MILK TIN TIN PLATING SYSTEM "L" SERLES

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要 約 :

전자산업의 발전은 전자분야 자체뿐 아니라, 관련 전산업분야의 발전을 기초로 하는 것이며, 납땜성이 뛰어난 전기 주석 도금 System의 개발도 그 일익을 담당하게 되는 것이다. 그러나 주석도금 System의 종류와 방법에 따라서 납땜성의 차이는 아주 크며, 그 이유로는 주석도금에 사용된 첨가제의 동시전착에 큰 영향이 있음을 알게되었다.

본 조사는 납땜이뛰어난 반광택 산성주석도금 방법에 대한 것으로 그 첨가제의 개발 및사용방법을 기술하고 있다.

1. Introduction

Today's more advanced electronic systems, computerized systems or robert production industries riquires more solderability guaranted piece parts, and make great demands on various technologies including that of tin or tin alloyed electrodeposition.

In This paper, discusses new tin plating solution which have special significance in tin/tin alloy plating for the electronic and steel plates.

The said Milk tin L system aims for both high speed tin plating with white luster deposition of the steel rolls and normal tin plating of general articles with lusterousness improved appearance for semicoductor packages and various bolts and nuts or terminals. On the high speed continuous tin plating for tinplates, it is very competive to all of processes, saying, the Ferrostan and Halogen.

Because of the dramatic changes in the price of the tin in current markets, the need for solutions that provides more economical tin/tin alloy plating is paramount. The auther have developed just such a solution, and the study relates primarily to the effects of the new additive.

This system in the acid tin baths the solderability performances were tested in the conditions of the 168 hour-bake at 150°c and 10 hour-steam age.

Technical advances have provided many mechanisms to work automatically by itself even at

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high temperature, thus signficant and functional criteria is added to be tested for tin/tin alloy coatings. It is felt that this trend will continue to a point where current materials may well be unacceptable and may lead to failure, since because some electronic components are operating continuously at 100°c. To validate the intergrity of a tin/tin alloy deposit under above conditions of higher operating temperatures. an accelerated test must be adopted. This comprises high temperature atmospheric (150°c) and steaming exposure as aforementioned, satifying requirements listed in the USA MIL spec MS-9554 A plus MIL-STD-883 Method 2003 with mild flux. Excellent, reproducible soldering results obtained from this said system were believed that L series additives are not going to be aborbed into the deposits, rather just playing roles in the diffusion layer modifying tin deposition with deep luster appearance.

The free-pores and uniform levelling effects gives to tinplates excellent shelf life or anti-corrosion characteristics.

2. Discus and Results

A. Solderability

Polarization at the electrode strongly is a function of the concentration of the additives and the species in the electrotinning bath. This should be the case if they adsorb at the surface and thus blocks or modifies sites for incorporation of metal atoms into the lattice, or inhibits the surface diffusion as adions. If they are consumed during the deposition process (e.g buried into the deposit or chemically changed by reduction and desorbed), a diffusion flux of the additive from the bulk of solution can determine the reaction resistance at the surface. This, in turn, should cause a secondary current distribution with the tendency to level the surface irregularities. Additives give various modification of the crystal growth, for an explanatary illustration, the increased nucleation rate, which produces grain refinement, may be due to the increase of overvoltage and/or the increase of free surface energy produced by adsorption of the additives. According to Haar an adsorbed film of certain additives would suppress the electrocrytallographic differences which lead to unequal growth of this various crystals and crystal faces. Metal deposition would then occur on the randomly distributed uncovered surface sites. With virtue of this observation and review, tin deposits of bright surface tends to contain some of reduced brightner substances.

Solderability failures in the plated semiconductor packages generally come from poor and/or improper preparation of metallic surface in the precleaning operations which are given prior to tin plating. Electrodeposition of an apparently perfect tin coating can occur in even onto a contaminated surface, but that may result in dewetting of the solder.

As the dewetting is defind, which occurs after intial metallurgical bond, has been developed, and the presence of unwettable, or nonmetallic inclusions in the basis metal surface interfers with the orderly growth of the intermetallic compound layer necessary to establish the metallurgical bond. When sufficient points of interference are present dewetting occurs. For an instance of copper base metal, when the wetting, occurring the intermetallic compound such as Cu_6Sn_5 produces between the tin in the solder and the basic metal surface. Thus a satisfactory soldered joint should be possible if the metallurgical bond required for wetting as formed.

As mentioned already, the first requirement for proper wetting is that the basis metal surface must be completely free of foreign materials such as organic and inorganic soils and oxides films, and the organics incorporated in the deposit might influence the trifling and slow wetting, particularly, pronounced in high temperature conditions. Here the organics might be changed to the oxidized substance therein and accordingly shows dewetting phenomena.

To assist the possibility, F.Nobel and P.E. Dairs suggested minimum additives should be used in the tin plating solution to achieve reliable solderability. And Wren and Haben also observed gas generation during soldering tests of the bright tin deposits that they concluded such phenomenon was attributed to the evolution of organic compounds adsorbed in the bright tin deposit.

To be conclusion, the inclusion of additives into the deposit might cause significant influences upon poor intermetallic compound formation and so on dewetting. If also chocsing improper mat tin plating system to overcome this problem, tin deposits being formed with almost invisible pores under low power magnification on the surface as shown in Fig.1 and leads to vitiate proper wetting even though the base substrate has been prepared enough thouroughly.

According to the technical data released from "L" and "T" companies, their additive systems are to be destroyed during electrolysis therefore suggesting a cycle replenishment of 400-600cc/ 1000 A.hr to maintain proper effects.

For evaluation and comparison on the solderability perfermances between this "L" series system and the pro duct of "L" company U.S.A., Haring Cell test and on-line scale production experiments, with barrel plating of Ceramic DIP packages were carried out, and solderabilities measured at conditions of at 168 hr bake at 150°C and steam age-10hr.

Plating conditions for VITAN "Milk Tin L1-L9" system (A-Sol) and "S" system from "L" company U.S.A (B-sol)

1) barrel size 6 ″x 9″ hexagonal with cylindrical center rod current contact (15.2cm^2)
   the perforated ratio of wall 9.3%
2) Articles: C-Dip (alloy 42) 14 leads unit (0.586 in^2)
3) H_2SO_4 (SP 1.84): 5.6~6.4 fl. OZ/gal, Sn: 3.0~4.8 OZ/gal
   Milk Tin L1: (2.5% Vol.), L9: 2.5% (Vol.), Temp 15°C
4) Total anode area: 1.17ft^2
5) Cathode C/D varied in the range of 1-24 A/ft^2, whereas anode C/D 4-4 3A/ft^2

Solderability performances from the Milk Tin process (A-sol) was provided by "F" Semiconductor Co., U.S.A., and the quality proved like the following data.

TEST Group *1	#1	#2	#3	#4	#5	#6	#7
Thickness(below 200 microinch)	0/60	0/60	0/60	0/60	0/20	0/20	1/20
$\bar{x}$ (micro inch)**	265	242	250	261	252	243	235
168hr bake/solder*3	0/20	0/20	0/20	0/20	0/20	0/20	0/20
10hr strem-age/solder	0/20	0/20	0/20	0/20	0/20	0/20	1/20*4

*1 Experimental, 40 lots have been classified into 7 groups upon the diversity of C/D and concentration changes of additives along with metallic tin ions.
**Measured by Betascope NH500 (Twin City) *3 Nonactivated rosin flux, Alpha 100
*4 Base Substate still shows oxidized scales unremoved.

Of serious concern to many users of high reliability components under such conditions is the possibility of system itself.

Therefore, the possibility canbe precheked and demonstrated by solerability testing.

Resultantly, there arouse a great deal efforts and attempts for set makers or system makers to enhance solderability by improving their soldering tools or developing of new tin plating baths.

Then, likely, "F" company decided to use this Milk Tin L1 and L9 additive system in his world wide subsidiary factories for tin plating various semiconductor units or packages, then fortunately, now invading into the tinplate manufacturer's factory to meet its high speed plating requirements.

Because of cosmetic requirement, lustrous or brilliant tin surface has been claimed for quite a long time before solderability performance of the bright surface has been known worse at high temperature for prolonsged cases than the case of mat or semibright finishes.

Therefore, semiconductor companies have the tin plating with mat rather than full bright.

B. Uniform deposition

This development characterizes ensuring uniform, free-pores surface so that protects the possible electrochemical corrosion problems.

By the current densities out of the noted range, the deposits becomes somewhat degree unto dullness with a tendency to have coarse crystal growth, particularly for higher side.

The structure of electrodeposited tin covers an extremely wide range, depending primarily on the electrolysis conditions as an example the choice of specific additive, generating a compact or a loose deposits, the latter is likely to be stripped away from the plating substrate during barrel plating therefore, in the barrel tin plating for mat tin finish it calls for considerable attentions on the selection of proper additive system which should reserve the high throwing

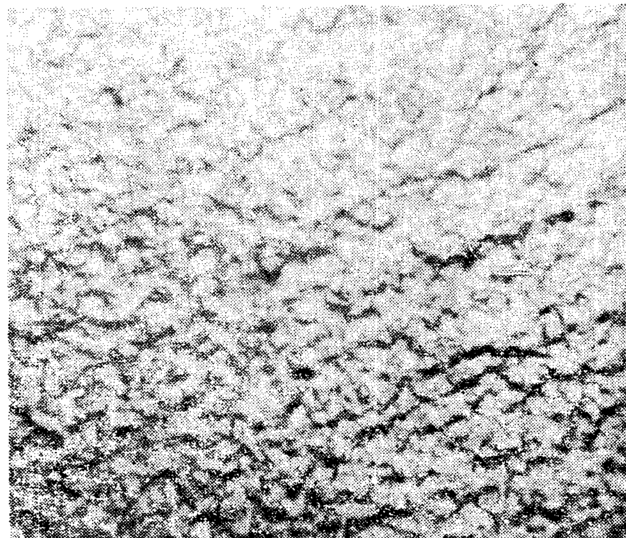

Fig. 1-1 Microscopic observation under 200 x of deposits from the "solution-A" onto the C Dip lead by current densisy 15A/ft^2 (obtained from 5-25A/ft^2)

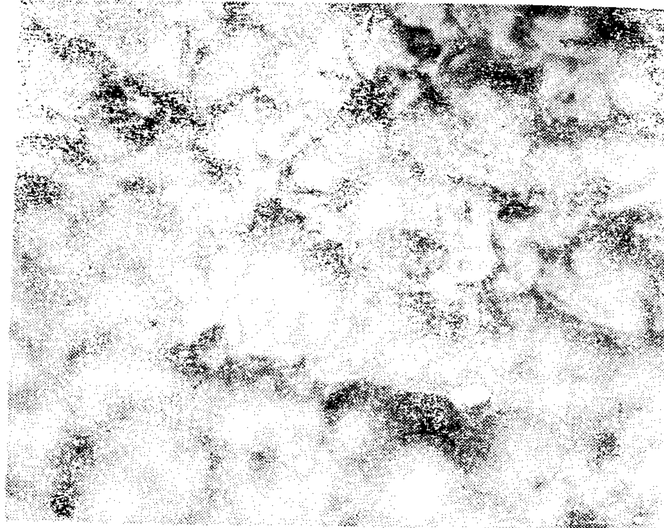

Fig. 1-2 Microsopic observation under 200×of the deposits from Solution-B onot the C-Dip lead by current density 13A/ft2 (obtained from 10-15/ft²)

power and coverage so that securing a strong structure in a moment of tin plating.

This author's development has been pointed on mechanism which creating a lot of new necleis in tremendeously fast speed on plating zone.

For an information, the structure of a deposit strongly relates on the rate of formation of new nuclei and the rate of the growth of the existing crystals, the grain size especially is very affected by the ratio of these two rates.

If the rate of nucleation is lower and the rate of crystal growth higher, a deposit with coarse grains results, if the case is contrary the deposit shall be fine.

C. High Conductivity

Author's solution is inproved rather with low tin concentration baths than that of high, One of appreciable features of this system, to be comparable to drastic performance of soderability, is the lower tin concentration system which is giving user a great deal advantages, improved coverage as well as throwing power owing to the solution conductivity increase, while producing milkish luster surface appearance without loose streaks of tin deposits.

Such deposits of tin aggromation is known relating with the so called tin bal problems that is pronounced with use of B-solution when tin concentration goes down below 4 oz/gal as well as high C/D has applied in.

With increase of tin concentration for overcome of this undersirable phenomenon leads to poor tin coverage due to relative decrease of solution conductivity, since because the metallic concentration increase affects the solution conductivity to be lower, consequently lowering differential throwing power and coverage upon the variation of plating zone.

This can be identified readily by use of Haring Cell testing or measuring of throwing power,

$$\% \text{ Throwing power} = \frac{\text{Primary ratio-meal ratio}}{\text{Primary ratio}}$$

With the help of theoretical reviews once more, describing the background, the critical factors

in the determination of throwing power are the degree of polarization and the bulk resistivity of the solution.

Upon the establishment of factors which control the throwing power, the author was able to develop this unique solution that should meet the needs of many plating specifications, high speed continuous along with rack or barrel operations.

In high metalic concentration, quantitively, concentration polarization dominates appreciably compared to the case of low metalic concentration because strong ionic atmospheric effection limits the metalic transportation. As the solution equivalent conductivity defines like

$$\Lambda = \frac{1000K}{C}$$

where Λ is equivalent conductivity, C equivalent concentration, K specific conductivity. Λ and C are in reciprocal relation, then with increase of C results in decrease of Λ.

This conductivity term thus is represented in throwing power term which was proposed by S.Craig Jr. as following in the berrel plating

$$J = \bar{J} e^{-rx}$$

where J in the charge transfer current density, $\bar{J}$ is the maximum charge transfer current density at the surface of the load and x is the distance from the surface of the load, r consti tutes of various parameters including solution conductivity K, say,

$$R = \frac{ZFJa}{KRT}^{1/2}$$

$\frac{ZFJ}{KRT}$ is thought of as the ease with whith current is transferred from the solution to the solid divided by the ease with which current is present through the solution, and is a function of the solution only and is the reciprocal of the polarization perameter. In case of small R the throwing power gets in improved state. Giving the tested results from the Haring cell, readers can see the remarkable improvements as compared to these those existing solutions as indicated in Fig-2

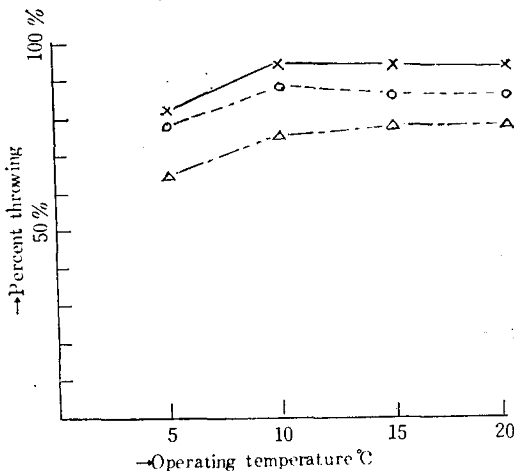

Fig. 2-1 The efffct of operating temperature on the throwing power of the A and B solutions.

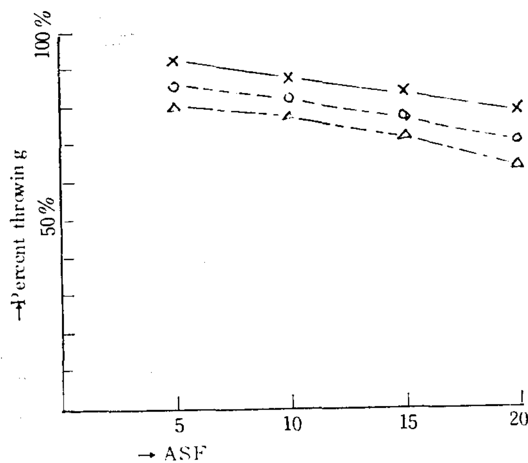

Fig. 2-2 The effect of C/D on the throwing power of A and B solutons.

Plating conditions

Author's sotutions: A(○) A'(×) "L"company solution:B(△)

Item	A	A'	B
Tin metal	4.8-6.2 oz/gal	1.8-2.2 oz/gal	8.0-10.0 oz/gal
H_2SO_4	4.5-8.0 fl oz/gal	7.4-8.3 oz/gal	5.5-6.5 fl. oz/gal
Vol %	L1 5%, L9 5%	L1 5%, L9 5%	0.5%, P10%

D. Cost Reduction

As aforementioned before the Milk Tin "L" series employes low tin concentration less than half of conventional or existing met systems, moreover the unit price of "L" series is cheaper less than half of existing systems.

Consequently the bath make up cost reduces down to 45% of the conventional baths.

One distinguishable cost save effectiveness lies on the small replenishment amounts since because it does'nt destroy in the course of electrolysis.

E. Recommended a typical Milk Tin Plationg Process (Dual System L1, L9)

E.1. Bath Make up (for barrel plating of elecronic parts)

Bath composition	Range	Optimum
Tin Metal	1.5-3.0 oz/gal	2.1 oz/gal
Surfuric acid	7-9fl. oz/gal	8.1 fl. oz/gal
L1	4-6% (Vol)	5%(Vol)
L9	4-6% (Vol)	5%(Vol)

—Operating Conditions—

Temperature	13-33°C	18-25°C
Cathode average C/D		
Rack		5-20ASF
Barrel		8-10ASF
Filteration		continuous recommended

—New bath makeup—100 Gallons

Stannous sulfate	251bs
Sulfuric acid (c.p.1.84)	6.34 ltr
L1	5 gallons
L9	5 gallons

D. 1 water is prefered to make up

—Maintenance additions—

Abbition should be carried out on a regular basis only to replace bath solution drag out loss.

E.2. Trouble Shooting guides with Hull Cell test

Current: 1 Amp

Agitation: None

Time: 5 minutes

Standard(resulting pannel) should be smooth and milkish appearance acrcss entire range at the preferred bath composition.

SYMPTOMS	CAUSES	CORRECTIONS
1. Dullness or powdery streaking in high C/D area	a) Low L9 content	a) Add L9 to the required content according to the Hull Cell tests.
	b) Low tin content	b) Adjust to the running concentration by analysis
	c) High concent of L1	c) Stop the L1 addition furthermore for sometime
	d) High ripple rate	d) Change the power supplier
2. Poor throwing power at low C/D area	a) Low surfuric acid content	a) Analysis and add the required amount.
	b) Low L1 content	b) Add required amount according to Hull Cell test.
	c) Excess L9 content	c) Omit the regular addition.

E.3. MILK Tin solution analysis

—Reagent Chemicals—

1. Hydrochloric acid
2. 0.25N Iodine
3. 5% Soluble starch solution
4. 0.1% thymol phthalein indicator
5. IN sodium hydroxide solution

—Tin metal concentration—

1. Pipette 5ml.sample in a 500ml erlenmeryer flask
2. Add 100ml. D.I. water and 50ml. concentrated hydrochlorioric acid, keep the flask under the hood while addition of acid is made
3. Titrate immediately with standard 0.25N Iodine solution to a dark blue color using starch as indicator
4. Caiculation process

   ml iodine ×N×1.58= oz/gal tin metal

   oz/gal deficient×vol(gal)×0.113=LBs, stannous sulfate to add

—Sulfuric acid—

1. Pipette 5ml. sample in a 500ml. erenmeyer flask
2. Add 50ml of D.I water and 10 drops of tymol phtalein indicator,
3. Titrate with IN sodium hydroxide solution to a blue end point
4. Calculation process

   ml. NaOH×N×0.738=fl oz/gal

fl oz/gal deficient×vol (gal)×0.0738=gal H_2SO_4 to add

F. Typical Properties of L1, L9

The L1 plays important role in enhancing throwing power along with coverage for the lower C/D areas, while L9 improving plating conditions in high C/D areas without loose, or cohedrent and powdery deposits or hydrogen gas evolution.

1. Physical appearance : clear or very slight pale straw color
2. Fluidity : can be pumped at ambient temperature
3. Specific grarity, 20°C : 1.01
4. PH, 5% in water : 6.9

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