component location on a PCB.
- During high-stress testing, SnPb solders were more reliable than lead-free. During low-stress testing, lead-free solders were more reliable.
- For promising lead-free solder alloys, system level demonstration/validation on aerospace/military electronic systems be achieved.
- To assess reliability of solder joints, all relevant tests should be considered, not only individual tests.

G.2. NASA-DoD Lead-Free Electronics (LFE) Project

The Joint Test Protocol[18] and the Project Plan[19] for the NASA-DoD LFE project is currently available. Following on from the JGPP/JCAA Lead-Free Solder Project, NASA-DoD established a project to further research the reliability performance of lead-free solders under environmental testing conditions of thermal cycling, vibration, mechanical shock, combined environments test, drop testing, interconnect stress test and copper dissolution. The aim was to evaluate lead-free solder joints on manufactured and reworked test vehicles, the reworked test vehicles subjected to solder-mixing (reworking SnPb vehicles with lead-free solder and vice versa). Only two lead-free solder alloys were involved in the project; SAC305 and Sn100C. The selected board finishes on the test vehicles were immersion silver and ENIG, and the flux types to be used were low residue or no-clean.

Testing has commenced but has yet to be completed.

G.3. Airworthiness Advisory 2008

This document was prepared by the Department of the Air Force, Headquarters Aeronautical Systems Centre (AFMC), Wright-Patterson Air Force Base Ohio. An earlier version was prepared in 2005[20] which expressed the concerns of using lead-free solder in military applications and stated in the recommendations that "the safety of USAF equipment must not be sacrificed in the transition to lead-free solder practices" and "None [of the alternative solder alloys] has passed the reliability testing required of aerospace-quality hardware."

The 2008 updated version acknowledges the difficulty in procuring SnPb soldered items due to the increasing number of manufacturers switching to production of lead-free solders, and therefore provided recommendations to assist in managing the transition to lead-free solders and finishes. A full list of the recommendations to manage lead-free solder is outlined in the Airworthiness Advisory 2008 document[21].

[18] NASA-DoD Lead-Free Electronics Project, Joint Test Protocol, October 8th 2007
[19] NASA-DoD Lead-Free Electronics Project Plan, Nov 17th 2008
[20] Airworthiness Advisory, AA-05-01, Lead- Free Electronics, May 2005
[21] Airworthiness Advisory, AA-08-02, Lead-Free Electronics, DoD Soldering Technologies Working Group, Mar 2008

G.4. Boeing (2000)

The Boeing Company commenced a test program to source a reliable lead-free solder replacement for wave soldering and reflow soldering[22]. Their test program consisted only of two candidate materials which were subjected to 4380 thermal cycles:

1. Sn/0.7Cu-wave soldering and
2. Sn/3.8Ag/0.7Cu-reflow soldering.

The results stated that the Sn/0.7Cu solder joint was reliable for surface mount wave soldering but the Sn/3.8Ag/0.7Cu was not as reliable as the SnPb solder for reflow soldering. Leachate tests for both candidate materials confirmed that no intolerable amounts of toxic metals leached from the solder.

In addition, lead-free board finishes were also examined for their reliability, in particular three types of finishes were involved in the study:

1. Immersion silver,
2. Electrolytic gold on nickel and
3. Organic solderability preservative (OSP).

Test solders were applied to the different board finishes and thermally cycled until failure.

For the reflow Sn/3.8Ag/0.7Cu solder:
The solder on all three lead-free board finishes resulted in underperformance, especially on the silver immersion board finish, compared to tin/lead. Additionally, the tests indicated that when Sn/3.8Ag/0.7Cu was contaminated with traces of lead this resulted in premature failure than otherwise expected during thermal cycling.

For the wave-solder Sn/0.7Cu:
The solder failed at a similar rate as tin/lead solder joints on all three surface finishes, therefore concluding that the Sn/0.7Cu solder is as reliable as tin/lead.

[22] Reliability and Leachate Testing of Lead Free Solder Joints- Woodrow, Thomas A., The Boeing Company, Seattle, WA- Final Potential Alternatives Report

G.5. Boeing (2002)

The Boeing Company completed another series of test in 2002[23] relating to the reliability of several lead-free solder joints when contaminated with lead (to simulate possible mishaps during the transition period). Results were compared to the control eutectic tin/lead solder.

Several solder materials were subjected to 3441 thermal cycles, and included in the study were:

Sn/3.8Ag/0.7Cu,
Sn/3.4Ag/4.8Bi,
Sn/3.5Ag,
Sn/0.7Cu,
Sn/3.4Ag/1Cu/3.3Bi, and
58Bi/42Sn

Results indicated that bismuth-containing lead-free solder materials and Sn/0.7Cu have a low tolerance to lead contamination, and failure is encountered prematurely in the thermal cycling process, especially with 58Bi/42Sn.

Sn/3.8Ag/0.7Cu and Sn/3.5Ag were not affected by lead contamination; in fact the lead contamination enhanced its reliability enabling it to proceed through more thermal cycles before failure.

If the candidate solders were *not* contaminated with lead, then the following conclusions were made;

1. Reflow Sn/3.8Ag/0.7Cu, Sn/3.5Ag and Sn/0.7Cu were less reliable than eutectic tin/lead
2. Sn/3.4Ag/4.8Bi is as reliable as eutectic tin/lead
3. Sn/3.4Ag/1Cu/3.3Bi is more reliable than eutectic tin/lead.

The full report can be viewed from the provided reference.

[23] The Effects of Trace Amounts of Lead on the Reliability of Six Lead-Free Solders, Woodrow, Thomas A., The Boeing Company, Seattle, WA

G.6. IPC SPVC- Round Robin Testing & Analysis

The IPC Round Robin Testing and Analysis report[24] provides the results from tests performed with lead-free alloys based on the SAC family (namely Sn/3.0Ag/0.5Cu, Sn/3.8Ag/0.7Cu and Sn/4.0Ag/0.5Cu). The test assemblies were based on surface-mount reflow technology, and only melt characteristics, wetting ability and solder spread of candidate alloys were surveyed.

The final recommendation of this round robin testing was the Sn/3.0Ag/0.5Cu for the electronics industry due to lower cost and equivalent performance than silver alloys with 3.8% silver or more[25].

G.7. NCMS (National Center for Manufacturing Sciences) Lead-Free Solder Project

The National Center for Manufacturing Sciences (NCMS) completed a four year program[26] aimed at identifying safe, reliable, non-toxic and cost-effective lead-free solder alloys.

In summary, several promising alloys were selected initially based on storage and operating temperature tolerance, divided into three temperature testing conditions; a) -55°C to 100°C for consumer electronics and telecommunications, b) -55°C to 125°C for military electronics and c) -55°C to 180°C for aerospace and automotive electronics.

The test included endurance through two thermal cycling profiles, through the -55°C to 100°C range and completing 6673 cycles, and through the more extreme -55°C to 180°C range and completing 5000 cycles.

In summary the alloy materials that performed with the minimum number of failures were:
(For the -55°C to 100°C thermal cycle)

1. Sn/3.4Ag/4.8Bi – no failures
2. Sn/58Bi - <1% failure
3. Sn/37Pb, Sn/3.5Ag, Sn/3Ag/2Bi- 2-5% failures
4. Sn/2.6Ag/0.8Cu/0.5Sb, Sn/2.8Ag/20In, Sn/3.5Ag/0.5Cu/1Zn- 8-11% failures

(For the -55°C to 125°C thermal cycle)

1. Sn/58Bi- 4% failures
2. Sn/37Pb, Sn/2.8Ag/20In- 13-16% failures
3. Sn/3.5Ag, Sn/3Ag/2Bi, Sn/2.6Ag/0.8Cu/0.5Sb, Sn/3.5Ag/0.5Cu/1Zn, Sn/2.8Ag/20In- 54-57% failures.

[24] IPC Solder Products Value Council, White Paper (IPC-SPVC-WP-006)
[25] IPC Solder Products Value Council, Round Robin Testing and Analysis of Lead Free Solder Pastes with Alloys of Tin, Silver and Copper, Final Report
[26] NCMS Lead-Free Solder Report (summary), <http://ieeexplore.ieee.org/stamp/stamp.jsp?arnumber=00747683> (accessed Dec 2009)

Another finding with respect to board finishes indicated that Ni/Au surface finish provided a similar wetting ability for lead-free solders to lead solders. Pure metallic finishes Sn, Pd or Au improved the wetting ability of all solders.

Fillet lifting was encountered in mostly high-tin alloys after reflow, which was attributed to the increase in pasty range.

Overall the recommendations of the NCMS participants included Sn/58Bi eutectic, Sn/3.4Ag/4.8Bi and Sn/3.5Ag eutectic.

However, though these are the recommendations of this particular project, the low to zero failure rates were possible under mild conditions. The test alloys under the higher temperature range profiles which were to simulate military conditions all failed, the lowest number of failure for one alloy being 4%.

G.8. Interflux® Electronics

Interflux® Electronics are a soldering flux manufacturing company for electronics and PCB assemblies. Their preferences of solder materials in the following are listed below[27]:
Reflow Soldering (solder paste):

Sn95.5/Ag4/Cu0.5
Sn95.5/Ag3.8/Cu0.7
Sn96.5/Ag3/Cu0.5
Sn96.5/Ag3.5

Wave soldering (solder bars)

Sn96.5/Ag3/Cu0.5
Sn99.3/Cu0.7

Rework or Manual Soldering (solder wire)

Sn95.5/Ag4/Cu0.5
Sn96.5/Ag3/Cu0.5
Sn96.5/Ag3.5
Sn99.3/Cu0.7

These solders are derived from their potential effectiveness in consumer/commercial products.

G.9. Summary

The recommendations of different alloys are derived from the tests under mostly mild conditions, because they are adapted to the commercial/consumer market. The variables for test projects included conditions, the number of test specimens, the types of alloys tested, the board surface finishes and the type of soldering process. Furthermore most of these would have been carried out under controlled laboratory conditions which would not simulate actual military conditions. Should a certain lead-free solder be selected based on the recommendations listed by the research body, further testing is strongly recommended to understand the solder joint behaviour under the appropriate military service conditions.

[27] W. Van Riet, Lead Free Soldering Start-up Guide presentation, Interflux® Electronics, 2004

Appendix H: Standards and Publications

H.1. Industry Standards and Publications

Standards/publications from organisations such as IPC and JEDEC, which address the issues of lead-free solder, are industry-approved and some of these standards have been adopted by the US Department of Defense (DoD). A summary of some relevant documents is provided below.

- *IPC-A-610*, *Acceptability of Electronic Assemblies*, is an industry standard which has been adopted for use by the DoD, and outlines the workmanship criteria for electronic assemblies using illustrative examples.
- *J-STD-001*, *Requirements for Soldered Electrical and Electronic Assemblies*, is an industry standard adopted by the DoD, which acts to complement IPC-A-610. It provides content which addresses aspects such as material requirements, soldering method and assembly requirements, cleaning requirements and rework/repair requirements.
- *J-STD-609*, *Marking and Labelling of Components, PCBs and PCBAs to Identify Lead (Pb), Pb-Free and Other Attributes*, is an industry standard adopted by the DoD which provides guidance on the processes used to distinguish and label lead-based and lead-free components.
- *IPC-7711/7721*, *Rework, Modification and Repair of Electronic Assemblies*, is an industry standard providing guidance on the rework/repair of electronic assemblies.
- *J-STD-004*, *Requirements for Soldering Fluxes*, is an industry standard providing guidance on the use of flux systems in SnPb and lead-free solder.
- *JP002*, *Current Tin Whisker Theory and Mitigation Practices Guideline*, a JEDEC/IPC Joint Publication, provides guidance in understanding the theory behind tin whiskers and some mitigation practices that are/have been used to alleviate the problem.

H.2. High Performance/Reliability Standards and Publications

The Government Electronics and Information Technology Association (GEIA) have produced a set of standards targeted towards those involved with lead-free components used in aerospace/military applications, including OEMs, suppliers, managers, engineers and product end-users. These documents can be sourced from the ITAA (Information Technology Association of America) online store at http://www.techstreet.com (accessed Jan 2010). A summary of relevant standards currently available for purchase is provided below.

- *GEIA-STD-0005-1*, *Performance Standard for Aerospace and High Performance Electronic Systems Containing Lead-Free Solder* outlines the requirements for documenting the processes which assure end-users that the high performance lead-free products will achieve the required performance, reliability, airworthiness and safety throughout the life of the product.
- *GEIA-STD-0005-2*, *Standard for Mitigating the Effects of Tin Whiskers in Aerospace and High Performance Electronic Systems* outlines the processes for documenting the mitigating steps taken to reduce the harmful effects of tin finishes in electronic systems. The document describes three types of control-levels that differ by the level of attention given to the risk of tin whiskers.

- *GEIA-STD-0005-3, Performance Testing for Aerospace and High Performance Electronic Interconnects Containing Pb-Free Solder and Finishes* aims to provide information regarding suitable designing and testing of aerospace/high reliability products. It does not detail specific methods to use for performance testing, but rather it provides guidance as to what should be included in a performance test to appropriately test the reliability of lead-free items.
- *GEIA-HB-0005-1, Program Management/ Systems Engineering Guidelines for Managing the Transition to Lead-Free Electronics* documents processes which are designed to assist program management and/or systems engineering management in managing the transition to lead-free electronics to assure product reliability and performance.
- *GEIA-HB-0005-2, Technical Guidelines for Aerospace and High Performance Electronic Systems containing Lead-Free Solder and Finishes* establishes guidelines for the use of lead-free solder and mixed SnPb/lead-free alloy systems while maintaining the high reliability standards required for aerospace electronic and electrical systems.
- *GEIA-HB-0005-3, Repair and Rework of Aerospace and High Performance Electronic Systems Containing Lead-Free Solder* is aimed at those involved in the repair/rework of high performance electronic assemblies and provides guidance on the known issues and impacts of working with lead-free solders. It also provides information on the processes used for rework and repair of lead-free solders.

Appendix I: Bibliography

The following articles provide additional information on lead-free solder in both commercial and military arenas. Note the references provided below are by no means an exhaustive list of information on lead-free solder.

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16. NASA-DoD "Lead-Free Electronics Project, Joint Test Protocol (JTP)," Oct 8th 2007

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26. J.R. Geibig, M.L. Socolof, "Solders in Electronics: A Life Cycle Assessment," EPA 744-R-05-001, United States Environmental Protection Agency, Aug 2005

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19. ABSTRACT

This report outlines the findings derived from a study into the issues associated with the use of lead-free solder in electronic systems. It provides an assessment of the potential problems that might arise from the transition from the traditional tin-lead solder to alternative lead-free solder alloys. The information will enable the Australian Defence Force (ADF) to better understand the differences in alternative alloy properties and behaviour that may affect ADF systems if implemented. There is currently no single recommended lead-free solder alloy for military environments. The use of current lead-free solders brings with it the risk of reduced reliability for electronic systems and the implications for ADF systems, especially mission critical systems, need to be understood.