Kuk Chol Ri, 2025, 13:6
ISSN (Online): 2348-4098
ISSN (Print): 2395-4752

International Journal of Science,
Engineering and Technology
An Open Access Journal

Direct electroplating of printed curcuit board through-hole by deposition of carbon black

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Abstract - Direct electrodeposition of PCB perforated holes by conductive carbon deposition is a promising process to reduce the cost of the process and reduce the environmental burden significantly compared to conventional electroless plating processes. For the deposition of conductive carbon into the perforated wall, an aqueous solution of polyamidoamine-epichlorohydrin copolymer was used as modifier. By measuring the streaming potential, when the pH of the modifier solution was 9.5, the deformed through-hole wall reached the isoelectric point and the amount of adsorbent of the modifier was maximized. Dynamic light scattering spectroscopy (DLS) was used to elucidate the effect of ultrasonic dispersion time, surfactant (SDS) and binder (Acrysol TT-935) on the dispersion of carbon black. The adhesion strength of the coating was investigated by conducting a soldered pin tensile test on the coated tubular holes using the conductive carbon deposition method. The results confirmed that the adhesion strength of the perforated coating coated using cationic copolymer modified and carbon dispersions was within the industrial standard.

Keywords - Carbon Black, Printed Circuit Boards, Hole electroplating, Conductivity, and bonding Strength.

I. INTRODUCTION

For the miniaturization and high-performance of devices, PCBs are mainly used with double-sided and multilayer substrates rather than with external ones. Both sides and multilayer substrates connect wires through holes. Therefore, after substrate drilling, a conductive layer must be formed in the hole for wire connection of the substrate [1-3]. There are two main ways to form a conductive layer inside the hole [4]. The first is the chemical copper plating method that has been widely used so far. The method of electroless plating is the method of obtaining a copper layer and electroplating it to form a coating in a hole. The second method is a direct electrocopper plating method that has been widely used recently. This method can overcome the disadvantages of the chemical copper plating method such as low adhesion, long process, high material consumption, short plating liquor life, environmental pollution, etc. This resulted in the development of direct plating techniques.

Due to the above drawbacks of electroless chemical plating, in 1963, IBM company D.A. Rhodovsky proposed the direct metallization theory, which has gained great popularity and has recently been rapidly developed and widely applied [5,6]. Through long-term research and practice, three types of direct metallization technologies have been developed. Direct metallization technology has matured and has been successfully industrialized for many industrial applications. The direct metallization technique is classified according to its metallization mechanism into three types [7-11] :

- Palladium and palladium compounds as conducting layers
- Graphite/carbon as the conductive layer of graphite/carbon black hole technology
- Organic conducting polymers such as polythiophene, polypyrrolidone, polyaniline, etc. as conducting layers.

The three direct metallization processes have advantages and disadvantages, respectively, and palladium limits its wide range of applications because of its direct use of high-cost metals. Graphite/carbon black direct plating has the lowest cost and short processing. However, after the micro-etching process, the black hole is prone to form a wedge-shaped hole [12].

The hole-plating process by conductive carbon deposition has the drawback of simplicity, reliability, low processing cost, but poor adhesion of the coating, as shown in the table. The studies of hole-coating by conductive carbon deposition have been reported in several literatures [13,14]. The deposition of conductive carbon takes place in two steps. In the first stage of the process, the water-soluble polymer is adsorbed onto the substrate, and in the second stage, the substrate is immersed in the dispersion to provide the matrix-induced deposition of the dispersed particles. Typical examples of water-soluble polymers are proteins (gelatin), polyacrylamide, carboxymethyl cellulose-Na salt, polyacrylate, polyvinyl alcohol, etc. In several patents [15−17], it was shown that a relatively low charge density (<0.5 meq g−1) cationic polyelectrolyte is a better coagulation initiator than the corresponding electrolyte of higher charge density.

In this work, a polyamidoamine-epichlorohydrin copolymer aqueous solution was used as a charge modifier on the pore walls to enhance the adhesion strength of the PCB through-hole coating by conductive carbon deposition. In addition, the carbon black dispersion with high dispersion stability by ultrasonic dispersion was prepared, and using it, the tube bore was directly coated and the pin tensile test was carried out.

II. EXPERIMENTAL

Materials

Polyamidoamine-epichlorohydrin copolymer (CALLAWAY 6818) (20 wt%) was supplied by Exxon Chemical Co., Ltd. Carbon black particles (SRB−8A) were purchased from NIPPON STEEL Carbon Co., Ltd. (Aichi, Japan). Polyethylene glycol p− (1,1,3,3, −tetramethylbutyl) −phenyl ether (Triton X−100 ; MW = 646.85) was purchased from Thermo Fisher Scientific (Geel, Belgium). Sodium dodecyl sulfate (SDS ; MW = 288.38) was purchased from Wako Pure Chemical Industries Ltd. Hexadecyltrimethylammonium bromide (CTAB MW = 364.45) was purchased from Tokyo Chemical Industries Ltd. (TCI ; Tokyo, Japan). Acrysol TT-935 (concentration 30 wt%) was purchased from Rome and Hass. NaOH, H2SO4 and H2O2 were of analytical grade.

Preparation of an aqueous solution of polyamidoamine-epichlorohydrin copolymer

According to the reports [15-17], 400 g of deionized water was added to a 1 L beaker, and 2 g of hexadecyltrimethylammonium bromide (CTAB) was added and stirred in a magnetic stirrer until complete dissolution. Then, 50 g of 20 wt% polyamidoamine-epichlorohydrin copolymer (CALLAWAY 6818) aqueous solution was added to the above solution and the mixture was stirred for about 10 min. Then, a certain amount of monoethanolamine was added as a pH regulator. Then, deionized water was added to adjust the volume of the solution to 1 L.

The streaming potential was measured to consider the PCB surface modification of the polyamidoamine-epichlorohydrin copolymer aqueous solution. The streaming potential was measured using an electrokinetic analyzer (Paar K.G., Graze, Austria). Using the Smoluchowski equation, the electrokinetic potential ξcan be calculated from the streaming potential [13]:

$$\xi = \mathrm{U}\eta\kappa/\Delta\mathrm{P}\varepsilon_0\varepsilon_r$$

where η is the viscosity of the liquid flowing through the channel, is the dielectric constant, κ is the conductivity, and ΔP is the pressure difference. To calculate the zeta potential with higher accuracy, the streaming potential was measured as a function of the pressure difference delta P (delta P is the pressure difference between the chamber inlet and outlet) in the range of 20−200 mbar. The channel shape value L/Q (cross-section − length) was estimated according to Fairbrother and Mastin [33] using the conductivity value of the solution. The streaming potential was measured as a function of pH of 0.001 mol L−1 KCl solution. The surface conductivity was not considered.

Preparation of carbon black dispersions

20 g of sodium dodecyl sulfate (SDS) was added to distilled water, dissolved completely, and then Acrysol TT-935 (concentration 30 wt%) was added to 10 g and dissolved completely. To the above

solution, 20 g of carbon black (SRB−8A) was added and treated in an ultrasonic bath (47 kHz, 130 W) for a certain time. After that, the particle size in the carbon black dispersion was analyzed by DLS analysis to characterize the dispersibility.

A DLS particle analyzer (DLS8000, Otsuka Electronics Co., Ltd., Kyoto, Japan) was used as a 45 mW He−Ne laser operating at a wavelength of 633 nm. Measurements were carried out using a quartz cell at a scattering angle of 90° and a measurement temperature of 25.0±0.1°C. Three replicates were used to calculate the mean. From the apparent diffusion coefficient obtained by DLS, the hydrodynamic particle size of the carbon black particles was determined using the Stokes-Einstein relation (Eq. (2)).

$$\mathrm{d} = \frac{\mathrm{k_B}T}{3m\eta D}$$

where kB is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the solvent, and dl is the calculated hydrodynamic diameter of the micelle.

Preparation of PCB

Fire retarding FR4-type printed circuit boards (PCBs) laminates were purchased from JUC Inc. (Japan). PCBs consist of glass fiber reinforced bromo-epoxy resin and copper foil. The thickness of PCB sample was 1.5 mm and was double sided. The thermal analysis of FR4− printed circuit board showed that it consisted of 40% epoxy resin and 60% glass fiber [1]. The dimensions of the PCB specimens were 4.5×2.5 cm2. The diameter and depth of the perforation were 0.3 and 1.8 mm, respectively. For the tests, 40 through holes were formed by the mechanical drilling on each sample. Before hole metallization, the samples were immersed in an ultrasonic bath (47Hz, 130W)to remove the smears formed on the hole wall during mechanical drilling.

Perforated coating of PCB by carbon black particle deposition on polymer modified surfaces

Figure 1 shows the through-hole plating process of PCB. First, the PCB samples prepared at room temperature were immersed in cationic wire polymer solution for 5 min, and then the samples were removed and washed with distilled water. The surface modified samples were immersed in a stirred immersion bath containing carbon black dispersions and the carbon black was deposited on the PCB. Printed circuit board samples with carbon black particles deposited were dried at 80 °C. The dried samples were immersed in a microetchant to remove the carbon black particles attached to the copper plate surface, put in an acidic copper plating bath and plated for about 15 min.

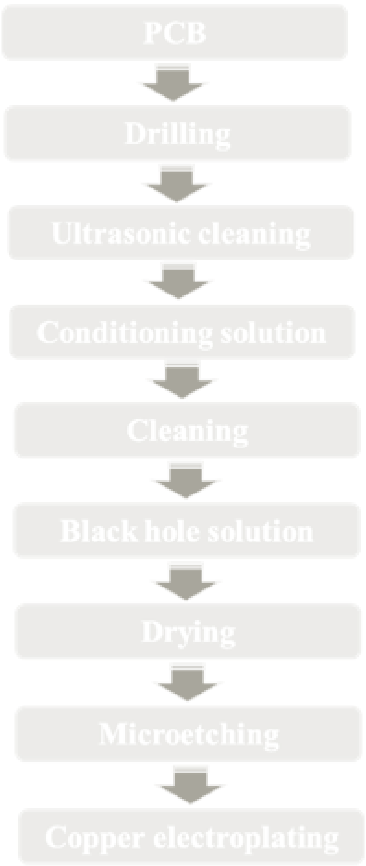

Fig. 1. Flow chart of the through-hole plating process on PCB.

The hole-plating experiments were carried out for 3600 s at a current density of 2A dm-2. The temperature of the plating bath was maintained at 298 K. The plating solution was stirred by air blowing. The plating solution was basically composed of 0.3 mol·L-1 CuSO4·5H2O, 1.8 mol·L-1 H2SO4, 2 mol·L-1 Cl- and added a small amount of bis- (sodium sulfopropyl) -disulfide (SPS) as a catalyst and polyethylene glycol (PEG 8000) as an inhibitor.

Determination of the deposition amount of carbon black by conductivity measurements

The surface conductivity of the carbon black coatings deposited on the polymer modified PCB surface was measured and the deposition amount was determined indirectly. The surface conductivity was determined using the van der Pau method, assuming uniform thickness of the deposited carbon black coatings [5]. It was assumed that the conductivity of the coating is proportional to the deposition amount of the carbon black.

Tensile tests of PCB perforated coatings

Tensile tests were carried out to evaluate the adhesion strength of copper layers plated on the carbon black layer of PCB perforated holes. First, a penetration hole of 10 mm diameter was drilled into a 1.5 mm thick PCB with a size of 40 mm × 40 mm, and the carbon black coating was deposited on it and then electroplated according to 2.5. Then, a 10 mm diameter copper pin was placed inside the hole and soldered. The soldered PCB specimens were fixed to a tensile tester and the pin tensile tests were carried out to measure the tensile strength when the copper layer electrodeposited on the hole wall was peeled out. For comparison, PCB samples obtained by conventional electrochemical copper plating were compared.

III. RESULTS AND DISCUSSION

Effect of pH on polymer modified PCB surface charge

The presence of the polyamidoamine-epichlorohydrin copolymer in the electrolyte solution changed the surface charge of PCB, hence the isoelectric point (IEP) value shifted from 5.4 to 9.5 (Fig. 2). The higher the amount of polymer adsorbed on the PCB surface, the higher the IEP shows positive charge.

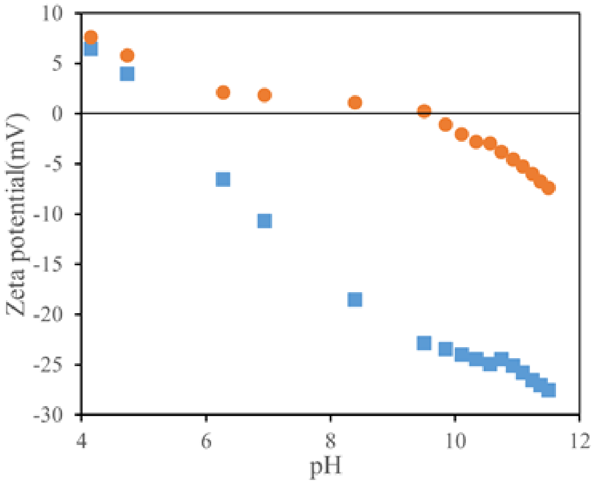

Fig. 2. PCB surface charge measured by pH in 0.001 mol·L-1 KCl solution. (–■–) the surface charge of the unmodified PCB, (–●–) the surface charge of the unmodified PCB.

The FR-4 type PCB consists of a bromo-epoxy resin and a glass fiber, from which the charge on the PCB surface changes with the pH of the solution in contact. In [1,2], it was shown that the surface of the polymer-unmodified FR-4 type PCB is negatively charged at pH above 5.4. Thus, the polymer-unmodified PCB surface is negatively charged, which prevents the carbon particles from agglomerating on the PCB surface due to electrostatic repulsion, as the carbon black particles are negatively charged when the PCB is immersed in the carbon black dispersion. By polymer modification, the PCB surface is positively charged and the carbon black particles can aggregate on its surface.

Dispersion of carbon black dispersions

To evaluate the dispersibility of the carbon black, the particle size of the carbon black particles was measured by dynamic light scattering analysis (Fig. 2) after adding 20 and 10 g of dodecylbenzene sulfonic acid (SDS) and Acrysol TT-935 as anionic surfactants to deionized water, followed by 20 g of carbon black and then 1 L of the carbon black particles as a function of the ultrasonic irradiation time.

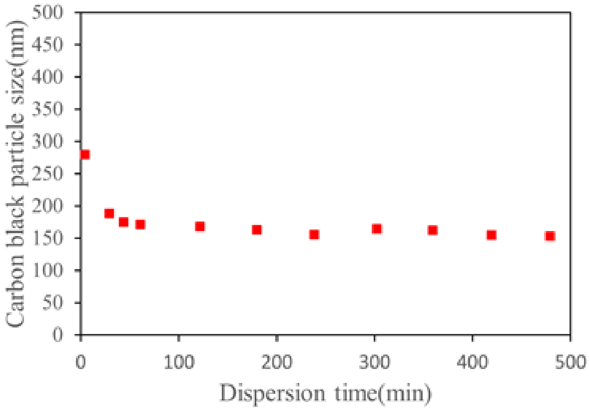

Fig. 3. Carbon Black particle size with time of ultrasonic (47 kHa, 130 W) dispersion. (To 1 L of the dispersion, 10 g of carbon black, 0.5 g of SDS, and 10 g of Acrysol TT-935 were added and dispersed at room temperature.)

As shown in Fig. 3, the carbon black particle size decreased by about 180 nm within 60 min when dispersed at 47 kHz and 130 W of ultrasound energy, and remained stable thereafter.

Then, the particle size changes of the carbon black were observed when the addition of SDS was changed to 0.1, 0.5, 1.0, 1.5, and 2.0 g L-1 without changing the addition of carbon black and Acrysol TT-935 for 60 min of ultrasonic dispersion (Fig. 4).

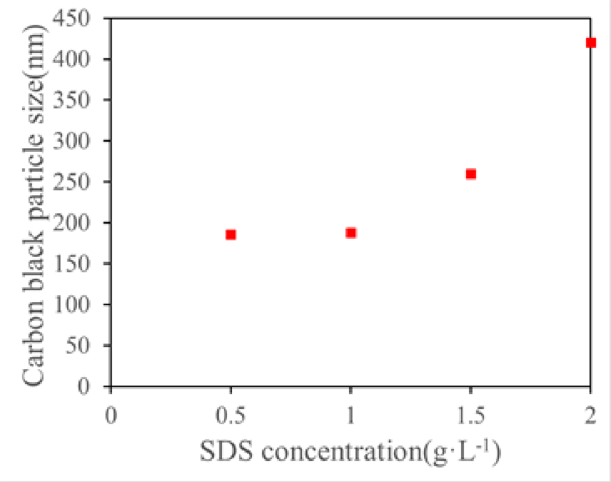

Fig. 4. Carbon Black particle size as a function of SDS concentration. (To 1 L of the dispersion, 10 g of carbon black, 0.5 g of SDS, and 10 g of Acrysol TT-935 were added and dispersed by ultrasound (47 kHa, 130 W) for 60 min at room temperature.)

As shown in Fig. 4, at SDS concentration of 0.1 g L-1, the carbon black particles were almost dispersed and the particle size increased rapidly beyond 1.5 g L-1.

This indicates that particle aggregation occurs when the SDS concentration is above 1.5 g L−1.

To investigate the effect of the addition of Acrysol TT-935 as a binder on the deposition of carbon black particles onto polymer modified PCB surfaces, the size of carbon black particles was observed by fixing the SDS dosage of 0.5 g L-1 and varying the addition of Acrysol TT-935 to 5, 10, 15, and 20 g L-1 (Fig. 5).

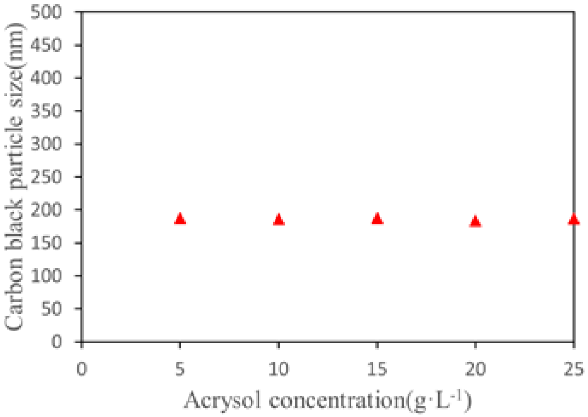

Fig. 5. Carbon Black particle size as a function of Acrysol TT-935 concentration. (1L of the dispersion was dispersed by ultrasonic (47 kHa, 130 W) for 60 min at room temperature, with 10 g of carbon black, 0.5 g of SDS.)

As shown in Fig. 5, the carbon black particle size did not change significantly with increasing Acrylsol concentration. This indicates that the acrylic emulsion in the dispersion of the carbon black does not contribute to the reduction of the size of the carbon black. However, the stability of the dispersion was higher when acrylic emulsion was added. When the acrylic emulsion was added to 10 g L −1, the dispersion remained stable for more than 1 year.

Determination of the deposition amount of carbon black on polymer modified PCB surfaces

The conductivity of the carbon coatings deposited on the polymer modified PCB surface has a crucial influence on the quality of the hole coating. Therefore, according to the procedure in Fig. 1, the polymer modified PCB was immersed in a carbon black dispersion to deposit a carbon black coating on the penetration hole of PCB, which was dried and then the conductivity was determined. The results of the measurements with varying concentrations of carbon black and binder in the carbon black dispersion are shown in Figs. 5 and 6. First, the conductivity of the carbon film deposited on the pore wall was measured by varying the concentration of carbon black at 10, 20, 30, 40 and 50 g L −1 (Fig. 6).

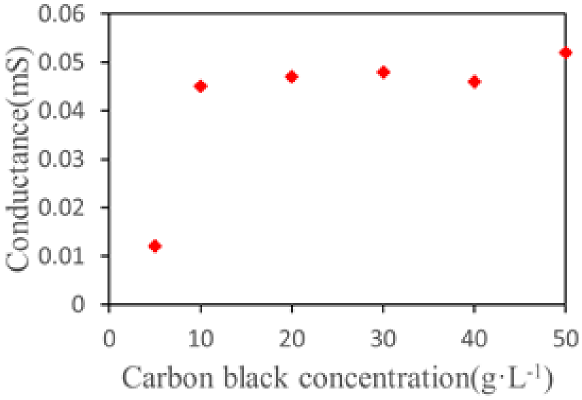

Fig. 6. Conductivity of the coating with concentration of Acrysol TT-935. (Polymer modified solutions and treatment conditions; 2 g L-1 of CTAB, 50 g·L-1 of CALLAWAY 6818, pH = 9.5, room temperature for 5 min: Carbon Black dispersions and treatment conditions; SDS 20 g · L-1, Acrysol TT-935 10 g L-1, room temperature for 5 min.)

As shown in Fig. 6, there is no significant change in surface conductivity over the concentration of 10 g·L−1 in the dispersion. This indicates that the amount of the black deposited on the pore wall does not increase even with increasing carbon black concentration at concentrations above 10 g L −1. On the other hand, when the amount of Black in the dispersion increased to more than 50 g·L−1, a non-uniform film was observed on the pore walls. This indicates that the particles agglomerated when the amount of Black is too high, and larger particles were deposited. The heterogeneous carbon black coating has a negative effect on the hole plating.

Next, the conductivity of the lifewall was measured by changing the concentration of Acrysol TT-935 in the carbon black dispersion to 5, 10, 15, 20 and 25 g L-1 (Fig. 7). As shown in the figure, the conductivity of the carbon black coatings increased with increasing binder concentration, which indicates that the deposition amount of the carbon black increased with binder concentration. The binder concentration did not change significantly above 20 g L −1. As shown in Fig. 5, the stability of the dispersion was good at 20 g L -1 of binder concentration.

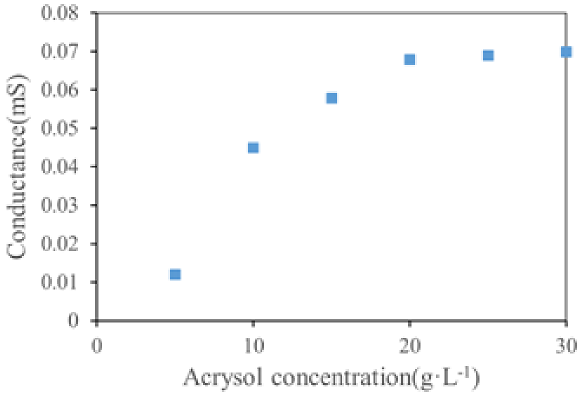

Fig. 7. Conductivity of the coating with concentration of Acrysol TT-935. (Polymer modified solutions and treatment conditions; 2 g·L-1 CTAB, 50 g·L-1 CALLAWAY 6818, pH = 9.5, 5 min at room temperature: Carbon black dispersions and treatment conditions; 10 g·L-1 carbon black, 20 g·L-1 SDS, and 5 min at room temperature.)

Pin tensile strength of the perforated coating

In Fig. 8, the results of pin tensile tests soldered to the through-hole copper-plated by carbon black deposition and electroless plating was shown. As shown in the figure, the maximum tensile force of the penetration hole plated by electroless plating was 13.4 N, and the maximum tensile force of the copper layer directly plated on the carbon black coating was 10.7 N. The tensile strength of copper layer plated on carbon black coating was slightly lower than that of electroless plated coating. However, tensile strength values above 10 N are acceptable for industrial applications.

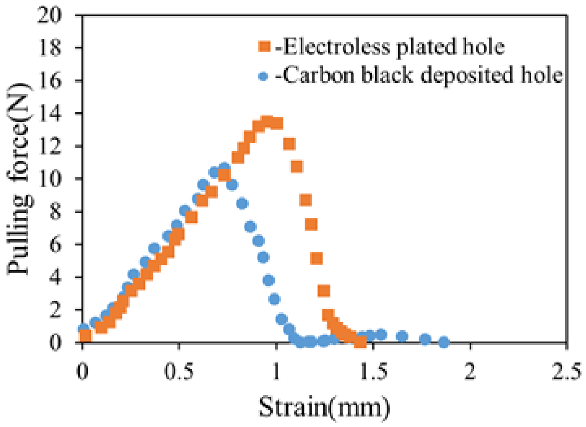

Fig. 8. Results of pin-pull test of copper plated by electroless and carbon black deposition.

IV. CONCLUSION

Through-hole coating of PCB was carried out by direct plating by carbon black deposition method and the effect of several factors on coating was investigated. By electrokinetic analysis, it was found that the isoelectric point on the PCB surface modified with the polyamidoamine-epichlorohydrin copolymer shifted from 5.4 to 9.5. Hence, pH of the cationic copolymer solution was adjusted to 9.5. Sodium dodecylbenzene sulfonate (SDS) as an anionic surfactant and sonication time were found to affect the dispersion of the carbon black. Acrysol TT-935, which was used as a binder of carbon black, did not affect the dispersion of carbon black. On the other hand, the concentration of carbon black and binder affected the conductivity of the carbon film deposited on the cationic copolymer modified through-hole surface. As a result, the carbon dispersions were the most suitable for the conductivity of the deposited coatings when 10 g L -1, SDS 0.5 g L -1 and Acrysol TT-935 were 20 g L -1. The maximum tensile force of the through-hole coating directly electrodeposited using the above cationic polymer solution and the carbon black dispersion is about 10 N, which is applicable to the PCB hole-plating process.

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