High Nickel Alloy & Tin-Silver Alloys

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A new generation of Zinc-Nickel alloy, which includes 11-15 percent of Ni in deposit, is now available. This system offers higher current efficiency and corrosion resistance performance. Especially under high temperature, environment corrosion resistance is extremely high.

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Zinc-Nickel Alloy – High Nickel

In today's competitive market place, consumers require higher quality products than ever before. The automobiles are used under severe conditions, especially in regions such as North America and Europe. During the winter, people spread salt with gravel for prevention of road ice. In the summer, sand particles causes erosion, which plays a role in initiating cavities. Dipsol of America provides several zinc-alloy plating processes against high corrosive environments. And we know high Zn-Ni alloy has higher corrosion performance.

General Alloy Plating

More than 100 types of electroplated alloy processes have been invented since zinc-copper alloy was developed in 1841. The merits of alloy plating are as follows:

1. We can achieve new phases that do not exist on metallography phase diagrams.
2. We can get the alloy which we can never get by melting method, as between high melting point metal and low melting point metal, because low melting point metal vaporizes as a high melting point temperature.
3. We can get a high performance deposit film while using a thin coating.

Feature

- Corrodes sacrificially to steel.
- Stability of its corrosive products.
- Adherent chromate conversion film.
- Low dissolution rate of chromate film against salt solution.

Corrosion of Steel Plated with Zn and Zn Alloy

By plating deposits of zinc and zinc alloys on steel substrate, steel substrate will be protected. Because of their poor ionization tendency, zinc and zinc alloys sacrificially dissolve prior to the iron.

We can estimate these tendencies by the electric potential values. (See **Table 1**.) By comparison with the electric potential value of iron the bigger a certain substance's value is, the sooner it dissolves. We can see the potential as the driving force of the dissolution.

We can also measure its sacrificiality by corrosive potential. (See **Table 2**.)
If the plating potential is on the minus side and close to iron, its dissolution speed is not high. Therefore theoretically corrosion resistance protection performance is following order:

Sn-Zn>high Zn-Ni>low Zn-NI>Zn-Co, Zn-Fe>Zn

Stability of its corrosive products
Corrosion is one of oxidation reaction from metal to salt. And corrosion protection for substrate depends on the stability of corrosive products.
Under general atmosphere, many types of anions produce many zinc salts, oxides and hydroxides. Zinc alloys make basic zinc salts easily. We have proven this by X-ray diffraction and X-ray fluorescent analysis. **Table 3** shows the products formed after 24 hours SST. **Table 4** shows the concentration of its elements.

Note: This analysis was carried out after sufficient water rinsing and drying, B117 so these products are insoluble. As seen in Table 3, corrosive products from zinc and zinc alloys are different.

For comparison, corrosive products that are formed from zinc alloys are all insoluble. These insoluble and nonconductive products form a barrier that prevents the contact with corrosive elements, as shown in the figure below.

TABLE 1 - ELECTROCHEMICAL SERIES

Electrochemical Reaction	Standard (Mono) Electrode Potential (V)		
$Au^{3+} + 3e^- = Au$	+1.50	(+)	Most Noble
$Pt^{2+} + 2e^- = Pt$	+1.20	↑	↑
$2H^+ + 2e^- = H_2$	0.00		
$Sn^{2+} + 2e^- = Sn$	-0.14		
$Ni^{2+} + 2e^- = Ni$	-0.25		
$Cd^{2+} + 2e^- = Cd$	-0.40	Electric	Ionization
$Fe^{2+} + 2e^- = Fe$	-0.44	Potential	Tendency
$Cr^{3+} + 3e^- = Cr$	-0.70		
$Zn^{2+} + 2e^- = Zn$	-0.76		
$Al^{3+} + 3e^- = Al$	-1.16	↓	↓
$Na^{2+} + e^- = Na$	-2.71	(-)	Least Noble

TABLE 2 - CORROSIVE POTENTIAL IN pH=6 BUFFER SOLUTION (VS. Ag-AgCl ELECTRODE)

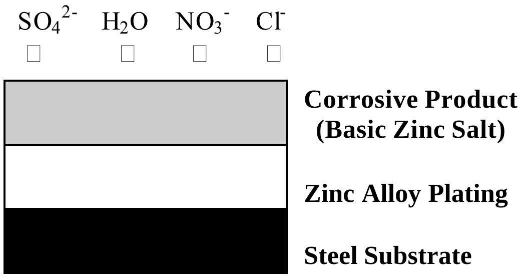
Metal	Corrosive Potential (V)	Co-Deposition Ratio
Fe	-0.70	
Sn-Zn	-0.90	Sn: 75%
Zn-Ni	-0.95	Ni: 15%
Zn-Ni	-1.00	Ni: 6%
Zn-Fe, Zn-Co	-1.10	Fe: 0.6% Co: 0.5%
Zn	-1.15	

TABLE 3 - X-RAY DIFFRACTION AFTER 24 HOURS SST

Zn	$ZnCl_2 \cdot 4Zn(OH)_2 \cdot H_2O$ $ZnCO_3 \cdot 3Zn(OH)_2 \cdot H_2O$	ZnO $ZnCl_2$
Zn-Ni	$ZnCl_2 \cdot 4Zn(OH)_2 \cdot H_2O$ $ZnCO_3 \cdot 3Zn(OH)_2 \cdot H_2O$	
Sn-Zn	$Zn(OH)_2$	$2ZnCO_3 \cdot 3Zn(OH)_2 \cdot H_2O$

TABLE 4 X-RAY FLUORESCENCE ANALYSIS AFTER 1 HOUR SST (40 SECOND COUNT)

Plating	Chloride	Zinc	Chloride-Zinc ratio
Zn	13,031	1,734,972	7.5×10^{-3}
Sn-Zn	19,103	368,581	5.2×10^{-2}
Zn-Ni	20,400	1,024,558	2.0×10^{-2}



Barrier Mechanism of Corrosive

TABLE 5 SOLUBILITY OF VARIOUS ZINC SALTS	
Zinc Salt	**Solubility (g/100 ml water)**
$2ZnCO_3 \cdot 3Zn(OH)_2 \cdot H_2O$	4.2×10^{-4}
$ZnCl_2 \cdot Zn(OH)_2$	8.4×10^{-2}
$ZnCl_2 \cdot 4Zn(OH)_2 \cdot H_2O$	3.3×10^{-3}
$ZnSO_4 \cdot 2ZnO$	1.2×10^{-1}
ZnO	4.2×10^{-4}
$ZnSO_4$	42
$ZnCO_3$	1.0×10^{-3}
$ZnCl_2$	432
$Zn(OH)_2$	5.2×10^{-4}

Adherent Chromate conversion film

Adhesion of Chromate Conversion Film

Adhesion of chromate conversion film on zinc alloy plating is superior to zinc. Their adherent property is due to the "anchor function" of the second metal to the chromate in addition to the zinc. In chromate solution, Tin, Nickel, Cobalt and Iron are not dissolved, so with increasing surface area, the co-deposition ratio rises.

Solubility of Chromate Film with Salt Water vs. Acid Solution

The dissolution rate of chromate film against salt water and acid solution is different for zinc and zinc alloys. Generally, the rate of dissolution of zinc alloys is lower than zinc. See **Figures 1** and **2**.

Figure 1 shows the relationship between the percentage of chromium that exists in the chromate film and acid solution (pH= 3) salt fog test time. From this result, we can expect that the zinc alloy's chromate protects its plating.

Figure 2 shows the relationship between the amount of zinc dissolution and salt spray test time. As seen in figure (2), the zinc chromate film loses its protection function faster than zinc alloy.

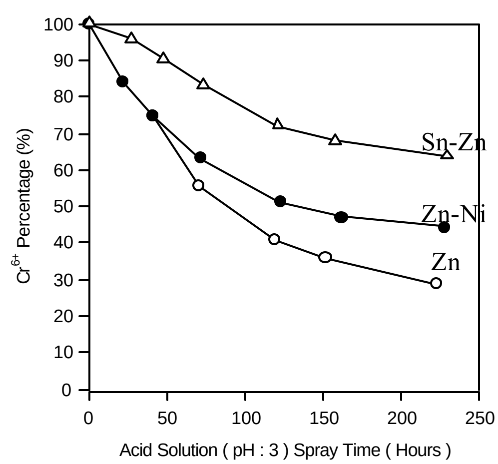


Figure 1

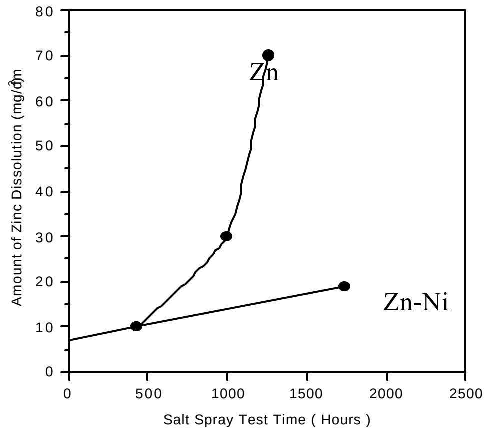


Figure 2

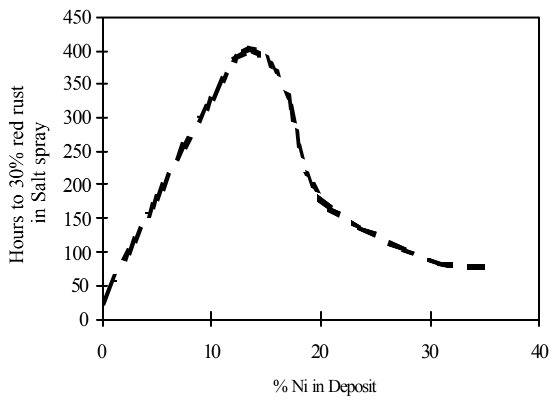
High Zn-Ni

Following is the feature of high Zn-Ni:

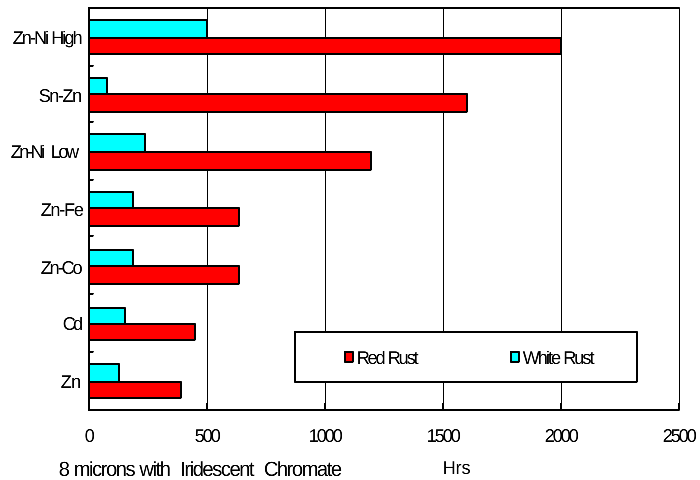
- Zinc- Nickel alloy contains 12-16% nickel.
- Over 4 times corrosion resistance to salt spray test than conventional zinc.
- Excellent adhesion and corrosion resistance in high temperature application.
- Higher hardness and scratch resistance.
- Excellent throwing power and covering power.

Corrosion Performance

Corrosion resistance varies depending on the Ni co-deposition ration, and at Ni 15% corrosion performance shows best.



Comparing with another plating, high Zn-Ni provides best corrosion resistance performance.



Hardness

Because of high contents of Ni , high Zn-Ni has high hardness. And this provides anti-scratch function and high corrosion performance under high temperature atmosphere.

Non-Cyanide Zinc	100 - 140 Vickers
Acid Chloride Zinc	60 - 80 Vickers
Zinc Cobalt (Acid)	180 - 210 Vickers
Acid Zinc Nickel	140 - 180 Vickers
Alkaline Zinc-Nickel	250 - 310 Vickers
High Zn-Ni	350 - 450 Vickers
Zinc Iron (Alkaline)	100 - 150 Vickers
Tin Zinc	13 - 17 Vickers

Bath Parameter

Plating speed is better than low Zn-Ni and running cost is slightly inexpensive.

	High Zinc-Nicke Barrel	Low Zn-Ni Barrel (5 - 9%)
Plating Speed at 9.3 ASF (micron/min)	0.15-0.17	0.09-0.13
Plating Time (min) for 8 microns at 9.3 ASF	50-60	65-90
Ni additive	1400 ml/KAH	830 ml/KAH
Brightener	140 ml/KAH	140 ml/KAH
Ni Stabilizer	-	50 ml/KAH
Additive#1	70 ml/KAH	40 ml/KAH
Additive#2	70 ml/KAH	30 ml/KAH
Running Cost	$13.28/KAH	$13.37/KAH

Operation condition is almost same as low Zn-Ni.

	Rack		Barrel	
	Start-up	Range	Start-up	Range
Zinc (g/L)	8	7 - 10	8	6 - 10
Nickel (g/L)	2.5	1.3 - 1.6	2.0	1.5 - 2.5
Caustic Soda (g/L)	130	100 - 150	100	100 - 150
Na_2CO_3 (g/L)	0	< 60	0	< 60
Brightener (%b.V.)	0.5	0.4 - 0.7	0.5	0.3 - 0.7
Additive#1	0.03	0.01- 0.05	0.03	0.01 - 0.05
Temp. (°F)	77	73 - 85	77	73 - 85
Cathode CD (ASF)	37	18 - 93	9.5	4.5 - 14.0
Anode CD (ASF)	45	45 >	45	45 >
Plating Speed (micron/min)	0.35	0.30 - 0.35	0.17	0.15 - 0.17

Operating Condition

Anode: Zinc 99.99% and nickel-plated steel. Or Nickel-plated steel with zinc generator tank.

Anode bag: Recommended.

Filtration: Continuous 2-3 turns over per hour.

Cathode rocker: 3-10 feet per min for rack system

Tank: PVC or lined steel tanks.

Spare tank: Similar capacity and material as process tank.

Rectifier: 15 Volt, 3 phases rectifier is usually satisfactory.

Others: A cooling system is recommended to remove sodium carbonate.

Standard Process Sequence

Process sequence is same as regular Zinc.

Soak
↓
Acid Pickling
↓
Electoroclean
↓
Acid Pickling
↓
Electoroclean
↓
Activation
↓
Plating
↓
Chromate
↓
Dry

(Rinse between each sequences)

Lineup of Chromate

Hexavalent Chromate

- Black
- Clear
- Iridescent

Trivalent Chromate

- Blue

Tin-Silver Alloy -- Pb Free Solder plating

Nowadays consumers are anxious about toxic substance content in their products. Pb is one of highest toxic elements. However Sn-Pb solder plating has been used for a long time due to its extremely high performance in the electronic industry, such as high bonding strength and inexpensive cost. Recently chemical suppliers started to develop Pb-free solder system in respond to environmental requirement.
Demands and Requirements in Market for Pb Free:

1. It must fit existing processes. Existing plating line and equipment must be used.
2. Chemicals are required to be non-toxic or toxicity needs to be less than Pb.
3. New processes should perform equal to if not better than the existing ones, example: Solderablity, bending property, and heat resistance.
4. Consistent supply of chemicals.
5. No cost increase.
6. Excellent conductivity of deposit.
7. Whisker free and ion migration free.
8. Acid and corrosion resistance are required.

This is the potential surface finishing for the replacement of Sn-Pb.

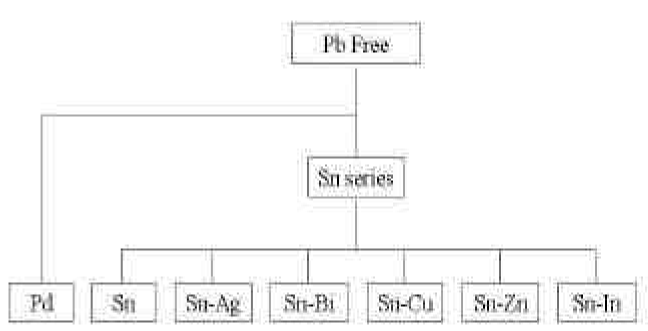


Fig 3 : Selection of Pb Free Solder Plating

Plating	Type of Bath	Type of Chemicals	Waste Treatment	Note
Pd	Acid	Ammonium Chloride	Acceptable	Thin thickness application approx. 0.1 µm.
	Neutral-Alkaline	Di-amino-nitrous acid	Acceptable	
Sn-Ag	Strong Acid	Organic sulfonic acid	Good, Easy	Ag will Displace to Sn Anode.
	Neutral	Diphosphate-Iodide	Acceptable	
	Alkaline	Di-methyl-hydantoin	Acceptable	
Sn-Bi	Strong Acid	Organic sulfonic acid	Good	Bi will Displace to Sn Anode.
	Neutral	Organic Carboxylic acid	Acceptable	
Sn-Cu	Strong Acid	Sulfuric acid	Good	Cu will Displace to Sn Anode.
	Neutral	Organic Carboxylic acid	Acceptable	
Sn-Zn	Neutral	Organic Carboxylic acid	Acceptable	Strong Acid type hasn't been developed yet.
	Alkaline	Stannic Acid -Zincate	Good	
Sn-In	Strong Acid	Organic sulfonic acid	Good	-
Sn	Strong Acid	Sulfuric acid	Good	Still be in use recently. Mature Product.
	Neutral	Organic Carboxylic acid	Acceptable	
	Alkaline	Stannic acid	Good	

Table-5 Feature of Pb Free Solder Plating Advantage and disadvantage for potential replacement.

Plating	Type of Bath	Type of Chemicals	Waste Treatment	Note
Pd	Acid	Ammonium Chloride	Acceptable	Thin thickness application approx. 0.1 µm.
	Neutral-Alkaline	Di-amino-nitrous acid	Acceptable	
Sn-Ag	Strong Acid	Organic sulfonic acid	Good, Easy	Ag will Displace to Sn Anode.
	Neutral	Diphosphate-Iodide	Acceptable	
	Alkaline	Di-methyl-hydantoin	Acceptable	
Sn-Bi	Strong Acid	Organic sulfonic acid	Good	Bi will Displace to Sn Anode.
	Neutral	Organic Carboxylic acid	Acceptable	
Sn-Cu	Strong Acid	Sulfuric acid	Good	Cu will Displace to Sn Anode.
	Neutral	Organic Carboxylic acid	Acceptable	
Sn-Zn	Neutral	Organic Carboxylic acid	Acceptable	Strong Acid type hasn't been developed yet.
	Alkaline	Stannic Acid-Zincate	Good	
Sn-In	Strong Acid	Organic sulfonic acid	Good	-
Sn	Strong Acid	Sulfuric acid	Good	Still be in use recently. Mature Product.
	Neutral	Organic Carboxylic acid	Acceptable	
	Alkaline	Stannic acid	Good	

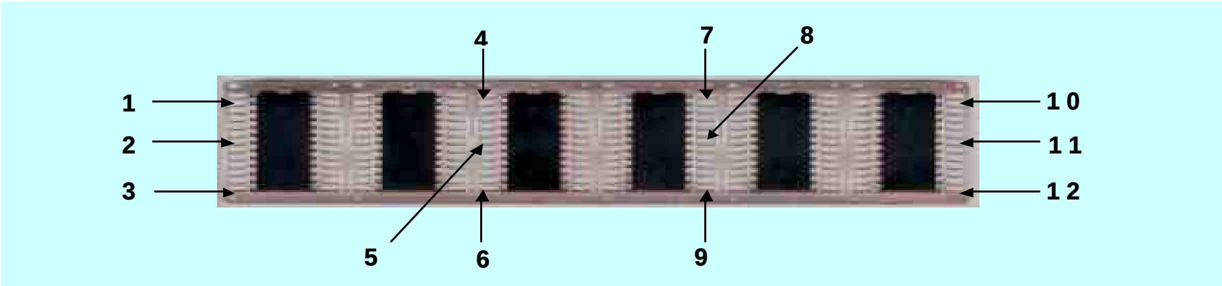
Table-6 Pb Free Plating Bath

Plating Type	Pd	Sn	Sn-3.5Ag	Sn-5Bi	Sn-0.75Cu	Sn-9Zn	Sn-20In	Sn-10Pb
Melting Point (^{o}C)	1554	232	221	225	227	199	189	221
Solderability	O	O	O	O	O	X	O	O
Bonding	O	O	⊕	⊕	⊕	⊕	⊕	O
Thermal Fatigue	-	O	O	x	?	O	-	O
Bending	-	O	O	x	O	O	Δ	⊕
Ion Migration	⊕	⊕	⊕	⊕	⊕	O	-	O
Whisker	O	X	O	O	X	O	-	O

⊕ : Excellent □: Good Δ : Inferior ×: Bad

Table-7 Property of Pb Free Solder Plating

Fig 4 : Measurement of Thickness & % Alloy for Sn-Ag Plating



#	Thickness (µm)	% Ag (wt%)	#	Thickness (µm)	% Ag (wt%)
1	10.8	3.12	9	9.2	2.98
2	10.5	3.65	10	0.7	3.19
3	11.2	2.87	11	10.3	3.29
4	9.3	3.34	12	11.1	2.95
5	8.8	3.78	Avg	10.0	3.31
6	9.5	3.44	Max	11.2	3.82
7	9.5	3.29	Min	8.8	2.87
8	8.9	3.82	Range	2.4	0.95

Thickness distribution and Ag contents are uniform.

Standard Process Sequence for Sn-Ag

Soak / Electroclean
↓
Activation by Acid Etching
↓
Pre-Dip
↓
Sn-Ag Plating
↓
Neutralization / Post-treatment
↓
Activation
↓
Plating
↓
Chromate
↓
Dry
(Rinse between each sequences)

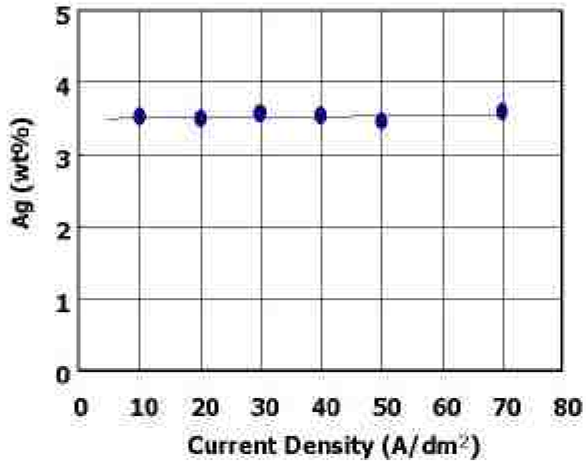
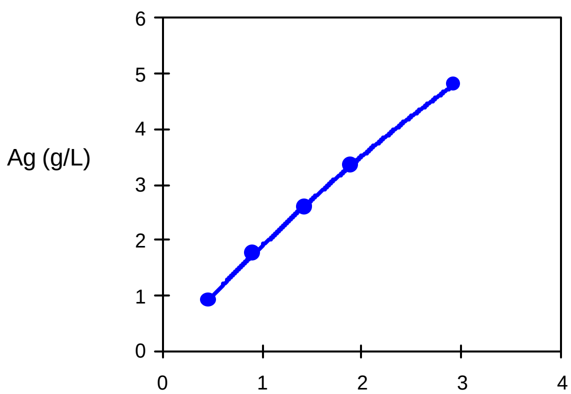


Fig 5 : Current Density – % Alloy of Silver

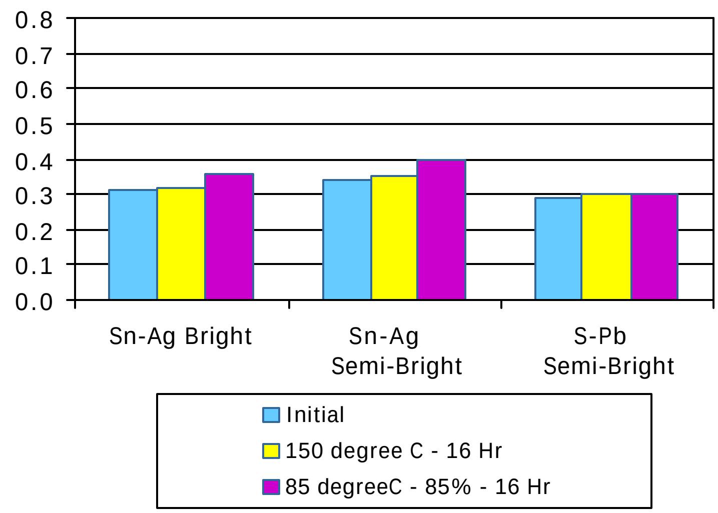
Ag contents are uniform for wide current density area.



Thickness : 10 mm
Bath Temp : 25 oC
Current Density : 30 A/dm2
Cathode Rocker : 5 m/mi

Fig 6 : Concentration of Silver in Bath (g/L)

Ag contents vary depending on the concentration of Ag in the plating solution.

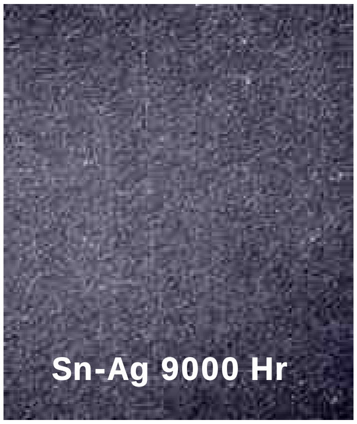


% Ag (wt %)

Width of Lead : 0.2 mm
Time : 10 sec
Thickness of Lead: 0.15 mm
Flux : Non-active Rosin
Depth : 1.0 mm
Solder : Sn-3.5Ag-0.75Cu, 250oC
Speed : 5 mm/sec

Fig 7 : Solderability (Cu, QFP Type)

Photo 1 : Whisker



Sn-Ag has no whisker.

Solderability is almost same as Sn-Pb

Table-8 : Hardness

	Sn-Ag	Sn-Ag	Sn-Pb
Appearance	Bright	Semi -Bright	Semi-Bright
Hardness (Hv)	15 - 20	15 -20	10 -15

Test Condition:
Thickness : 25 - 30 micron Ag(wt%) : 2.7 – 3.5
Test Device : Vickers Hardness MVK-G2
Test Load : 1 – 3 gm
Load Speed : 1 mm/sec
Holding Time : 10 sec