Effects of the Surface State of Plastics on Adhesive Strength in Electroless Plating

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SYNOPSIS

Adhesive resins with high adhesive strength and high heat resistance have been studied in developing a novel iron-core printed circuit board with high mechanical strength and high heat radiation capability. A reticular pattern formed on the surface of an adhesive resin composed of nitrile rubber, phenolic resin, and epoxy resin. It caused blisters in the plating or reduced the heat resistance of the printed board. This pattern was formed as a result of phase separation of epoxy resin or phenolic resin from the nitrile rubber. Using a high-molecular-weight epoxy resin led to high adhesive strength and high heat resistance, without phase separation. The relationships between the composition of adhesive resins and their characteristics were discussed on the basis of the state of their surface after being roughened by chemical etching. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

We have developed functional printed circuit boards by forming circuit patterns additively on an insulated iron board by electroless plating.[1-4]

Resin composed of nitrile rubber and phenolic resin is commonly used for its high heat resistance and high peeling strength when its surface is roughened in a chromic acid–sulfuric acid etching solution.[5] In this paper, we discuss several problems encountered in forming circuit patterns on the substrate's resin coating and reveal, on the basis of their roughened states, that the poor miscibility of resin components causes blisters in the plating and plating inhomogeneities. These problems are overcome by developing a new composite resin that has excellent miscibility.

EXPERIMENTAL

Nitrile rubber, phenolic resin, and epoxy resin were dissolved separately in methyl ethyl ketone. These solutions were mixed to form a 10% resin solution. The resin components are shown in Tables I–III.

The resin was coated onto a commercial glass fiber–epoxy resin board by dipping the board into the resin solution. The board was cured for 30 min at 140–160°C, yielding a resin layer about 40 μm thick.

The sample board was immersed in an etching solution composed of 1.2 kg potassium dichromate, 11 kg sulfuric acid, and 5 kg water (chromic etchant) for 5 min at 35°C. The board was neutralized with aqueous sodium thiosulfate and dried.

An ethanol–ammonia solution of disilver glutamate (14 w/v %) was coated onto the roughened sample with a spinner. After the sample dried for 10 min at 40°C, it was activated by dipping it into a sodium hydroxide solution for 1 min.

The activated substrate was placed in an electroless plating solution, Copper Mix 328 (Shipley from Muromachi Chemical Industries, Tokyo, Japan), at 30°C for 20 min. A 0.4-μm-thick copper foil was deposited onto the substrate and it was then electroplated in copper sulfate plating solution to a copper thickness of 35 μm.

Adhesive strength was derived from the peeling strength when the copper foil was peeled at right angles to the substrate with an Instron peeling instrument. The sample was 1 cm wide and 10 cm long and the peeling speed was 50 mm/min.

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Journal of Applied Polymer Science, Vol. 59, 1751–1758 (1996)
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Table I Nitrile Rubber Examined

Symbol	Trade Name	Nitrile Content	Description
R_2	Nipol 1001	36–41%	Light yellow bulk

A 2.5-cm-square piece was cut from the plated sample and placed in fused solder 1 cm below the surface. The time required for the onset of changes such as plating swell and turbidity was measured. We judged the heat resistance to be good when no change was observed for 20 s.

RESULTS AND DISCUSSION

Small blisters often formed during electroless plating onto the substrate coated with the resin composed of nitrile rubber, phenolic resin, and epoxy resin. These blisters were observed at three stages: during electroless plating, electroplating, and heat resistance testing.

Two kinds of blisters were observed in the heat-resistance test. One was voids in the adhesive resin layer and the other was blisters between the resin and the plated copper foil. One of a few possible reasons for this is that the degree of resin curing is low and, as a result, vapors such as condensed water, ammonia, and formaldehyde are formed as the curing proceeds. Another is that excess silver oxide powder formed by the reduction of the photosensitive activator stays on the resin surface, which reduces the adhesion between the resin and the copper foil deposited onto it.

To reduce the number of voids in the resin layer, the precuring conditions were made more severe: the curing temperature was raised from 140°C to 150°C.

Because blisters were observed more frequently than voids, they were examined in more detail. The surface state of the roughened resin is an important factor that affects the various adhesion characteristics, peeling strength, blisters in the plating, and heat resistance in the process of forming the circuit by electroless plating. To form a suitable surface state, the resin surface must be physically and chemically roughened.

Blisters Between Adhesive and Plated Copper

Resins were prepared, as shown in Table IV, by mixing the components shown in Tables I–III. A reticular pattern was observed on the resin surface when the sample was roughened with chromic etchant [Fig. 1(a)]. In some cases the pattern remained unchanged after the sample was electrolessly plated [Fig. 1(b)], while in others the pattern was not plated [Fig. 1(c)]. One possible reason for this reticular pattern is related to the resin compositions: 10% epoxy resin, 60% phenolic resin, and 30% nitrile rubber (No. 1 in Table IV). This pattern was first observed during the resin coating stage and became clearer as etching proceeded. Therefore, the pattern seemed to originate from the low-molecular-weight epoxy resin or phenolic resin. The epoxy resin was eliminated from the adhesive resin to determine which one causes the pattern to form. Although the reticular pattern was reduced, as shown in Figure 2, it is slightly visible in resin No. 2, indicating that the epoxy resin was not the only cause.

The pattern became clearer with increased etching time, which became clearest at 10 min and faded

Table II Phenolic Resins Examined

Symbol	Trade Name	Type	Characteristic
P_1	PR 12687	Novolak	High tensile strength
P_2	PR 11078	Resol	Heat resistant
P_3	Plyophen 5023	Resol	Water resistant
P_4	PR 7031A	Novolak	Good adhesion
P_5	PR 50232	Resol	Heat resistant
P_6	PR 50217	Resol	Heat resistant
P_7	PR 50775	Novolak	Good adhesion
P_8	PR 12987	Novolak	Heat resistant

Table III Epoxy Resins Examined

Symbol	Trade Name	Type	Form	MW	mp (°C)	Epoxy Equiv.
E_1	Epikote 828	Bisphenol A	liquid	380	< rt	184–194
E_2	Epikote 1001	Bisphenol A	solid	900	64–74	450–500

after 20 min, as the pattern itself was etched. Figure 3 shows changes in the reticular part with increased etching time, as observed with an electron microscope. An uneven "snake scale" pattern forms along the reticular pattern boundary. It is gradually eroded by the chromic etchant until the surface "snake scale" membrane breaks and the inner adhesive resin appears. Figure 4 is a micrograph of the underside of the copper foil plated on the roughened resin which was etched for 10 min. The smooth reversal "match head" replica against the resin surface was formed along the pattern boundary. This part of the copper foil has a low-strength adhesion to the substrate, which will cause blisters to form during the process. This pattern is a result of either the lack of miscibility of the two components—phenolic resin and nitrile rubber—or of nitrile rubber additives.

The solubility parameters, which indicate miscibility, are 11.5 for phenolic resin and 9.4–9.5 for nitrile rubber. Though the miscibility is not high from the viewpoint of the solubility parameters, there are several types of phenolic resin. P_1 and P_4 in Table II have better miscibility with nitrile rubber than do P_2 and P_3. The miscibility with rubber is in the following order: $P_1 > P_4 > P_2 = P_3$.

It was deduced from this result that the low miscibility of resin No. 2, containing phenolic resin of resol type P_2, causes the reticular pattern to form and that the pattern boundary, which looks hard but is eroded by the etchant, is made of low-molecular-weight phenolic resin or its mixture with nitrile rubber additives.[6] Even though this part was coated with a photosensitive activator, the silver powder was washed out and, as a result, this part was not plated. Strong adhesion would not be expected even if the silver oxide remained on the resin, as when plating on pure phenolic resin.

Next, resins composed of phenolic resin of the Novolak type with high miscibility, P_1 or P_4, and nitrile rubber were prepared. Although a slight reticular pattern formed on their roughened surfaces, the miscibility was greatly improved and blisters in the plating due to the reticular pattern did not occur. Examples of the roughened surface are shown in Figure 5.

Relation Between Adhesive Strength and Roughened Surface State

The influence of the surface state on adhesive strength between the plated copper foil and the substrate was studied next. Even after resin No. 2 was roughened for 1 min, the adhesive strength remained

Table IV Resin Composition and Characteristics (No. 1)

No.	Composition (%)	Roughening Facility	Miscibility	Peeling Strength (kg/cm)	Heat Resistance
1	R_2 (30) P_2 (60) E_1 (10)	○	X	2.5	△
2	R_2 (33) P_2 (67)	○	△	1.5	△
3	R_2 (50) P_1 (50)	○	○	3.5	○
4	R_2 (50) P_4 (50)	△	○	3.8	○
5	R_2 (70) P_4 (30)	○	○	3.0	○
6	R_2 (50) P_5 (50)	○	△	3.5	△
7	R_2 (16) P_5 (84)	X	△	0	X
8	R_2 (50) P_6 (50)	○	X	1.2	X
9	R_2 (50) P_7 (50)	△	△	6.1	○
10	R_2 (33) P_7 (67)	X	△	—	—
11	R_2 (50) P_8 (50)	○	○	6.7	○

○: good; △: standard; X: poor.
R = nitrile rubber; P = phenolic resin; E = epoxy resin.

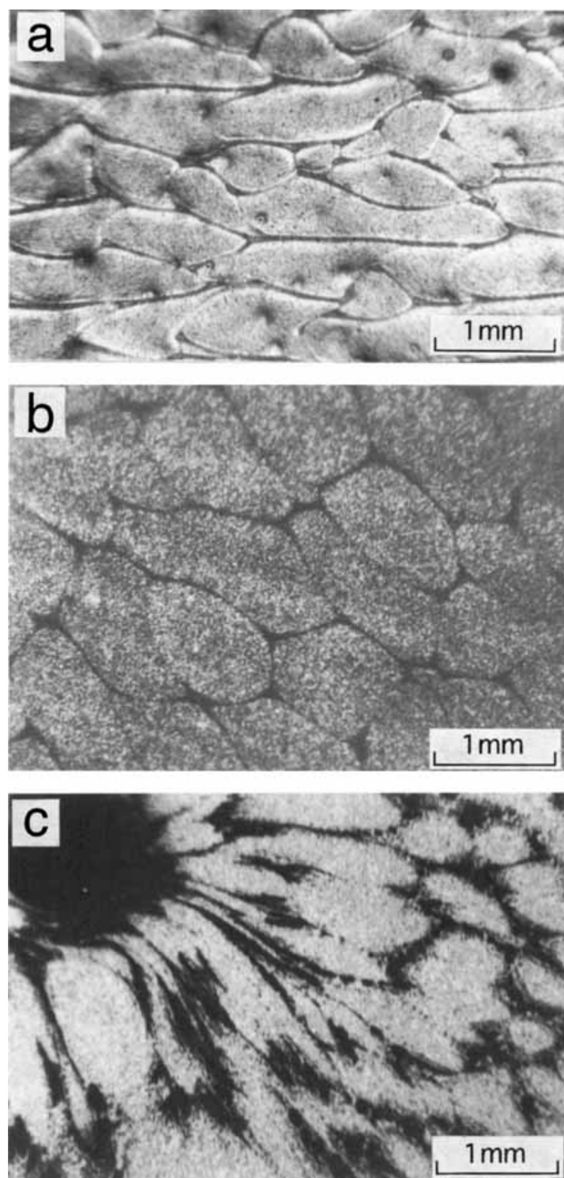

Figure 1 Reticular pattern of resin No. 1 consisting of three components (see Table I). (a) surface before chemical etching; (b) surface after electroless plating; (c) partially plated surface.

low and peeling was observed at the interface between the resin and copper foil. After 5 min of roughening, the adhesive strength increased and peeling was replaced by a cohesive break in the resin. We reported in a previous paper[5] that the plating metal was deposited on the resin surface, enveloping the ball-like phenolic resin, and a kind of mechanical anchoring effect caused the adhesion as reported by others.[7-14] In this study, however, the highly miscible adhesive resins No. 3 and No. 4 had the roughened surfaces that did not affect anchoring, as shown in Figure 5. A similar result was obtained for resin No. 2 after slight roughening (1 min). These results can only be explained by the chemical affinity of resin to copper foil.[15] It is considered that the adhesion in this system resulted from the inductive polarization of the nitrile group[10]; chelation of copper atoms to the double bond of the butadiene fraction; and electrostatic attraction by carboxyl, carbonyl, and hydroxyl groups[16] existing on the resin surface as a result of the chromic-acid treatment.

Figure 6 shows the change in peeling strength with increasing roughening time. Though every resin has a smooth surface after 1 min of roughening, high adhesion is achieved due to the inherent chemical affinity of the individual resins.

Resin Composition for High Adhesive Strength

Resins of the Nitrile Rubber–Phenolic Resin System

New resin compositions were studied to obtain a homogeneously roughened state by chemical etching,

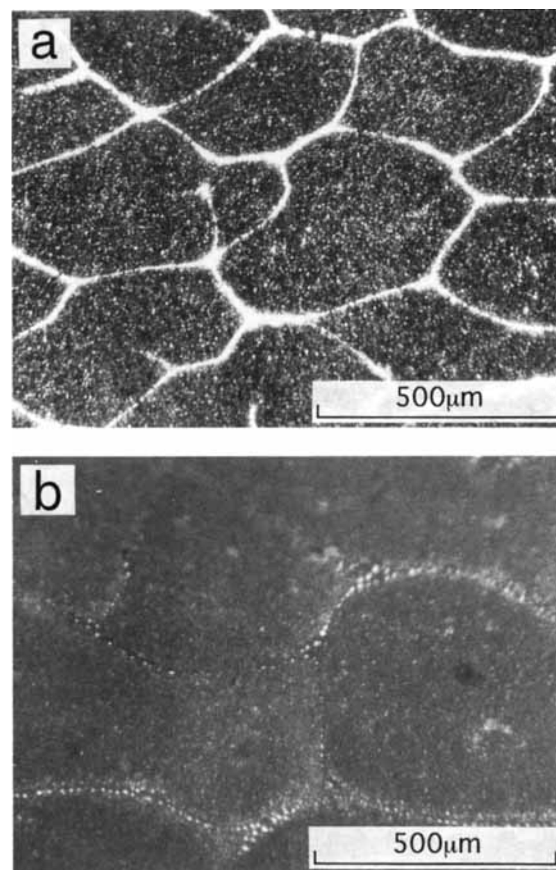

Figure 2 Pattern formed on the underside of copper foil plated on resins. Pattern (a) degrades to (b) when epoxy resin is removed.

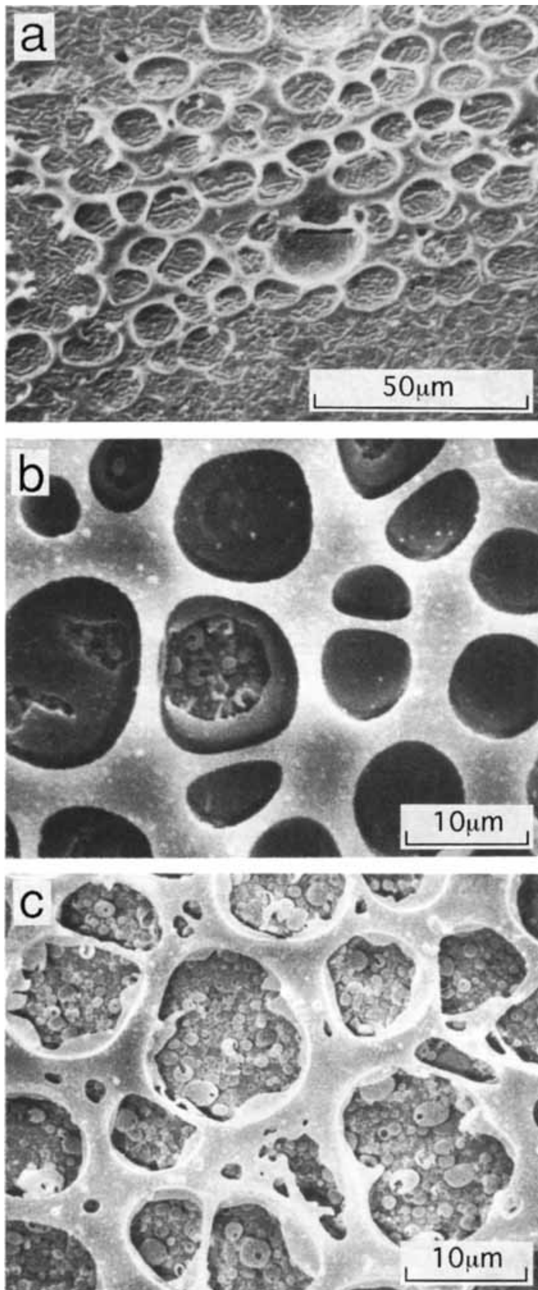

Figure 3 Change in pattern boundary of resin No. 2 due to chemical etching. Etching time: (a) 0 min; (b) 5 min; (c) 20 min.

leading to strong adhesion and high heat resistance. We examined the phenolic resins using Nipol 1001, the nitrile rubber which, so far, has provided the best adhesion. These resins have different melting points, gel points, and cured resin specifications.

We must take into consideration the miscibility of the phenolic resin with nitrile rubber to avoid blisters in the plating, as mentioned before. In general, the Novolak type has better miscibility but worse adhesion to metal than the Resol type, so we took the balance of these two characteristics into consideration. Typical characteristics of phenolic resins are outlined in Table II. Resins containing

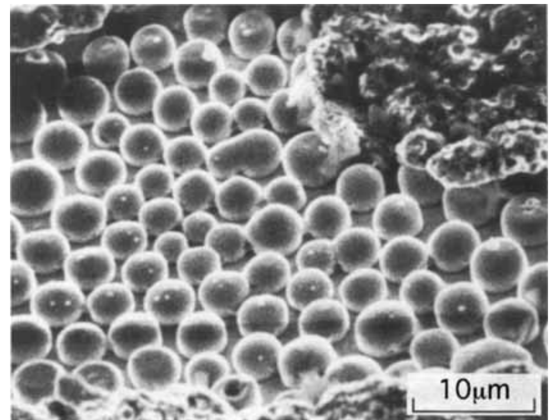

Figure 4 **Micrograph of** pattern boundary on copper foil peeled from resin No. 2.

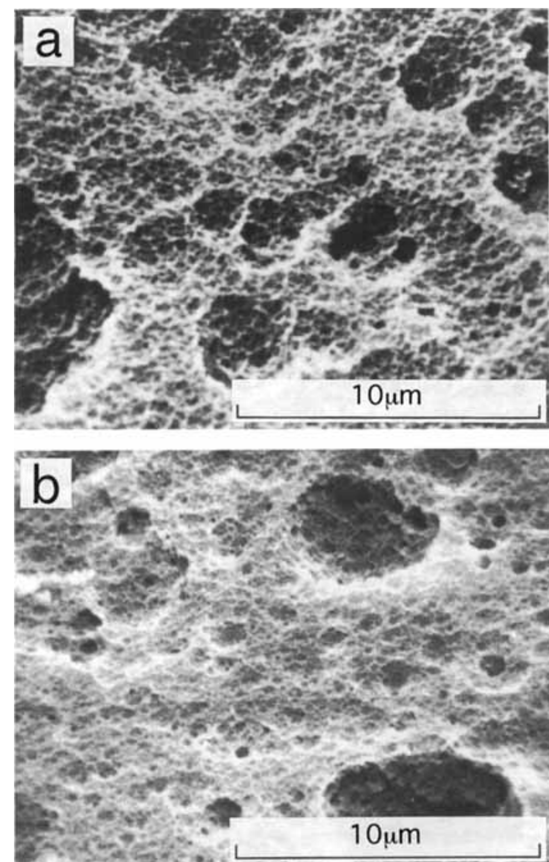

Figure 5 Micrographs of the roughened surface of resins (a) No. 3 and (b) No. 4 (see Table II). Etching time: 20 min.

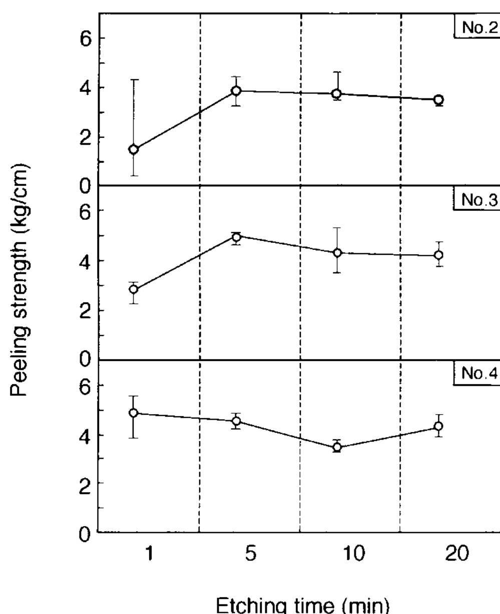

Figure 6 Change in peeling strength with etching time.

phenolic resin with a low gel point, P_4 and P_7 (resins No. 4 and No. 9 in Table IV), and those containing a high proportion of phenolic resin (No. 7 and No. 10) were etched after being swollen in acetone to facilitate roughening.

The miscibility estimated from the roughened state was excellent in phenolic resin P_4, poor in P_6, and average in P_5 and P_7. A slight reticular pattern was observed for the last phenolic group. Heat resistance was fair, as shown in Table IV, except for resin No. 8 with its low miscibility, and No. 7 and No. 10 which were not roughened. This indicates that heat resistance is closely related to adhesive strength. Resins No. 9 and No. 11 had high peel strength over 6.0 kg/cm and high heat resistance. Phenolic resin P_8 is almost Novolak-type, in which a small amount of Resol-type phenolic resin is added to resin P_7 for adhesion improvement.

In summary, the ease of roughening and the roughened state of the cured resin, as well as the adhesive strength and heat resistance, varied according to the kind of phenolic resin used and the resin composition. Regarding the phenolic resins examined in this study: as the melting point decreased, the curing speed increased; the resins became more difficult to roughen; and the heat resistance decreased, although the adhesive strength was high. Regarding the composition: when the nitrile rubber content increased to over 50%, the resin became soft, thus decreasing the chemical resistance and allowing blisters or reticular patterns to form. In contrast, when the relative content of phenolic resin increased, the chemical resistance also increased; but the adhesive became difficult to roughen, thus decreasing the adhesive strength. This caused a reduction in heat resistance because of its correlation to adhesive strength.

As seen in Table IV, resins No. 9 and No. 11 have good miscibility and were plated successfully. They have high adhesive strength and heat resistance, as mentioned previously. The roughened state of resin No. 9, a finely roughened surface similar to that of nitrile rubber, is shown in Figure 7.

Epoxy resin, an alternative to phenolic resin, was examined as a thermosetting resin for blending with nitrile rubber to increase the adhesive strength and heat resistance, and to lighten the color of the resin. Although the reticular pattern was not observed, the resin was corroded by the alkaline plating solution, causing fine blisters to form on the surface. Furthermore, the adhesive strength was relatively low because the epoxy resin does not react with nitrile rubber; it cures by itself, forming stonelike clusters. Consequently, phenolic resin is essential and cannot be replaced by epoxy resin.

Resins of the Nitrile Rubber–Phenolic Resin–Epoxy Resin System

This system was examined initially, but the miscibility of the epoxy resin was low and a reticular pattern formed. It was examined again using the high-molecular-weight epoxy resin listed in Table III, with which better miscibility was expected. In this system, the epoxy resin will be cured by the Resol-type phenolic resin itself and by hexamethylene tetramine included in a Novolak-type phenolic resin.

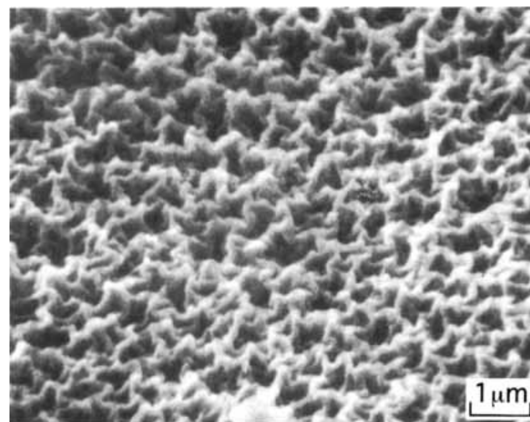

Figure 7 Micrograph of resin No. 9 roughened by chemical etching for 3 min.

Table V Resin Composition and Characteristics (No. 2)

No.	Composition (%)	Roughening Facility	Peeling Strength (kg/cm)	Heat Resistance	
12	R_2 (40) P_7 (20) E_1 (40)	△	3.7	X[a]	X[b]
13	R_2 (40) P_7 (30) E_2 (30)	△	4.1	X	⊙
14	R_2 (40) P_7 (40) E_2 (20)	X	2.2	X	—
15	R_2 (40) P_7 (50) E_2 (10)	X	2.7	X	X
16	R_2 (50) P_7 (20) E_2 (30)	○	4.8	⊙	⊙
17	R_2 (60) P_7 (20) E_2 (20)	○	4.0	⊙	⊙

⊙: excellent; ○: good; △: standard; X: poor.
R = nitrile rubber; P = phenolic resin; E = epoxy resin.
[a] Before postbaking.
[b] After postbaking.

Phenolic resin P_7 in Table IV was used in this study for its high adhesive strength. The resin composition is shown in Table V.

Resins with a rubber content of less than 40% and with a phenolic resin content of more than 40% were impossible to roughen (No. 14 and No. 15). The total content of the thermosetting resin was kept constant, but it became easier to roughen as the phenolic resin content was decreased (No. 17). Among those resins which could be roughened, No. 16 and No. 17 had both high adhesion strength and high heat resistance. Resin No. 13 includes more phenolic resin than No. 16 and No. 17, and it forms a slightly more prominent reticular pattern as a result; however, it has good adhesion and heat resistance. Figure 8 shows the roughened surface of resin No. 17, which has excellent adhesive strength and heat resistance. It resembles the roughened surface of resin No. 9 (Fig. 7), but this resin has better heat resistance even before postbaking because it contains epoxy resin.

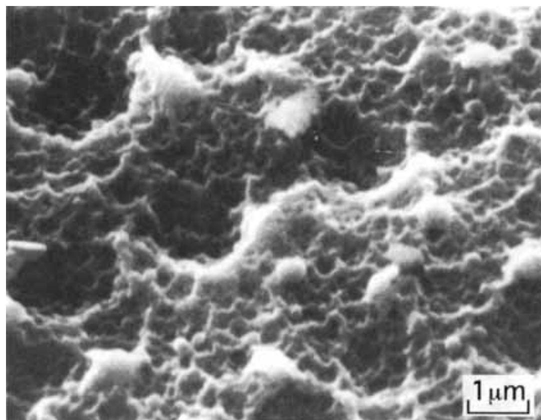

Figure 8 Micrograph of resin No. 17 roughened by chemical etching.

Electric Properties of Resins

A printed circuit board fabricated by this process using resins No. 3 and No. 9 was tested for electrolytic corrosion. The space between the lines is 1 mm. Electrolytic corrosion was evaluated by the insulation resistance after applying a 200-V dc for 96 h at 90% relative humidity (RH). The insulation resistance was measured 1 min after applying a 500-V dc. Figure 9 shows the change in insulation resistance after electrolytic corrosion. As seen in the figure, resistance decreased by one order of magnitude after the corrosion test but still maintained more than 10^8 Ω. It recovered to its original level when the printed board was left at 20°C at 60% RH. The withstood voltage was more than 750 V dc for 1 min.

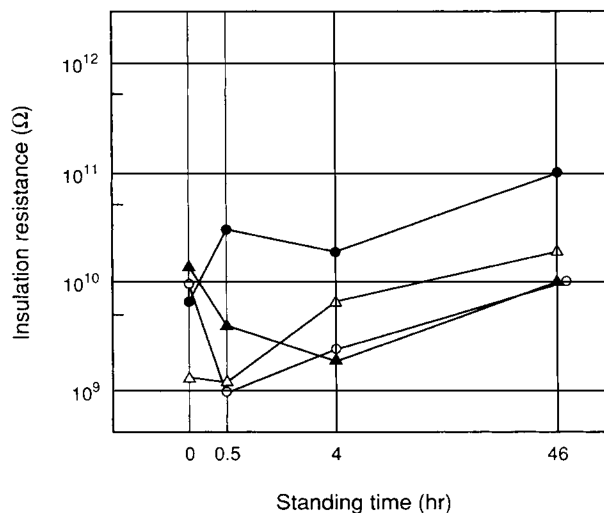

Figure 9 Change in insulation resistance of printed circuit boards with standing time after electrolytic corrosion. Boards made by A Co. (○); B Co. (●); C Co. (△); D Co. (▲).

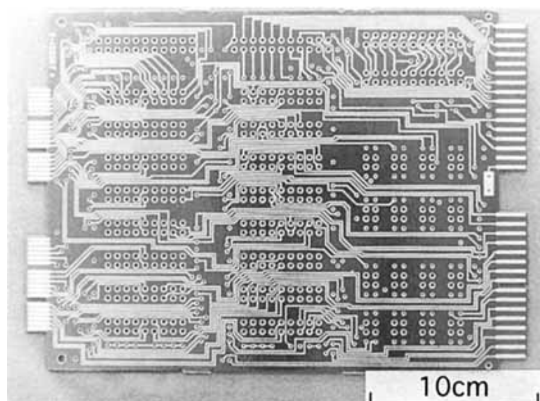

Figure 10 Sample of iron-core printed circuit board using resin No. 3.

Figure 10 shows the iron-core printed circuit board fabricated with resin No. 3.

CONCLUSION

A reticular pattern was observed on the resin surface when various resins composed of nitrile rubber, phenolic resin, and epoxy resin were coated onto a plate and roughened in a chromic acid–sulfuric acid solution. The pattern was caused by the isolation of the epoxy resin owing to its low miscibility. Resins without epoxy resin still formed such patterns when they were composed of Resol-type phenolic resin having low miscibility with nitrile rubber. When such resin-coated boards were electrolessly plated, the reticular pattern remained a stripe, causing the plating to swell during solder heating treatment. This problem was solved by using phenolic resin having high miscibility with nitrile rubber, resulting in a fine, homogeneously roughened surface. The resin prepared by adding a higher-molecular-weight epoxy resin to this composite showed no phase separation, which resulted in excellent heat resistance and high adhesive strength. This revealed the fact that adhesive strength and heat resistance are closely related to the roughened surface state. An iron-core printed circuit board, fabricated with one of the resins examined in this study, exhibited excellent characteristics and high reliability.

The authors thank Kentaro Matsuyama of Hitachi Chemicals Co.; Hisao Tabei of NTT Advance Technology Co.; and Akinobu Tanaka, Akira Iwasawa, Katsuhide Onose, and Noboru Asano of NTT Laboratories for their encouragement and helpful discussions.

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Received March 21, 1995
Accepted May 25, 1995