Mirror-Bright Silver Plating from a Cyanide-Free Bath

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Silver has good electric conductivity and solderability and possesses excellent electric characteristics as a contact and is thus widely used for plating electronic industrial parts. A cyanide plating bath is most often used, but the cyanide compounds have strong toxicity and a large amount of the cost is required for securing safe working conditions and waste treatment. Because of this, many cyanide-free baths have been proposed and reported, such as the silver chloride-sodium thiosulfate system,[1] the silver nitrate-tartaric acid system,[2] and the silver iodide system added with gelatin,[3] but none of them is in practical use. The authors found that a plated coat having performance comparable to that of the cyanide silver plating bath can be obtained from a silver methane sulfonate-potassium iodide bath to which *N*-(3-hydroxyl-1-butylidene)-*p*-sulfanilic acid (HBPSA) is added and has succeeded for industrialization; however, the plated coat obtained from this bath has poor brightness. The authors have carried out research and development work on a cyanide-free bath capable of providing a bright silver plate.[4–6] It was determined that a bright coating can be obtained from silver succinimide.[7,8] Jayakrishnan and Natarajan[9] reported an alkaline silver plating using succinimide, but they gave no information for the stabilization of the bath. The authors found that the bath can be stabilized by adding boric acid and that mirror-bright silver plating can be obtained by adding polyethyleneimine (PEI) as a brightener.

In the development work reported in this article the influences of adding PEI on the appearance of the plate coat, current efficiency, surface morphology, cathodic polarization characteristics, and the like were examined. The solderability, contact electric resistance, and hardness obtained were compared with those obtained from a conventional cyanide bath.

EXPERIMENTAL METHOD

Bath Composition and Operating Conditions

Table I shows the composition, pH, temperature, and current density of the plating bath. The pH was adjusted using methane sulfonic acid and potassium hydroxide.

Evaluation of the characteristic value of the deposit was obtained by comparing it with that obtained from a bright cyanide bath. The composition and operating conditions of the cyanide bath are shown in Table II. For both the cyanide-free bath and cyanide bath plating was performed using a cathode rocker (4 m/min) except for the Hull cell test. Also, when performing silver plating from the bright cyanide bath, a silver strike (0.1 to 0.2 μm) was applied on a copper plate in advance.

Table I. Basic Bath Composition and Operating Conditions for Cyanide-Free Bath

Composition	*Concentration*
CH_3SO_3Ag	0.45 M
$C_4H_5O_2N$	1.5 M
H_3BO_3	0.50 M
Polyethyleneimine	0.50 g/L
pH	10.0
Temperature	25°C
Current density	2.0 A/dm^2

Table II. Bath Composition and Operating Conditions for Bright Cyanide Bath

Composition	*Concentration*
AgCN	0.37 M
KCN	1.80 M
K_2CO_3	0.25 M
Commercial brightener	30.0 ml/L
pH	12.5
Temperature	25°C
Current density	2.0 A/dm^2

Hull Cell Test

The influence of changes in PEI molecular weight on the appearance of the plated coat was examined. Copper plates were used for samples and silver plates (99.99%) were adopted as the anode. The amount of a plating solution was 250 mL. The bath was agitated with a stirrer (500 rpm), and the plating was performed for 5 minutes with a total current of 1A in the Hull cell condition. The chemical formula of PEI is shown in Figure 1.

Cathode Current Efficiency

For the cathode current efficiency a copper plate 25 mm × 25 mm with 0.3 mm thickness was used. Electrolysis of 117 coulombs was performed, and the efficiency was determined from the difference in weight before and after plating. A bath temperature of 25°C was used as the base, and the cathode rocker was set at 4 m/min.

Surface Observation

Silver plating was performed to a coating thickness of 0.3 mm on a 10 mm × 10 mm copper plate 0.3 mm thick and the surface morphology of

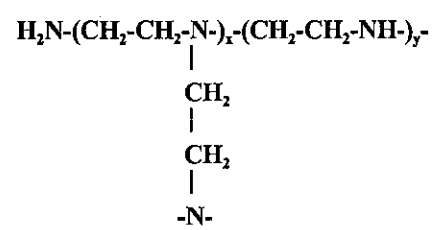

Figure 1. Chemical structure for polyethyleneimine (molecular weight 300 to 1,000).

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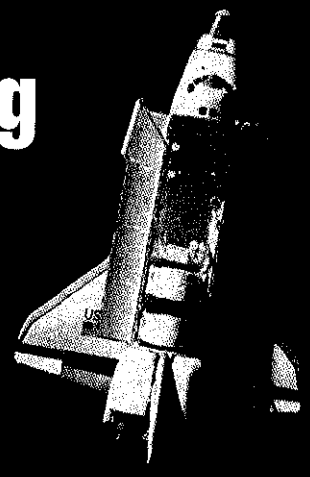

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Table III. Electrical Resistance and Hardness of the Deposits

Number	*Property of Solution/Deposit*	*Value*
Contact electric resistance:		
1	Cyanide-free bath, PEI 0 g/L, 5 μm, 5 g load	1.23 mΩ
2	Cyanide-free bath, PEI 0.5 g/L, 5 μm, 5 g load	1.02 mΩ
3	Cyanide bath, 5 μm, 5 g load	2.10 mΩ
Vickers microhardness:		
4	Cyanide-free bath, PEI 0 g/L, 100 μm, 100 g load	Hv 113
5	Cyanide-free bath, PEI 0 g/L, 100 μm, 100 g load	Hv 121
6	Cyanide bath, 100 μm, 100 g load	Hv 105

the plated coat was observed using a scanning electron microscope.

Cathodic Polarization Curve

The basic bath shown in Table I was used as a test solution. A test electrode of 0.3 × 10 × 50 mm copper plate was used, and a resist seal was made leaving an active area of 2 cm^2. This was used for measurement after degreasing and acid cleaning. A platinum wire was used as a counterelectrode and a Ag/AgCl electrode was used as reference electrode. Automatic polarization equipment was used for the measurement. Agitation (500 rpm) by stirrer was conducted at 25°C with the potential scanning speed of 25 mV/min. Also, cathode electrolysis was performed for 5 minutes at a constant current density of 1 A/dm^2 in advance before the measurement, and silver plating was applied to the surface of the copper plate of the test electrode and then the measurement was started.

Solderability Test

Solderability was evaluated using the Menisco graph method.[10] A 20 mm × 45 mm copper plate 0.3 mm thick, silver plated with 5 μm was used as a sample. It was cleaned with acetone before the test and immersed in 25% rosin/alcohol flux for 5 seconds. As a test bath, molten solder with a tin to lead weight ratio of 65:35 was used. The test condition comprised a bath temperature of 220 to 260°C, immersion time of 3 seconds, immersion speed of 25.4 mm/sec, and immersion depth of 8 mm.

Contact Electric Resistance

A 30 mm × 30 mm copper plate 0.3 mm thick, plated with silver to 5 μm was used, and the contact electric resistance was measured with an electric contact simulator. Four terminal method was used for measurement, with gold wire for measuring probe, an applied current of 10 mA, a reciprocating speed of 1 mm/min, and a loading weight of 5 g_f.

Hardness of Plating

A 25 mm × 30 mm stainless steel sheet 0.5 mm thick was plated with silver to a thickness of about 100 μm. The plated coat was then peeled off from the stainless steel base. The hardness on the rear surface of the coat was measured by using microhardness meter. Measuring load was 100 g_f.

RESULTS AND DISCUSSION

Effect of Adding Boric Acid

Change in pH with time is shown in Figure 2. In the case of the basic bath to which 0.5 M boric acid (H_3BO_3) was added, the bath pH almost retained the initial pH even after the elapse of 120 hr; and in the case where H_3BO_3 was not added, a phenomenon of a sudden drop in pH as the time elapsed was recognized. A pH around 10 was found to be excellent for silver plating using succinimide as a complexing agent, and it was clarified that the complex became unstable when pH was less than 7, resulting in settlement

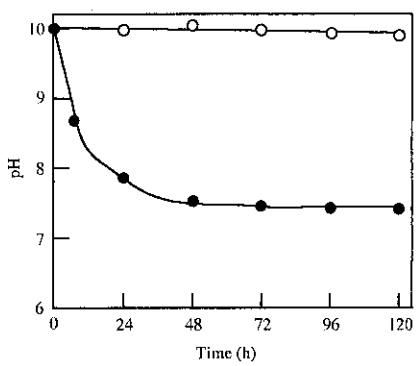


Figure 2. Effect of boric acid addition on pH (0.5 M H_3BO_3 above, no H_3BO_3 below).

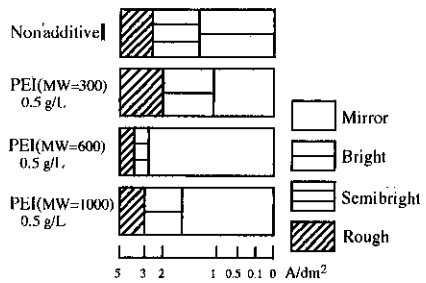


Figure 3. Effect of polyethyleneimine molecular weight on the appearance of Hull cell test panels.

in the bath and poor appearance of the deposit.[7,9]

Hull Cell Appearance

Figure 3 shows the influence of adding PEI with different molecular weights on the Hull cell appearance. The amount of PEI added was set to 0.5 g/L regardless of its molecular weight. When PEI was not added a bright appearance occurred up to about 1.5 A/dm^2, semibright up to 2.5 A/dm^2, and nonbright with rough graining occurred above this value. On the other hand, if PEI is added, a mirror appearance occurred even from a low current density in every molecular weight. The mirror brightness was especially noted in the widest range of current density particularly when the molecular weight was 600. Also, the range of current density, where the mirror brightness was obtained, hardly changed even when PEI amounts larger than 0.5 g/L were added.

Cathode Current Efficiency

Figure 4 shows the influence of the current density on the cathode current efficiency. A bath with no PEI added had a significant tendency of decreas-

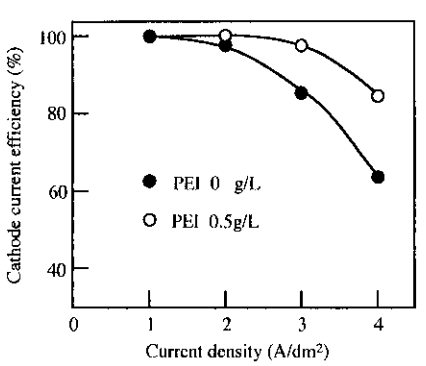
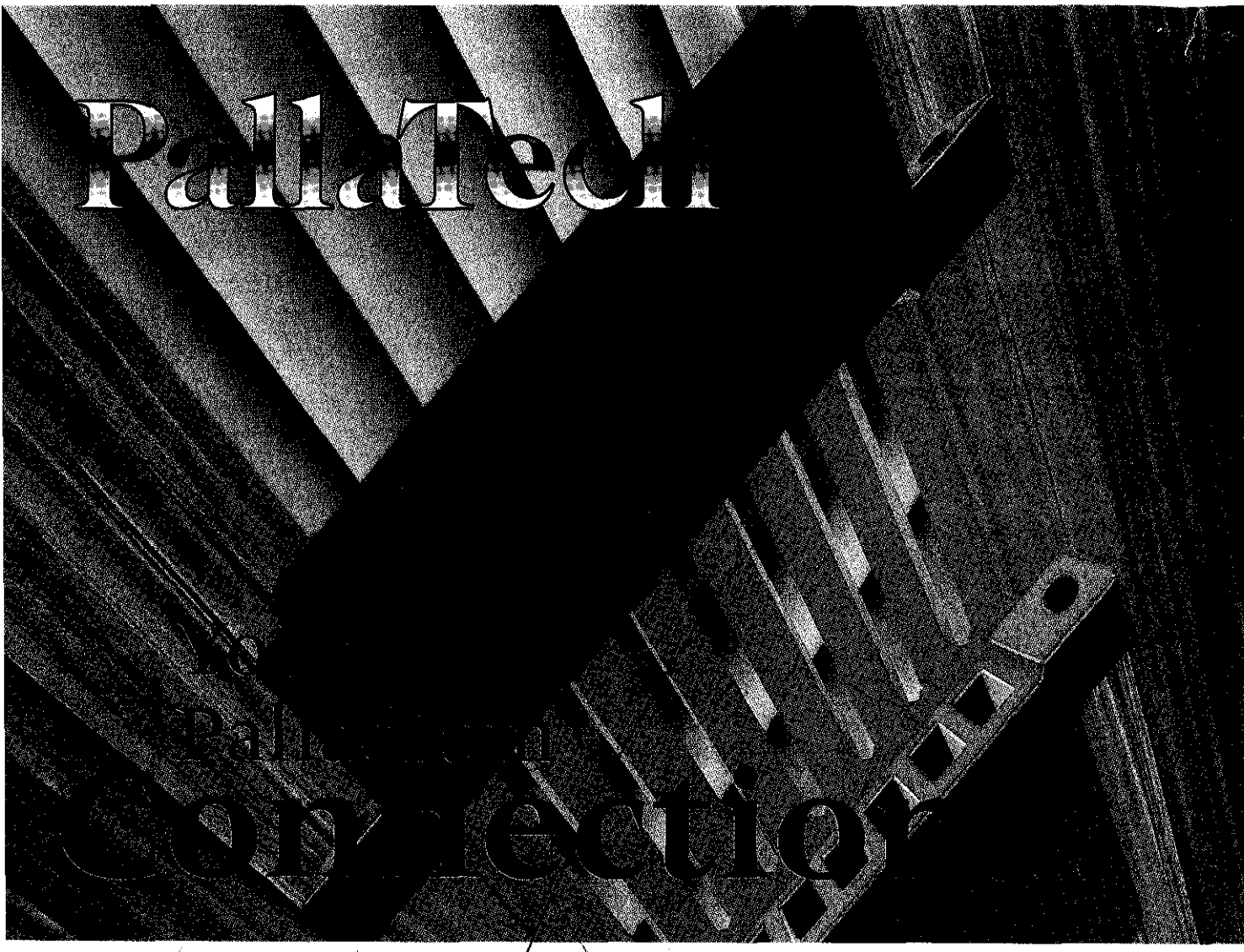


Figure 4. Effect of current density on cathode current efficiency.



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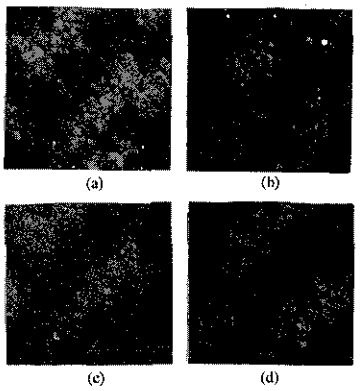

Figure 5. Effect of polyethyleneimine on surface morphology (a) none, 2 A/dm^2; (b) None, 3 A/dm^2; (c) 0.5 g/L (MW 600), 2 A/dm^2; (d) 0.5 g/L (MW 600), 3 A/dm^2.

ing in current efficiency owing to an increase in current density compared with a bath with PEI added. When PEI (MW = 600) was added the current efficiency was 84% at 4 A/dm^2 but, if not added, a low value of 63% was obtained. As shown in the results of Hull cell appearance in Figure 3, a deposit with relatively rough grains was formed when 3 A/dm^2 was exceeded without adding PEI. The current efficiency seemed to have dropped greatly because the deposit was removed by rinsing with water during or after electrolysis.

Surface Morphology

Figure 5 shows the influence of adding PEI (MW = 600) on the surface morphology of the silver deposit. When no PEI was added, 2 A/dm^2 created bright and 3 A/dm^2 semibright to the naked eye; and microscopically the crystal was slightly finer at 2 A/dm^2 (photo a) than 3 A/dm^2 (photo b). When PEI was added (photos c and d), the crystal was made finer at any current density and the most dense surface morphology occurred at 2 A/dm^2 (photo c).

Cathode Polarization Curve

Figure 6 shows the influence of the PEI added on the cathode polarization curve. When comparing the polarization curves of a bath added with PEI to a bath without PEI, the former is polarized much greater than the latter in the potential range higher than −700 mV. This seemed to have occurred because the PEI added was absorbed by

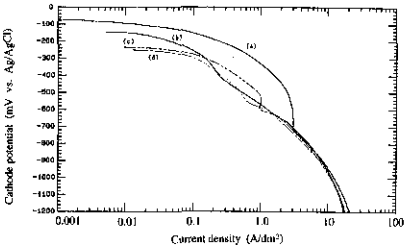

Figure 6. Effect of polyethyleneimine molecular weight on cathodic polarization (a) None; (b) MW 300; (c) MW 600; (d) MW 1,000.

active site and thus overvoltage increased when compared based on the same (apparent) current density. It is known that the radius of the crystalline nucleus, which can grow continuously in a growth layer of an object to be plated, is inversely proportional to overvoltage.[11] Mirror brightening (Fig. 3) of a plated object by adding the PEI is considered to have been brought on by the crystal grain being made finer (Fig. 5) owing to an increase in the overvoltage.

Solderability

As with gold or silver, the silver-plated coat does not melt at the joining temperature but quickly dissolves into the solder and thus is classified a soluble coating. The solderability of silver-plated deposits obtained from the cyanide bath and the cyanide-free bath was evaluated by using the Menisco graph method. The solderability was then examined by using zero cross time (Tπ) as one of the parameters obtained from the Menisco graph curve. As the wettability of solder becomes better, Tπ becomes shorter.[12] Figure 7 shows the influence of the solder bath temperature on the solderability. As the solder bath temperature

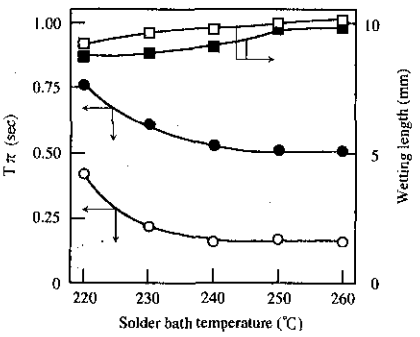

Figure 7. Effect of solder bath temperature on solderability. ○ □ cyanide-free bath, 0.5 g/L (MW 600); ● ■ cyanide bath.

rises, Tπ decreases and the wetted length tends to increase, but each of them becomes constant at about 250°C. When comparing the baths to each other, there is no great difference in wetted length, but Tπ for the cyanide-free bath with PEI added has a shorter value, and thus this bath is judged to have good solderability.

Contact Electric Resistance and Hardness

Silver plating is much used for the surface treatment of contact materials. The contact electric resistance is thus considered to be one of the important evaluation items. Table III shows the contact electric resistance value and hardness of silver-plated deposits obtained from both the cyanide bath and the cyanide-free bath. The resistance value becomes smaller in the order as listed below.

Cyanide bath > cyanide-free bath (no PEI) > cyanide-free (PEI) bath.

The deposit obtained from the cyanide-free bath with PEI added has the smallest resistance value.

In the case of the hardness, to the contrary, the hardness increased in the order as listed below.

Cyanide bath < cyanide-free bath (no PEI) < cyanide-free (PEI) bath.

The deposit obtained from the cyanide-free bath with PEI added is considered to be slightly better in both the contact electric resistance and hardness than the coat obtained from the cyanide bath.

CONCLUSION

With respect to mirror-bright silver plating from a silver methane sulfonate succinimide-based bath, the authors examined bath stability as well as appearance due to addition of PEI, current efficiency, surface morphology, and influence on cathode polarization curves and the like and further compared the characteristic values of the deposits on the plated objects to those obtained from a cyanide bath, and the following results and findings have been obtained.

1. The pH of bath is maintained at around 10 by adding boric acid.
2. The mirror-bright silver plating can be achieved through addition of PEI.
3. PEI with a molecular weight of

600 creates a mirror-bright deposit over the widest range of current density.
4. PEI is adsorbed at the electrode surface with indications of the densest surface morphology at 2 A/dm^2 and a current efficiency of almost 100%.
5. Solderability and contact current resistance are better than those obtained from the bright cyanide bath.
6. Hardness of plating indicates values slightly higher than those from the bright cyanide bath.

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