Lead-free Coatings in High Speed Electronic Connectors

by Sudarshan Lal,* James A. Kopec and Stephen R. Angeli

As a result of legislative pressures and customer demands, the connector industry is at a crossroads with respect to the selection of tangible lead-free coatings. The materials, component finishes and processes that make up the backbone of electronic assembly operations pose challenges to connector manufacturing companies. Lead-free solders and coatings require higher assembly processing temperatures. Consequently, plastics, printed circuit boards and connector housings must in turn be evaluated to determine if higher temperatures can be tolerated. Two lead-free coatings, pure tin and tin-copper, have been proposed as possible alternative surface finishes to tin-lead. Whisker formation in these coatings is also a major concern. Higher reflow temperatures pose another concern because of questionable dimensional stability of resin materials. This paper critically examines the application of matte tin and bright tin-copper chemistries with respect to process applications in high-speed reel-to-reel operations. Results of process parameters, metrology, deposit characteristics, solderability, propensity of whisker formation and its mitigation are discussed in detail. In order to cope with higher solder temperatures and meet the challenges that arise from use of lead-free coatings, suitable resins for connector housings are proposed.

Proposed legislation in Europe and environmental directives from the Council on Waste Electrical & Electronic Equipment (WEEE) and Restrictions of Hazardous Substances (ROHS) for removal of toxic substances such as lead, mercury, cadmium and chromium in coatings and particular classes of halogens in plastic materials is a hot issue. The implementation timetable is not fixed and continues to change. Currently, European countries are aiming to remove lead from electronic products by July 1, 2006. Japan and the Asia Pacific Rim seem to be more advanced in this effort and OEMs were expected to roll out products by the end of year 2002. This puts immense pressure on finishing companies, board finishers and component assemblers for qualification of lead-free processes in order to capture market share of the business. An orderly transition from leaded products to lead-free products requires a systematic approach without disrupting the supply chain and causing concerns to end-users. Most likely, a gradual offering of lead-free products will occur alongside the eventual phasing out of leaded products. Some suppliers are also working on reducing the content of lead in their products rather than eliminating it altogether.

Presently, the electronic industry is facing crucial decisions in selection of coating finishes, of lead-free solders for superior joint reliability and suitable plastics for the housing materials to withstand higher reflow temperatures. Initial lead-free development work was presented by the author earlier.[1-3] This paper will address issues relating to coating selection, reflow temperatures, tendency toward whisker formation and resin material selection.

Experimental

Two commercial matte tin and two bright tin-copper baths were prepared according to the vendors' recipes. Reel-to-reel electroplating was performed on stamped terminals of phosphor bronze 510 at a line speed of 3.05 m/min (10 ft/min). A dedicated sump tank was employed for all lead-free work. This tank and two 0.36-m (14-inch) long tin plating cells were leached first with 15% NaOH and then with 15% methane-sulfonic acid (MSA) overnight with thorough and repeated rinsing in between steps. This is intended to reduce the leachate from lead and copper contamination to less than 2 ppm. Coupons of Alloy 42 were also plated in a 2-L (0.53 gal) bath for estimation of copper in the Sn-Cu deposit. The tin-copper deposited coupons were dissolved in aqua regia and the copper in the deposit was determined by atomic absorption spectroscopy (AAS). Current densities on the plating line were adjusted to obtain desired thicknesses of tin or tin-copper on the compliant section of the contacts with proper shielding of carrier strips. A thickness of 1.5 to 2.0 µm (60 to 80 µ-in.) of matte nickel as an underlayer was applied all over the test parts using a sulfamate nickel bath. Plating thickness

Nuts & Bolts: What This Paper Means to You

The connector industry is at a crossroads with respect to the selection of tangible lead-free coatings. Two lead-free coatings, pure tin and tin-copper, are possible alternatives to tin-lead solders. Whisker formation and higher reflow temperatures pose concerns. This paper looks at these coatings in high-speed reel-to-reel operations, and gives a pretty thorough examination of what can and can't be accomplished with them.

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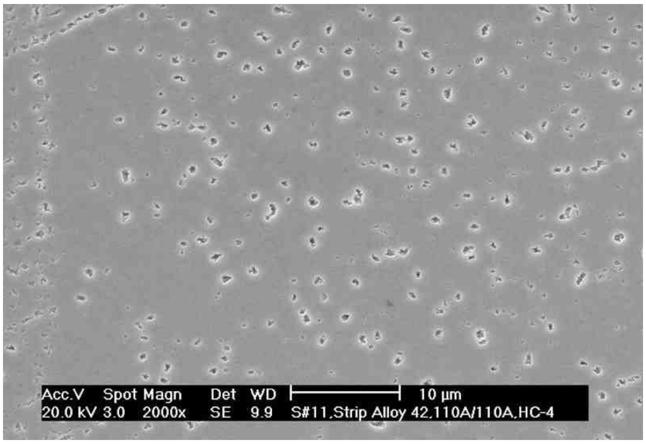

Figure 1—Bright tin-copper bath C coating @ 3.0 m/min (10 ft/min).

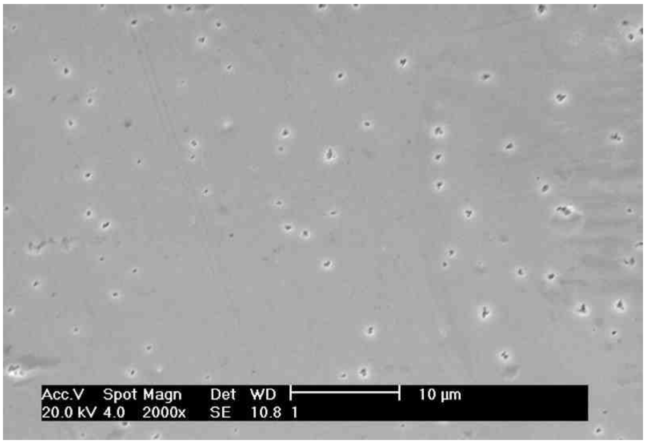

Figure 2—Bright tin-copper bath B coating @ 3.0 m/min (10 ft/min).

was measured by x-ray fluorescence spectroscopy (XRF).[4] Samples for total carbon in the deposit were plated on oxygen-free high conductivity copper (OFHC) using a rotating disk electrode (RDE) and carbon was determined by gas fusion analysis. The coating morphology rating (CMR) of the deposits was determined from SEM microphotographs. Coating adhesion was determined according to ASTM procedure.[5] Solderability testing[6-7] of deposits was carried out using a wetting balance on samples "as is", after steam aging for 8 hr and 72 hr using lead-free solder, Sn-Ag-Cu, and compared with 63 Sn/37 Pb solder as per the ANSI/J-STD-002 method.

Whisker testing was studied a) as is, b) after bending at 90°, c) at 55°C (131°F), ambient humidity and d) at 55°C (131°F) in the presence of 85% humidity. Three contacts were included for each set of conditions in whisker testing. Whisker growth examination was carried out every week or every two weeks depending on the samples, using SEM at 1000X to 2000X at a 15° to 30° tilt.

The coating stress was monitored using a stress analyzer. Commercial beryllium-copper strips were plated at a known current density and from the knowledge of total deflection between the legs, the deposit stress was calculated.

Results and Discussion

The following baths were included in this study:

Bath A: Matte Tin vendor A
Bath B: Bright Tin-Cu vendor B
Bath C: Bright Tin-Cu vendor C
Bath D: Matte Tin vendor D

These proprietary baths were critically examined in view of their general function and maintenance of their chemistries, smell, handling, stability, deposit characteristics, ease of operation on the plating line and variability of the process.

Metrology

Plating Thickness: Samples were plated with 1.5 to 2.0 μm (60 to 80 μ-in.) of matte nickel from a sulfamate bath. The compliant section was plated with various lead-free coatings and thickness varied between 3.0 and 7.6 μm (120 and 300 μ-in.) in the compliant section. Copper in the Sn-Cu coating could not be measured accurately by EDX because of interference, spot size, non-uniform distribution of copper in the deposit and lack of availability of proper XRF standards. However, copper content was confirmed by plating Alloy 42 test strips run on the plating line and also on laboratory coupons with subsequent dissolution in aqua regia and analysis by AAS. Copper values ranged from 1.0 to 1.5% in the tin-copper deposit.

Adhesion: Adhesion of all coatings was tested according to ASTM procedure[5] on samples as is and also bent at 90°. This test also indicated the ductile behavior of the coatings. All coatings passed the test and no microcracks were noticed in the bend areas.

Appearance: All coatings were visually examined for general appearance. The Sn-Cu coatings were extremely bright, smooth and free of visual defects such as blisters, flakes, slivers and cracks. The pure tin bath gave a satin-gray appearance. A bright tin-copper coating is preferred by customers because of its appearance and resistance to tarnishing while in storage.

Morphology: The morphology of these coatings is shown in the SEM photos in Figs. 1-4. Bright Sn-Cu appeared to be smoother

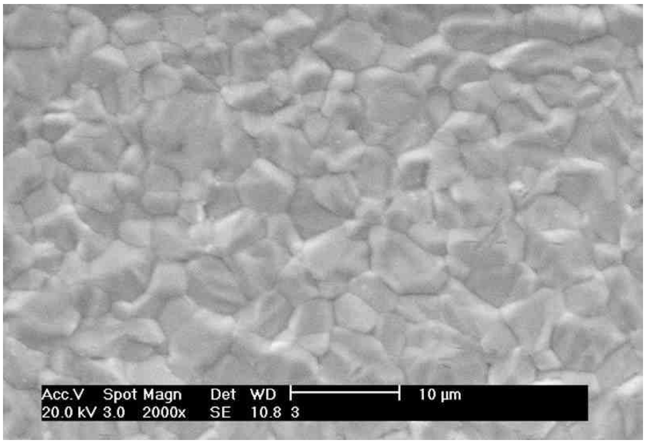

Figure 3—Morphology of matte tin coating bath D.

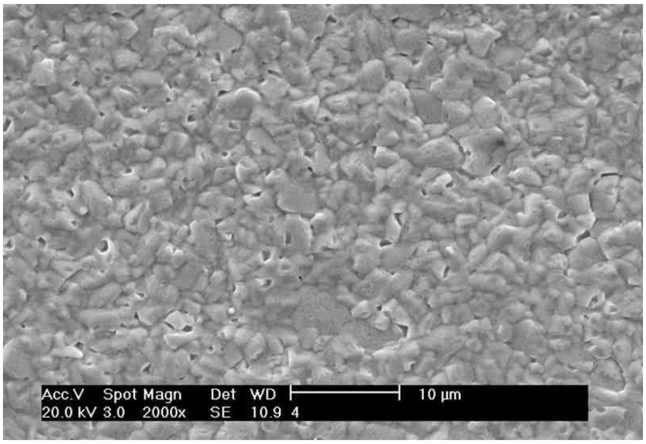

Figure 4—Morphology of matte tin coating bath A.

Table 1
Solderability Comparisons of Various Baths with 95.5 Sn/4.0 Ag/0.5 Cu Solder

Property	Matte Tin Bath A	Bright Sn-Cu Bath B	Bright Sn-Cu Bath C	Matte Tin Bath D
Deposit appearance	Satin gray	Shiny bright	Mirror bright	Satin gray
Wetting time, as is, sec	0.42	0.50	0.69	0.61
Wetting time, 8 hr steam, sec	3.66	0.75	0.69	1.87
Wetting time, 72 hr steam, sec	4.67	1.35	0.73	1.35
Wetting forces @ 4.5 sec, as is, μN/mm (lbf/ft.)	415 (0.028)	405 (0.027)	415 (0.028)	412 (0.028)
Wetting forces @ 4.5 sec, 8 hr steam, μN/mm (lbf/ft.)	15 (0.001)	448 (0.030)	449 (0.030)	51 (0.003)
Wetting forces @ 4.5 sec, 72 hr steam, μN/mm (lbf/ft.)	-40 (-0.003)	298 (0.020)	414 (0.028)	298 (0.020)
% Coverage, as is	100	99	100	100
% Coverage, 8 hr steam	100	92	100	93
% Coverage, 72 hr steam	100	78	100	59

and fine-grain whereas the matte tin coatings were comprised of larger grains. The CMR rating for these coatings was 2 to 3. This rating is empirical, 1 being the smoothest and 10 the coarsest.

Solderability: The coatings were subjected to solderability tests using 95.5 Sn/4.0 Ag/0.5 Cu solder and were compared with a standard 63 Sn/37 Pb solder in: a) as-is condition, b) after 8 hr of steam aging and c) after 72 hr of steam aging using a non-activated rosin flux.* The results of this study are summarized in Tables 1 and 2.

Wetting Times: All baths had wetting times of less than 1 sec in the as-plated condition. It is apparent that there was no significant difference in wetting times between the lead-free solder and tin-lead. After 8 hr of steam aging, coating A exhibited highest wetting time in the presence of both solders. The wetting times for both bright tin-copper coatings were still less than 1 sec. After 72 hr of steam aging, matte tin bath A exhibited the highest wetting times in both solders. Wetting times for bright Sn-Cu bath C were the shortest in both solders.

Bright Sn-Cu coatings from bath B show wetting times below 0.6 sec. The wetting times for a given coating vary with the type of solder used and trends change with the duration of steam aging. Coatings from matte tin baths A and D exhibited longer wetting times after 8 hr of steam aging. This tended to be worse after 72 hr of steam aging. It is probable that thicker surface oxide films, formed during steam aging are responsible for this behavior.

Wetting Forces: All coatings exhibited appreciable wetting forces ranging from 321 to 415 μN/mm (0.022 to 0.028 lbf/ft) in both solders in as plated conditions. The wetting forces for lead-free solder were higher than those for Sn-Pb, indicating good bonding. After 8 hr of steam-aging, the matte Sn coating A showed the lowest (and even negative) forces with both solders. This indicated poor wettability. Both tin-copper samples showed appreciable forces at 4.5 sec under these conditions. After 72 hr of steam aging, matte tin sample A performed poorly whereas both tin-copper samples displayed appreciable forces. The wetting forces for sample C were always higher than those for sample B under all conditions, showing its better performance.

The wetting forces for these coatings without steam aging were less than 400 μN/mm (0.27 lbf/ft). The wetting forces for bright Sn-Cu after 8 hr were the highest for both solders and decreased with 72 hr of steam aging. The matte tin coatings exhibited negative forces for steam-aged samples, which indicated poor wettability from oxide films. This behavior improved considerably in the presence of #809 active flux.

Solder Coverage: All coatings showed better than 99% coverage under "as is" conditions in both solders. With 8 hr of steam aging, coatings B (Sn-Cu) and D (matte Sn) displayed only 93% coverage with Sn/Ag/Cu solder and failed the test. Among the bright tin-coppers, coating C always showed 100% coverage irrespective of the steam aging time whereas coating B gave only 92% coverage. This may be due to excessive surface oxidation. All coatings exhibited better than 95% coverage with Sn-Pb solder under "as is" conditions, 8 hr and 72 hr of steam aging except for Sn-Cu coating B.

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* *Alpha 100 Flux (Type R), Cookson Electronics Assembly Materials, Jersey City, NJ.*

Table 2
Solderability comparisons of various baths with 63 Sn / 37 Pb solder

Property	Matte Tin Bath A	Bright Sn-Cu Bath B	Bright Sn-Cu Bath C	Matte Tin Bath D
Deposit appearance	Satin gray	Shiny bright	Mirror bright	Satin gray
Wetting time, as is, sec	0.54	0.53	0.63	0.68
Wetting time, 8 hr steam, sec	4.83	0.83	0.79	1.35
Wetting time, 72 hr steam, sec	4.63	1.82	1.13	2.42
Wetting forces @ 4.5 sec, as is, μN/mm (lbf/ft.)	321 (0.022)	375 (0.025)	408 (0.028)	334 (0.022)
Wetting forces @ 4.5 sec, 8 hr steam, μN/mm (lbf/ft.)	-55 (-0.004)	371 (0.025)	394 (0.026)	197 (0.013)
Wetting forces @ 4.5 sec, 72 hr steam, μN/mm (lbf/ft.)	-13 (-0.001)	274 (0.018)	355 (0.024)	19 (0.001)
% Coverage, as is	100	100	100	100
% Coverage, 8 hr steam	100	100	100	100
% Coverage, 72 hr steam	100	78	100	98

Whisker Testing

The electronics industry has extensively employed tin and tin-lead coatings for their superior properties such as solderability, corrosion resistance, mechanical and electrical properties. However, electrodeposited tin and tin alloy coatings are susceptible to whisker formation, depending on the environment, the substrate and any intrinsic microstress during the deposition process. Whisker formation seems to be a mechanical phenomenon and their appearance is aided primarily by stresses in deposited film.[8-14] Their growth may be accentuated by environmental factors such as temperature, humidity, intermetallic compound formation and its interdiffusion in grain boundaries, and growth of oxide films. The whisker phenomenon is a major concern to electronic engineers.

Table 3 summarizes the results of whisker growth to date when a set of three samples were subjected to 55°C (131°F) dry heat, 55°C and 85% relative humidity as is, and bent at 90°. The samples were examined every week and later on examined every second week when whisker growth on the samples was detected. The purpose of the study was to evaluate the tendency of coatings to produce whiskers by inducing external stress either by mechanical bending or exposing to various environmental conditions. Any relationship if any between carbon content and whisker formation was also sought. Figures 5 thru 7 depict some of the representative photomicrographs of whiskers found in this study. Samples not exhibiting whiskers are exposed in controlled chambers for ongoing observations. A critical examination of the results led to following conclusions:

- Except for a few instances, most of the whisker growth was noted in the presence of temperature and humidity. Only in some cases whiskers were also observed in dry heat. This is not in concurrence with previously published reports.
- Some whiskers were observed on flat areas but more were observed near edges after eight weeks. The preponderance of whiskers near the edges may be from stress in the metal substrate caused during stamping operations.
- EDX analysis of whiskers showed the presence of pure tin. Neither the presence of intermetallics, nor Cu or Ni were noted.
- The size of whiskers varied from coating to coating. There was no hard and fast rule for their growth, size and shapes. We noticed all kinds of odd shape eruptions and also twisted striated pillars with domes. A bright tin-copper exhibited odd shape eruptions after 18 months, but the size of these eruptions were so small that they might have been of no consequence in practical applications. The length ranged from 5 to 40 μm (0.20 to 1.57 mil) and the diameter from 5 to 15 μm (0.20 to 0.59 mil).
- Whiskers were observed even in matte coatings with low carbon levels. For example, one matte Sn-Cu coating indicated a whisker (10 μm x 3 μm; 0.39 x 0.12 mil) in the compressive area after eight weeks and that grew to 60 μm (2.36 mil) in length after 12 weeks.
- Whiskers were even observed for tin-lead coatings.

It is well known that the incidence of whisker formation can be minimized by optimizing plating conditions with decreased microstresses, but their formation may not be eliminated entirely. There is no accelerated standard procedure to grow whiskers. A National Electronics Manufacturing Initiative (NEMI) group is

Table 3
Whisker Study on Various Baths

Bath	Type	Condition	Time Found	Growth	Dimensions, L/D* μm	% Carbon
A	Matte tin	55°C (131°F), 85% RH, bent	8 wks	At 12 wks	Multiple, small whiskers	0.0059
		55°C (131°F), 85% RH, unbent	30 wks	Some growth	25/5	0.0059
B	Bright Sn-Cu	55°C (131°F), 85% RH, unbent	30 wks	N/A	Small whiskers	0.3550
		55°C (131°F), dry, unbent	22 wks	N/A	Small whiskers	0.3550
C	Bright Sn-Cu	55°C (131°F), 85% RH, unbent	8 wks	None thru 12 wks	8/5	0.0575
		55°C (131°F), 85% RH, unbent	12 wks	N/A	40/5	0.0575
D	Matte Tin	55°C (131°F), 85% RH, unbent	8 wks	At 12 wks	Multiple, small whiskers	0.0024
		55°C (131°F), 85% RH, 90° bent	10 wks	Multiple growth	25/5	0.0024
H	Bright Sn-Pb (90/10)	55°C (131°F), 85% RH, unbent	8 wks	None thru 12 wks	Initial, one small whisker	0.4500

* L/D = Length / Diameter

engaged in conducting a designed experiment for this purpose. All tin and tin-copper coatings may be amenable to whisker formation. However the whisker density and dimensions should be taken into consideration for product recommendation keeping in view that even tin-lead coatings form whiskers. Mechanical and external environmental factors contribute to inducing whiskers on existing coatings. However, if a given coating does not produce appreciable whiskers for six months under aggressive environmental conditions, one may feel more comfortable that the coating may not cause any significant failures during the normal service life of a product. The selection of a given coating for potential electrical contacts should not just be made in consideration of its resistance to whisker formation. Other important properties such as formability, ductility, solderability, fretting corrosion, porosity and tribological properties, should also be considered.

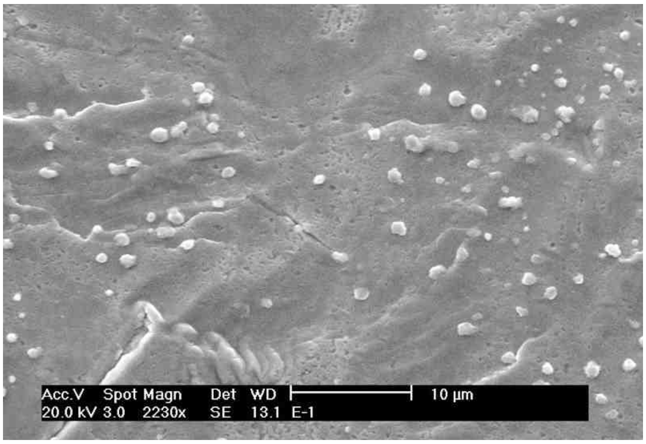
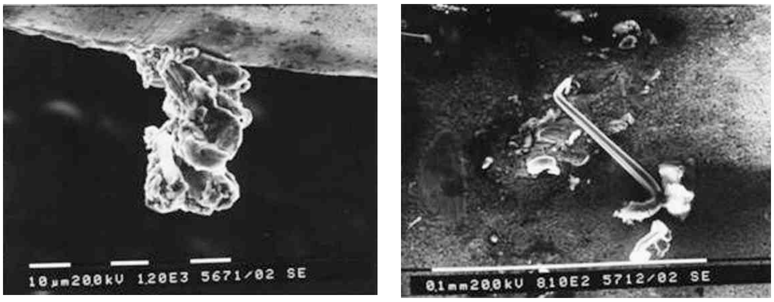


Figure 5—Odd-shaped eruptions in a bright tin-copper coating after 18 months' storage in a central office environment.

The mechanism of whisker formation is complex and not well understood. However, tangible explanations have been put forward especially referring to compressive stress, carbon content and matte vs. bright coatings.[16-19] Because there is no universally accepted standard whisker growth test, several international consortiums are attempting to come up with a standard protocol. The task seems difficult with the complexity of multi-variables that tend to influence the outcome. Our data does not point to any generalizations as we have observed whiskers both in dry heat at 55°C (131°F) as well as at 55°C and 85% relative humidity. Rather, our data shows a preponderance of more whiskers in a hot, humid environment (Table 3). The compositional study of grown whiskers showed mostly pure tin in all cases. No indication of intermetallics such as Cu_3Sn, Cu_6Sn_5, Ni_3Sn_4 or $NiSn_3$ was noted.

Stress Measurements

The stress in the deposit was measured by plating beryllium-copper strips in a given bath at optimum current density. The Be-Cu strips were coated with photoresist on opposite sides of legs so that only one side of each leg was plated. The nature of the bend on the plated legs dictated the stress (concave bend for tensile stress and convex bend for compressive stress). After measuring the total deflection between the legs, the stress in the deposit was calculated by the simplified formula based on Stoney's equation,[15]



Figures 6a and 6b—Typical tin whiskers in tin deposits.

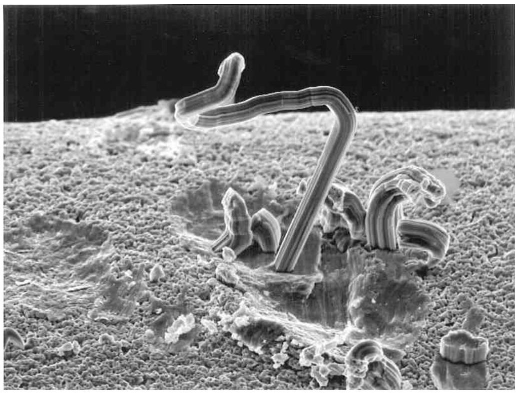


Figure 7—Tin whiskers for tin-copper coating after 12 weeks @ 55°C (131°F) and 85% humidity.

$$S = U . K/3. t$$

where U is total deflection between the legs, K is a constant, and t is the deposit thickness in inches. The stress in these deposits was tensile in nature. It varied with current densities and was in the range of 17.2 to 27.6 MPa (2500 to 4000 lb./in^2).

General Bath Comparisons

Most of the Sn-Cu baths contained MSA-based chemistries containing at least two additives and a carrier. From practical considerations, these additives can be controlled by Hull cell results and/or A-hr usage. Concentrations in some baths could be determined using high performance liquid chromatography (HPLC) which may not be feasible in routine production. Cyclic voltammetric stripping (CVS) method for some bath components may be applicable.

The coating on the parts could be applied selectively either by control depth or by masking on a plating wheel. This was contingent on the ability of the bath not to generate extra foam in the plating cells as well as in the sump. In some cases, sporadic sprays of defoamer were necessary to diminish foaming in the sump and or cells. Some parts can pose problems in plating into recesses or certain areas of parts where the solution could hardly reach, depending on geometry of parts because of the limited throwing power of the bath.

The thickness of the deposit was controlled by varying the line speed and/or DC amperage. At higher amperage most of these baths appeared less efficient. Treeing was also noticed with burning on the edges. The appearance also got darker at high amperes and microcracks were observed to form. Finally, total carbon content of the various baths did not seem to affect their solderability behavior.

Intermetallics & Oxide Films

The oxide formation and its thickness on matte tin coatings were studied by x-ray photoelectron spectroscopy (XPS). It was noticed that oxide films grew in thickness with prolonged steam aging. The composition of the oxide layer was mainly SnO. The thickness of oxide layers were:

Ambient "as is"	25-50 Å
After 8 hr steamed	100 Å
After 72 hr steamed	200 Å

The tin-copper coating seemed to be more resistant to oxidation and grew thinner oxide films when compared with pure tin coatings. This was also indicated from the solderability data of the steam aged samples.

Intermetallic formation was observed in samples with and without a nickel underlayer. The intermetallic layer was thicker in samples without a nickel underlayer. Also, its thickness increased with annealing time. This study also showed that the presence of a nickel layer was helpful in the mitigation of whiskers.

Housing Material Resistance To Higher Reflow Temperatures

Lead-free solders are expected to have an increase in their liquidus temperature of 30 to 50C° (54 to 90F°). This increase results in

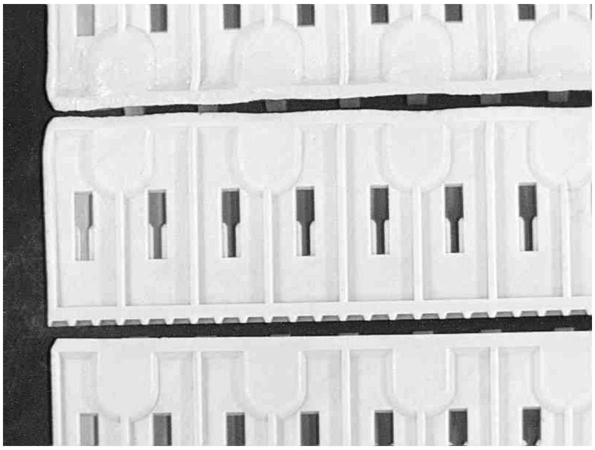


Figure 8—Metral headers showing results of reflow: bottom part, 223°C (433°F); middle part, 262°C (504°F) and top part, 272°C (522°F) board temperatures, respectively. Parts are made from liquid crystalline polymer (LCP) with a melting point of 280°C (536°F).

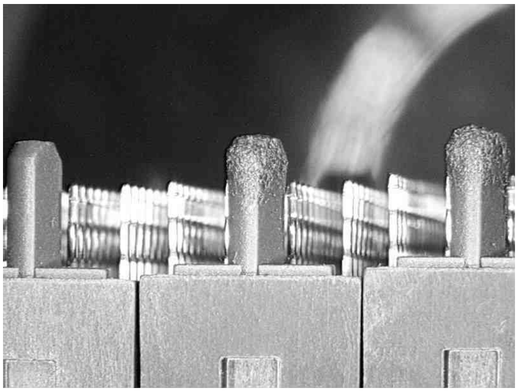


Figure 9—Card Edge: left to right shows effects of parts through reflow at 223°C (433°F), 262°C (504°F) and 272°C (522°F) board temperatures. Material is polyphenylene sulfide (PPS).

Table 4
Reflow Resin Sample Description

Resin	MP, °C (°F)	% Filler	Connector Type
LCP #1	330 (626)	40	Ball grid array
LCP #2	335 (635)	30	Thru-hole receptacle
LCP #3	335 (635)	30	SMT mobile phone
LCP #4	280 (536)	40	Press-fit header
LCP #5	350 (662)	30	Thru-hole
PPS	280 (536)	40	Press-fit card edge
SPS	270 (518)	30	Surface mount
PCT #1	285 (545)	30	Slot 1Thru-hole
PCT #2	285 (545)	40	Slot 1Press-fit
PCT #3	285 (545)	30	SMT Header
PA46 Nylon	295 (563)	45	Thru-hole
PPA Nylon	300 (572)	30	Thru-hole

an increase of reflow temperatures on the printed circuit board of an expected 20 to 40C° (36 to 72F°) for surface mount/reflow soldering. The impending increase in reflow temperatures has caused concern about the thermal capability of polymeric dielectric materials used in connector housings. Therefore, simple screening experiments were performed to examine the impact of elevated reflow temperatures on various resin materials.

Surface Mount Reflow Resins

There are twelve resins commonly used in products that belong to six generic classes of polymers. These classes are: (1) liquid crystalline polymer (LCP), (2) polyphenylene sulfide (PPS), (3) syndiotactic polystyrene (SPS), (4) polycyclohexylene dimethylene terphthalate (PCT), (5) nylon 4,6 (PA46) and (6) polyphthalamide (PPA). Table 4 lists the resin melting point, percent filler and corresponding connector style used.

Three reflow temperatures of 220°C, 260°C and 270°C (428°F, 500°F and 518°F) were studied. To reach these board temperatures, oven air temperatures of 251°C, 287°C, and 302°C (484°F, 549°F and 576°F), respectively, were needed. In all cases the parts were placed on boards for oven travel, but no actual soldering was performed.

The samples were also exposed to two pre-conditioning treatments to simulate shipping and storage conditions: dry and wet (soaked). Drying was achieved by baking the samples in a dry heat oven for 4 hr at 110°C (230°F). Wet samples were obtained via exposure in a steady state humidity chamber for 96 hr at 40°C (104°F) and 95% RH. The moisture content was obtained just prior to reflow using coulometric Karl Fischer titration analysis.[20]

Measured responses were both qualitative and quantitative. Qualitative measurements consisted of visual examination for blisters, discoloration, deformation/warpage and melting. Quantitative measurements included quantity of blisters and connector physical dimension stability.

Materials LCP #4, PPS, SPS, and PCT #2 resins failed to withstand the industry anticipated 260°C (500°F) peak reflow temperature for lead free soldering. LCP #4 failed at both 262°C (504°F) and 272°C (522°F) temperatures due to melting and warpage. PPS and SPS resins failed in both wet and dry states at 262°C (504°F) and higher temperatures. The locating posts of the PPS card edge sample exhibited melting and the SPS sample exhibited melting and housing warpage. PCT sample #2 exhibited a significant amount of bow at the 262°C (504°F) temperature and some melting at 272°C (522°F). At 272°C (522°F), the wet samples of PCT #2 also exhibited blistering. PCT #1 and #4 failed only at 272°C (522°F) in both wet and dry states because of melting and change in dimensions.

Both high temperature nylons passed at all reflow temperatures in the dry state. However, PA 46 and PPA failed at all reflow temperatures (even the current 223°C (433°F)) in the wet state via blistering. The failures were related to the hygroscopic property of the material and outgassing of moisture at all elevated reflow temperatures.

In general, surface mount housing materials with a melting point of 285°C (545°F) and lower exhibited visual and/or dimensional defects following exposure to 260°C (500°F) and higher reflow temperatures(Figs. 8 and 9). All resins with melting points greater than 285°C (545°F) successfully sustained the industry anticipated 260°C (500°F) peak reflow profile without visual/dimensional damage.

Wave Solder Resins

An identical experiment was performed for wave solder resins. Two resins used in the electronics industry for thru-hole soldered connectors were studied: polybutylene teraphthalate (PBT) and polyethylene teraphthalate (PET). The melting points of the resins were 225°C (437°F) and 250°C (482°F) respectively. The general composition of both resins was 30% glass-filled.

Samples of both resins were conditioned wet and dry identically to the reflow resins. Samples were exposed to wave solder bath temperatures of 245°C (473°F) (control), 265°C (509°F) (predicted lead-free process temperature) and 280°C (536°F).

Both PBT and PET successfully withstood all wave solder bath temperatures in both wet and dry states with no dimensional and physical damage. Although this test was limited, the data indicates that both resins will sustain higher lead-free wave solder bath temperatures.

Table 5
Baby H Insertion/Retention Force (lb)

PCB Hole Finish	Insertion		Retention		Avg. Drill Diam. (in.)	
	MIN PTH	MAX PTH	MIN PTH	MAX PTH	MIN PTH	MAX PTH
Immersion Sn	13.2	12.38	9.64	10.83	0.0300	0.0332
Cu / OSP	10.9	4.39	8.21	3.57	0.0304	0.0334
Immersion Ag	14.01	15.07	8.36	11.68	0.0304	0.0328
Tin-Lead	15.5	12.83	13.34	11.07	0.0304	0.0328

Table 6
EON Insertion/Retention Force (lb)

PCB Hole Finish	Insertion		Retention		Avg. Drill Diam. (in.)	
	MIN PTH	MAX PTH	MIN PTH	MAX PTH	MIN PTH	MAX PTH
Immersion Sn	4.41	3.55	2.15	2.96	0.0300	0.0332
Cu / OSP	3.41	1.82	1.98	1.70	0.0304	0.0334
Immersion Ag	5.12	4.04	2.05	3.58	0.0304	0.0328
Tin-Lead	4.66	4.69	2.55	4.41	0.0304	0.0328

Compliant or press-fit applications

The purpose of this test was to determine the effect, if any, of pin–to-PCB insertion/retention forces of compliant pins possessing a matte tin finish. Pin-to-PCB insertion and retention forces were measured on 25 of two compliant types (Baby H and EON) in each PCB hole size and plated-thru-hole (PTH) finish. Tables 5 and 6 summarize the average insertion and retention force measurements on two types of contacts. Copper-organic surface protectant (Cu/OSP) finish PTHs exhibited the lowest insertion and retention forces of both contact styles. The behavior was similar to a Sn-Pb coating. Experiments were performed on lead-free compliant pins in press-fit applications to determine any insertion/retention force effects of lead-free compliant pins in Cu/OSP and immersion tin, immersion silver plated-thru-holes both for minimum PTH (0.76 mm; 0.030 in.) and maximum PTH (0.84 mm; 0.033 in.) hole diameters. The test was performed for three insertion/withdrawal cycles using a virgin pin at each insertion for the same PTH. The results clearly indicate that lead-free finishes do not affect insertion or retention forces in immersion tin and copper plated thru holes.

One important facet of press-fit application involves the application of excessive stresses imposed on the substrate and the lead-free coating. The seal at the inner areas is supposed to be gas tight and whisker growth in those areas may or may not happen and is of no consequence. There is some concern with respect to the exposed areas of the eye of the needle inside the hole. In addition, the lead-free coated pin protruding from either side of the board may tend to whisker. However, because of low coating thickness, chances of whisker formation seem remote. Whisker tests on representative press-fit parts have not shown any whisker formation. The whisker formation is coating dependent and extra care should be exercised in selection of a finish. Another plausible solution is to anneal the part at 150 to 170°C (302 to 338°F) for one hour to relieve any residual stresses prior to assembly.

Conclusions

Both matte tin and bright tin-copper baths were suitable for control depth plating. Some baths required defoamers to quell excessive foaming.

All coatings qualified standard tests such as appearance, adhesion and solderability in as-plated conditions. Solderabilty response for steam-aged samples for matte tin coatings was poor in the presence of non-active flux in the presence of oxide films. The behavior improved dramatically in the presence of highly active flux, which seemed rather aggressive for the removal of passivated surface films.

The propensity of whisker formation was the highest in matte tin coatings when compared to bright tin-copper finishes. The whisker tendency could not be correlated to total carbon in the deposit.

There were odd shape eruptions and whiskers near the edges of terminals. This arises from stress in the substrate which is introduced during stamping of the raw material.

The macrostress in these deposits was tensile. This possibly transforms into compressive stress from contributions of stresses in the substrate, environment, intermetallic compounds or impurities in plating baths. The role of tin–copper intermetallic formation diminishes with the application of a 2.0 μm (80 μ-in.) thick nickel underlayer.

In tin and tin-copper coatings, for solderability, there is a need to qualify resin materials to withstand higher temperatures. This will impact the production cost contributed by equipment, materials and energy.

This study summarizes our overall experience in utilizing the bright tin-copper and matte tin as lead-free chemistries for desired surface finishes. It is apparent that there is no easy solution for the replacement of tin-lead coatings. The tin-lead coating processes have been utilized for the past 50 years and our knowledge base and experience in using these coatings is mature. On the other hand, alternative baths for lead replacement are being developed and tested and are still in their infancy. There are several important issues confronting lead-free processes such as stable bath formulations, stability on storage, long term behavior on high speed plating lines, additive replenishment, uniformity in alloy compositions, deposit metrological and tribological properties, uniformity in coatings, stability and shelf life of coatings, phenomena of whisker formation, solderability characteristics and high reflow temperatures. The elevated temperatures required for reflow pose another challenge and our results show only a few resin candidates qualifying the tests. Considering all these aspects, it seems that industry has to adopt certain achievable specifications.

In regards to propensity of whisker formation, the selected coating should behave similar to a 90 Sn/10 Pb coating. Our preliminary results with bright Sn–Cu chemistry seem promising and this coating may be suitable for lead-free applications. Equally, optimized processes using pure tin chemistries are also attractive as drop in replacement. The whisker fear factor will be always there in these coatings. For high reliability applications, precious metal finishes are the preferred choice. It is apparent that implementation of lead-free processes will impact production costs because of special additives, multiple baths, increased reflow temperatures and special resins needed for coping with high temperatures. However, the evolution of no-lead chemistries has begun and with further developments and experimentation, the engineering community will collect enough data to meet the demands of customers as well as satisfy the environmentalists. Binary alloys appear to be a viable solution whereas ternary alloys seem more difficult to control in plating composition of levels of total carbon. We have also sporadically observed whiskers in tin-lead (90-10) baths. Based on the specifications, substrate, type of product and its product cycle, one may select a suitable lead-free coating for a given application.

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References

1. S. Lal, Proc. *AESF SUR/FIN'2001,* AESF, Orlando, FL, 2001; p. 367.
2. S. Lal, S. Angeli and J. Kopec, *Proc. IPC 2001,* IPC, Northbrook, IL, 2001.
3. S. Lal, S. Angeli and J. Kopec, *Proc. APEX 2002,* IPC, Northbrook, IL, 2002.
4. *Standard test method for measurement of coating thickness by X-Ray Spectrometry, ASTM Method B568-98,* ASTM, Philadelphia, PA, 1998.
5. *Standard test method for adhesion of metallic coatings, ASTM method B571-97,* ASTM, Philadelphia, PA, 1997.
6. *Standard test method for solderability, ASTM method B678-93, ASTM,* Philadelphia, PA, 1993.
7. *Joint Industry Standard, ANSI/J-STD-002, April 1992, Test E,*
8. R. M. Fisher, L. S. Darken and K. G. Carroll, *Acta Met.,* **2**, 368 (1954).
9. K. N. Tu, *Acta Met.,* **21,** 347 (1973).
10. S. C. Britton, *Trans. IMF,* **52,** 95 (1974).
11. U. Lindborg, *Metall. Trans.,* **6A,** 1581 (1975).
12. T. Nagai, K. Natori, and T. Furusawa, *J. Japan Inst. Metals,* **53,** 303 (1989).
13. S. C. Britton, *Spontaneous Growth of Whiskers on Tin Coatings: 20 Years of Observations,* Publication 487, International Tin Research Institute, London.
14. L. Zakraysek, *Plating and Surface Finishing,* **64,** 38 (March 1977).
15. G. G. Stoney, *Proc. Royal Soc.,* **82,** 173 (1909).
16. K. M. Cunningham and M. P. Donahue, *Proc. 4th International SAMPE Electronics Conf.,* 569, (1990).
17. G. W. Stupian, *Tin Whiskers in Electronics, Aerospace Technical Report #92,* 2925 (1992).
18. B. Z. Lee and D. N. Lee, *Acta Met.,* **46,** 3701 (1998).
19. T. Hasigawa, *et al., J. Mat. Sci.,* **17,** 2560 (1982).
20. *Standard test method for determination of moisture content of polyamide, ASTM Method D789-98, Vol. 08.01,* ASTM, Philadelphia, PA, 2000.

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