Formation of Precise Electrically-Conductive Pattern Using Metal Colloid I-J Ink

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Abstract

A precise electrically conductive pattern was formed by the I-J technique using ink composed of a highly concentrated colloidal dispersion of nano-meter sized silver particles. The silver particles were encapsulated with a block copolymer to form protected metal colloid. The I-J Ink was formulated using the metal colloid to form an extremely precise electrically-conductive pattern. The ink exhibited a low viscosity at high colloid concentrations and maintained excellent spontaneous dispersing characteristics that prevented I-J head clogging or "Kogation". A printed line width as small as 20 μm was obtained using a commercial thermal I-J printer. The silver colloid particles were strongly combined with each other to form a dense particle layer on a substrate surface. The electrical resistivity of less than 10^{-3} Ω was obtained through baking at a temperature of lower than 300°C. The resistivity was reduced to the order of 10^{-5} Ω when a metal plating copper layer was formed on the metal colloid layer surface. The practical issues in applying the technique to the preparation of a precise print circuit pattern are discussed.

Introduction

Many trials have been made to form electrically-conductive patterns by depositing a metal powder on the insulating substrate surface.

For the pattern formation with electrophotographic toner, metal particles such as silver, copper and nickel were used as a main component. The dry toner as well as the liquid toner was used in this technique.

Metal pastes that are a mixture of heat curable resin and fine metal particles dispersed in the organic solvent were used for patterning through a silk stencil. The silk stencil printing technique has been improving over years and a line width of less than 50 μm was obtained recently.

This report relates to the formation of a precise electrically-conductive pattern with I-J ink containing silver colloid particles. The colloid particles that have a nano-meter particle size provide I-J ink with excellent stability. Ink preparation, printing characteristics, evaluation of the printed layer, in particular concerning the electrical properties, and other issues relevant to the application of the ink to the preparation of the precise print circuit pattern are discussed below.

Experimental

Preparation of Silver Colloid

Figure 1 shows a process for preparing the silver colloid particles. The colloid particles were deposited slowly from an aqueous solution of silver nitrate with the addition of a tertiary amine that acts as a strong reducing agent. Obtained colloid particles were encapsulated with a hydrophilic block copolymer as shown in fig. 2 to prepare protected silver colloid particles. Nitrate ions and excess amine molecules remaining in the aqueous solution were removed through ultrafiltration and electrodialysis to obtain a hydrosol that contains the silver colloid particles.

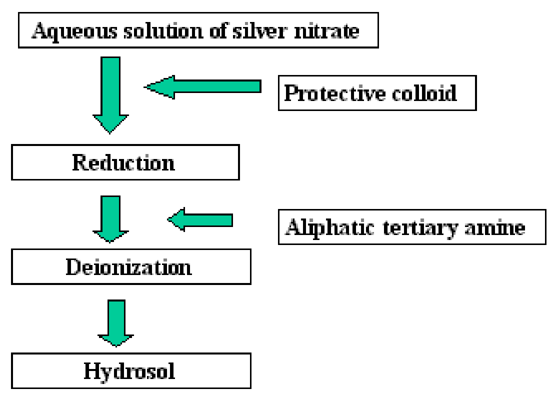

Figure 1. Preparation process for silver colloid

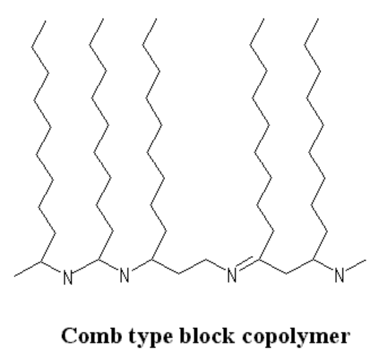

Figure 2. Structual formula of polymer for protected colloid

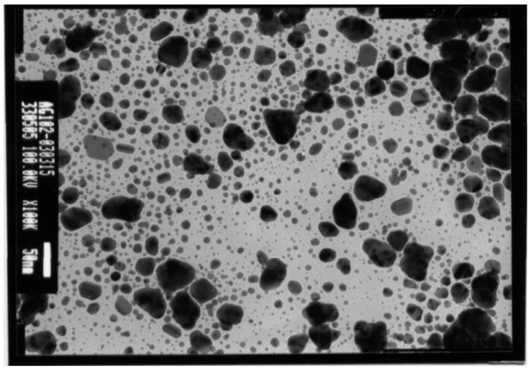

Figure 3. TEM photograph of silver colloid

It was possible to remove the water in the hydrosol completely. Then the xerosol that contained 95wt% silver particles and 5wt% protective polymer was obtained. Thus a xerosol can re-dispersed spontaneously in water to yield hydrosol.

Figure 3 shows a TEM photograph of the silver colloid. The particle size distribution measured with a light scattering particle analyzer is shown in Figure 4. The particles showed sharp size distribution, yielding an average particle size of about 20 nm.

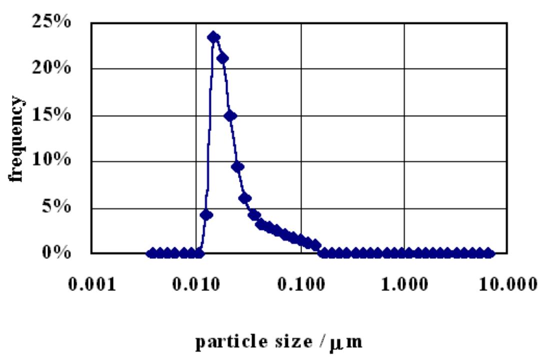

Figure 4. particle distribution of silver colloid

Preparation of the Silver Colloid I-J Ink

Surfactants such as a colloid dispersion stabilizing agent, viscosity and flowability adjusting agent, and surface tension adjusting agent were added to the hydrosol containing 30wt% silver colloid particles to provide the silver colloid I-J ink. Components such as an organic solvent with a high boiling point and/or polymers with a high molecular weight that form an insulating layer during the formation of conductive circuit pattern were excluded from the ink formulation. The typical physico-chemical properties of the silver colloid ink (MAI-1) that shows a high reliability for the I-J printing operation are shown in Table 1. The values of the principal characteristics of the MAI-1 ink such as viscosity, surface tension, solid content, pH and conductivity were nearly equal to those of the pigment disperse type I-J ink available in the market.

Table 1. Properties of MAI-1 inl

	Ag Colloid	Pigment I-J Ink	MAI-1 Ink
Viscosity (mPa・s)	16	20〜50	36
Surface tension (mN/m)	50	30〜40	32
Solid content %	30	15〜20	20
PH	7.0	7〜9	11.0
Conductivity (ms/cm)	440	500〜3,000	1,300

Substrate for the I-J Printing

High glossy photo-paper, a polyester film, polyimide film, glass and glass wool impregnated by an epoxy resin (glass-epoxy plate) were used as the substrate for the formation of conductive pattern.

Printer and Test Process

A commercial I-J printer with a thermal I-J head that can reproduce a precise pattern of 4800 dpi (horizontal) x 1200 dpi (vertical) was used as the test printer. Fifteen ml of MAI-1 ink was filled into the ink cartridge for the test printer, and designed patterns were printed directly according to the output data of a computer. The printed pattern was dried at room temperature and used as the evaluation sample for measuring printing resolution, conductivity, silver particle migration, and adhesion strength.

Results and Discussion

Storage Stability of MAI-1 Ink and Printing Reliability

The MAI-1 ink sealed hermetically in a container showed excellent stability. After storage under a temperature range of 10 to 40°C for six months, the variation of the values of above physico-chemical properties proved to be less than ±5%.

The MAI-1 ink shows excellent reliability for the ink drop ejection from I-J head. Head clogging was not observed to the end of the ink cartridge. The stability against the Kogation that is sometimes an issue for a commercial thermal type print head was also excellent.

Printing Resolution and Characteristics

Figure 5 shows a micrograph of the finest line pattern printed on the I-J photopaper surface obtained by using a commercial I-J printer with the thermal type print head. In the lateral direction, the printer can realize the finest resolution of 4800 dpi. As shown in the micrograph, the edge of the finest lateral line was sharp, and realizing a width of about 20 µm. The edge of the line was sharper than the anticipation from the ink drop size of 2 pl (equivalent diameter of about 25 µm) ejected from the nozzle tip.

In the vertical direction, on the other hand, the finest line width was 50 to 100 µm.

Figures 6 and 7 show the printed examples of a print circuit pattern using the silver colloid I-J ink MAI-1.

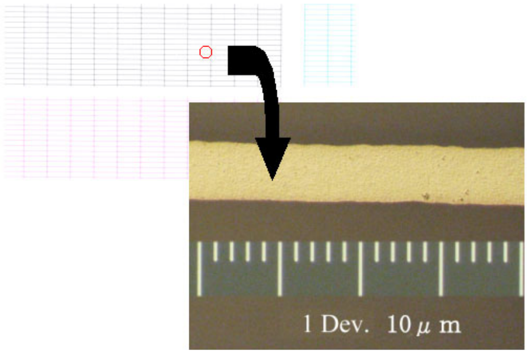

Figure 5. Presice electrically conductive pattern

Image Blurring

In general, the ink drop landing on the substrate surface sometimes spreads and yield a blurred image. It is a critical issue to obtain a fine precise pattern on the various substrate surfaces by I-J printing. Following measures were effective for the formation of a clearly printed precise pattern on the substrate surfaces used in this experiment: (a) Increase of the surface tension of ink to 30 mN/m or above, (b) preheating of the substrate, and (c) reduction of the surface tension of the substrate surface. In practice, surface treatment with oxygen plasma and/or fluorocarbon plasma was very effective for the prevention of drop spreading.

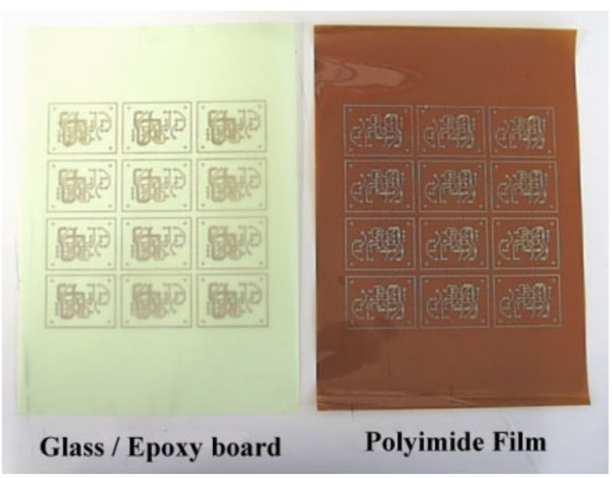

Figure 6. Circuit pattern using silver colloid ink

Conductivity of the Printed Silver Layer

Conductivity was evaluated by surface resistivity measurements. The resistivity was measured by a four point probe measuring system.

The surface resistivity of the silver colloid layer on the glass substrate baked at 150°C for 30 min. was 0.8 Ω. The surface resistivity of the same layer baked at 300°C for 1 hour was reduced to 10mΩ.

From the printed MAI-1 ink layer on the substrate surface, almost all parts of volatile liquid such as water and volatile organic solvents were evaporated at room temperature. The dried up solid layer consists mainly of the silver colloid and a small amount of volatile additives. Usually, the layer at this point is an insulator having a resistivity of higher than 10^{10} Ω because of the polymer encapsulating the silver particles.

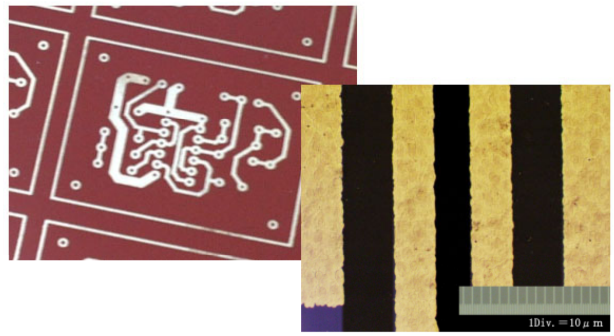

Figure 7. Circuit pattern using silver colloid ink

As already mentioned, the layer after baking at 150°C shows conductivity. At 150°C, the weak part of the encapsulating polymer layer was destroyed and the silver colloid particles came in direct contact with each other. Then the sintering of the particles started. It is well known that the starting temperature of the sintering of ultra-fine metal particles is much lower than the melting point. The melting point of the silver, for example, is 961°C. The result shows that, through such an extreme melting point reduction at the interface between the silver colloid particles, the conductive layer was obtained by baking at such a lower temperature.

The conductivity is increases by increasing the baking temperature of the silver colloid layer. The low surface resistiviity observed for the layer baked at 300°C shows that the formation of networks with the sintered silver particles has thoroughly progressed.

Figure 8 shows the electron micrograph (SEM) of the silver colloid layer on the polyimide film baked at 150°C. The layer thickness was about 0.5 μm and a flawless fine structured layer was formed on the polyimide film surface.

The surface resistivity of the copper layer that is plated on the silver colloid layer on the polyimide film with baked at 150°C for 30 min wasa order of 10^{-5}Ω. The thickness of the copper layer was 1 to 2 μm. From the electron micrograph observation, it was confirmed that the plated layer was as dense and uniform as the baked silver layer shown in figure 8.

Migration Test

A line pattern having a line width of 100 μm, a line space of 100 μm and a thickness of the printed thickness layer of 0.5 μm was printed on the epoxy/glass sheet surface with MAI-1 ink. The printed pattern was baked at

150°C and a copper layer was plated on the baked layer. The thickness of the plated copper layer was 2.0 μm. The obtained pattern was used as the sample plate for the migration test, in which a DC Voltage of 20V was applied between the two lines on the sample plate and the plate was kept at 80°C, 85%RH atmosphere for 300 hrs.

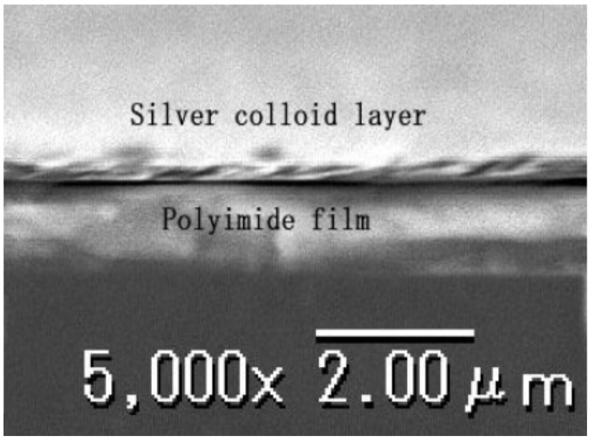

Figure 8. Silver colloid layer on polyimide film

Figure 9. Copper/silver layer on glass/epoxy substrate

After 300 hr storage, no short circuit formation by the migration of silver particles between the two lines was recognized. The result suggests that the migration of the silver particles under such a high temperature and high relative humidity atmosphere can be prevented by the selection of the species of plating metal and metal/silver thickness ratio.

Adhesion Strength

Adhesion strength was evaluated by a peeling off test using an adhesive tape.

In the case of the copper/silver circuit layer on the glass/epoxy plate, the pattern was maintained as a whole after the peeling off operation. The electron micrograph shown in fig. 9 suggests that the copper/silver layer penetrates into the uneven hole on the substrate surface and contributes to the enhancement of the adhesion strength through the anchor effect.

The improvement of the adhesion strength for the polyester film, polyimide film, and glass plate was confirmed by the surface treatment with oxygen plasma and/or fluorocarbon plasma.

Conclusion

A precise electrically conductive pattern was formed by the I-J technique using ink containing a silver colloid of high concentration. A 20 μm line width pattern was obtained using a commercial I-J printer. The stability of the silver colloid ink and printing characteristics were excellent, and troubles such as head clogging and Kogation were not observed. By baking the printed pattern, the surface resistivity was decreased to the order of 10^{-3} Ω. The surface resistivity of the 10^{-5} Ω was obtained by adding a plating layer of copper on the silver colloid printed layer. The technique is useful for the formation of precise conductive pattern and also for the preparation of electric circuit pattern.

References

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Biography

Toshihiko Oguchi joined Morimura chemicals Ltd. In April 2000. He is responsible for new product development and application research. Previously at R & D center in Toshiba Corporation his work has primary focused on the development of liquid and dry toners for electro-photography and perpendicularly recording media. He is a chief member of ISJ's Technical Committee part III meeting (The technical committee of toner-based material). He received his BS from Tokyo Metropolitan University in 1967 and Dr. of Engineering from Tokyo Institute of Technology in 1988.