The Advantages of Mildly Alkaline Immersion Silver as a Final Finish for Solderability

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Abstract

The immersion silver process has become the first choice of final finishing for many original equipment manufacturers (OEM) because of its shortened process flow, good conductivity, even deposition, good solderability and bonding function, and suitability for vertical and horizontal-automated production lines. Some popular immersion silver solutions on the market contain acid that will attack copper to cause circuit break and trace undercutting. The acidity of these processes limit immersion times for silver deposition that can in turn lead to no deposition in the bottoms of blind vias. These processes also frequently use inhibitors or penetrating agents that can contribute to massive voiding and brittle solder deposits. This in turn leads to decreased solder strength.

The shortcomings of these acidic systems are overcome using a mildly alkaline immersion silver. This process has a pH greater than 7 making it possible for longer dwell times that ensures a complete deposition in blind vias. The new process does not contain inhibitors so that the deposited silver possesses higher purity, higher corrosion resistance, lower contact resistance, high soldering strength, and no electromigration. This technology is fully compliant for RoHS and WEEE regulations.

Introduction

Final finish of a printed circuit board (PCB) is the final process after soldermask application. The PCB is the carrier of electronic components that are frequently connected through soldering and bonding. So, the final finish of a PCB must satisfy a number of demands, like solderability, bondability, appearance, anticorrosion ability, suitability, expansibility, cost, shelf-life, and so on.

Hot-air solder leveling (HASL) has been the most important final finish for many years, but tin-lead solders contain about 36% lead. The lead in waste electronic products will dissolve into the soil and ground water and from there be absorbed by plants and animals. Lead can accumulate in the human body and cause diseases of the kidney, thyroid, and gastrointestinal system. Lead has become a regulated cancer causing substance.

The design of electronic circuits continues to become more complicated due to demand for reduced circuitry sizes and the use of a variety of fabrication and mounting methods. Alternative final finishes to tin-lead must have the following characteristics in order to meet these design demands as well as meet regulatory criteria:

- 1. Deposits or coatings can not contain materials banned by regulation, especially lead.
- 2. Deposits or coatings must be even and planar for surface mount technology (SMT) applications.
- 3. The solderability of alternative technologies must be similar to tin-lead finishes.
- 4. The alternative technology must be suitable for aluminum (Al) or gold (Au) wire bonding.
- 5. The alternative technology must be able to meet industry standards for thermal shock and stress testing.
- 6. The alternative technology must operate under 100°C.

The following technologies are alternatives to HASL processes:

- 1. Electroless Nickel / Immersion Gold (EN/IG) is an excellent alternative to HASL. It is suitable for Al or Au wire bonding and lead-free soldering. However, the process is lengthy, costly, difficult to control and not always suitable for the fine lines and spaces of high-density interconnect (HDI) applications.
- 2. Electroplating Nickel / Electroplating Gold provides excellent solderability and the best gold wire bonding, but the process becomes very complicated because all of the circuits must be connected before electroplating.
- 3. Organic Solderability Preservative (OSP) coatings are an inexpensive alternative to HASL. Operating times are short and easy to control. The coating typically has good solderability, but it tends to fail after only three thermal shock cycles.
- 4. Immersion Tin (ImSn) forms a smooth, even, and fine particle size (a 1 micron deposit can pass three thermal cycles), and it is suitable for rigid or flex PCB manufacture. However, ImSn can attack and dissolve soldermask easily to undercut copper traces.
- 5. Immersion Silver (ImAg) is also an excellent alternative to HASL and EN/IG because of its excellent solderability and

Al wire bonding performance. The process is short and simple and provides excellent results in thermal shock and stress testing.

		r			r
	HASL	EN/IG	ImSn	OSP	ImAg
Cost per sq. ft.	\$0.12 - \$0.26	0.40 - 0.50	\$0.26 - \$0.30	\$0.12 - \$0.18	\$0.26 - \$0.40
Waste Treatment	Simple	Complicated	Complicated	Simple	Simple
Equipment	Vert. / Hor.	Vertical	Vert. / Hor.	Vert. / Hor.	Vert. / Hor.
Shelf Life	1 year	1 year	6 months	6 months	6 months
Process Time	5 minutes	1 hour	15-25 minutes	6 - 10 minutes	6 - 10 minutes
Rework	Easy	Difficult	Easy	Easy	Easy
Wire Bonding	Can not	Au / Al wire	Can not	Can not	Al wire
Surface evenness	Poor	Excellent	Excellent	Excellent	Excellent
Thickness	50 – 500 µin	160 – 240 µin	30 – 50 µin	8 – 20 μin	4 – 12 µin
Reaction time	1 - 1 seconds	40 minutes	8 - 12 minutes	0.5 - 1.5 minutes	1-2 minutes
Process Temp.	240 – 260 °C	80 – 85 °C	60 – 80 °C	40−48 °C	50 – 60 °C
Soldermask restrictions	Yes	Yes	Yes	No	No

Table 1 - Performance Comparison between HASL & Alternative Technologies

Table 1 identifies a number of characteristics of these alternatives to HASL.

Problems of current acidic silver processes

ACID ATTACK

Nitric acid used in the formulation of most immersion silver products is a very strong oxidizing and corroding agent that will attack the copper circuit and cause stress corrosion. The circuit trace can be broken after plating for 3 or more minutes. Acid solution penetrating under the soldermask results in undercut. Figure 1 shows photos of broken copper circuits and undercut after plating for 3 min and 5 min.

Plating time: 3minutes



Plating time: 5minutes





Corrosion under solder mask



Figure 1 - Copper circuit is broken when plating for 3 min and 5 min.

When immersion time is restricted to one minute or less to control the acid corrosion effects, then the bottom of blind vias may be only partially covered with silver. Figure 2(A) shows a lack of silver coverage in a blind via resulting from decreased deposition time in the acid immersion silver. Figure 2(B) gives the EDS analysis results from the blind via bottom. We can see that the bottom of the blind via still is copper with no silver.



Figure 2 - (A) Blind via bottom detected by EDS



Figure 2 - (B) EDS analysis result of blind via bottom

HIGH CARBON CONTENT OF SILVER DEPOSIT

Hydrocarbon based inhibiting and wetting agents are added to acid type immersion silver formulations to inhibit the attack on copper by nitric acid and promote solution penetration into the bottom of blind vias. These organic molecules can co-deposit with silver and form so called "organo-silver" deposits. In these organo-silver deposits, the purity of silver is only 70% to 80%, while the remaining 20-30% is organic addition agent or organic carbon. Excess organic content has been linked to out gassing during reflow operations.

X-ray photoelectronic spectrum (XPS) depth analysis is an advanced surface element analysis method used to characterize the purity of metal deposits. Figure 3 shows the XPS depth profile analysis figures of acidic immersion silver of company A and company M.



Figure 3 - XPS depth profile analysis figure of acidic immersion

We can see from Figure 3 that immersion silver deposit of company A contains about 5% carbon, and the immersion silver deposit of company M contains more than 30% carbon. High carbon content will decrease the conductivity, contribute to high frequency loss, lower anticorrosion ability, and decrease solderability and bondability of silver deposits.

In addition, acidic immersion silver deposits containing a high quantity of carbon compounds can be oxidized by oxygen in air to form CO or CO_2 during soldering. The CO or CO_2 then is trapped in the melted solder to form voids or blisters in cooled solder. The number and size of voids increase with an increase in carbon content and with an increase in thickness of the silver deposit. These voids normally are concentrated above a pad and influence the soldering strength and reliability. Figure 4 shows photos of voids caused by CO or CO_2 in the immersion deposits from company A and company M acid immersion products. We find that the void is very large when the immersion silver deposit contains close to 30% carbon.

Company A - Voids in immersion silver deposit caused by carbon contamination



Company M – Voids in immersion silver deposit caused by carbon contamination



Figure 4 - SEM photos of voids of acidic immersion silver for Company A And Company M

Figure 5 shows photos of cross-sections of a BGA soldering point. The most voids are concentrated just above the pad surface where the gases have entered into the solder during reflow. Figures 6 and 7 show examples of out gassing in through holes after soldering.





Figure 5 - The SEM photos of voids of acidic immersion silver for Company A and Company B

Company M – Voids Concentrated above pad surface



Figure 5 - photos of cross-section of BGA soldering Point from acidic immersion deposits of companies A and M



Figure 6 - The photos of cross-section of BGA soldering Point



Figure 7 - The photo of cross-section of out gassing in through hole after soldering

New mildly alkaline immersion silver process

We have listed the process features of mildly alkaline immersion silver

- 1. Silver bath contains no nitric acid, thus no copper corrosion or undercut.
- 2. Bath contains no inhibitor and penetrating agents that lead to voids in solder balls.
- 3. Bath uses full complexing agent system; silver deposit is pure silver and doesn't contain carbon or organic compound, thus no out gassing during solder operation.
- 4. Pure silver deposits do not produce voids in solder balls and have a high solder strength.
- 5. Special antitarnish agent can form a very thin hydrophobic film that do not influence soldering and bonding.
- 6. Immersion time can be selected between 1 to 5 minutes, this can ensure complete deposition of silver at the bottom of blind vias.
- 7. Bath is mildly alkaline (pH 8.5) and doesn't attack soldermask.

Table 2 shows the basic process steps of the new mildly alkaline immersion silver process. Both vertical and horizontal processing can be used.

Step	Temperature	Time (min) Horizontal	Time (min) Vertical
1.Acid clean	50 °C	1.5	4
2.Microetch	25 °C	1.5	2
3.Acid dip	25 °C	0.5	0.5
4.Predip	25 °C	0.5	0.5
5.Immersion Silver	55 °C	2	2
6.Antitarnish	40 °C	1.5	2
7.Dry	70 °C	1	1
8.Package			

Table 2 - Mildly Alkaline Immersion Silver Process Steps

Influences of bath composition and operating condition on deposition rate of mildly alkaline immersion silver

• Influences of silver concentration

To illustrate the influence of silver concentration on deposition rate bare copper boards were immersed into solutions with different Ag^+ concentrations: 0.5g/L, 1.0 g/L, 1.5 g/L, 2.0g/L, and 2.5 g/L of solution at 60°C for 2 minutes, and then silver thickness was determined using X-ray thickness instrument. The results are shown in Figure 8.



Figure 8 - Relationship of Ag deposit thickness and Ag⁺ concentration in bath

The results in Figure 8 show that deposition rates increase with increased silver concentration in the bath. For example, when Ag^+ concentration is 1 g/L, at 60°C for 2 min the silver deposit thickness is 8 micro inches

• Influence of copper ion concentration

Immersion silver is a replacement reaction. Copper from the circuit is dissolved while at the same time silver is deposited on copper, thus the copper ion concentration in the bath will be increased as the reaction proceeds. Figure 9 shows how the copper ion concentration increases proportionally with the silver deposition rate.



Figure 9 - the curve of silver deposition rate with copper ion concentration in bath

• Influence of bath pH value

Bath pH can change the composition and state of complex ions and influence the rate of silver deposition. Figure 10 shows the change in silver deposition rate relative to change in bath pH. It shows that the deposition rate increases slowly with increasing bath pH. However, if the bath pH value is too high (pH>11), there will be attack on the soldermask. Therefore, the bath is maintained at about pH 8.5.



Figure 10 - Relationship of bath pH value with thickness of silver deposit

• Influence of bath temperature

Normally the rate of a chemical reaction increases with increased bath temperature. Figure 11 shows the silver deposition rate relative to bath operating temperature. It shows that silver deposition will be lower than about 8 micro inches in 2 minutes 0.2 μ m (8 microinches) bath temperature is kept at 30°C. When bath temperature is controlled at about 75°C for 2 min, the thickness of silver deposit will reach 0.3 μ m (12 micro inches).



Figure 11 - Relationship of bath temperature with thickness of silver deposit

• Influence of plating time

Immersion silver reaction is a replacement reaction

 $2 [Ag Xn] + Cu \implies 2Ag + Cu^{2+} + Xn$ (X : is the complexing agent)

No reducing agent is used in the bath, so silver thickness will reach a maximum when the entire copper surface is covered by silver. The replacement reaction will stop and silver thickness will remain stable. Figure 12 shows the relation between immersion time and thickness of silver deposit. It shows that silver reaches $0.25 \ \mu m$ (10 micro inches) at 2 minutes.



Figure 12 - Relation curve of plating time with thickness of silver deposit

Solderability of mildly alkaline immersion silver compared to acid immersion silver and Electroless nickel immersion gold

Solderability determination was tested in a DAGE-BT 2400PX model solder ball shear test machine. Specimen boards from each of the alternative final finishes applied to BGA boards were coated with Sparkle Flux WF-6050. And then φ 0.5mm solder balls were placed on BGA pad, then solder balls were reflowed onto the BGA pads. Finally the solder balls were pushed by a moving arm in the solder shear test machine, the shear force in grams required for removing solder balls was recorded .The higher the shear force (g), the better the solderability and solder joint strength.

Solderability of mildly alkaline immersion silver deposit (A), acid immersion silver deposit (B) and electroless nickel immersion gold (EN/IG) deposit before and after heat treatment of at 155°C.

Figure 13 shows shear force results of the different immersion silver deposits and EN/IG deposit after thermal exposure at 155 C for four hours. The results show the shear force for mildly alkaline immersion silver deposits remain close to 1400 g, essentially equal to EN/IG, while the acid immersion silver dropped slightly to just over 1300g Normally surface mount (SMT) manufacturers demand shear forces greater than 800g, that means that the solderability of mildly alkaline immersion silver deposit after 155°C for 4 hours is still at an excellent level and comparable to EN/IG deposit. Thus mildly alkaline immersion silver process is a good alternative for EN/IG and performs slightly better than acid immersion silver.



Figure 13 - Figure of shear force of different immersion silver and EN/IG deposits after 155°C for 0~4 hours

Solderability of different immersion silver deposit before and after 8 days of humidity testing

Fig 14 is the figure of shear force of different immersion silver and EN/IG deposit after exposure to 90% relative humidity (RH), 40°C and 8 days of humidity testing. The results indicate that the ball shear force still remained over 1400g, less than EN/IG, but more than acid immersion silver after 8 days of humidity testing. This means that the solderability of mildly alkaline immersion silver deposits after 8 days of humidity testing is better than acidic immersion silver while not quite as good as the EN/IG deposit.



Figure 14 - Figure of shear force of different immersion silver and EN/IG deposits after RH 90% 40 for 0~8 days of humidity testing.

Solderability of different immersion silver deposits before and after reflow

Fig 15 gives the shear force of different immersion silver types and EN/IG before and after each of three reflow cycles. The results show that ball shear force for mildly alkaline immersion silver after three reflows still remains above 1400g and are very close with EN/IG deposit and slightly better than acid type immersion silver.





Solderability of different immersion silver deposit before and after tarnishing in H₂S gas

Silver deposits are tarnished easily in industrial air and especially in H_2S gas. To determine if tarnish on mildly alkaline immersion silver effects solderability differently from other types of final finishes, specimens with mildly alkaline silver and acid immersion silver were exposed to H_2S gas in a desiccator until tarnished to a bluish purple color then tested for shear force against EN/IG deposits. The results in Figure 16 show that blue-purple tarnished silver deposits still have excellent shear force (1400g). This is similar to EN/IG deposits and significantly better than tarnished acid immersion silver.



Figure 16 - Figure of shear force of no-tarnished and tarnished silver deposits in H₂S gas.

Aluminum wire bondability of different immersion silver deposits.

Bonding determination was carried out on AB 509A type of Aluminum Wire Wedge Bonder. $31.25\mu m$ ($\phi 1.25 m$) of aluminum wire is heated and pressed onto the silver pad, and then the aluminum wire is mounted in a pull tester and pulled until the wire is broken, the pulling force (g) is recorded. The greater the pulling force, the better the bondability .Normally SMT plants demands that the pulling force must greater than 7g.

Bondability of different immersion silver deposit and EN/IG deposit before and after baking at 155°C

Figure 17 shows the pulling force of different immersion silver deposits and EN/IG deposit before and different immersion silver deposits after baking at 155°C, for 3~4 hours. These results indicate that the initial pulling force on mildly alkaline immersion silver can reach 11.5g which is greater than for acid immersion silver deposit or EN/IG deposit. The pulling force on mildly alkaline immersion silver remains above 8 g after baking at 155°C for 4 hours.

This means that it has excellent aluminum wire bondability. It can generally be regarded as having better aluminum wire bondability than either acid immersion silver or EN/IG.



Figure 17 - Figure of pulling force of different immersion silver and EN/IG deposits before and different immersion silver deposits after baking at 155°C for three and four hours

Bond ability of different immersion silver deposits and EN/IG deposits before and after 8 days of humidity testing. The aluminum wire pulling forces of different immersion silver deposits and EN/IG deposit before and after 4 and 8 days humidity testing at RH 90%, 40°C are shown in Figure 18. The results show that the pulling force of mildly alkaline immersion silver deposit remains above 9 g after 8 day humidity testing. This is better than acid immersion silver deposit and is very close to EN/IG deposit.



Figure 19 - Pulling force comparison of different immersion silver deposits and EN/IG deposits before and after 4 & 8 days humidity testing

Bondability of different immersion silver deposits and EN/IG deposits before and after reflow .

Figure 20 shows the pulling force comparison of different types of immersion silver and EN/IG deposits before reflow and for the immersion silver systems after two and three reflows. The results show that the pulling force of mildly alkaline immersion silver can remain above 8.5g after three reflows. This means that mildly alkaline immersion silver still has very good aluminum wire bondability after three reflows.



Figure 20 - Pulling force comparison of different immersion silver and EN/IG deposits before reflow and different immersion silver systems after two and three reflows.

Bondability of different immersion silver deposits before and after tarnish in H₂S gas

Mildly alkaline and acid type immersion silver specimens were placed in a desiccator flooded with H_2S gas until the silver deposit was tarnished to blue-purple color, and then pulling force was tested on the tarnished silver deposits. The results are shown in Figure 21. They show that blue-purple silver deposits still yield excellent pulling force (9 g). This means that tarnish of silver has little influence on bonding performance of silver deposit.



Figure 21 - Pulling force before and after tarnish of silver deposit

Void determination of a mildly alkaline immersion silver after soldering

A silver-plated BGA board is coated with Sparkle Flux WF6050, and then φ 0.5mm solder ball is placed on BGA pad. After reflow, the solder ball is attached to the BGA pad. Figure 22 shows no voids above the pad. This is markedly different from Figure 5 which are cross-sections from two acidic immersion silver systems. The mildly alkaline immersion silver is a pure deposit whereas the acidic immersion system forms an "organic silver" that is more prone to voiding.



Figure 22 - Cross-section of solder ball and silver pad applied with mildly alkaline immersion silver after soldering.

Lack of out gassing in a mildly alkaline immersion silver system

Figure 23 shows the absence of out gassing in the silver coating deposited using a mildly alkaline immersion silver process. Figures 7 and 8 show out gassing in silver coatings deposited with an acidic systems.



Figure 23 - Cross sections of through holes that have had silver applied with a mildly alkaline system after soldering

Conclusions

- 1. A mildly alkaline immersion silver process can overcome the following problems of acidic immersion silver: copper attack, undercutting, solder voiding and low solder joint strength.
- 2. Silver deposited with a mildly alkaline immersion process performs better than acidic formulations for thermal shock and stress testing.
- 3. The adhesion of silver deposited with a mildly alkaline immersion process after thermal shocking is better than the adhesion of silver deposited by an acidic immersion formulation.
- 4. Tarnishing of immersion silver deposits doesn't affect soldering or Al wire bonding.
- 5. Special anti-tarnish coatings do not affect soldering or Al wire bonding.

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CharterSILVER IAG-377 New Weak Alkaline Immersion Silver Proces

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CharterSILVER®

Introduction of Prof. FANG Jing Li

Mr. Fang was a Professor of Chemistry Department and Coordination chemistry Institute of Nanjing University, he studied surface treatment technologies for more 30 years, He was worked in following companies from 1995

- **1.** Gul Technologies Singapore Ltd., Principal Engineer
- 2. Plaschem (Singapore) Pte Ltd., TEO
- 3. Taiwan Uyemura Ltd., Senior consultant
- 4. Chartermate Electronics (HK) Ltd., Technic Director

Edited books:

- 1. "Comprehensive Review of electroplating additives"
- 2. "Multiple Complex Electroplating"
- 3. "Electroplating on Plastics"
- 4. "Brush plating technology"
- 5. "Polishing Technology of Metallic materials"
- 6. "Handbook of Surface treatment technologies"
- 7. "Theory and Application of Electroplating Additives"

Five demands of PCB Final Finish

1.Cost

Rough materials,equipment,waste water,HR,production yield,end product 2.Suitability and expansibility of process: Lead-free < rigid-flex board < fine line < solder mask

3.Solderability performance:

Solder wetness ,soldering reliability 4.Shelf-life of solution and PCB 5. Demand of ET test

Five choices of Final Finishing

Lead-free HASL
 ENIG
 OSP
 Immersion Tin(ImSn)
 Immersion silver(ImAg)

Performance comparison of Final Finish

	ENIG	ImSn	lmAg	OSP	HASL
Running cost RMB/ft ²	3-4	2-3	2 – 3	1.0-1.5	1 - 2
Waste treat.	Complicate	Complicate	simple	simple	simple
equipment	vertical	Vert./Hor.	Vert./Hor.	Vert./Hor.	Vert./Hor.
Store period	1 year	6 month	6 month	6 month	1 year
Time,min	60	15 ~25	6 ~ 10	6 ~ 10	5
Rework	difficult	easy	easy	easy	easy
Bonding	Al,Au wire	can't	Al wire	can't	can't

Performance comparison of Final Finish

	ENIG	I. Silver	OSP	HASL	I. Tin
Surface evenness	Excellent	Excellent	Excellent	bad	Excellent
Thickness , μ''	160 - 240	4 -1 2	8 - 20	50 - 500	40 - 60
Reaction time	40 min	1-2 min	0.5-1.5 min	1-3 sec	6-10 min
Reaction temp. ℃	80- 85	50-60	40-48	240-260	60-80
Restrict of soldermask	Yes	No	No	yes	Yes

Current status of HASL

- HASL of Sn/Pb will be stopped until Jul., 2006 by WEEE and RoSH
- Horizontal operation will increase evenness, decrease the change of size, but the cost of horizontal line is 2 times of vertical line
- Defect of lead-free HASL(Sn-Cu-Ni)
- ✤ 1. soldering temperature is increased 30-40 °C
- ✤ 2. etched Cu is 2 µm higher than HASL
- 3. Cu is accumulated in solder easily and must be removed periodically
- ✤ 4. soldering strength is lower than HASL

Advantage of ENIG

- Excellent Heat Resistance, Permit Multi- Reflow soldering
- Lower Contact Resistance Suitable for Key Pad
- Long Shelf-life, one year)
 Good solder Wetting
- Suitable for Al or Au wire bonding
- Ni-P deposit can inhibit copper diffusion

Disadvantage of Electroless Ni-P

- Process control is difficult
- Heat diffusion of Ni-P is bad, Ni surface is attacked by Immersion Au solution and produce black pad;
- Gold-plated hole is easily corroded electrochemically)
- The Pd catalysis is difficult for fine line of HDI, overplating, short circuit are formed easily
- High temperature(>80°C) operation, long reaction time(30min) is harmful for size of soldermask

Advantage of OSP

The cost is close to HASL

 Process and operting time is short and easy control

Easy to rework

 Competition is come from Immersion silver mainly

Disadvantage of OSP

- Copper surface is oxidized easily in lead-free multi-soldering and solderability will decrease
- It can't be used for multi soldering and multi-bonding of PCB
- Easily change surface color of gold key pad, gold finger to brown
- The cost is little lower than immersion silver only
- The thickness variation $(0.2 \sim 0.35 \sim 0.5 \,\mu \,\mathrm{m})$ of OSP coating will influence ET, high frequency or high speed signal

Advantage of Immersion Tin

- 1. Deposit is smooth, even, condense, fine particle and non porosity
- 2 Thickness of tin is 0.8-1.2um, it can pass multisoldering
- 3. It also can pass 155 °C for 4h; 40 °C, RH93% for 8 day and 3 refolws
- 4. Solution is stable, operation is simple
- 5. It can be used in vertical and horizontal autoline
- 6. It can be used for rigid, flex and rigid-flex board

Disadvantage of Immersion Tin

1. Solution can attacks and dissolve soldermask easily

2. Solution can cause undercut of copper line

- 3. 3. Immersion time needs 10-12 min, horizontal line will be very long and very expansive
- 4. Pure tin forms tin whisker easily
- 5. 5. Tin deposit will formed a dewetting Cu/Sn alloy layer with copper at high temperature

Competition Advantage of Immersion Silver

- 1. Immersion Ag is only one which can satisfy all 5 demands of final finishing
- 2. The cost is low and close to OSP
- **3.** It is suitable for rigid, flex and rigid-flex board
- Process is simple, operating temperature is low ,immersion time is short (1 min ≒ 0.2 µm)
- 5. Reliability at 72 °C,RH 85%,48 weeks is the best one in IPC 2003 comparison
- 6. Ag deposit has the best conductivity, and favorable for high speed and high frequency signal
- 7. Excellent covering power of blind via
- 8. It can be used for AI wire bonding

Disadvantage of Current acidic Immersion silver process

- Board will be wasted when line is stopped
- Ag deposit easily tarnished
- Organic inclusion in Ag coating will increase carbon content in coating ,form void in solder and cause dewetting in reflow operation
- Process needs super pure water (conductivity<10µs) rinse</p>
- Bath contains nitric acid, it will attack and broken copper circuit
- Bottom of blind via can't be covered partially by silver if immersion time only is one minute
 - Prolong immersion time will attack copper circuit and cause undercut

Ag deposit of A company contains 5% carbon



Ag deposit of B company contains 15% carbon



Cu circuit is broken when plating 3 min and more







plating time:3 min







Plating time: 5min

Void is formed when SMT

(when SMT, $C + O_2 \rightarrow CO/CO_2$)





Void observation

Acompany



X35 500 Am 0000 23 31 SEI



X120 100 mm 0000 21 31 SEI



15kU X480 0000 21 31 SEI 50.4m

Bcompany



Void observation









X278 58xm 8888 19 48 SET







Cu is finded on bottom of blind via after 1 min immersion



盲孔縱橫比:

最大=115:147 最小=86.9:147



Cu is finded in bottom of blind via with EDS analysis







Roadmap of developing new immersion Ag

- 1. Remove nitric acid can eliminate attack copper and undercut
- 2. Remove inhibitor and penetrating agent can eliminate carbon codeposition and avoid microvoid in solder ball
- 3. Only full complexing agent system can satisfy above demands

Process feature of CharterSILVER® IAG-377

- 1 Silver bath contains no nitric acid, so no Cu attack and undercut
- 2 Bath contains no inhibitor and penetrating agent, so no void in solder ball
- 3. Bath uses full complexing agent system ,so Ag deposit is pure silver and don't contain carbon
- 4 Pure Ag deposit don't produce void in solder ball and has high soldering strength
- 5 Special antitarnish agent don't influence soldering and bonding
- 6 Immersion time can be selected between 1-5 min,it can insure deposition Ag to bottom of blind via
- 7 Bath is weak alkaline(pH 8.5) and don't attack soldermask

IAg-377 Immersion Silver Process Flow

CharterSILVER[®] IAG-377 化学银工艺流程 Process Flow

			水平
酸除油 Acid Clean	AC - 19	50° C	1.5min
微蚀 Soft Etching	SPS or H ₂ O ₂	25°C	1min
浸酸 Soft Etching	5%H2SO4	25°C	10sec.
预浸 Predip	PX - 313	25°C	0.5mm
浸银 Imm. Ag	IAG - 377	60°C	1.5min
防变色 Anti-Tarnish	ANT - 39	40°C	1min

注意:要侵工艺正常运行,全程清洗用水必须是高质素去离水

Note) D.I. water rinse must be applied between each process items. The above process shall be able to be arranged with applications.

Influence of bath components and operating conditions on deposition rate

1.Deposition rate is increased with increase Ag concentration

2.Silver thickness is 0.2µm when Ag concentration is 1 g/L

Influence of Ag concentration on deposition rate



Influence of [Cu²⁺] on deposition rate

Deposition rate is increased with increase Cu²⁺ concentration

The increase of rate changes to stable when [Cu²⁺] arrived 60 mg/L

Influence of [Cu²⁺] on deposition rate



Influence of bath pH on deposit thickness

Deposition rate is increased with increase bath pH

 Bath with over high pH will attacks soldermask

 Bath pH of IAG 377 must be controlled lower than 9

Influence of bath pH on deposit thickness



Influence of bath temperature on deposit thickness

Silver thickness is lower than 0.2 µm at 30 °C for 2 min

Silver thickness is 0.2 µm at 60
 °C for 1.5 min

Influence of bath temperature on deposit thickness



Influence of immersion time on deposit thickness

Silver thickness will arrive stable after 3 min immersion

 Silver thickness will arrive 0.2 µm at 60 °C for 1.5 min

Influence of immersion time on deposit thickness



Solderability of immersion silver deposit

 Solderability is very good and similar to B company's level after 155 °C for 4 h

Solderability of immersion silver is similar to ENIG after 155 °C for 4 h

Ball shear strength of different immersion Ag deposit before and after 155 °C for 1-4h



Ball shear strength of different immersion Ag deposit after 40°C,RH 90% for 8 d

Ball shear strength of IAG 377 immersion Ag deposit after 40°C,RH 90% for 8 d is very good and better than B company

Ball shear strength of different immersion Ag deposit after 40°C,RH 90% for 8 d

表2 不同铝层经潮湿试验前后的可焊性 剪切力/g □ IAG-377银层 ■B公司银层 ■ EN/IG ι (潮湿试验时间)/d

Ball shear strength of different immersion Ag deposit after 1-3 reflows

 shear strength of IAG 377 immersion Ag deposit after 1-3 reflows is excellent and better than B company

Ball shear strength of IAG 377 immersion Ag deposit after 1-4 reflows is close to ENIG

shear strength of different immersion Ag deposit after 1-3 reflows



Ball shear strength of different immersion Ag deposits before and after H₂S tarnish

 Ball shear strength of different immersion Ag deposits before and after H₂S tarnish still are very good

shear strength of different immersion Ag deposits before and after H₂S tarnish







IAG-377 silver + flux

IAG-377 silver +ANT-39 antitarnish + flux

Conclusion:no microvoid is finded after soldering of IAG-377 silver deposit

IAG-377化学银切片(40X)



IAG-377化学银切片(100X)



Bonding strength of IAG 377 Immersion Ag

Bonding strength of IAG 377 Immersion Ag before and after 155 °C for 4 h is better than B company and similar to ENIG

Bonding strength of different Immersion Ag before and after 155 °C for 4 h



Bonding strength of different Immersion Ag before and after 40 °C,RH90%,8 days

Bonding strength of different Immersion Ag before and after 40 °C,RH90%,8 days is better than B company and close to ENIG

Bonding strength of different Immersion Ag before and after 40 °C,RH90%,8 days



8 -

Bonding strength of different Immersion Ag before and after 3 reflow

Bonding strength of IAG 377 Immersion Ag before and after 3 reflow is better than B company and close to ENIG

Bonding strength of different Immersion Ag before and after 3 reflow



Bonding strength of different Immersion Ag before and after H₂S tarnish

Bonding strengths of different Immersion Ag before and after H₂S tarnish are still excellent, that means tarnish of silver don't influence Al wire bonding

Bonding strength of different Immersion Ag before and after H₂S tarnish



CharterSTRIP AGS-1 silver stripper

Advantage

- No cyanide and other toxic materials, it is a green environmental product
- strip rate is fast as 0.1-0.2µm/min
- strip solution possesses some chemical polish action and don't cause over corrosion
- Operating is proceeded in room temperature and bath maintain is easy

II. Solution composition and operating conditions

- Silver stripper AGS-1A
- Silver stripper AGS-1B
- pH
- T -
- Time

500 ml/L 200 ml/L 8.7(8.5-9.0) Room temperature 3-10 min

- Replenish:AGS-1B : AGS-1A= 1:1
- Rework can proceed after brush treatment

-- Conclusion--

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- IAG 377 immersion Ag overcomed following problems of acidic immersion Ag: copper attack, undercut, solder void and low solderjoin strength etc.
- 2. Ball shear strength of IAG 377 immersion Ag deposit before and after 155 °C 4 h, 40°C-90% RH 8 d and 1-3 reflows is better than B company and close to ENIG
 - Bonding strength of IAG 377 immersion Ag deposit before and after 155 °C 4 h, 40°C-90% RH 8 d and 1-3 reflows is better than B company and close to ENIG
- 4. Ball shear and Bonding strengths of IAG 377 Immersion Ag before and after H₂S tarnish are still excellent, that means tarnish of silver don't influence soldering and Al wire
- 5. CharterSILVER IAG 377 process has been used in PCB plant of UK and Italy. The results are satisfied

CharterSILVER®