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The electroless plating of Cu-Ni-P alloy onto cotton fabrics

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Abstract−The objective of this study is to apply the electroless plating of Cu-Ni-P alloy on cotton fabrics to the preparation of conductive fabrics. The alloy composed of infinit small amount of nickel and phosphorus particle originated from sodium hypophosphite and nickel sulphate respectively as reducing agent and hypophosphite oxidation accelerator. Electroless plating of Cu-Ni-P alloy on cotton fabrics and effect of plating on the physical and mechanical properties of alloy coated fabrics as well as electromagnetic interference (EMI) shielding effectiveness were reported in detail. In this research highly washing and abrasion durable conductive fabrics obtained with supreme shielding effectiveness.

Key words: Electroless Plating of Cu-Ni-P Alloy, Cotton Fabric, Surface Morphology

INTRODUCTION

Because of the high conductivity of copper, electroless copper plating is currently used to manufacture conductive fabrics with high shielding effectiveness (SE). It can be performed at any step of the textile production, such as yarn, stock, fabric or clothing [1].

Electroless copper plating as a non-electrolytic method of deposition from solution on fabrics has been studied by some researchers [1-9]. The early reported copper electroless deposition method uses a catalytic redox reaction between metal ions and dissolved reduction agent of formaldhyde at high temperature and alkaline medium [1,2]. Despite the advantages of the technique, such as low cost, excellent conductivity, easy formation of a continuous and uniform coating, experimental safety risks appear through the formation of hazardous gasous product during the plating process, especially for industruial scale.

Further research has been conducted to substitute formaldhdyde with other reducing agents coupled with oxidation accelerator such as sodium hypophosphite and nickel sulphate [4-8]. Incorporation of nickel and phosphhrus particles provides good potential for creation of fabrics with a metallic appearance and good handling characteristics. These properies are practically viable if the plating process is followed by finishing process in optimized pH and in presence of ferrocyanide.Revealing the performance of electroless plating of Cu-Ni-P alloy on cotton fabrics is an essential research area in textile finishing processing and for technological design [4-9].

The main aim of this paper is to explore the possibility of applying electroless plating of Cu-Ni-P alloy onto cotton fabric to obtain the highest level of conductivity, washing and abrasion fastness, room condition durability and EMI shielding effectivness. The fabrication and properties of Cu-Ni-P alloy plated cotton fabric are investigated in accordance with standard testing methods.

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EXPERIMENTAL

Cotton fabrics (53×48 count/cm^2, 140 g/m^2, taffeta fabric) were used as substrate. The surface area of each specimen was 100 cm^2. The electroless copper plating process was conducted by multistep processes: pre-cleaning, sensitization, activation, electroless Cu-Ni-P alloy deposition and post-treatment.

The fabric specimens (10 cm×10 cm) were cleaned with non-ionic detergent (0.5 g/*l*) and $NaHCO_3$ (0.5 g/*l*) solution for 10 minutes prior to use. The samples then were rinsed in distilled water. Surface sensitization was conducted by immersion of the samples into an aqueous solution containing $SnCl_2$ and HCl. The specimens were then rinsed in deionized water and activated through immersion in an activator containing $PdCl_2$ and HCl. The substrates were then rinsed in a large volume of deionized water for 10 min to prevent contamination the plating bath. The electroless plating process was carried out immediately after activation. Then all samples were immersed in the electroless bath containing copper sulfate, nickel sulfate, sodium hypophosphite, sodium citrate, boric acid and potassium ferrocyanide. In the post-treatment stage, the Cu-Ni-P plated cotton fabric samples were rinsed with deionized water, ethylalcohol at home temperature for 20 min immediately after the metallizing reaction of electroless Cu-Ni-P plating. Then the plated sample was dried in an oven at 70 °C.

The weights (g) of fabric specimens with the size of 100 mm×100 mm square before and after treatment were measured by a weight meter (HR200, AND Ltd., Japan). The percentage for the weight change of the fabric is calculated in Eq. (1).

$$I_W = \frac{W_f - W_0}{W_0} \times 100\% \tag{1}$$

where I_w is the percentage of increased weight, W_f is the final weight after treatment, W_o is the original weight.

The thickness of fabric before and after treatment was measured by a fabric thickness tester (M034A, SDL Ltd., England) with a pressure of 10 g/cm^2. The percentage of thickness increment was calculated in accordance to Eq. (2).

$$T_I = \frac{T_F - T_0}{T_0} \times 100\% \quad (2)$$

where T_I is the percentage of thickness increment, T_f is the final thickness after treatment, T_o is the original thickness.

A bending meter (003B, SDL Ltd., England) was employed to measure the degree of bending of the fabric in both warp and weft directions. The flexural rigidity of fabric samples expressed in Ncm is calculated in Eq. (3).

$$G = W \times C^3 \quad (3)$$

where G (N-cm) is the average flexural rigidity, W (N/cm^2) is the fabric mass per unit area, C (cm) is the fabric bending length.

The dimensional changes of the fabrics were conducted to assess shrinkage in length for both warp and weft directions and tested with (M003A, SDL Ltd., England) in accordance with stansdard testing method (BS EN 22313:1992). The degree of shrinkage in length expressed in percentage for both warp and weft directions was calculated according in accordance with Eq. (4).

$$D_c = \frac{D_f - D_0}{D_0} \times 100 \quad (4)$$

where D_c is the average dimensional change of the treated swatch, D_o is the original dimension, D_f is the final dimension after laundering.

Tensile properties and elongation at break were measured with standard testing method ISO 13934-1:1999 using a Micro 250 tensile tester.

Color changing under different application conditions for two standard testing methods, namely, (1) ISO 105-C06:1994 (color fastness to domestic and commercial laundering, (2) ISO 105-A02:1993 (color fastness to rubbing) was used for estimate.

Scanning electron microscope (SEM, XL30 PHILIPS) was used to characterize the surface morphology of deposits. WDX analysis (3PC, Microspec Ltd., USA) was used for the metallic particles over surface Cu-Ni-P alloy plated cotton fabrics. The chemical composition of the deposits was determined using X-ray energy dispersive spectrum (EDS) analysis attached to the SEM.

The coaxial transmission line method as described in ASTM D 4935-99 was used to test the EMI shielding effectiveness of the conductive fabrics. The set-up consisted of an SE tester that was connected to a spectrum analyzer. The frequency scanned from 50 MHz to 2.7 GHz is taken in transmission. The attenuation under transmission was measured equivalent to the SE.

RESULTS AND DISCUSSION

1. Energy Dispersive Elemental Analysis

The composition of the deposits was investigated using X-ray energy dispersive spectrum (EDS) elemental analysis. The deposits consisted mainly of copper with small amounts of nickel and phosphorus. Table 1 shows the weight pecent of all detectd elemental analysis.

The nickel and phosphorus atoms in the copper lattice possibly increase the crystal defects in the deposit. Moreover, as a non-conductor, phosphorus will make the electrical resistivity of the deposits higher than pure copper. Electroless plating of copper conductive layer on fabric surface employs hypophosphite ion to reduce copper ion to neutral copper particle. However, the reduction process extremely accelerates by addition of Ni^{2+}. Addition of Ni^{2+} also sediments tiny amount of nickel and phosphorus elements. Follwing formulations show the mechanism of copper electroless plating using hypophosphite.

Table 1. Elemental analysis of electroless copper plated using hypophosphite and nickel ions

Element	Copper	Nickel	Phosphorous
~wt%	96.5	3	0.5

$$2H_2PO_2^- + Ni^{2+} + 2OH^- \rightleftharpoons Ni^0 + 2H_2PO_3^- + H_2$$

$$2H_2PO_2^- + 2OH^- \xrightarrow[surface]{Ni} 2e^- + 2H_2PO_3^- + H_2$$

$$Cu^{2+} + 2e^- \rightleftharpoons Cu^0$$

$$Ni^0 + Cu^{2+} \rightleftharpoons Ni^{2+} + Cu^0$$

2. Fabric Weight and Thickness

The change in weight and thickness of the untreated cotton and Cu-Ni-P alloy plated cotton fabrics is shown in Table 1.

The results showed that the weight of chemically induced Cu-Ni-P-plated cotton fabric was heavier than the untreated one. The measured increased percentage of weight was 18.47%. This confirmed that Cu-Ni-P alloy had clung on the surface of cotton fabric effectively. In the case of thickness measurement, the cotton fabric exhibited a 5.7% increase after being subjected to metallization.

3. Fabric Bending Rigidity

Fabric bending rigidity is a fabric flexural behavior that is important for evaluating the handling of the fabric. The bending rigidity of the untreated cotton and Cu-Ni-P-plated cotton fabrics is shown in Table 2.

The results proved that the chemical plating solutions had reacted with the original fabrics during the entire process of both acid sensitization and alkaline plating treatment. After electroless Cu-Ni-P alloy plating, the increase in bending rigidity level of the Cu-Ni-P-plated cotton fabrics was estimated at 11.39% in warp direction and 30.95% in weft direction. The result of bending indicated that the Cu-Ni-P-plated cotton fabrics became stiffer to handle than the un-

Table 2. Weight and thickness of the untreated and Cu-Ni-P-plated cotton fabrics

Specimen (10cm×10 cm)	Weight (g)	Thickness (mm)
Untreated cotton	2.76	0.4378
Cu-Ni-P plated cotton	3.72 (↑18.47%)	0.696 (↑5.7%)

Table 3. Bending rigidity of the untreated and Cu-Ni-P-plated cotton fabrics

Specimen	Bending (N·cm)	
	Warp	Weft
Untreated cotton	1	0.51
Cu-Ni-P plated cotton	1.17 (↑11.39%)	0.66 (↑30.95%)

Table 4. Dimensional change of the untreated and Cu-Ni-P-plated cotton fabrics

Specimen	Shrinkage (%)	
	Warp	Weft
Untreated cotton	0	0
Cu-Ni-P plated cotton	−8	−13.3

treated cotton fabric.

4. Fabric Shrinkage

The results for the fabric Shrinkage of the untreated cotton and Cu-Ni-P-plated cotton fabrics are shown in Table 3.

The measured results demonstrated that the shrinkage level of the Cu-Ni-P-plated cotton fabric was reduced by 8% in warp direction and 13.3% in weft direction.

After the Cu-Ni-P-plated, the copper particles could occupy the space between the fibers and hence more copper particles were adhered on the surface of fibers. Therefore, the surface friction in the yarns and fibers caused by the Cu-Ni-P particles could then be increased. When compared with the untreated cotton fabric, the Cu-Ni-P-plated cotton fabrics showed a stable structure.

5. -Fabric Tensile Strength and Elongation

The tensile strength and elongation of cotton fabrics was enhanced by the electroless Cu-Ni-P alloy plating process as shown in Table 4.

The metallized cotton fabrics had a higher breaking load with a 28.44% increase in warp direction and a 35.62% increase in weft direction than the untreated cotton fabric. This was due to the fact that more force was required to pull the additional metal-layer coating.

The results of elongation at break were 12.5% increase in warp direction and 7.8% increase in weft direction, indicating that the Cu-Ni-P-plated fabric encountered little change when compared with the untreated cotton fabric. This confirmed that with the metallizing treatment, the specimens plated with metal particles demonstrated a higher frictional force of fibers. In addition, the deposited metal particles developed a linkage force to hamper the movement caused by the applied load.

Table 6. Washing and rubbing fastness of the untreated and Cu-Ni-P Fabrics plated cotton fabrics

Specimen	Washing	Rubbing	
		Dry	Wet
Cu-Ni-P plated cotton	5	4-5	3-4

6. Color Change Assessment

The results of evaluation of color change under different application conditions, washing, rubbing are shown in Table 5.

The result of the washing for the Cu-Ni-P-plated cotton fabric was grade 5 in color change. This confirms that the copper particles had good performance during washing. The result of the rubbing fastness is shown in Table 5. According to the test result, under dry rubbing condition, the degree of staining was recorded to be grade 4-5, and the wet rubbing fastness showed grade 3-4 in color change. This result showed that the dry rubbing fastness had a lower color change in comparison with the wet crocking fastness. In view of the overall results, the rubbing fastness of the Cu-Ni-P-plated cotton fabric was relatively good when compared with the commercial standard.

7. Surface Morphology

Scanning electron microscopy (SEM) of the untreated and Cu-Ni-P-plated cotton fabric is shown in Fig. 1 with magnification of 250×. Microscopic evidence of copper-coated fabrics shows the formation of evenness of copper particles on the fabric surface and structure.

Table 5. Tensile strength and percentage of elongation at break load of the untreated and Cu-Ni-P- Fabrics plated cotton fabrics

Specimen	Percentage of elongation (%)		Breaking load (N)	
	Warp	Weft	Warp	Weft
Untreated cotton	6.12	6.05	188.1	174.97
Cu-Ni-P plated cotton	6.98 (↑12.5%)	6.52 (↑7.8%)	241.5 (↑28.4%)	237.3 (↑35.62%)

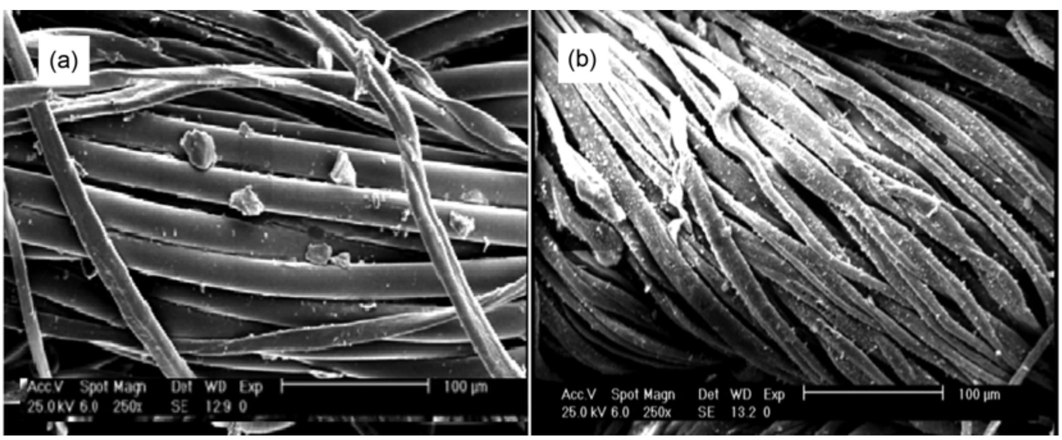

Fig. 1. SEM photographs of the (a)untreated cotton fabric (b) Cu-Ni-P plated cotton fabric.

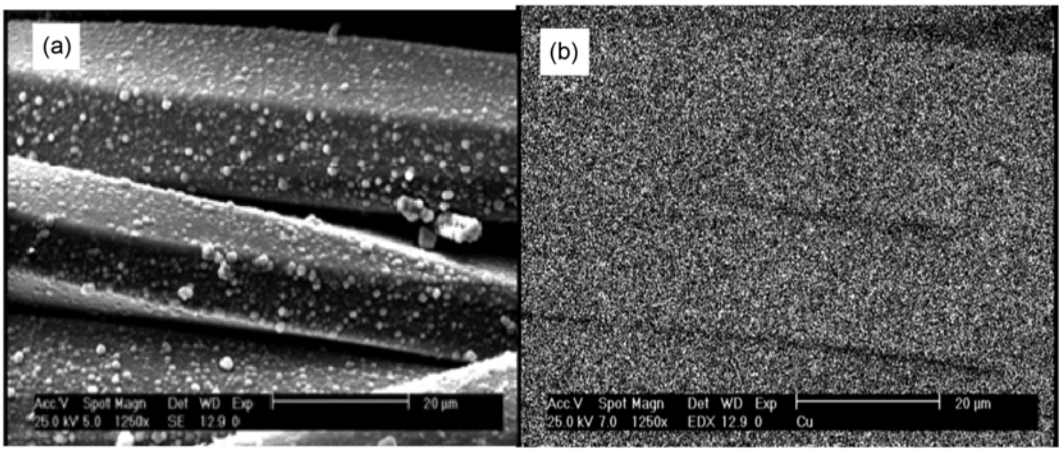

Fig. 2. (a) SEM photograph of the Cu-Ni-P plated cotton fabric (b) WDX analysis of the Cu-Ni-P plated cotton fabric.

Fig. 2 shows the SEM and WDX analysis copper-plated surfaces of cotton fiber. It was observed that the cotton fiber surface was covered by Cu-Ni-P alloy particles composed of an evenly distributed mass. In addition, WDX analysis indicated that the deposits became more compact, uniform and smoother; also, there exists a homogeneous metal particle distribution over the coated fabric surface. These results indicate that the effect of chemical copper plating is sufficient and effective to provide a highly conductive surface applicable for EMI shielding use.

8. Shielding Effectiveness

Electromagnetic shielding means that the energy of electromagnetic radiation is attenuated by reflection or absorption of an electromagnetic shielding material, which is one of the effective methods to realize electromagnetic compatibility. The unit of EMISE is given in decibels (dB). The EMI shielding effectiveness value was calculated from the ratio of the incident to transmitted power of the electromagnetic wave in the following equation:

$$SE = 10\log\left|\frac{P_1}{P_2}\right| = 20\left|\frac{E_1}{E_2}\right| \tag{5}$$

where P_1 (E_1) and P_2 (E_2) are the incident power (incident electric field) and the transmitted power (transmitted electric field), respectively. Fig. 3 indicates the shielding effectiveness (SE) of the copper-coated fabrics with 1 ppm $K_4Fe(CN)_6$ compared to copper foil and other sample after washing and rubbing fastness test. The shielding effectivness test was applied on five different conductive sample including copper foil, electroless plating of Cu-Ni-P alloy particle on cotton fabric, electroless plated fabric after washing test, electroless plated fabric after dry and wet rubbing. As can be expected, copper foil with completely metallic structure shows the best shielding effectivness performance according to higher conductivity compared to other conductive fabric samples. However, SE of copper-coated cotton fabric was above 90 dB and the tendency of SE kept similarity at the frequencies 50 MHz to 2.7 GHz. The acquired results for samples after washing fastness test show nearly 10% decrease over the frequency range, which is still applicable for practical EMI shielding use. Two other samples after rubbing show, respectively, 12% and 15% reduction in shielding effectiveness value, but the presented results still show an accepted level of shielding around 80 dB. The SE reduction after fastness tests is a quite normal behavior, which is likely due to removing of conductive particles from the fabric surface. However, the compact and homogeneous distribution of conductive particles provides a great conductive coating on the fabric surface with high durability even after washing or rubbing tests. The copper-coated cotton fabric has a practical usage for many EMI shielding application requirements.

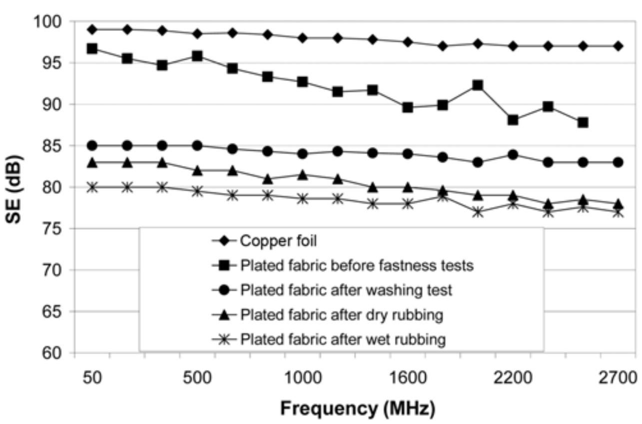

Fig. 3. The shielding effectiveness of various conductive sample.

CONCLUSION

Electroless plating of Cu-Ni-P alloy process onto cotton fabrics was demonstrated. Both uncoated and Cu-Ni-P alloy coated cotton fabrics were evaluated with measurement weight change, fabric thickness, bending rigidity, fabric shrinkage, tensile strength, percentage of elongation at break load and color change assessment. The results showed significant increase in weight and thickness of chemically plated cotton fabric. Coated samples showed better properties and stable structure with uniformly distributed metal particles. The SE of copper-coated cotton fabric was above 90 dB, and the tendency of SE kept similarity at the frequencies 50 MHz to 2.7 GHz. Also, the evaluaton of SE after standard washing and abration confirms the supreme durable shielding behavior. The copper-coated cotton fabric has a practical usage for many EMI shielding application requirements.

REFERENCES

1. R. H. Guo, S. Q. Jiang, C. W. M. Yuen and M. C. F. Ng, *J. Mater. Sci.*: Mater Electron, DOI 10.1007/s10854-008-9594-4 (2008).
2. Y. M. Lin and S. H. Yen, *Appl. Surf. Sci*., **178**(1-4), 116 (2001).
3. G. Xueping, W. Yating, L. Lei, Sh. Bin and H. Wenbin, *J. Alloys Compounds*, **455**, 308 (2008).
4. J. Li, H. Hayden and P. A. Kohl, *Electrochim. Acta*, **49**, 1789 (2004).
5. H. Larhzil, M. Cisse, R. Touir, M. Ebn Touhami and M. Cherkaoui, *Electrochim. Acta*, **53**, 622 (2007).
6. J. G. Gaudiello and G. L. Ballard, *IBM J. RES. DEVELOP*, **37**(2) (1993).
7. G. Xueping, W. Yating, L. Lei, Sh. Bin and H. Wenbin, *Surface & Coatings Technology*, **201**, 7018 (2007).
8. E. G. Han, E. A. Kim and K. W. Oh, *Synth. Met*., **123**, 469 (2001).
9. S. Q. Jiang and R. H. Guo, *Fibers and Polymers*, **9**(6), 755 (2008).
10. S. S. Djokic, Fundamental Aspects of Electrometallurgy: Chapter 10, Metal Deposition without an External Current, Eds., K. I. Popov, S. S. Djokic B. N. Grgur, pp. 249-270, Kluwer Academic Publishers, New York (2002).
11. O. Mallory and B. J. Hajdu, Eds., Electroless Plating: Fundamentals and Applications, Noyes Publication, New York (1990).
12. R. C. Agarwala and V. Agarwala, *Sadhana*, **28**, 475 (2003).
13. M. Paunovic, *Plating*, **51**, 1161 (1968).
14. H. F. Chang and W. H. Lin, *Korean J. Chem. Eng*., **15**(5), 559 (1998).