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Plating fog generation in the forming of printed circuits by the additive method

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Plating fog is often observed when metallizing a latent pattern by electroless copper plating. Metallic elements in the nuclei of plating fog particles are analysed using electron probe microanalysis (EPMA). Silver and iron are invariably found in the particles. The iron is driven into the board during the liquid honing process and reduces silver ions in the photosensitive material to silver metal which causes plating fog. Plating fog also arises from reduced copper particles or generated hydrogen gas bubbles when they are trapped on the unpatterned region. Mechanical stirring accompanied by substrate oscillation is an effective method of avoiding plating fog.

1. Introduction

Novel photosensitive materials [1–3], substrate resins [4–8] and fabrication processes [9, 10] have been studied with a view to developing printed circuit boards produced by the additive method. The copper plating fog which forms while the catalyst pattern is being metallized has also been studied. Other factors which have been examined include the effects of substrate roughness, plating solution composition, exposure time and activation by palladium [11]. This paper describes an investigation of the origin of plating fog and a way of suppressing it so that a method can be established for producing printed circuit board by the additive process.

2. Experimental details

As reported previously [11], the substrate was coated with an adhesive resin composed of nitrile rubber, phenolic resin, epoxy resin and zinc oxide filler. It was heated at 160 °C for 30 min to cure the resin. It was then roughened with a liquid honing apparatus using Alundum 200 abrasive and coated with photosensitive material (disilver glutamate). Then it was u.v. irradiated to form the catalyst pattern. Fixing with 20% aqueous acetic acid solution and 20% aqueous ammonia solution, took place for 20 min. Finally it was electrolessly plated with copper plating solution (Cuposit CP-70, Shipley Co.) for 15 h at 30 °C. The copper fog particles, which had been deposited on the substrate, were then peeled off and the metal elements on both peeled surfaces were analysed using electron probe microanalysis (EPMA).

3. Results and discussion

3.1. *Elemental analysis of fog particle nuclei*

Four kinds of sample were analysed by EPMA as shown in Fig. 1. Wavelength analysis and area analysis results are shown in Table 1 and Figs 2 and 3, respectively. Only copper was detected at the outer edges of the fog particles (3B and C), but silver, iron and zinc, in addition to copper, were detected in the nucleus (3A). The same elements were detected at the nucleus mark on the substrate (4A), but no iron was detected in the outer edge of the trace (4B).

The silver originates from the disilver glutamate and the zinc from the zinc oxide filler in the coating resin. The fact that iron and silver are invariably present in the particle nucleus indicates that they are responsible for the fog generation. We believe that the iron originates from the abrasive used in the liquid honing apparatus because the iron image is about 20 μm in diameter. It is clear that the iron and silver are localized in the nucleus of the fog particles as shown in Fig. 2. Copper and zinc are homogeneously distributed throughout the peeled surface. By contrast, the iron is localized in the nucleus of the particle on the substrate, whereas the copper and zinc are homogeneously distributed and no silver is detected (Fig. 3). These results suggest that iron is driven into the substrate, where some of it remains, but that the silver, which coexisted with the iron in the nucleus, migrates to the fog particles.

The above experiment indicates the strong likelihood that iron causes plating fog. To confirm this, we investigated whether there was any iron in the samples shown in Table 2. Iron was found in all the

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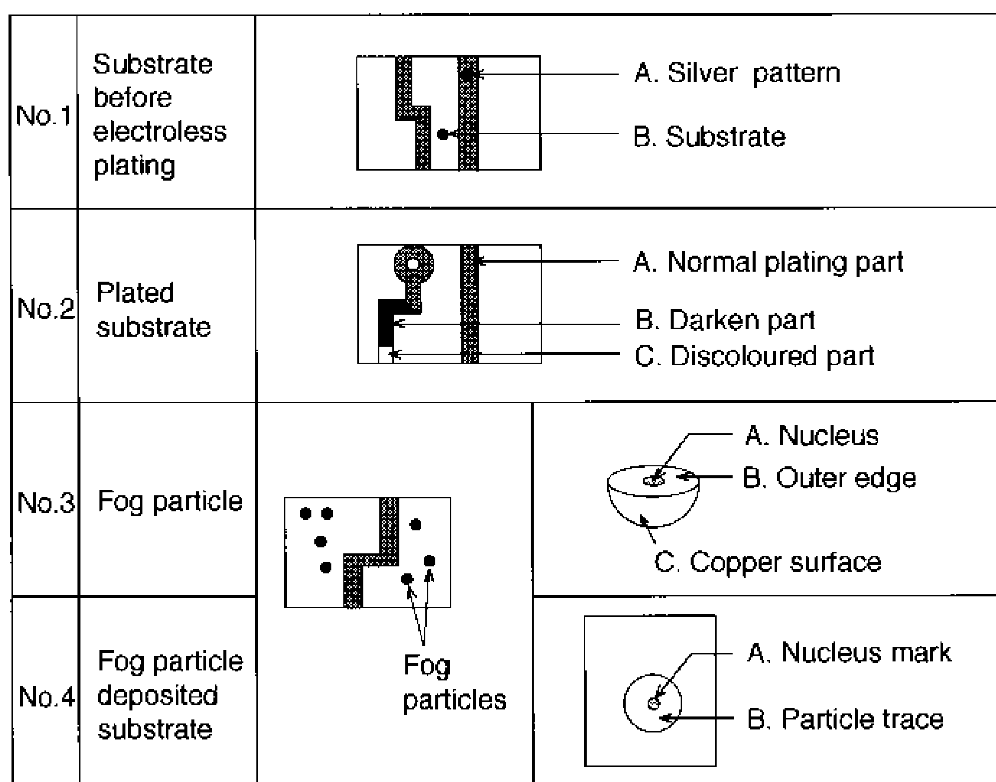

Fig. 1. Samples of plated pattern and copper fog for electron microanalysis.

samples, except for the blank test (no. 1). This result reveals that iron is introduced into the substrate from the liquid honing apparatus and causes plating fog.

The results suggest that the plating fog is either caused solely by the iron from the liquid honing apparatus or as the result of the iron reacting with the photosensitive material or the fixing agent. Ferrous ion acts as a plating catalyst whereas ferric ion does not; the substrate coated with ammonium ferrous sulfate is wholly plated but one coated with ammonium ferric sulfate is not plated. We therefore examined the influence of combinations of various iron compounds with photosensitive material on the plating fog. The results are presented in Table 3. We also investigated the reactions of iron compounds with the fixing solution and these results are shown in Table 4. The following facts are revealed: (i) iron, ferrous oxide and ferric oxide have low catalytic effect for plating but disilver glutamate enhances the catalysis of iron and causes plating fog; and (ii) plating fog forms when iron powder and photosensitive material coexist on the substrate. There are two possible causes of plating fog formation. One is that the iron powder driven into substrate forms ferrous ion through dissolution in acetic acid (fixing solution), and directly reduces the plating solution. The other is that iron powder on the substrate reduces the silver ion of the disilver glutamate, thus generating a plating catalyst, though iron powder does not markedly react with disilver glutamate. The fact that silver is invariably detected in the nuclei of the fog particles suggests the latter explanation.

3.2. *Plating fog generation along with reduction of plating solution*

Almost all copper ions are stabilized with a chelating agent such as EDTA in the plating solution. When

Table 1. Elements detected by EPMA wavelength analysis

Sample	*Measured part*	*Detected element*
1(A)	Silver pattern before plating	Ag, Zn, S, Fe
1(B)	Substrate surface before plating	Zn, Ag, Cl, S, Fe
2(A)	Normally plated pattern	Cu, Zn
2(B)	Darkened part of plated pattern	Cu, Ag, Zn, Cl, Hg, Pd
2(C)	Discoloured part of plated pattern	Cu, Zn, Ag
3(A)	Nucleus of fog particle	Cu, Ag, Fe, Zn
3(B)	Outer edge of fog particle	Cu
3(C)	Suface of fog particle	Cu
4(A)	Nucleus mark of substrate	Cu, Fe, Zn, Ag
4(B)	Particle trace of substrate	Zn, Ag, Cl, S, Cu

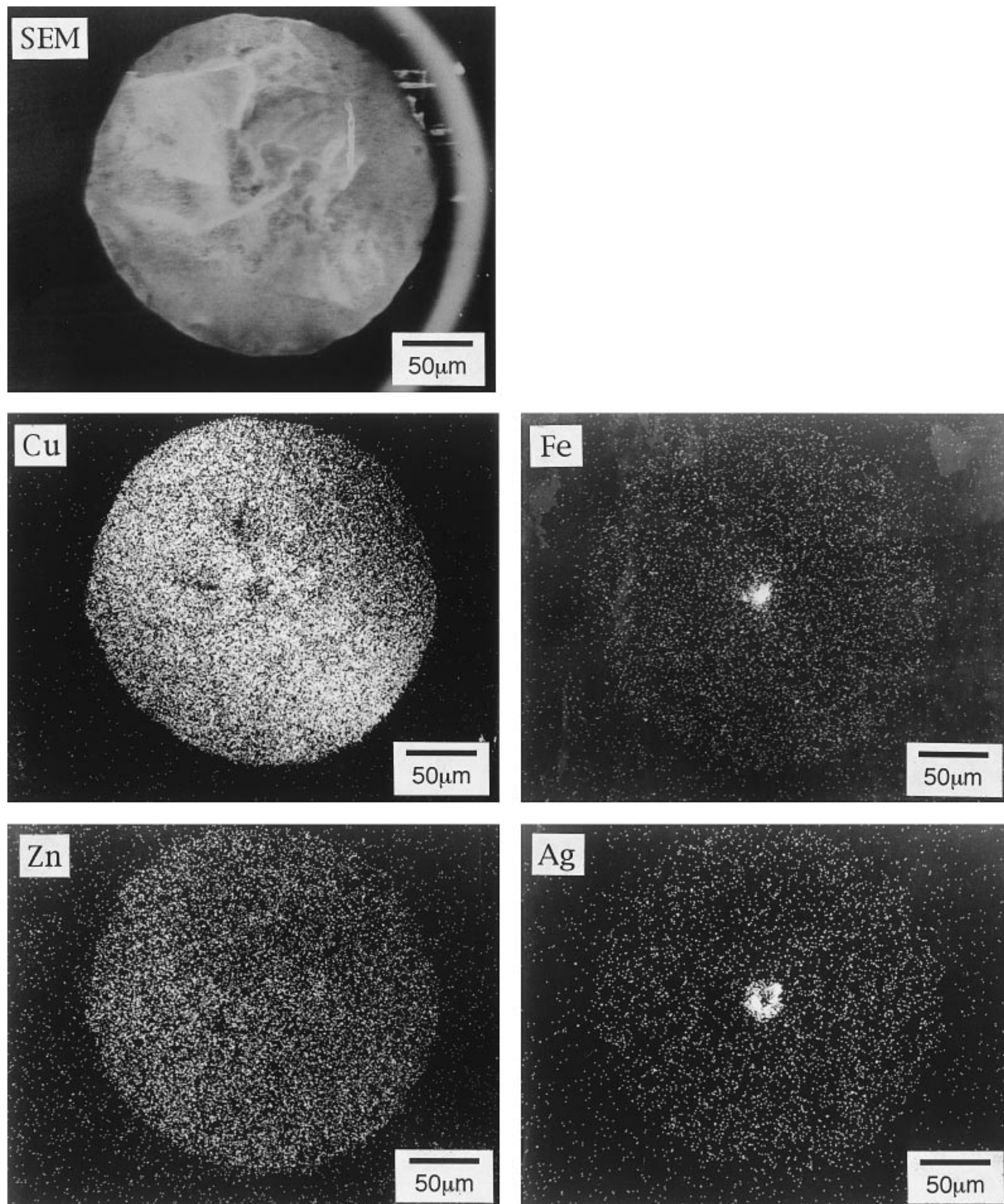

Fig. 2. EPMA image of peeled surface of copper fog particle.

the substrate is placed in this solution, it is negatively charged and a monolayer or bilayer of noncomplexed copper ions is formed on the pattern surface. This means that a reducible layer of copper ions is formed only on the metal pattern. The copper is selectively deposited on the pattern through the reduction of the noncomplexed copper ions by formaldehyde [12, 13].

The plating fog results from the fact that the copper particles generated on the pattern by the normal reductive reaction are not deposited on the

Table 2. Prepared sample and element detection

Sample	*Sample*	*Analysis results*
1	Substrate coated with ZnO containing resin	Iron not detected
2	Abrasive water containing Alundum in liquid honing apparatus	Ferrous ion detected*
3	Substrate roughened by almost iron-free abrasive	Very little iron detected
4	Nucleus of fog particle deposited on sample 3	Iron, silver and zinc detected in more than 2/3 of particles

* Ion testing paper was used.

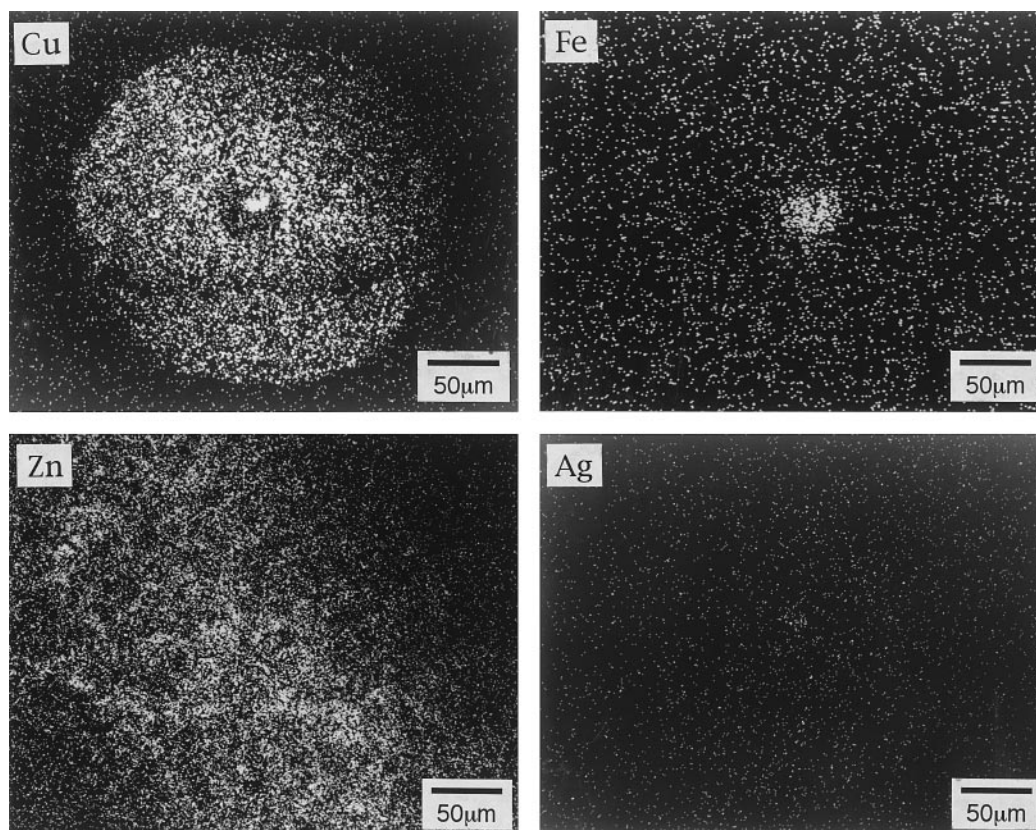

Fig. 3. EPMA image of substrate surface from which a fog particle was peeled.

pattern but become attached to the noncatalytic part near the pattern [14]. Figure 4 shows examples of this possibility. The sample substrate is prepared by etching a copper-laminated glass–epoxy board, so that the unpatterned region is not catalytic. When the substrate was placed in the plating solution, plating fog was observed near the pattern (a). Here, the solution flowed slowly upward, so the direction of the

Table 3. Plating catalysis of various iron compounds

Sample	*Plating fog results*
1. Powder (Fe, Fe_3O_4, Fe_2O_3) buried resin board	Fog partially formed. Their catalysis is low.
2. Sample 1 with photosensitive material coating and fixing treatment	Fog formed. Catalysis is $Fe > Fe_3O_4 \simeq Fe_2O_3$
3. Sample 1 with dilute photosensitive material coating and u.v. irradiation	Fog formed only by silver element. Little fog formed by other powder.

Table 4. Reaction between iron compounds and fixing solution

Powder	*Photosensitive or fixing solution*	*Reaction*
	NH_4OH(20%)	none
Fe	CH_3COOH(20%)	$Fe \rightarrow Fe^{2+}$
	Disilver glutamate*	none
	NH_4OH(20%)	none
Fe_2O_3	CH_3COOH(20%)	$Fe_2O_3 \rightarrow Fe^{3+}$, ($Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$)
	Disilver glutamate*	none
	NH_4OH(20%)	none
Fe_3O_4	CH_3COOH(20%)	$Fe_3O_4 \rightarrow Fe^{3+}$, ($Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$)
	Disilver glutamate*	none

* Solvents are ethanol (52 vol%) and aqueous ammonia (11 vol%)
Reaction in parenthesis occurs in electroless plating solution.

plating fog was the same as that of the solution flow. By contrast, no plating fog was generated when the solution was vigorously stirred as shown in (b). This indicates that the reattachment of copper particles is prevented by stirring. The copper particles deposited on the scratch, are attributed to the flow and reattachment of copper particles reduced on the pattern.

Figure 5 shows the state of the plating fog formed in a gently stirred solution. When the flow of the solution is perpendicular to the pattern, the fog particles are only deposited downstream of the pattern and the upstream pattern has a sharp edge. When the flow is parallel to the pattern, little plating fog forms on the unpatterned region. This indicates that the copper particles, which form on the pattern as a result of cupric ion reduction, flow in the downstream direction and are trapped on the unpatterned region where the plating fog is formed.

Particles such as copper metal, cuprous oxide and dust generally destabilize the plating solution [14–18]. The layer of noncomplexed copper ions also forms around hydrogen gas bubbles generated by the reduction of the cupric ion. This does not present a problem if the bubbles are immediately removed from the substrate. However, if they move along the substrate surface and are attached to the unpatterned part, the reduction of copper ions is initiated at the contact point and leads to plating fog. An example of this is shown in Fig. 6. The depression which can be seen at the centre of the fog particle is believed to be the impression of a hydrogen bubble attached to the substrate.

To suppress plating fog caused by the above mechanisms, we stirred the plating solution in various ways and examined the effects on plating and plating fog formation. The results are shown in Table 5. When the solution was not stirred (1), a large amount of plating fog was formed in the upstream region as seen in Fig. 4(a). The flow was due to the evolution of hydrogen. This phenomenon was not observed with mechanical stirring (2). Stirring is effective in preventing the formation of cuprous oxide and in suppressing the self decomposition of plating solution [18–21]. With air bubbling (3, 5), however, the deposited copper was partially oxidized and lost its catalytic activity as seen in Fig. 7(a) (darkened region). This was confirmed by X-ray analysis as copper was detected in the darkened region. It was preferable to oscillate the substrate in order to change the flow direction. The best pattern plating result was obtained with method (4) and is shown in Fig. 7(b).

4. Conclusion

Mechanisms of plating fog formation and ways in which to suppress it were examined. The following can be stated:

(i) Silver and iron were detected at the nucleus of all fog particles, but they were not detected at the outer edges. The iron was driven into the substrate from

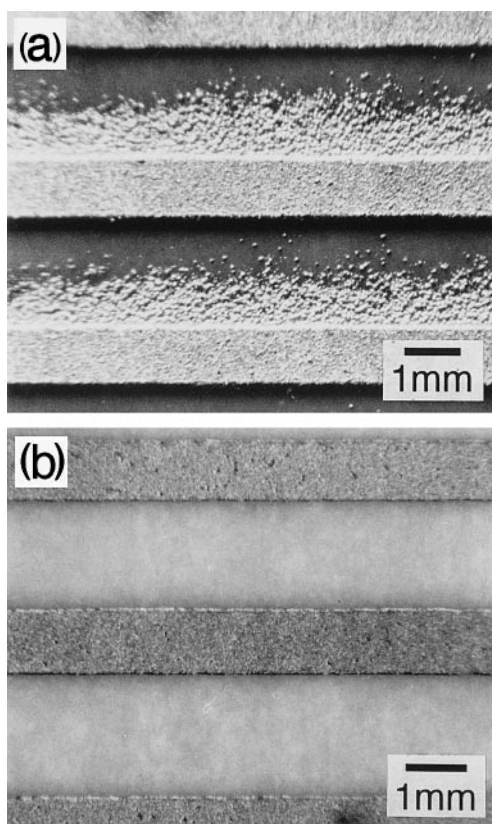

Fig. 4. Effect of mechanical stirring of plating solution on plating fog: (a) no stirring, (b) vigorous stirring.

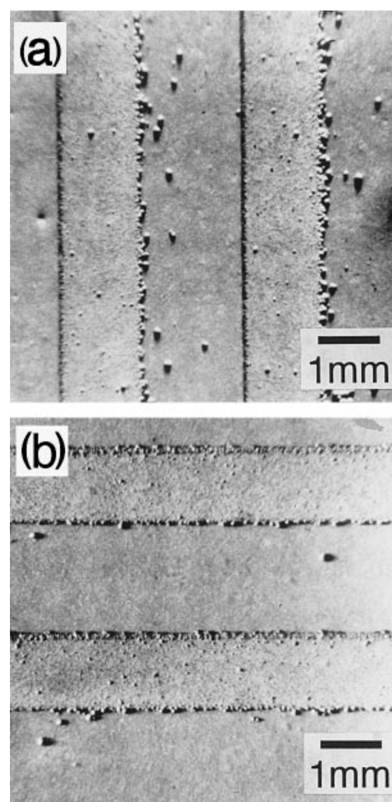

Fig. 5. Influence of flow direction of plating solution on fog formation: (a) perpendicular to pattern, (b) parallel to pattern.

Table 5. Effect of bath stirring on pattern plating and plating fog

No.	Stirring condition			Results*	
	Mechanical stirring	*Air bubbling*	*Oscillation of substrate*	*Pattern plating*	*Fog on unpatterned region*
1	–	–	–	◎	×
2	○	–	–	◎	◎
3	–	○	–	×	◎
4	○	–	○	◎	◎
5	○	○	○	×	◎

* ◎excellent, × poor, ○ adopted

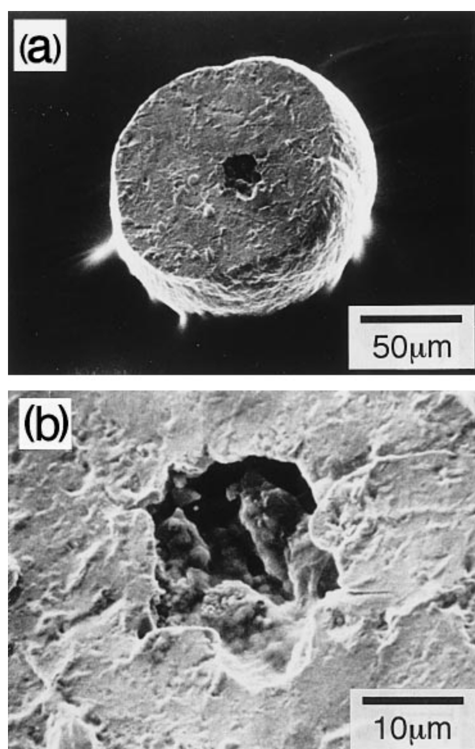

Fig. 6. Plating fog particle generated by a hydrogen bubble: (a) underside of particle, (b) centre of (a).

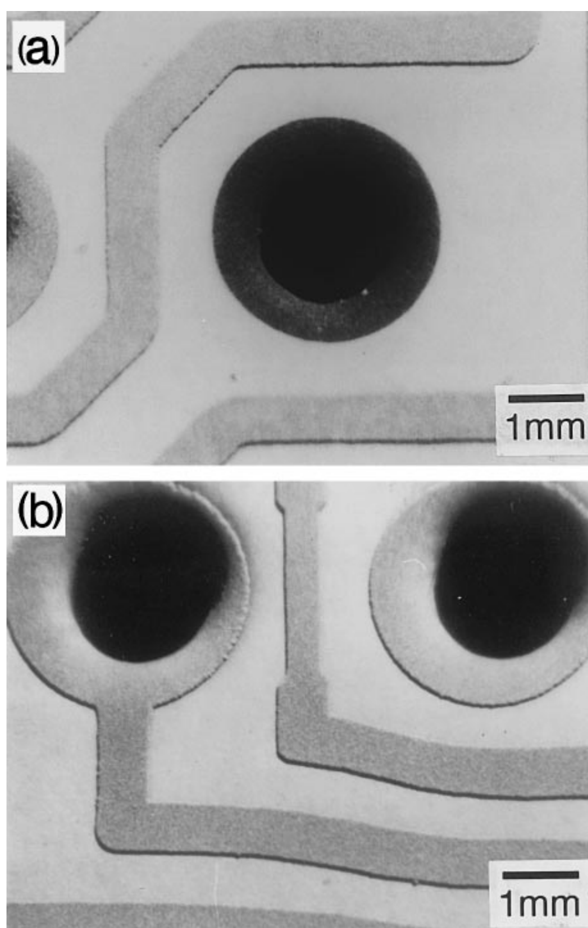

Fig. 7. Two states of electroless plating: (a) unplated part observed in air-bubbled plating solution, (b) printed circuit pattern obtained in mechanically stirred solution with substrate oscillation.

liquid honing apparatus and reduced the silver ion in the photosensitive material, thus causing plating fog.
(ii) Plating fog forms when copper particles generated on the pattern are detached from it by solution flow and are attached to the unpatterned part.
(iii) Plating fog also arises due to hydrogen gas bubbles generated by the reduction of cupric ions.
(iv) Mechanical stirring accompanied by substrate oscillation was effective in preventing the reattachment of copper particles and hydrogen gas bubbles, and led to the achievement of a fogless pattern.

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