A Study of Antimony in Solder*

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Antimony

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

Antimony has been used in a variety of applications for 2,000 years, and today is most commonly found alloyed with other elements. Antimony is used to harden lead for batteries and in cable sheaths, as well as in bearing alloys and in babbit alloys, both leaded and unleaded. Antimony also has been used to manufacture semiconductors. Antimony is one of the main ingredients in food-grade pewter, and is found in most lead-free plumbing solders. Additional information about antimony in terms of physical properties, history, uses, and consumption is attached.[1]

The Advantages of Antimony in Solder Alloys

Antimony has demonstrated several advantages when used as a doping agent in solder alloys. When used in tin-lead solders in the 0.3% - 0.5 % range, the alloys exhibit better thermal fatigue resistance than alloys that do not contain antimony. When added to tin-based solders, antimony forms intermetallic structures with other materials, such as silver and copper, which adds to the strength of the alloy. In Ames Research Laboratory's patent on an SnAgCu alloy, it is stated that, "In another embodiment of the invention, the solder may include at least one alloy component selected from the group consisting essentially of Si, Sb, Zn, Mg, Ca, a rare earth element, and such metals in a collective amount not exceeding about 1% weight for example, to improve wettability, enhance fatigue strength, and/or refine solder joint grain size".[2] This is similar to a report from the IDEALS project, which states that, "A lead-free soldering technology based on Sn (Ag, Cu, Bi, Sb) alloys, possibly with minor additions to enhance aspects of soldering performance, is technically and industrially viable".[3] Furthermore, there have been tests that demonstrate that antimony slows and reduces the growth of intermetallics with copper and other base metals when forming electrical interconnects. Additional information and documentation concerning the above-stated advantages is available from the author.

The "Toxicity" of Antimony

The issue of the toxicity of antimony has come up as the search for viable lead-free alloys continues. Confusion regarding the toxicity of antimony has developed as a result of the

* This paper makes several references to "attached documents". To receive a copy of these documents in their entirety (approximately 150 pages), please contact the author.

[1] Attached Documents A, B, C, D & E

[2] U.S. Patent Number 5,527,628

[3] "IDEALS Improved Design Life and Environmentally Aware Manufacturing of Electronic Assemblies by Lead-Free Soldering", Martin R Harrison & James H Vincent, Marconi Materials Technology Limited.

outlawing of antimony trioxide. Antimony trioxide, used as a fire retardant, is toxic at .5 mg per cubic meter of air. However, antimony trioxide is not formed during soldering or reclamation processes. This paper shall detail third party and governmental studies and legislation concerning antimony and its "toxicity", and shall compare this data to that which concerns "safe" metals such as silver, copper, zinc, compounds of tin, as well as lead.

CERCLA Priority List of Hazardous Substances

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) requires the U.S. Environmental Protection Agency (EPA) and Agency for Toxic Substances and Disease Registry (ATSDR) to prepare a list, in order of priority, of substances "which are deemed to pose the most significant potential threat to human health due to their known or suspected toxicity and potential for human exposure".[4] Substances considered to be the most hazardous are listed in order from 1 to 275. ATSDR/EPA also publish a "Top 20 Hazardous Substances" list[5], which are simply the first 20 of the 275 elements that listed on the CERCLA Priority List of Hazardous Substances. The rankings of the metals of interest are:

Metal	Ranking (in order of priority)
Lead[6]	2
Zinc[7]	68
Bismuth[8]	131
Copper[9]	136
Silver[10]	196
Antimony[11]	241

It is interesting to note that, according to the ATSDR and EPA, antimony is ranked below zinc, bismuth, copper, and silver (all of which are constituents of lead-free alloys), as well as lead, in terms of its potential threat to human health.

TCLP Testing

The Toxicity Characteristic Leaching Procedure (TCLP) is a test mandated by the U.S. Government under the Code of Federal Regulations (CFR), Title 40, Volume 18, Parts 260 to 265. The specifics of this test are dictated by the U.S. EPA. The purpose of this test is to determine if:

4 Attached Document 1, 1997 CERCLA Priority List of Hazardous Substances
5 Attached Document 2, Top 20 Hazardous Substances
6 Attached Document 1, page 2
7 Attached Document 1, page3
8 Attached Document 1, page 5
9 Attached Document 1, page 5
10 Attached Document 1, page 7
11 Attached Document 1, page 8

> "A solid waste exhibits the characteristic of toxicity if, using the Toxicity Characteristic Leaching Procedure, test method 1311 in 'Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,' EPA Publication SW-846, as incorporated by reference in Sec. 260.11 of this chapter, the extract from a representative sample of the waste contains any of the contaminants listed in table 1 at the concentration equal to or greater than the respective value given in that table."[12]

TCLP testing is used to determine whether a solid waste cannot be discarded in a landfill due to it leaching more than a pre-determined amount of a "toxic" element. There are 40 of these elements specified by Federal TCLP testing procedures to be monitored.[13] Of these 40 elements, eight of the elements are metals, all of which have different maximum allowable concentrations.[14] These metals are Arsenic, Barium, Cadmium, Chromium, Lead, Mercury, Selenium, and Silver.[15] **Antimony is not listed under TCLP regulations, and thus is not considered a toxic element in the scope of the U.S. Federal TCLP**. It is of interest to note that **silver is listed with a maximum allowable concentration of 0.05 mg/l**, as silver is a constituent of the majority of lead-free, "environmentally friendly" solders.

AIM has had a third party laboratory perform TCLP testing on the CASTIN alloy, which is comprised of Sn/Ag2.5/Cu0.8/Sb0.5.[16] Testing was performed on CASTIN solder paste, CASTIN bar, and a crushed PCB that had been soldered with CASTIN. As demonstrated by the attached document #3, **CASTIN passed all TCLP testing performed to the U.S. Federal Standard, and therefore will not leach the "toxic" substances specified by TCLP at a rate to prevent it from being disposed of in a landfill**.

OSHA Limits for Air Contaminants

The Occupational Safety & Health Administration (OSHA) of the U.S. Department of Labor, under Code of Federal Regulations (CFR), Title 29, has regulated the maximum level of air contaminants of certain elements to which workers are allowed to be exposed over the course of eight hours[17]. These limits for air contaminants are intended to protect workers from the harmful effects of certain elements, and are listed under Table Z-1 of this document. Following are the expressed limits of metals of interest:

[12] Attached Document 3, 40 CFR 261.24
[13] Attached Document 3
[14] Attached Document 3
[15] Attached Document 4, 40 CFR 264, lists these elements individually
[16] Attached Document 5, ESS Labs of Cranston RI, TCLP Test Data
[17] Attached Document 6, OSHA Table Z-1, Limits for Air Contaminants

Metal	Limit (mg/m^3)
Antimony[18]	0.5
Silver[19]	0.01
Organic Tin Compounds[20]	0.1
Copper fumes[21]	0.1

This serves as further evidence that antimony is not considered more toxic than certain elements with a "safe" reputation, and in fact often is less-stringently regulated than these elements.

The above OSHA Limits for air contaminants is corroborated by The National Institute for Occupational Safety and Health (NIOSH), a division of the U.S. Centers for Disease Control and Prevention (CDC). NIOSH has published The Documentation for Immediate Dangerous to Life or Health Concentrations (IDLHs)[22], which lists the elements specified by the OSHA Limits for Air Contaminants with the same limitations. **Again, antimony is less-stringently regulated than silver, organic compounds of tin, and copper fume.**

Toxic Chemical Release: Community Right to Know

The U.S. Government, under the Code of Federal Regulations (CFR), Title 40, Volume 20, Parts 300 to 399, dictates that when certain elements are released over certain quantities, the organization responsible for this must report this action.[23] Part 302.4 of this document lists the "reportable quantity adjustment for each hazardous substance in pounds."

Metal	Limitation (lbs)
Antimony[24]	5000
Copper[25]	5000
Silver[26]	1000
Lead[27]	10

Once again, the above serves as further evidence of the more stringent regulation in terms of the toxicity of silver as compared to that of antimony. It also is interesting to note the very strict guidelines imposed upon lead, an element with "proven" toxicity, as compared to those imposed upon antimony.

[18] Attached Document 6, page 2
[19] Attached Document 6, page 12
[20] Attached Document 6, page 13
[21] Attached Document 6, page 5
[22] Attached Documents 7, 8, & 9, NIOSH Chemical Listing, NIOSH Pocket Guide for Antimony, & NIOSH Pocket Guide for Silver
[23] Attached Document 10, 40 CFR 372.65
[24] Attached Document 10, page 2
[25] Attached Document 10, page 4
[26] Attached Document 10, page 12
[27] Attached Document 10, page 8

Nonwastewater and Wastewater Treatment Standard Levels for Hazardous Wastes

The U.S. Government, under the Code of Federal Regulations (CFR), Title 40, Part 268.48, dictates the maximum allowable levels of hazardous wastes to be disposed of via nonwastewater and wastewater treatment. This standard may disallow certain solid wastes from being land disposed of, if they exceed the leachate standards listed for the below elements. This falls under the title of "268.48 Universal Treatment Standards (UTS)".[28] According to this list, metals fall under the heading of "Inorganic Constituents."[29] Following is a how certain metals of interest are ranked according to the UTS:

Metal	Wastewater Standard (mg/l^3)	Nonwastewater Standard (mg/l)
Antimony[30]	1.9	1.15
Lead[31]	0.69	0.75
Silver[32]	0.43	0.14
Zinc[33]	2.61	4.3

Thus, in terms of this standard, the order of the most stringently regulated metals may be represented as: Pb < Ag < Sb < Zn. **It is interesting to note that silver is far more strictly regulated than antimony according to the Federal UTS.** In fact, silver is more strictly regulated than lead according to this standard.

Carcinogenicity

Antimony is not classified as a carcinogen. According to the ATSDR Tox FAQ[34], "The Department of Health and Human Services, the International Agency for Research on Cancer, and the (EPA) have not classified antimony as to its human carcinogenicity".[35] This is nearly identical to the carcinogenicity reports given by the ATSDR ToxFAQs for zinc[36] and tin[37].

Furthermore, Toxicology Excellence for Risk Assessment (TERA) has published a matrix of health/cancer risks versus worldwide health organization's determinations of these. Below is a summation of the reports for antimony and silver. The individual matrixes for antimony[38] and silver[39] are attached to this paper, and a detailed report for

[28] Attached Document 11, 40 CFR 268.48
[29] Attached Document 11, page 281
[30] Attached Document 11, page 281
[31] Attached Document 11, page 282
[32] Attached Document 11, page 282
[33] Attached Document 11, page 282
[34] Attached Document 12, Antimony ToxFAQ
[35] Attached Document 12, page 2
[36] Attached Document 13, Zinc ToxFAQ
[37] Attached Document 14, Tin ToxFAQ
[38] Attached Document 15, TERA Antimony Matrix
[39] Attached Document 16, TERA Silver Matrix

each of these elements and the specific details of each health standard and organization may be found at the website: < http://www.epa.gov/iris/subst/index.html>.[40]

Risk Value	ATSDR	Health Canada	IPCS	RIVM	TERA	U.S. EPA	WHO
Noncancer Oral	Sb & Ag	Neither	Neither	Neither	Neither	Sb & Ag	Neither
Cancer Oral	Sb & Ag	Neither	Neither	Neither	Neither	Ag	Neither
Noncancer Inhalation	Sb & Ag	Neither	Neither	Neither	Neither	Neither	Neither
Cancer Inhalation	Sb & Ag	Neither	Neither	Neither	Neither	Ag	Neither

As shown above, when judged according to the classifications of various worldwide health organizations, silver is more highly regulated/deemed as more of a health threat than antimony.

General Exposure Limits

As mentioned above, OSHA has established exposure limits for certain elements over an eight-hour period. Following is the complete list of exposure limits for antimony and silver (all figures are mg/m^3).

Metal	General Ind. Std	Construction Ind. Std.	Threshold Limit Value	Rec. Exposure Limit
Sb[41]	0.5	0.5	0.5	0.5
Ag[42]	0.01	0.01	0.01	0.01

As demonstrated in the above OSHA exposure limits, silver is more strictly regulated than antimony for hazardous air contaminants according to a variety of standards.

EPA/IRIS Elemental Summaries

The Integrated Risk Information System (IRIS) is a division of the EPA that has compiled summaries of various elements. Attached are reports on antimony[43], silver[44], zinc[45], and lead[46]. These reports are quite detailed, with the most important aspect of these to note being that all of the elements summarized have shown some undesirable effects when in certain forms and/or when these are exposed to humans at levels deemed

[40] TERA Website Index Page
[41] Attached Document 17, OSHA Antimony Sampling Information
[42] Attached Document 18, ,OSHA Silver Sampling Information
[43] Attached Document 19, IRIS Antimony
[44] Attached Document 20, IRIS Silver
[45] Attached Document 21, IRIS Zinc and Compounds
[46] Attached Document 22, IRIS Lead and Compounds (inorganic)

to be excessive. Of additional interest is the fact that of all of the aforementioned metals, only lead has officially been classified as carcinogenic[47].

Conclusion

In conclusion, it should be noted that all metals can be toxic in one form or another at certain quantities. **The aforementioned data indicates that antimony is no more "toxic," and perhaps more importantly, is no more regulated, than many of the "safe" elements that comprise the majority of lead-free solders. In fact, antimony is often far less-stringently regulated and is often classified as less of a health threat than silver, zinc, bismuth, copper, and compounds of tin.** In addition, lead has been deemed to be much more "hazardous" than antimony according to the above specifications.

For additional information, please contact the author at:
AIM, tel 1-800-CALL-AIM or 401-463-5605, fax 401-463-0203,
or visit us on the web at www.aimsolder.com.

[47] Attached Document 22, page 5