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Immersion, Non-Electrolytic, Tin/Lead Plating Process

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Abstract
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The technological development and characteristics of an innovative process and composition for immersion plating and fusing of a solderable tin/lead deposit over copper are discussed (Ref. 1). The process offers a viable alternative to hot air solder leveling, electrodeposition/selective stripping, or inhibitor coatings for maintaining solderability of printed wiring boards.

A flat, uniform solderable tin/lead coating on all feature surfaces and edges is achieved. A number of important benefits are derived. The ability to uniformly coat any copper surface, including fine pitch features, is substantially enhanced. Solderability is improved because of a thick, flat, co-planar and uniform Tin/Lead deposit on all copper surfaces.

Typical thickness and composition of the fused alloy are 150 to 300 microinches (4 to 8 microns) and 65 to 75% tin.

Introduction

With the emergence of Solder Mask Over Bare Copper (SMOBC) and Surface Mount Technology (SMT), a number of processes have been developed for maintaining solderability of Printed Wiring Boards (PWBs): Hot Air Solder Leveling (HASL), imaging processes with selective plating or stripping of electrodeposited solder and subsequent fusing, and organic inhibitor coatings.

This paper will discuss an innovative process for maintaining solderability. The key to this new technology is an immersion, non-electrolytic, solder plating bath (SPB) that plates a fuseable tin/lead deposit by a chemical displacement reaction with copper (Ref. 2). The major benefits include a flat, uniform solderable tin/lead coating on all feature surfaces and edges (Fig. 1a,b,c,d).

***Fig. 1a.**—Hole Corner, As Plated*

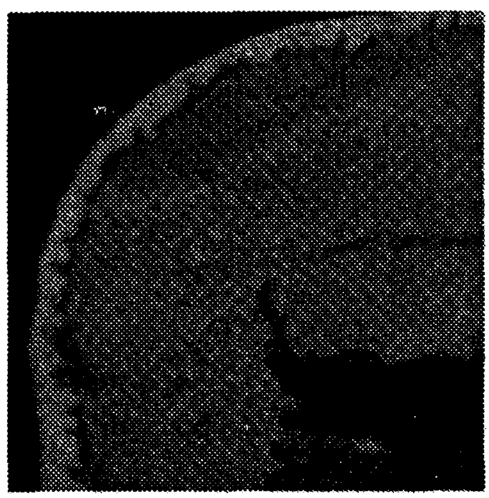

***Fig. 1b.**—Hole Corner, Fused*

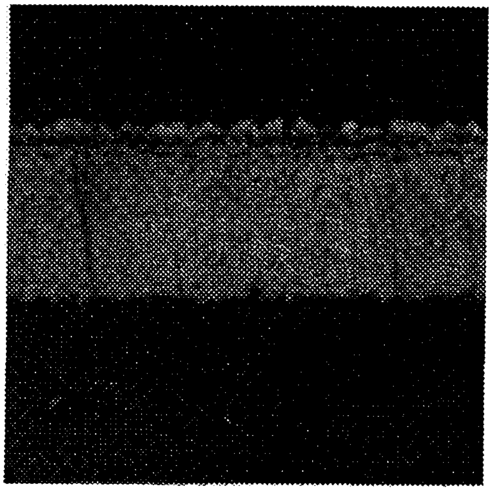

Fig. 1c.—Line, As Plated

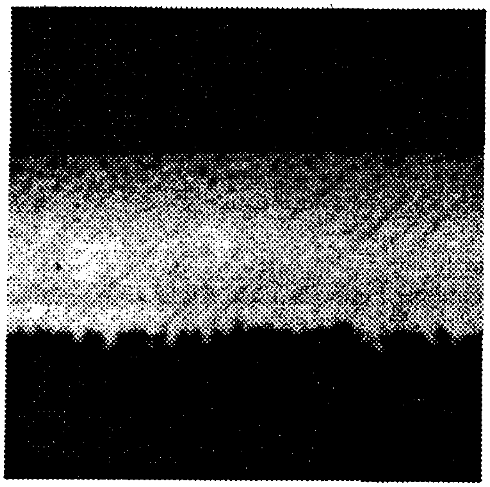

Fig. 1d.—Line, Fused

Solderability is made possible by a thick tin lead deposit with uniformity and conformality on all copper surfaces of the circuit lines and plated through holes. Peaking and thinning differences are minimized between the circuit line center and edge or between the hole center and corner (Fig. 2,3).

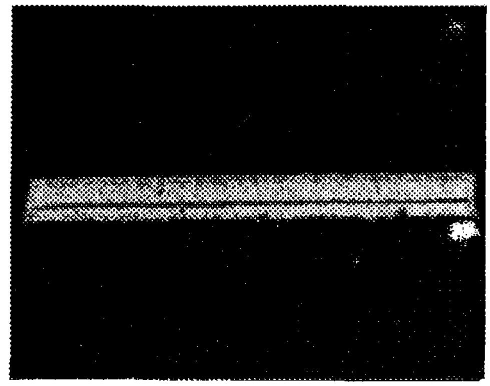

Fig. 2.—Uniform Fused Thickness on Circuit Line

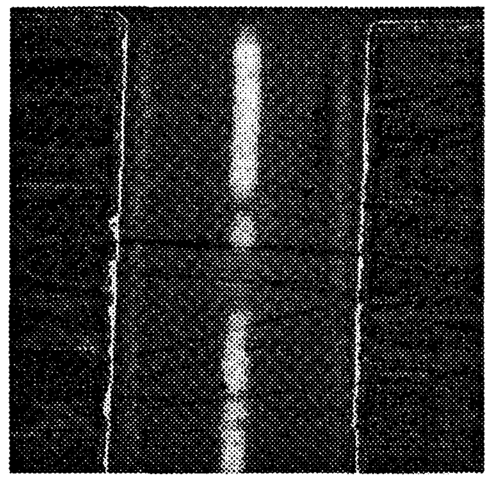

Fig. 3.—Uniform Fused Thickness in Hole

Additionally, it is possible to uniformly plate fine pitch circuit features and surface mount pads (Fig. 4a,b).

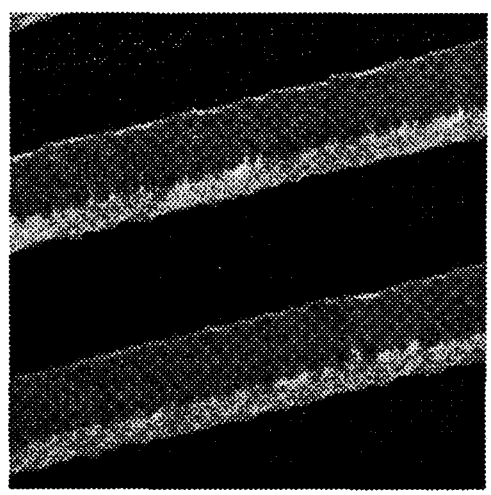

Fig. 4a.—Uniform Fused Thickness on 2 mil Lines

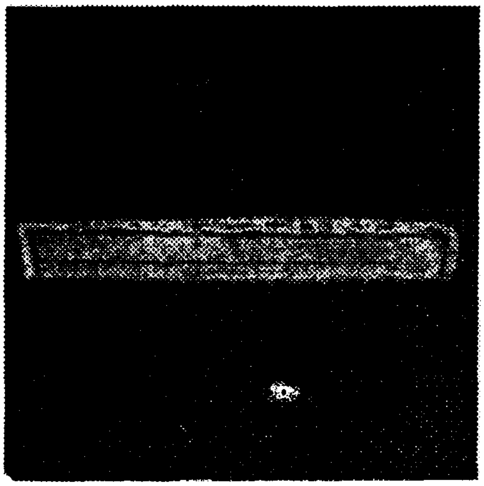

Fig. 4b.—Uniform Fused Coating on Surface Mount Pad

Typical thickness and composition ranges of the fused alloy are 150 to 300 microinches (4-8 microns) and 65 to 75% tin content. Average thickness and composition are controlled to about 240 microinches (6 microns) and 70% tin content.

The topics discussed in this paper are as follows: 1) Plating Mechanism in the SPB, 2) Deposit Characteristics, 3) Process Description, and 4) Operational Results.

1. Displacement Plating Mechanism

The solder plating bath represents an entirely new technology for depositing tin and lead in a near eutectic ratio onto copper surfaces. It operates most like the familiar immersion chemistries that displace a more noble metal onto a less noble metal in accordance with the electromotive force series. Under normal conditions, tin and lead would not be expected to plate on the more noble metal copper. However, the presence of a complexing agent (L-Ligand) shifts the Sn, Pb, and Cu potentials to more favorable values (Fig. 5).

$$Sn^{2+} + 2Cu \longrightarrow Sn^{0} + 2Cu^{1+} (L)$$

$$Pb^{2+} + 2Cu \longrightarrow Pb^{0} + 2Cu^{1+} (L)$$

Fig. 5.—Displacement Reaction

If the deposit were compact, it would be expected that this reaction would essentially be unable to continue after the deposition of the first monolayer of tin and lead. However, the deposit is porous, and deposition continues at a constant rate until the pores begin to fill, as evidenced by the knee in the plating thickness vs. time graph (Fig. 6). This accounts for the ability of the SPB to deposit sufficient thickness for fuseability.

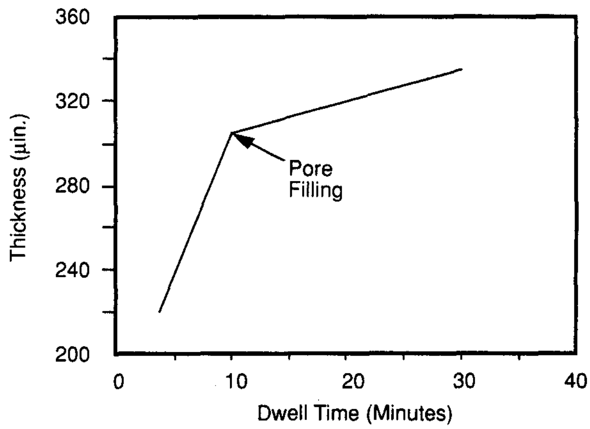

Fig. 6.—Deposit Thickness Versus Dwell Time

One possible reason that other chemistries of the displacement type, notably immersion tin, are not useful is because of their inability to deposit adequate thickness before pore closure. The solder plating bath utilizes unique rate enhancers that ensure that the reaction continues until adequate thickness is deposited.

Since copper is removed from the printed wiring, not only during displacement in the solder plating bath but also in the cleaning process, it is required to plate an additional copper thickness of approximately 300 microinches to maintain minimum final copper thickness specifications. About 100 microinches of copper is removed in the copper etch cleaning step and about 200 microinches of copper is displaced for each 300 microinches of tin/lead deposited (Fig. 7).

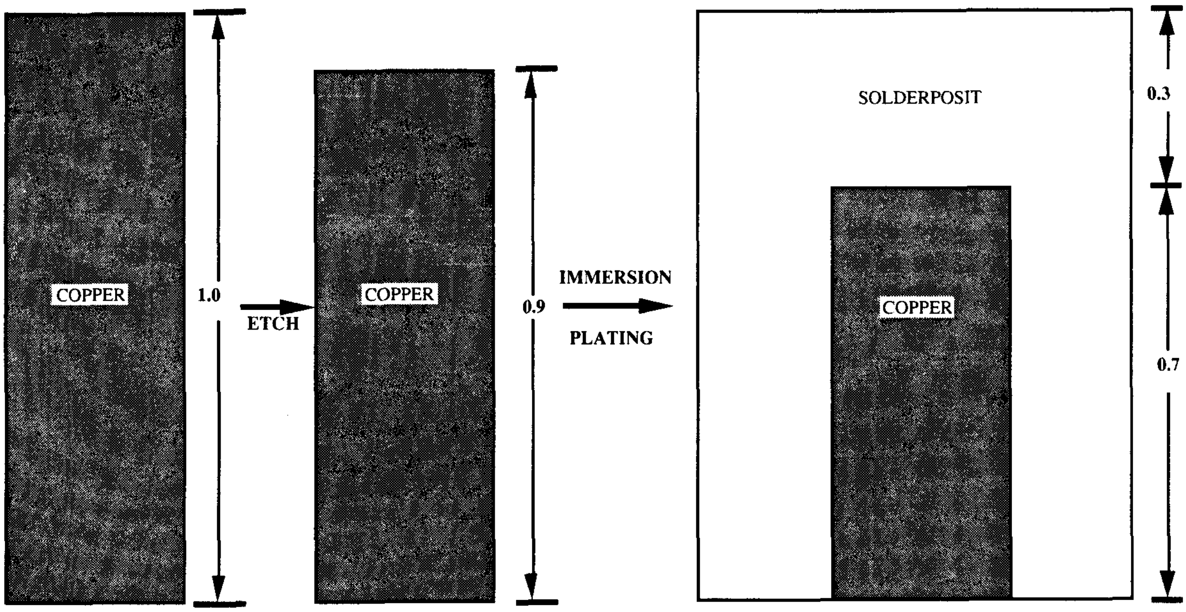

Fig. 7.—Immersion Plating Schematic

The chemistry is such that several interactive factors determine the useful bath life. The factors involved in determining bath life are pot life time, time at elevated temperature, cumulative total of replenishment, total ligand concentration, daily throughput and copper concentration (Fig. 8a).

a) Pot life time typically 2 weeks.
b) Time at elevated temperature up to 80 hours.
c) More than 1/2 cycle of replenishment (one cycle = replenishment of 18 g Sn/L).
d) Greater than 12 square feet of copper surface coated to an average thickness of 225 microinches (with higher daily throughput, the bath yield will be increased).
e) Daily throughput of 1.2 to 18 sq. ft.of copper surface per gallon of bath per day.
f) Copper concentration of 12 - 18 g/l, depending on the daily throughput.

Fig. 8a.—SPB Bath Life

Replenishment of the chemical components of the SPB is based primarily on determination of tin concentration by titration. Secondary adjustments to the bath component concentrations may be made in order to alter the deposit thickness and composition within the specified ranges by reference to thickness and composition measurements made by X-Ray Fluorescence (XRF) analysis.

The functional components of the immersion tin/lead bath are listed in Fig. 8b.

Tin
Lead
Acid
Buffer
Ligand
Reaction Enhancer
Composition Adjuster
Thickness Adjuster

Fig. 8b.—Functional Components of SPB

2. Deposit Characteristics

The tin/lead deposit has the typical characteristics shown in Fig. 9.

1. Average thickness on all feature types between 150 and 300 microinches.
2. Tin content between 65% and 75%.
3. Fused deposits meet IPC-S-804A criteria for acceptable solderability.
4. 100% Adhesion to copper substrate (no interfacial delamination).
5. Ratio of thickness of annular pad to non-annular pad in the range between 0.7 to 1 and 1.5 to 1.

Fig. 9. *—SPB Deposit Characteristics*

Without magnification, the surface before fusing is typically dull and matte, with reflective crystals distributed throughout.

With a scanning electron microscope at 200 and 1000X magnification roughness and porosity of the deposited tin/lead are more easily observed (Fig. 10a,b).

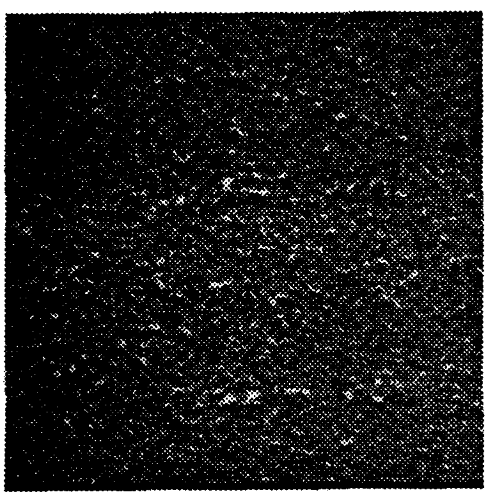

Fig. 10a. *—Surface as plated, 200x*

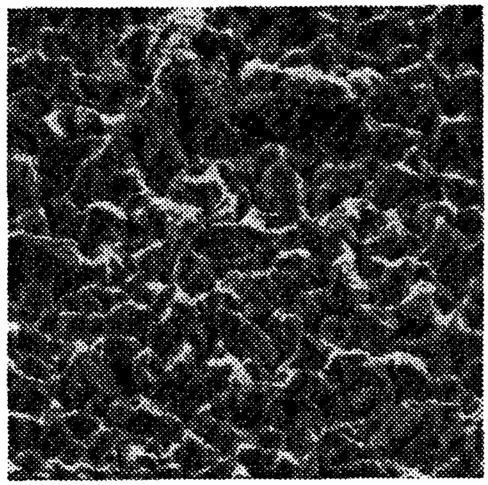

Fig. 10b. *—Surface as plated, 1000x*

The analysis of the top surface of the as plated deposit shows a high tin content and low lead content (Fig.11a,b).

Fig. 11a. *—Plated Surface*

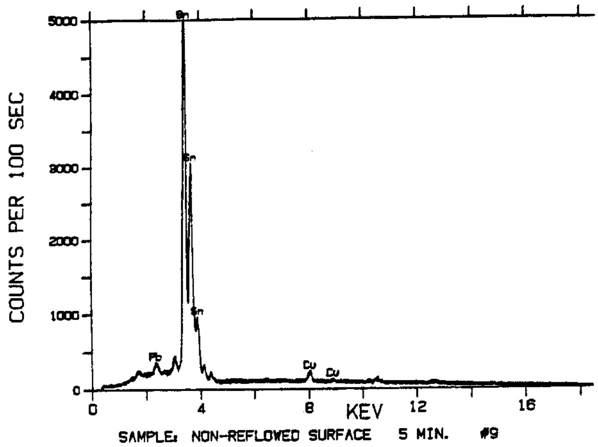

Fig. 11b.—X-ray scan of plated surface

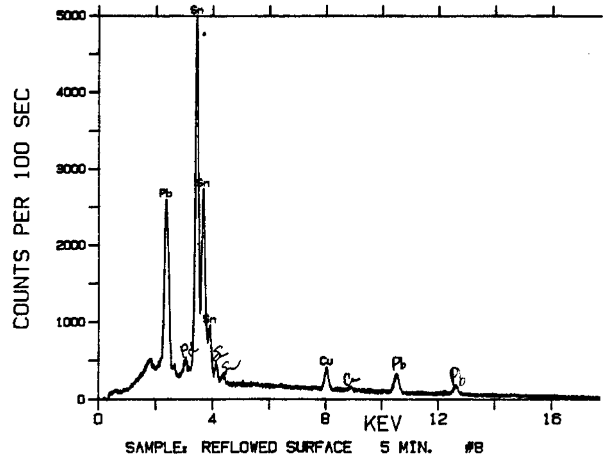

Fig. 11d.—X-ray scan of fused surface

Analysis of the same surface after fusing shows tin and lead to be present in the amount expected for the homogeneous alloy (Fig. 11c,d).

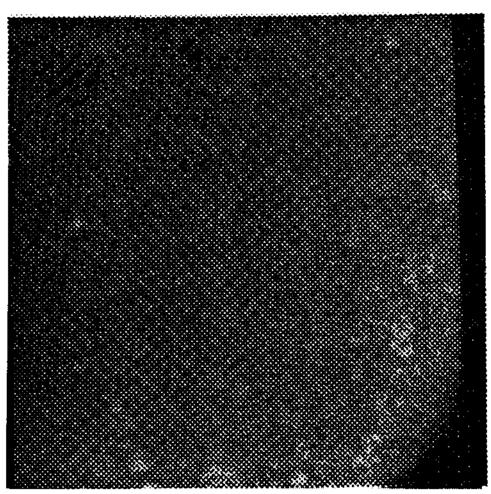

Fig. 11c.—Fused surface

The before and after fusing cross-sections show that the uniformity of thickness of the deposit is retained, and that the deposit is of the same homogeneous appearance as obtained with other methods of solder application (Fig. 12a,b).

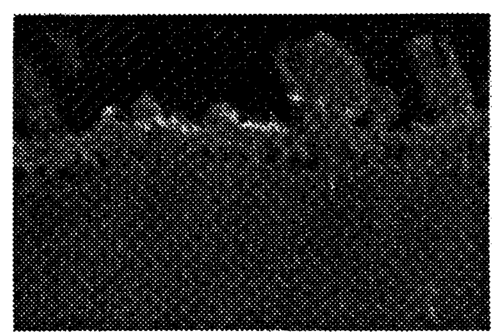

Fig. 12a.—Plated Cross-Section

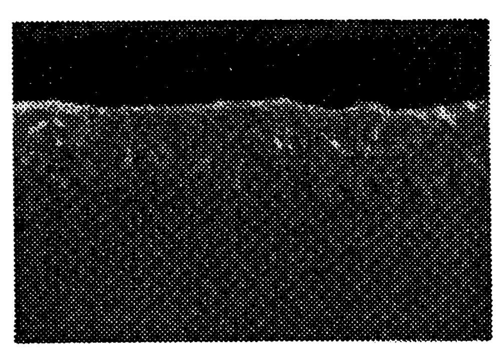

Fig. 12b.—Fused Cross-Section

The tin and lead distribution maps of the preceeding cross-sections show the changes in the deposit composition distribution which occur due to fusing (Fig. 13a,b,c,d).

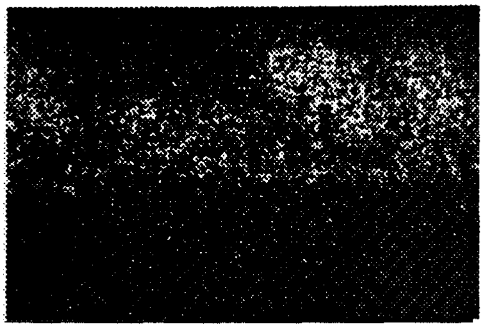

Fig. 13a.—*Tin map as plated*

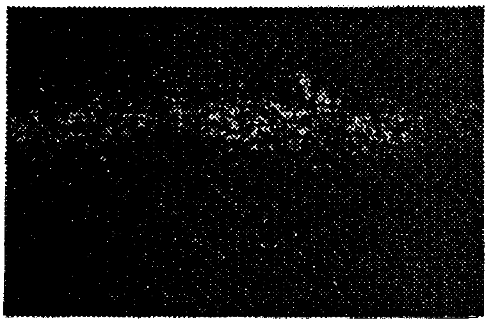

Fig. 13b.—*Lead map as plated*

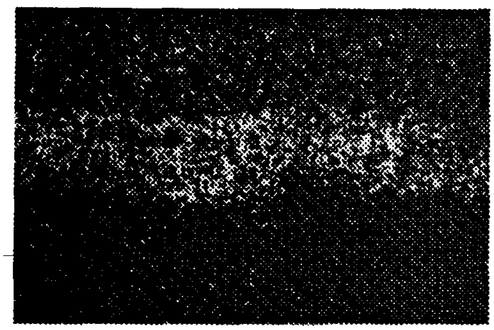

Fig. 13c.—*Tin map as fused*

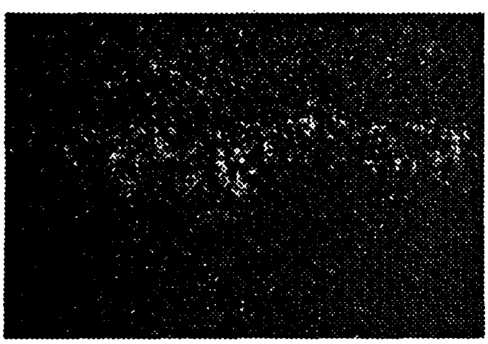

Fig. 13d.—*Lead map as fused*

The tin and lead distribution maps of the fused surface shows a uniform distibution of tin and lead at the surface (Fig. 13e,f).

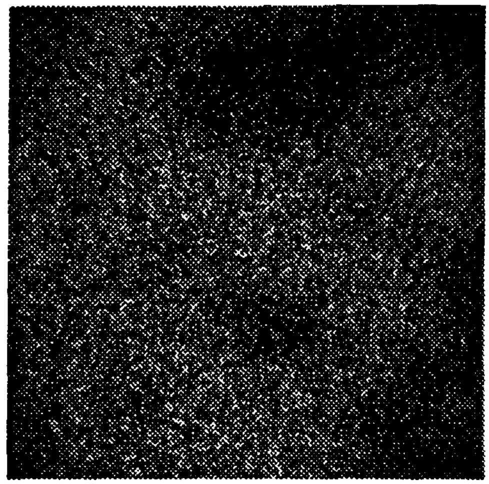

Fig. 13e.—*Fused Surface Tin Map*

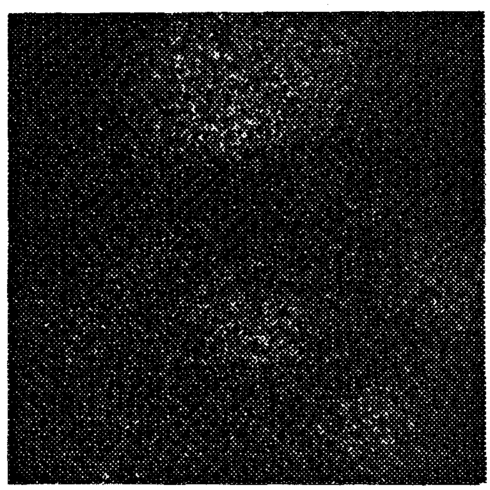

Fig. 13f.—*Fused Surface Lead Map*

XRF contour mapping of the thickness and composition of the deposit after fusing illustrates the degree of uniformity and flatness that can be achieved (Fig.14a,b).

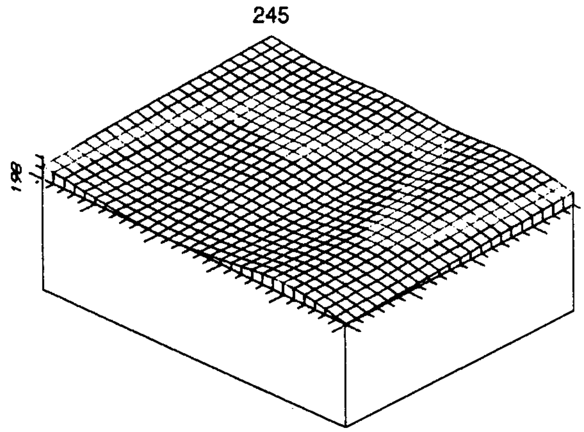

Fig. 14a.—Fused thickness (microinches) contour map

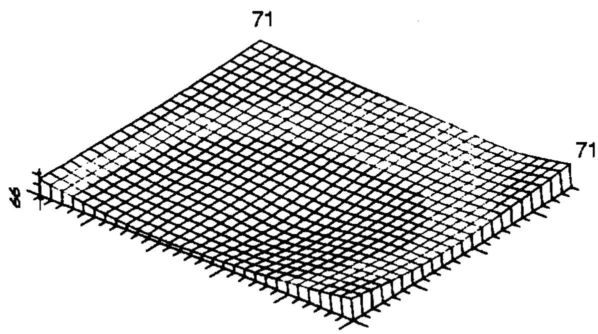

Fig. 14b.—Fused composition (% tin) contour map

Comparative studies on roughness and ionic contamination indicate the similarity of the results with original substrate and other processes (Fig. 15a,b).

Comparative Surface Roughness (Angstroms)		
Sample	Average Roughness	Maximum Peak to Valley
0.5 oz Cu Clad	5048	16437
1.0 oz Cu Clad	4159	13112
Bare Cu Circuit	2281	14183
Reflowed Immersion Sn/Pb	2147	14974

Fig.15a.—Surface Roughness

Ionic Contamination	
Before Reflow	0.0017 mg NaCl/in^2
After Reflow	0.0080 mg NaCl/in^2
Military Specification	0.0140 mg NaCl/in^2
Commercial Specification	0.0600 mg NaCl/in^2

Fig. 15b.—Ionic Contamination

Industry specifications for solderability were met in independent testing (Fig. 16).

IPC S804A Method 4

9 IPC B25 PWBs - one specimen from each

Results: All meet requirements.

MIL-STD-202F; method 208 D and 208 F

1 area aged over boiling water for 1 hour
1 area aged over boiling water for 4 hours

Results: Acceptable solderability and both meet requirements

Fig. 16.—Solderability Tests (Ref. 3)

As shown in Fig.17a, three circuit cards, coated with immersion tin/lead and fused using separate techniques, were micro-sectioned and evaluated at 200X magnification for tin-lead and intermetallic thickness.

Fusing Method	Tin-Lead	Intermetallic
Hot oil	0.0003-0.0004"	0.0001"
Std. IR	0.0003-0.0004"	0.0001"
2 X IR	0.0001-0.0004"	0.0001"

Fig. 17a.—Intermetallic Thickness Measurements (Ref. 3)

Figures 17b,c,d illustrate the layered structure of the as-plated deposit. The layers vary in tin content. Fig. 17e shows the homogeneity of the deposit after fusing, and also the 50-100 microinch intermetallic layer, in the total 300 microinch coating.

Fig. 17b.—As Plated, 1500x

Fig. 17c.—As Plated, 3500x

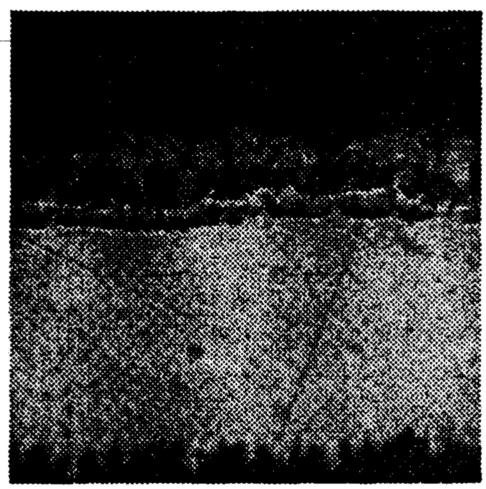

Fig. 17d.—As Plated layers, 1500x

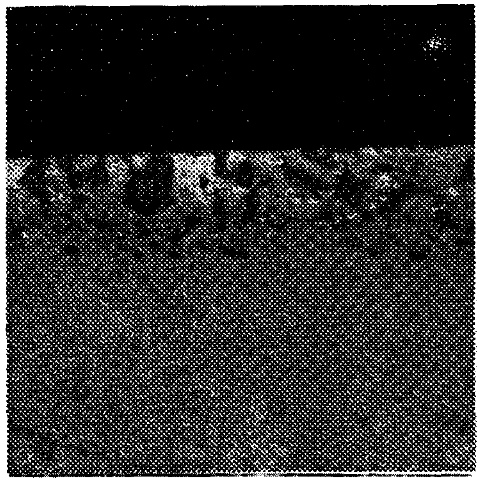

Fig. 17e.—Fused, 1500x

3. Process Description

The process is composed of two parts: 1) the immersion tin/lead plating process of solder masked (SMOBC) panels and 2) the fusing process.The preferred method is to operate these two parts as one continuous process. The general process flows are shown in Fig. 18a,b.

Acid Cleaner
Microetch
Pre-Dip
No rinse
SPB
Post-Dip

Fig. 18a.—Plating Process

Immersion Tin
Clean/Flux
Pre-Heat
Fuse
Post-Heat
Clean/Dry

Fig. 18b.—Fusing Process

The process for plating involves cleaning of light soils and removal of oxides, etching, dipping into a compatible solution, followed by direct immersion (no rinsing) prior to plating with immersion tin/lead for about 8 minutes at 162°F, followed by a compatible post-dip for maintaining solubility of SPB constituents and localizing drag-out, rinsing and drying. The process for fusing is typical and requires an initial immersion tin.

The more specific process flows are shown in Fig. 19a,b.

Immersion Tin/Lead Plating Process		
Optimize solder mask, plating, fusing, and associated processes for specific applications.		
Product	Temperature (°F)	Time (min)
1. ACID CLEANER	110-120	3-5
2. Rinse*	60-90	1
3. Rinse	60-90	1
4. MICROETCH**	95-105	1-2
5. Rinse	60-90	1
6. Rinse	60-90	1
7. Rinse	60-90	1
8. PRE-DIP	100-120	1-2
9. IMMERSION TIN/LEAD	160-164	7.5-8.5
10. POST-DIP	60-80	1-2
11. Rinse	60-90	1
12. Rinse	60-90	1
13. Rinse	60-90	1
14. Dry		as necessary (minimize)

* DI water rinsing is preferred for all rinsing operations, and is necessary for all post-microetch rinses.

** Removal of 80-100 µin. of copper is recommended.

Fig. 19a.—Plating Process Flow

Hot Oil Fusing Process		
Optimize solder mask, plating, fusing, and associated processes for your specific application.		
Product	Temperature (°F)	Time (min)
1. IMMERSION TIN*	70-160	30-180 sec.
2. Rinse**	60-90	
3. Rinse	60-90	
4. Rinse	60-90	
5. Dry		as necessary (minimize)
6. FLUX	60-80	typically 10-15 sec. (as necessary)
7. REFLOW OIL	250	typically 30 sec. (as necessary)
8. REFLOW OIL	400	typically 20 sec. (as necessary)
9. REFLOW OIL***	250	typically 20 sec. (as necessary)
10. Rinse	120	1
11. Rinse	60-90	1
12. Rinse	60-90	1
13. Clean		
14. Dry		as necessary (minimize)

* There should be minimal delay between IMMERSION TIN and FUSING.

** DI water rinsing is preferred for all rinsing operations.

*** Alternatively, hot {greater than 120°F (49°C)} DI water may be used for the necessary time.

Fig. 19b.—Hot Oil Fusing Process Flow

SMOBC panels are required to have clean copper surfaces free of residues and the solder mask must be compatible with the process. Also, an additional 300 microinches of copper thickness is required, as previously explained.

The fusing process which was used during the early stages of evaluation was hot oil fusing, which is presented here in more detail. Infrared fusing is also being used. It is expected that most fusing processes may be used. However, some critical requirements common to all methods need to be emphasized (Fig. 20).

A. The requirement to use immersion tin.
B. Minimal delay between immersion tin and fusing.
C. Continuous sequence between immersion tin and fusing.
D. Optimization of fusing parameters for specific applications.

Fig. 20.*—Critical Fusing Requirements*

4. Operational Results

The solder plating bath (SPB) described here overcomes the limitations of the prior art that led many investigators to believe that a non-electrolytic tin/lead plating bath would not be practical (Ref. 4). Previous experiences, going back over 20 years, to develop a SPB were frustrated by a number of factors: a. uncontrollable thickness and composition; b. exfoliation of the deposit; c. short pot-life; d. low tolerance to copper concentration; e. poor solderability due to excessive intermetallic content; f. solderability degradation with aging; and g. high cost associated with low yield/throughput. The typical operational results at full scale production conditions (50 - 150 gallon process lines) indicate that these problems are resolved. (Fig. 21).

a) Pot life time typically up to 2 weeks.
b) Time at elevated temperature up to 80 hours.
c) More than 1/2 cycle of replenishment (one cycle = replenishment of 18 g Sn/L).
d) Greater than 12 square feet of copper surface coated to an average thickness of 225 microinches (with higher daily throughput, the bath yield will be increased).
e) Daily throughput of 1.2 to 18 sq. ft.of copper surface per gallon of bath per day.
f) Copper concentration of 12 - 18 g/l, depending on the daily throughput.
g) Average thickness on all feature types between 150 and 300 microinches.
h) Tin content between 65% and 75%.
i) Fused deposits meet IPC-S-804A criteria for acceptable solderability.
j) 100% Adhesion to copper substrate (no interfacial delamination).
k) Ratio of thickness of annular pad to non-annular pad in the range between 0.7 to 1 and 1.5 to 1.

Fig. 21.*—Results from standard operation*

About 70,000 (18 X 24 inch) panels have been produced over the past 2 years at five production facilities.

Figures 22a,b illustrate the controllability and consistency of thickness within specifications throughout a bath life.

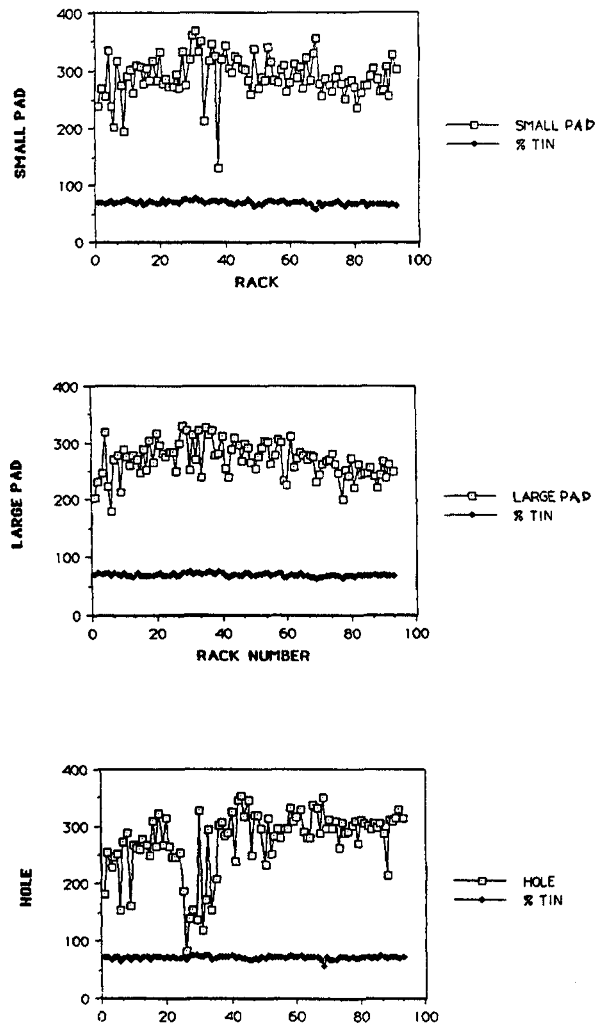

Fig. 22a.*—Thickness and composition on small pad, large pad, and annular ring*

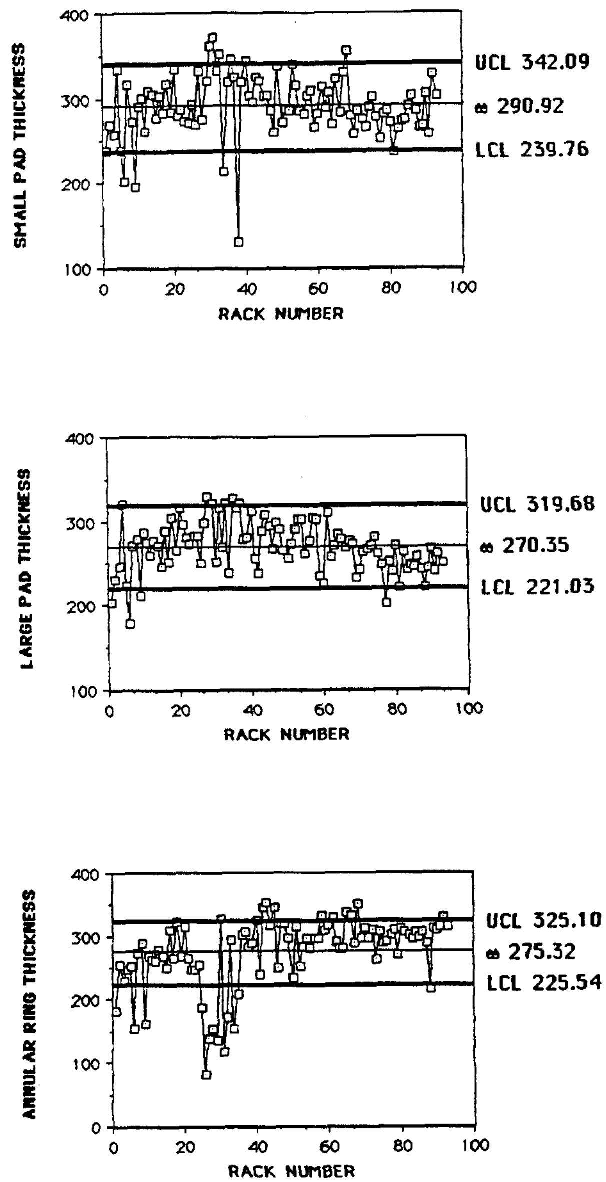

Fig. 22b.—*Thickness and Composition on Small Pads, Large Pads, and Annular Rings, with One Sigma Limits*

Figure 22c shows all the thickness data for all three features. At startup, the bath was adjusted for the particular copper substrate being plated. Racks 22-37 plated low thicknesses on the annular rings due to inadvertant shutdown of the deionized water rinses during production (Fig. 22c).

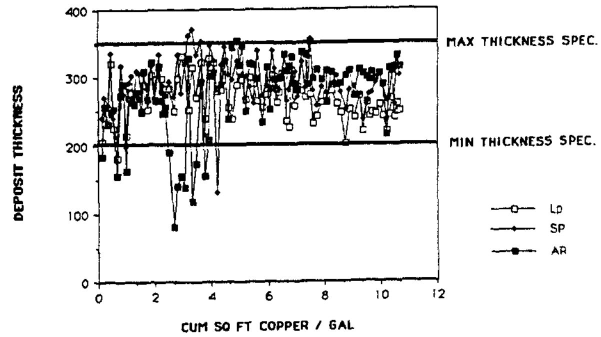

Fig. 22c.—*Summary of Data from 22a and 22b*

In the prior data, this production facility specified 200 to 350 microinches thickness in order to accomodate infrared fusing.

In Fig. 23a,b, the consistency and controllability of the average thickness and tin content in the deposit throughout a bath life at another test site is shown. At this location, the thickness specification was 150 to 300 microinches for hot oil fusing.

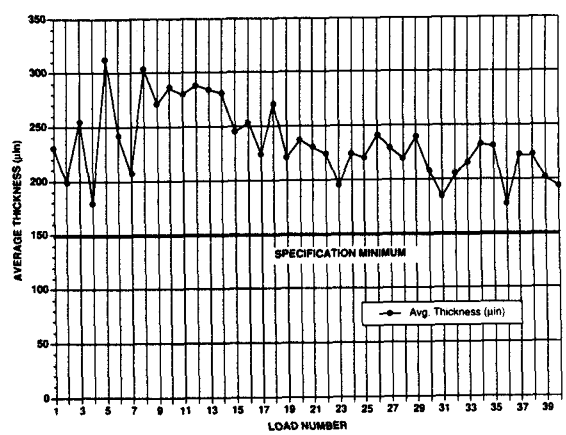

Fig. 23a.—*Average Thickness*

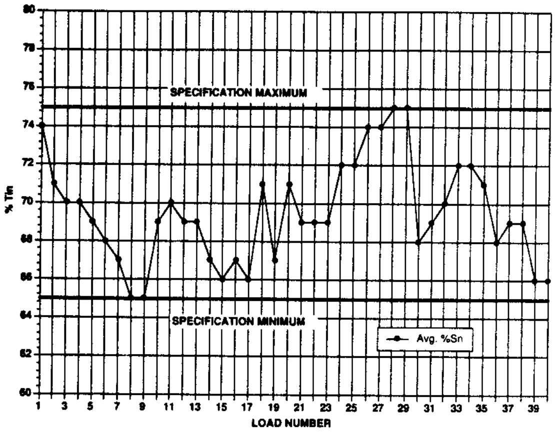

Fig. 23b.—Average Composition

Figures 23c,d,e,f contain the individual data points for four different feature types on two boards from the same rack. (Legend: ■ = annular ring, ● = small SMD pad, ▲ = large pad, ◆ = circuit line)

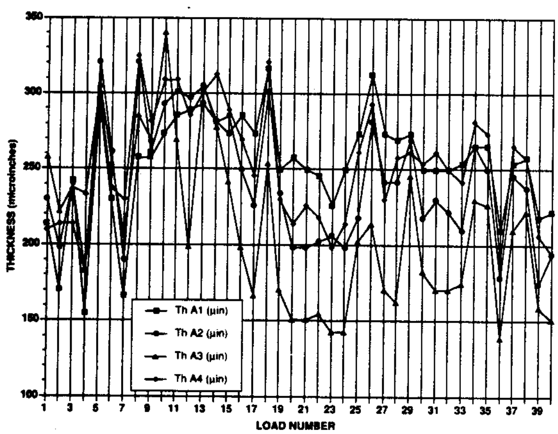

Fig. 23c.—Thickness on "A" Panels

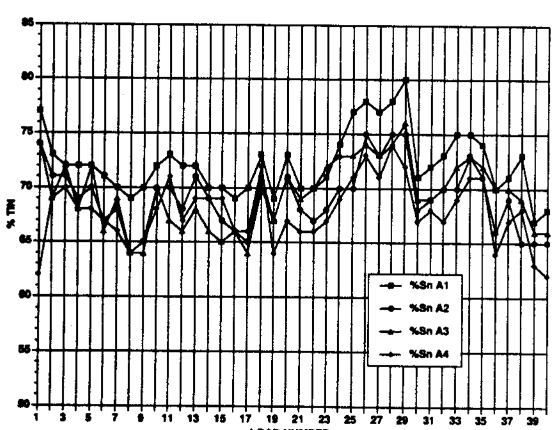

Fig. 23d.—Composition on "A" Panels

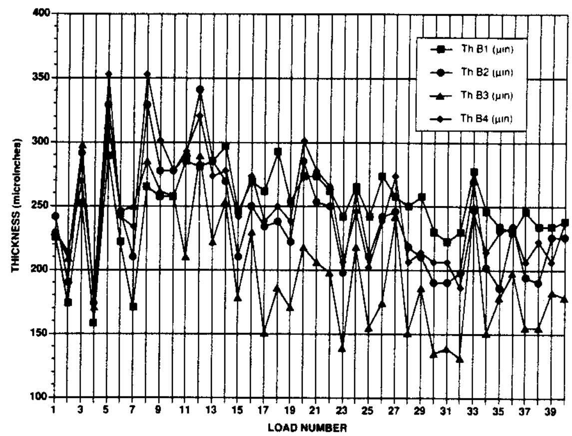

Fig. 23e.—Thickness on "B" Panels

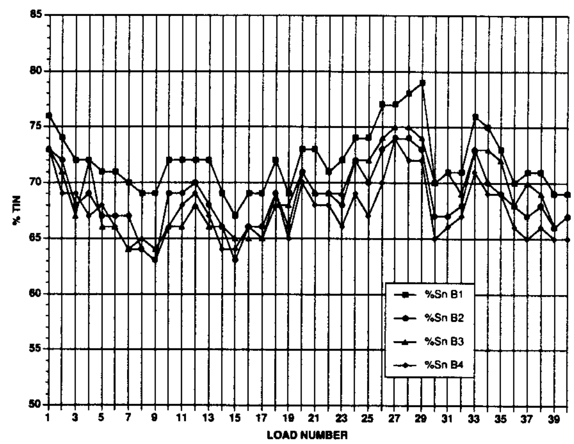

Fig. 23f.—Composition on "B" Panels

Figure 23g shows 100% adhesion and increasing cohesion by tape test throughout the bath life.

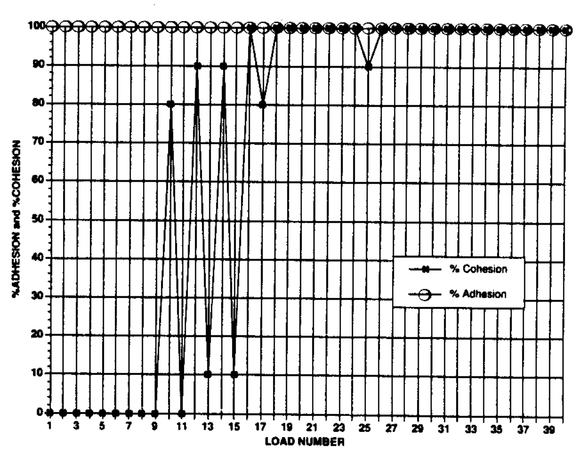

Fig. 23g.—Adhesion and Cohesion

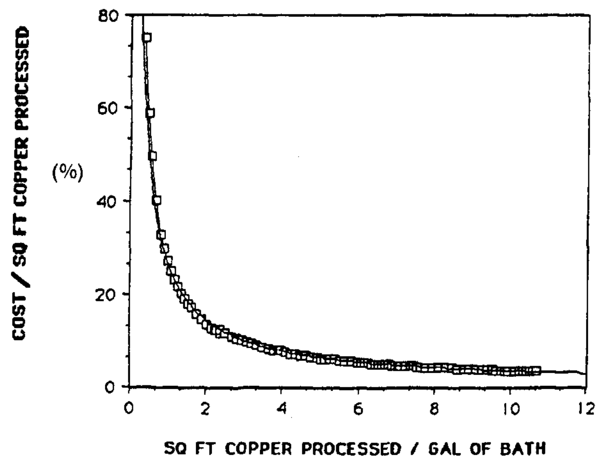

Fig. 24.—Amortization of Bath Makeup Cost

Figure 24 illustrates the amortization of the bath makeup and replenishment with throughput.

A statistical study of composition and thickness for a control production method and the SPB method was performed over a ten rackload span (Fig. 25). The SPB produced much less variability in thickness and composition after fusing.

Control		
	Composition (% Sn)	Thickness (µin)
Range Average	49 - 69 61 ± **7**	38 - 201 103 ± **56**
Solder Plating Bath		
	Composition (% Sn)	Thickness (µin)
Range Average	62 - 70 67 ± **2**	246 - 412 371 ± **33**

Fig. 25.—Average Results from 10 Rack Loads

The typical yield is greater than 12 square feet of exposed copper surface per gallon of SPB at an average thickness of 225 microinches when replenished through more than 1/2 cycle of replenishment (one cycle is the replenishment of 18 g Sn/liter). Loading and throughput are important to maximize the yield. Higher loading and throughput increase the yield to about 18 square feet of exposed copper surface per gallon of bath when replenished through more than 3/4 of a cycle of replenishment (Fig. 26).

Loading:	0.1 to 0.5 sq. ft. of copper surface per gallon of bath.
Throughput:	1.2 to 18 sq. ft. of copper surface per gallon of bath per day.

Fig. 26.—Usage Requirements

Figure 27 shows the increase of copper concentration with throughput.

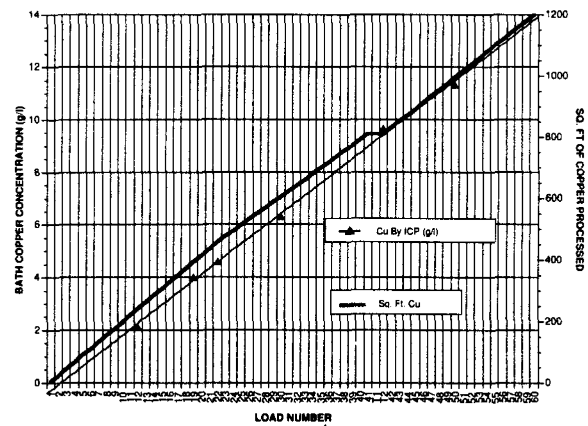

Fig. 27.—Increase of Copper Concentration for 100 gallon bath

Figures 28 and 29 show the solderability results after dry aging and autoclave aging.

Dry Aging (2 boards per evaluation) Percentage of solder paste wetting after reflow.		
	Control	Solder Plating Bath
6 hours	98%	100%
12 hours	95%	100%
24 hours	90%	98%
36 hours	80%	95%
48 hours	70%	95%

Fig. 28.—Solderability: % Wetting vs Hours in Oven at 150°C

Autoclave Aging (3 boards per evaluation) Percentage of solder paste wetting after reflow.		
	Control	Solder Plating Bath
6 hours	70%	90%
12 hours	60%	80%
24 hours	55%	70%
36 hours	50%	60%
48 hours	30%	40%

Fig. 29.—*Solderability: % Wetting vs Hours at 120°C, 100% R.H., and 2 Atmospheres*

Summary

Although originally expected to be used mainly for SMT and advanced fine pitch applications, current users are investigating the use of the immersion, non-electrolytic tin/lead plating process for all applications where fused tin/lead is used for maintaining solderability and the benefits of chemical deposition can be realized.

Acknowledgments

We wish to recognize that this paper has many contributors both within and outside of Shipley Company Inc. Also, that this innovative technology is the result of a strong team effort comprising many members of our world wide, european and far east operations in partnership with vendors, customers, assemblers and manufacturers of original equipment. In particular, we would like to thank: the process inventor, Richard Iantosca of RAICO, W. Palm Beach, Fl, and John Carter and Michael Gulla of Shipley Company Inc. for the opportunity to further research and develop this exciting and enabling technology.

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