Handbook of Lead-Free Solder Technology for Microelectronic Assemblies

edited by
Karl J. Puttlitz
Kathleen A. Stalter

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Preface

The inspiration and need for this book arose from our task at IBM of implementing lead-free/reduced products to be in conformity with legislation proposed by the European Union (i.e. the RoHS Directive), and from the growing worldwide concern about the toxic agents utilized in electronics manufacture and products, particularly lead. The lead (Pb)-free implementation issue is of paramount interest to the electronics industry due to the magnitude of the undertaking and the many unanswered questions that must be addressed. It is an area that has been much discussed in trade press publications, at workshops, and it has been the subject of portions or entire international conferences. Given the importance and level of activity worldwide, it is both timely and appropriate to assemble the information surrounding the key aspects of the lead-free issue, particularly as they relate to electronic assemblies, from among the most knowledgeable practitioners and researchers in the world.

Virtually every major electronics component or product manufacturer is involved in activities in response to both legislative and market pressures to eliminate toxic materials, particularly lead, from their products.

The purpose of this book, therefore, is to serve as a handbook/primer for those who are contemplating or have already started the process of conversion, from standard Sn-Pb solder microelectronic assemblies to Pb-free. The book serves as a single source that covers all key aspects associated with this issue, including health, total environmental impact, legislation, market economics, and the materials, process, and reliability challenges; not just a narrow focus on a particular aspect. Accordingly, the book also serves as a valuable resource for those actively engaged in procuring, manufacturing, and utilizing lead-free products in all regions comprising the world market.

The audience for this book includes almost everyone either peripherally or directly involved in bringing microelectronics products to the marketplace, and users as well. This book would certainly be a valuable resource for individuals engaged in producing and marketing low-end products such as cameras, camcorders, cell phones, pagers, games, lap- and desktop computers, and other consumer products. Some of these products have been targeted for conversion to lead elimination/reduction and are already available in the marketplace. Typically, these products tend to be high-volume items, destined for disposal in landfills. Although high-end product disposal at end of life is likely to be by recycling, or refurbishing for the secondary market, individuals involved with high-end products will also find the book very useful. While this handbook thoroughly discusses the technological aspects surrounding lead-free implementation, it also provides a detailed understanding of lead-related health issues, tradeoffs and implications in changing over to Pb-free/reduced assemblies; and global regulations, consequences, dispensations, and exemptions with

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regard to utilizing lead. Since the book contains material that relates to a wide range of electronics products from low- to high-end applications, the book will be useful to a very large audience.

The book will serve as a primer for newcomers in the field, as it does not assume prior knowledge of the subjects discussed and provides the necessary background information. It will be a valuable resource tool for those already in the field. Specifically, the book is intended for:

- Scientists and engineers engaged in research, development and design, assembly, manufacturing, applications, quality, reliability, equipment engineers and testing
- Management, to gain a thorough understanding of the technology challenges, risks, and trade-offs
- Marketing, sales, intellectual-property-oriented individuals, and others peripherally involved, who require a working knowledge or a general understanding of the issues
- Students, for a thorough understanding of the forces that come into play in shaping business decisions such as "green" manufacturing, especially in electronics; materials technology fundamentals and issues, and potential solutions surrounding Pb-free solders

This book is written in a manner that assumes the reader has some knowledge or facility with science or engineering-based principles, but does not assume prior knowledge of the material discussed here. In addition to serving as a handbook, it can be used for instructional purposes, with each chapter being a self-contained unit. That is, those key concepts or principles necessary to understand the material introduced in a chapter are briefly explained in the early sections of a chapter, or at the point of discussion. Also, brief segments may be introduced as restatements or summaries of concepts discussed in some detail in another chapter. This is done as a convenience to the reader, to avoid interruption in seeking information in other chapters. However, this book is well cross-referenced, providing the reader the opportunity for a more thorough explanation and understanding concerning a particular area of interest if desired.

The introduction in Chapter 1 provides an overview of why the lead-free matter has become a worldwide issue, some concerns in introducing lead-free substitutes, and perspectives for a successful introduction.

The book is divided into three parts, each addressing a major aspect related to the elimination of lead in electronic assemblies: the driving forces; the impact on manufacturing; and reliability-related factors.

In Part I, "Background and Driving Forces," Chapters 2 through 5 provide an understanding of the key issues associated with the worldwide lead-free movement, and the forces that are shaping and driving the movement. For example, Chapter 2 provides a detailed discussion of the toxic effects of lead on humans, how lead enters the body and its effect on various organ systems. Chapter 3 addresses the potential environmental impacts of substituting various materials utilized in microelectronic assemblies. In addition to health and environmental issues, there are also significant legislative drivers, both national and regional, discussed in Chapter 4 that manufacturers and users alike must be aware of because of the constraints and requirements they impose. The marketplace provides a significant driving force for lead-free products (Chapter 5), which is steadily increasing in importance due to worldwide identification with, and sentiment for, the removal of toxic materials in the manufacture of products. This driver may, in fact, ultimately require manufacturers to convert their products to lead-free long before legislation requires it.

In Part II, "Materials and Manufacturing Considerations," Chapters 6 through 18 provide detailed discussions of the changes and impacts associated with various materials utilized, as well as manufacturing practices associated with the fabrication of microelectronic assemblies. Chapter 6 describes the key features of the Pb-Sn system, which the industry unanimously adopted worldwide and successfully utilized for the past 40 years, and serves as a reference or benchmark for comparing replacement systems. Chapter 7 defines the nature and mechanical properties that a solder material must collectively possess to meet the requirements imposed by solder joints in microelectronic assemblies at both the die and package levels. Chapters 8 and 9 describe the melting characteristics, microstructural features, morphology and other characteristics that determine the properties of interest for various binary, ternary and higher-order alloy systems considered as potential candidates to replace the Pb-Sn system.

Although Pb-Sn solders possess many characteristics desirable for solder joints, they are not ideal, exhibiting low shear strength and creep resistance, particularly at elevated-temperature application conditions. Chapter 10 describes several dispersion-strengthening methods for Pb-free solders to help overcome these traditional shortcomings of solder materials. Chapter 11 addresses the fundamentals governing wetting and spreading of liquids on solid surfaces and how they relate to lead-free solders on metallized terminal pads to assure sound connections. The mechanism and role of fluxing agents are also discussed. As a follow-on, Chapter 12 describes the metallurgical compatibility, processing advantages/disadvantages and reliability aspects associated with various types of lead-free board and component finishes in combination with several popular lead-free solder candidates under consideration. Chapter 13 discusses the method of formation, morphology, stability, and properties of intermetallic compounds (IMC) that form at solder/metallized surface interfaces that play an integral part in the quality and reliability of solder joints. Chapter 14 discusses the assembly differences that arise when utilizing lead-free solders as compared to eutectic Sn-Pb, and the impacts of those differences. Of particular interest are situations that necessitate and benefit from inert atmospheres (Chapter 15), which is a significant departure from standard eutectic Sn-Pb practice. Chapter 16 discusses some logistical and other impacts in changing over to a lead-free soldering assembly operation. The manufacturing experiences of various organizations that successfully introduced lead-free technology to their product lines are also reviewed. Numerous studies have been conducted by consortia around the world to determine which solder systems or alloys exhibited the most promise as suitable replacements for eutectic Sn-Pb solder. The major studies and their findings are reviewed in Chapter 17. It is anticipated that non-solder alternatives (Chapter 18) will play an increasing role in providing suitable, cost-effective interconnection solutions for some product segments, particularly in the area of consumer electronics.

In Part III, "Reliability Considerations," Chapters 19 through 22 describe a variety of reliability issues of concern in solders utilized in electronic assemblies, but particularly so for high Sn-based solders typical of lead-free solder alloys. Chapter 19 discusses general reliability concepts in relation to solder alloy composition, phasing, and morphology. Reliability aspects reported in the literature in relation to the use of lead-free alloys for flip-chip and various package-level interconnections are also reviewed. Chapter 20 describes the factors associated with thermomigration and electromigration, which are of particular increased interest due to higher electrical power levels in flip-chip solder joints, and the introduction of lead-free solders. Tin-whisker formation and the potential for creating electrical shorts in the field is an issue mostly confined to Sn-rich finishes on components and boards. Chapter 21 describes how and why they form, and addresses the issue from the perspective that most lead-free replacement alloys are Sn-rich, and what the studies in this area have revealed. Finally, Chapter 22 provides a comprehensive explanation of various phe-

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nomena associated with Sn-based systems that can have significant reliability implications, among them, soft-error problems due to the presence of radioactive species, catastrophic degradation as a result of an allotrophic phase transformation, and structure-related issues.

We are most grateful to our parents for their unending devotion, sacrifices, and love. They instilled the desire to seek the truth and enlightenment to better understand "how" and "why," and to freely share our talents and knowledge with others in helping to give back what was given to us.

We are also thankful to our spouses, Dianne Puttlitz and Mark Stalter, being ever mindful of their understanding and patience over the many months the manuscript was in preparation, and without whose support and encouragement the completion of this book would have been impossible.

Finally, we are very appreciative of the effort put forth and information provided by the many contributors to this book who so generously shared their knowledge and expertise, and devoted so much of their precious free time to make this book a reality.

Karl J. Puttlitz
Kathleen A. Stalter

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1

Overview of Lead-Free Solder Issues Including Selection

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I. INTRODUCTION

The use of lead (Pb) has been widely accepted in the electronics industry (utilized in a variety of applications for more than five decades), but most notably the use of eutectic tin–lead (Sn–Pb) solders to attach discrete components to printed circuit boards (PCBs). These attachments typically also serve as the electrical interconnection between the attached components and the PCB. Lead-based solders are also used as a coating or finish on metal terminations on PCBs, and on the peripheral leads of components.

A. Lead Utilization and Consumption

Approximately 5 million tons of Pb are consumed annually on a global basis, of which storage batteries represent the largest single application (about 81%) by far. Lead oxides (for glass, ceramic products, chemicals, etc.) and ammunition together account for about 10%, and solders for electronic assemblies account for only about 0.5%, as noted in Table 1 [1]. Although storage batteries constitute a large percentage of consumption due to an alleged near-100% recycling practice, batteries have not been targeted for a ban because they are believed not to contribute to pollution or contamination, and hence do not pose a problem [2].

The largest use of Pb in electronics is in the manufacture of cathode ray tubes as a component of the glass that protects TV and computer monitor viewers from undue exposure to x-radiation. Only about one tenth of the total (0.05%) is currently used in solder alloys [3].

There are laws in the United States that control the use of lead in gasoline and plumbing solder, and banned its use in consumer paint since 1978 [4].

B. Efforts to Restrict Lead Use

However, due to an increased awareness of the potential health hazards associated with the toxicity of lead in humans, which can lead to disorders of the nervous and reproductive systems, and also affect neurological and physical development, actions have been taken to eliminate or reduce the use of Pb in a variety of products. Among these are solders used for plumbing, and additives in paint and gasoline since the late 1970s. Banning or restricting the use of Pb did not become an issue until the early 1990s in the United States, but the proposed legislation to ban Pb was never enacted into law due, in large part, to pressures brought about by the electronics

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TABLE 1 Lead Consumption by Product

Product	Consumption (%)
Storage batteries	80.81
Oxides used for glass, ceramic products, pigments, and chemicals	4.78
Ammunition	4.69
Sheet lead	1.79
Cable covering	1.40
Casting metals	1.13
Brass and bronze billets and ingots	0.72
Pipes, traps, and other extruded products	0.72
Solder (excluding electronic solder)	0.70
Electronic solder	0.49
Miscellaneous	2.77

Source: Ref. 1.

industry. However, there has been a growing worldwide movement to eliminate the use of lead in products due mainly to health-related concerns. This will now be mandated through European Union (EU) legislation banning the use of lead in electronics products with some exemptions starting July 1, 2006. Environmental issues, particularly lead elimination, had not received much attention in the electronics industry until the late 1990s when the initial Waste from Electrical and Electronic Equipment (WEEE) Directive was drafted by the EU. It became clear that responsible environmental practices can have a positive impact on business. Failure to embrace prescribed environmental practices would result in a degraded competitive posture and an erosion in market share. Cleaning procedures that were, at one time, an integral part of PCB assembly today have mostly converted to no-clean processes. This shift, like many others, benefits the environment while also contributing to the bottom line [5].

C. This Handbook

This handbook discusses all the key aspects of the lead-free issue as it relates the implementation of lead-free soldering technology in the electronics industry. Among those areas discussed in detail are the background issues that give rise to the driving forces for lead-free implementation; the factors related to selecting alternative material systems such as flux, printed circuit board, board/component lead finishes, and lead-free solder alloys suitable for both reflow and wave soldering; and also manufacturing and reliability-related considerations.

II. DRIVING FORCES FOR LEAD-FREE SOLDERS

A. Health-Related Aspects

Candidate solder materials to replace eutectic Sn–Pb solders must satisfy toxicity regulations and limits set by the government. U.S. occupational exposure limits for selected materials are listed in Table 2 [6]. These are generally the same as for other industrialized countries (e.g., UK limits are the same for inorganic Pb) [6].

Despite the long-term utilization of Pb, it is now well recognized that Pb can have some very serious ill effects on humans. Depending on the aspects, Pb poisoning is sometimes classified as alimentary, neuromotor, or encephalic. Lead poisoning is the result of prolonged exposure to Pb or its compounds.

TABLE 2 Occupational Exposure Limits of Selected Materials

Material	U.S. Occupational Safety and Health Administration, permissible exposure lights (mg/m^{-3})
Zinc oxide fume	5
Inorganic tin	2
Copper dust	1
Antimony and compounds	0.5
Copper fume	0.1
Organic tin	0.1
Indium	0.1
Silver dust and fume	0.1
Silver, soluble compounds	0.01
Inorganic lead	0.05
Bismuth	Not assigned
Gallium	Not assigned

Source: Ref. 6.

1. Contaminated Drinking Water

Historians have speculated that Pb poisoning played a role in the collapse of the Roman Empire because of the widespread use of Pb for drinking water pipelines [7]. However, this source of Pb was recognized early on as a source for ingesting Pb, so the use of Pb pipes and lead-containing solders for plumbing of drinking-water lines has been prohibited by federal legislation in the United States (Section 1417, Amendment to the Safe Drinking Water Act, June 19, 1986).

a. Leachate from Landfills. Based on similar concerns, the electronics industry is quickly moving ahead with lead-free assemblies and components to avoid potentially Pb-contaminated drinking water. This time, however, the source is alleged to be Pb leached from landfills containing electronic wastes (lead from component finishes, printed circuit board assemblies, etc.) of consumer products such as TVs, PCs, telephones, camcorders, handheld games, refrigerators, microwaves, etc. It is contended that the leachate would find its way into the groundwater system with the potential of contaminating municipal water supplies, as illustrated in Fig. 1.

b. Lead Concentration Limits. In Japan, the Pb elution environmental standard in landfills in 0.3 mg/L. In toxic materials detection tests conducted by the Japanese Environmental Agency, it was determined that the amount of lead leaching from the pulverized remains of TV cathode ray tubes, PCBs from PCs, and pachinko machines far exceeded the environmental standard [8]. In the United States, the regulatory limit for Pb in drinking water is 0.015 mg/L (EPA 40 CFR 141). In utilizing the Toxicity Characteristics Leaching Procedure (TCLP) per EPA 40 CFR 261, the concentration limit is 5 mg/L [2]. It has been demonstrated that the concentration of lead leached from solders can be several hundred times higher than the acceptable limit [9].

B. Legislation

There are several forces driving the movement toward the elimination of Pb. An initial driving force is the fear of legislation, the most important of which is the EU's proposal (RoHS Directive) to ban lead in *all* electronics products, including information technology (IT) products such as monitors, printers, and computers. The basis for the legislation is the allegation that Pb could be leached from electronic wastes discarded in landfills, and that the leachate will find its way into the groundwater system, ultimately contaminating the drinking water supplies of municipalities.

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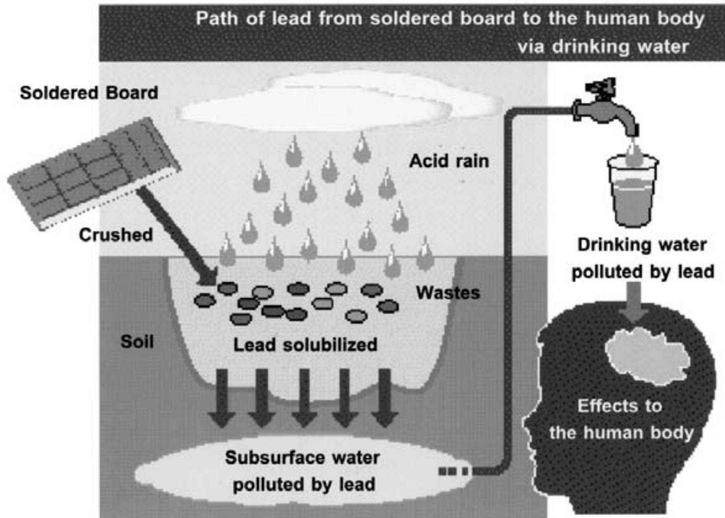

FIG. 1 An illustration depicting the sequence of events that results in the ingestion of lead leached from electronic wastes in landfills. (From Ref. 69. Courtesy of Panasonic Corporation.)

This legislation, which will have a major impact on the electronics industry, is a precautionary measure because there are no known instances of water supplies having been contaminated in this manner. Nevertheless, there is a growing concern about electronic wastes and their Pb content because they are increasing at a rate three times greater than other solid wastes [10].

C. Market Advantages

Japan has taken aggressive steps in instituting recycling laws to reduce the volume of wastes to be disposed. Because Japan is a small, highly populated country, it does not wish to utilize its precious space for landfills. Accordingly, it requires many products at end-of-life to meet prescribed specifications for disposition, including the removal of lead-bearing parts. To help reduce disassembly costs at end-of-life, Japanese original equipment manufacturers (OEMs) took the approach of introducing lead-free technology into their assemblies, particularly the solders used to reflow attach components to printed circuit boards, and lead-free components and board finishes. This strategy put the Japanese OEMs at the forefront of lead-free implementation. They have made lead-free products available in several niche markets, such as laptop and desktop computers, and some handheld consumer electronic products.

Many observers of the lead-free solder issue feel that the market-driven aspect is more important than legal mandates because the market can force a transition to lead-free solders much more quickly as it can provide a substantial marketing advantage in some geographies, particularly for consumer products. Japanese electronics manufacturers have taken the lead in "green" marketing and manufacturing. Consider, for example, a lead-free minidisc player made by Panasonic, bearing a green leaf environmentally safe symbol that was released in October 1998. The product gained a significant increase in market share, moving from 4.7% of the minidisc player market to 15% in a very short time. Much of this success was attributed to the product's green status. In Japan, products bearing a green sticker are typically not more expensive than competitors' lead-bearing products—in some instances even less expensive. It appears that there are tradeoffs that can be made to work around cost issues [11].

Although not as pervasive as in Japan, there have been some early lead-free activities in both Europe and the United States as well. For example, the Ford Motor Company launched a large

green marketing campaign, having declared targets of 2002 for lead-free electronic assemblies, and totally lead-free vehicles by 2004 [12].

Green marketing is rapidly being viewed as a powerful and effective marketing tool. Many respected companies attribute some of their success to having taken a proactive environmental approach. Corporate executives are becoming increasingly aware that benefiting the environment can lead to bottom-line benefits. Among the benefits are a reduction in expenses and the creation of new sources of revenue [13,14].

D. Mechanical Properties

There are technology-based reasons for eliminating Pb–Sn solders. The trend for continued densification in electronic packages is driving the need for even tighter pitches, which, correspondingly, requires finer-line circuitry. Because this trend results in solder joints with smaller cross sections, it also requires solders whose inherent mechanical properties are better suited to withstand the increasingly severe mechanical demands compared to eutectic Sn–Pb solder. It has been reported that many lead-free candidate solders exhibit significantly better strength and fatigue life properties than eutectic Sn–Pb [6].

E. International Standards Organization (ISO) 14001 Certification

The international community is becoming ever more environmentally conscious, causing manufacturers and their materials and equipment supplies to develop products and processes that reduce the impact on the environment. The two primary factors are: the growing support for and embracement of the worldwide lead-free movement, and ISO 14001 certification. The certification is a standard for environmental management published by the ISO in 1996. It emphasizes establishing management systems that ensure environmentally sound business practices as opposed to focusing on specific performance targets. ISO 14001, whose attributes and features are listed in Table 3, can also be tailored to individual companies owing to its generic structure. The intent is to integrate the environmental management system (EMS) with company-wide business management practices and decisions [15]. The certification supports techniques that are environmentally friendly. Electronics manufacturers are turning to vendors that can provide products that meet "green" standards. For example, the implementation of ISO 14000 prevents volatiles from flux to escape into the atmosphere, a problem aggravated by lead-free solders due to the higher reflow temperatures of furnaces. The reduced flux volume that results in enhanced throughput and efficiency also serves to preserve the internal cleanliness of reflow furnaces by minimizing interruptions for maintenance purposes. Some flux separation and collection systems can remove 95% of flux residues from an oven interior, and extend maintenance for 30–90 days in high-volume operations [16].

TABLE 3 Attributes and Features of Environmental Standard ISO 14001

Standard	Description
Sponsor	International Standards Organization
Purpose of standard	Provide an environmental management system
Emphasis	Environmentally sound business practices
Structure	Can be tailored to individual organizations, big or small
Intent	Integration of environmental management system with company-wide business practices and decisions
Advantage	Benefits the environment, and users are increasingly turning to products that meet "green" standards

TABLE 4 Some Useful Standards Related to Lead-Free Technology

Standard	Subject
Association of Connecting Electronics Industries, IPC-J0Std-006	Detailed list of both tin–lead and lead-free solders
ICP-J-Std-002, 003	Board and component lead solderability
MIL-M-38510	Plating thickness for good component lead solderability
JEDEC J-Std-620A	Plastic package moisture sensitivity, heat tolerance

F. Standards/Practices/Information

Because lead-free technology entered the scene relatively recently, practices are still being established and few standards exist. Some useful standards that do exist are listed in Table 4.

III. WORLDWIDE ACTIVITIES/PRACTICES

A. Early Initiatives

Some of the efforts to ban lead were initiated in the U.S. Congress. In 1991, the U.S. Senate proposed the Reid Bill (S.391, Lead Exposure Reduction Act), which proposed restrictions on lead solders, limiting the lead content to 0.1% or less. Subsequently, the bill was modified (S.729, 1993) to propose a ban on all lead-bearing alloys including electronic solders, and a tax of US$1.69 per kilogram on primary lead and US$0.83 per kilogram on secondary lead used in the industry. Although Pb solders were ultimately removed from the bill due to intense lobbying by the U.S. electronics industry, it serves to provide global awareness that Sn–Pb solders may, at some point, be restricted. As a result, many companies worldwide instituted investigations addressing the feasibility of a variety of Pb-free solders [2].

Environmental consciousness was firmly in place in industries, including the electronics industry, which responded to several challenges, most notably the ban on chlorofluorocarbon (CFC) cleaning agents. Prior to 1992, flux residues from soldering operations were removed mainly by industry choice. After the Montreal Protocol and subsequent Amsterdam Regulations that banned manufacturers from using ozone-depleting chemicals effective January 1, 1996, the industry responded by implementing suitable solutions [17].

B. Europe

In 1994, Denmark, Sweden, Norway, Finland, and Iceland signed a pact to phase out Pb, with Swedish manufacturers under a voluntary ban effective 2000. There are producer responsibility laws in effect in Holland, Switzerland, and Norway.

In 1997, the Swedish government identified Pb as an element it intended to eliminate from products over the following 10 years. The Sweden Environmental Quality Objectives direct that new products, including batteries, introduced in Sweden should be mostly Pb-free by 2020 [18]. In 1991, the UK, in collaboration with GEC, BNR-Europe, Multicore Solders, and ITRI, and supported by the Department of Trade and Industry (DTI), undertook a project to make an initial assessment of alternative solders for electronic assemblies. That was followed by a European collaboration in 1994 to address issues associated with the implementation of Pb-free soldering technologies as did several large companies in the UK.

1. WEEE Directive

The EU introduced a draft directive (law) called the WEEE, which called for a ban on Pb in all electronics, except automotives. The scope of the ban is far-reaching, banning the selling or

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import of electronics containing lead, normally as part of interconnections that attach components to printed wiring boards (PWBs). But Pb can also be present as part of finishes on cards/boards, peripheral leads of components, or materials used to fabricate components and peripherals (e.g., monitors).

2. Take Back/Recycling

In parallel with initial investigations of lead-free alternatives that commenced in the early 1990s, there were also recycling laws proposed, mostly in Asian countries, that addressed the related issue of an ever-increasing volume of end-of-life electronic wastes to be disposed in landfills. Products must be designed for disassembly to remove parts containing environmentally objectionable materials, including Pb. Various product "take-back" schemes involving electronic wastes have been devised whereby manufacturers of these products are mainly responsible for the collection of wastes from designated locations, businesses, and households when owners decide to discard electrical and electronics products.

So-called "producer responsibility" laws for electronics and electrical waste equipment are anticipated to be widespread in Europe. Such laws have already been in effect for some time in Holland and Switzerland, and are also in effect in Norway (1999) and Sweden (2000). Threshold limits for recycling specified materials are typically defined [2].

C. Asia Pacific

There is a wide disparity in the approach to environmental matters among Asian countries, from virtually no regulations to strict legislation diverting discarded electronic products from landfills. In those cases where regulation is lax, it is most often due to a corresponding lack of infrastructure. For example, in 1995, Thailand had a staff of 43 to oversee 50,000 industrial plants. A reliance on self-regulation of the private sector is not uncommon in these areas where the trend is to adopt environmental standards such as ISO 14000, the environmental impact assessment required by the World Bank and the Asian Development Bank. Although "command-and-control" regulations will likely increase in the United States, Europe, Japan, and South Asian countries, other Asian countries will more likely use market-driven regulation and self-regulation because they have experience with these methods and lack necessary resources [19].

1. Recycling

Due to the very significant involvement on the part of the electronics industry, there is a high degree of interest and activity in the Pb-free issue in Japan, Singapore, South Korea, and Taiwan. For example, there has been a recycling law in effect in Taiwan since March 1998 requiring that all electronics products undergo proper waste processing at a product's end-of-life.

Japan enacted the "Electronics Appliance Recycling" law in June 1998 requiring appliance manufacturers by 2001 to collect and recycle their own products. Japan appears to be leaning toward high-technology disassembly coupled with material recovery (i.e., recycling) with many private-operated and government-operated recycling plants coming on-line. An example of these is the highly automated plant that went into operation in April 1998 that has the capacity to service a population center of about 1 million people, equivalent to about 150,000 units (TVs, washing machines, etc.) [19]. So as the EU is focused on a Pb ban, the Japanese Ministry of International Trade and Industry (MITI) is approaching the issue quite differently through so-called "take-back" legislation (i.e., recycling). In the European Directive, the manufacturer or importer is responsible for the cost of recycling [20].

2. Lead Reduction/Elimination

Whereas the official Japanese approach to the "Pb in landfills" issue is recycling, Japanese OEMs, and material and component suppliers, apparently motivated by the benefits of reducing disassembly costs at end-of-life by eliminating lead-containing parts and the specter of significant potential market opportunities, are moving in the Pb reduction/elimination direction. Early in 1998, the Japanese Electronics Industry Development Association (JEIDA) and the Japanese

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Institute of Electronics Packaging presented a Pb-free roadmap. Japanese OEMs announced their own plans to drastically reduce Pb levels in their products by 2002, and some even earlier [21]. The targets of several Japanese OEMs who were among the first to promote and adapt lead-free manufacturing to their products are listed in Table 5.

D. North America

Since the initial attempts in congress to pass lead-free legislation in relation to electronic products, there has been little activity in the United States until the late 1990s, when it was clear that the Japanese were well positioned to exclude products from Japan that did not meet standards they might require owing to their early lead-free activities. Furthermore, because some Japanese lead-free products were being offered in some niche markets, it demonstrated the viability and manufacturability of lead-free technology, thus justifying the EU-proposed legislation to ban the use of Pb in electronics products.

1. *Low Activity Level Early On*

Significant levels of lead-free activities were carried out over a wide range of consumer and industrial electronic products in the early 1990s. These initiatives were gradually abandoned in many areas due to the lack of legislative pressures to pursue alternatives to lead-containing products and materials, particularly solders for PWB assemblies. A notable exception was the automobile industry, where companies such as Delco, Ford, and Motorola continued to investigate and qualify lead-free products. Some of these activities were motivated by the desire to achieve higher strength and greater fatigue resistance characteristic of most lead-free alloys compared to eutectic Sn–Pb at higher service temperatures. Nortel Networks was one of the few North American companies to utilize lead-free solders in consumer electronics (Meridian phones). Texas Instruments (TI) provided Ni/Pd finishes for its component leads early on, replacing Sn–Pb coatings. TI also replaced the use of high-Pb solder for chip attachments to components with Ag-filled epoxies. These joints, however, are not suitable for high-power applications [19].

2. *Drivers Motivate Activity*

Aside from these few exceptions, it was both market-driven concerns and legislative concerns that served to revive interest in the lead-free issue among manufacturers in the United States. Although industry associations initially lobbied against the issue, they eventually supported it since the movement gained support worldwide. In fact, National Electronics Manufacturers Initiative (NEMI) initiated a very ambitious and aggressive lead-free effort that sought to select a suitable lead-free alloy, define a process window, produce populated cards/boards, and demonstrate the reliability of the solder joints of a broad variety of components through standard stress testing.

TABLE 5 Several Early Manufacturers to Initiate Lead Reduction/Elimination in a Variety of Products

Company	Action	Year
Hitachi	50% reduction from 1997 levels	1999
	Eliminate Pb interconnects	April 2001
Toshiba	Elimination in mobile phones	2001
Sony	All Pb eliminated, except high density electronics	2001
Matsushita (Panasonic)	All Pb from products	2001
	Been producing 40,000 minidisc players per month Pb-free	October 1998
NEC	50% reduction from 1997 levels	2002
NTT	No Pb or Cd in newly purchased equipment	Now

Source: Ref. 21.

An IPC statement probably reflects the opinion of most U.S. manufacturers, "... 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" [22].

IV. LEAD-FREE SOLDERS AND SELECTION CONSIDERATIONS

A. Solder Alloys

1. *Brief History*

The use of solders extends back to about 4000 BC and, as indicated in the timeline of Fig. 2, served as an important factor through the Bronze and Iron Ages up to the current so-called "Silicon Age." The oldest archaeological evidence relates to gold-based hard solders since gold is impervious to corrosion, so an ample number of objects have been discovered. The earliest of these date back to about 4000 BC when gold-based hard solders were developed by artisans in Mesopotamia [24]. Both the Celts and the Gauls performed high-quality soft soldering using the same solder alloy. The use of Sn–Pb solders in ancient cultures is much more obscure, but by 350 BC, the Greeks sealed bronze-based water pumps and air pumps with Sn–Pb alloys, and the Romans used Sn–Pb solders extensively in the construction of aqueducts [25] and to close the seams of lead water pipes. They used an alloy, "terrarium," consisting of one part Sn and two parts Pb, still used today for that purpose. There are references to lead–tin soldering going back to biblical days, where its use to solder water pipes is mentioned in the Old Testament [26]. There were few changes to soldering practice during the Iron Age and Middle Age; however, its use was greatly expanded during the Industrial Revolution, such as the use of soft solders for plumbing (i.e., copper tubing). Early in the 20th century, soldering was introduced to the electronics industry as a reliable method of connecting copper wires. More recently, the solder joint took on the dual function of serving both a mechanical and electrical connection, challenging the strength, creep, and fatigue resistance of Sn–Pb solders [23]. In electronics, soldering continues to be the predominant means to attach devices to printed circuit boards or microelectronic chip carrier packages.

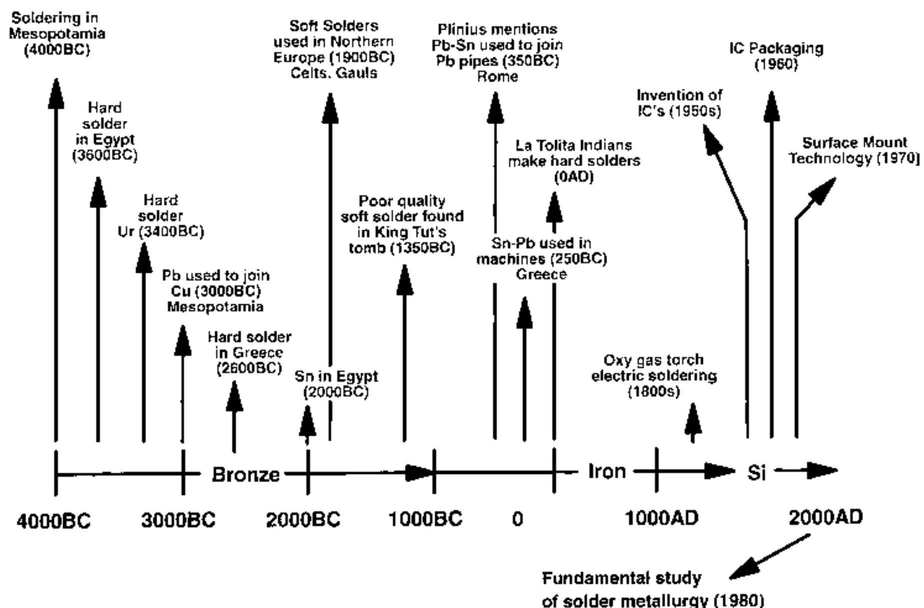

FIG. 2 Solder utilization time line. (From Ref. 23.)

2. Definition and Classification

Soldering may be defined as the joining of metals by utilizing another metal, which has a melting point or range below about 450°C (1000°F) and is lower than the metals to be joined. This differs from brazing, in which the added metal generally has a melting range above 450°C (1000°F), but also below the metals to be joined [27]. Fig. 3 illustrates the melting ranges of some typical solder and braze materials.

Solders are typically classified as either soft or hard. Some confusion often results from this convention because some hard solders are really braze materials if the melting temperature criterion is applied. Soft solders typically consist of alloys containing lead and tin, but also often contain indium (In), bismuth (Bi), antimony (Sb), or silver (Ag). In practice, most soft alloys melt at temperatures lower than 450°C, usually between 180°C and 300°C. High-tin solders, typical of lead-free solders, tend to be stiffer, harder, and less ductile compared to high-lead solders. Hard solders often contain metals such as Au, Zn, Al, and Si.

3. Traditional Electronics-Based Solders

Lead-bearing solders had become the largest group of alloys utilized in electronics products; among these were eutectic (63Sn–37Pb) and near-eutectic (60Sn–40Pb) solders used extensively for PCB assemblies. The melting point or range of these alloys is sufficiently low to maintain the integrity of both components and laminate materials, such as FR-4, typically used for PCBs. There are some specialized applications of several high-Pb alloys (Table 6) utilized as flip-chip solder bumps (e.g., 97Pb–Sn, 95Pb–Sn), and as high-melt balls or columns (90Pb–10Sn) for ball

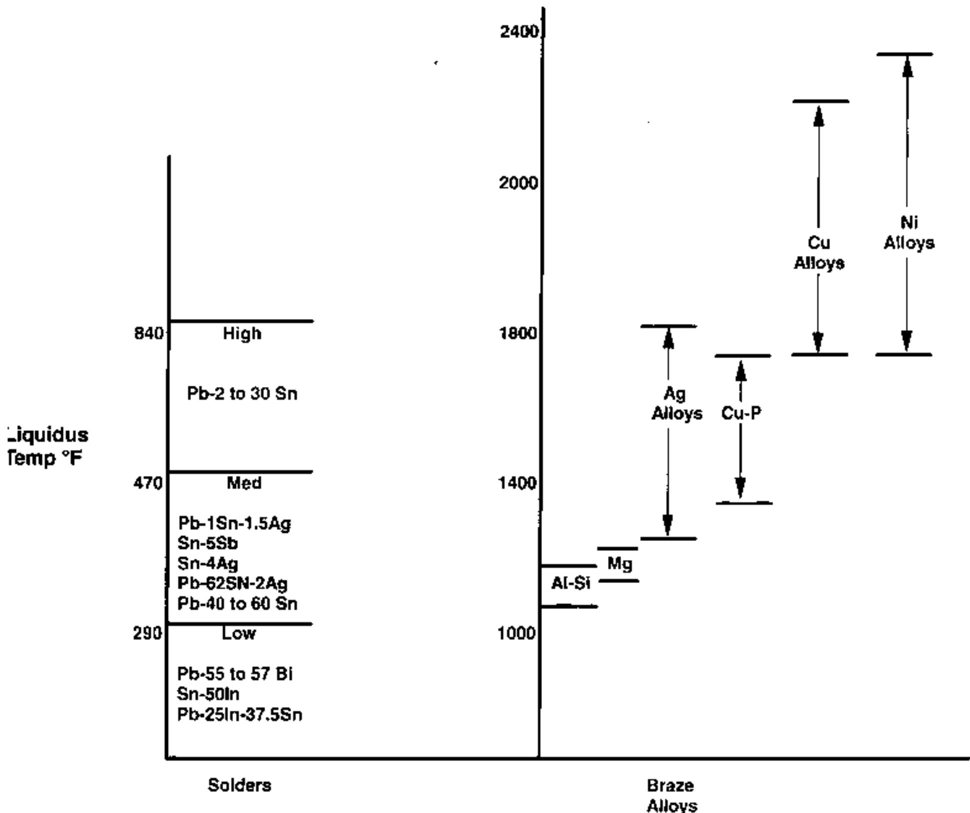

FIG. 3 Melting ranges for fusible alloys. (From Ref. 27.)

TABLE 6 Some Solders Utilized for Electronic Assemblies

Application	Solder alloys
Flip-chip solder bumps	Pb–3Sn, Pb–5Sn, Pb–50In, eutectic Sn–Cu
BGA solder bumps	Dual-solder bumps: Pb–10Sn (ball) and eutectic Sn–37Pb (ball and card attachments) Single-solder bumps; eutectic Sn–37Pb, eutectic Sn–Pb–2Ag, Sn–Ag–Cu
Soldering to thick film metallizations (e.g., Au–Pd, Au–Pt, Ag–Pd)	Pb–10Sn, Pb–50In
Soldering to thin films (e.g., Cu, Ni, Au)	Eutectic Sn–37Pb, Au–20Sn
Low-temperature operations (e.g., attaching temperature-sensitive components, last step in a temperature hierarchy)	Eutectic Sn–Bi

and column grid array components attached to cards or boards with a low-melt solder (eutectic Sn–Pb) [28]. In all Pb–Sn alloys, Pb is not a metallurgically active species (i.e., does not enter into any reactions with bonding pads or surface metallizations), so that there are no interfacial intermetallic compounds (IMCs) containing Pb, nor any such compounds dispersed within the bulk solder. The presence of lead, however, affects the solid-state growth kinetics of Sn–Cu intermetallic compounds. These factors are all discussed in detail in Chap. 6. The presence of Pb also helps to prevent the white tin (β)-to-gray tin (α) allotropic phase transformation from occurring in high-Sn solders upon cooling below 13°C. The loss of structural integrity that accompanies this transformation during cold-temperature service is referred to as tin pest [29]. The details of this phenomenon are discussed in Chap. 22.

There are several non Pb–Sn solders utilized in electronics for specialized applications. One of these, 50Pb–50In, is utilized for hybrid microcircuit applications involving soldering to precious metal (Au–Pd, Au–Pt), thick film, and thin film circuits [30]. One advantage of this solder is that its Au thieving (dissolution rate) is much slower than Sn–Pb solders.

a. Role of Lead in Lead–Tin Solders. Lead plays a very important and unusual role in Sn–Pb solder alloys in general, as noted in Table 7, and in solder joints of electronic assemblies in particular. As noted earlier, Pb does not participate in the formation of any intermetallic compounds, neither at the terminal ends of solder joints nor distributed within the bulk solder. Pb is effectively a "neutral diluent" for Sn. It reduces the melt temperature of alloys with Sn, and improves the mechanical characteristics of Sn as a solder joint material (i.e., reduces stiffness, increases plasticity, etc.) without significantly affecting solder chemistry (i.e., interactions between Sn and terminal metallizations, namely Cu and Ni) [31].

TABLE 7 Role of Lead (Pb) in Tin–Lead Solders

Feature	Comments
Melting point	Reduces the melting point of Sn
Surface tension	Reduces surface tension of molten Sn–Pb solders, providing their characteristic good wetting properties
Activity	Does not participate in reactions with circuit metallizations (e.g., Cu, Ni) Intermetallic compounds formed by reaction with Sn
Cost	Trade off for Sn content reduces alloy cost

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B. Lead-Free Definition

There is no universally accepted lead-free definition. In fact, even the EU has not provided (and is not required to provide) a definition until 1 year *after* the RoHS Directive goes into effect. However, various industry organizations have adopted a 0.1% maximum residual lead content. This value appears somewhat arbitrary (i.e., not based on some health-related threshold value).

C. Selection Criteria for Suitable Lead-Free Solder Candidates

Lead-free solders must conform to a broad range of properties and characteristics to be considered as suitable candidates to replace eutectic Sn–Pb solders for use in electronic assemblies [31]. Lead-free solder candidates must also be compatible with product packaging trends of ever-increasing densification to meet the demands for more functionality and portability. Decreases in package size correspondingly result in smaller solder joint interconnections. While undergoing size reductions, solder joints of high-density, high-performance electronic packages are expected to withstand increasing mechanical, electrical, and thermal burdens, which can lead to reduced reliability and even failure during manufacture or in the field [32]. There are two basic requirements that all solder interconnection alloys must satisfy. First, they must wet and bond to metallic terminals or features on components and substrates. This implies that the solder must be capable of forming intermetallic compounds with Cu, Ni, and other metals routinely utilized in microelectronic packages. Second, a solder must have a melting point that is sufficiently low to be reflowed as a paste when surface mount reflow attaching components to printed circuit boards, yet high enough to avoid any ill effects due to operating temperatures in the field.

The most important characteristics that must be considered in selecting suitable lead-free solder candidates are listed in Table 8.

Many of the lead-free solder systems of interest consist of some minor additions of third or fourth elements to binary alloy systems to achieve a desired benefit such as enhanced wettability or reliability, etc.

1. Toxicity

Clearly, the toxic metallic elements cadmium (Cd), thallium (Th), and mercury (Hg) can be eliminated immediately. It should be noted that some geographies (e.g., Japan, Scandinavia) regard Sb as toxic [33]. Although the metal itself is generally not thought to be toxic, the trioxide compound—not typically formed at soldering temperatures but can be formed at incineration temperatures—is considered toxic. Because incineration is widely practiced in Europe and Japan to dispose wastes as opposed to using landfills, alloys containing Sb are not likely candidates for widespread application.

TABLE 8 Criteria and Desired Attributes for Candidate Lead-Free Solders

Criteria and desired attributes
• Not toxic
• Available in sufficient quantities to meet current and future requirements
• Exhibit sufficient electrical and thermal conductivity
• Possess adequate mechanical properties: strength, toughness, fatigue and creep resistance
• Compatible with typical terminal metallizations (e.g., Cu, Ni, Ag, Au, Sn, etc.)
• Affordable (i.e., economically viable)
• Have acceptable melt and process temperatures
Not too different from eutectic Sn–Pb
Avoid deleterious temperature effects on cards, boards, and components
Low dressing characteristics

2. Supply and Abundance

The number of viable elements to replace Pb is significantly reduced when factoring in the condition of sufficient abundance and availability. Availability refers to the quantity that is produced and therefore in most cases is available to manufacture products, whereas abundance refers to world reserves in the Earth's crust. It should be noted that politics and a region's stability can play an important role (i.e., a particular element can be both sufficiently abundant and be in substantial supply, but not readily available due to manipulation by cartels or restrictions imposed by governments). Reserve implies that, in addition to its state of abundance, the metal can be economically extracted by utilizing current technologies at the posted market price.

Availability is an important consideration, as can be deduced from Table 9, which provides a comparison for those elements most likely to be substituted for Pb. Consider, for example, the case of Bi. If the entire world's supply of Bi were utilized for microelectronics applications, only about 7800 tons of eutectic Sn–Bi could be produced, or only a maximum of 8% Bi could be added to Sn to produce a weight of solders equivalent to the use of eutectic Sn–Pb in electronics, about 60,000 tons. Thus, an alloy that contains a significant amount of scarce elements is not a viable replacement for eutectic Sn–Pb solder [6].

3. Cost

Because lead is one of the least expensive elements on Earth, any substitute will have some impact on cost, particularly so because it is likely that the substitutes will be from the group of elements Sn, Ag, Cu, and In. If either In or Ag is utilized, their contents must be kept low because both are relatively expensive when compared to lead, as noted in Table 10. Besides idium's high cost (typically in the range of US$200.00 per kilogram), it also has a supply problem. Only about 200 tons of indium are produced globally each year [36].

a. Metal Density Factor. There is a significant difference on a cost-per-pound basis between the elements that comprise most of the leading lead-free alloy candidates and the baseline eutectic Sn–Pb solder. Solders are purchased on the basis of weight, not volume. For example, solder paste is typically purchased by the kilogram, and solder wire or bar is purchased by the pound. The candidate substitute metals are much less dense compared to Pb (Table 11). Similarly, Table 12 shows that the density of the most popular Pb-free candidate alloys is much less than eutectic Sn–Pb solders. For example, the popular lead-free alloy, Sn–3Ag–0.7Cu, is nearly 20% less dense. The implication is that 1 kg of eutectic Sn–Pb yields about 1000 jars of solder paste,

TABLE 9 Cost and World Reserves of Metals Utilized in Microelectronic Assemblies

Metal	World reserves (thousand metric tons)	Price (US$/lb)
Antimony (Sb)	3,200	0.68
Bismuth (Bi)	260	3.50
Copper (Cu)	650,000	0.89
Gold (Au)	77	4480
Indium	6	85.45
Lead (Pb)	130,000	0.44
Nickel (Ni)	150,000	3.91
Palladium (Pd)	79,000	5700
Platinum (Pt)	—	8602
Silver (Ag)	420	76.54
Tin (Sn)	12,000	3.70
Zinc (Zn)	440,000	0.65

Source: Ref. 34.

TABLE 10 Relative Cost of Some Candidate Element Replacements for Lead in Electronic Assemblies

Replacement elements for lead	Relative cost
Lead (Pb) reference	1
Zinc (Zn)	1.3
Antimony (Sb)	2.2
Copper (Cu)	2.5
Tin (Sn)	6.4
Bismuth (Bi)	7.1
Indium (In)	194
Silver (Ag)	212

Source: Ref. 35.

whereas it only requires about 0.8 kg of the Pb-free solder to yield 1000 jars of solder paste [37]. Thus, the increased cost for materials is substantially offset by the differential density factor because a solder joint requires essentially the same solder volume independent of whether it consists of lead-bearing or lead-free solders.

b. Metal Processing Factor. The processing costs associated with fabricated products such as solder pastes often dominate over the material cost. Therefore, there is little difference between eutectic Sn–Pb and lead-free solder alloy paste, as is shown in Table 13. The table also shows, however, that the cost of products that do not have significant process costs associated with them, such as a bar stock utilized for wave soldering or a wire for repair operations, is dictated by the cost of raw materials [38].

4. Melt Temperature and Range

Both gallium (Ga) and mercury (Hg) can be eliminated from consideration as base materials just based on their low melting points. The melting point of the elements Ag, Cu, Ni, and Au are too high to serve as base materials and some are also too expensive, only leaving In and Sn. Indium is too expensive to use in quantities required of a base alloy. That leaves Sn, whose solder alloy melt points are typically between about 120°C and 280°C, providing a baseline for lead-free solder alternatives to eutectic Sn–Pb. Eutectic alloys with either Cu or Ag have melt points close to pure Sn, so only a few percent of these elements can be added to Sn before the melting point level is considered unacceptable [31].

TABLE 11 Relative Cost of Candidate Elements to Replace Lead in Electronic Assemblies Based on Volume

Element	Metal cost per pound (US$, approximately)	Density at 25°C(lb/in^3)	Cost per standard volume (US$/$in^3$)	Cost factor relative to Pb
Zinc (Zn)	0.50	0.258	0.129	0.70
Lead (Pb)	0.45	0.416	0.184	1
Antimony (Sb)	0.80	0.239	0.191	1.04
Copper (Cu)	0.65	0.324	0.211	1.15
Tin (Sn)	3.50	0.354	1.20	6.52
Bismuth (Bi)	3.40	0.354	1.20	6.52
Silver (Ag)	84.20	0.379	31.91	173.40
Indium (In)	125.00	0.264	33.00	173.30

Source: Ref. 37.

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TABLE 12 Relative Cost of Some Candidate Lead-Free Alloys to Replace Eutectic Sn–Pb Solders in Electronic Assemblies Based on Their Densities

Alloy	Melting range (°C)	Metal cost (US$/lb)	Density at 25°C (lb/in^3)	Metal cost (US$/in^3)	Percent increase cost/in^3 compared to 63Sn–37Pb
62 Sn–37 Pb	183	2.37	0.318	0.75	0
42 Sn–58 Bi	139	3.44	0.316	1.09	45
77.2 Sn–20 In–2.8 Ag	179–189	30.06	0.267	8.02	970
91 Sn–9 Zn	199	3.23	0.263	0.85	13
91.8 Sn–3.4 Ag–4.8 Bi	208–215	6.24	0.272	1.7	125
90 Sn–7.5 Bi–20.5 Ag–Cu	186–212	5.09	0.273	1.39	85
96.2 Sn–2.5 Ag–0.8 Cu–0.5 Sb	213–219	5.48	0.267	1.46	95
96.3 Sn–3 Ag–0.7 Cu	217–218	5.90	0.268	1.58	110
95 Sn–3.5 Ag–1.5 In	218	8.15	0.268	2.18	190
93.5 Sn–3.5 Ag–3 Bi	216–220	5.92	0.269	1.59	110
96.5 Sn–3.5 Ag	221	6.32	0.368	2.33	125
99.3 Sn–0.7 Cu	227	3.48	0.264	0.92	23
95 Sn–5 Sb	232–240	3.37	0.263	0.88	17

Source: Ref. 41.

To be compatible with standard surface mount and wave soldering processes, and to avoid PCB and component damage require a solder alloy melting point not higher than about 230°C, whereas operating requirements may be as broad as a −55°C to 155°C. This implies a minimum melting point of at least 175°C [31].

The compositions of some lead-free solder alloys and their corresponding melt temperatures are listed in Tables 14–Tables 16, covering melt temperatures between about 180°C and 200°C. Some higher-temperature compositions are listed in Table 17, but are only of utility for niche applications owing to such issues as cost (Au–Sn) and health concerns (Sb-containing alloys).

TABLE 13 Relative Cost of Some Lead-Free Solders in Bar Stock and Solder Paste Form

Solder alloy	Bar relative cost (US$/kg)	Paste relative cost (US$/kg)
Sn–63 Pb (baseline)	1	1
Sn–3.5 Ag	2.9	1.07
Sn–3 Ag–2 Bi	2.17	1.06
Sn–2.6 Ag–0.8 Cu–0.5 Sb	2.06	1.05
Sn–3.4 Ag–4.8 Bi	2.26	1.06
Sn–3.5 Ag–0.5 Cu–1 Zn	2.27	1.06
Sn–4.6 Ag–1.7 Cu	2.25	1.08
Sn–3.2 Ag–0.7 Cu	2.21	1.06
Sn–3.5 Ag–1.3 Cu	2.28	1.06
Relative cost of selected metals		
Pb = 1, Zn = 1.7, Cu = 3, Sb = 3.9, Bi = 8.6, Sn = 11, Ag = 260, Au = 15,000		

Source: Ref. 38.

TABLE 14 Some Lead-Free Solder Alloys with a Melting Point or Liquidus Temperature Below 150°C

Composition	Melting range (°C)
Bi–33 In	109 (E)
Sn–52 In	118 (E)
Sn–50 In	118–125
Sn–58 Bi	138 (E)
Sn–57 Bi–0.1 Ag	138–140

E = eutectic composition.

For lower-temperature applications, 42Sn–58Bi (eutectic, mp = 139°C), near-eutectic compositions, and Sn–Bi with Cu, In, Au, Sb, or Zn additions are possibilities, but a special flux may be required because a standard flux may not be sufficiently active at lower temperatures [39].

a. Minimize Pasty Range. A solder with a discrete melting point is preferred (i.e., one with a eutectic composition). However, if this is not possible, the melting range should be no more than 10°C, and less than 5°C is desirable. Alloys with a so-called large pasty or mushy range are known to be susceptible to hot cracking during solidification, causing solders to lift away from annular metallization surrounding the tops of plated through-holes (PTHs), a condition referred to as fillet lifting [40]. Accordingly, eutectic or near-eutectic composition alloys are desired to prevent this condition.

5. Wettability

Solder wettability is the capability of an alloy in the molten state to spread over the solid surface of another metal, usually metallization on a terminal pad. It is the precursor of "solderability," which describes the solder's ability to form a solder joint on a PCB. Joint formation includes such aspects as fillet formation between a vertical surface and a horizontal surface, and capillary flow of the solder as required to fill holes or gaps.

a. Effect of Elemental Additions on Surface Tension of Tin. All high-Sn solder alloys exhibit a higher surface tension and are more chemically aggressive (i.e., greater tendency to form intermetallic compounds with termination pad metallizations) compared to eutectic Sn–Pb solder [41]. Lead has the important effect of lowering the surface tension of Sn–Pb solders. For example, the surface tension of eutectic Sn–Pb at 280°C is about 470 dyn/cm compared with 550 dyn/cm for pure Sn at its melting point of 232°C [42]. Minimizing surface tension improves wetting and solderability. None of the elemental additions made to Sn in forming lead-free alloys duplicates the effects of Pb in terms of lowering surface tension, thus is likely the reason that the

TABLE 15 Some Lead-Free Solder Alloys with a Melting Point or Liquidus Temperature Between 150°C and 200°C

Composition	Melting range (°C)
Sn–20 Bi–10 In	143–193
Sn–20 In–2.8 Ag	175–186
Sn–8 Zn–3 Bi	189–199
Sn–9 Zn	198.5 (E)

E = eutectic composition.

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TABLE 16 Some Lead-Free Solder Alloys with a Melting Point or Liquidus Temperature Between 200°C and 230°C

Composition	Melting range
Sn–3.4 Ag–4.8 Bi	205–210
Sn–7.5 Bi–2.0 Ag	207–212
Sn–7.5 Bi–2.0 Ag–0.5 Cu	186–212
Sn–3.5 Ag–3.0 Bi	206–213[a]
	216–220[a]
Sn–3.5 Ag–5.0 Bi–0.7 Cu	210–215
Sn–2.0 Ag–3.0 Bi–0.75 Cu	210–215
Sn–2.0 Ag–4.0 Bi–0.5 Cu–0.1 Ge	216
Sn–3.4 Ag–4.8 Bi	208–216[a]
	200–216[a]
Sn–3.5 Ag–0.7 Cu	217 (E)
Sn–3.0 Ag–0.7 Cu	217–218
Sn–3.5 Sb–2.0 Bi–1.5 Cu	218 (E)
Sn–3.5 Ag–1.5 In	218 (E)
Sn–3.2 Ag–0.5 Cu	217–218
Sn–4.7 Ag–1.7 Cu	216–218
Sn–2.5 Ag–0.8 Cu–0.5 Sb	213–218
Sn–3.8 Ag–0.7 Cu	217–219[a]
Sn–2.0 Ag–0.8 Cu–0.5 Sb	213–219[a]
	216–222
Sn–2.0 Ag–0.75 Cu	217–219
Sn–4.0 Ag–0.5 Cu	217–219
Sn–4.0 Ag–1.0 Cu	217–219
Sn–3.5 Ag–1 Zn	218–221
Sn–3.5 Ag	221 (E)
Sn–2.0 Ag	221–226
Sn–0.7 Cu	227 (E)
Sn–2.0 Cu–0.8 Sb–0.2 Ag	226–228
Sn–5 Sb	232–240[a]
	236–240[a]

E = eutectic composition.
[a] Different values reported in the literature.

TABLE 17 Some Lead-Free Solder Alloys with a Melting Point or Liquidus Temperature Above 230°C

Composition	Melting range (°C)	Characteristics
Sn–5 Sb	232–240	Poor wetting
Au–20 Sn	280 (E)	Very expensive
Sn–25 Ag–10 Sb	365 (E)	Low ductility
		Unsuitable thermomechanical fatigue resistance for die attach

E = eutectic composition.

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TABLE 18 Effect of Temperature on the Surface Tension of Near-Eutectic (60Sn–40Pb) Solder

Conditions (°C)	Surface tension (dyn/cm)	Reference
211	489.9	Schwaneke et al. [43]
260	483.3	Schwaneke et al. [43]
260, with rosin (R) flux on Cu	390 ± 40	Vianco et al. [42]
260, with rosin mildly activated (RMA) flux on Cu	382 ± 8	Vianco et al. [42]

wettability of lead-free alloys is typically worse when compared to studies that use eutectic Sn–Pb as the benchmark.

b. Effect of Temperature on the Surface Tension of Pb–Sn Solder. Surface tension has not been found to be a strong function of temperature over the range of temperatures associated with typical solder assembly operations, as noted in Table 18.

The wettability and solderability of lead-free solder candidates must be of sufficient adequacy to form solder joints whose reliability is not degraded relative to eutectic Sn–Pb joints due to wettability-related issues.

6. Minimum Complexity in Materials Fabrication

It is significantly more difficult to manufacture powder for a multielement (ternary or higher-order) alloy than for a binary alloy. Consider, for example, that the powder for a Sn–Pb eutectic solder paste is prepared by melting ingots of pure Sn and Pb whose weight ratio is 63% and 37% in a pot, respectively. The molten solder alloy is atomized by a special process to form powder that is sieved to be in compliance with specified particle size limits. However, ternary, quaternary, and higher-order alloys require tight control and accuracy of composition. Manufacture will likely require an additional precomposing step. For example, to prepare an alloy consisting of three elements of weight percentages 96.3, 3.0, and 0.7, respectively (i.e., for a Sn–Ag–Cu alloy) demands a high degree of precision, which will result in additional cost [37].

7. Minimum Metallurgical Complexity

It is generally agreed upon that none of the lead-free binary systems investigated is likely to be a consensus replacement for eutectic Sn–Pb in assembly reflow applications, although this may be the case for wave soldering. Viable candidates typically consist of a small quantity of a third or fourth element added to a lead-free binary alloy compared to the relatively uncomplicated eutectic Sn–Pb solder.

TABLE 19 Required Mechanical Property Enhancements Beyond Eutectic Sn–Pb

Properties	Remarks
Shear strength	• Solder joints typically experience shear loading –Often due to coefficient of thermal expansion (CTE) mismatches
Fatigue resistance	• Increased number of consumer electronics products –Particularly communication, handheld devices –Experiences many on/off cycles
Elevated temperature compatibility	• Increased applications involving harsh conditions (e.g., vehicle engine compartment) –Needs improved creep resistance and microstructural stability

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a. Enhanced Properties Required. There are an increasing number of applications that require significantly enhanced mechanical properties, as listed in Table 19. For example, the operating temperature range for consumer and telecommunications electronics products normally can span the range from about −55°C to 100°C. In addition, there are critical applications such as avionics and automotive where under-the-hood, engine-mounted electronics typically experience many thermal cycles, which in some cases span the range from −55°C to 165°C and higher. Accordingly, there are now numerous demanding applications that require solder characteristics to exceed those of eutectic Sn–Pb [44–48], independent of the need to define a lead-free solder, making it necessary to mutually satisfy both requirements.

b. Effect of Elemental Additions. Both Cu and Ag have a low solubility in Sn, forming intermetallic compounds instead, so there is little opportunity for solid solution strengthening. The hypereutectic alloys contain primary IMCs.

The elements Zn, Bi, and In all exhibit some solid solubility in Sn, and so can contribute to strengthening the Sn matrix. They must be introduced as higher-order additions because the binary systems with Sn (e.g., Sn–In and Sn–Bi) have melting points too low for mainstream electronic assembly. Whereas Zn additions can cause several concerns (poor corrosion properties), the stability of ZnO necessitates the use of highly active fluxes, and pastes containing fine Zn particles can be expected to be unstable due to interactions between the powder and the medium, resulting in unacceptably short shelf-lives [33].

8. Adequate Properties for Operational Requirements

a. Eutectic Sn–Pb Solder Was Satisfactory. For most applications, the processing and reliability characteristics of Sn–Pb-based solders have served the electronics industry well for more than 40 years, providing a comfort factor that will not be easy to emulate, although a

TABLE 20 Summary of the Base Metal Selection for Lead-Free Solders in Consideration of Key Elimination Factors

Elimination factor	Metal	Symbol	Melting point (°C)
Unstable	Cesium	Cs	29
	Rubidium	Rb	39
	Potassium	K	64
	Sodium	Na	98
	Lithium	Li	179
	Magnesium	Mg	651
Too toxic	Mercury	Hg	−39
	Thallium	Tl	304
	Cadmium	Cd	321
	Lead	Pb	327
Abundance	Gallium	Ga	29.8
	Indium	In	157
	Bismuth	Bi	271
MP too high/cost	Copper	Cu	1083
	Nickel	Ni	1453
	Silver	Ag	960
	Gold	Au	1063
Remainder	Tin[a]	Sn	630
	Zinc[b]	Zn	232
	Antimony[c]	Sb	419

[a] Tin (Sn) is the best choice, taking all key aspects into consideration.
[b] Zinc (Zn) is very active chemically, causes corrosion and oxidation issues.
[c] Antimony (Sb) has some components known to be very toxic.

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significant number of studies on lead-free alloys, some of which are discussed in Chaps. 8 and 9, have demonstrated more than adequate reliability characteristics [36].

D. Major Lead-Free Candidate Solder Alloys

Although there has been a significant worldwide effort to identify a drop-in replacement for eutectic Sn–Pb solder, none has been found. Based on elemental selection criteria and considerations such as cost, abundance, toxicity, etc., discussed earlier and summarized in Table 20, the industry has focused on several lead-free solder candidates that appear suitable for the assembly of most electronics products in consideration of the various factors noted in Section C Many of these alloys offer a distinct advantage over eutectic Sn–Pb, such as high joint strength, enhanced fatigue resistance, improved high-temperature life, and harder solder joints [36]; all are noted as desired and sought-after characteristics in Table 19. Both tin and indium would serve as good base materials in that both readily wet the metallizations used for terminations in electronic assemblies and form IMCs with those metals to achieve good bonding. However, there is both a cost and a supply issue associated with In, thus leaving Sn. Another advantage is the existence of substantial experience and database in the use of tin solders compiled over a long history. Tin typically cannot be utilized elementally as a solder owing to its high melting point (232°C). Elemental additions are therefore necessary to reduce the melting point of Sn. Typically, Ag, Al, Bi, Ga, and In are used for that purpose. Other elemental additions such as Ni and Sb, which do not lower the melting point of Sn, are added to enhance the properties of the Sn matrix. The

TABLE 21 Major Lead-Free Solder System Candidates to Replace Eutectic Sn–Pb

Alloy system	Remarks
Binary	
Sn–Ag	Fairly high melt temperature (221°C)
	Alternative for wave soldering, but cost an issue
	Some reliability concerns related to Ag_3Sn platelet growth
Su–Cu	Fairly high melt temperature (227°C)
	Wave solder candidate
	Only moderate wetting, but sufficient for most applications
Sn–Bi	Not applicable as a general assembly solder due to cost, low melt temperature (138°C), and availability
	Good for low-temperature end of a solder hierarchy
Sn–Zn	Cheap
	Lower melt temperature than most Pb-free solders
	Zn is highly active, presents potential corrosion and process concerns
Ternary	
Sn–Ag–Cu	Leading candidate system for reflow soldering
	Lower melt point than Sn–Ag, Sn–Cu binary alloys
	Adequate wetting, mechanical properties
	Much reduced Cu scavenger characteristics compared to Sn–Ag
Sn–Ag–Bi	Even lower melt temperature than Su–Ag–Cu
	Best fatigue characteristics among most popular Pb-free alloys
	Poses some reliability and end-of-life reclamation concerns
Other additions	
Ag, Al, Bi, Ga, In, Cu	Reduce melting temperature of Sn-based solders, and some enhance mechanical properties
Ni, Sb	Do not reduce the melt temperature of Sn-based solders, but added to enhance properties

most popular Pb-free alloy candidates are listed in Table 21 and are discussed in the following sections.

1. Based on Sn–Ag System

The most promising alloys identified are primarily based on the Sn–Ag system, with high tin contents, typically greater than 90%, and with a small addition of either Cu or Bi to create a ternary alloy. Sometimes a very minor addition, less than 1%, of a fourth element is made to enhance a particular desired characteristic, such as strength or reliability. In most cases, the binary eutectic (Sn–3.5Ag) is not adequate for several reasons, which include a high melting point (221°C) that would necessitate subjecting electronic assemblies to high temperatures during manufacture, and exhibits the worst wetting characteristics among high-Sn solder alloys [2]. However, there is a substantial experience base in the use of eutectic Sn–Ag for a variety of niche applications over the years.

2. Bismuth Addition to the Sn–Ag System

Several alloys have been created through the addition of 5% Bi or less to lower the melting point of eutectic Sn–Ag. A typical example is Sn–3.4Ag–4.8Bi, which melts between 208°C and 215°C. In addition to lowering the melting point, Bi also improves the wettability of eutectic Sn–Ag. In fact, Sn–Ag–Bi alloys within the $\leq$5% Bi range generally exhibit the best solderability among the group of the most popular lead-free solder alloys [38]. The addition of Bi greatly increases the fatigue resistance of eutectic Sn–Ag solder. A fourth element such as Ge or Cu is sometimes added to improve alloy strength characteristics.

However, the addition of Bi can also have adverse effects, as it can result in the brittleness of Sn–Ag–Bi alloys, and the presence of Pb on components and board finishes can form a low-melting (96°C) eutectic, which in turn can result in poor fatigue resistance. In addition, fillet lifting has been observed at through-hole joints as wave-soldered joints cool down. Alloys with a solidification range, such as Sn–Ag–Cu alloys, are susceptible to this condition where the solder separates from the IMC layer. Although favored, even alloys without a so-called pasty range, such as eutectic alloys, are not necessarily immune to fillet lifting, as discussed in Chap. 17. Bismuth also has the tendency to easily oxidize, so fluxes that are active at lower temperatures should be used.

3. Copper Addition to Sn–Ag System

The addition of minor amounts of Cu, typically in the range of 0.7%, lowers the melting point of eutectic Sn–Ag. The melting point of Sn–Ag–Cu alloys is slightly higher than Sn–Ag–Bi alloys, but is less costly. The ternary eutectic Sn–Ag–Cu alloy melts at 217°C. The presence of Cu in the solder greatly reduces the Cu dissolution rate from terminal pads with which the solder is in contact. In addition, the yields and reliability of eutectic Sn–Ag–Cu or near-eutectic alloys have been found to be at least comparable to eutectic Sn–Pb. These alloys are also reported to exhibit better solderability and reliability compared to eutectic Sn–Ag or Sn–Cu binary alloys [2].

4. An Assembly Approach

An approach which many in the electronic assembly industry believe is viable in utilizing lead-free solders consists not of a single solder, as in the past with eutectic Sn–Pb, but the choice of a small number of solders depending on the type of soldering operation. An alloy from either the Sn–Ag–Cu or Sn–Ag–Bi system is suitable for solder reflow operations (e.g., the attachment of components to PWBs by reflowing solder paste). The use of Sn–0.7Cu (mp = 227°C) has been considered as a candidate for wave soldering applications because it is the least expensive of the lead-free alloy candidates of interest. Material cost is a key consideration in wave soldering because of the need to periodically change the entire contents of the bath due to contamination buildup. The alloy has soldering qualities equivalent to eutectic Sn–Pb. Although the eutectic Sn–Cu alloy also possesses the poorest mechanical properties among the lead-free solder candidates [2], it is sufficient for most applications. The Sn–Ag–Cu and Sn–Ag alloys can be utilized for wave soldering, and so, too, for rework operations.

TABLE 22 Partial List of U.S. Patents on Lead-Free Solders

US patent number	Assignees	Sn (wt.%)	Bi (wt.%)	Ag	In	Sb	Cu	Zn	Others	Major composition
4758407	Harris	87–93		0.1–0.5		4–6	3–5		Nl (1)	Sn Sb Cu
4778733	Engelhard	92–99		0.05–3			0.7–6			Sn Cu Ag
4806309	Willard	90–95	1–4	0.1–0.5		3–5				Sn Sb Bi
5229070	Motorola	90	5		5					Sn Bi In
5328860	IBM	78	10	2	10					Sn Bi In Ag
5344607	IBM	90	2		8					Sn In Bi
5393188	IBM	93	2	3		1	1			Sn Ag Bi Sb
5411703	IBM	94	2			3	1			Sn Sb Bi Cu
5368814	IBM	42	58		2					Bi Sn In
5414303	IBM	70–90	2–10		8–20					Sn In Bi
5455004	Indium Co.	82–90	1–5		3–6			4–6		Sn In Ag Bi
5580520	Indium Co.	71–92		2–4	4–26					Sn In Ag
5410184	Motorola	92–97					3–8			Sn Cu
5435955	Touchston	79–97	0–1	0–4			3–15		Set (1)	Sn Cu Ag
5429689	Ford	80	4–15	0.5	5–15					Sn Bi In
5538686	Lucent	86			5			9		Sn Zn Ag
5589433	Lucent	40–60	40–60	0.2–0.5						Sn Bi Ag
5698160	Lucent	59–82		2–11				16–30		Sn Zn Ag
5352407	Seelig	93–98		1.5–3.5		0.2–2	0.2–2			Sn Ag Sb Cu
5405577	Seelig	90–99		0.5–3.5		0.2–2	0.1–3			Sn Ag Sb Cu
5520572	US Army	86–97	0–5	0.3–4.5	0–9.3		0.5		Interim	Sn Ag Bi In Cu

5527628	Iowa St. U.	89		3.5–7.7			1–4			Sn Ag Cu
5658258	Mitsui	90	0.5–1.5	1–4	3–4					Sn In Ag Bi
5733501	Toyota	65–95	0.1–9.5	0.8–5	0.1–9.5	0.1–10				Sn Sb Bi In Ag
5730932	IBM	80	12	3	5					Sn Bi In Ag
5762866	Lucent	76–96	0.2–6	1–6	0.2–6			0.2–8		Sn Ag Bi In Zn
5755898	Ford	37–57	37–57		6–10					Bi Sn In
		48–58	40–60		2–5					Sn Bi Ln
5833921	Ford	43–58	38–52	1–2	2	5–15	1–4			Sn Bi Sb Cu In
5837191	Johnson	95		0.6		0.75–2	0.6		Nl (0.6)	Sn Sb Ag
5843371	Samsung	77–89	6–14	3–4	2–5					Sn Bi Ag In
5851482	KIMM	80	1–20		0.1–3			0.01	Al Mg	Sn Bi In Zn
5863493	Ford	91–97		2–5			0–3		Ni(0–3)	Sn Ag Cu Nl
5874043	IBM	70–74		6.5–7.5	12–24					Sn In Ag
5938862	Delco	84–90		2.5–3.5	7–11		0.5–1.5			Sn In Ag Cu
5985212	H-Tech	> 75			D-6		0.1–9.5		Ga (<5)	Sn Cu In Ga
5993736	Mitsui	91–95	2–3	2–4				0.5–2		Sn Ag Bi Zn
5942185	Hitachi	72–87	10–23					3–5		Sn Bi Zn
6077477	Matsushita	81–91	5–10	3–6	0.1–1.0		0.1–2			Sn Bi Ag Cu
6086687	Alpha Fry	> 90	0–9.25	0–0.25	0–9.25	0–9.25	0–9.25	0–0.2	Tl (0.2)	Sn[a]
6139979	Murata	92–96				3–5	0.7–2.0		Nl (0.5)	Sn Sb Cu Nl
6156132	Fuji Elec	40–70	30–58	0–5		0–5	0–1	Ge	Nl (0.2)	Sn Bi Ag Sb

E. Patented Alloys

A large number of patents relating to lead-free solder compositions and processing originate from Europe, North America, and Asia Pacific, as is evident from the partial list of U.S. patents granted, which is presented in Table 22. Accordingly, one or more patents cover many lead-free candidate alloys, whose composition lies within the general family of alloys in which there is substantial interest. Patented lead-free alloys cover a wide range of Sn, Ag, Cu, Bi, Sb, and other elemental combinations, including many in the Sn–Ag–Cu family of alloys. Interestingly, there are often gaps in the patent coverage of an alloy system, and in some cases, no real performance differences between those that lie within the patented composition range and those that do not. Therefore, users are urged to be aware of the patent coverage as it relates to the lead-free solder system they contemplate on utilizing in a product. The use of a patented alloy is anticipated to add between 2% and 8% of the cost of the alloy [37]. A nonpatented alloy may serve the purpose just as well. A partial list of patented and unpatented alloys in the Sn–Ag–Cu system is listed in Table 23.

F. Conductive Adhesives Alternative

It is generally agreed upon that conductive adhesives that consist of a polymer material such as an epoxy that is filled with conductive metal particles will play an increasing role in the attachment of components to PCBs independent of the lead-free issue. This is particularly true in the case of games, consumer electronics, and some handheld communication products. The technology is uncomplicated, utilizing stencil printing techniques similar to solder paste deposition and therefore extendable to high production volumes. It is also generally agreed upon that conductive polymer lead-free alternatives are best suited for cost-driven, high-volume applications, as opposed to those where performance and reliability are key priorities.

1. General Categories

There are general classifications of conductive adhesive materials based on the method by which conduction is achieved. Isotropic adhesives are the most common, and have been used in flexible connections. They normally contain about 70 wt.% Ag particles, but other metals are used as well [6]. The quantity of metal loading is sufficient to assure that the adhesive is electrically conductive in all directions upon curing, as illustrated in Fig. 4, hence the term isotropic. This is in contrast to adhesives with much lower metal filling, such that there are an insufficient number of particle-to-particle contacts to render the adhesive conductive, as depicted in Fig. 5a. However, if the adhesive is sandwiched and compressed between a pair of terminal pads, the particles between the

TABLE 23 Patent Status of Some Alloys in the Sn–Ag–Cu System

Allow composition (wt.%)				
Sn	Ag	Cu	Melt temperature (°C)	Patent status
93.6	4.7	1.7	216–218	Ames Labs, covers any alloy containing 3.5–7.7% Ag and 1–4% Cu
95	4.0	1.0	217–219	Ames Labs
96.5	3.0	0.5	—	Harris Brazing Co.
95.5	4.0	0.5	217–219	Unpatentable, published 50 years ago
95.5	3.8	0.7	217–219	Unpatented
96.3	3.2	0.5	217–218	Unpatented
95.75	3.5	0.75	—	Senju

Source: Ref. 2.

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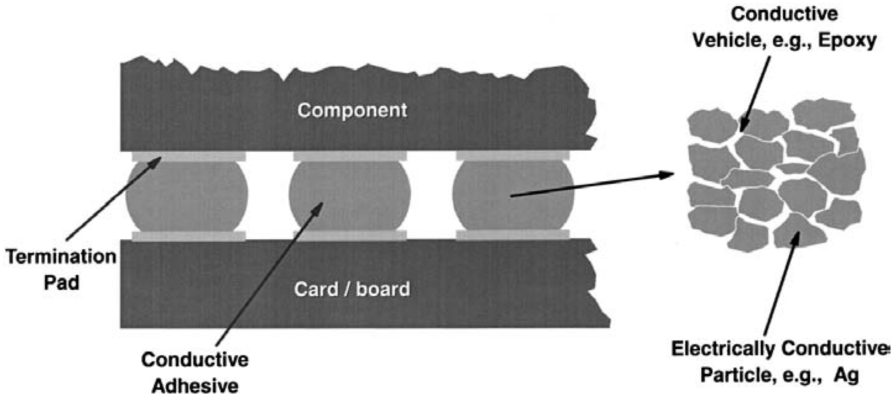

FIG. 4 Illustration depicting an isotropic conductive adhesive alternative.

pads are made to contact each other or the terminal pads. Under these conditions, the adhesive is electrically conductive between the terminal pads, but not to either side of the terminal pads, as depicted in Fig. 5b. Because the conduction path is limited in these types of conductive adhesives, they are referred to as anisotropic.

2. *Advantages*

Conductive adhesive materials are very cost-competitive with solder materials, only require a relatively low-temperature cure, and leave no residues, and thus require no subsequent cleaning step. This is a significant advantage compared to lead-free solders that require a high-temperature reflow and, depending on the flux utilized, may also require a subsequent cleaning step. The print speeds of conductive adhesives are comparable to solder pastes.

3. *Disadvantages*

Conductive adhesives are not anticipated to make significant inroads into high-performance, high-reliability products, however, because of the physical and electrical instability they typically

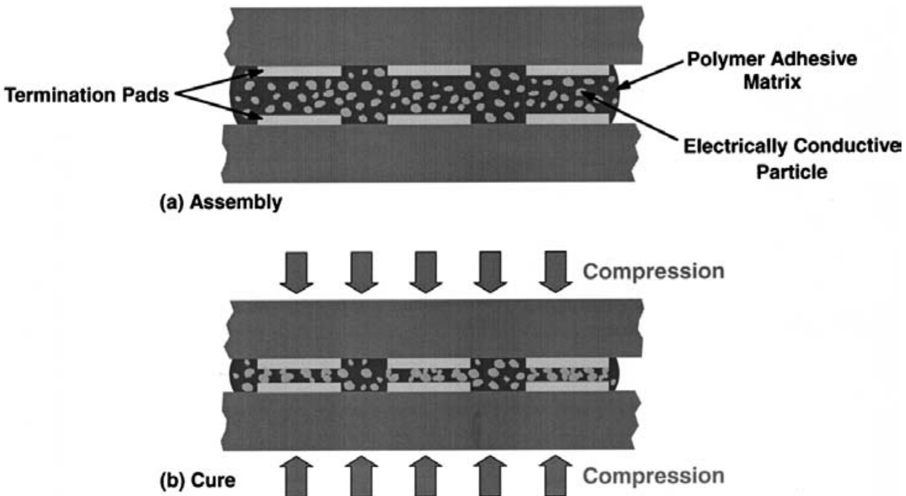

FIG. 5 Illustration depicting an anisotropic conductive adhesive alternative.

exhibit under thermal conditions. In addition, there are joint reliability concerns associated with their adhesive bonding integrity, moisture adsorption characteristics, and typically poor impact resistance. Small passive components attached to PCBs with conductive adhesives typically pass standard drop tests, but higher mass packages do not [21]. There are other issues as well, including a lack of self-centering as occurs during reflow with soldered components, and rework difficulties (i.e., removing and replacing components) [36].

Generally, having a nonsolder surface finish to bond a conductive adhesive improves contact resistance [49]. For example, conductive adhesives perform well with palladium-based terminated components. Lead-free board finishes such as nickel/gold and copper/palladium have been evaluated. Failures at the interface between component terminations and conductive adhesives is a typical failure mode observed in durability tests, and also the cause of an increase in electrical resistance. Oxidation and corrosion of Sn–Pb finishes take place at the interface [21].

V. ISSUES AND CONCERNS IN IMPLEMENTING LEAD-FREE SOLDER TECHNOLOGY

There are several important issues that arise as a consequence of switching from eutectic Sn–Pb to a lead-free solder technology for microelectronic chips, packages, and assemblies. The key issues are discussed in this section.

A. Implementation Approach

Implementing Pb-free manufacturing in electronic assemblies will occur over time (as noted in Table 24) in several stages that will have some overlaps.

1. Step 1: Lead-Free Solder

There has been a significant worldwide effort to identify suitable lead-free solder candidates to replace eutectic Sn–Pb utilized for both the reflow and wave solder attachment of components to PWBs utilized in microelectronic assemblies. Because this effort has consumed much of the initial focus in the lead-free movement within the electronics industry, it is not surprising that the introduction of lead-free solders will represent the initial implementation step. It must be recognized, however, that electronic assemblies will, for the most part, be hybrids (i.e., while the solder is utilized for assembly, both reflow and wave solder operations will be lead-free). It is possible in some assemblies that nothing else will be lead-free, including the components and board finishes, as illustrated in Fig. 6.

Early on, there was little agreement which lead-free alloy(s) should replace eutectic Sn–Pb, a variety of which were utilized in some niche products, as noted in Table 25. The benefits of having a consensus agreement for a very reduced number of alloys is, of course, recognized. In essence,

TABLE 24 Staged Implementation of Lead-Free Materials in Microelectronic Assemblies

	Lead-free				
Implementation stage	Reflow solder	Wave solder	Component finish or I/O	Board finish	Component internal
1	Yes	Yes	Perhaps	Perhaps	No
2	Yes	Yes	Perhaps	Yes	No
3	Yes	Yes	Yes	Yes	Perhaps
4	Yes	Yes	Yes	Yes	No

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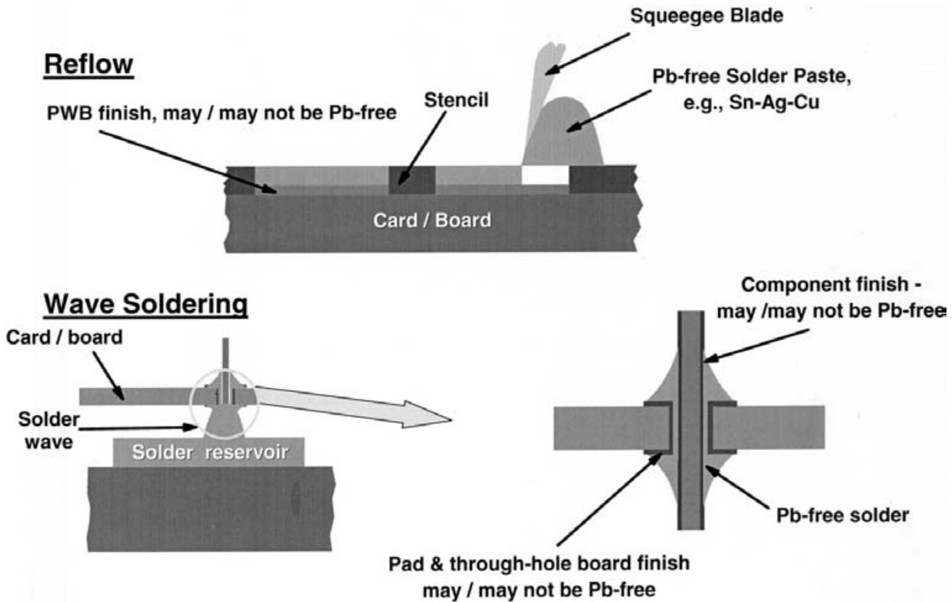

FIG. 6 Illustration depicting the combination of solders and finish materials achieved through reflow and wave soldering operations.

TABLE 25 Lead-Free Solders Utilized Based on the Industry Served

Solder	Melting range (°C)	Industry served	Company
Sn–Ag	221–226	Automotive	Visteron (Ford)
Sn–Ag–Bi	206–213	Military/aerospace/consumer	Panasonic
			Hitachi
Sn–Ag–Bi–Cu		Military/aerospace	Panasonic
Sn–Ag–Bi–Cu–Ge		Consumer	Sony
Sn–Ag–Bi–X	206–213	Consumer	Panasonic
Sn–Ag–Cu	217	Automotive	Panasonic
			Nokia
			Nortel
		Telecommunications	Panasonic
			Toshiba
Sn–Bi	138	Consumer	Panasonic
Sn–Cu	227	Consumer	Panasonic
		Telecommunications	Nortel
Sn–Zn	198.5	Consumer	NEC
			Panasonic
			Toshiba

Source: Ref. 50.

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that has occurred, having selected the Sn–Ag–Cu system with or without the addition of a fourth element as the most popular alternative solders selected. The Sn–Cu system has emerged as a low-cost alternative for wave soldering, and is compatible with most lead-bearing finishes, whereas alloys in the Sn–Ag–Bi system are considered attractive for surface mount reflow attachment applications and as a lower-operating-temperature alternative to Sn–Ag–Cu alloys. However, as noted in Section 4, there is a fillet lifting concern associated with Pb-based through-hole applications. Although the bulk of the industry's soldering will likely be conducted with just a few lead-free alloys, it is anticipated that a variety of alloy systems will still be utilized to satisfy the needs of specific applications. The initial lead-free implementation step, therefore, is to introduce lead-free wave (bar) solders and solder pastes.

2. Step 2: Lead-Free Finishes

The next phase will address eliminating lead from board finishes—the protective coatings applied to termination pads on printed wiring boards to protect metal conductors from degradation (e.g., oxidation, corrosion) and remain solder-wettable. Finishes are applied in a number of ways, including dipping into a molten metal bath (e.g., tin, solder), electroless plating, etc. Alternative finishes must, of course, be compatible with the lead-free alloy selected in Step 1.

3. Step 3: Lead-Free Components

Completely eliminating Pb from electronic assemblies will require its elimination from components that utilize lead in some aspects integral to a component's structure and function. Examples of this are lead used in wiring cable sheaths to provide resistance to degradation, lead used in monitor glass for protection against radiation, lead used as the dielectric material ($PbTiO_3$) in some capacitors, etc. This last stage will require the longest time, owing to the number of alternative solutions that must be identified and demonstrated as suitable.

TABLE 26 Effect of Higher Process Temperatures on Various Microelectronic Board Assembly Items

Board assembly items	Effects
Components	
Ceramic chip carriers	Little to none
Organic chip carriers	Degradation can be substantial, depends on T_g of material Increased moisture sensitivity level
Specials: electrolytic capacitors, wound components, etc.	Susceptible to damage, typically designed for 230° maximum temperature, some up to 260°C
Printed circuit board material	Standard FR-4, $T_g \sim 140$°C Subject to degradation Higher T_g materials Will survive proposed ~240°C Typically will not survive ≥260°C
Plastic overmold material	Thermal plastics may undergo shrinking or warping, or cause critical features to move (creep) Thermal setting compounds, typically not affected by MSL-related effects
Fluxes	Must be formulated to be active near and at the alloy melt point temperature Must not create charred masses that hinder soldering, or allow surface reoxidation

B. Higher Process Temperatures

Most lead-free alloys of interest have a melt temperature that is about 40°C higher than eutectic Sn–Pb (mp = 183°C), which can have a drastic effect on the integrity, reliability, and functionality of printed wiring boards, components, and other attachments (e.g., connectors) [18]. The bulk of lead-free research has focused on identifying suitable solder candidate alloys to replace eutectic Sn–Pb. Solder pastes, wires, and bar stocks are only a part of the issue. The effects of the increase in process temperature necessary for utilizing most Pb-free solders are listed in Table 26 and discussed in the following sections.

1. *Effect on Components*

Electrolytic capacitors are very susceptible to high-temperature damage, as are wound components, such as relays [2]. Surface mount packages are not rated for temperature exposures beyond 230°C, but some survive up to about 250°C, and a few beyond that temperature. Pin-in-hole components are typically rated to survive up to 260°C. In standard reflow assembly practice, the solder liquidus temperature is less than 200°C (e.g., eutectic Sn–Pb, mp = 183°C) and the reflow temperature is typically below 230°C.

In addition, parametric damage can occur to memory integrated circuits (ICs) if exposed to process temperatures around 250°C [38].

2. *Effect on Organic Packaging Materials*

The higher processing temperatures required of lead-free alloys are incompatible with most organic-base materials utilized in microelectronic assemblies including laminate components and PWBs. FR-4 has been the laminate of choice for years, whose T_g is around 140°C. There are higher temperature-resistant laminates available, but at a higher cost.

a. Plastic Components. Plastic components are also constructed of a laminate base and may experience internal damage in several ways when exposed to excessive temperatures. The most common of these is due to water that diffuses into the body of the component between the time that the seal on a plastic bag that contains a set of components and a dessicant is broken, and the time when it is oven-reflowed. The sudden increase in temperature during reflow causes the water to become converted to steam, which is accompanied by a significant increase in pressure within the package, because the gas (i.e., steam) cannot escape the package quickly enough. The pressure is relieved by causing cracks within the package, a process referred to as "popcorning," due to the sound created. The cracks most often consist of the mold compound delaminating from the lead frame or die paddle. Cracks created due to popcorning are not unusual even when processing at eutectic Sn–Pb assembly temperatures (e.g., 200–225°C) if the moisture in parts is not properly removed through a bakeout procedure. Popcorning is anticipated to be aggravated at increased process temperatures required of most lead-free solder alloys. Cracks created due to popcorning typically are large and may cover half of the package dimension, so are likely to be revealed by electrical tests (i.e., large cracks usually sever one or more interconnections). Delamination, on the other hand, including small separations along a lead frame or die paddle, will usually not be immediately discovered by electrical testing. Delamination areas become collection points for atmospheric humidity and contaminants. Chemical reactions can cause a trace finger to corrode, metal migration between adjacent fingers, and other electrical problems, resulting in failure [51,52].

b. Package Overmoldings. Plastic molded electronic packages are also subject to thermal degradation, ranging from simple discoloration to a complete meltdown of the packaging material. Many thermal plastic materials utilized may undergo shrinking and warping, or have critical features that move (creep) when exposed to thermal profiles utilized when processing lead-free solder alloys. Molded electronic packages consisting of thermal setting compounds typically do not exhibit visible signs of distress due to lead-free processing temperatures, but still can be compromised due to the effects of popcorning discussed earlier. This, of course, puts the burden of package integrity on the end user, requiring that components be prebaked and/or that tighter

process controls be utilized. Ultimately, the solution will be to formulate more robust molding compounds that withstand lead-free process temperatures [52].

c. Printed Circuit Boards. A material referred to as FR-4, whose T_g is approximately 240°C, has long been the PWB material of choice in the industry. There are two key concerns associated with the higher soldering temperatures: *z*-axis expansion and decomposition of the laminate. Higher process temperatures cause higher levels of *z*-axis expansion that may affect through-hole reliability. Excessive *z*-axis expansion can be prevented by utilizing laminate materials whose glass transition temperature (T_g) is compatible with increased process temperatures. Plastic materials typically undergo a very significant increase in expansion and a loss of strength at temperatures beyond the T_g, which can result in warping and mechanical instability problems.

Decomposition, or the breaking of polymeric bonds in PWB materials, can also occur during high-temperature solder reflow operations. Some tests on laminate materials require a 280°C and higher exposure for 15–20 min. However, for most laminate materials utilized in microelectronics applications, exposure for a mere few seconds at those temperatures results in breaking of polymeric bonds within the material. Although the percentage of broken bonds is quite small (3–5%), this can still lead to moisture inclusion, or even a degraded T_g.

Higher process temperatures can cause several other PCB-related issues such as warpage, which can cause attachment problems especially with large components; it can adversely affect adhesives, markings, and the adhesion of copper circuitry [50].

3. *Effect on Flux*

Flux plays several important roles during a reflow operation to assure adequate solder wetting and bond formation between the solder and metallization on a termination pad. Its main function is to remove and prevent oxidation in the molten solder and pad surfaces to assure the exposure and intimate contact between fresh, uncontaminated surfaces, and to provide a protective layer to prevent reoxidation during the soldering process. Fluxes are formulated to exhibit their optimum activity over specific temperature ranges that normally are close to the solder melting temperature to reduce oxides. If the flux is exposed to moderate temperatures for long periods or excessive temperatures for even short periods, it forms a hardened mass of charred residue that prevents soldering and is not protective, allowing the surfaces to be reoxidized. Accordingly, many fluxes utilized for eutectic Sn–Pb solder would not be effective with lead-free alloys whose melting temperatures are substantially higher than eutectic Sn–Pb, causing poor wetting and leading to poor manufacturing yields [32]. For reflow processes, a flux should be compatible with peak temperatures above the liquidus temperature up to 250°C, whereas for wave soldering, a suitable flux for a lead-free solder must be capable of withstanding a 130°C preheat and a 280°C temperature in contact with the solder in the molten state for a period of approximately 3 sec [53].

4. *Dissolution of Terminal Pad Metallization*

Higher reflow temperatures increase dissolution rates that can result in an increased concentration of termination pads and surface finish elements in solder joints. Copper is the main circuitizing material utilized for PCBs and also some component lead frames (e.g., small outline—SO; quad flat pack—QFP; plastic leaded chip carrier—PLCC), owing to its good electrical conductivity and solder wetting properties. Tin has a high affinity for copper, so the high tin composition of many lead-free solders and their high melt temperatures have a much increased tendency to dissolve copper termination pads compared to eutectic Sn–Pb, as shown in Fig. 7 [20]. The lead-free alloys noted in Fig. 7 all have significantly greater Sn contents and melting points than eutectic Sn–Pb, which both serve to increase the Cu dissolution rate between about two and seven times faster compared to 60Sn–40Pb. Excessive intermetallic compound formation (Cu_6Sn_5) can adversely affect solder joint reliability due to the brittle nature of this compound, particularly under impulsive load conditions [54].

Nickel/gold is another popular board finish when combined with a gold finish on a component terminal pad. Care must be exercised to not exceed the rule-of-thumb Au threshold concentration in a solder joint (approximately 3%) [55].

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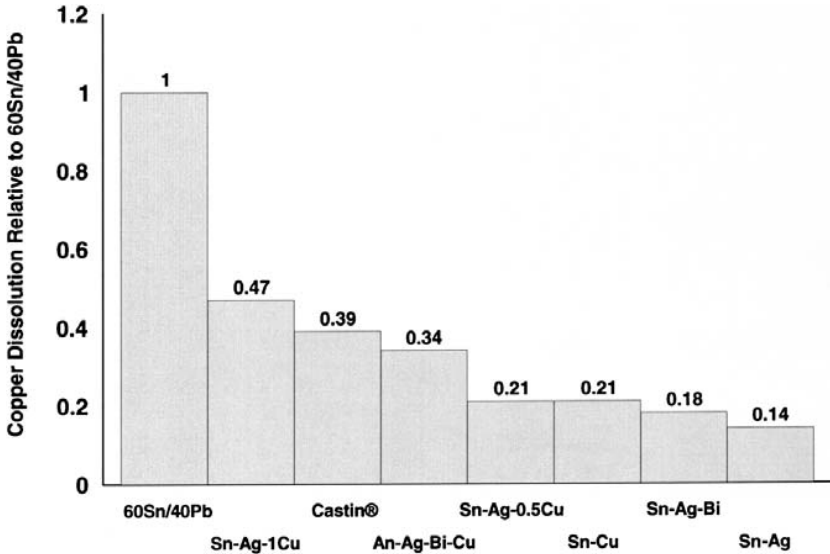

FIG. 7 Dissolution rate of copper for several lead-free solder alloys relative to 60Sn–40Pb solders. (From Ref. 20.)

C. Finishes

Lead-free manufacturing does not only pertain to solder pastes and solder bars for wave soldering, but also as a substitute for lead-bearing finishes utilized for component leads and solder bumps. Lead-free alloys are also used to pretin and protect the copper features on PWBs against oxidation.

1. Component Finishes

In general, the change to lead-free finishes for components is anticipated to be a portion of electronic assemblies to convert to lead-free manufacturing later and is thought to be the most

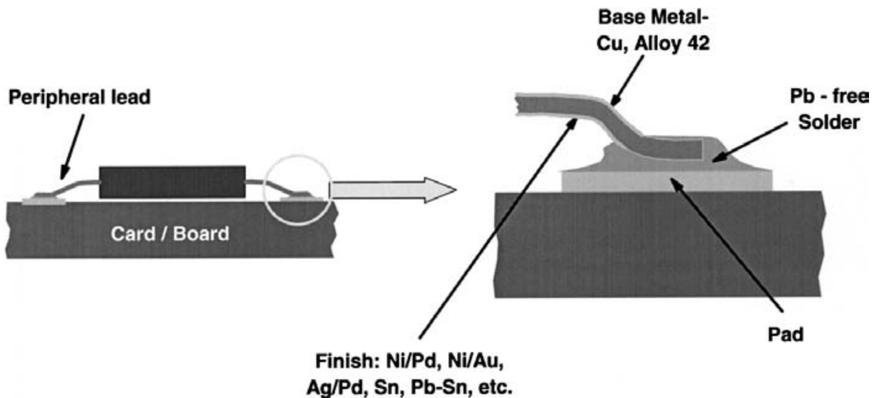

FIG. 8 Illustration depicting typical wetting characteristics of peripherally leaded components with lead-free solders.

difficult to implement. Component manufacturers have reliability concerns both in relation to the impacts of devising suitable processes to provide consistent, high-quality finishes with new materials, and also on the effects these finishes will have on the integrity of solder joints. As noted earlier, there is also the concern of the effect that increased process temperatures will have on the components themselves [53].

a. Peripheral Lead Frames. Many peripherally leaded components, as depicted in Fig. 8, utilize Sn–Pb finishes for peripheral leads. It is likely that lead-free solders will be implemented before component leads with lead-free finishes become available. Nickel/palladium, nickel/gold, silver/platinum, silver/palladium, pure tin, and nickel finishes have been utilized in the past and are likely to be key contenders in completely lead-free systems [26]. Several companies have supplied components with Ni/Pd terminations for several years. The Pd dissolves into the molten solder, wetting the underlying nickel. This works well in the case of eutectic Sn–Pb. Nickel/palladium finished terminations have been evaluated with several lead-free solders and found to provide solderability comparable to eutectic Sn–Pb [52]. Tin–bismuth-based finishes have also been utilized with component lead frames for some time. These finishes exhibit excellent mechanical properties when used with Sn–Ag–Bi solders [56].

Several plated, tin-based lead-free finishes such as Sn, Sn–Ag, Sn–Bi, Sn–Cu, and others have been found suitable with both Cu and alloy 42 component terminations (i.e., lead frames) [57].

b. Ball Grid Arrays (BGAs). Area array components (i.e., ball grid arrays) typically consist of eutectic Sn–Pb of Sn–Pb–2% Ag solder ball terminations, as depicted in Fig. 9. It appears that the major lead-free solder candidates are also suitable as BGA solder ball materials. However, there are dual-solder versions utilizing a high-melt solder ball (90Pb–10Sn) that do not melt during the ball attachment to the component and component attachment to the card processes, each utilizing low-melting (183°C) eutectic Sn–Pb solder paste. The high-melt solder ball assures a substantial standoff height between the component and the card, which has a direct effect on enhancing the solder joint fatigue life. However, a suitable high-melt, lead-free alloy that meets the condition of low cost and whose melting point is within the range of 250–300°C has not

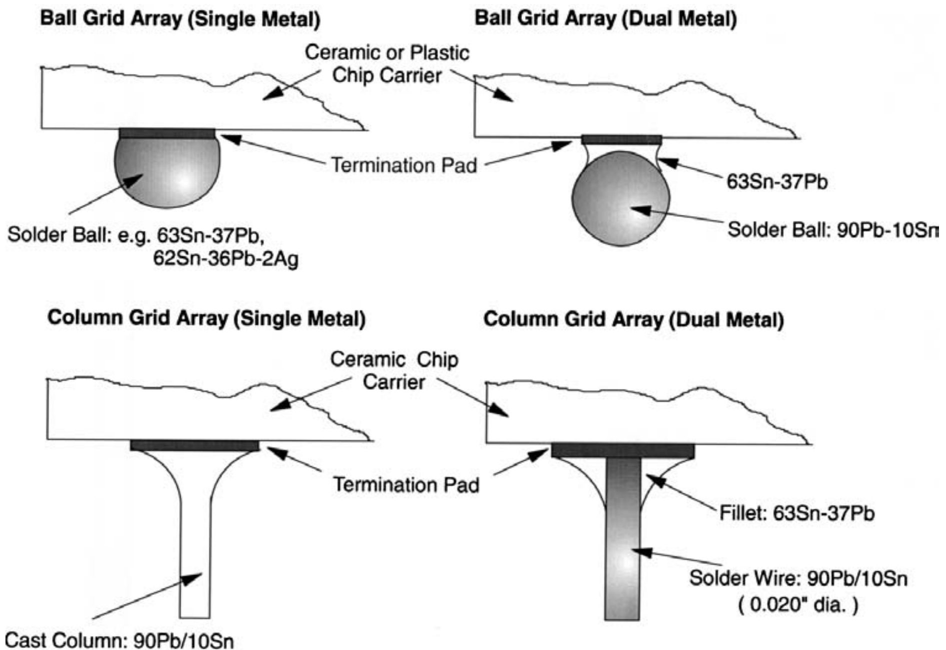

FIG. 9 Illustration depicting typical ball and column grid array terminations.

been identified. The only established lead-free alloy in this temperature range is 80Au–20Sn, which is too expensive to be utilized for this application [58].

There are concerns with lead-free terminated BGA components; among them are wetting and self-centering characteristics that impact placement accuracy requirements and manufacturing yields [49].

2. Card/Board Finishes

The PCB industry produces a number of lead-free finishes; among them are nickel/immersion gold (Ni/Imm Au), Imm Ag, Sn, Ni/Pd, and organic solderability protectants (OSPs).

a. Hot Air Solder Leveling (HASL). Hot air solder leveling accounts for over 60% of the finishes on printed circuit assemblies (PCA). Tin–lead is the PCA material of choice to attach surface-mounted or through-hole components [58]. The PCB industry has been exploring alternatives to HASL to eliminate thermal shock to boards and components, which will be further aggravated by the increased process temperature required by most lead-free alloys.

b. Plated Finishes. The trend is to provide thinner, more uniform, and planar finishes that enable fine-pitch assembly. These conditions are more easily achieved by utilizing plated finish solutions:

1. Nickel/gold—However, the Interconnection Technology Research Institute (ITRI) and others have investigated the failure of SMT parts, particularly eutectic Sn–Pb BGA component solder joint failures associated with electroless Ni/Imm Au metallization on card termination pads. The failures occur under mechanical shock test conditions. Given the root cause theory of failure, it is anticipated that lead-free solders will experience the same failure mechanism. Nickel/gold finishes are often utilized for higher temperatures and multisoldering purposes. The cost of Ni/Au is about 25% higher than for OSP finishes [53].
2. Electroplated tin—Electroplated Sn exhibits excellent solderability and corrosion resistance, but is prone to Sn whisker growth. Thin, hairlike whiskers grow from the surface and pose as a potential reliability problem due to electrical shorts caused in the field. Heat fusing or reflow is used to eliminate tin whiskers [53].

c. Effect of Higher Process Temperatures. The higher process temperatures typical of lead-free solders may cause some lead-free surface finishes to react differently compared to eutectic Sn–Pb conditions. For example, after several reflow or rework cycles, the degree of protection offered by a finish could be compromised. OSP finishes, typically available at approximately the same price as HASL finishes, are easily processed and relatively free of organic contaminants.

Oxidation problems can result upon exposure to several soldering processes, particularly at elevated lead-free soldering temperature conditions. Utilizing an inert atmosphere and reformulating OSPs to withstand higher process temperatures will help [53].

d. Solder Reactions/Process Effects. Another area of concern is the reaction rate between lead-free solders and terminal metallurgy systems. The formation of Ni–Sn IMCs at the interface is much slower compared to the formation of Cu–Sn IMCs. This is an important aspect to take into consideration because Sn content and process temperature are both significantly higher for lead-free solders compared to eutectic Sn–Pb, so the reaction rates are quicker. The formulation of excessive thicknesses of IMC layers is to be avoided to prevent weak solder joints. However, even with a reduced formation rate, a thicker Ni layer is required than for eutectic Sn–Pb solders [52].

D. Process Challenges

1. Process Window

As noted earlier, the preliminary challenge that lead-free solders present to IC and component manufacturers, and electronic assemblers is the higher process temperatures typically required of

lead-free solders, as noted previously. The generally accepted limit that IC packages can withstand is approximately 235–240°C and the lower limit to reliably reflow eutectic Sn–Pb solders is about 200–205°C. This provides approximately a 30°C process window, which is sufficient in a properly monitored line to produce a low-defect-rate, high-yield product with little concern for creating process drift-related defects. However, with lead-free assemblies, the process window shrinks dramatically, as illustrated in Fig. 10. With bismuth-containing alloys, whose liquidus temperatures typically range between 206°C and 213°C, the window shrinks by one third, to approximately a 20°C operating range. For Sn–Ag–Cu alloys, whose liquidus is 217°C, the window is reduced by two thirds, with an operating range of only 10°C. Given that assemblers desire to remain within 5°C of their control limits, the true process window is very small. However, it has been determined that the soldering process can be significantly optimized by obtaining and analyzing data on a real-time basis in a reflow oven. Process control can be aided by utilizing a prediction software that customizes a profile for a specific solder paste, product type, and user-defined input process limit [12].

a. Processing at Lower Peak Temperatures. The industry initially assumed that a 260°C peak reflow temperature was necessary, predicated on the following reasoning. The eutectic Sn–Pb melting temperature is 183°C and the working temperature is typically 220°C, which corresponds to a superheat (temperature span above the liquidus) of approximately 40°C. Considering the fact that the most popular lead-free alloys (i.e., those based on Sn–Ag–Cu) have a liquidus temperature in the range of about 215–220°C, and applying a superheat of 40°C as a reflow temperature results in a suggested peak temperature of about 260°C. However, numerous studies [59–62] have reported that metallurgically and physically sound solder joints can be achieved by utilizing peak temperatures of 245°C or less, significantly below the 260°C initial de facto maximum requirement.

b. Temperature Uniformity. Although adequate solder joints can be achieved at lower temperatures, the issue then becomes how well temperatures can be controlled to assure that all the solder joints of an assembly achieve the minimum reflow temperature prescribed within a process window. With eutectic Sn–Pb, it was permissible to have a variation of 30°C to accommodate various size components, boards, and board cross-section complexities, and still have a viable process (i.e., a window between 210°C and 240°C). However, owing to the approximately 40°C higher melt temperatures of Pb-free solders, the process window must be reduced to lower the peak temperature to a level where it does not degrade the integrity of the board and some components, and severely impact the moisture sensitivity of laminate materials. It has been determined that the peak temperatures that components experience during reflow

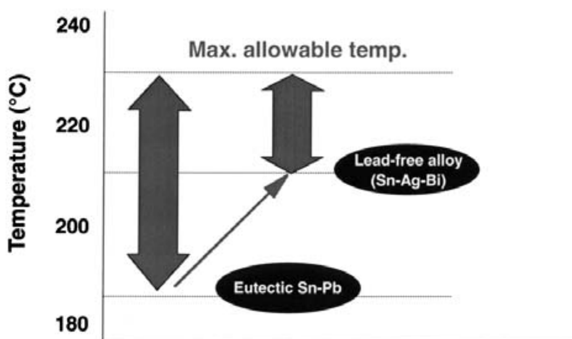

FIG. 10 Process window comparison between eutectic Sn–Pb and Sn–Ag–Bi solder alloys. (From Ref. 56.)

track best on the basis of their volume compared to their mass [63]. Accordingly, Joint Electron Device Engineering Council (JEDEC) defined a standard, JSTD-020, for the reflow attachment of components with lead-free solders: components whose volume is 350 mm^3 or greater must be 245°C (+0,−5) whereas those less than 350 mm^3 must not exceed 250°C (+0,−5). These limits are based on several studies conducted.

It was demonstrated using a forced convection production furnace with a 12-zone heating system and two nitrogen cooling zones that assemblies consisting of a very broad range of component volumes populated on various board cross sections could achieve the JEDEC criteria. Table 27 indicates that all the components are maintained between 232°C and 245°C for a typical disc drive assembly (Assembly A) with a 6s2p card cross section. The components on a laptop assembly (Assembly B) consisting of a card with larger dimensions (8.49 × 8.05 in. vs. 5.3 × 4.3 in.) and an 8s2p cross section were maintained at a peak temperature between 231°C and 237°C. Two significantly more complicated cases were considered typical of server applications. Assembly C consisted of a large board (19.6×15.0 in.) with components ranging to 5700 mm^3, but whose board cross section was the same as Assembly B (i.e., 8s2p). In this case, the peak temperature range was maintained at 227–238°C. The peak temperature range of a server assembly (Assembly D) with a smaller dimension card (10.6 × 6.0 in.) but with a 12s10p cross section and component volumes ranging to 12,300 mm^3 was determined to be between 226°C and 245°C. The complexity represented in most of the test assemblies is much greater (e.g., card size, card cross section, and range of component volumes) than most typical applications. But the test conditions demonstrate that the ΔT across an assembly can be held to about 10–15°C in moderate to complex conditions. In many applications, ΔT can reasonably be held to about 5–7°C in a manufacturing environment. To do so, however, requires that profiles for lead-free assembly must be appropriately modified. Useful modifications are to increase the preheat temperature and to lower the peak temperature to the extent possible. Rapid heating rates should be avoided (rates greater than 4°C/sec), which cause thermal instability and excessive demands on flux makeup [61].

TABLE 27 Peak Temperatures for a Range of Component Volumes When Attached to Various Assemblies using a Convection Belt Furnace

Assembly A: disk drive 5.3 × 4.3 in., 6s2p												
Component volume (mm^3)	1.2	3.3	26.4	34.5	50	100	240	274	274	1239		
Temperature (°C)	240	240	245	239	245	240	235	237	236	232		
Assembly B: laptop 8.49 × 8.05 in., 86s2p												
Component volume (mm^3)	3.6	12.8	50.4	62	69	140	429	800	1634			
Temperature (°C)	235	237	237	233	233	236	238	234	231			
Assembly C: server 19.6 × 15.0 in., 8s6p												
Component volume (mm^3)	1.2	26.2	68.2	226	226	270	369	1207	1400	2400	5700	5700
Temperature (°C)	235	237	237	233	233	236	238	234	231	227	231	232
Assembly D: server 10.6 × 6.0 in., 12s10p												
Component volume (mm^3)	2.3	3.3	13.2	36.4	59	134	160	274	550	2143	7600	12,300
Temperature (°C)	238	245	242	239	238	241	241	242	239	235	226	230

Source: IBM Corporation.

2. Solder Hierarchy

To facilitate the manufacturing of electronic assemblies and to increase both yield and reliability, it is a standard assembly practice that any process step requiring an elevated temperature, such as solder reflow or curing of a polymeric material, does not cause existing solder joints within an assembly to undergo melting. Therefore, if various components are to be added to an assembly at different stages of a process, solders with progressively lower melting points are utilized. For example, flip chip solder bumps (97Pb–3Sn, mp ~ 322°C) are reflowed to ceramic BGA chip carriers, which, in turn, are attached to cards with eutectic Sn–Pb (mp = 183°C). The flip-chip solder bumps do not become molten during the component-to-card attachment step. Utilizing a solder hierarchy prevents soldering at successive process steps from inadvertently melting previously soldered joints. Unfortunately, there are no high-temperature, lead-free substitutes other than 80Au–20Sn (mp = 280°C) a situation that causes board design and manufacturing issues. At the low end, 58Bi–42Sn is available for a low-temperature step [58].

3. Equipment

Accommodating the heating profiles of lead-free solders will require that some reflow and wave soldering equipment be modified or reconfigured.

a. Reflow Soldering Machines. As noted earlier in Section 5.D.1 (Fig. 10), increasing the melt temperature causes the process window to become narrower. Efficient heat transfer becomes increasingly more important as the process window shrinks. A choice must be made among the common heating methods utilized in reflow ovens, namely radiation, hot air/nitrogen convection, or vapor phase. Radiation (lamps) will not meet lead-free requirements, and the throughput of a vapor-phase process is too slow and expensive due to liquid dragout replacement costs. Convection is the method most suited to reflowing lead-free solders. Meeting the process specifications depends on oven configuration, including heating and cooling lengths, number of zones, and other factors such as target throughput, board dimensions and complexity, loading (i.e., distance between boards), required exit temperature, and, of course, the solder paste composition and component specifications. Several peak zones may be required. The equipment should be configured that the heating set points are capable of achieving a nearly uniform assembly temperature (i.e., small ΔT across the board) when entering the peak zone. The goal is to maintain a board above the liquidus temperature for a sufficient period to allow the coolest spot on the board to solder properly while not exceeding the maximum limit at the hottest location on the board. Furnace design and configuration are very important. Reflow furnaces that utilize advanced technology capable of operating at high peak temperatures while still maintaining a relatively small ΔT across fairly large boards with components and attachments that range in size and weight are available, as illustrated in Table 27. Clearly, the alloy melting temperature plays a dominant role in the process, excluding alloys with high melting points. Accordingly, alloys such as Sn–Cu (mp = 227°C) will probably not be utilized for reflow applications. Whereas alloys such as Sn–Cu–Bi (whose melting range is typically between 200°C and 216°C), Sn–Ag–Cu (mp = 217°C), and Sn–Ag (mp = 221°C) are better suited for this purpose.

Reflow equipment utilized for lead-free PCB assemblies should be flexible, especially in the ability to manipulate and control heating and cooling rates, because temperature control is critical. In general, lead-free soldering suffers from a lack of standardization [53].

b. Wave Soldering Machines. Due to the high melting points of lead-free solders, wave soldering machines require a higher preheat temperature to assure that the thermal shock upon entering the first wave does not exceed 100°C. Both VOC-free or water-based fluxes are recommended for lead-free soldering because they are compatible with higher-temperature operation and are environmentally friendly. If a VOC water-based flux is to be utilized, it is be necessary to retrofit the fluxing machine with a spray fluxer because flux suppliers typically do not support foam fluxing VOC water-based fluxes. If not retrofitted, a robust, heat-resistant flux must be selected for foam fluxing, and foam tube and density control must be verified with the flux to be dispensed.

During preheat, the topside of a board should achieve a temperature of about 110–130°C upon having passed through the last preheat zone to limit the thermal shock upon entering the

first wave. The board is to be heated to 100°C as quickly as possible to evaporate water in through-holes, areas underneath components, and between pallets and boards. Continue heating with forced convection to simultaneously equilibrate the assembly temperature. Depending on the type of production, the system may consist of a third preheat zone, consisting of hot air, infrared lamps (for mixed component assemblies), or calrod heaters. All water must be removed from these VOC fluxes before entering the first wave to prevent spattering. Achieving the necessary preheat conditions requires a minimum of 180 cm of heating length for conveyor speeds of 120 cm/min and higher. In the case of high-speed soldering (180 cm/min), a preheating length of 240 cm is required. If high throughput is a priority, which requires increased belt speeds, the preheat zone and the soldering temperature must be increased.

The solderpot temperature, of course, depends on the alloy melting temperature. Therefore, for Sn–Ag–Cu (mp = 217°C), the solder temperature will typically range between 250°C and 270°C. However, for high melting point alloys such as Sn–Cu, the soldering temperature will range between 260°C and 280°C. In general, the higher the solder temperature is, the better is the solderability and the shorter is the required contact time between the solder wave and terminal metallization. Solderability can be improved by using an inerting atmosphere such as nitrogen, a more aggressive flux, or a "smart" wave, as shown in Fig. 11. As the figure illustrates, the main difference between eutectic Sn–Pb and lead-free wave soldering is the increased preheat and solder temperature of lead-free alloys. If the peak soldering temperature is limited, as it typically is, then it is necessary to increase the solder wave contact time to achieve good wetting [53].

E. Mixed Technology

It is anticipated that there will be a hybrid transition period where some components or board finishes will be a mixture of both lead-bearing and lead-free solders. Some studies have been conducted to evaluate the effort of mixing leaded and lead-free technologies on the same board. Some of these have included fairly complicated assemblies such as double-sided, FR-4 high-density microvia test boards with an electroless nickel/immersion gold surface finish. Standard off-the-shelf components consisting of lead-bearing terminations were reflow-attached to the boards utilizing a Sn–Ag–Cu–Sb solder paste composition. Various area arrays, ceramic leadless chip carriers, standard leaded components (small outline integrated circuits–SOICs), and a variety of passives (resistors, capacitors, and inductors) were utilized. Mixing lead-free and Pb technologies increases the difficulty of predicting an assembly's long-term reliability, but the results in this study [59] were encouraging. Good solder joints were observed at reflow temperatures even somewhat below 245°C without board and component damage. In addition, the reliability was superior to eutectic Sn–Pb solder joints based on accelerated thermal cycle (ATC) and drop tests.

F. Inspection

Visual inspection, refined over the years to identify defects and faults that have been correlated to mechanical property behavior and reliability in the field, is a very important aspect of the electronic assembly process. Accordingly, a set of visual inspection criteria has been identified and generally practiced across the industry for eutectic Sn–Pb solder joints. However, the mechanical properties, visual appearance, and solder joint geometry of lead-free solders, in combination with lead-free and lead-containing terminations, are markedly different from those of Pb–Sn, as listed in Table 28. Therefore, new visual inspection guidelines must be developed [19].

Lead-free alloys typically exhibit a dull, mottled, and matte surface appearance compared to the bright and shiny appearance characteristic of Sn–Pb solder joints. In addition, lead-free solder joints tend to have a higher intermetallic compound content, in part due to the higher reaction temperature during processing. Additionally, lead-free alloys have been observed not to wet various termination metallurgies (e.g., Ni, Cu, Pd, etc.) typically utilized in microelectronic packages as well, compared to Sn–Pb solders. Lead coverage, fillet geometries, and working characteristics differ considerably for lead-free alloys compared to eutectic Sn–Pb [64]. Many pads exhibit "copper halos" because wetting does not take place at the edge of the pads. The

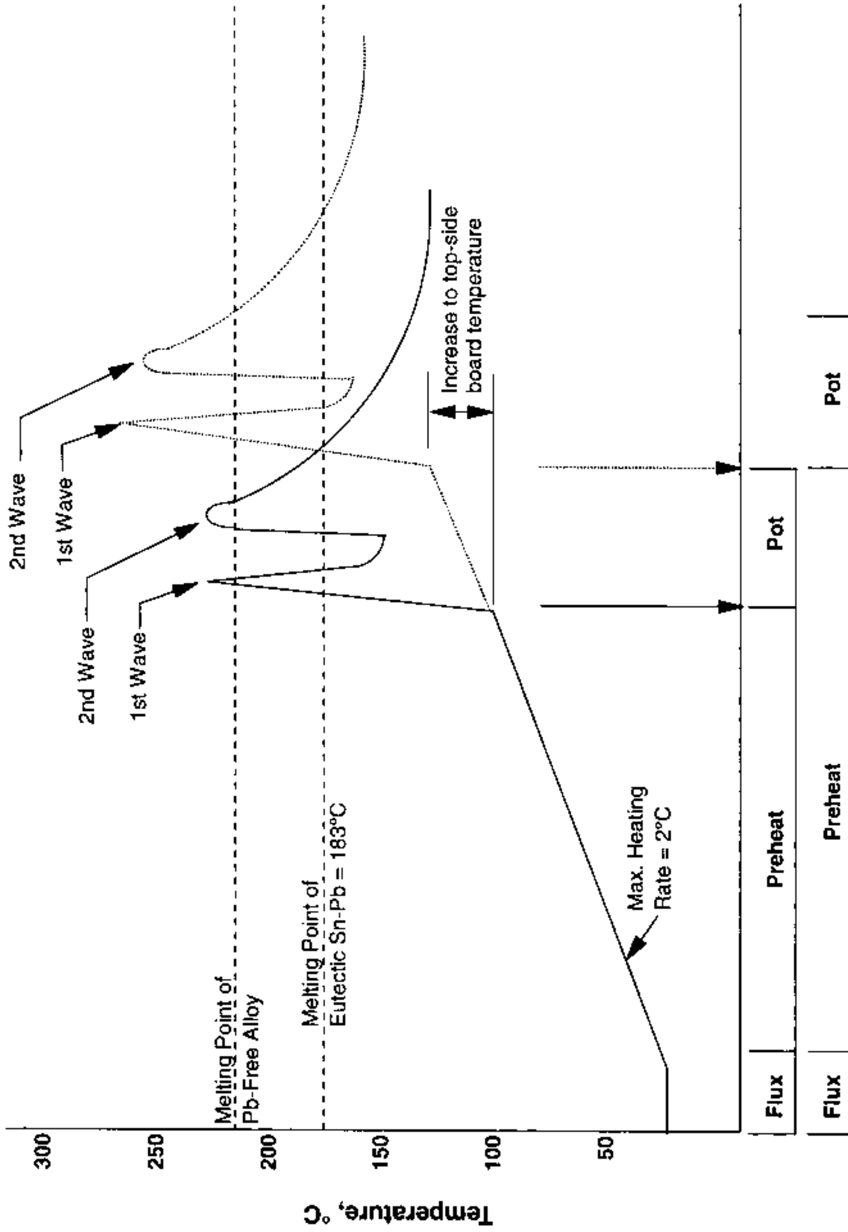

FIG. 11 Comparison of wave soldering profile for eutectic Sn–Pb and lead-free solders. The main differences are increased preheat and soldering temperatures. (From Ref. 53.)

TABLE 28 Comparison of Physical Characteristics Between Sn–Pb and Lead-Free Solders

Features	Pb–Sn solders	Pb-free solders
Visual appearance	Bight, shiny	Matte, dull
Dispersed intermetallic compound content	Low to moderate	More due to higher Sn content and higher reaction temperature
Wetting characteristics	Excellent	Fair to good, pads typically exhibit "Cu halos"
Fillet formation	Wicks up lead, full fillet at lead heel and toe	Does not wick up a lead, partial fillet at lead heel and toe

presence of any of these conditions would be sufficient cause for rejection based on the standard inspection criteria applied to Sn–Pb solder joints. However, many of these differences may not be a cause for improper or unacceptable lead-free solder joints. Considerable learning will be necessary to establish standard inspection criteria and a thorough retraining will be necessary on the part of quality and manufacturing inspectors [59]. The reprogramming of automated optical inspection and x-ray systems is likely. For example, higher voltages may be required to compensate for the poorer image resolution afforded by lead-free solders. There have been reports of only minor software tweaks in some cases. The algorithms used to analyze solder joints are still all applicable. But lead-free alloys yield a lighter image because they absorb about 10% less energy compared to lead-bearing solders. This difference can be compensated for by modifications to the solder thickness tables of the inspection system software.

There are other differences compared to Sn–Pb practice that also require resolution, such as darker and more persistent flux residues and fillet lifting in terms of acceptability [58].

G. Rework

Rework is the term in the electronics industry that pertains to removing and subsequently replacing one or more of the components or other attachments on a PWB, as depicted in Fig. 12. The procedure typically consists of locally heating the solder joints of peripheral or area array

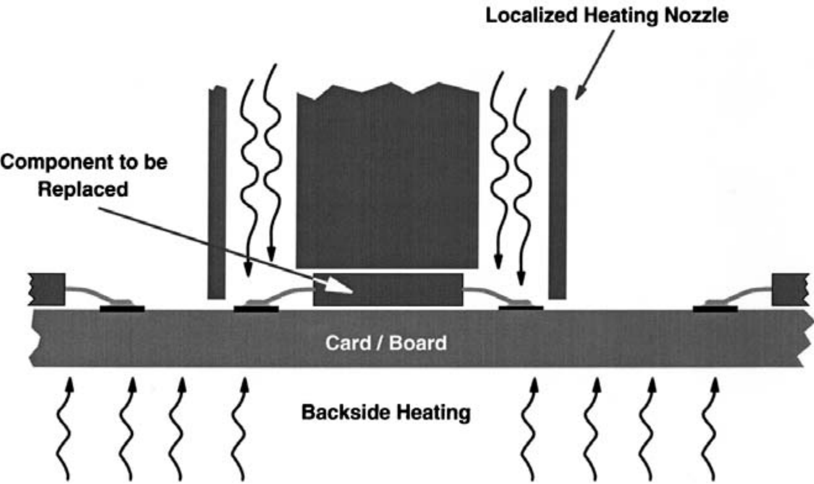

FIG. 12 Illustration depicting the replacement of a component attached to a printed circuit board (PCB) utilizing a localized heating technique.

leaded components. When the solder joints melt, the component is lifted away from the board either by mechanical means or by a vacuum-activated device. A replacement component is locally reflowed to the same site. Sometimes the board is also heated from the underside to lower the thermal gradient and to help eliminate warping.

Rework is an important aspect of manufacturing that helps meet required yields to achieve economic viability—another aspect that is anticipated to be substantially affected by a change to lead-free technology. Rework operators, such as inspectors, will require additional training, and development will be necessary because the properties and melting points of the solders can be significantly altered from component to component across an assembly because of elemental additions introduced to the solder from the PWB and terminal pad metallization systems.

1. Increased Temperature Effects

As the melt temperatures increase, so does the difficulty of reworking the assembly without damage to the board, surrounding components, and other attachments. For example, it is estimated that for manual rework operations, it will probably be necessary for the soldering iron tip temperature to be beyond 300°C. Accordingly, rework operators will require training to develop skills to minimize the exposure time of temperature-sensitive replacement components to higher temperatures [64]. Studies (including one by the NEMI) focused on rework practices for removing and replacing through-hole and surface-mount components attached with lead-free solders have been reported. Of particular interest is the local degradation a PCB may undergo when subjected to multiple replacement cycles at the same component location on a board [65]. Repeated exposure to high localized temperatures may cause board delamination, thermal degradation (charring, brittleness), and delamination of copper traces (i.e., loss of adhesion to the board).

2. Reclamation Implications

Ease of component removal also affects reclamation efforts. Cradle-to-grave ownership of products by their manufacturers or others in the chain of commerce requires a careful evaluation of the recycling cost of an assembly. The processing required to remove several components from an assembly can be substantially reduced by selecting components with a common termination metallurgy, so they can all be removed at a common removal temperature. The selection of a lead-free alloy for component and board finishes should be with subsequent reclamation in mind [59].

3. Feasibility Demonstrated

The rework of lead-free solder joints has been shown to be technically feasible. Concerns associated with locally heating printed circuit boards or attachments at high temperatures are mostly manifested in reworking heavy and complex components such as BGAs that require a high level of heat to effectively achieve removal and reflow. It appears that rework can be accomplished without damaging temperature-sensitive parts, and board warpage can be minimized if the process is optimized. The same issues apply to rework as general assembly operations, soldering temperatures, and other parameters must be tightly controlled.

4. Required Suitable Marking System

Because there is no single lead-free drop-in replacement for eutectic Sn–Pb, there must be a suitable marking system to indicate the particular alloy (and its melt temperature) used for assembly. This is necessary for an operator to subsequently remove a component and select a metallurgically compatible replacement component (i.e., compatible with the rework alloy, component termination finish, and original assembly alloy). Numerous investigations indicating a variety of lead-free finishes compatible with the Sn–Ag–Cu family of alloys have been conducted [64].

H. Cost

The potential cost impact of implementing lead-free technology is foremost on the minds of both manufacturers and users alike. A study conducted by the National Center for Manufacturing

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Science (NCMS) estimated that replacing Pb in electronic assemblies will result in a material cost of US$140–900 million dollars in the United States alone, with supply chain costs likely to run in the tens of billions of dollars [66]. Cost issues are related to materials (solders, components, boards, protective atmospheres during processing, additional energy consumption due to the higher process temperatures required for most lead-free solders, and operational costs).

1. *Solder materials*

a. Paste. As noted earlier, the cost of solders purchased as bar stocks depends on the raw material cost (Table 11), but for fabricated products such as solder pastes, the processing cost to manufacture the product is often the dominant factor, so the difference between Sn–Pb and Pb–free solder pastes becomes very small [2].

b. Bar Stock. The situation is different in the case of solder bar stock. Consider, for example, a wave solder pot that requires 760 kg of eutectic Sn–Pb alloy (density = 8.4 g/mm^3) to fill the pot at a cost of about US$4000. The cost to fill the same pot with any of several lead-free solders is given in Table 29. The Cu–Sn alloy has some cost–benefit over other candidates.

c. Components. Changing the finish on peripherally leaded components is not perceived to be a major issue because several lead-free finishes have been available for some time. The process costs for lead-free component finishes are not anticipated to increase dramatically because the techniques to apply them are already in place. However, reliability issues such as tin whisker growth of some newer finishes must be thoroughly addressed.

The solder balls for area array components (e.g., ceramic ball grid arrays—CBGAs; plastic ball grid arrays—PBGAs; chip scale packages—CSPs) do have, of course, a processing-related cost that will not have as much effect in blurring the cost differential between lead and lead-free solders as occurs with solder pastes. Like solder bars, the cost of solder will likely track more closely with the raw material cost.

2. *Card/Board Materials*

In addition to converting to lead-free board finishes, the industry also desires to eliminate halogenated flame retardants as a board material due to the negative impact they have on the environment. Thus new boards that simultaneously meet the requirements of higher temperature resistance to be compatible with the higher reflow temperatures necessary for most lead-free solders, alternative flame retardants, and lead-free finishes are necessary. The new board materials will require higher glass transition temperatures (T_g) to maintain integrity and shape at the higher process temperatures. Accommodating all the required changes in the new cards and boards will result in a cost increase; the extent will not be clear until the material sections and their fabrication processes have been finalized and optimized [67].

3. *Consumables*

a. Flux. Flux plays a major role in the quality of solder joint formation because it removes oxides and other materials to provide solderable surfaces with fewer defects. A "green" soldering process would typically utilize VOC-free, water-based fluxes, which have some advantages

TABLE 29 Cost Comparison Between Eutectic Sn–Pb and Several Lead-Free Solder Alloys

Solder alloy	Cost factor relative to eutectic Sn–Pb	Cost to fill solder pot (US$)[a]
Eutectic Sn–Pb	1	3,960
Eutectic Sn–Cu	1.28	5,068
Eutectic Sn–Ag	1.35	5,346
Su–Ag–Cu	1.45	5,742

[a] Assumes a pot capacity of 760 kg of eutectic Sn–Pb solder.
Source: Ref. 67.

compared to alcohol-based fluxes. Some studies have shown that VOC-free fluxes provide better results on lead-free solders than no-clean fluxes, particularly as they relate to residuals left on the board and solderability. There are less residues because the required flux volume is less. The activators and chemicals in the flux react more aggressively in water than alcohol. Although VOC-free fluxes are more expensive, the actual cost is about the same or less because the required flux volume is less. Cost savings also result from the fact that as solderability improves, the amount of rework decreases. In addition, a reduced amount of flux reduces maintenance: Cleaning can be achieved more easily and can be done with hot water rather than chemicals.

To achieve the desired VOC-free fluxes for lead-free soldering, flux suppliers are developing ways to dissolve rosin into water-based fluxes [67].

b. Inert Atmosphere (Nitrogen). With the reduced solderability of lead-free alloys compared to eutectic Sn–Pb, the use of an inert atmosphere generally, but not always, improves wettability and has other benefits (Table 30) to improve solder joint reliability. The use of inert atmospheres along with glycol submersion minimizes dross formation in wave soldering machines.

Excessive flow rates must be avoided in reflow furnaces to avoid a condition referred to as tombstoning in small passive components (e.g., chip resistors, capacitors, etc.). Tombstoning is a term used to describe a condition whereby a small rectangular component with a terminal at each end is lifted away from a board at one end. It remains soldered at the opposite end, and so is oriented perpendicular to the board, having an appearance similar to a tombstone—hence the term.

In the end, a cost–benefit tradeoff analysis must be made for a particular product that considers the advantage of enhanced wettability, thus better yield and reliability, and reduced dross formation compared to the additional nitrogen cost.

Use in reflow furnaces—The cost justification for utilizing inerting depends upon the degree of enhancement in wettability and the application's reliability requirements. Geographic location can be an important consideration as well. For example, the cost of a cubic meter of nitrogen in Switzerland is about 10 times as great as that in Germany. When production flexibility is a priority, a reflow oven should be capable of both air and inert gas (i.e., nitrogen) operation. When the use of nitrogen is a significant cost consideration and it is not needed, it should not be utilized. However, with the trend toward reduced pitches in electronic assemblies and more complex designs, the flexibility to utilize nitrogen, if desired, should exist [67].

Use in wave soldering machines—Lead-free solders, such as Sn–Pb solders, oxidize very quickly in the liquid state. In both cases, the oxides form at the surface immediately after the oxide skin has been removed. Dross, the material formed at the molten wave in a wave soldering machine, consists of solder metal surrounded by an oxide skin. The tendency to form dross in the case of lead-free solders is greater than that in eutectic Sn–

TABLE 30 Considerations in the Use of Inert Atmospheres

Factors	Remarks
Inert atmospheres	H_2, N_2, and mixtures of N_2, H_2, and Ar
Benefits	Increases solder wettability
	Reduces oxidation of solder and solderable surfaces due to:
	Increased temperature required for Pb-free solders
	Increased Sn content of Pb-free solders
	Reduced dross formation in wave soldering operations
Concerns	Cost, tombstoning of passives due to excessive flow rates

Pb, owing to their greater tin content and higher melt temperatures to increase the reaction rate. By far, most oxides comprising dross are tin oxides (i.e., SnO and SnO_2). Dross also forms at the solder pump shaft, but wave solder machines that seal this area to prevent its formation are available. Dross formation at the wave can be reduced by lowering the wave face height (i.e., the distance from the wave crest to the solder pool level).

The use of nitrogen, therefore, provides several benefits in wave soldering applications: enhanced wettability and reduced dross formation. These factors must be balanced against the cost of inerting. It should be noted that losses due to dross formation can be significantly reduced because oxides only constitute a small part of dross. Dross can be compressed to partly separate the solder metal from oxide cells [67].

4. Operating Costs

a. Energy Consumption. More energy is typically required to heat up a board assembly utilizing a lead-free solder compared to that of a eutectic Sn–Pb solder owing to the former's high melting and process temperatures. The same is true for wave soldering, where there are two areas that require increased energy consumption. A higher preheat temperature is required to heat an assembly in preparation for wave soldering, up to about 25%. As in reflow ovens, due to the higher melting points of lead-free solders, higher solder pot temperatures are required in wave soldering machines with lead-free solders. The result of one study comparing the energy consumption for a pot operating at 280°C (for Cu–Sn) and 250°C (for Sn–Pb) is given in Table 31, where consumption measurements were made without a load (i.e., boards were not passed through the reflow oven). The higher melting points of lead-free solders necessitate up to 25% more energy consumption during the preheat stage to raise the assembly to an adequate temperature prior to being passed over the solder bath. In addition, because the solder melt point is higher, it is necessary to provide additional power to melt the solder [67]. Additional energy is also required if forced cooling is utilized subsequent to solder solidification.

b. Throughput Impact. There are several important factors that contribute to a reduction of throughput with lead-free solders compared to eutectic Sn–Pb. In general, lead-free solders require longer contact times with the molten solder wave to achieve good wetting with the board features (i.e., termination pads, plated through-holes). A wave soldering machine can be retrofitted with a different wave former to increase contact time. If the wetting still is not sufficient, then the conveyor speed must be reduced, which also results in a lower throughput [67].

c. Repair. Typically, higher temperatures are required for repair operations to quickly heat a localized region to remove a component or other attachments mounted to a board, and reflow a replacement without melting the solder joints of neighboring components. As noted earlier, reflow and process temperatures of lead-free alloys are already significantly higher (about 40°C) compared to eutectic Sn–Pb. The temperatures necessary for rework only aggravate the situation because they are even higher.

TABLE 31 Comparison of Solder Pot Power Consumption for Eutectic Sn–Pb (250°C) and Eutectic Sn–Cu (280°C)

Factors	Sn–Pb (250°C)	Sn–Cu (280°C)
Power consumption to setpoint (kW hr)	34	36
Time to setpoint (hr)	3.5	5.5
Power consumption per hour at setpoint (kW hr)	5.0	5.0

Source: Ref. 67.

As pointed out earlier, the appearance and shape of lead-free solder joints differ from eutectic Sn–Pb. However, it should be pointed out that this has not caused an increase in defects requiring rework. This is true even though new defects such as fillet lifting occur with some lead-free alloys. Reliability tests have not indicated these defects, including fillet lifting, have lower quality, and thus are believed to not require repair [67]. More experience is required to verify that this is the case.

d. Maintenance. Although some aspects of utilizing lead-free solder alloys will result in increased operating costs, maintenance is not anticipated to be a contributing factor. In fact, practices such as utilizing VOC-free, water-based fluxes may even result in reduced maintenance time and increase maintenance intervals compared to no-clean fluxes [67].

I. Reliability

1. Lacking Sufficient Database

Although the mechanical properties of eutectic Sn–Pb are not outstanding, they are adequate for most applications. This is important given the many other attributes a suitable solder must mutually satisfy. Additionally, a very substantial database has been put in place over the last 50 years from which both designers and users alike can draw upon in determining long-term reliability under a multitude of field conditions for eutectic Sn–Pb solder joints. There is no such database for lead-free solders, and even with accelerated testing, it will take years to generate an understanding equivalent to eutectic Sn–Pb. Possessing this level of understanding is admittedly less critical for consumer electronics applications such as games, mobile telephones, or other handheld telecommunication devices, etc.; but for applications requiring service lifetimes that span from a few years to a decade or more, this lack of information is of real concern. Not all lead-free alloys are devoid of a reliability database. For example, both Sn–Ag and Sn–Bi have been utilized in various applications for some time. Numerous studies have indicated that, in general, lead-free alloys including Sn–Ag–Cu exhibit reliability under accelerated testing conditions that are at least equivalent to eutectic Sn–Pb solder joints, and in many cases substantially better. The field data of several lead-free solders utilized in some niche products such as phones (Nortel), minidisc players (Panasonic), laptop and tabletop personal computers available from several manufacturers, etc., have not indicated any major reliability problems. However, more accelerated laboratory test and field data are necessary before drawing conclusions about the long-term reliability of these solder materials that have been used in a limited number of solder joint configurations and field conditions.

2. Information and Comparisons

It is important to recognize in assessing and comparing the reliability results of tests, or those reported in the literature, that test conditions, regime, and materials are all taken into account. Contradicting claims regarding reliability can arise from inappropriate comparisons [19]. For example, it has been reported that significant wetting differences have been observed to exist for the same nominal composition lead-free alloy pastes but from different vendors, reflowed exactly in the same manner [68]. The poor wetting observed for an alloy that also exhibited good wetting occurred by utilizing solder pastes from different vendors. The wettability clearly is not related to the composition of the alloy, but rather to another factor, such as the effectiveness of the flux. However, in the early stages of lead-free technology, not all parameters were necessarily optimized in an experiment that resulted in erroneous characterizations and reliability results.

J. Logistics

Although several lead-free solders have been identified (e.g., Sn–Ag–Cu and Sn–Ag–Bi for reflows; Sn–Cu for wave soldering), no single drop-in replacement has been identified with global consensus suitable for all aspects of assembly soldering: reflow, wave, and repair. The lack of a universally adopted lead-free alternative to eutectic Sn–Pb creates logistical problems in implementing lead-free soldering in electronic assembly operations. Contract manufacturers, who are increasingly assuming OEM solder assembly operations, will be faced with the need to

run multiple assembly lines to satisfy the range of their customers solder requests. The logistical problem is very evident in the case of wave soldering, where emptying and refilling the solder bath is a nontrivial exercise [19].

VI. SUMMARY

Although there are no easy answers for the rapid pace of the global electronics industry in moving toward the implementation of lead-free products, there are several reasons that can be identified:

The fear of potential legislation and potential trade barriers—The proposed EU RoHS Directive will restrict the sale of lead-bearing electronic products, effective July 1, 2006 with some exceptions.

The concern of competition and loss of market share resulting from market-driven pressures—Momentum has gathered due to a voluntary program initiated by many Japanese electronics OEMs to eliminate lead from their products and the very favorable preference for them in some geographies.

The need for enhanced properties over those provided by eutectic Sn–Pb to meet the requirements of even more challenging service conditions such as high-temperature capability demanded my many automotive applications.

The cost and process impacts in implementing lead-free electronic assembly, although significant, do not appear to be as great as initially perceived in many cases. These concerns are mainly based on the fact that lead is relatively inexpensive, and replacing it will add expense. It should not, however, have a major impact on the final product in most cases. In addition, as is typically the case for any new technology, the cost is eventually reduced. At first, it was also believed that it was necessary to conduct lead-free reflow and wave operations at 260°C temperature and above, which would have had severe implications on the structural and functional integrity of cards and circuit boards, attachments including components, the plastic component moisture sensitivity level (MSL), and activity of fluxes. It is now known that solder joints with adequate wetting, metallurgical characteristics, and mechanical properties can be achieved at much lower temperatures (i.e., in the range of 240°C) for most lead-free alloys of interest. This also greatly reduces the concern that significantly elevated process temperatures have on the infrastructure that is already in place. It now appears that most reflow ovens and wave soldering machines used for eutectic Sn–Pb assembly will be suitable, or only require relatively minor modifications.

In fact, from various studies conducted globally by industrial organizations, consortia, government-sponsored laboratories, and universities, it has been demonstrated there are some substantial benefits for the use of lead-free solders over eutectic Sn–Pb such as enhanced strength and fatigue resistance properties, with higher maximum operational temperatures of finished products [58].

There will, of course, be many hurdles and issues to overcome, many of which are discussed in this handbook, in driving to implement lead-free soldering of electronic assemblies around the world. But very significant progress has been made in a relatively short period, which is also discussed in this handbook, with no known "show stoppers" having been identified. Long-term reliability remains a major unknown and is a key concern in the industry, notwithstanding early encouraging results reported in the literature. Given the momentum of green manufacturing and the worldwide support for the movement, it appears that the issue is when lead-free technology (including soldering operations in electronic products) will be implemented, and not if.

REFERENCES

1. National Center for Manufacturing Science. Lead and the Electronics Industry: A Proactive Approach, NCMS, Ann Arbor, May, 1995.
2. Lee, N.-C. Lead-free soldering—where the world is going, Adv. Microelectron. September/October 1999, 29–35.

3. Ellis, B. Environmental issues in electronics manufacturing: a review, Circuit World January 2000, *26* (2), 17–21.
4. Prasad, R. Lead-free solder, Surf. Mount Technol. January 2000, *14* (1), 26–28.
5. Reed, G. The greening of SMT, Surf. Mount Technol. June 2000, *14* (6), 16.
6. Wood, E.P.; Nimmo, K.L. In search of new lead-free electronic solders, J. Electron. Mater. 1994, *23* (8), 709–713.
7. Sax, N.I. *Dangerous Properties of Industrial Materials*; 6th Ed. Van Nostrand Co.: New York, 1984.
8. Lead-free roadmap—a scenario for commercial application, JEIDA, February 3, 1998.
9. Smith, E.B. III; Swanger, L.K. Are lead-free solders really environmentally friendly? Surf. Mount Technol. March 1999, 64–66.
10. Jones, Greg Are you ready for lead-free assembly? Surf. Mount Technol. June 2000, *14* (6), 60–62.
11. Jorgensen, C. Lead-free electronics: full steam ahead. Surf. Mount Technol. May 2000, *14* (5), 87–89.
12. Jones, G. The effect of lead-free assembly on the semiconductor industry. Chip Scale Rev. March/April 2000, *4* (2), 49–55.
13. Environmental book to benefit the workplace, Surf. Mount Technol. June 2000, *14* (6), 48.
14. Selvaduray, G.S. Is design for the environment strictly academic? Chip Scale Rev. September/October 2000, *4* (5), 15.
15. Feilding, S. What is ISO 14001? Electron. Packag. Prod. April 2000, *40* (4), 22.
16. Peo, M.; DeAngelo, D. Are you ready for lead-free reflow? Surf. Mount Technol. May 2000, *14* (5).
17. Palmer, M.A. Alternative processing for forming solder joints with lead-free solder alloys. SMT August 2000, *14* (8), 61–66.
18. Lead Free Soldering 1, HDP User Group International, Inc., Scottsdale, Project No. 032, Rev. A, June 1999.
19. Linton, J. Asia and the environment. Circuits Assem. August 1999, *10* (8), 22–24.
20. Grusd, A. Connecting to lead-free solders. Circuits Assem. August 1999, *10* (8), 32–38.
21. Crum, S. Targeting lead-free solutions. Electron. Packag. Prod. 28–36.
22. Buetow, M. The latest on the lead-free issue. Technical Source; IPC. 1999, spring/summer publication.
23. Vianco, P.T.; Frear, D.R. Issues in the replacement of lead-bearing solders. July 1993, *45* (7), 14–19.
24. Wolters, J. *Zur Geschichte der Lottechnik*; Degussa: Frankfurt, Germany, 1978.
25. Racklam, H. *Pliny's Natural History*; Heinemann: London, 1968; Vol. 33.
26. Mahidhara, R. A primer on lead-free solder, Chip Scale Rev. Mar/April 2000, *4* (2), 40–41.
27. Groover, M.P. *Fundamentals of Modern Manufacturing*; Prentice-Hall: Saddle River, NJ, 1996; 777–779.
28. Puttlitz, K.; Totta, P.A. *Area Array Interconnection Handbook*; Kluwer Academic Publishers: Boston, 2001 (Chaps. 8, 15, and 17).
29. MacIntosh, R. Tin in cold service. Tin Uses 1966, *72*, 7.
30. Holmes, P.; Loasby, R., Eds.; *Handbook of Thick Film Technology*; Electrochemical Pub. Ltd.: Ayr, Scotland, 290–305.
31. Harrison, M.R.; Vincent, J.H.; Steen, H.A.H. Lead-free reflow soldering for electronics assembly. Solder. Surf. Mount Technol. 2001, *13* (3), 21–38.
32. McCormack, M.; Jin, S. New lead-free solders. J. Electron. Mater. July 1994, *23* (7), 635–640.
33. Vincent, J.H.; Humpston, G. Lead-free solders for electronics assembly. GEC J. Res. 1994, *11* (2), 76–89.
34. U.S. Bureau of Mines. U.S. Geological Survey, 2000.
35. Knapp, D. NCMS lead-free electronic interconnection program. Proc. Surf. Mount Int. 1994, 425–431.
36. Suraski, D.; Seelig, K. The current status of lead-free solder alloys. IEEE Trans. Electron. Packag. Manuf. October 2001, *24* (4), 244–248.
37. Zarrow, P. The true cost of lead free. Circuits Assem. June 2001, *12* (6), 20–22.
38. Lee, N.C. Lead-free soldering of chip scale packages. Chip Scale Rev. March/April 2000, *4* (2), 42–47.
39. Prasad, R. Lead-free solders and their properties. Spec. Suppl. Surf. Mount Technol. June 2000, *14* (6), 9–10.
40. Zarrow, P. Lead-free: don't fight a fact, deal with it. Circuits Assem. August 1999, *10*, 18–20.
41. Bulwith, R.A.; Mackay, C.A. Silver scavenging inhibition of some silver loaded solders. Weld. J. (Weld. Res. Suppl.) June 2000, *79* (6), 9–10.
42. Vianco, P.; Hosking, F.; Rejent Wettability analysis of tin-based, lead-free solders. Proc. NEPCON WEST (Des Plains, IL) 2000, 3017.
43. Schwaneke, A.; Falke, W.; Miller, V. Surface tension and density of liquid tin–lead solder alloys. J. Chem. Eng. Data 1978, *23*.
44. Millor, C.M.; Anderson, I.E.; Smith, J.K. A viable tin–lead solder substitute: Sn–Ag–Cu. J. Electron. Mater. 1994, *23* (7), 595–601.
45. Jin, S. Developing lead-free solders: a challenge and opportunity. J. Met. 1993, *45* (7), 20–24.
46. Winterbottom, W.L. Converting to lead-free solders: an automotive industry perspective. J. Met. 1993, *45* (7), 20–24.

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47. Melton, C. Proceedings of the IEEE International Symposium on Electronics and the Environment, Month 1993; 94 pp.
48. Kang, S.; Sarkhal, A. Lead (Pb)-free solders for electronic packaging. J. Electron. Mater. 1994, *23* (8), 701–707.
49. Raby, J.D.; Johnson, R.W. Is a lead-free future wishful thinking? Electron. Packag. Prod. August 1999; 81–20.
50. Jorgensen, C. Can you paint a rosy picture with green paint? P.C. Fab October 2000, *23* (10), 38–44.
51. Tonga, Y.; Adams, T. Lead free processing: thermal effect on components. Spec. Suppl. Surf. Mount Technol. June 2001, (Guide to Lead-Free Soldering) *15*, 10–11.
52. Yang, L.; Berstein, J.B.; Chung, K. The impact of lead-free soldering on electronics packages. Microelectron. Int. 2001, *18* (3), 20–26.
53. Barbini, D.; Diepstraten, G. Five steps to successful lead-free soldering. Circuits Assem. April 2001, *12* (4), 42–49.
54. Humpston, G.; Jacobson, D.M. *Principles of Soldering and Brazing*; ASM International: Materials Park, OH, 1993.
55. Glazer, J., et al. Effect of gold on the reliability of fine pitch surface mount solder joints. Circuit World August 1992, *18* (4), 14–46.
56. Baggio, T.; Suetsugu, K. Guidelines for lead-free processing. Surf. Mount Technol. September 1999, *13* (9), 60–66.
57. Parker, R.D. The next no-lead hurdle: the components supply chain, August 2000. http://www.circuitree.com.
58. Bell, R. Lead free: will alternative alloys really work? Circuits Assem. September 2000, *11* (9), 120.
59. Dunford, S.O.; Viswanadham, P.; Rantila, P. On the road to lead free. Circuits Assem. April 2001, *12* (4), 34–40.
60. Tonapi, S., et al. Effects of flux and reflow parameters on lead free chip assembly. Proc. APEX, January 2001; AT5-2.
61. Bartelo, J.; Cain, S.; Caletka, D.; Darbha, K.; Gosselin, T.; Henderson, D.; King, D.; Knadle, K.; Sarkhel, A.; Thiel, G.; Woychik, C.; Shih, D.Y.; Kang, S.K.; Puttlitz, K.J.; Woods, J. Thermomechanical fatigue behavior of selected lead-free solders. Proc. APEX, January 2001; LF2-2.
62. Shina, S., et al. Selecting material and process parameters for lead-free SMT soldering using design of experiments. Proc. APEX, January 2001; LF1-1.
63. Susko, R.; McCullen, J. Peak reflow temperature vs. package volume for lead-free solder data. Presented at JEDEC/JEITA Meeting, Arlington, VA, September 17–19, 2001.
64. Richards, B.; Nimmo, K. Update 2000–an analysis of the current status of lead-free soldering—one year on, UK Department of Trade and Industry (DIT), London, www.lead-free.org/download/dti form 2000 html.
65. NEMI lead free interconnect project: statement of work, National Electronics Manufacturers Initiative, Herndon, VA, May 9, 2000, www.nemi.org/PbFreePUBLIC/index.html/.
66. Kallender, P. Lead a heavy problem at industry meeting. Print. Circuit Fabr. July 2001, *24* (7), 18.
67. Diepstraten, G. Five steps to successful lead-free soldering: step 5. Circuits Assem. August 2001, *12* (8), 47–54.
68. Hart, P.J.; Henderson, D.; Puttlitz, K.J.; Tonsi, N.; Sarkhel, A.; Woychik, C. Characteristics of some lead-free solder pastes for microelectronics package assembly. Semicon West 2000 (San Jose, CA) July 2000.
69. Panasonic Corporation, http://www.semicon,panasonic.co.jp/lead-free/e-index.html#menu1.

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2

Health and Environmental Effects of Lead and Other Commonly Used Elements in Microelectronics

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I. INTRODUCTION

A. Background

Lead is used in many aspects of human endeavor. The primary use is lead-acid batteries, with lesser amounts used in ammunition, fishing weights, electronic and non-electronic solders and components, cosmetics, stained glass, and medicines [1]. Some uses, particularly as an automotive fuel additive, have already been banned in most industrialized nations. Lead use in food canning has also been banned by many nations. Uses such as electronic solders are also banned, in the process of being banned, or becoming more closely regulated. Other toxic metals used in electronics such as silver and antimony are currently regulated by several nations' environmental authorities and may ultimately be further regulated or banned [2].

B. Health Related Factors

Lead and other heavy metals such as silver, copper, cadmium, lead and bismuth have been known to have toxic effects on humans and our environment since ancient time [3]. These metals have become mainstays in the electronic world in which we live. As a result, human and environmental exposure to these metals has increased significantly over the past several decades, leading to significant health concern and environmental degradation. Lead and other metals enter the environment and the human body through several routes, which environmental and health regulations seek to reduce or eliminate.

Several metals are essential to human and other life. Table 1 [4–6] categorizes these for humans into macronutrients, for which 100 or more mg/day are necessary for the body to function effectively and efficiently, and into micronutrients, which require only a few mg/day. Intake of less metal than required for the body to function adequately can result in both acute and chronic disease, while intake of excess metal can be toxic to the body, resulting in yet other diseases. The human body, as well as many animal and plant species, has metabolic pathways to remove the excess of some toxic metal elements. Animals and plants have their own essential metal requirements. If there are excesses or deficiencies in nutrient intake or the ingestion of

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TABLE 1 Metals Essential to Human Nutrition

Metal elements and human metabolic needs
Nutrient elements (100mg/day or more): Ca, Cl, Mg, P, K, Na, S
Micronutrients (no more than a few mg/day): Cr, Co, Cu, F, I, Fe, Mn, Se, Zn
Possibly essential micronutrients: Ni, Si, Sn, V
Generally recognized as toxic elements: Ag, Al, As, Ba, Cd, Pb, Hg

potentially toxic metals over time, vegetation, animals, and fish can adapt to degrading ecosystem conditions in their growth environment or discriminate against uptake; other species do not. The inability to discriminate can result in disease, diminished growth, and failure to reproduce. Some animals and plants accumulate metal elements in their tissues, referred to as bioaccumulation. Toxic metals bioaccumulated in the food web continue up the food chain to humans and other higher level consumers leading to disease, disabling effects, or death [7].

II. TOXICITY MECHANISMS

A. History

The toxicity of heavy metals, particularly lead, has been known since ancient times. In fact, pharmacology owes its early existence to the study of metal poisoning. The term pharmacology derives from pharmakon, which is the Greek word for poison [3]. Assimilation of heavy metals into the human body causes disruption in several biological processes. The mechanisms for these disruptions include heavy metal ions masquerading as beneficial metal ions as well as binding to active sites on biological molecules, thus rendering these molecules unable to perform their function.

Toxicology examines the dose and time-dependence of interactions between external agents (chemicals and elements) and normal metabolic agents. The first and most important principle of toxicology is that of dose-response, which states that there is a toxic dose and a safe dose for every external agent. Just as there are no inherently "safe chemicals" (safe under all conditions of exposure), there are also no agents that cannot be used safely by simply reducing the exposure.

B. General Effects

Lead is a divalent metal and often competes with other divalent ions such as iron, calcium, and zinc with respect to absorption and biochemical physiological processes. It may also substitute for the "normal" roles of some other ions, but with deleterious consequences. Overall, lead appears clinically to exert its toxic effects more in some tissues as opposed to others. The nervous, renal, and circulatory systems appear to be sites where lead has its greatest toxic impact. Furthermore, much like some other minerals, lead can cross the placenta and have consequences upon a developing fetus. Children are much more sensitive to lead's toxic effects than are adults; and governmental agencies in the United States and other countries have many special departments and programs to aid in reducing lead exposure in children's environments. Special concern has been given to the influence of even small levels of lead exposure in young children, and the effects it has on learning processes. Lead affects most organs and organ systems in the human body. Table 2 [4–6,8] displays a summary of its effects on human metabolism and organ systems.

C. Target Organs for Heavy Metals

Neurotoxin problems associated with lead ingestion are well documented as a major danger to young children [9]. Other organs are impacted by toxic exposure to lead and other heavy metals. A principle source is dust in homes that have lead-based paints or soils containing paint scrapings

TABLE 2 Effects of Lead on Human Organ Systems

Lead metabolism and toxicity	
Organ	Pathology
Central nervous system	Memory loss and learning difficulties
	Brain cellular morphology
	Neurotransmitter release
	Encephalopathy
	Cognitive intelligence
	Brain edema
Cardiovascular	Hypertension
	Cardiac electrical function
	Cardiac calcium use
	Cardiac Na/K metabolism
Blood	Hemoglobin synthesis
Kidney	Impairment of overall function
	Gout
Skeletal (Bone)	Development (skeletal as well as dental)
	Osteocalcin and protein synthesis
Reproductive	Spontaneous abortions
	Sperm morphology and count
	Pregnancy, gestation period, implantation influences

that children play on or transfer from hand to mouth. Vegetables grown in contaminated soils provide another pathway to the human population. In Eastern Europe, evidence of lead and cadmium toxicity in humans is found in populations living near smelter areas. This global problem has existed and still occurs from smelter and mining operations where economic development goals supercede environmental sensitivity and the health of at-risk populations [10].

1. Central Nervous System and Developmental Effects

Exposure to low lead levels in children can result in behavioral and learning difficulties. The ability of lead to have such dire effects at relatively low levels gives testimony to its reputation as a potent neurotoxin. Memory loss and learning difficulties have been the subject of numerous reports [9,11]. Several regions of the brain appear to be targeted by lead, including the hippocampus, the region of the brain most often associated with the cellular basis of memory and learning.

The developing nervous system is sensitive to lead, even when exposure has ceased the functional effects are long term and may lead to a permanent deficit. The mechanism by which lead may affect brain physiology and biochemistry could be due either to a direct influence upon nerve endings or by influence on neurotransmitter release in some fashion [4,6].

Depending on the level of lead exposure, children have been reported to have symptoms such as ataxia, convulsions, headache, and learning disabilities and tend to exhibit hyperactive behaviors. Encephalopathy has been reported in lead-toxic children. Learning and behavioral deficits in children have been reported. Blood levels of less than 10 micrograms per deciliter, which are comparatively low, could result in such deficits in children. Blood lead levels have demonstrated an inverse relation to the neuropsychological performance of children. Children 2 to 4 years of age had slower mental development as blood lead levels increased [4,6,9].

Lead has been shown to stimulate the release of dopamine, acetylcholine, and gamma-aminobutyric acid which are all essential neurotransmitters produced by the brain. Some of these effects may be due to the ability of lead to alter calcium entry into nerve cells or in some way cause

an increase in the intracellular calcium level. Lead may enter the cells through the calcium channels, while calcium channel blockers may inhibit lead uptake in the same cells. Lead is known to substitute for calcium as a second messenger and can bind to cellular proteins. Many proteins that would normally bind to calcium and other nutrient metals bind to lead when it is present. Calmodulin (a protein in the nervous system) has a greater affinity for lead than for calcium. These lead-protein complexes cannot properly regulate neurotransmitter levels, as do their nutrient metal-protein analogs. Lead activates brain enzymes that regulate voltage levels in the brain. This overactivation impairs learning in children.

The encephalopathy induced by lead toxicity is most likely due to a compromise in the blood-brain barrier. Brain edema occurs in the interstitial area and appears due to compromised blood vessels integrity. The brain capillaries and blood vessels have endothelial cells that contain tight junctions and act as a seal or carrier that excludes many plasma proteins and organic molecules and impedes Na and K exchange. Elevated lead levels disrupt these vessels, and plasma proteins such as albumin enter the interstitial spaces, as do some ions. This increases osmotic pressure, and water accumulates in response. The increased interstitial fluid flows into the cerebrospinal fluid. The edema causes in an increase in intracranial pressure and restricts blood flow to the brain. The direct mechanisms by which the blood-brain barrier and blood vessels that compose the barrier may be compromised may be due to astrocytes appearing to be vulnerable to the toxic effects of lead. The astrocytes cover the walls of the brain blood vessels, and lead can injure these structures.

2. Lead Effects on Blood

Exposure to toxic levels of lead leads to blood disease and anemia by: competing for absorption with elemental iron; inhibiting hemoglobin synthesis; and altering the relative composition of cell membranes, including red blood cells, making them more fragile and thus prone to premature breakdown and death. Lead and other heavy metals can also affect white blood cells, leading to a deceased capacity for immune system response.

Anemia is a classic indication of lead toxicity. Hemoglobin synthesis impairment results because lead can inhibit the enzyme that creates its predecessor molecules. This reaction occurs in the mitochondria; and is significantly impaired by lead toxicity. It is interesting to note that this enzymatic reaction does requires zinc, another metal element, to continue to completion, illustrative of the need for some metal elements in the human body but the exclusion of other toxic elements [4].

3. Renal (Kidney) Toxicity [4,8]

The kidney is also sensitive to lead exposure, with kidney failure resulting from long-term exposure to toxic levels of lead. Furthermore, toxic levels of lead inhibit other functions of the kidney aside from the primary function of urine production. The nephron of a kidney, which is that portion where blood filtering and urine production takes place, is sensitive to lead. It is well known that the active form of vitamin D^3 is produced in the proximal tubules of the nephron. Decreased levels of vitamin D3 in the body results in decreased calcium absorption by the gut, and ultimately affect the strength of bones in a lead-exposed body. Increased levels of lead in blood can lead to protein-lead complexes in the nephron tubules. Gout may be a symptom of such toxicity due to increased reabsorption of uric acid into the bloodstream. Typical measures of renal failure (e.g., blood urea nitrogen, creatine) are elevated as a consequence of lead-induced renal failure.

Other metals (e.g., calcium, copper, zinc, etc) have an impact upon kidney damage from lead toxicity. Some mitigate the effects of lead, while others magnify lead's toxic effects. Other heavy metals such as cadmium also attack the kidney.

4. Cardiovascular Toxicity

Lead has been linked with hypertension by some epidemiological studies. Even low levels are associated with elevated blood pressure [4]. Some of lead's influence upon blood pressure may also be related to renal toxicity discussed previously. Calcium and lead are known to have antagonistic biochemical roles, as previously discussed regarding brain protein binding. However, the influence of calcium upon lead-induced increases in blood pressure appears paradoxical.

Feeding rats a high level of calcium does not appear to block or dampen the effect of lead hypertension. [5,8,9]

5. Bone Integrity

Lead has a high affinity for bone, partly due to its antagonistic relationship with calcium. The greatest amount of lead in the body is the skeleton, which acts as a reservoir for lead. The influence of lead upon bone must be considered from the perspective of vitamin $D_{3,}$ the metabolism of which is significantly altered in lead toxicity. Bone structure is in a constant state of self-renewal, with continual controlled destruction, reduction, and rebuilding. Lead is known to influence the various biochemical and physiological events involved with this process.

Lead may accumulate in bone beginning in fetal life. Young children with growing bones are apparently more susceptible to the toxicity of lead than are adults. Impaired dental development and delayed skeletal maturation have been reported in congenital lead poisoning cases. In children, the NHANES II (second National Health and Nutrition Examination Survey) study documented decreased height and chest circumference with increased blood lead levels for children 7 years and younger [9]. Levels of plasma osteocalcin, a bone protein, are lower in children exposed to toxic levels of lead [4]. Bone matrix synthesis is impaired with low-to-high lead exposure. Bone formation rate and healing from fractures are both decreased with exposure to lead. Bone structures may also be less dense. Many of the processes of bone turnover are not only attributed to the direct influences of lead on bone dynamics; but also indirect mechanism, as lead may influence hormones targeting calcium and bone metabolic processes. The active form of vitamin $D_{3,}$ 1,25-dihydroxycholcalciferol, appears to be lower in children with elevated blood lead levels.

6. Reproductive Toxicity

Toxic quantities of lead in the human body impact the reproductive processes of both men and women. An increased incidence of spontaneous abortions has been documented in female lead workers and in the wives of male lead workers, i.e. persons working in lead smelting or manufacture of lead containing products. Male lead workers with blood lead concentrations of 53 to 75 ug/dl have been reported to have decreased sperm counts as well as altered morphology of the sperm. [4].

D. Elimination from the Human Body

Metals are elements- they cannot be detoxified. They are already in their simplest state and cannot be changed, other than their valance. The toxic activity of metals is thus not mitigated in the body by biotransformation as it can be with organic pollutants such as pesticides. Biotransformation includes processes that change the toxin into another chemical agent, which tends to be less toxic. Excretion is therefore the major process by which the body removes the threat from metal exposure. Sequestration is the most effective for mitigation of metals toxicity in the body. It is a process whereby a metal ion is moved to a site and placed in "metabolic storage" so that it cannot move to and act upon a vulnerable metabolic site. The human body also has several processes with which to excrete or otherwise remove heavy metals. Once having gained access to the human body, metals undergo diverse but sequential mechanisms of absorption, distribution, sequestration, biotransformation and elimination. These considerations apply irrespective of the mode of entry to the body. This whole chain of events in its entirety, designated the biodynamics of a substance, is depicted in Figure 1 [9]. Central to processes for toxin removal from the body is the blood stream. It serves as the medium both for uptake of metals for distribution through bodily tissues and for removal by excretory routes. Removal of foreign substances and metabolites already absorbed into the body is achieved in a variety of ways. The principal routes of exit are via the kidney and the bile, while excretion into feces, sweat, saliva and breast milk represent minor routes of elimination.

Exercise of a toxic or nutrient effect of a metal primarily depends on its ability to enter the body and then move to sites within the body where it can have an effect (i.e. replacement of calcium in bone). The ability to reach a site is mitigated by the balance between the relative rates

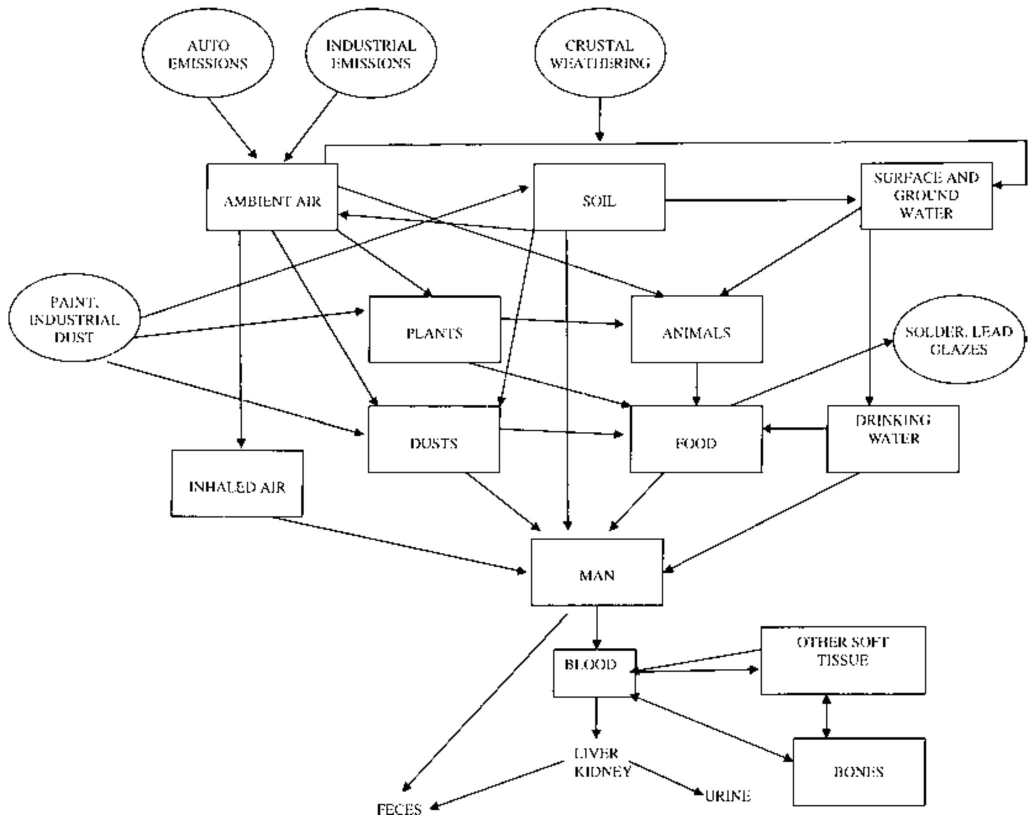

FIG. 1 Biodynamics of lead in the human body.

of opposed biodynamic processes to remove metals and other exogenous substances from the body. Some processes in the body improve absorption of lead and thus facilitate the ease which any compound reaches metabolic sites (moisture on mucous membranes).

1. Respiratory Tract

Metals can be removed from the body while still in the respiratory tract and not yet absorbed. The walls of the nasal passages are lined with mucus membranes. Nose blowing, sneezing, and coughing each act to remove particles from the body. In the lungs both scavenger cells and cilia help to move metal particles up the respiratory tract to where the physical actions mentioned above then remove the particles.

2. The Renal System

Three separate processes in the kidney, consisting of ultrafiltration, passive reabsorption, and active secretion regulate kidney excretion. Kidney function is efficient for polarized molecules such as salt (sodium chloride). Non-ionized foreign substances such as metal ions bound to proteins are subject to passive reabsorption into the blood stream after delivery into the kidney. This results in a low net rate of excretion for these substances, in contrast to more polar, lipid-insoluble molecules. Consequently, metabolic conversion of a compound into one with a higher polarity, favors excretion. Manipulations of this kind may be beneficial in the prevention of poisoning by certain substances. Protein binding constitutes another factor determining the speed of removal of foreign compounds by the kidney. When lead is tightly bound to proteins, as is the case with the previously discussed brain proteins, excretion by the kidneys is reduced.

3. The Liver and Bilary System

Toxic metabolites formed in the liver may be secreted into the bile. A portion of these may enter the intestinal tract and eventually undergo fecal excretion. A larger portion is usually reabsorbed by the intestines to be transferred to the blood, and thence to the kidney. Extra-hepatic circulation, which consists of passage of the compound via the liver back to the gall bladder, and its ultimate degradation by gut bacteria, also takes place. Thus, biliary excretion may lead to three distinctive terminal processes: fecal excretion, enterohepatic circulation and enterobacterial metabolism.

4. Other Species Metal Elimination and Synthetic Aids to Elimination

While the processes for excretion of heavy metals are reasonably well developed in humans, they do not exist in all species; and have limitations in humans as well. In fact, the active processes undertaken by organs such as the kidneys to excrete metals also causes a breakdown of sensitive tissues and structures within the kidney, leading to chronic disease if exposure to the metal continues. Many animal and plant species simply store the metal elements as ions in their tissues. When these animals and plants die or are taken by a higher-level consumer as live prey, the stored metals enter the food web. As higher-level consumers ingest greater quantities of the metal, metal elements become magnified in the food web.

Excretion can be assisted in humans and many other animal species. Ethylenedinitrilotetra-acetic acid (EDTA) is a common chelating agent, which is infused via the bloodstream into patients in order to remove metal ions from the body. Chelation refers to the formation of metal complexes by bonding a chelating agent or ligand with a metal to form a heterocyclic ring. Initially, the medical use of chelating agents was to treat heavy metal poisonings, for example, British Anti-Lewisite (2,3-dimercaptopropanol) for arsenic poisoning. EDTA was also used to treat lead poisoning in a young child [12] and following its initial approval by the Food and Drug Administration (FDA) in 1953, EDTA was utilized to treat other heavy metal poisonings. EDTA chelates various divalent metal ions with differing affinities. It is excreted mainly by the kidney, with about 50% excretion in one hour, and more than 95% within 24 hours. Almost none of the compound is metabolized. This inability to be metabolized coupled with its excretion by the kidney makes EDTA an excellent agent for removal of heavy metals from the human body [13].

III. EXPOSURE ROUTES

Lead and other heavy metals enter the human body as well as the ecosystem at large via several routes. Human exposure to lead typically occurs through ingestion rather than inhalation or other routes. United States Environmental Protection Agency (USEPA) and other regulatory agencies' air quality standards, solid waste disposal regulations, and drinking water standards are based in part on this proportion of exposure in the general population. These routes have some amount of crossover exposure such as airborne lead falling onto plants and other surfaces from which subsequent ingestion occurs.

A. Air

The human respiratory system has the two primary functions of delivering oxygen to the bloodstream for delivery to tissues and removal of carbon dioxide, a waste product of cellular metabolism. The respiratory system is vulnerable to contaminants in the air including heavy metal particles. In addition to loading the lungs with metal, inhaled metal particles make their way into the digestive system as mucus from the respiratory system is swallowed. Lead in the atmosphere and in soils near heavily traveled roads has been eliminated as a source in many countries by the use of unleaded gasoline; however, lead contaminated soils adjacent to these roads are still in place. Inhaled dusts from these roads provide a means for lead to be inhaled. Another source is lead smelter operation. Much smelter-originated atmospheric lead has been eliminated from the atmosphere by terminating operation of some smelters and by utilization of chemical scrubber-electrical precipitator systems in chimneys of modern or modified operations.

Many older smelter operations still load the atmosphere and the surrounding soil with lead and other elemental species such as arsenic, cadmium, chromium, mercury, nickel, vanadium, and zinc. This source of inhalable metals is mostly associated with old mining operations, heavy metal industries, oil refineries and energy generation facilities. However, in highly environmentally regulated societies such as Western Europe, the United States, and Japan, airborne exposure to lead has decreased significantly over recent past decades. An excerpt from the USEPA performance standards for lead smelters is found below. This portion of USEPA regulations moderates the amount of particulates, which would be expected to contain lead that can be discharged into the ambient air from a lead smelter [14].

> §60.182 Standard for particulate matter.
> (a) On and after the date on which the performance test required to be conducted by §60.8 is completed, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any blast furnace, dross reverberatory furnace, or sintering machine discharge end any gases which contain particulate matter in excess of 50 mg/dscm (0.022 gr/dscf).

B. Ingestion

Ingestion of lead-based paint is the primary cause of lead poisoning of children in the United States, according to the Centers for Disease Control [15]. The mouth, stomach, and intestines are all capable of lead absorption, which ultimately transport the metal to the bloodstream. Other toxic metals can also be absorbed after ingestion, to greater or lesser degrees.

1. Route and Body Destinations

Once absorption is completed, the substance enters the circulatory system, leading to its distribution throughout the body. Access into the tissues of the body is not gained until the substance has passed across various tissue boundaries and cell membranes. These boundaries and barriers behave as typical fat-containing membranes; therefore, in order for substances in the environment, such as metals, to pass through these barriers, they must possess certain chemical properties such as non-ionization on an atomic level and low polarity on a molecular level. From an ingestion standpoint the barriers in the lining of the stomach, remainder of the gut and placenta are of greatest importance [16].

2. Uneven Distribution

Various parts of the body have a greater or lesser affinity for various metals and this affects the extent and areas of distribution in the body. Generally speaking, foreign compounds and metals are unevenly distributed among the various tissues, and selective accumulation at particular locations is the rule rather than the exception. The target tissues or organs where the compound exhibits its characteristic activity often are not those with the greatest accumulation of foreign compounds or metals. In fact, foreign compounds are usually segregated in non-sensitive tissues such as fat layers, which function as storage depots. The fat layers allow for the accumulation of toxic compounds and metals that it then releases. Fatty tissues, connective tissues, and the skeleton are specifically adapted to serving as reservoirs for toxic agents.

3. Exchange and Transport

Materials deposited in storage areas are constantly exchanged with circulation. Blood serum proteins function as major carriers for the transport of foreign molecules, especially in the case of fat-soluble materials such as DDT and its metabolites (pp' DDE), and fat-soluble compounds of toxic metals. For metals in particular, transport requires preliminary binding between a protein and a metal compound to be stored or transported. Protein binding, also termed sequestration, is a reversible process the degree of which is governed by the affinity of a foreign compound for specific receptor sites on a protein. Since only the unbound (free metal) form is freely transported across a cellular membrane, dissociation of the sequestrated molecule is necessary to effect passage through cellular membranes. In short, metals must be bound to a protein in order to be

carried to a target site or storage depot, but must disassociate in order to pass through a cellular membrane and actually enter the cell once at the site. As mentioned above, metals that remain in the bloodstream are excreted at a slow rate, or stored and thus rendered harmless.

4. Drinking Water

Drinking water is another avenue for the ingestion route of exposure to lead and other metals. Lead occurs naturally in some drinking water supplies. Lead also enters the drinking water supply through both natural and human sources. Treated drinking water leaches lead from the pipes of the drinking water distribution stream. This is believed to have been the primary means for lead poisoning of citizens of the Roman Empire. Lead pipes distributed drinking water to baths, fountains, and other end uses. Lead-containing solders have been banned from commercial and household piping in many countries since the 1970s to prevent lead exposure through drinking water. In addition, the USEPA and other environmental agencies have put into place regulations which require drinking water treatment facilities to ensure that drinking water has an appropriate pH and other chemical factors to assume a low propensity to leach lead from pipes. These regulations are a portion of the Lead and Copper Rule [17], whose purpose is to help minimize the levels of lead and copper in drinking water. Other environmental authorities worldwide have adopted similar rules and regulatory levels of these metals that are listed in Table 3. The USEPA has set action levels of 0.015 mg/L for lead and 1.3 mg/L for copper, or Maximum Contaminant Level Goals [17,18] established by the Lead and Copper Rule ("the rule"), which are 0 mg/L for lead and 1.3 mg/L for copper. This rule includes basic requirements for drinking water treatment facilities to optimize corrosion control (lead and copper leaching from the water distribution pipes) and, if appropriate, treat source water, provide public education, and replace lead service lines. Appropriate actions must be taken if the drinking water fails to meet the action levels cited. Metal content measurements are taken at end user's (homes, schools, etc.) tap. Over the past several years, many worldwide environmental agencies have lowered the allowable lead concentration in drinking water from 0.050 mg/L to 0.015 mg/L. A few agencies have continued to lower the maximum allowable level, and with many setting a lead concentration goal of zero, or undetectable in drinking water. Lower allowable levels are being put into practice, as the effects of lead, especially on children, are now better understood.

A large percentage of the worldwide population obtains its drinking water from underground sources rather than lakes or streams. Pollution of these groundwater sources by metals

TABLE 3 Worldwide Regulated Levels of Lead in Drinking Water

Element	Limit, mg/L	Source
Indium	None found	
Bismuth	None found	
Tin	None found	
Silver	0.10	USEPA 40 CFR 141
Antimony	0.006	USEPA 40 CFR 141
Antimony	0.002	Japanese legislation
Antimony	0.005	98/83/EEC
Copper	1.0	USEPA 40 CFR 141; Japanese legislation; Thai legislation
Copper	2.0	98/83/EEC
Lead	0.015	USEPA 40 CFR 141
Lead	0.05	Japanese legislation; Thai legislation
Lead	0.010	98/83/EEC
Zinc	1.0	Japanese Legislation
Zinc	5.0	Thai Legislation

such as lead causes potential harm to these populations. One source of this pollution is improper solid waste disposal. World Health Organization (WHO) and USEPA scientists estimate groundwater accounts for more than 95% of all fresh water available for use worldwide. Approximately 50% of the United States population obtains all or part of their drinking water from groundwater, with nearly 95% of rural residents relying on groundwater for their drinking supply. About half of irrigated cropland on United States farms uses groundwater and approximately one third of industrial water needs are fulfilled by using groundwater [19]. The issues related to solid waste disposal and contaminated drinking water are discussed in detail in Section 2.4.

5. *Food*

In most cases, food is not a significant avenue of lead exposure. Lead-free solder is used in canneries to ensure that lead is not leached from the canning materials by acidic foodstuffs. One area that lead can pose a hazard to the food supply is lead-coated cookware and tableware. In many countries lead continues to be used as a pottery colorant and glaze. Acidic foods can leach and absorb lead from these decorated surfaces. Crops can absorb lead and other metals into their edible parts. Table 4 lists some examples of metal contamination in crops.

C. Direct Contact

Lead can also become a health issue through direct contact, which then leads to ingestion and to a much lesser extent, absorption through the skin. The primary route of exposure by direct contact has been chips and dust from lead-based paint. Infants and children make contact with lead chips and dust as lead containing paint flakes off painted surfaces and onto the floor and other horizontal surfaces. Infants and children collect the chips and dust on their hands, feet, clothing, and hair. When the children eat or place their hands in their mouth, lead ingestion occurs. Children exposed to lead are at risk to several health problems including developmental and neurological impairment. Lead poisoning has been linked to mental retardation, poor academic performance and juvenile delinquency. It is estimated that nearly one million children in the United States alone have dangerously elevated levels of lead in their blood [9]. Because of the potential dangers, any exposure to deteriorated lead-based paint presents a hazard. Lead, to a much lesser degree, can absorb through the skin. Direct contact is a minor exposure route, and effects primarily industrial lead workers rather than the public. These workers are normally protected against lead exposure, at least in industrialized countries.

D. National Standards

In the late 1990s, the USEPA published new national standards to identify dangerous levels of lead in paint, dust and soil. These standards provide homeowners, school and playground administrators, childcare providers and others with guidelines to protect children from hazards posed by lead. The standards provide the general public benchmarks for remedial actions to safeguard children and the public from the dangers of lead. The standards also apply to other Federal lead provisions, such as the EPA's real estate disclosure requirements when selling or

TABLE 4 Metal Contamination in Crops

Metal element	Edible plants that accumulate this metal
Cadmium	Lettuce, Spinach, Celery, Cabbage
Lead	Kale, Ryegrass, Celery
Copper	Sugar Beet
Nickel	Sugar Beet, Ryegrass, Turnip
Zinc	Sugar Beet, Spinach

TABLE 5 Lead Standards for Real Estate (United States)

Media	Maximum lead concentration allowed
Dried paint, applied, surface area	1.0 mg/cm^2
Dried paint, applied, by weight	0.5 percent by weight
Dust, on residence floor	40 $ug/foot^2$
Air	1.5 ug/m^3
Soil, bare, childrens' play areas	400 mg/kg (parts per million)
Soil, bare, surrounding a residence (average concentration)	1200 mg/kg (parts per million)

renting a home or apartment. These hazard standards also provide guidance for other EPA programs engaged in toxic waste cleanups. These standards also provide landlords, parents, and childcare providers with specific levels on which to make informed decisions regarding lead found in their homes, yards, or play areas as noted in Table 5. Under the new standards, lead is considered a hazard if there are greater than: 40 micrograms of lead in dust per square foot on floors; 250 micrograms of lead in dust per square foot on interior window sills and 400 parts per million (ppm) of lead in bare soil in children's play areas or 1200 ppm average for bare soil in the rest of the yard. The standards allow inspectors and risk assessors to assist property owners in deciding how to address problems which may include lead paint abatement, covering or removing soil or professional cleaning of lead dust. Lead in dwellings is normally abated by sealing it, which may be as simple as repainting the area from which lead dust is flaking, or by removing and disposing lead-containing building materials. Both methods significantly reduce or eliminate direct contact with lead-containing paint chips and dusts.

E. Mobility

The mobilized form determines the route (s) of exposure to plant and animal life: gases or vapors that evaporate or sublime from liquids or solids, dust or fumes, solid metal or metal oxide particulates on or in the soil, and dissolved in aqueous media. Whether the ions or ionic and anionic complexes are mobilized or precipitated and then perhaps remobilized, is dictated by changes in physical, chemical and biological conditions in source areas and areas where the metals are ultimately deposited. In soils and sediments the controlling parameters that influence mobility and deposition of metals are many. These include: pH, redox potential, concentrations, chemical gradients, cation exchange capacity (CEC) of the soil/rock, presence of clay minerals, Fe/Mn oxyhydroxides, adsorption-desorption, and bioaccumulation. The interaction of these parameters and varying responses of metals to them can make prediction of environmental influences complex. In fact, somewhat random factors such as animals can have a significant impact on the transport of metals and other pollutants. No models have yet been devised to consider all these factors. As with all pollutants, it is best to minimize migration from the source into the environment. The element chromium, for example, is tightly bound in the residual phase and not easily mobilized, whereas cadmium has more distribution in easily soluble and exchangeable phases than the other elements considered.

IV. SOLID WASTE DISPOSAL AND CONTAMINATED WATER

A. Landfill Issues

Research indicates that other metals currently used in electronics, as well as those contemplated as replacements for lead in electronics, are leachable into landfill leachates [20,21]. The clean up of metal-element polluted aquifers is a very costly affair and yet necessary to prevent present-day and future metal exposures. Landfill leachate escapes through poor landfill construction and

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design, breaks in the landfill liner, or overflow due to excess leachate in the landfill, typically from rainfall (Fig. 2). All modern landfills have leachate treatment systems, but these can be overloaded through heavy short-term rainfall or treatment system malfunction. If not quickly corrected the escaped leachate may migrate into the surrounding surface soil or below the surface. This can lead to the pollution of private and communal water wells, or the seepage of polluted groundwater into surface water where it can directly cause visibly detrimental environmental effects. Aquifer remediation may take a long time, since the pore volume of an aquifer must be flushed a number of times to remove metal pollutants, which adsorbs to the soil and rock.

B. Contamination Mechanisms

The United States Environmental Protection Agency (USEPA) has found waste sites in which lead-containing wastes disposed in landfills did leach and reached environmental receptors located beyond the landfill area [22]. Leaching from landfills is the primary means by which human activity causes lead and other toxic metals to enter groundwater. When solid wastes are disposed in landfills, rainfall and chemical reactions within the wastes release metal elements within the waste. These reactions occur because rainwater is acidic after dissolving nitrate and sulfuric radicals from the air as it falls, and because putrification reactions (rotting) of food wastes produce acidic byproducts such as acetic acid. These acids leach the metal elements from waste items, such as lead from electronic wastes, and the rainwater carries the metals into the leachate that collects within landfills. Thus, groundwater and solid waste disposal are grouped together in this chapter. A search of the USEPA Superfund NPL Assessment Program database for USEPA Region Two (northeastern United States) shows leachate from three landfills, which contains

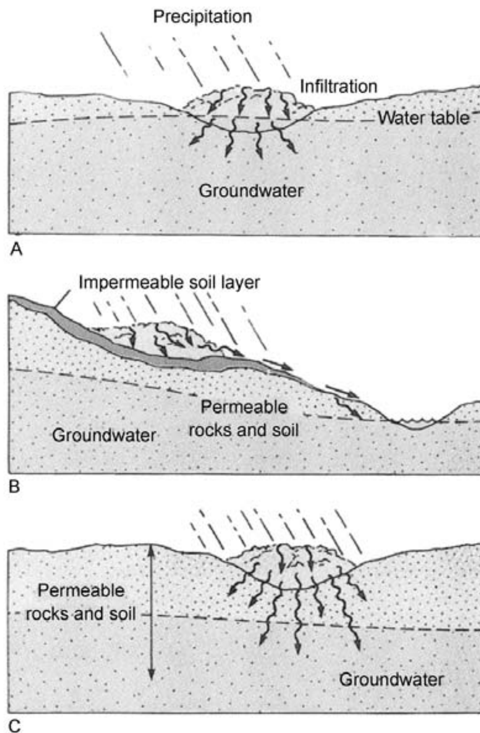

FIG. 2 Release of toxic metals via landfill breakage or flooding. (After Smith and Swanger, Ref. [20], 1999.)

lead and/or other heavy metals; and this leachate has reached groundwater or surface water. The data also showed two landfills where leachate is heavy metal contaminated, but has not yet reached groundwater or surface water sources. Sites in Harris County, Texas also show groundwater lead contamination via improperly managed activities over the area of the aquifer [23]. As a result of these sites with contaminated groundwater, USEPA and State environmental agencies have enacted regulations regarding disposal of hazardous materials as well as recycling. Both regulations and recycling tend to minimize exposure of groundwater to potential contaminants released from a landfill. When released, leachate may move across the land surface or into the subsoil, or both. If the leachate is contaminated with metal ions or compounds, these may deposit into the surface soils or move through the subsurface soils and rock. The rate of metal movement depends upon the geology of local soils and rock. If we look closely in the pores of topsoil (Figure 3), we see that many reactions are occurring while groundwater is generated from rainwater, and while leachate moves over the soil.

1. *Leachate Reactions*

The most important leachate reactions are dissolution and precipitation of solids and minerals, redox (reduction/oxidation) reactions with organic matter, and ion exchange and sorption on clay minerals and organic matter.

Metal element concentrations in surface and near-surface earth systems and the atmosphere are the result of mobility, precipitation, and deposition of free ions, ionic compounds and anionic complexes of those metals.

a. Effect of pH. The pH factor is critical in the geomovement of metal contaminants [24,25]. Under acidic conditions, metals such as Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn become more soluble and mobile. This enhances their uptake by grasses and other vegetation. Increased acidity (decreased pH) also increases the amount of dissolved organic carbon in soils, swamps, or wetland environments. Under oxidizing conditions in nature, decomposing organic matter releases associated metals and causes greater acidity, in much the same manner as man-made waste disposal landfills. The acidity increases the mobility of the metals cited above. Conversely, increases in pH to basic conditions establish a geochemical barrier, so many toxic metals with low solubility constants (K_{sp}) are immobilized and their uptake by vegetation is restricted. For example, a pH rise from 7.4 to 9.0 in aquatic systems favors the adsorption of Zn, Cr and Cd onto suspended matter. Indeed, liming of agricultural soils increases pH and dissolved organic carbon; and can immobilize metals, including lead, that are potentially harmful to crop growth or because of their movement through the food chain into feed and food crops. At the same time, however, other metals such as molybdenum can be mobilized and made bioavailable to fodder.

b. The Redox Factor. Metals may have different mobility responses when a reduction-oxidation (redox) factor is combined with pH as summarized in Table 6 [24]. As examples arsenic

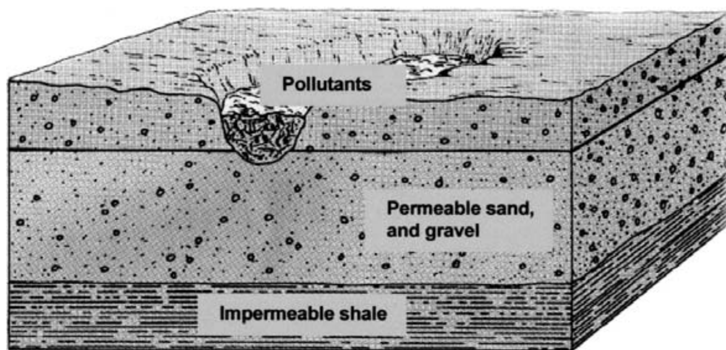

FIG. 3 Topsoil structure and porosity allows pollutants to enter groundwater. (After Smith and Swanger, Ref. [20], 1999.)

TABLE 6 Metal Mobility at Various pH and Redox Levels

Metal Element	Mobility Favored at pH	Mobility Favored Under Conditions	Best Combination for Mobility	Precipitates in Reducing Environments with Sulfide
Cadmium	lower	oxidizing	near pH = 6, mildly oxidizing	Slightly
Chromium	lower	oxidizing	low pH, highly oxidizing	Slightly
Copper	lower	oxidizing	pH = 4, highly oxidizing	Yes
Manganese	lower	reducing	low pH, highly reducing	Slightly
Nickel	lower	oxidizing	near pH = 6, mildly oxidizing	Yes
Lead	lower	oxidizing	pH = 4, highly oxidizing	Yes
Molybdenum	higher	reducing	low pH, highly reducing	Yes
Mercury	slightly lower (pH = 6)	oxidizing	near pH = 6, mildly oxidizing	Yes
Zinc	lower	oxidizing	pH = 4, highly oxidizing	Yes

and manganese, increase in mobility with decreasing pH and greater reduction potential (to As^{3+} and Mn^{2+}); Fe^{2+} and Mo as Mo^{2+} react similarly. Under weakly acidic conditions (about pH 6) the elements Cd, Ni and Hg possess increased mobility. With decreasing pH to four or less, soil borne zinc, copper, and lead mobilize as does Fe and Mn at pH of less than two. Under reducing conditions and in the presence of sulfide, chalcophile elements such as zinc, copper, iron, mercury, nickel, lead and others precipitate as sulfide mineral phases. Changes in oxidation or reduction potentials in a subsurface environment can lead to the separation of elements. The separation may be geographic due to changing reduction potential from decaying organics and bacterial activity. Thus, in many subsurface environments some metals are immobilized and precipitated under conditions where others are still mobile and transported to precipitate elsewhere. Natural pH values for most soils are in the range of about 3 to 8.5 and redox potentials from −0.35 to +0.8. Shallow sub surfaces waters have more restricted ranges with pH from 5.5 to 8.5 and redox potentials from −0.08 to +0.6 resulting in a wide range of metal element transport behaviors.

c. Cation Exchange Capacity Factor. The concentrations and chemical gradients of metals in the soil and rock have an effect on their speed of transport. Just as in any free liquid medium, diffusion of metals occurs at some maximum rate. Concentrations of ions that compete for adsorption sites or in other ways hamper the diffusion process, can impact the speed of transport through a soil or rock medium. Cation Exchange Capacity (CEC) also impacts a soil's ability to adsorb and retain metal ions. The CEC of a soil refers to the amount of positively charged ions a soil can hold. When dissolved in water, the resulting metal ions have a positive charge. Soils have a slight excess of negative charge sites due to the presence of clay particles and organic matter. Therefore, the higher the clay and organic matter content, the higher the CEC of the soil. Soils with a high CEC tend to hold onto positively charged nutrients better than soils with a low CEC. The CEC of a soil can be increased somewhat by increasing the soil's organic matter content and by increasing the pH of a soil. A higher CEC is an indicator that a soil can hold and retain a higher concentration of metals compared to a soil with a lower CEC.

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d. Adsorption and Retention. Adsorption is a function of the density of unsatisfied surface charges on colloids and clay-size particulates. The charges may be negative in the case of clay minerals, manganese oxyhydroxides and organic colloids (especially humic compounds), thus providing absorption sites for cations including heavy metals. Unsatisfied charges may also be positive as is the case for iron oxyhydroxides and provide capture sites for anionic complexes such as arsenate, molybdate, chromate, vanadate, and phosphate. Like pH and redox, adsorption capacity varies with environmental conditions. For example, oxyhydroxides have the strongest adsorption sites followed by particulate organics and clay minerals. The presence of clay minerals can have a great impact on metal transport, especially in soils in which clay minerals dominate. The clay minerals act on metal transport in two ways. One is the adsorption of the metal ion; the other is the physical barrier that high-clay soils create to the movement of liquid contaminants. It is a common practice to use clay soils in landfill construction, and for temporary barriers in construction projects. This is due to the poor permeability of high-clay soils, especially those with little-to-no sand particle content. These soils exhibit permeability as low as 1×10^{-6} milliliters of water per day per inch of soil compared with rocky soils may have a permeability of several milliliters of water moving through an inch of soil per day. In addition, adsorption of most metals increases with increasing pH as is predictable from the mobilization of metals in soils or sediments discussed earlier.

There is a finite capacity of soil or rock to store metal contaminants under any set of conditions. When this capacity is exceeded, the contaminant may diffuse into the surrounding soil or rock. If the conditions change to decrease the level of adsorption or increase the level of desorption from the soil or rock, there may be a release of contaminants into the surroundings. For example, peat is a known accumulator of metals. Peat is acidic and has sulfide present, so precipitates metals such as lead as lead sulfide. For example, in one case adjacent river waters, with a basic pH, flowed into a peat deposit area and allowed the precipitated metals to be released. This resulted in declines of forests and fish stocks in the adjacent wetlands. In addition, the impact of metal contamination on some parasites and predators lessened the natural control of forests pests [25].

e. Biomethylation and Bioaccumulation. Biomethylation or the microbial mediated formation of organometallic compounds from inorganic precursors is an important process that affects the toxicity potential of several metals. It creates the toxic species of Hg that enter the food web as CH_3Hg^+ or $(CH_3)Hg_2$ after its release from a microbe cell. Other metals which undergo biomethylation in minor amounts include As, Cr, Sb, Se, Sn and T1. Biomethylation is stimulated in minor waters, which are slightly acidic, rich in organic matter and have high bacterial activity. Related to biomethylation is bioaccumulation. Both plants and animals bioaccumulate metals under certain conditions. In this process, metal ions undergo uptake by an organism. This organism may or may not suffer ill effects from the metal intake. If this organism is later ingested by another organism higher in the food web, then the metal may bioaccumulate in this second organism, as more food contaminated with metal is eaten. Ultimately the metal concentration per unit of body weight increases until at some point on the food web the organisms at that level suffer an ill effect. These may be low-level effects such as stunted growth, reduced ability to reproduce, or higher-level and more visible effects such as death.

V. TOXICOLOGY OF ELECTRONIC MATERIALS

Management of waste in industrialized countries ranges from highly regulated, specific, government-controlled operations to practical non-existence. Most industrialized countries that significantly regulate industrial/commercial hazardous waste fall within this range. This includes those that do or do not regulate household hazardous waste disposal. 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" [26]. When waste is disposed, 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 storm water, groundwater, or to migrate into groundwater, local drinking water supplies are threatened with contamination.

A. Definition of a Hazardous Substance

1. United States Government Agencies

a. USEPA. The USEPA identified four characteristics of hazardous waste: 1) toxicity, 2) corrosivity, 3) reactivity, and 4) ignitability. EPA also developed standardized procedures and criteria for determining whether a waste exhibits one of these characteristics. These characteristics and criteria are codified at 40 CFR Part 261 [26]. Testing procedures are detailed in SW-846 [24].

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.

b. USDOT. The United States Department of Transportation (USDOT) has published its own hazardous classification system based on impact to human safety and health in the event of a mishap in the transportation system. The hazard class of dangerous goods is indicated either by its class (or division) number or name. For a placard corresponding to the primary hazard class of a material, the hazard class or division number must be displayed in the lower corner of the placard. However, no hazard class or division number may be displayed on a placard representing the subsidiary hazard of a material. For other than Class 7 or the OXYGEN placard, text indicating a hazard (for example, "CORROSIVE") is not required. Text is shown only in the U.S. The hazard class or division number must appear on the shipping document after each shipping name. [Appendix I]

2. European Union and Other Organizations Worldwide

The European Union as well as many governments worldwide utilizes United Nations regulations for definition and shipment of hazardous materials. These requirements are developed by the United Nations Committee of Experts for transport of all types of non-radioactive dangerous goods. Other organizations such as the International Airline Transport Association (IATA) turn these requirements from the United Nations into operational and technical requirements and practices.

B. Electronic Materials Toxicity

The study of the relative toxicity of various metal elements used in electronics is important as the industry evaluates new solder alloys and new component materials. The Surface Mount Council reported various elements comprising lead-free solder alternatives [27] (Table 7). Based on this and other data cited in the report, toxicity ranking assigned to the common lead-free solders alloying elements are as follows:

Every cited environmental, health, and safety organization worldwide classifies lead containing materials as "dangerous," "hazardous," or by some other similar term. Some organizations place a maximum allowable concentration limit for lead on materials above which they are noted to be "dangerous" or some similar classification. These classifications form the basis for environmental, occupational safety, and other regulations pertaining to lead. Other metal elements used in electronics are regulated for waste disposal and/or occupational exposure in many jurisdictions worldwide as discussed in the following sections. As metal exposure to humans is discussed, it is important to remember that environmental contamination is a significant variable. For example, rural populations that would see little to no metal exposure can be given

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TABLE 7 Summary Results from the Surface Mount Council Study. (After Allenby, et.al., Ref. [27],1999)

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

Note a: OSHA PEL; Note b: ACGIH TLV; Note c: ACGIH TLV is 0.15 mg/m^3.

harmful doses of metal through drinking water contamination arising from nearby mining operations with improper mine waste disposal.

C. Lead

1. *Sources from Electronic Assemblies*

Lead exposure and use in electronic assemblies is mainly associated with printed wiring boards (PWB), solder joints, and the electronic components themselves.

a. Components. Several classes of electronic components contain lead either as part of their active and functioning elements, or as part of their interconnection structure. Piezoelectric devices often use lead in their piezo elements inside the device casing. Most devices produced today use a metallized surface finish on their solderable surfaces. This surface finish has traditionally been tin-lead solder, but sometimes consists of palladium, pure tin, or other lead-free alloys.

b. Printed Wiring Boards. Most printed wiring boards produced today use tin-lead surface finishes on their solderable surfaces. Although alternative surface finishes are increasing in use, tin-lead solders finished pads and through holes are still the norms worldwide. Thus, a finished printed circuit board may have lead in the printed wiring board, the components, and to attach the solder joints themselves if lead is used as part of the solder paste in the wave machine to attach surface mounted components or pin-in-hole components.

c. Cable Sheathing. Some cable sheathing utilizes lead to enhance thermal stability, ductility, increase weight for density intense applications, or to decrease susceptibility to corrosives. If the sheathing is exposed, lead is easily leached from the sheathing surface.

d. Monitors. Portions of computer monitors and other cathode ray tube driven devices contain lead. Cathode ray tubes (CRTs) are often referred to as being a hazardous waste because of the leaded glass of which they are constructed. A study involving 36 CRTs was conducted at the University of Florida [28] to quantify the leachable lead from CRTs using the USEPA's toxicity characteristic leaching procedure (TCLP). The study revealed that the color CRTs leached approximately 18.5 mg/L, well above the USEPA limit of 5.0 mg/L of leachable lead, thus characterized as hazardous waste. None of the monochrome CRTs exceeded this limit. Most jurisdictions in industrialized countries have put recycling programs into place for television sets and computer monitors to reduce this source of leachable lead in municipal landfills.

e. Batteries. By far the most prevalent use of lead worldwide is in the production of batteries for electrical energy storage [29]. Over half of worldwide lead consumption goes into

battery production. In contrast, approximately 0.6% of worldwide lead consumption goes toward electronics manufacture. Lead batteries do undergo one of the oldest and most successful recycling programs worldwide, thus their impact to the environment is not as great as their proportional use relative to other lead uses such as ammunition. Ammunition by its nature and use is non-recyclable.

2. Blood Levels

Lead in the human body can be measured through several media and organs. Lead blood level is the best measure of impact to a particular person or population. Analysis of metals in blood is well understood and characterized in terms of accuracy and precision, which are both quite good relative to use of other sample media (i.e. teeth and hair).

a. Action Levels. Action levels for lead in various environmental media are provided by several sources. These are primarily environmental regulatory bodies. Researchers also promulgate action levels. Tables 8 and 9 provide example action levels across various media.

b. Levels over History. Man's use of lead has been the only significant variable in the environmental availability and thus exposure to lead. In prehistoric times, a seventy-kilogram human had about 0.3 mg of lead in the body. Humans in North America currently contain about 500 times that amount or about 150 mg per seventy kilograms of body weight. When lead was utilized as common gasoline additive, airborne lead concentrations were roughly one thousand times prehistoric levels [1].

c. Exposure Routes. The human population is exposed to lead via all three principal routes: ingestion, inhalation, and direct contact. The proportion of lead intake from these routes varies significantly depending on the subject's age, social status, and occupation. The primary route of lead exposure in children is lead based paint dust and chips [9]. As lead based paint ages it becomes dislodged from the painted surface and transforms from a sheet to dust and chip sized particles. Children, especially children who are crawling, gather the paint particles on their hands and clothing. These particles are then ingested as the child places his or her hand in the mouth. Adults are also impacted by lead ingestion from lead glazed cookware and by traditional medicines containing lead [1,9]. Awareness of lead poisoning, both acute and chronic is lessening

TABLE 8 Action Levels for Metals in Liquid Media. (After Smith, Ref. [21], 1999)

Element	Media	Limit, mg/L	Source
Indium	All	None found	
Bismuth	All	None found	
Tin	All	None found	
Silver	Drinking Water	0.10	USEPA 40 CFR 141
Antimony	Drinking Water	0.006	USEPA 40 CFR 141
Antimony	Drinking Water	0.002	Japanese legislation
Antimony	Drinking Water	0.005	98/83/EEC
Copper	Drinking Water	1.0	USEPA 40 CFR 141; Japanese legislation; Thai legislation
Copper	Drinking Water	2.0	98/83/EEC
Lead	Drinking Water	0.015	USEPA 40 CFR 141
Lead	Drinking Water	0.05	Japanese legislation; Thai legislation
Lead	Drinking Water	0.010	98/83/EEC
Zinc	Drinking Water	1.0	Japanese Legislation
Zinc	Drinking Water	5.0	Thai Legislation

TABLE 9 Action Levels for Metals in Solid Media. (After Smith and Swanger, Ref . [20], 1999, and Smith, Ref. [21], 1999)

Element	Media	Limit, mg/L unless noted	Source
Antimony	TCLP Leachate	1.0	TNRCC 30 TAC 335[a]
Copper	TCLP Leachate	500	various State (USA) regulations
Lead	TCLP Leachate	5.0	USEPA 40 CFR 261[b]
Lead	Soil, bare, children's' play areas	400 mg/Kg	TSCA section 403
Lead	Soil, bare, surrounding a residence (average concentration)	1200 mg/Kg	TSCA section 403
Silver	TCLP Leachate	5.0	USEPA 40 CFR 261

[a] TNRCC 30 TAC 335 refers to State of Texas statutes.
[b] Some jurisdiction observe a 1.5mg/L limit, based on a multiple of the 0.015 mg/L drinking water limit.

the incidence of this route of lead exposure. In contrast, the primary exposure route for the adult population is inhalation. Lead particles in the air derive from the burning of leaded gasoline, and to a lesser extent from lead smelting and other lead processing in industry. With the ban on lead containing gasoline in many countries, this route of exposure has much less risk than in the past. Lead exposure via inhalation is geographically related, favoring those near roadways and lead smelters with a higher airborne lead concentration. Lead workers, persons involved in the actual processing of lead materials such as battery plates, are the only significant population impacted by direct contact with lead. The adult population, regardless of age, has little opportunity for direct contact with significant quantities of lead. Children are impacted by direct contact via the ingestion mechanism described above.

d. Various Populations. The Center for Disease Control (CDC, Atlanta, Georgia, USA) has conducted several blood-lead studies. These studies sampled both children and adults. Various State and Local health departments have also studied blood lead levels. Table 10 shows a compilation of some of these studies.

Blood lead levels in children ages one to two years have dramatically decreased. In 1976, 88% of children in this age group had blood lead levels greater than 10 ug/dl, but that number declined to 5.9% by 1994[1,9,30].

e. Steady Decline and Reasons. After it was banned as a gasoline additive, average population blood lead levels fell precipitously. From 1976, where one study [9,30] measured an average blood lead of 100 ug/dl in a population near roadways, the study measured 40 ug/dl in 1980 in the same population of subjects. Other contributors to the reduction of blood lead levels include reduced lead levels in plumbing and canning solders, bans on lead in residential paints, education and screening programs by public health agencies, and destruction of older dwelling structures which contained lead-based paint.

D. Zinc

1. Uses

Zinc is used primarily in galvanizing metals and metal alloys, but zinc compounds also have wide commercial applications as chemical intermediates, catalysts, pigments, vulcanization activators and accelerators in the rubber industry, UV stabilizers, and supplements in animal feeds and fertilizers. They are also used in rayon manufacture, smoke bombs, soldering fluxes, mordents for

TABLE 10 Compilation of Lead in Blood Studies. (After US-EPA, Ref. [9], 1998)

Attribute	Sample Size	Geometric Mean (95 % Confidence Interval)	Selected Percentiles (95% Confidence Interval)				
			10th	25th	50th	75th	90th
Total, age 1 and older	3,189	1.6 (1.4–1.8)	0.7 (0.6–0.7)	1.0 (0.9–1.1)	1.5 (1.4–1.7)	2.3 (2.2–2.6)	3.7 (3.2–4.3)
Gender							
Males	1,594	1.9 (1.7–2.1)	0.8 (0.7–0.9)	1.2 (1.1–1.4)	1.8 (1.7–2.0)	2.7 (2.5–3.1)	4.3 (3.7–5.3)
Females	1,595	1.3 (1.2–1.5)	0.6 (0.4–0.7)	0.8 (0.7–0.9)	1.2 (1.1–1.4)	1.9 (1.7–2.1)	3.0 (2.6–3.5)
Race/Ethnicity							
Black, non-Hispanic	693	1.7 (1.5–2.0)	0.8 (0.6–0.8)	1.1 (0.9–1.3)	1.6 (1.4–1.8)	2.5 (2.2–3.0)	4.2 (3.3–5.2)
Mexican American	1,289	1.8 (1.6–2.0)	0.7 (0.6–0.8)	1.1 (0.9–1.2)	1.6 (1.4–1.9)	2.8 (2.3–3.3)	4.1 (3.8–5.2)
White, [a] non-Hispanic	1,207	1.5 (1.4–1.7)	0.6 (0.5–0.7)	1.0 (0.8–1.1)	1.5 (1.3–1.6)	2.3 (2.1–2.5)	3.5 (3.1–4.1)
Age group							
1–5 years	254	2.0 (1.7–2.3)	0.9[b] (0.5–1.1)	1.3 (1.1–1.5)	1.9 (1.6–2.1)	2.7 (2.2–4.4)	4.7[b] (3.5–9.8)
6–11 years	419	1.3 (1.0–1.6)	0.6 (0.5–0.7)	0.8 (0.7–1.0)	1.2 (1.0–1.5)	1.7 (1.4–2.2)	2.7 (1.9–4.7)
12–19 years	868	1.0 (0.8–1.2)	0.4 (0.2–0.5)	0.6 (0.5–0.8)	0.9 (0.8–1.1)	1.4 (1.2–1.6)	2.1 (1.9–2.4)
20–39 years	595	1.4 (1.2–1.5)	0.6 (0.5–0.7)	0.8 (0.8–1.0)	1.3 (1.1–1.5)	2.0 (1.7–2.2)	2.8 (2.5–3.2)
40–59 years	471	1.9 (1.7–2.0)	0.9 (0.7–1.0)	1.2 (1.1–1.3)	1.8 (1.6–1.9)	2.7 (2.4–3.2)	3.8 (3.6–4.4)
60 + years	582	2.5 (2.2–2.8)	1.2 (1.1–1.3)	1.6 (1.5–1.9)	2.3 (2.1–2.7)	3.5 (3.0–4.3)	5.0 (4.5–6.4)

Numbers in parentheses are 95% confidence intervals.
[a] Includes other race/ethnic groups.
[b] Estimate meets minimum standards of reliability but should be interpreted with caution.

printing and dyeing, wood preservatives, mildew inhibitors, deodorants, antiseptics, and astringents. In addition, zinc phosphide is used as a rodenticide. Zinc is an essential element with recommended daily allowances ranging from 5 mg for infants to 15 mg for adult males [31].

2. Ingestion

In humans, acutely toxic oral doses of zinc cause nausea, vomiting, diarrhea, and abdominal cramps and in some cases gastric bleeding. Ingestion of zinc chloride can cause burning in the mouth and throat, vomiting, pharyngitis, esophagitis, hypocalcemia, and elevated amylase activity indicative of pancreatitis. Zinc phosphide, which releases phosphine gas under acidic conditions in the stomach, can cause vomiting, anorexia, abdominal pain, lethargy, hypotension, cardiac arrhythmias, circulatory collapse, pulmonary edema, seizures, renal damage, leukopenia, and coma and death in days to weeks. The estimated fatal dose is 40 mg/kg of body weight.

Gastrointestinal upset has also been reported in individuals taking daily dietary zinc supplements for up to 6 weeks. There is also limited evidence that the human immune system may be impaired by sub chronic exposures. Chronic oral exposures to zinc have resulted in hypochromic microcytic anemia associated with hypoceruloplasminemia, hypocupremia, and neutropenia in some individuals.

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Gastrointestinal absorption of zinc is variable (20–80%) and depends on the chemical compound as well as on zinc levels in the body and dietary concentrations of other. In individuals with normal zinc levels in the body, gastrointestinal absorption is 20–30%. Information on pulmonary absorption is limited and complicated by the potential for gastrointestinal absorption due to the swallowing of zinc-containing mucus from the respiratory tract. Zinc is present in all tissues with the highest concentrations in the prostate, kidney, liver, heart, and pancreas. Zinc is a vital component of many enzymes such as carbonic anhydrase, which regulates CO_2 exchange.

3. Inhalation

Under occupational exposure conditions, inhalation of zinc compounds (mainly zinc oxide fumes) can result in a condition identified as "metal fume fever," which is characterized by nasal passage irritation, cough, headache, altered taste, fever, weakness, hyperpnea, sweating, pains in the legs and chest, leukocytosis, reduced lung volume, and decreased diffusing capacity of carbon monoxide. Inhalation of zinc chloride can result in nose and throat irritation, dyspnea, cough, chest pain, headache, fever, nausea and vomiting, and respiratory disorders such as pneumonitis and pulmonary fibrosis. Although "metal fume fever" occurs in occupationally exposed workers, it is primarily an acute and reversible effect that is unlikely to occur under chronic exposure conditions when zinc air concentrations are less than 8–12 mg/m^3. Gastrointestinal distress, as well as enzyme changes indicative of liver dysfunction, have also been reported in workers occupationally exposed to zinc fumes. However, it is not clear to what extent these effects may have been caused by pulmonary clearance (swallowing respiratory mucus) and subsequent gastrointestinal absorption. Consequently, there are no clearly defined toxic effects that can be identified as resulting specifically from pulmonary absorption following chronic low level inhalation exposures to zinc.

4. Low Toxic Concern/Regulation

No case studies or epidemiologic evidence is known to suggest that zinc is carcinogenic in humans by the oral or inhalation route. Zinc has received little environmental regulatory attention as it is a necessary nutrient and is ubiquitous in the natural environment. It is regulated at high levels in the TCLP test (500 mg/L) in some jurisdictions in the United States.

E. Bismuth

1. Uses

Used in medicines for decades, bismuth has many medically beneficial uses. At higher doses chronic bismuth poisoning can occur. Symptoms of chronic bismuth toxicity in humans consist of decreased appetite, weakness, diarrhea, fever, and metal line on the gums, foul breath, gingivitis and dermatitis. Jaundice and conjunctival hemorrhage are rare, but have been reported. Bismuth nephropathy with proteinuria may occur, as the kidney is the site of highest concentration, with the liver being considerably lower. Bismuth does pass into the amniotic fluid and into the fetus. Bismuth and/or bismuth compounds have been suggested to be a carcinogen or a co-carcinogen in rats. In addition, some studies have shown that bismuth can cause chromosomal aberrations in rats. More epidemiological studies are required for a more complete determination. Little has been studied as to the potential toxic effects of bismuth in the natural environment.

2. Human Exposure

Bismuth has similar human exposure pathways as lead. Its overall exposure opportunity to the human population is much less than lead since bismuth has seen many fewer uses in industry. The opportunity for exposure from ingestion is low, except in its use in medicines. The general population is not subject to bismuth exposure by direct contact. Bismuth is a byproduct of lead smelting and thus there is human exposure from airborne lead smelting emissions.

3. Regulation

Bismuth currently sees little regulation from any governmental authority worldwide. This is due to its perceived low toxicity and generally low industrial use.

F. Copper

Copper occurs naturally in elemental form and as a component of many minerals. Because of its high electrical and thermal conductivity, it is widely used in the manufacture of electrical equipment. Common copper salts, such as the sulfate, carbonate, cyanide, oxide, and sulfide are used as fungicides, as components of ceramics and pyrotechnics, for electroplating, and for numerous other industrial applications. Copper can be absorbed by the oral, inhalation, and dermal routes of exposure. It is an essential nutrient that is normally present in a wide variety of tissues.

1. Ingestion

In humans, ingestion of gram quantities of copper salts may cause gastrointestinal, hepatic, and renal effects with symptoms such as severe abdominal pain, vomiting, diarrhea, hemolysis, hepatic necrosis, hematuria, proteinuria, hypotension, tachycardia, convulsions, coma, and death. Gastrointestinal disturbances and liver toxicity have also resulted from long-term exposure to drinking water containing 2.2–7.8 mg Cu/L. The chronic toxicity of copper has been characterized in patients with Wilson's disease, a genetic disorder causing copper accumulation in tissues. The clinical manifestations of Wilson's disease include cirrhosis of the liver, hemolytic anemia, neurological abnormalities, and corneal opacities.

2. Inhalation

Acute inhalation exposure to copper dust or fumes at concentrations of 0.075–0.12 mg Cu/m^3 may cause metal fume fever with symptoms such as cough, chills and muscle ache-similar to zinc fumes. Among the reported effects in workers exposed to copper dust are gastrointestinal disturbances, headache, vertigo, drowsiness, and hepatomegaly. Vineyard workers chronically exposed to Bordeaux mixture (copper sulfate and lime) exhibit degenerative changes of the lungs and liver.

3. Direct Contact

Opportunities for direct contact with copper are minimal in the general population. Occupational exposure is possible, particularly in the electrical equipment manufacturing industry. Dermal exposure to copper may cause contact dermatitis in some individuals.

4. Regulation

Copper and copper compounds are regulated under Superfund, SARA 313, Clean Water Act Toxic Pollutant, California State Superfund Hazardous Substances, CAL-OSHA Director's List of Hazardous Substances, and California HWCL Hazardous Wastes.

G. Silver

Silver is a relatively rare metal that occurs naturally in the earth's crust and is released to the environment from various industrial sources. Human exposure to silver and silver compounds can occur orally, dermally, or by inhalation. Silver is found in most tissues in small amounts, but has no known physiologic function. Other than occupational exposures, the general population is not at extensive risk of exposure to silver by any route.

1. Ingestion

In humans, accidental or intentional ingestion of large doses of silver nitrate has produced corrosive damage of the gastrointestinal tract, abdominal pain, diarrhea, vomiting, shock, convulsions, and death.

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2. Inhalation

Respiratory irritation was noted following acute inhalation exposure to silver or silver compounds. Silver nitrate solutions are highly irritating to the skin, mucous membranes, and eyes. Ingestion, inhalation, or dermal absorption of silver may cause argyria, the most common indicator of long-term exposure to silver or silver compounds in humans. Argyria is a gray or blue-gray, permanent discoloration of the skin and mucous membranes that is not a toxic effect per se, but is considered cosmetically disfiguring. Chronic inhalation exposure of workers to silver oxide and silver nitrate dusts results in upper and lower respiratory irritation, deposition of granular silver-containing deposits in the eyes, impaired night vision, and abdominal pain.

3. Direct contact

Mild allergic responses have been attributed to dermal contact with silver.

4. Regulation

Silver and silver compounds are regulated under Superfund, SARA 313, RCRA, Clean Water Act Toxic Pollutant, California State Superfund Hazardous Substances, CAL-OSHA Director's List of Hazardous Substances, and California HWCL Hazardous Wastes.

H. Antimony

Antimony (Sb) is a naturally occurring metal that is used in various manufacturing processes. Antimony is sparingly absorbed following ingestion or inhalation. Both gastrointestinal and pulmonary absorption are a function of compound solubility. Antimony is transported in the blood, its distribution varying among species and dependent on its valence state. Antimony is not metabolized but may bind to macromolecules and react covalently with sulfhydryl and phosphate groups. Excretion of antimony is primarily via the urine and feces, and is dependent upon valence state.

1. Ingestion

Acute oral exposure to high doses of antimony or antimony-containing compounds may cause gastrointestinal disorders (vomiting, diarrhea), respiratory difficulties, and death at extremely high doses. Subchronic and chronic oral exposure may affect blood cell production and blood chemistry.

2. Inhalation

Acute inhalation exposure of humans may cause gastrointestinal disorders, probably due to ingestion of airborne antimony. Long-term occupational exposure of humans has resulted in electrocardiac disorders, respiratory disorders, and possibly increased mortality. Antimony levels for these occupational exposure evaluations ranged from 2.2 to 11.98 mg Sb/m^3. Based on limited data, occupational exposure of women to metallic antimony and several antimony compounds has reportedly caused alterations in the menstrual cycle and an increased incidence of spontaneous abortions.

3. Direct Contact

Exposure to antimony from direct contact is unlikely except under occupational conditions.

4. Regulation

Antimony and antimony compounds are regulated under Superfund, SARA 313, Clean Air Act Hazardous Air Pollutant, Clean Water Act Toxic Pollutant, California State Superfund Hazardous Substances, CAL-OSHA Director's List of Hazardous Substances, and California HWCL Hazardous Wastes. It is interesting to note that where a set of several metals are regulated in drinking water by a given jurisdiction, antimony typically carries the lowest maximum allowable concentration. This attests to its chronic toxicity relative to other toxic metals.

I. Indium

The information available on the toxic properties of indium in humans is limited due to its low use in industry and its rarity in the earth's crust. It is known that soluble indium salts are extremely toxic when injected into laboratory animals with a direct effect on the heart, liver, kidneys and blood. However, indium salts are far less toxic when administered orally or by inhalation. Teratogenic effects have also been reported in laboratory animals injected with indium but its applicability to human exposure is unknown.

1. Toxicity in Humans

The inhalation route is by far the most significant route in occupational settings. Indium metal is not irritating to the eyes or skin other than by direct abrasive action of metal particles on eye or skin tissue. Soluble indium salts; however, are very irritating to the eyes. Inhalation of indium fume or dust may cause irritation and damage to the respiratory tract. It may also irritate the gastrointestinal tract if ingested. The mechanisms of these irritations are probably similar to the irritations caused by other toxic metals used in electronics. Prolonged exposure to indium fume or dust may cause irritation and damage to the lung. Workers exposed to indium compounds during the production of indium complained of tooth decay, pain in joints and bones, nervous and gastrointestinal disorders, heart pains, and general debility.

2. Regulation

Indium and indium oxide are not listed as human carcinogens by the Occupational Safety and Health Administration (OSHA), the National Toxicology Program (NTP), the International Agency for Research on Cancer (IARC), the American Conference of Governmental Industrial Hygienists (ACGIH) or the European Union (EU). Indium and its salts are not heavily regulated by worldwide environmental authorities. If bismuth and indium alloys are selected by the industry, their use will dramatically increase. Regulation may follow as environmental agencies deem them as having an adverse impact on the environment as the electronics industry solidifies its commitment to a given lead-free alloy or alloys.

J. Nickel

Nickel is a naturally occurring element that exists in various mineral forms. It is used in a wide variety of applications including metallurgical processes and electrical components, such as batteries. Some evidence suggests that nickel may be an essential trace element for mammals.

1. Ingestion

Most nickel enters the human body via food and water consumption. The absorption of nickel is dependent on its physicochemical form, with water-soluble forms being more readily absorbed. The metabolism of nickel involves conversion to various chemical forms and binding to various ligands in the body. Nickel is excreted in the urine and feces.

2. Inhalation

Inhalation is the primary route for occupational nickel exposure. Inhalation exposure to some nickel compounds cause toxic effects in the respiratory tract and immune system. Acute inhalation exposure of humans to nickel may produce headache, nausea, respiratory disorders, and death. Asthmatic conditions have also been documented for inhalation exposure to nickel. Data on nickel-induced reproductive/developmental effects in humans following inhalation exposure are mixed, with some studies pointing to reproductive effects from inhalation exposure to nickel, while other studies found no observable effects. The primary target organs for nickel-induced systemic toxicity are the lungs and upper respiratory tract for inhalation exposure and the kidneys for oral exposure. Other target organs include the cardiovascular system, immune system, and the blood.

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3. Direct Contact

Exposure from contact with nickel is not a significant pathway in humans.

K. Tin

1. Ingestion

Tin compounds have variable toxicity. Elemental tin and organic compounds have low toxicity and are poorly absorbed when ingested Tin and tin compounds can cause biological effects such as severe digestive tract irritation with abdominal pain, nausea, vomiting, diarrhea, and permanent tissue destruction of the esophagus and digestive tract. Tin salts may cause systemic toxic effects on the nervous system, heart, and liver. Tin may interact with the absorption of biologically essential metals such as copper, zinc, and iron and can inhibit various enzymes and metabolism. Ecotoxicity, reproductive effects, and mutagenicity have been observed in laboratory studies.

2. Inhalation

Some inorganic tin salts are irritating or can liberate toxic fumes on decomposition. Inhalation of tin dusts over a period of years may cause pneumoconiosis. Like other toxic metals, inhalation typically causes irritation to the nose and throat. Prolonged or repeated exposure may cause pneumoconiosis.

3. Direct Contact

Exposure from direct contact with tin is not a significant pathway in humans.

4. Regulation

A literature search uncovered no regulation on elemental tin. There is regulation of organic tin containing materials used to kill and remove barnacles from ship hulls (tributyltin) due to their extreme toxicity to shellfish.

L. Cadmium

Cadmium is a naturally occurring metal that is used in various chemical forms in metallurgical and other industrial processes including the production of pigments.

1. Ingestion

Cadmium exposure can occur via the diet and drinking water, accumulating primarily in the liver and kidneys. An acute oral exposure to 20–30 g has caused fatalities in humans. Exposure to lower amounts may cause gastrointestinal irritation, vomiting, abdominal pain, and diarrhea. Chronic exposure to cadmium primarily affects the kidneys, although other conditions such as "itai-itai" disease may involve the skeletal system. Cadmium is excreted primarily in the urine.

2. Inhalation

Cadmium is absorbed more efficiently by the lungs (30 to 60%) than by the gastrointestinal tract. For inhalation exposure, both the lungs and kidneys are target organs for cadmium-induced toxicity. Inhalation exposure to cadmium and cadmium compounds may result in effects including headache, chest pains, muscular weakness, pulmonary edema, and death. Renal toxicity (tubular proteinosis) may also result from inhalation exposure to cadmium.

3. Direct Contact

Exposure to cadmium for the general population via direct contact is not significant.

4. Regulation

Due to its use in industry, cadmium containing solid waste disposal is regulated in many industrialized countries. These countries also have regulated the acceptable levels of cadmium in drinking water and wastewater.

VI. TOXICITY TEST METHODS AND ISSUES

A. Basis for Toxicity Testing

Materials are tested for toxicity using standardized laboratory methods. These methods are believed to produce results that correlate to the perceived risks of their use in the environment, and particularly their potential harm if released into the environment. Many environmental authorities worldwide have published test methods. These vary from jurisdiction to jurisdiction, but each has the same goal stated above. Additionally the results of the laboratory testing undergo a variety of interpretive steps to classify materials and wastes as hazardous and non-hazardous. The results leading to these classifications also vary depending on the media under test, i.e. drinking water has the lowest allowable contaminant levels while solid wastes typically have the highest allowable concentrations before declared "hazardous."

B. Total vs. Leachate Concentration

There are two primary groupings related to materials testing for environmental contamination potential. These are total concentration and leachable concentration methods. Total concentration methods require the analyst to use the sample material in its "as received" state, with no physical or chemical modifications before analysis for the contaminants of interest. Leachable concentration methods require that the sample material be taken through a leaching process before the leachate is analyzed for the contaminant of interest. With leaching methods, one takes a sample of material and creates a leachate sample that is analyzed. The leached material is normally disposed after the leaching process is completed.

1. Comparison and Usefulness to Estimating Exposure

Total concentration methods are useful in estimating exposure to the environment from a contaminant of interest, as the exposure cannot exceed the total concentration in the material. If the environmental characteristics (such as weathering) of a material are well characterized, then a total concentration analysis allows researchers to estimate the impact to the environment as the material releases or retains a contaminant of interest. Leach methods serve to simulate the action of weathering on a material. When acids are used in the leachate fluid, these methods may also simulate the effects of acid rain (nitric and sulfuric acids are used) and landfill leachate exposure (acetic acid is used). The USEPA has determined experimentally that the leaching fluid pH is a significant variable in the variability and thus the usefulness of leaching method results [24].

C. General Test Methodology for Solid Wastes

1. Procedure

Table 11 lists a summary of the primary leach methods published by environmental agencies [32–34] In general, the waste is sampled using techniques to ensure that the sample represents the waste stream or lot. After sampling and transport to the laboratory, the sample is analyzed for characteristics such as ignitability, reactivity, and corrosivity, that many jurisdictions consider a hazardous characteristic if a substance exhibits any one or more of them. After these preliminary tests, the waste sample is checked for particle size. Most leach methods require that the waste material be ground so that the maximum particle size does not exceed some dimension. Leaching is a surface phenomenon; and sizing the waste allows for an adequate surface area to volume of waste material to provide sufficient conditions for leaching to occur. The leaching fluid of choice is added to the sized waste sample in a prescribed sample weight to fluid weight ratio. The sample is then tumbled (for the USEPA TCLP leach) or shaken and then allowed to settle without further agitation. Agitation is used to simulate weathering and makes the leaching process more aggressive. After the prescribed leaching time, the leachate is filtered typically through a 0.45 um filter to simulate the inability for solids to percolate through soil or rock in the case of a landfill liner breach or leachate overflow across a soil surface.

TABLE 11 Leach Methods Used Worldwide. (Information from Refs. [32–34])

Jurisdiction	Method Name	Leach Media	pH of Leach Media	Dilution Factor
United States	TCLP	Acetic acid, buffered	4.88	20
United States	SPLP	Nitric + Sulfuric Acids	5.00	20
California (USA)	STLC	Citric acid, buffered	5.00	10
European Community	PrEN	Deionized water	Neutral	10
Japan	JST-13	Deionized water	neutral	10

PrEN 12457 parts 1–3. Compliance test for granular waste materials (CEN TC292 2002)	Two-step (ls$_2$, ls$_{2-10}$) or one-step (ls$_{10}$) agitated leaching with deionised water on granular (<4mm) materials. Tested on equivalent of 100 g dry solids after removal and quanitification of non-crushable portion.	To assess leachability under mild extraction conditions for waste disposal or material reuse options. Two step test indicates of relative timescales for release particularly when compared with availability for leaching. *As required by Environment Agency RGN2 (2001) for waste acceptance to landfill*. Threshold values for inert wastes have been published. Values for hazardous wastes are expected during 2002.
Maximum availability leaching test (NEN 7431, 1995)	Two step agitated leaching test at pH 7 and 4 on ground material	To determine the potential (maximum) availability of leaching under worst case environmental conditions.
Tank test (NEN 7345, 1995)	Sequential extraction of solidified materials at pH4, 8 or 12.5 over a maximum of 64 days.	To assess leachability of products which have been solidified for reuse or disposal.
pH dependence test (draft)	24 hour extraction of granular materials at controlled pH. Replicate samples are tested over a range of pH values between pH 4 and 12.	To determine the effect of falling or increasing pH conditions on leachability, once a material has been placed in situ.
Column leach test (NEN 7343, 1995) and draft percolation simulation test	Sequential flushing of column of granular (<2mm) material with acidified water at increasing liquid to solid ratios (0.1–10).	To determine the rate of leaching of various contaminants as a function of time or solid to liquid ratio, particularly at low ratios prevailing in disposal scenarios.
BS 6920 Part 2 Section 2.6 (extraction of metals)	Sequential extraction of cubes of solidified materials in test water over 9 days.	To examine leaching of metals from non-metallic materials used for the supply of potable water (e.g. ready-mixed concrete, plastic pipes, coatings and epoxy resins).
NRA interim test for contaminated soils (NRA 1994)	Two step or one-step agitated leaching with deionised water on granular (<5mm) materials. Tested on equivalent of 100 g dry solids.	To examine leachabilty of soils under mild extraction conditions which mimic rainfall infiltration, to assess the potential for groundwater contamination during site development.

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This filtered leachate is then subjected to a variety of tests. When metals are the constituents of interest, the filtered leachate is digested by adding nitric acid and perhaps other oxidizing agents. The leachate undergoes digestion and then is brought to a prescribed standard volume for analysis. The digestion process ensures the complete breakdown of metal complexes, dissolution of metallic solids smaller than 0.45 um but larger than atomic size (provide dimension), and stability of the metal ions in solution while the digested leachate awaits analysis. Undigested filtered leachates can result in unreliable results because the metals may be non-uniformly dispersed through the leachate, and unstabilized metals may leave the liquid solution and plate onto the container wall, causing low readings in the metal analysis. Therefore, the analysis for the metals of interest follows digestion. The filtered leachate is ready to be analyzed for metals, volatile organic compounds, or non-volatile organic compounds such as pesticides. It is interesting to note that in the environment, the transport of metal elements in leachate is determined by the anions (sulfate, sulfide, chloride, bromide, etc.) in the leachate. The laboratory tests discussed do a poor job of emulating the effects of these anions on the toxic metals' ability to migrate through the environment. The presence, concentration, and types of anions present in landfill leachates varies significantly from landfill to landfill [22] and thus no standardized test could hope to mimic the range of these conditions. Specialized (non-standard) tests can seek to better model the behavior of toxic metals from a particular leachate; however, these tests are only approved by environmental authorities on a case-by-case basis.

2. Analyses

The analyses for metals in the leachate are undertaken primarily by Atomic Absorption Spectroscopy (AAS) or by Inductively Coupled Plasma Emission Spectroscopy (ICP). These methods make use of the unique absorption or emission spectra that all metal elements possess to quantify their presence in the leachate. The analytical instrument is standardized using multiple concentration levels of the metal elements being tested in the leachate. The absorption or emission is proportional to the concentration of the metal in solution. After standardization, the leachates are aspirated into the analytical instrument, where the metal concentrations are determined by the correlation with the absorption or emission spectra.

D. Toxicity Characteristic Leaching Procedure (TCLP)

The Toxicity Characteristic Leaching Procedure (TCLP) was developed by USEPA for determining whether a waste is hazardous by virtue of its toxicity. In this context, waste is hazardous if it presents a threat to human health and the environment when "improperly managed." The USEPA reasons that the most likely pathway for human exposure to toxic constituents is through drinking water contaminated by leachate from a landfill. Accordingly, the TCLP defines the toxicity of a waste by measuring the potential for the toxic constituents present in a 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.

The TCLP specifically requires analyzing a liquid waste extract to determine whether it contains unacceptably high concentrations (Table 12) of any of eight toxic metal constituents identified in the USEPA National Interim Primary Drinking Water Standards. These are: arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. Some states have added copper, nickel, and zinc to this list.

1. Extraction Solution

Consistent with the mismanagement scenario, a leachate is obtained from solid waste by exposing the waste to organic acids as these are the acids likely to be found in a landfill containing decomposing municipal wastes. Prior to leaching the alkalinity of the sample must first be determined in order to properly select which of two different extraction fluids should be used. This determination is accomplished by reviewing the waste sample's pH, or experimentally by adding acid or base until a pH change occurs. Samples with a low alkalinity utilize a sodium acetate extraction solution with a pH of 4.93, whereas those with a high alkalinity (often alkali stabilized

TABLE 12 STLC and TTLC Values. (Information from Refs. [35,36])

	STLC, TTLC, TCLP METALS-MAXIMUM LIMITS		
Analyte	STLC max. limit mg/L (ppm)	TTLC max. limit mg/Kg (ppm)	TCLP max. limit mg/L (ppm)
Antimony	15	500	
Arsenic	5.0	500	5.0
Barium	100	10,000	100
Beryllium	0.75	75	
Cadmium	1.0	100	1.0
Chromium, total	5.0	2,500	5.0
Cobalt	80	8,000	
Copper	25	2,500	
Lead	5.0	1,000	5.0
Mercury	0.20	20	0.20
Molybdenum	350	3,500	
Nickel	20	2,000	
Selenium	1.0	100	1.0
Silver	5.0	500	5.0
Thallium	7.0	700	
Vanadium	24	2,400	
Zinc	250	5,000	

wastes with a pH greater than 11) utilize a dilute acetic acid extraction solution with a pH of 2.8. Samples are tumbled in the appropriate extraction fluid for 18 hours. However, the choice of extraction fluids does not apply to volatiles, where the sodium acetate solution is always used. Analysis for volatile organics also requires a pressurized device to maintain these volatile compounds in the liquid leachate. This device is called a Zero Headspace Extraction (ZHE) apparatus. Results from the leachate are compared against the published TCLP regulatory limits. The TCLP is considered a relatively aggressive leaching procedure relative to other methods in use worldwide.

E. Synthetic Precipitation Leaching Procedure (SPLP)

Aside from the deionized water leaching methods, there are methods that utilize leaching fluids containing various acids. These methods are used to simulate both acid rain and improper waste disposal mixing household and industrial waste in the same disposal unit. The Synthetic Precipitation Leaching Procedure (SPLP), developed by the USEPA, is one such test. The leaching fluid in the SPLP contains nitric and sulfuric acids, diluted to a pH of 5.00. Some European environmental agencies use a similar leaching fluid. These fluids contain either sulfuric acid or sodium nitrate.

F. Distilled Water Methods

Many members of the European Community, including France and Germany, as well as Japan utilize deionized (demineralized) water-leaching tests. A European Community test method also specifies deionized water leaching. The State of Texas and other environmental regulators, utilize seven-day, but less aggressive leach method than the TCLP. Methods based on deionized water leaching are used to demonstrate the contamination potential to drinking water and groundwater from a waste that is exposed to potable (drinkable) water. The storm-water contamination potential can also be predicted using the seven-day leach method. In this method, a portion of the material under study is mixed with some multiple of its weight in distilled or deionized water,

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shaken, tumbled, or left to leach undisturbed for some prescribed period. The leachate is then filtered and analyzed for the constituents of interest. In jurisdictions where this test is used, if the leachate shows constituents of interest higher than local drinking water standards, the material is considered to have failed the test.

1. *Distilled Water with Salts Methods*

Other leach methods, used in the European Community, call for chloride salts and nitrate salts to be added to the deionized-water leaching fluid. These leachates are believed to give a more accurate simulation of actual leaching processes in waste disposal areas in these geographic areas. Indeed, acid rain consisting of primarily nitrate anions, and soils with high chloride contents are better represented by these fluids than by the USEPA or other leachate compositions.

G. Total Threshold Leaching Concentration (TTLC) and Soluble Threshold Limit Concentration (STLC)

The State of California, in addition to its use of the STLC [35] and the USEPA TCLP test, also provides regulations for the Total Threshold Limit Concentration (TTLC). The TTLC is simply a measure of the physical composition of the substance under study, with no regard for its leachability. Substances containing regulated elements or compounds over the TTLC value are deemed hazardous by the State of California. Table 12 lists the STLC and TTLC values, along with the associated maximum percentages a solder alloy can contain without failing the TTLC value. TTLC and STLC are used when determining a hazardous waste characterization under California State regulations [36].

1. *Soluble Threshold Limit Concentration*

(STLC) this analysis determines the amount of each analyte that is soluble in the "Waste Extraction Test" (W.E.T.) [35] leachate. This W.E.T. leachate procedure is used for solid samples or those containing $>$ 0.5% solids. The sample is tumbled in 10 times its weight of a 0.2M sodium citrate buffer for 48 hours. This leachate is then analyzed to determine the soluble concentrations.

2. *Total Threshold Limit Concentration*

(TTLC) this analysis determines the total concentration of each target analyte in a sample. Samples are analyzed using published EPA 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. This is done 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. The concentration of analyte in the leachate is compared against the STLC and TTLC regulatory values. These elemental allowances are much smaller than the lead-free alternative alloys typically considered. In fact, the limit values are much less, than allow concentrations expected to materially change the properties of tin-based solders. This presents a significant concern for California-based assemblers and fabricators. It appears unlikely that there will be a lead-free alloy that will pass the TTLC values (thus non-hazardous under California law). Any alloying elements added to tin will likely be in an amount greater than the TTLC limit in order for the alloying element to have any noticeable effect on the alloys physical properties such as melting point.

H. General Interpretation of Results

The results of the leachate tests are compared against local regulatory limits. If these are exceeded then either the waste is declared "hazardous" or the waste is designated for further treatment to reduce leachable concentrations. In jurisdictions where total concentrations rather than leach-

able concentrations are used, it is presumed that if the total concentration of a contaminant in the material is less than the leach concentration limit, then the material is "non-hazardous" since it is impossible to have a leachable concentration higher than a total concentration. Along with the results from the sample come various quality control analyses. These include matrix spike samples analyzed in the same analytical run as the actual leachate sample. A matrix spike is an aliquot of sample to which a known amount of the contaminant has been added before analysis. This spiked sample aliquot is subjected to exactly the same sample preparation, instrument calibration, and the like as an actual sample aliquot. It serves at the control for the actual sample test. The recovery of the known amount of contaminant is determined during analysis; and if an inadequate amount is recovered, or if the apparent amount recovered is excessive, it may invalidate the leachate sample results. In some cases, other metals interfere with the metal of interest. In these cases, the results are reported with the matrix spike recovery noted as an exception, or a different analytical technique is chosen—one without the sensitivity to the analytical interference of the first analytical method. A "blank" sample is also prepared and analyzed along with the waste samples of interest and spiked samples. A blank sample theoretically has an undetectable amount of the contaminant of interest. If the blank sample shows elevated levels of the contaminant of interest, it causes the associated analytical run to be suspect. After removing the source of the unwanted contamination of the analytical system, the waste sample is re-analyzed.

VII. SUMMARY

Human exposure to lead had increased significantly from prehistoric times to the present. Man's activities have released lead into the air, the soil, and into the various water supplies. Lead and other heavy metals used in electronics also have entered the environment and given rise to human exposure. Lead and other metals enter the environment and the human body through several routes, the most prevalent being ingestion by children. Ingestion of lead causes neurological dysfunction. This effect is especially marked in children, whose nervous systems are developing. Other organ systems are also affected by lead exposure, including the skeletal system, cardiovascular system, and the renal system. The human body, as well as other animal species, has metabolic processes that can remove lead. Drugs such as EDTA can augment these metal removal processes in the body.

When solid wastes are disposed in landfills, rainfall and chemical reactions within the wastes release metals contained in the wastes' solder, components, and circuit boards. As these metals are leached from the waste, the metals may enter the local groundwater. In many communities, groundwater is the source for drinking water. The metal-contaminated leachate liquid may also deposit into surface soils and rocks where humans, animals, and plants come into contact with the toxic metals. Plants may absorb toxic metals and thus enter the food web as animals eat the plants.

The heavily industrialized countries regulate the disposal of wastes to prevent contamination of the environment as discussed above. These regulations include landfill construction requirements, landfill leachate monitoring requirements, and inbound waste screening for hazardous and toxic constituents. The inbound waste screening normally involves laboratory tests on the waste material. The tests vary from country to country but typically simulations of landfill leaching, often characteristic of a particular region. The laboratory-generated leachate is then tested for toxic constituents and if present at predefined levels, results in the waste material being classified as "hazardous" by regulation. Hazardous waste is more closely monitored after disposal than is waste classified as "non-hazardous." Controls on waste disposal including the removal of lead compounds from automotive gasoline, building paints, and food containers have combined to cause a decline in blood lead levels in the United States' general population. The dramatic reductions observed provide conclusive evidence that efforts taken to remove lead and other toxics from our environment has had a corresponding significant effect on our uptake, thus a very positive impact on our health.

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The reader is also directed to:
The Lead-Free Soldering Forum at IPC PCEXPO'99, Long Beach, California; March 1999.
J. Miller, J. *The Environmental and Health Risks of Lead in Electronics;* Proceedings of IPC Works '99, Chicago: IPC, 1999.
Stern, Arthur Cecil. *Fundamentals of Air Pollution*; Academic Press: London, 1984.

REFERENCES

1. Christian, B. "Lead Pollution, A Good Story," Proceedings of IPC Works '99; IPC: Chicago, IL, 1999.
2. Code of Federal Regulations, Chapter 40, Parts 136 (wastewater), 141 (drinking water), 261 (hazardous and solid waste); United States Government Printing Office, 2001.
3. Nriagu, Jerome O. *Lead and Lead Poisoning in Antiquity*; John Wiley and Sons: New York, 1983; 378–382.
4. Massaro, Edward, Ed.; Handbook of Human Toxicology; CRC Press: Boca Raton, Florida, 1997.
5. Tortora, Gerard, J.; Grabowski, Sandra Reynolds. *Principles of Anatomy and Physiology*; 9th Ed.; John Wiley and Sons: New York, 2001.
6. Rose, John. *Environmental Toxicology: Current Developments*; Overseas Publishers Association: New Delhi, 1998; 10, 81–100.
7. Mason, R.P.; Sullivan, K.A. "Mercury in Lake Michigan". Environmental Science and Technology 1997, *31* (3), 942–947.
8. Jacob, S.W.; Francone, C. *Elements of Anatomy and Physiology*; W. B. Saunders and Co: Philadelphia, 1989.
9. United States Environmental Protection Agency. *Risk Analysis to Support Standards for Lead in Paint, Dust, and Soil*; EPA-747-R-97-006, Washington, D.C., 1998.
10. Legge, Allan H.; Krupa, Sagar. *Air Pollutants and their Effects on the Terrestrial Ecosystem*; John Wiley and Sons: New Jersey, 1986; 197–205, 354–359.
11. Prasad, A., Ed.; *Essential and Trace Elements in Human Health and Disease: An Update*; Wiley-Liss, Inc.: New York, 1993.
12. National Institutes of Health, National Center for Complementary and Alternative Medicine. "*EDTA Chelation Therapy for Coronary Artery Disease*"; RFA-AT-01-004, 1994.
13. Morgan, Jean "Chelation Therapy in Lead Neuopathy." Southern Medical Journal Aug. 1975, *168* (8), 1001, 1003.
14. Code of Federal Regulations, Chapter 40, Part 60.
15. Centers for Disease Control. "*What Every Parent Should Know about Lead Poisoning in Children*"; Centers for Disease Control: Atlanta,GA, 1997.
16. Bruin, A. *Environmental Toxicology of Environmental Agents*; Elsevier: The Netherlands, 1976.
17. Federal Register: January 12, 2000 (Volume 65, Number 8), 1949–2015.
18. Code of Federal Regulations, Chapter 40, Parts 9, 141, 142.
19. United States Environmental Protection Agency. *Water on Tap*; EPA 815-K-97-002, 1997.
20. Smith, Edwin B. III; Swanger, Kristine L. "Lead Free Solders: A Push in the Wrong Direction?" Proceedings of IPC PCB Expo '99; Long Beach, California, pp. F-10-1 to end, March 1999.
21. Smith, Edwin B. III. "Environmental Impacts and Toxicity of Lead Free Solders, Including Japanese and European Union Regulations,." Proc. IPC Works '99; Minneapolis, MN, Oct. 1999.
22. Saleem, Zubair. "*Summary of Comments on: Management and Disposal of Lead-Base Paint Debris; Proposed Rule*"; United States Environmental Protection Agency, Docket No. F98-LBPD-FFFFF, September 1999.
23. For documents concerning an example site, see Texas Register, (12 TexReg 3858-3859) and Texas Register, (13 TexReg 427-428) for items pertaining to the "Houston Lead" site, and displaying groundwater impact statements.
24. United States Environmental Protection Agency. SW-846: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 2001.
25. Appelo, C.A.J.; Postma, D. *Geochemistry, Groundwater and Pollution*; A. A. Balkema: Rotterdam, 1993.
26. Code of Federal Regulations, Chapter 40, Part 261.

27. Allenby, B.R.; Ciccarelli, J.P.; Artaki, I.; Fisher, J.R.; Schocnthaler, D.; Carroll, T.A.; Lyons, A.M.; Dahringer, D.W.; Degani, Y.; Gradel, T.E.; Plewes J.T.; Freund, R.S.; Gherman, C.; Solomon, H.; Melton, C.; Munie, G.C.; Socolowski, N. *An Assessment of the Use of Lead in Electronic Assembly*; Surface Mount Council, Northbrook, Illinois, 1999.
28. Townsend, Timothy G. *Characterization of Lead Leachability from Cathode Ray Tubes Using the Toxicity Characteristic Leaching Procedure*; State University System of Florida, Gainesville, Florida, December 1999.
29. Thornton, Iain; Rautiu, Adu; Brush, Susan. *Lead, the Facts*; IC Consultants Ltd: London, UK, December 2001.
30. United States Environmental Protection Agency. A Summary of Studies Addressing the Source of Soil-Lead. Technical Summary 1998, Volume I, EPA 747-R-98-001A, 1998.
31. Centers for Disease Control (CDC). Agency for Toxic Substances and Disease Registry, "ToxFAQ's", available for all metals discussed in this chapter from the CDC, Atlanta, GA, and National Institutes of Safety and Health (NIOSH). Registry of Toxic Effects of Chemical Substances (RTECS), 1999.
32. Jackson. L.P.; Rohlik, A.R.; Conway, C., Eds.; "Hazardous and Industrial Waste Management and Testing: 3rd Symposium"; ASTM Special Technical Publication 851, Publication Code Number 04-851000-16, Philadelphia, PA, 1983.
33. Test Method PrEN 12457 parts one through three, published by the European Union; available from British Standards Institute, 389 Chiswick High Road, London, England W4 4AL.
34. Test Method BS6920, available from British Standards Institute, 389 Chiswick High Road, London, England W4 4AL.
35. California Environmental Protection Agency. Waste Classification Regulation Guidance Manual, August 1994.
36. California Code of Regulations, Title 26.
37. International Air Transport Association. *Dangerous Goods Regulations*; 40th edition; International Air Transport Association: Geneva, 1999.

3
Environmental Impact of Lead and Alternatives in Electronics

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I. INTRODUCTION

The environmental impact of lead dates back to 1887 when U.S. medical authorities diagnosed lead poisoning in children and later, (1904), linked this poisoning to lead-based paint. In 1921 Thomas Midgley discovered that tetraethyl lead curbs engine knock when added to gasoline. The following year the public health service warned of the dangers of leaded gasoline. In spite of that warning, leaded gasoline went on sale in 1923 [1] and continued to be sold in the USA until the late 1990s when it was banned.

With the Clean Air Act of 1970, the U.S. Environmental Protection Agency (EPA) proposed the phase-out of lead in gasoline in 1972. Eleven years later, the EPA reported that the amount of lead in gasoline had dropped 50% and lead levels in blood dropped 37% between 1976 and 1980. By 1991, there was a 78% reduction in lead-levels in blood [1].

In the United States, the Clean Water Act of 1986 banned the use of lead alloy solders for potable water systems, and lead in household paint has been prohibited since before 1970. The dramatic decline in blood lead levels in adults and children since 1970 has been the result of regulatory and voluntary elimination of lead in gasoline, drinking water plumbing connections and fittings, and paint.

In the past, the health and safety concerns with lead poisoning have focused on lead-based paint and lead in gasoline. However, the increasing quantity of scrap electronic products disposed into landfills has raised the question of the environmental impact of this source of lead. Studies in 1991 by Allenby, et al. [2] examined the potential for replacing lead-based solder and concluded that there were no viable alternatives at that time. They also suggested that the total environmental impact of lead and its alternatives, from mining, through manufacture, use, and end-of-life should be considered.

In the early 1990s, legislation was proposed in the US, but no regulatory action was taken. The movement toward lead-free electronics emerged into concrete legislation in Europe on June 13, 2000 when the European Commission adopted two proposals: A Directive on Waste of Electrical and Electronic Equipment (WEEE), and a Directive on the Restriction of Hazardous Substances (ROHS). The WEEE requires Member States to set up take-back centers for end-of-life recovery at no cost to the consumer. The initial WEEE included the ROHS requirements and

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set 2004 as the date for lead-free electronics (lead in cathode ray tubes (CRTs) is exempt). Since then the deadline was established as July 01, 2006. In Japan, the Japan Electronic Industry Development Association (JEIDA) developed the Roadmap 2000 for Commercialization of Lead-free Solder. Thus, the environmental impact of lead from electronics and lead-free alternatives is an important issue to explore.

A. Overview of Issues/Concerns

The regulatory actions banning the use of lead for a variety of applications, such as plumbing, household paint, gasoline, solder in food cans, shot, etc. was based on scientific evidence that lead from these sources can cause harm to human health and to the environment. The action to prohibit lead in electronic products appears to be guilt by association. There is no evidence that lead in electronic products is causing human lead poisoning or is leaching into ground water from obsolete products placed in landfills. It is not known whether alternative solder alloys incorporating tin, silver, copper with additions of other metals such as bismuth, antimony, indium, and nickel, may be even more harmful to the environment. Consideration must be given to the total cycle of metal usage, including mining, smelting, manufacturing, energy requirements, reliability, and leaching potential.

The issue is not only a ban on the use of lead solders in electronics, but also a plan to recycle electronics at end-of-life instead of discarding them into landfills.

B. Lead Utilization

Lead storage batteries represent the major use of lead in the United States, according to data from the U.S. Geological Survey [3] noted in Table 1. The use of lead in electronic solder is only 0.3% of the total lead usage. If one considers consumer electronics, which includes television sets and computers, approximately 90% of the lead utilized in electronics is contained in cathode ray tubes (CRTs) which are exempt under the ROHS Directive.

C. Obsolete Electronics

The proliferation of electronic technology, particularly for communications and computer applications, is increasingly prevalent in business and home applications. Consumers want smaller, faster, more capable and convenient electronic products. The amount of electronic waste is expected to increase rapidly with most of it destined for landfill.

TABLE 1 Major Uses and Consumption of Lead in the United States (After U.S. Geological Survey, Ref. [3], 2000)

Product	U.S. consumption (%)
Storage batteries	86.6
Ammunition	3.6
Paints, ceramics, pigments, chemicals	3.0
Casting metals	2.0
Sheet lead	1.4
Cable covering	0.2
Solder (excluding electronic solder)	0.4
Electronic solder	0.3
Brass, bronze billets and ingots	0.1
Pipes, traps, extruded products	0.1
Miscellaneous	2.3

1. Quantity/Rate of Growth

Technological obsolescence is creating a stockpile of used electronic products. Computers are a prime example. Every year in the United States 36.7 million computers are manufactured [4]. In 1998, 20.6 million computers became obsolete and only 2.3 million were recycled. The remaining computers are sitting in closets, garages, attics, etc. awaiting future disposal. These obsolete computers, TV sets, VCRs, radios, compact disc players, etc. contain important natural resources which must be considered when evaluating their end-of-life scenarios. In Canada, 1,356 tons of lead from computers and monitors were discarded in landfills in 1999. A report from Enviros RIS for Environment Canada predicts that 67,324 tons of computers, laptops, peripherals and monitors will be disposed in 2005, and another 91,219 tons will be reused or recycled [5].

In Europe [6] the rapid growth in WEEE is projected to be three times higher than the growth of average municipal waste. While 6 million tons were generated in 1998, the volume is expected to increase at least 3 to 5% annually resulting in 16 to 28% more WEEE by 2003 and a doubling of this amount by 2010. Thus, the recovery and reuse of the material resources represented by WEEE must be addressed.

2. Composition of Landfills and Electronic Waste

Household trash in the U.S. is normally sent to a Municipal Solid Waste (MSW) facility for placement into a landfill site. Fig. 1 shows graphically the content of this waste stream prior to recycling, with metals representing 8%. The amount of MSW generated in the U.S. in 2000 was nearly 232 million tons (Fig. 2) [7] with the average amount of solid waste generated daily per person increasing from 2.7 pounds in 1960 to 4.5 pounds in 2000. While recycling has increased from 5.6 to 69.9 million tons/year during the same period, the recycling rate also increased from less than 5% to about 30% (Fig. 3) [7]. Though 96.4% of automobile batteries are recycled, their presence in landfills (Table 2) represents the major source of lead at these sites [8].

D. Replacing Lead-Bearing Solders in Electronics

The solder alloys most commonly used for electronics assembly contain tin (Sn) and lead (Pb) with a standard composition being Sn63Pb37. Compared to the tin-lead solder alloy, most lead-free alloys under consideration melt at much higher temperatures, while only a few melt at lower

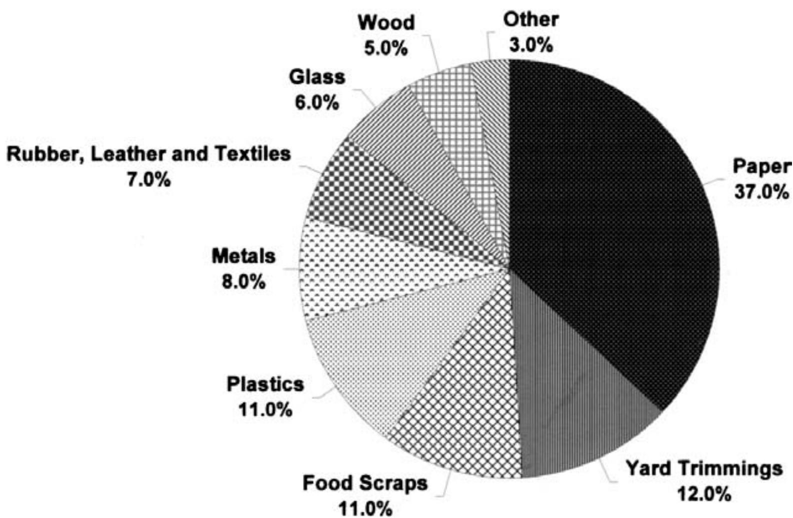

FIG. 1 Graphical representation of waste streams prior to implementing recycling. (After U.S. Environmental Protection Agency, Ref. [7], 2000.)

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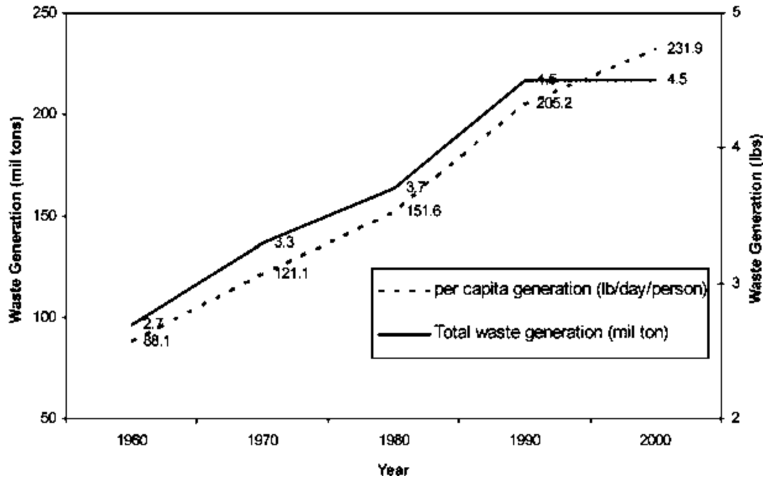

FIG. 2 Trends in municipal solid waste generation from 1960 to 2000. (After U.S. Environmental Protection Agency, Ref. [7], 2000.)

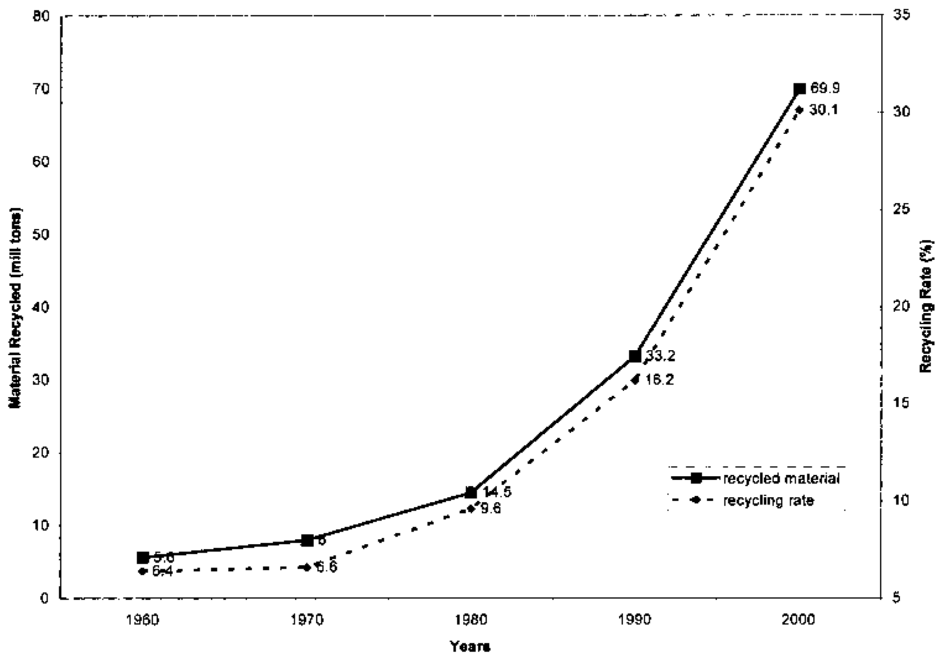

FIG. 3 Trends in the weight and percentage of recycled solid waste materials. (After U.S. Environmental Protection Agency, Ref. [7], 2000.)

TABLE 2 Major Lead-Containing Municipal Solid Waste Discards and their Content (After Industry Economics Company, Ref. [8], 1991)

Lead-containing MSW discards	Percent by weight
Lead acid batteries	48.1
Television picture tubes	35.8
Other consumer electronics	4.4
Glass and ceramics	5.5
Plastics	2.5
Cans and other shipping containers	1.4
Other	2.3

temperatures. Some solder replacement candidates are eutectic alloys melting at a single temperature, while others are non-eutectic alloys that melt over a temperature range. Table 3 lists some of the many alloys that have been investigated along with their melting points or melting range.

1. Major Sources in Electronics

In addition to computer monitors (which account for almost 90% by weight of the lead (Pb) in electronic waste found in landfills) printed wiring assemblies are the other major source of Pb in electronic products. The tin-lead solder alloys used in components and on solderable terminations, and as a preservative coating on cards and boards, are the applications for lead-free solder compositions.

Solder is used to join electronic components and other attachments to printed wiring boards. Soldering can be accomplished by hand with soldering irons or with automation using wave soldering machines or reflow ovens. Automation allows the soldering of hundreds of electrical connections per second. Wave soldering machines convey assembled printed wiring assemblies across fluxing and preheating stations, and then over the wave of molten solder. The lead-free solder alloys selected for hand or wave soldering applications include tin-copper (Sn-Cu), tin-silver (Sn-Ag), and tin-silver-copper (Sn-Ag-Cu).

TABLE 3 Partial List of Lead-Free Alloys and their Melting Temperatures

Alloy	Melting point (°C)
Sn-Pb37	183
Sn-Bi58	138
Sn-Zn9.0	198.5
Sn-Cu0.7	227
Sn-Ag3.5	221
Sn-Ag3.8-Cu0.7	217
Sn-Ag3.0-Cu0.5	217–220
Sn-Ag2.5-Cu0.8-Sb0.5	217–219
Sn-Ag3.5-Bi4.8	205–210
Sn-Ag2.0-Bi7.5Cu0.5	217–218
Sn-Ag2.0-Bi4.0-Cu0.5-Ge0.1	210–217
Sn-Ag3.5-In1.5	218
Sn-Ag2.8-In20.0	175–187

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