JOURNAL OF APPLIED ELECTROCHEMISTRY **26** (1996) 63–71

Study of electroless plating fog on plastic surfaces

S. SUGIHARA

Faculty of Engineering, Tokushima Bunri University, Shido-cho, Okawa-gun, Kagawa 769-21 Japan

A. IWASAWA, K. ONOSE, J. YAMAKI

NTT Interdisciplinary Research Laboratories, Tokai-mura, Naka-gun, Ibaraki 319-11 Japan

Received 4 July 1994; revised 12th May 1995

Plating fog is often observed on the substrate when printed circuit boards are produced by photoadditive electroless plating. Thus unwanted metal is deposited on the unpatterned region, where there should be no plating activity, when a substrate with a catalytic plating pattern is immersed in plating solution. This metal deposition phenomenon observed on roughened resin substrates is examined in terms of (i) the physical state of substrate surface, (ii) the chemical state of substrate surface and (iii) the exposure and activation process.

1. Introduction

Many kinds of printed circuit board (PCB) are being produced for use in electronic exchange and information processing systems. However, only a small quantity of each type is fabricated and the printed patterns are becoming more complex to enable systems to be assembled economically and appropriately. This trend causes the manufacturer unavoidable cost increases and makes it impossible to take advantage of the benefits of mass production.

With a view to overcoming this problem, we have studied a novel PCB production method in which a latent image of silver atoms is formed by the photolysis of silver carboxylates [1–12]; the image is then metallized by electroless copper plating [13, 14]. Figure 1 outlines this method, which meets the need for the small-scale production of many kinds of board. This is because even one board can be made economically with this process involving a small number of steps without photo masks.

To establish this photoadditive method, we have developed highly photosensitive materials which catalyse the electroless copper plating [1–3], and adhesive resins which provide high peeling strength between the substrate and plated copper metal [3, 15]. Here, we study the remaining problem, which is the plating fog often observed during the process of metallizing the latent silver pattern by electroless copper plating. Although there is little literature on this subject [16], we consider the plating fog is caused by the following three factors: (a) metal or metallic ions of plating catalyst on the PCB surface, (b) instability of the electroless plating solution and (c) the diffusion layer which reduces copper ions formed around the pattern.

With respect to (a), if metal M is the plating catalyst, copper metal is deposited on metal M by the following reaction.

$$Cu^{2+} + 2HCHO + 4OH^- \xrightarrow{M} Cu^0 + 2HCOO^- + 2H_2O + H_2 \qquad (1)$$

If there is any noble metal, M, in the unpatterned region, it will lead to plating fog because Reaction 1 proceeds by self catalysis, that is, the deposited copper metal catalyses Reaction 1 again. In addition, reductive metallic ions M^+ (e.g. Fe^{2+}) reduce the copper ions and generate copper deposits as shown by Reaction 2 and this causes plating fog.

$$2M^+ + Cu^{2+} \longrightarrow 2M^{2+} + Cu^0 \qquad (2)$$

Therefore, it is important to remove the catalytic metal or metal ions completely from the unpatterned region in order to prevent plating fog.

With respect to (b), the side reactions described below may occur in the plating solution in addition to Reaction 1, above. Formaldehyde, as a copper ion reducing agent, is subject to a disproportionation reaction (Cannizzaro reaction)

$$2HCHO + OH^- \longrightarrow CH_3OH + HCOO^- \qquad (3)$$

This reaction consumes formaldehyde, forms formic acid, and then accelerates the ageing of the plating solution. Furthermore, formaldehyde partially reduces cupric ions to cuprous ions in alkaline solution.

$$Cu^{2+} + HCHO + 3OH^- \longrightarrow Cu_2O + HCOO^- + H_2O + H_2 \qquad (4)$$

Cuprous oxide thus formed is subject to disproportionation and yields copper metal in alkaline solution.

$$Cu_2O + H_2O \longrightarrow Cu^0 + Cu^{2+} + 2OH^- \qquad (5)$$

The copper metal particles formed are suspended in the plating solution and this is considered to be the most likely reason for the solution to be unstable. When these particles are trapped on the substrate, they cause plating fog.

With respect to (c), an important role is played by the interfacial electrochemistry between the plating solution and the substrate surface. The plating fog caused is markedly reduced by mechanical stirring

0021-891X

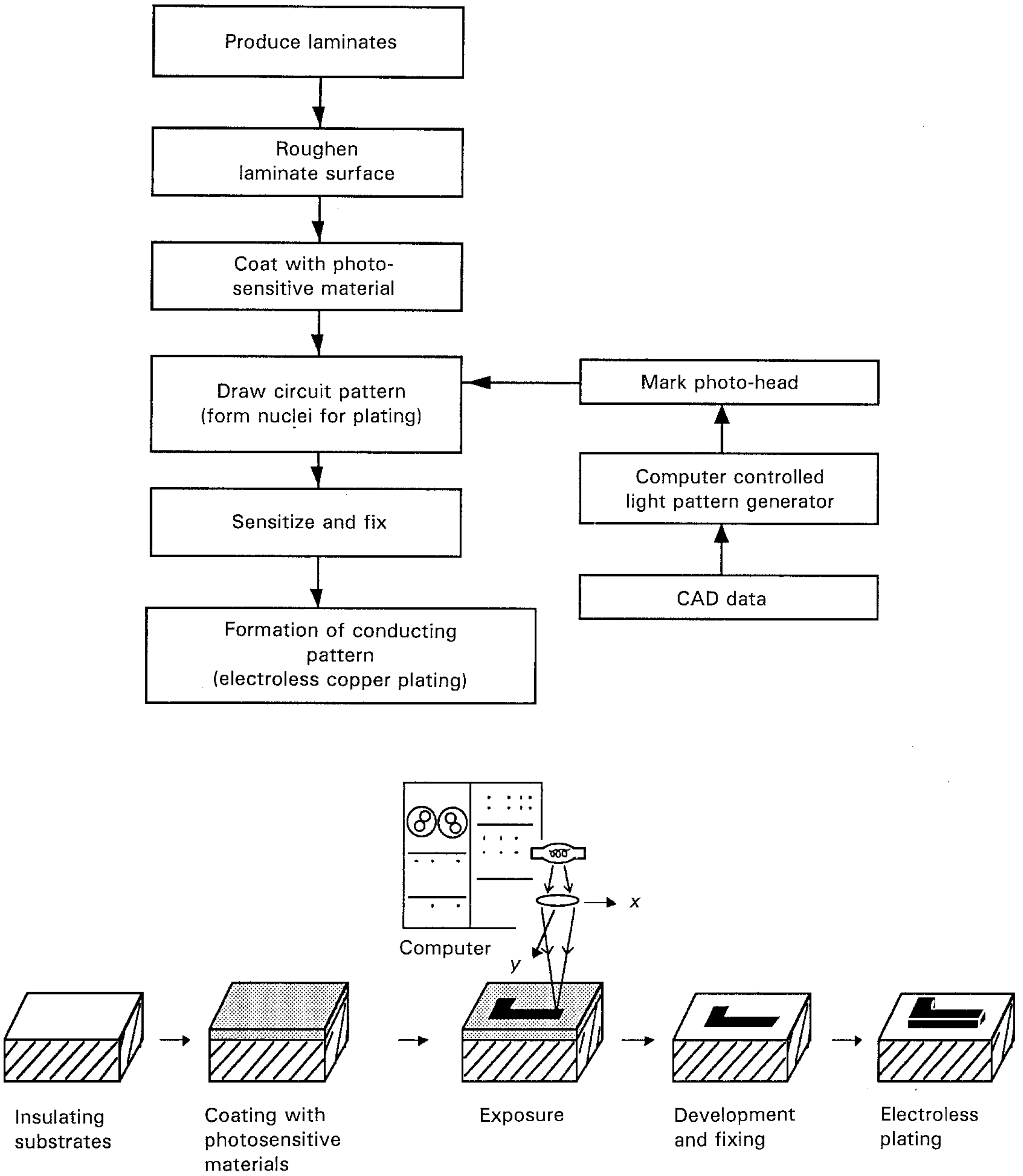

Fig. 1. Printed circuit board production by photoadditive process.

or air bubbling. Mechanical stirring is considered to decrease the reductive diffusion layer and air bubbling deactivates the self catalysis of copper by oxidation.

In this study, we examine the effects of the surface state of the substrate and the catalysis of metals.

2. Experimental details

Samples were prepared using the process for forming a copper circuit pattern shown in Fig. 1 with the exception of the exposure stage. In this case the exposure was carried out by irradiating the photosensitive substrates with negative photo masks. The composition of the adhesive resins used for coating the substrates is shown in Table 1. The substrates coated with each resin were cured at 160 °C for 30 or 60 min and then roughened by liquid honing using an abrasive composed of Alundum 200, 280 or 400 at a roughening pressure of 1–3 kg cm^{-2}. A 14 w/v % solution of disilver glutamate was coated on the substrate with a spin coater and it was then sensitized by u.v. light exposure generated by a 3 kW super high pressure mercury lamp (7 mW cm^{-2}) for 5 min. It was activated with an acidic 0.05% palladium

Table 1. Composition of adhesive resins

Resin	*Phenolic resin**		*Nitrile rubber*†	*Epoxy resin*‡	*Filler*
	P_7	P_8	R_2	E_2	*ZnO*
1	–	30	40	30	–
2	–	20	50	30	150
3	10	–	40	50	150

* P_7: Sumilite PR50775, P_8: Sumilite PR12987 (Sumitomo Durez Co.)
† R_2: Nipol 1001 (Nippon Zeon Co.)
‡ E_2: Epikote 1001 (Shell Petrochemical Co.)

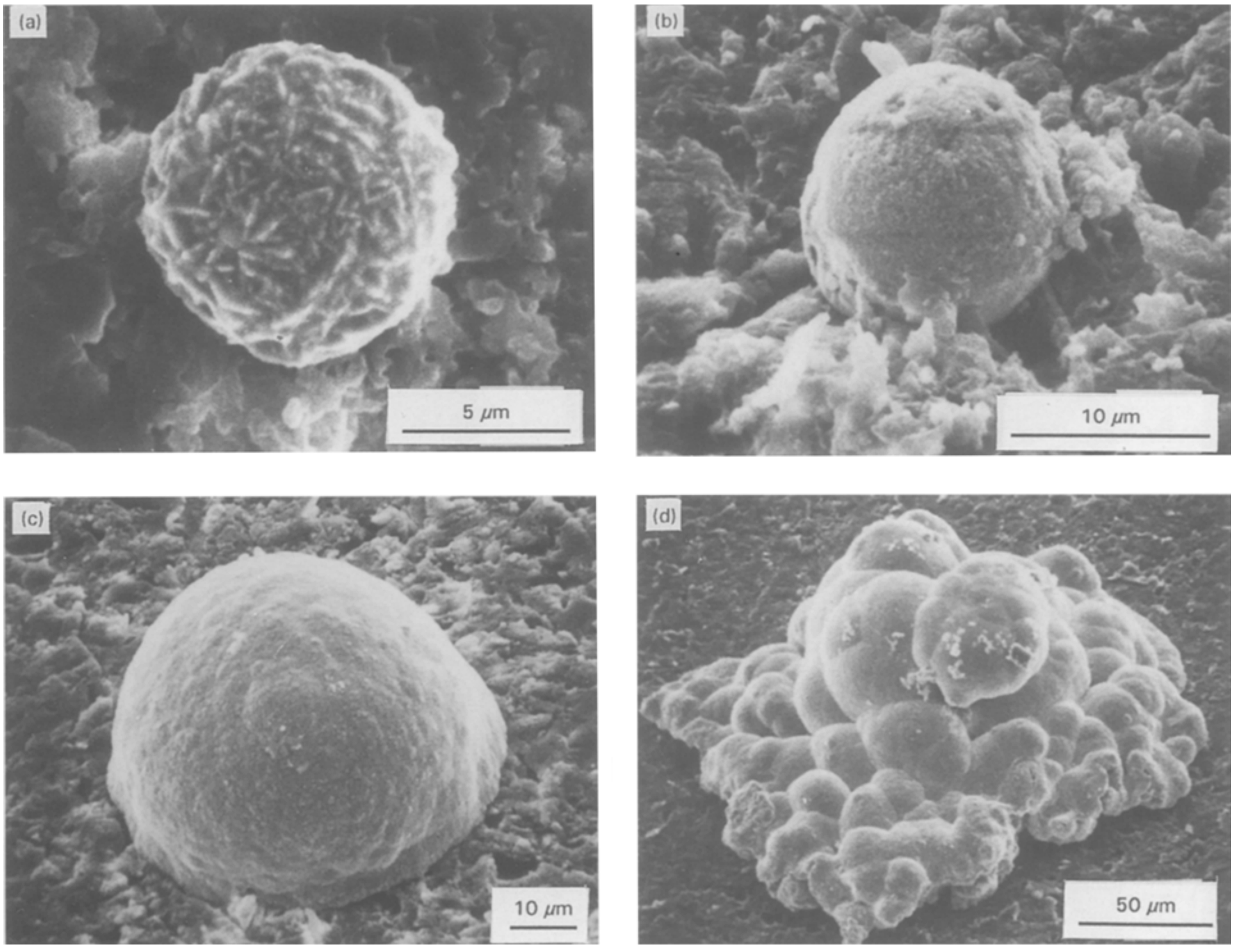

Fig. 2. Plating fog of various size formed on the surface of resin substrate after 24 h at 50 °C.

chloride solution and then fixed with a 20% aqueous acetic acid solution and then a 20% aqueous ammonia solution, each for 20 min. It was then electrolessly plated by placing it in Cuposit CP-70 plating solution (Shipley Co.) at 30 °C or 50 °C for 1–24 h. During this period the solution was stirred mechanically and filtered with a 10 μm filter. The plated board was finally cured at 120 °C or 160 °C for 30 min.

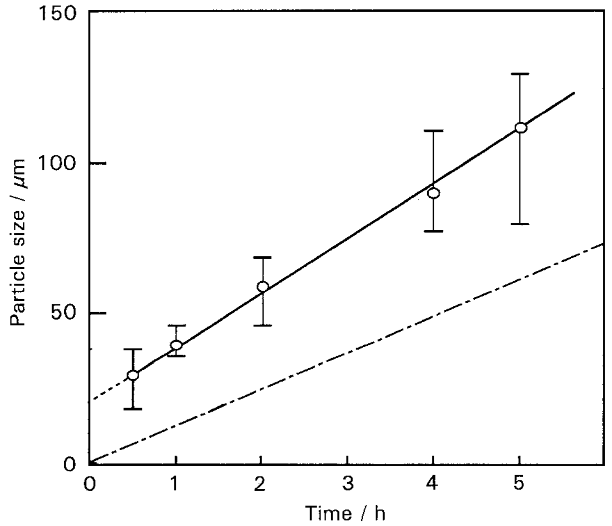

Fig. 3. Change in fog particle size with time (50 °C).

3. Results and discussion

3.1. *Plating fog on a photosensitive material free substrate*

Figure 2 shows micrographs of copper plating fog particles of various size formed on the substrate 24 h after placing in the plating solution at 50 °C. The particles grow from a small sphere (a) and (b) to a hemisphere (c) and some particles aggregate to form a large cluster (d). These fog particles grow with time; the particle size increases linearly with time as shown in Fig. 3. This indicates that the activity of the plating solution remains constant during this period. In addition, the fact that the extrapolation of the particle size to zero (time) does not coincide with the origin indicates that copper particles of some size are already suspended in the plating solution before introduction of the substrate. A carbon mesh was dipped into the plating solution four hours after preparation and trapped particles were examined by TEM. Particles of 0.15 μm in diameter and needle-like crystals 1 μm in length, as shown in Fig. 4, were observed and were identified as cuprous oxide by electron diffraction analysis. These oxides yield copper metal according to Reaction 5, and small suspended particles are continuously generated in the plating solution because small copper particles, as shown in Fig. 2(a), are

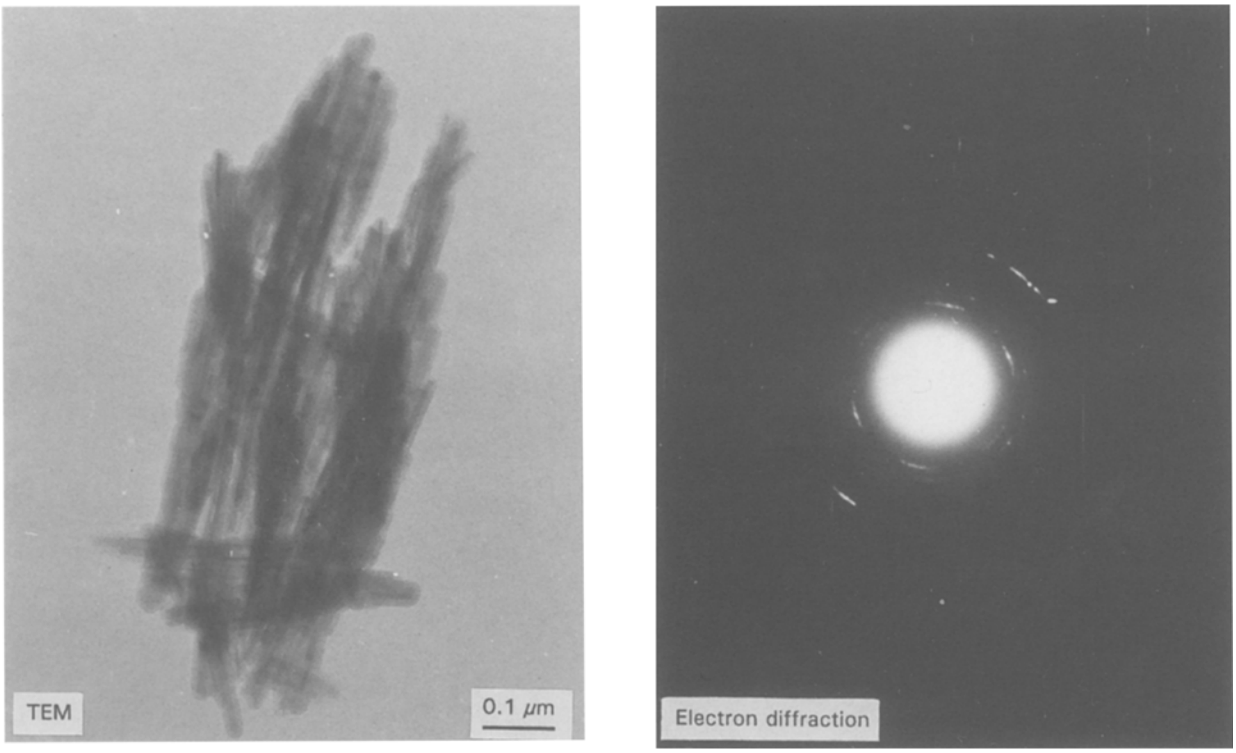

Fig. 4. TEM image and electron diffraction pattern of suspended particle in the plating solution (4 h after preparation).

observed on the substrate even 24 h after solution preparation. Sometimes, needle-like crystals grow on the particle surface at 30 °C as shown in Fig. 5. The underside of a large particle has a nucleus and a ring-like growth pattern as shown in Figure 6. In this case, many small particles gather together to form a mass of fog and the manner of the growth obviously differs from that shown in Fig. 5.

The probability of a suspended particle attaching itself to the substrate depends on the form and the chemical properties of the substrate surface. In addition, abrasives may cause plating fog if they are left on the substrate. To investigate this, substrates were prepared with different surface states and their effect on plating fog was examined. The samples and the surface preparation processes are listed in Table 2. Figure 7 shows the surface of a substrate before plating; this surface was coated with resin 1 (Table 1) and roughened by liquid honing. The amount of plating fog on the substrates is also given in Table 2. Heat treatment significantly changes the surface state; a surface roughened at 2 kg cm^{-2} pressure became smooth when heated at 160 °C for 20 min, as shown in Fig. 7(a2). Extensive surface smoothing results in a slight decrease in the size and number of fog particles.

Chromium ions (Cr^{6+} or Cr^{3+}) on the substrate cause a large amount of fog (b3). This indicates that chromium ions catalyse the deposition process. Similarly, the abrasive Alundum causes a large number of fog particles (b4). This fog is believed to be due to the iron contained in the abrasive or eroded from the nozzle of the honing apparatus. The resin surface becomes fairly smooth in an alkaline solution,

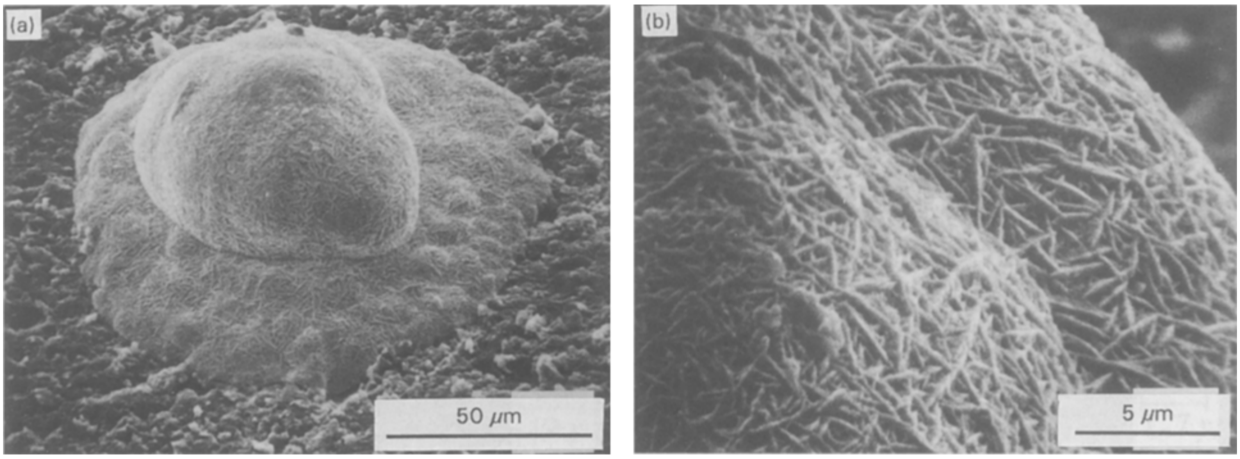

Fig. 5. Micrographs of a fog particle and its surface formed at 30 °C.

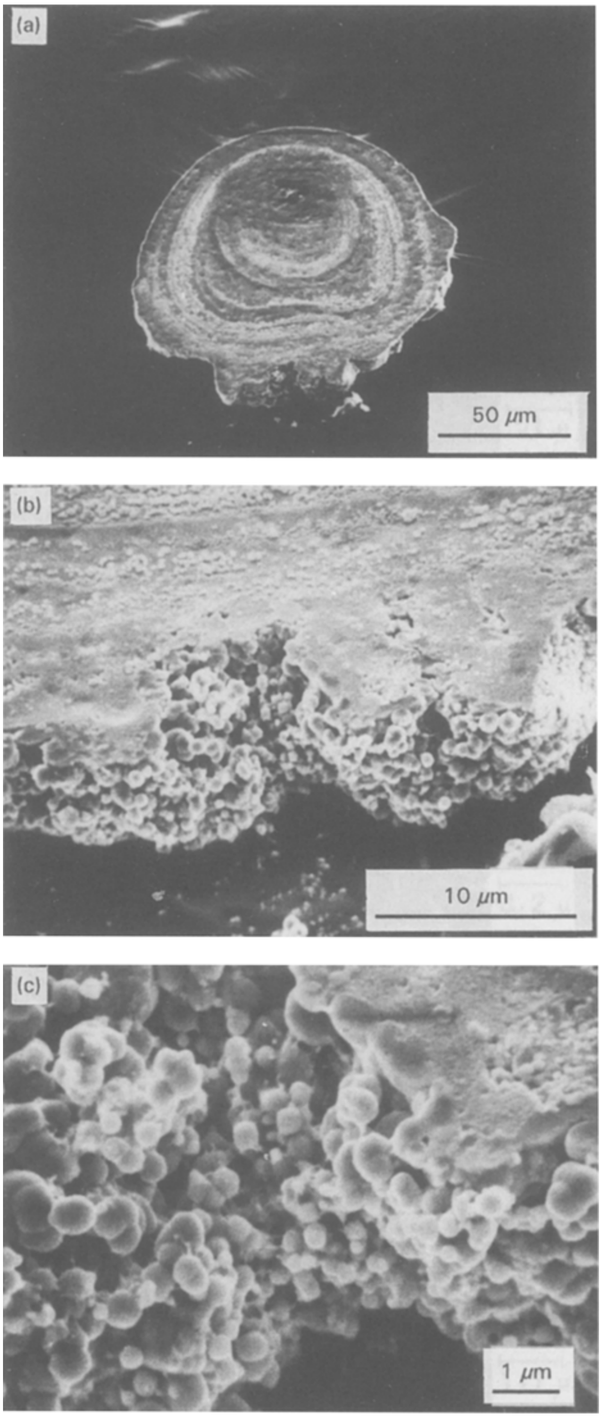

Fig. 6. SEM images of the underside of a large particle.

which leads to a decrease in plating fog (b5). Thus, even if the substrate surface is modified by placing it in alkaline plating solution for a long time, there should be no increase in plating fog. Changes in the standing time of the substrate have no effect either on the surface shape or on the plating fog.

Macroscopic scratches do not cause plating fog (c) but fine cuts do; there is a specific type of flaw shape which leads to plating fog formation.

3.2. *Plating fog on a substrate patterned with photosensitive material*

3.2.1. Shape of fog particle. A parallel silver pattern was formed by u.v. exposure and the shape of the fog particles deposited on the unpatterned region was examined. The particle generated after 20 h at 26 °C is approximately hemispherical, the average size being 112–115 μm in diameter in the direction parallel to the surface, and 61 μm in height. The thickness of the plated pattern was 62 μm. This result indicates that fog deposition starts at the same time as the normal deposition of the pattern because the fog particle height is almost the same as that of the metal pattern.

3.2.2. Influence of surface roughness. The influence of the surface shape of the substrate on the plating fog is slight compared with metallic impurity in the case of a photosensitive material free system (Section 3.1). However, in a system containing photosensitive material, the ease with which the photosensitive material can be removed by fixation, in other words, the amount of catalyst remaining on the substrate, varies with surface shape. This naturally affects the plating fog. So, a substrate coated with resin 2 (Table 1) was prepared and roughened under various pressures with a liquid honing apparatus using Alundum 200. The prepared substrate was dipped in a solution of photosensitive material and, after silver metal had been deposited by u.v. light exposure, it was fixed using the standard method and then electrolessly plated at 30 °C for 15 h. The surface roughness is shown in Fig. 8. The number of plating fog particles rose with increase in surface roughness. This tendency was increased by activation treatment with palladium chloride (Section 3.2.4.). These results indicate that it is more difficult to remove the photosensitive material or the abrasive with increasing roughness and that these materials are activated by palladium.

3.2.3. Influence of exposure time. The following factors are considered to cause plating fog as a result of long exposure: (i) the thermal decomposition of photosensitive material by increase in temperature; (ii) the leakage of light to the unpatterned region due to poor light blocking of the negative photo mask; (iii) light scattering from the patterned part (transparent) to the unpatterned region (blocking) of the negative photo mask; (iv) light transmitting through pinholes in the unpatterned region of the negative photo mask; and (v) insufficient fixation due to surface deformation caused by temperature increases and pressure from the photo mask.

It was found that the factors due to the photo mask (ii–iv) were negligible because the same results were observed when a double layer photo mask was used. The temperature increase in the unpatterned region of the substrate in the exposure apparatus is shown in Fig. 9. Because the photosensitive material, disilver glutamate is stable below 80 °C, there is no possibility of thermal degradation by long exposure, even if it decomposes in air. The changes in the number of plating fog particles with u.v. exposures of up to 5 min are

Table 2. Methods of surface preparation and its effect on plating fog

Item	Liquid honing		Postcuring	Plating fog particle	
	a[1]	*b*[2]	160 °C, 60 min	*Amount* 10^{-4} g cm^{-2}	*Size*[7]
a1 Baking	○	–	–	1.7	D
a2 Baking	○	–	○	∼0	A
b1 Baking	–	○	–	2.2	B
b2 Baking	–	○	○	3.3	A
b3 Cr^{6+}contamination[3]	–	○	–	16.6	B, C
b4 Metallic residue[4]	–	○	–	25.3	C
b5 Alkaline change[5]	–	○	–	1.8	C
a6 Time change[6]	○	–	–	∼0	E
b6 Time change[6]	–	○	–	∼0	B
c Scratching	–	–	–	∼0	B

[1] Pressure of 2 kg cm^{-2}, once.
[2] Pressure of 4 kg cm^{-2}, twice.
[3] Placing in 10% $K_2Cr_2O_7$ solution for 2 min.
[4] Roughening by liquid honing and only placing in water.
[5] Placing in 20% NaOH solution at 30 °C for 7 days.
[6] Standing at r.t. for 7 days.
[7] Order of size: A < B < C < D < E.

shown in Fig. 10. It appeared that variations in exposure had very little effect. There are differences in the plating fog produced at different roughness; the plating fog increases somewhat as the roughness increases. This result is consistent with the experiments described earlier (Section 3.2.2).

3.2.4. Effect of activation. The silver patterned substrate was activated by palladium chloride and fixed. The results with regard to plating fog are shown in Fig. 11. The fog is slight and constant without activation, whereas with activation it increases with exposure time by about a maximum of nine times, and reaches a very high level with severe roughness. This indicates that the silver catalyst on the unpatterned region is washed away sufficiently by the fixation process and is difficult to wash away by palladium substitution or it has greater catalytic effect, even if its size and quantity are kept small. The effect of roughness indicates that the photosensitive material sinks into the substrate with a highly roughened surface and, as a result, it is difficult to remove by washing or fixation.

3.2.5. Limiting concentration of heavy metal ions for electroless plating. The limiting concentrations of catalytic palladium, silver and iron on the substrate were examined in order to reveal the influence of heavy metal on the plating fog. Substrates coated with adhesive resin 3 (Table 1) were immersed in solutions of palladium chloride, disilver glutamate, and ferric chloride of various concentrations. After being dried for 10 min at 40 °C, they were placed in the plating solution. The minimum concentration at which the substrate is plated is defined as the limiting concentration of the metal. The metal ion concentration was evaluated on the assumption that a 5 μm thick layer was formed on the substrate from the preliminary experiments using disilver glutamate. The plating activity of each metal was compared in terms of limiting concentration. The relationship between the metal ion concentration and plating state is shown in Table 3 and Fig. 12. Silver does not provide catalysis for plating below a concentration of 3.6×10^{-5} mg cm^{-2}. The substrate darkens with exposure, but is only partially plated at 3.6×10^{-4} mg cm^{-2}. The whole area was plated at 3.6×10^{-3} mg cm^{-2}. It is, therefore, clear that silver is washed away by fixation below a concentration of 10^{-3} mg cm^{-2}. With palladium, plating was possible at concentrations above 6.4×10^{-5} mg cm^{-2}. With iron, no plating was observed even at high concentrations (2 w/v%). This shows that iron ions

Table 3. Lower limit of silver and palladium concentration for electroless deposition

*Silver atom concentration** /mg cm^{-2}	*State of deposition*
3.6×10^{-3}	whole area plated
3.6×10^{-4}	partially plated
3.6×10^{-5}	not plated, very little fog
3.6×10^{-8}	not plated, very little fog
3.6×10^{-11}	not plated, no fog
Blank	not plated, no fog

* 24∼26 °C.

*Palladium atom concentration** /mg cm^{-2}	*State of deposition*
6.4×10^{-5}	half area plated
1.2×10^{-5}	not plated, no fog
1.2×10^{-6}	not plated, no fog
1.2×10^{-7}	not plated, no fog

* 27 °C.

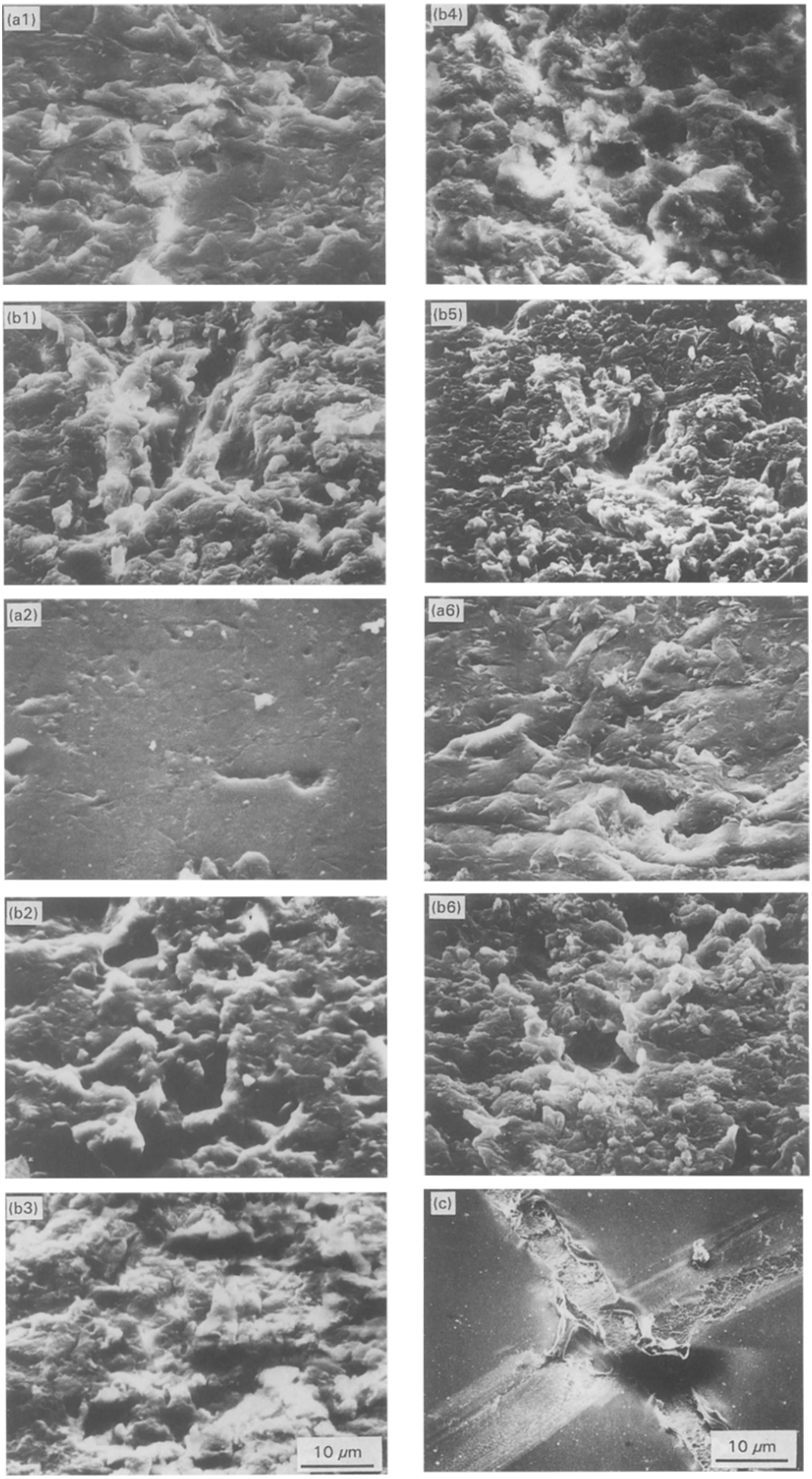

Fig. 7. Surface of substrates roughened by liquid honing and then treated by various methods. Legend as in Table 2.

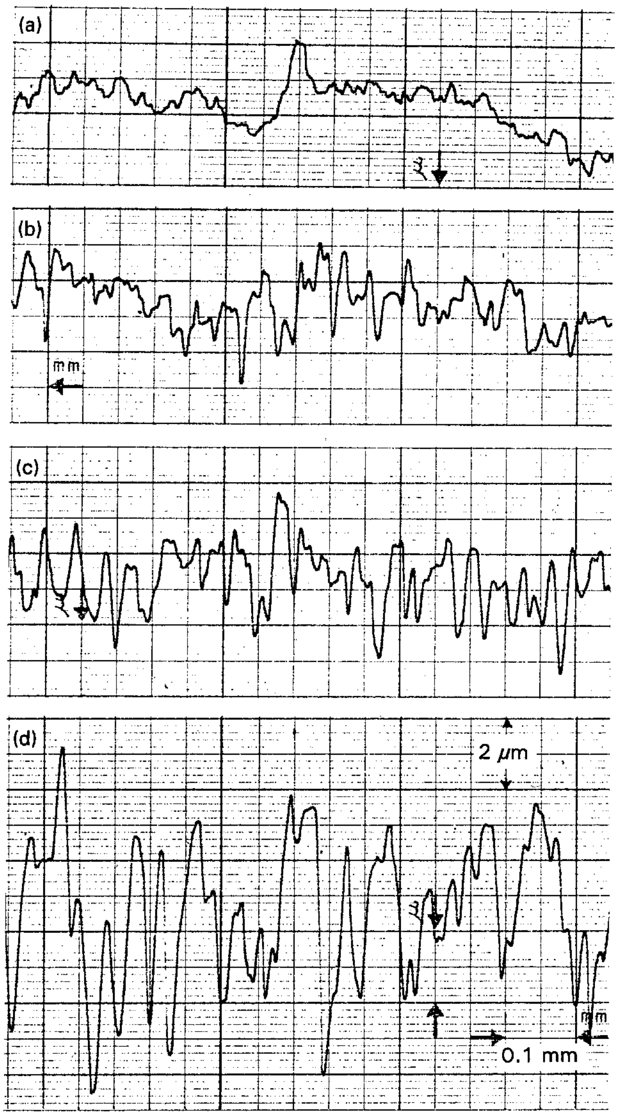

Fig. 8. Change in surface roughness with liquid honing roughening pressure, (a) original, (b) 1, (c) 2 and (d) 3 kg cm^{-2}.

never provide catalysis even taking into consideration the fact that ferric chloride is soluble in the plating solution.

From the above results, when the plating activity is compared in terms of the limiting concentration, which is reasonable because the atomic weights of silver and palladium are nearly the same, the activity of palladium is about ten times higher than silver.

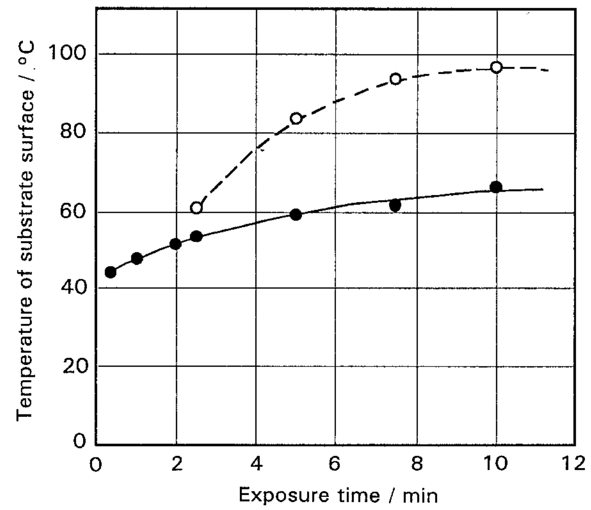

Fig. 9. Temperature increase in substrate exposed to u.v. light. Key: (○) in air, (●) in vacuum.

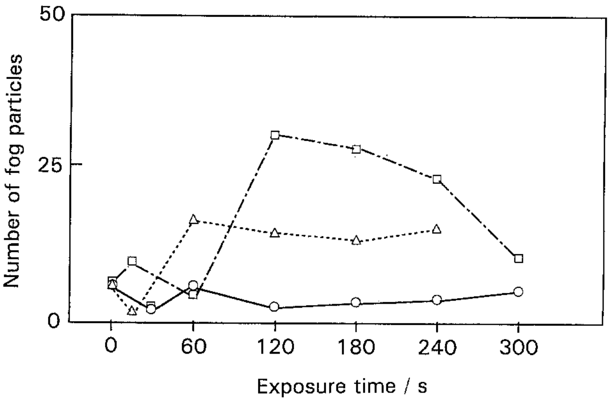

Fig. 10. Change in number of fog particles with exposure time. Roughening pressure: (○) 1, (△) 2 and (□) 3 kg cm^{-2}.

Activity ratio,

$$\frac{\mathrm{Pd}}{\mathrm{Ag}} = \frac{3.6 \times 10^{-4} \sim 3.4 \times 10^{-3}}{6.4 \times 10^{-5}} = 5.6 \sim 56$$

This result is consistent with the effect of activation by palladium on plating fog mentioned in Section 3.2.4.

4. Conclusion

Copper plating fog, formed on metallization of a silver pattern has been examined. The following remarks can now be made.

(i) Based on results showing that copper particles are deposited on a nonactive substrate, cuprous

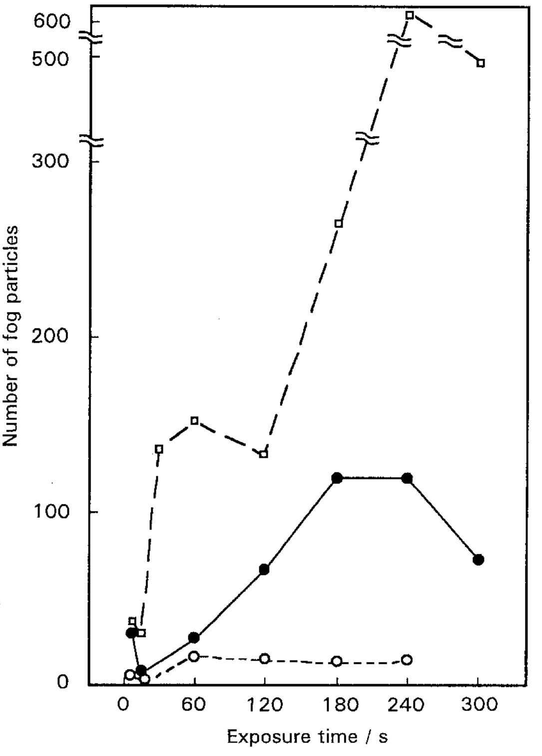

Fig. 11. Influence of palladium activation on plating fog. Roughening pressure: (○) 2 (activation free), (●) 2 and (□) 3 kg cm^{-2}.

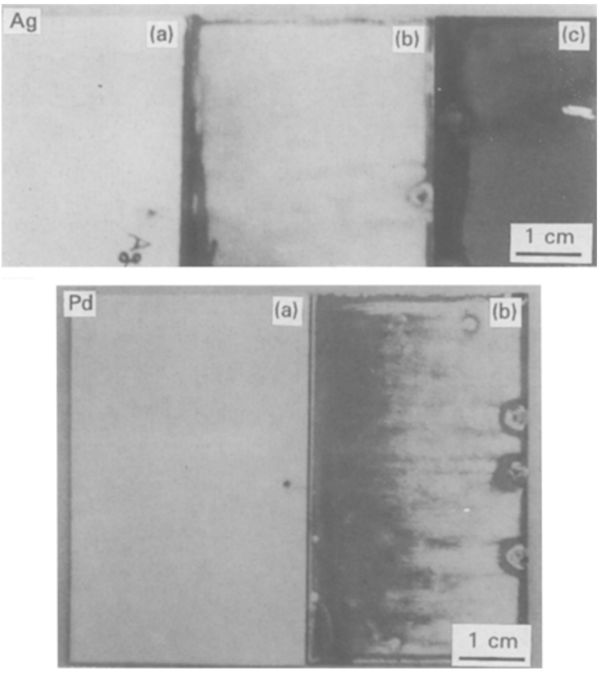

Fig. 12. Plating state with silver and palladium catalysts at various area concentrations. Darken area is plated. Ag: (a) 3.6×10^{-5}, (b) 3.6×10^{-4} and (c) $3.6 \times 10^{-3}\,\mathrm{mg\,cm^{-2}}$ Pd: (a) 1.2×10^{-5} and (b) $6.4 \times 10^{-5}\,\mathrm{mg\,cm^{-2}}$.

oxide particles of size 0.15–1 μm are continuously suspended in the plating solution and are sometimes deposited on the substrate, thus forming plating fog. The amount of plating fog, however, hardly depends on substrate roughness because the number of particles is small.

(ii) Chromium ion and iron metal on the substrate cause plating fog, even in catalyst pattern free system.

(iii) The normal plating deposition on the patterned part and the plating fog are found to start at the same time, because the size of the fog particles is almost the same as the thickness of the pattern.

(iv) Long exposure does not cause the thermal decomposition of photosensitive material, and gives no effect on the plating fog.

(v) The amount of plating fog depends on the surface roughness when the substrate is roughened with a liquid honing apparatus and a silver pattern is formed. This plating fog is attributed to iron from abrasive, silver from photosensitive material and palladium from activator. The degree of fog increase by palladium activation corresponds to the plating activity ratio of palladium and silver.

Acknowledgement

The authors thank A. Tanaka, H. Tabei and N. Asano for their encouragement and helpful discussions.

References

[1] H. Tabei, S. Nara and K. Matsuyama, *J. Electrochem. Soc.* **121** (1974) 67.
[2] A. Iwasawa, H. Tabei, S. Nara and K. Matsuyama, *Photogr. Sci. & Eng.* **20** (1976) 246.
[3] S. Sugihara, Kobunshi *Ronbunshu* **39** (1982) 115.
[4] S. Sugihara, A. Iwasawa, H. Tabel and J. Yamaki, *J. Chem. Soc. Japan* **1994** (1994) 992.
[5] J. Kubal, *Nature* **193** (1962) 1175.
[6] Y. Konishi, H. Hada and M. Tamura, *J. Chem. Soc. Japan* **86** (1965) 1132.
[7] M. Tamura, H. Hada and Y. Konishi, *ibid.* **86** (1965) 1135.
[8] H. Nozaki, T. Iida, *Hyomenn* **8** (1970) 807.
[9] Y. Konishi, H. Hada and M. Tamura, *J. Chem. Soc. Japan* **90** (1969) 992.
[10] Y. Konishi, H. Hada and M. Tamura, *ibid.* **92** (1971) 1091.
[11] Y. Konishi and H. Saijo, *Chem. Lett.* (1973) 137.
[12] Y.Yonezawa, Y. Konishi, H. Hada, K. Yamamoto and H. Ishida, *Thin Solid Films* **218** (1992) 109.
[13] S. Nara, H. Tabei, K. Onose and A. Iwasawa, *Electr. Commun. Lab. Tech. J.* **25** (1977) 617.
[14] A. Iwasawa, H. Tabei, S. Nara, S. Sugihara and K. Onose, *Rev. Electr. Commun. Lab. Jpn.* **25** (1977) 570.
[15] S. Sugihara, *J. Adhesion Society of Japan* **31** (1995) 12.
[16] K. Takahashi, K. Iraki, K. Kano, J. Takamura and T. Tsunoda, *Electrocomponent Sci. Technol.* **8** (1981) 99.