An Empirical Study into Whisker-Growth of Tin & Tin Alloy Electrodeposits

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A whisker classification system based on the length and frequency of occurrence of whiskers is used to present results from a major study of whisker formation. Samples in this study include 22 different finishes (including matte and bright tin, tin-lead, and tin-copper, matte tin-silver and matte tin-bismuth deposits) applied to brass, Olin 194 and Alloy 42 etched lead-frame substrates, with and without nickel barrier layers and with and without post-plate annealing. Samples were stored at 52°C/98%RH and examined by scanning electron microscopy at monthly intervals. Various approaches to statistical analysis are used to differentiate the performance of the various process/substrate combinations. In general the results confirm the benefits of nickel barrier layers, thicker deposits and post-plate annealing for minimisation of the whisker risk. An unexpected result is the total freedom from whiskering seen with some bright tin and tin-copper deposits with high carbon content and fine grain structure. Some key questions remain: Can any tin or tin-alloy deposit claim to be truly whisker-free? Is there an "acceptable" level of whisker growth? There is a strong need for internationally agreed standards for whisker test methods and specifications.

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Introduction

The trend to eliminate lead from electronic devices, driven by both legislative[1,2] and marketing pressures, continues and is unlikely to be reversed. Progress has been made in the identification and characterisation of lead-free solder alloys to replace the traditional tin-lead solders[3,4], but satisfactory alternatives to the electroplated tin-lead component finishes widely used in electronics fabrication remain elusive. The well-documented[5] phenomenon of tin whiskering in lead-free tin and tin-alloy electrodeposits remains a cause for concern and practical methods for the control and elimination of tin whiskers are essential to ensure reliability in lead-free electronic components. As a contribution to this goal, we report here the results from a major study of whisker formation in some 22 different finishes applied to 3 different lead-frame substrates, with and without nickel and copper barrier layers and with and without post-plate annealing.

Experimental Methods

The substrates were commercially produced etched lead-frames in brass, Olin 194 or Alloy 42. The 22 plating processes, all proprietary formulations, comprised matte 90/10 tin/lead (1 type), matte tin (4 types), matte tin/copper (5 types), matte tin/silver (3 types), matte tin/bismuth (3 types), bright tin (3 types), bright 90/10 tin/lead (1 type) and bright tin/copper (2 types). The lead-frame samples were plated at a cathode current density of 10 A/dm² in a 1 litre volume of the working bath using reciprocal agitation. An identical pre-treatment was used in all cases and consisted of cathodic alkaline clean (proprietary formulation), rinse, dip in 10% sulphuric acid, rinse, and electroplate. Average deposit thicknesses were confirmed by accurate measurement of weight gain during plating onto test pieces of known surface area. Where applicable, alloy composition of deposits was checked by complete dissolution of a test piece in aqua regia followed by volumetric dilution of the stripping solution and analysis of the diluted solution by atomic absorption spectrophotometry. For samples with barrier layers, the nickel layer was provided from a proprietary sulphamate-based process and the copper layer from a proprietary bright acid copper process. For samples subjected to post-plate annealing the annealing condition was 150°C for 1 hour.

Samples were examined by Scanning Electron Microscopy (SEM) to assess whisker formation in the deposits. Initially, all samples were examined in the 'as-plated' condition although in most cases this examination was done between 1 and 2 weeks after plating with the samples having been stored under ambient conditions during this period. Thereafter the samples were stored in an environmental test chamber under controlled conditions of 52±1°C and 98% Relative Humidity and re-examined at 1 monthly intervals for a total of three months.

Any whiskers observed in the SEM examinations were assessed according to an internal classification system described previously[6]. In essence, this is as follows:

- Class 0 - no observable whisker growth
- Class 1 - infrequent, short length (<5µm)
- Class 2 - infrequent, moderate length (5-25µm)
- Class 3 - more frequent, short or moderate length (<25µm)
- Class 4 - long (>25µm), classic whisker shape, 3-4µm

Results

Results from the SEM examinations of all samples according to the whisker classification system (vide supra) for the 3-month test period are shown in Appendix 1.

To facilitate comparison between the various process/substrate combinations a whisker index has been created from the whisker classification results. This index combines the severity of the whiskering and the rate of whisker growth into a single value.

Index = (as is*1) + (1 month*0.75) + (2 month*0.5) + (3 months*0.25)

	As is	1month	2month	3month	Index
Example 1	0	0	0	0	0
Example 2	4	4	4	4	10
Example 3	0	0	1	2	1
Example 4	0	1	2	3	2.5

An index of “0” is whisker free over the 3-month test. An index of “10” indicates severe whiskering from the beginning. As a general guide an index of <1 may be considered acceptable.

There are various methods of looking at the results. Perhaps the simplest representation is a 22x8 matrix (see Table 1). There are some missing values, indicated by “*”. This is because some newer processes were added after the original matrix tests were started and it was felt that some substrates could be eliminated, and annealing was only carried out on selected samples.

Table 1 – Matrix of Results by Whisker Index

		Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8	Average
A1	Matte 90/10 tin/lead	0	0	0	0	0	5	0	*	0.71
A2	Matte pure tin (1)	6	10	4.75	10	0.25	10	1	0	5.25
A3	Matte pure tin (2)	6	5	3.25	10	2.5	10	2.5	0.5	4.97
A4	Matte pure tin (3)	4.5	5	2	7.5	0	7.5	0	0	3.31
A5	Matte tin/copper (1), 1% Cu	4.5	10	1.5	10	0	10	9.25	0	5.66
A6	Matte tin/copper (1), 4% Cu	8	10	2.25	10	0	10	10	0	6.28
A7	Matte tin/copper (2), 1% Cu	4.75	7.5	3	10	0	5	5.25	*	5.07
A8	Matte tin/copper (2), 4% Cu	1.75	7	4.5	2.5	1.75	7.5	8	*	4.71
A9	Matte tin/bismuth, 2% Bi	3	2.25	5.25	0.75	0	0.5	0.5	*	1.75
A10	Matte tin/bismuth, 5% Bi	0.75	0.5	0.5	0	0.5	0.75	0	*	0.43
A11	Matte tin/bismuth, 10% Bi	0	0	0.5	0.5	0	1	0	*	0.29
A12	Matte tin/silver, 2% Ag	6	0.5	4.5	10	5.25	9	0	*	5.04
A13	Matte tin/silver, 3.5% Ag	4.5	1.75	4.5	10	2.5	10	0	*	4.75
A14	Matte tin/silver, 5% Ag	5.25	1.75	6	7.5	0.75	7.5	0	*	4.11
A15	Bright 90/10 tin/lead	0	0	0	0	0	0	0	*	0.00
A16	Bright pure tin (1)	3	7	0	3.25	0	10	6	*	4.18
A17	Bright pure tin (2)	1.5	0	0	5	0	1.5	0.75	*	1.25
A18	Bright tin/copper (1), 2% Cu	3	0	0	10	0	5	0	*	2.57
A19	Bright pure tin (3)	*	0	*	*	0	*	0	*	0.00
A20	Bright tin/copper (2), 2% Cu	*	0	*	*	0	*	0	*	0.00
A21	Matte tin/copper (3), 2% Cu	6	3	0	*	*	*	0	0	1.80
A22	Matte pure tin (4)	7	3.25	0.5	*	*	*	0	0.5	2.25
	Average	3.78	3.39	2.15	5.94	0.68	6.13	1.97	0.14	

Z1	brass
Z2	Olin 194 3 µm
Z3	Alloy 42
Z4	brass+copper
Z5	brass+nickel
Z6	Olin 194+copper
Z7	Olin 194 10 µm
Z8	Olin 10 µm Anneal

Examining this table reveals some interesting trends. The two copper plated substrates gave very poor results. The reason for this is currently unknown. It has been suggested that copper undercoats can reduce whiskering[7]. This was clearly not the case in this study, but it has been shown[8] that compressive stress in a copper undercoat can accelerate whisker growth in a tin deposit. It may well be that the type of copper undercoat (acid, cyanide, neutral) and additive type has an important affect. This is currently being studied. Alloy 42, with a few notable exceptions, gave generally good results. This substrate is of less practical importance since copper alloy based lead-frames, because of their cost advantage, are more prevalent. The 3 micron coatings on either brass or Olin 194 gave generally poor results. The 10 micron coatings on Olin 194 had a much lower whisker tendency than the 3 micron coatings. The nickel undercoat was very effective in minimising whiskers on the brass substrate.

The matte 90/10 tin/lead process gave very good results and the only other matte processes that came close to the performance of the matte 90/10 tin/lead were the 95/5 and 90/10 tin/bismuth. Matte tin/copper processes (1) and (2) were very bad. The results were improved considerably by annealing. Matte tin/copper (3) is the most recent tin/copper development and was whisker free at 10 microns on the Olin 194 substrate. Matte pure tin processes (3) and (4), the three tin/bismuth alloys and the three tin/silver alloys were all whisker free at 10 microns on Olin 194.

The bright processes gave remarkably good whisker performance. This was unexpected as historical literature[7] suggests whiskering should be much worse for bight deposits. The reason for this is that the additive systems used in modern bright processes are very different to those used 20-30 years ago and the new additives clearly produce coatings that are resistant to whisker growth. This is as a result of the crystal orientation and structure and not related to whether the deposits are bright or matte.

The results for each process on Olin 194 with 3 and 10 micron coatings, on brass, and on brass with nickel undercoat are depicted graphically in figures 1 – 4. A summary chart combining these data is in figure 5.

Figure 1 – Whisker Index for 3µm Deposits on Olin 194

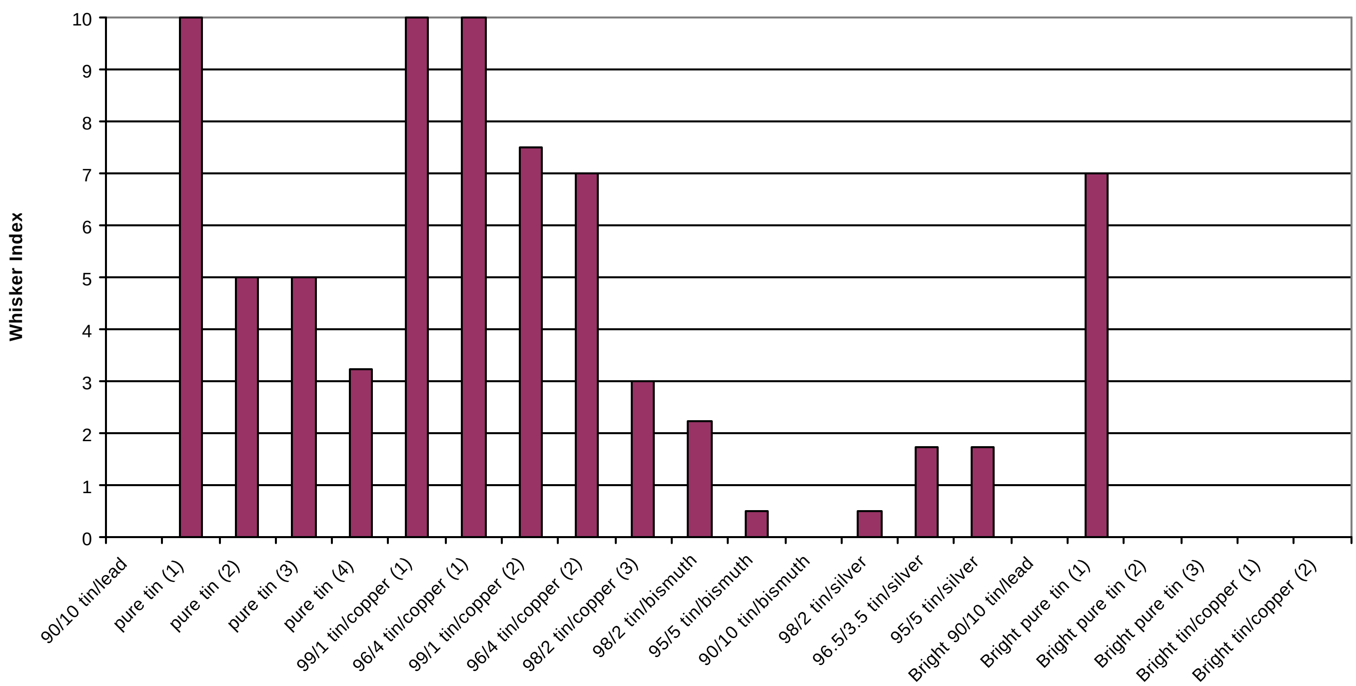


Figure 2 – Whisker Index for 10µm Deposits on Olin 194

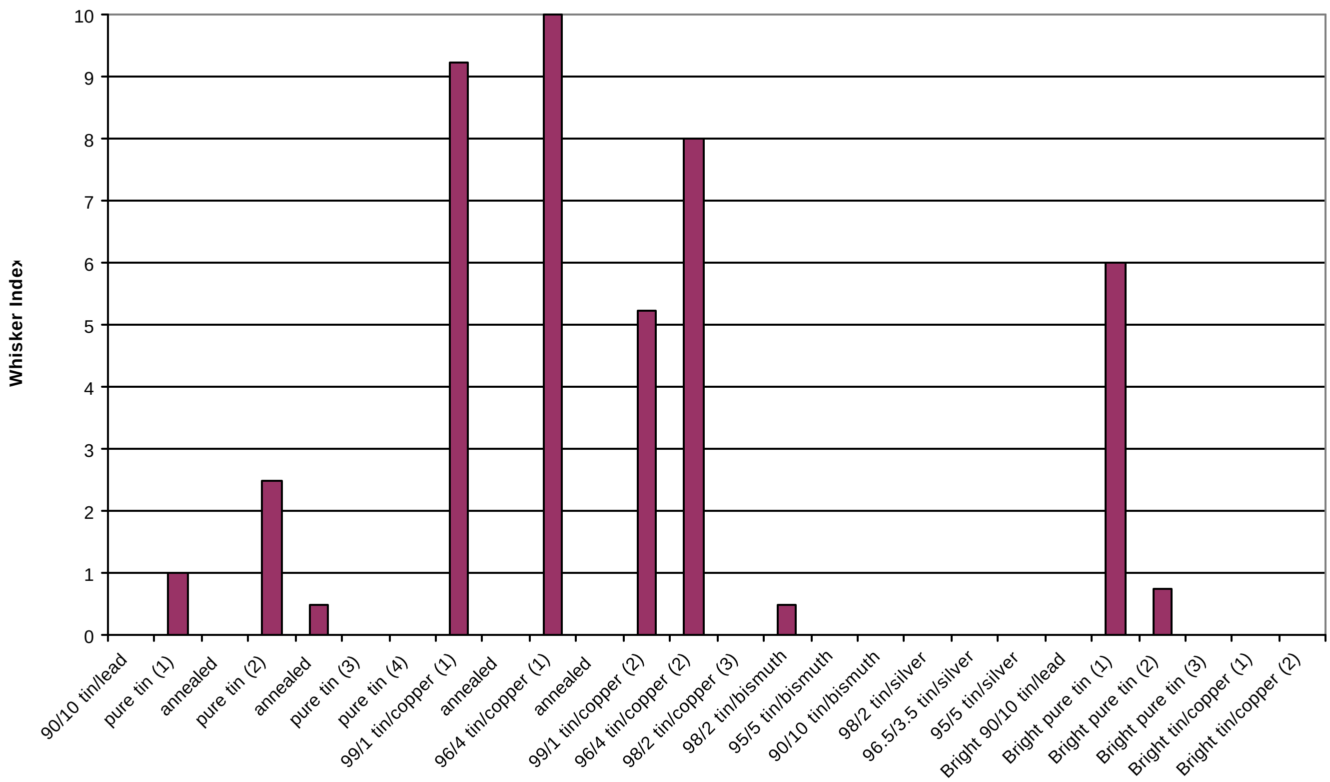


Figure 3 – Whisker Index for 3µm Deposits on Brass

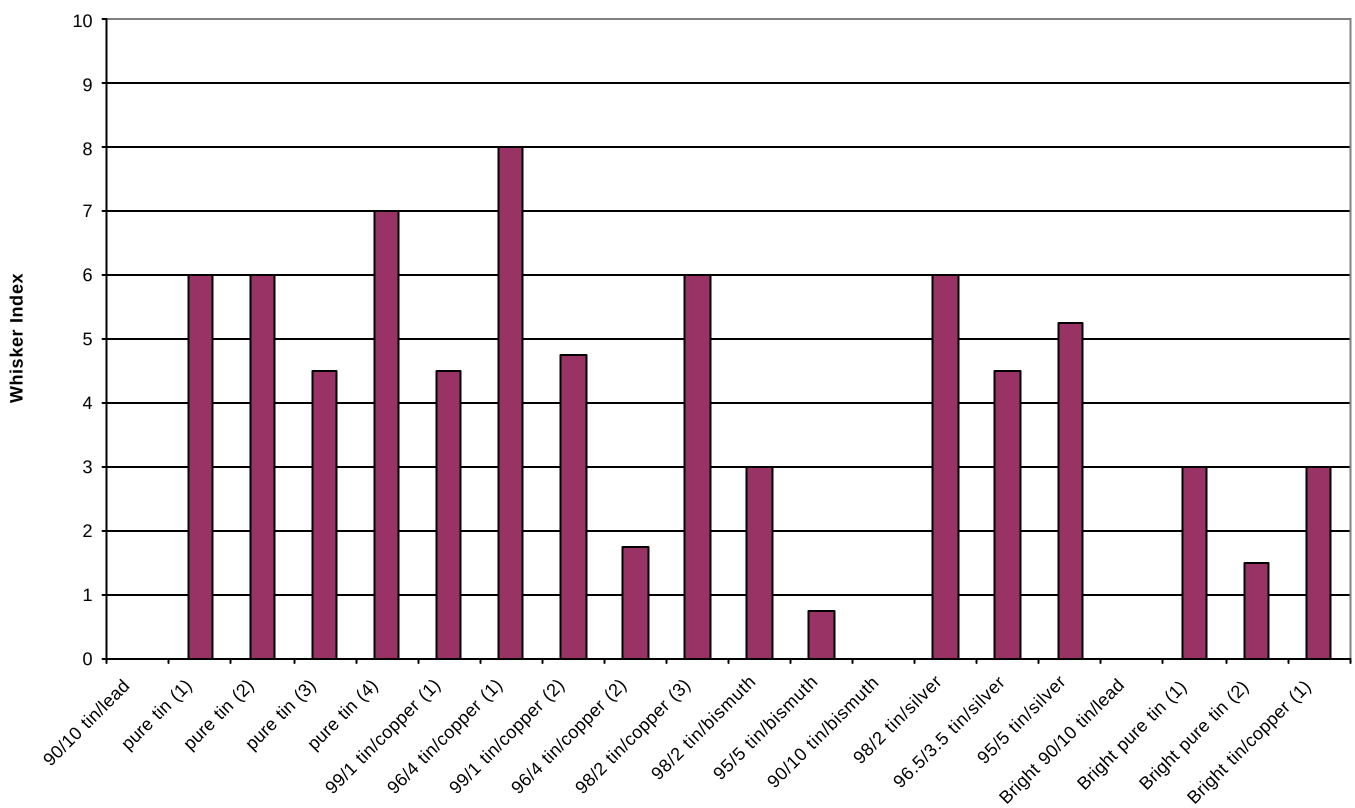


Figure 4 - Whisker Index for 3µm Deposits on Brass With Nickel Undercoat

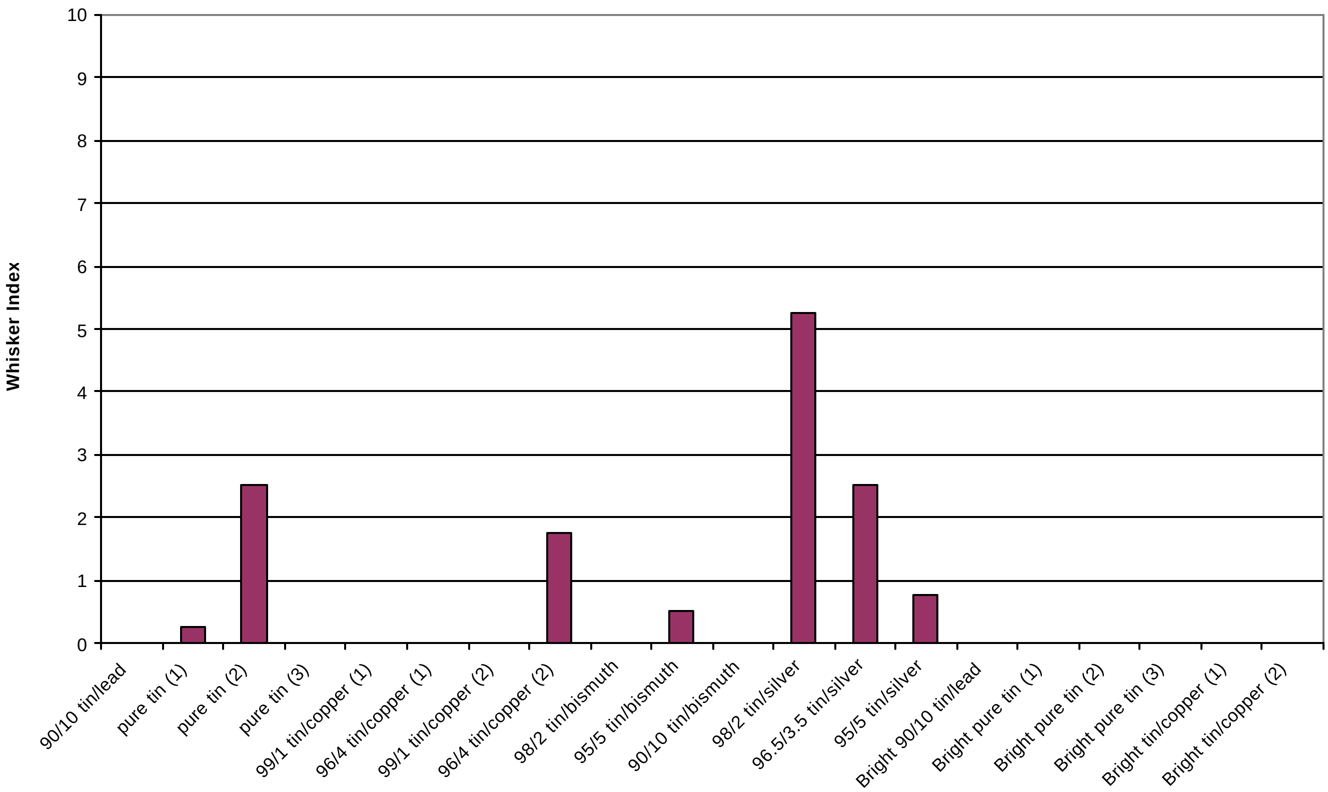
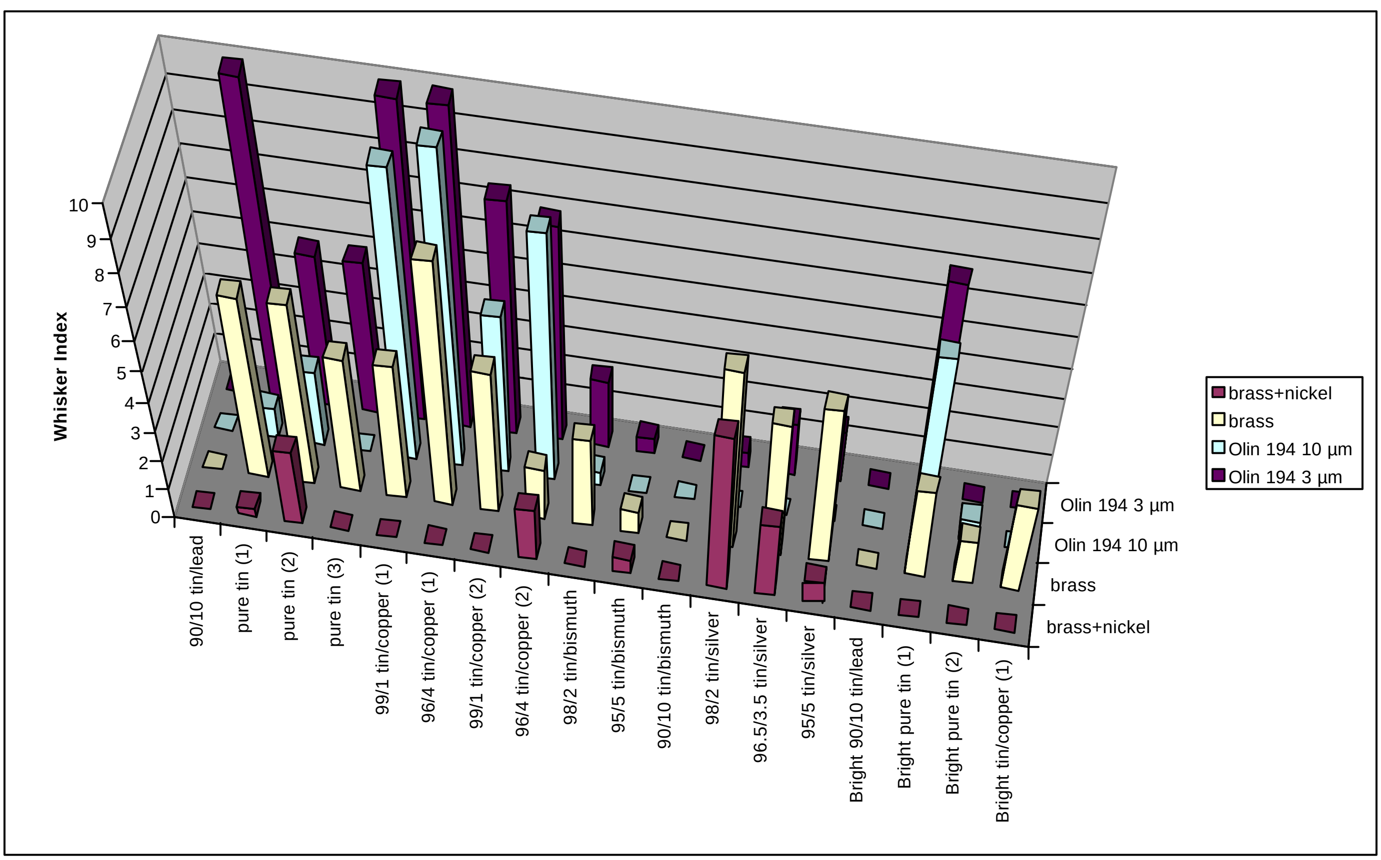


Figure 5 – Summary of All Whisker Index Data



Statistical Analysis

One of the simplest methods of analysis of a matrix of results is just to compare the mean values for each row and column. Care should be exercised when looking at mean values with many missing values because of the possibility that the missing values might have had a large effect. A sorted matrix (lowest to highest, top to bottom and left to right) is shown in Table 2. The trends and results outlined above can be seen more easily using this sorted matrix.

Ordinary least squares regression analysis is not really appropriate for data sets such as this because assumptions are made about the underlying distribution which are not valid. Neither the actual values nor the errors are normally distributed. Various methods of multisample non-parametric analysis (e.g. Quade, Friedmann) were evaluated but did reveal much of interest.

Although mathematical purists may frown upon the use of regression analysis for a data set such as this one, the use of a general linear model is useful for multiple comparisons for multilevel categorical variables and, if we code each combination by using dummy variables, regression analysis can be used and does provide some interesting information. It is beyond the scope of this paper (or indeed the knowledge of the authors!) to go into detail relating to the statistical techniques used for this analysis. Reference 9 provides a good insight into these methods.

The output from the regression analysis is shown in Table 3. The Unistat[10] statistical analysis package was used. Only the original matrix is used for this analysis. The missing values can be handled but provide unnecessary complications.

Table 2 – Sorted Matrix of Results by Whisker Index

		Z8	Z5	Z7	Z3	Z2	Z1	Z4	Z6	Average
A15	Bright 90/10 tin/lead	*	0	0	0	0	0	0	0	0.00
A19	Bright pure tin (3)	*	0	0	*	0	*	*	*	0.00
A20	Bright tin/copper (2), 2% Cu	*	0	0	*	0	*	*	*	0.00
A11	Matte tin/bismuth, 10% Bi	*	0	0	0.5	0	0	0.5	1	0.29
A10	Matte tin/bismuth, 5% Bi	*	0.5	0	0.5	0.5	0.75	0	0.75	0.43
A1	Matte 90/10 tin/lead	*	0	0	0	0	0	0	5	0.71
A17	Bright pure tin (2)	*	0	0.75	0	0	1.5	5	1.5	1.25
A9	Matte tin/bismuth, 2% Bi	*	0	0.5	5.25	2.25	3	0.75	0.5	1.75
A21	Matte tin/copper (3), 2% Cu	0	*	0	0	3	6	*	*	1.80
A22	Matte pure tin (4)	0.5	*	0	0.5	3.25	7	*	*	2.25
A18	Bright tin/copper (1), 2% Cu	*	0	0	0	0	3	10	5	2.57
A4	Matte pure tin (3)	0	0	0	2	5	4.5	7.5	7.5	3.31
A14	Matte tin/silver, 5% Ag	*	0.75	0	6	1.75	5.25	7.5	7.5	4.11
A16	Bright pure tin (1)	*	0	6	0	7	3	3.25	10	4.18
A8	Matte tin/copper (2), 4% Cu	*	1.75	8	4.5	7	1.75	2.5	7.5	4.71
A13	Matte tin/silver, 3.5% Ag	*	2.5	0	4.5	1.75	4.5	10	10	4.75
A3	Matte pure tin (2)	0.5	2.5	2.5	3.25	5	6	10	10	4.97
A12	Matte tin/silver, 2% Ag	*	5.25	0	4.5	0.5	6	10	9	5.04
A7	Matte tin/copper (2), 1% Cu	*	0	5.25	3	7.5	4.75	10	5	5.07
A2	Matte pure tin (1)	0	0.25	1	4.75	10	6	10	10	5.25
A5	Matte tin/copper (1), 1% Cu	0	0	9.25	1.5	10	4.5	10	10	5.66
A6	Matte tin/copper (1), 4% Cu	0	0	10	2.25	10	8	10	10	6.28
	Average	0.14	0.68	1.97	2.15	3.39	3.78	5.94	6.13	

Z8	Olin 10 µm Anneal
Z5	brass+nickel
Z7	Olin 194 10 µm
Z3	Alloy 42
Z2	Olin 194 3 µm
Z1	brass
Z4	brass+copper
Z6	Olin 194+copper

Table 3 – Output From Regression Analysis

Valid Number of Cases: 126, 0 Omitted
Dependent Variable: Index

	Coefficient	Standard Error	t-Statistic
Constant	0.6448	1.0868	0.5933
Process = A2	5.1429	1.3311	3.8636
A3	4.8929	1.3311	3.6758
A4	3.0714	1.3311	2.3075
A5	5.7500	1.3311	4.3198
A6	6.4643	1.3311	4.8564
A7	4.3571	1.3311	3.2734
A8	4.0000	1.3311	3.0051
A9	1.0357	1.3311	0.7781
A10	-0.2857	1.3311	-0.2146
A11	-0.4286	1.3311	-0.3220
A12	4.3214	1.3311	3.2465
A13	4.0357	1.3311	3.0319
A14	3.3929	1.3311	2.5489
A15	-0.7143	1.3311	-0.5366
A16	3.4643	1.3311	2.6026
A17	0.5357	1.3311	0.4025
A18	1.8571	1.3311	1.3952
Substrate = Z2	0.3194	0.8301	0.3848
Z3	-1.1111	0.8301	-1.3386
Z4	2.4722	0.8301	2.9783
Z5	-2.7222	0.8301	-3.2795
Z6	2.6528	0.8301	3.1958
Z7	-1.4444	0.8301	-1.7401

Residual Sum of Squares = 632.5337
Standard Error = 2.4902
Mean of Index = 3.5417
Stand Dev of Index = 3.6634
Correlation Coefficient = 0.7893
R-squared = 0.6230
Adjusted R-squared = 0.5379
F(23,102) = 7.3271
significance of F = 0.0000

This is a non-replicated experiment and the values, although objectively calculated, are based on a subjective assessment. Therefore theoretical statisticians may well argue that interactions, which are clearly present, are being ignored (the single replicate does not produce sufficient observations to compute all interactions). However, if a t-value of 2 is chosen as an arbitrary cut-off point (again with apologies to statistical purists) then some interesting conclusions can be drawn. Confidence in these conclusions is enhanced since they are in agreement with those determined from examination of the raw data.

The coefficients for each process are by comparison with A1 (matte 90/10 tin/lead) and the coefficients for each substrate are by comparison with Z1 (brass). If the coefficients are positive then the whisker tendency is higher than the standard (the more positive the higher the whisker index and the more negative the lower). If the t-statistics are above 2 (absolute value, positive or negative) then the trend can be considered as significant. The higher the value the more significant.

All the pure tin processes are significantly worse than the tin/lead base case with process (3) being the best. The three tin/bismuth coatings, bright 90/10 tin/lead, two of the bright pure tin coatings and the bright tin/copper process are not statistically significantly different to the matte 90/10 tin/lead. The three tin/silver alloys and bright pure tin (1) have statistically significantly worse whiskering than the standard matte 90/10 tin/lead.

The coefficients and t-statistics for the substrates show that the two copper plated substrates are significantly worse than the brass base case. Nickel-plated brass is significantly better than brass. The Olin substrate (3 or 10 ìm) and alloy 42 are not statistically different to brass.

Discussion

Although the bright coatings are originally designed for connector applications, the question can be reasonably asked “Could these coating be used for IC packaging?” The whisker free bright pure tin or tin/copper coatings have excellent solderability (even after ageing) and, although they are bright, they have excellent ductility. The only issues are that they contain high carbon contents (ca. 0.5%) therefore not conforming to US Mil Specification (maximum 0.05%) and there is a concern that the high organic content of these deposits may give rise to outgassing during reflow soldering, leading to voids in the solder joint as it freezes.

At first sight the 90/10 tin bismuth coating looks an attractive alternative to 90/10 tin/lead. However, the tin/bismuth solution deposits bismuth onto the tin anodes during operation. This creates operational, process control and solution maintenance difficulties.

The tin/silver and tin/copper processes have similar problems to the tin/bismuth solution in that the alloying element is lost by immersion onto the pure tin anodes. This can be mitigated to some extent by chemical means but these chelating agents create waste water treatment complications. Pure tin may well be the optimum whisker-free lead-free coating of the future provided that additive systems or modus operandi can be found which will ensure whisker freedom under all practicable operating conditions.

In this series of experiments etched lead frames were used. It has been reported that faster whisker growth occurs on stamped lead frames because of the higher stress levels produced at the cut and damaged edges of the leads.

Thermal cycling tests (-35°C, 125°C, 500 cycles, 7 minutes at each temperature) and the Highly Accelerated Stress Test (HAST, also known as the autoclave or pressure cooker test, typically 105°C, 100% relative humidity, 1.22×10^5 Pa, 100-500 hours) are now being proposed as accelerated whisker tests. These tests should be compared to the test used in these studies.

Conclusions

No drop-in replacement for 90/10 tin/lead exists for lead frame applications. 90/10 tin/bismuth comes closest but operational difficulties with this plating solution will limit its use.

The use of a nickel barrier layer or deposit annealing both reduce whiskering but retrofitting nickel to an existing plating line is expensive and difficult to implement and annealing is time consuming and reduces solderability shelf-life.

Small amounts of alloying elements are insufficient to prevent whiskering.

Thicker coatings are helpful in reducing whiskering

Future development of a truly whisker free pure tin process is still a goal. A process that will produce whisker freedom at 3 microns on brass or Olin substrates will ensure equivalence to 90/10 tin/lead.

The whisker test of 52°C and 98% relative humidity for 3 months has proved to be a good test for discrimination between 90/10 tin/lead and candidate lead-free processes using brass or Olin 194 lead frames.

Bright pure tin or tin copper alloys are shown to be whisker-free lead-free solutions for connector applications.

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References

1. Draft EC Directive on Waste Electrical and Electronic Equipment (WEEE Directive).
2. Draft EC Directive on Restriction of Hazardous Materials (RHS Directive).
3. "*An Analysis of the Current Status of Lead-Free Soldering*", April 1999, UK government (DTI) report co-authored by ITRI and NPL.
4. "*Update 2000*", April 2000, UK government (DTI) update to "*An Analysis of Lead-Free Soldering*", co-authored by ITRI and NPL.
5. M. Toben et al., "*Tin Whiskers in Electrodeposits: An Overview of the Mechanisms That Drive Their Growth*", SURFIN 2001, Nashville, TN, June 2001 (and references therein).
6. R. Schetty, "*Minimization of Tin Whisker Formation for Lead-Free Electronics Finishing*", IPC Works Conference, Miami, FL, September 2000.
7. S.C. Britton, *Trans. Inst. Metal Finishing*, **52**, 95 (1974).
8. A. Politcycki & H-P. Kehrer, *Z. Metallkunde*, **59**, 309 (1968).

9. R.J. Wonnacott & T.H Wonnacott, *Regression: A Second Course in Statistics*, J. Wiley & Sons, 1981; pp. 104-115.
10. UNISTAT Statistical Package Version 5, Unistat Ltd., 4 Shirland Mews, London W9 3DY, UK.