Immersion Tin as a High Performance Solderable Finish for Fine Pitch PWBs

David H. Ormerod - Enthone division of Polyclad Technologies.

<u>Abstract</u> - "A new high performance immersion tin incorporating a co-deposited organic provides a highly solderable PWB surface finish. The process is described and includes solderability data after accelerated aging and extended processing. Studies of SIR, metallic dendritic growth and ionic contamination are included. A final section shows the benefits for fine pitch assembly, including the yield improvements seen at Reflow, ICT and final inspection. The reliability questions are answered and conclude that the flat solderable tin process provides a cost effective and yield-enhancing planar alternative to Nickel-Gold, HASL and OSPs."

"Nothing solders like solder" - so it is written. The application of molten Tin/Lead onto clean copper gives an excellent electrical and mechanical interconnection. The copper/tin/lead metallurgy is very well understood and documented, and the solder joints formed have a well-established track record for reliability. However, the use of the 63/37 tin-lead Hot Air Solder Level (HASL) process, which has been the finish of choice for several decades, continues to decline. HASL is a cost-effective finish but has several technical drawbacks related to the difficulty of application and to the assembly limitations with fine pitch technology. For this reason, it has already been superseded by a range of flat, so called "planar", finishes which offer significant benefits with regard to the improved paste screening, the control of solder joint volumes and the fast, accurate placement of small components

These selective planar finishes include several metallization processes such as Electroless Nickel-Immersion Gold and Electroless Nickel-Electroless Palladium which are not surprisingly at the high end of the cost spectrum. At the opposite end resides a whole group of substituted Imidazole type coatings that form the basis of the Organic Solderabiliy Preservatives (OSPs). These OSPs are relatively cheaper to apply than HASL and, in many cases, provide adequate solderability for the assembler. It is not surprising, however, that the unrelenting trend of miniaturization continues to challenge not just HASL but in fact all the finishes. The explosive growth of the Ball Grid Array technology, which has critical planarity needs, has seen its solder joint reliability plagued by incidences of interfacial stress fractures associated with Nickel/Gold . On the other hand, the use of mixed technology in the assembly process, (i.e. surface mount components on both sides of the printed circuit board together with through-hole interconnects), demands that the surface finish has a high tolerance to multiple heat cycles. This, in turn, is now challenging the OSPs which, in many cases, have limitations in withstanding the multiple thermal excursions, particularly when less aggressive and/or low solids fluxes are applied (an increasing trend).

As a direct result, there has been a growing demand for further alternatives, and a new generation of thin immersion metallization processes has entered the market. These include both silver and tin technologies, both of which offer lower cost-of-use relative to gold and palladium. The modified immersion tin process offers a very novel solution to this problem, largely because it provides a very comparable copper/tin/lead metallurgy to that of HASL when used with tin-lead solder pastes and solder-wave. This paper goes on to review the case history of one such modified proprietary flat solderable tin process, and the benefits demonstrated to the assembler.

Flat solderable tin, or any other new finish, has to unequivocally satisfy the stringent requirements of planarity, solderability, ionic cleanliness and surface insulation resistance. It is important that the new process can be readily integrated into the PWB fabrication operation. Coupled with this, an ability to deal effectively with the emerging volume production and assembly of fine pitch and area-array technologies represents the ideal. It is also 2

extremely important to demonstrate that the tin finish, whether soldered or unsoldered, will not whisker and will not be subject to any corrosion, dendritic growth or any other mechanical or thermal breakdown which could conceivably affect the long term performance or reliability of the device.

Basis of the Flat Solderable Tin process

Immersion tin deposition on copper has been well researched and documented. The tin is applied in the form of a stannous fluoborate, sulfate or chloride solution and a displacement reaction occurs with the copper. This can be represented as follows: $Sn^{2+} + Cu \rightarrow Cu^{2+} + Sn$. Thiourea is used to drive the forward reaction by overcoming the reverse potential as copper builds up in the solution. The reduced tin is deposited on the surface of the copper and the reaction begins to self limit as soon as the tin coating prevents any further transfer of copper into the solution. As a consequence, the coatings are relatively thin i.e. of the order $0.1 - 1.0 \mu$ 40 millionths) depending (4 on concentration, temperature, and porosity of the deposit. Having described the basic immersion tin reaction, it is now important to understand the differences incorporated in the modified flat solderable tin system. The first major distinction is that the tin bath incorporates a novel organic complex that is co-deposited with the tin. This is shown schematically below.



As a result a more random and polygonized deposit structure is formed which has a much lower propensity towards oxidation, dendritic growth and whiskering. The deposition mechanism creates a "coating" which retards the formation of

copper-tin intermetallic growth (mainly Cu₆Sn₅ at storage temperatures and also Cu₃Sn during assembly heat cycles). The second key differentiator is the tolerance of the tin bath to copper. Normally, a typical immersion tin will lose its ability to provide a consistent deposit thickness with low porosity, once the copper level attains 1-2grams per liter. This would typically arise after 0.25 - 0.5 square meters of copper surface / liter of bath volume (10.5 - 21)square feet copper / US gallon) have been plated to 1µ thickness. The modified bath has been developed to have a much higher tolerance to copper and it is not uncommon to attain 8 square meters / liter (325 square feet / US gallon) of copper surface. This offers three important process benefits: 1) The process plating characteristics, and hence the solderability after aging, remain very consistent. 2) The chemical utilization is improved with a corresponding and significant reduction in process cost. 3) There is a greatly reduced need for bath disposal and this has a large environmental impact, as most immersion tin baths contain thiourea. The flat solderable tin process uses a conventional pre-treatment sequence to clean, condition and etch the copper substrate, prior to the tin deposition. An acid cleaner followed by a persulfate micro-etch would be standard. The tin plating bath itself operates typically at 65°C (149°F) and an important step is to follow this with a warm water rinse at 43 - 45°C (109 - 113°F). This ensures that organic by-products are not left on the surface, which could cause long term degradation of the surface, or poor solder wetting. Although the modified tin process uses a displacement reaction, a small part of the mechanism is autocatalytic. This ensures a very uniform deposit. For this reason, and to be completely effective, a minimum immersion time is used to eliminate any porosity and to increase the oxidation and corrosion resistance of the coating.

Solderability of the Finish after Aging

With a conventional immersion tin deposit, the formation of copper/tin inter-metallics consumes the tin during the aging and assembly processes. Good residual solderability of the coating is dependent on the amount of free tin remaining on the surface and is impaired by any atmospheric oxidation. The latter reduces the wettability, particularly if lower activity fluxes are used. It is noteworthy that tin and tin lead alloys. when applied to copper, have comparable Cu/Sn inter-metallic growth rates and also comparable tin oxidation rates at 155°C (311°F). It has also been postulated that each 4 hours of aging (at this temperature) nominally represents 1 year of shelf life.



As a consequence, the 155°C dry heat test is appropriate, and has become an arbitrary standard for testing this type of finish. On this basis, the proprietary flat solderable tin finish shows much improved resistance to thermal excursions. Extensive test results have borne out that the flat solderable tin process routinely provides complete (98 -100%) hole filling and pad wetting (on a solder float or solder wave test) after 8 hours aging at 155°C. In reality, this means that the finish will provide good solderability for 5 assembly heat cycles following a minimum of 6 months storage, which has evolved as a basic acceptance or approval criterion in the European market. The above chart shows the solder wetting forces with the flat solderable tin finish after 4 and 8 hours aging at 155°C.

One potential concern with plated tin finishes, is the susceptibility to moisture,

both during storage and processing. Steam aging tests e.g. J-Std 003, do not seem to be appropriate for non-fused finishes and most alternative finishes do not fair well under such conditions. To assess the effects of humidity on shelf life, it is much more appropriate to use damp heat aging tests such as 85°C / 85% relative humidity prior to solderability testing.



To simulate medium term storage under warm, more humid conditions, 21-day tests at 40°C /92% relative humidity or 28 day tests at 35°C /85% RH have been used with good results. Maximum wetting forces held up well and the most noticeable effect was the increase in time to 2/3 Maximum Wetting Force Relative to Aging from 0.9 seconds to approximately 2.2 seconds Typical results for solder wetting forces are shown in below.



The results of several evaluations have confirmed that, although the finish is affected by the humidity, the effects are inconsequential, and the modified tin finish retains good solderability, even in a "worse case" storage and transportation situation. Dry pack of PCB's could possibly extend the shelf life, although this has not been tested. However, water must not be left standing on a board or in the plated through holes prior to completing all soldering operations.

Surface Insulation Resistance and Ionic Residues.

Hot air solder level coatings have, in many cases, struggled to consistently meet the industry needs for surface insulation resistance (SIR) and ionics, because of the high levels of residual halides. These halides can cause major concerns relative to the accepted Bellcore limit of 6.5 ugs NaCl $/in^2$. As a consequence, typical results for surface insulation resistance (SIRs), as measured by, say, the Bellcore 78 test, or Electromigration as measured by the IPC 2.650.14, can be a problem. HASL finished PWBs often struggle to consistently meet the minimum Bellcore specification limit of 3×10^9 ohms, unless extensive improvements are made to the HASL postwash units in the form of 'cool-down chemical flux cleaners, soft stages'. brushing and multiple cascade hot water rinsing followed by DI water. Applying such procedures will normally increase the SIRs by 1.0 - 1.5 decades. A study of electromigration comparative numbers (TM650 2.6.14) of alternative surface finishes are shown below.



A direct comparison, on bare FR4 boards, showed the modified immersion tin system capable of providing values greater that 3 x 10^{10} ohms, which are typically one decade higher than normal HASL results, and also higher than for bare copper.

In the chart below it can also be seen that the residual ionics of 0.9 - 1.5 μ gs/in² (= NaCl), are comparable to the best in class (Nickel/Gold). When tested with solder resisted boards, the ionic results become dependent on the mask type and the degree of cure. Full or partial solvent-based solder-masks like, Probimer® 52 and 65, give excellent results with very low levels of



detectable ionics. By contrast, the results with aqueous acrylic-epoxy solder resists are more subjective, due to the hydrophilic nature of the mask materials including the resin-photopolymer systems and the fillers. Much depends on the LPSM process parameters and on the degree of final cure. However, typical numbers of 1.0 ugs/NaCl equivalents 3.0 are achievable with several masks providing that the LPSM process is optimized. In some cases the use of a post treatment (ionic cleaner) may be required. The testing has shown that, as the tin bath ages, there is little influence or further degradation of the ionics results, which is a latent benefit of the system.

Resistance to Dendritic Growth and Whisker formation.

The next chart below shows the results of the IPC 650 TM 2.6.13 testing for metallic dendritic growth, as conducted by an independent laboratory. The results for the flat solderable tin, using the 20 mil pitch coupons were significantly better than for bare copper, HASL and OSP. The 12 mil pitch numbers were similar. More importantly, with extended use of the bath, the results for metallic dendritic growth remained steady, further confirming the longer-term consistency of the bath.

SEM photomicrographs @ 5,000 X



With the strong emphasis on the reliablity needed from a surface finish, and with the historical propensity of thicker electroplated tin coatings towards whisker formation, this raises a possible concern with tin areas which may not be soldered (and not covered with solder mask). These areas include: via-hole pads not covered with solder mask on a 100% SMT PCB; compliant pin connector holes; exposed ground rings or other traces.

Several whisker studies on the flat solderable finish have been completed using a wide range of test conditions. Because of the random nature of such a phenomenon, there is no test-method that can give 100% assurance that a finish will not whisker. However, product manufactured as early as 1994 has been examined, with no evidence of any whisker growth. Testing to the DIN 41640 specification (56 days at 55°C, 20%) relative humidity - an ideal condition for whisker growth) has also been successfully completed with no problems reported. It is important to note that FST is not an electroplated finish and has reduced plating stress (stress areas may serve as sites for whisker growth). Secondly, FST has a precisely controlled thickness that is below the threshold normally associated with whisker formation. Thirdly, whilst the surface of the coating contains a high percentage of tin (>99%), it is not 100% tin and contains a proprietary co-deposit.



"Sharp" and Irregular grain structure -- Well Polygonized grain structure --Tin whiskers potential is substantial 1-3µm - very difficult to grow whiskers

Conventional Tin Flat Solderable Tin The comparative SEM photographs show the different structure of conventional immersion tin (which may be more prone to whiskers) and the flat solderable tin (FST). With a grain size of 1-3 μ m and a "well polygonized" (rounded and uniform) grain structure, FST meets the criteria "Very difficult to grow whiskers" as defined by Kakeshita, Shimizu, Kawanaka, Hasegawa, Journal of Matls.Sci.,17, 1982, pp 2560-2566.

Application of Flat Solderable Tin to Fine Pitch Assembly

Now re-looking at the alternatives, from the assembler's standpoint, the driving factors for any replacement PCB finish, other than HASL, come down to 3 major points:

- 1. To improve fine pitch SMT yields at assembly pitches of less than, or equal to, 0.65 mm (25 mil.). This is the point at which the any variability in the PCB finish begins to play a significant role.
- 2. To facilitate production processes at 0.4 mm. Pitch (16 mil.).
- 3. To enable the reliable soldering of finepitch area array technology devices (BGA's under 1mm pitch) where any variations in process and solder volume become much greater concerns.

A key question is the solder volume variability. The HASL specification requires the Sn/Pb thickness to be from 50 to 1000 microinches (1.25 -40μ), with a pad to pad variance not greater than 750 microinches (19 μ). This doesn't come close to eliminating the variability. In calculating the deposit volumes, the resulting variability of

the HASL finish contributes from 2.3% to as much as 54% of the solder joint volume! The ultimate goal is to improve the yields whilst increasing the joint reliability and lowering the cost of use. In concert with this, in order to replace the existing HASL finish, any new planar alternative should ideally be a "drop-in replacement" at assembly. The finish must be compatible with the flux systems used (SMT and Wave Solder) and also with the Reflow processing profiles (Air or Nitrogen). The treated boards must meet all the Bellcore reliability criteria and the holes must be compatible with press-fit and compliant pin insertion and metallurgy. The product must have excellent storage and handling capability with at least 6 and preferably 12 months shelf life and be completely suited to "in circuit test". Finally from the Fabricator's standpoint, the finish must be easy to apply and the process needs to be easily integrated into the existing PCB manufacturing operation. A 2 year study by a major OEM / assembler, concluded that the flat solderable tin gave good compatibility with all these requirements. The data emerging from the preliminary study follows:

Assembly Production Experience of Flat Solderable Tin

Initial testing at а communications equipment manufacturer showed that the assembly characteristics of the flat solderable tin were virtually identical to HASL. No process changes were required, when the finish was evaluated in a plant using Bellcore qualified no-clean processes throughout. The product was actually run through the plant during one set of tests without anyone noticing, except that the yields increased. The only area where a difference was recorded was triggered by the moisture sensitivity following solderpaste re-washes after misprinting. In this case, it was found to be important to carefully blow out any water from the plated through holes, or a wave soldering problem would be experienced. This is really something that should be done for HASL boards anyway, but it was definitely more critical with the non-fused tin finish. This prompted some further "in-depth" humidity testing (reviewed previously), which went to confirm that the FST actually had a good tolerance to high humidity accelerated aging.

First Time Production Tests

The first controlled production pilot testing was on a small run of 30 boards, processed 4 months after the fabrication. The boards run were 2-sided SMT mixed technology with through holes, and with a 2mm compliant pin connector. The second side was processed with a glue and wave assembly process. The board assembly consisted of a substantial number of .025 inch (0.65 mm) devices plus a substantial mix of other SMT components. The first pass yield results at In Circuit Test were as follows:

Flat Solderable Tin	-FPY 97%.
Typical HASL ICT	-FPY 87%.

There was one faulty component on this assembly but no defects were found relating to the SMT or soldering processes. The Post Glue, Post Wave Solder, and Final QA inspections all yielded 100% and no defects were related to the SMT or soldering processes.

HASL Rework Experience

Approximately 1500, HASL finished PCB boards, from old stock, (on average over 2 years old) had badly failed solderability testing and could not be used. These boards were reworked with FST, after stripping the HASL finish. The most complex of these boards was a 2 sided assembly with SMT/mixed technology, glue and wave bottom side, and over 2000 components. The SMT reflow side included 25 mil pitch devices plus two 304 pin, 0.5mm pitch, 40 mm body, MQFP's The results are shown as follows:

Historical HASL FPY,

Cumulative	50.6%	
FPQA:	753/814	92.5%
ICT:	1207/1569	76.9%
P_Wave:	1783/2192	81.3%
P_Reflow:	1544/1762	87.6%
(4Q95+1Q96)	+2Q96)	

Flat Solderable Tin First Pass Yield Data:

P_Reflow:	487/510	95.5%
P_Wave:	477/581	82%
ICT:	627/705	88.9%
FPQA:	267/282	94.7%
Cumulative F	65.9%	

The test data showed an increase in postreflow yields of 8%, an increase in first pass ICT yields of 12%, and a cumulative first pass yield improvement of 15%. The very next run of these assemblies in the factory after switching back to HASL finished boards resulted in a 21% drop in post reflow inspection yields!

Flat Solderable Tin Reliability

The reliability expectation is probably the most searching question to be addressed before any new finish can be used in a production environment. A number of important questions must be addressed. The performance aspects of the new tin system, particularly with regard to ionics, surface insulation resistance, electromigration, metallic-dendritic growth and propensity to whiskering, were reviewed earlier. A key question remains: What is the solderjoint reliability?

Solder Joint Reliability

Thermal cycling of the flat solderable tin has been carried out in some extensive European studies, where volume production experience dates back to 1994/5 and where dependable data exists. The approach used in this OEM study was to qualify solder joint reliability based on the "equivalence" of the metallurgy relative to HASL. In the case of a flat solderable tin, the plating process is self-limiting with a typical maximum thickness is around 45µinches (1.1μ) . Based on this fact, an analysis of the contribution of tin to the tin-lead alloy of the solder joint can be made. Using a 0.005 inch thick stencil, the tin percentage in the final solder joint increases less than 2%, and industry data readily supports that a 10% change in the tin-lead ratio would have no measurable difference on solder joint photographs reliability. SEM for comparable HASL and FST solder joints have identified the intermetallic region and are shown below

The distribution of tin and lead in several solder joints was reviewed for both the HASL and the tin finished boards that were assembled at the same time..



SEM Photographs - Tin-Copper Intermetallic thickness in both cases is ~ $1 \mu m$

This was to ensure that tin rich areas or other anomalies were not formed with the flat solderable tin finish. SEM analysis of many dot-mapped areas was also completed. Overall, a tin range of 75.5% to 79.8% was recorded between the two finishes. The study concluded that the resulting tin-copper intermetallics and alloy solder after soldering are indistinguishable on a flat solderable tin finished PCB compared to a HASL finished PCB. Based on this testing, it was felt that thermal cycle reliability testing was not required, but pull strength testing was undertaken to completely ensure the solder joints were truly the same. The purpose of this was to verify that: Firstly, the adhesion strength and failure mechanisms were equivalent; and secondly, that there were no hidden differences.

Solder Joint Pull Testing

The study compared HASL, OSP, FST, and Ni-Au finishes and all the pull tests resulted in cohesive failures. The tests revealed an interesting set of observations. Firstly, it was discovered that a difference in the pull strength results existed between the planar finishes tested and the HASL. The planar surfaces generated lower pull values and the results are shown below.

Pull Test Results

Sample	Size	Pull-lbs.	Std-Dev.
HASL	50	2.91	0.40
FST	50	2.37	0.25
OSP	52	2.36	0.33
Ni/Au	55	2.09	0.31

This difference was related to a "honeycombing" effect (or voiding) on the planar joints, which was not observed on the HASL joints and appeared to stem from flux out-gassing from the solder paste. By contrast, in the HASL joints, the flux outgassing typically coalesced into a single void, generally in the heel of the solder joint. The variability due to the solder joint volume appeared to cause the large standard deviation. It was hypothesized that, for the honeycombed planar solder joints, the small micro-voids formed, appeared to reduce the joint surface area with a proportionate reduction in pull. The flat solderable tin and OSPs pull numbers were comparable but the tin finish had by far the lowest standard The Ni-Au finish resulted in deviation. substantially lower average pull strength values. At this point, a conclusive cause for this difference has not been determined, but it is theorized that this is may have been related to the Au-Sn intermetallics in the solder joint.

These findings created the question: Were these micro-voids a problem for solder joint reliability? Solder joints fail by crack initiation and propagation. Voids in the solder joint stop the crack propagation and require the crack to re-initiate prior to further progression. One example reference: SMI Proceedings 1996, Vol 1, pp 121-126, "The Effects of Solder Joint Voiding on Plastic Ball Grid Array Reliability", Banks, Burnett, Cho, DeMarco, Mawer:

"Solder joint voiding at the maximum levels observed in this study (where the voided areas was up to 24% of pad area) caused no negative effect on PBGA board level reliability. In fact, PBGA solder joints with voids had 16 percent <u>better</u> reliability than those without voids." "It is probable that the observed reliability improvement results because once a crack propagates to a void, it must re-initiate to proceed further. This re-initiation requires additional energy, thereby retarding the fracture of the joint."

From this and other studies, it was concluded that the solder voids are not a reliability problem and that the increased standard deviation probably related to the differences in the solderability of the finishes.

Conclusions from the Assembly Studies.

The first impressions derived at the assembly stage, using Bellcore no clean flux technology, were that the tin finish gave compatibility excellent with 'HASL' soldering processes. The key difference is that the planarity reduces the variance in solder joint volume by up to 50%. This can impact not only the speed and efficiency of component mounting but, on direct comparison with HASL, can also facilitate some signifcant yield increases at assembly. In the case history described, the ICT yield increased from 87% to 97% on 0.025' pitch technology, and the tin process facilitated the reclamation of over 1000 unsolderable HASL boards with a cumulative FPY yield increase of 15.9% actual. The flat solderable tin finish did withstand solder paste rewashes providing that the holes were dried after rewash. The moisture sensitivity of the tin coating was not a problem for solderability, which held up extremely well after high %RH aging.

The area of interface with aqueous liquid photo-imageable soldermasks has shown that some work well but some of the

nickel/immersion gold process. In this case, the mask curing needs to be optimized and a post clean added if necessary. Such optimization will also improve the tape testing integrity which can also be an issue for incorrectly cured mask material.

The overriding conclusion, from the metallurgical studies completed, is that the modified flat solderable tin finish produces a solderjoint which is very comparable to that from the HASL finish, for which a lot of reliability data exists. The pull tests were the best (highest pull and lowest Std.Dev.) of the planar alternatives tried.

Finally, The many tests conducted for SIRs, E Migration, metallic dendritic growth and whisker testing all gave repeatedly good results. On this basis, the flat solderable tin finish offers a good planarity solution for fine-pitch assembly product not requiring direct wire bonding. It is appreciably less expensive than the precious metal based alternatives and has better heat cycle durability and through hole solderability than other alternatives.

Acknowledgement.

This paper was written with the input from, and benefit of, a substantial amount of work

carried out by DSC Communications (now Alcatel) in Plano, TX and kindly provided by Joe Smetana.

References - with appropriate thanks to:

- "Alternate PCB Surface Finishes", Joe Smetana Jr., DSC Communications (Alcatel) Future Circuits 1998
- 2. IPC-TM- 650 Test Methods Manual
- "Measuring and Predicting Solderability". Christopher Hunt, National Physical Lab.
- "Alternativen zur Heiβverzinnung". Von Odfried Inderfurth, Galvanotechnik 84 (1993)
- Kakeshita, Shimizu, Kawanaka, Hasegawa, Journal of Matls.Sci.,17, 1982, pp 2560-2566.
- "The Effects of Solder Joint Voiding on Plastic Ball Grid Array Reliability" Banks, Burnett, Cho, DeMarco, Mawer, SMI Proceedings 1996, Vol 1, pp 121-126.
- The Development and Use of a Modified Immersion Tin as a High Performance Solderable Finish. David H.Ormerod, Dexter Electronic Materials (September 1997)
- 8. Internal Dexter technical papers. Mir Ali, Janet Semensi et al., Dexter Electronic Materials, Londonderry,NH.