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ELECTROLESS METAL PLATING OVER ABS PLASTIC

ABSRACT

Plating is used to decorate objects, for corrosion inhibition, to improve solder ability, to harden, to improve wear ability, to reduce friction, to improve paint adhesion, to alter conductivity and for other purposes. Electroless plating is a fundamental step in the metal plating on the plastic. In this study, the electroless copper plating on Acrylonitrile butadiene styrene (ABS) was investigated. The effects of the ionic liquids as catalyst, plating time and sanding paper size were investigated on metal plating. Experiments were carried out with two different types of ionic liquids: EMIC and DCA and with 120, 240, 320 and 500 grit sandpaper by applying sand attrition process, and constant bath temperature as 60^0C with 60-150 minutes of deposition times. Due to the results, the copper plating on ABS plastic was a success. The surface morphology and amount of deposit analysis were performed using the Fischerscope X-Ray XDL-B System, X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Hence, it is determined that the maximum amount of deposit is obtained in the sample which EMIC is used as catalyst with 150 min deposition time and 500 grit sandpaper size.

Keywords: Electroless Plating, ABS Plastic, Copper Plating, Lonic Liquid, X-Ray XDL-B System

1. INTRODUCTION

Metal plating on the plastic industry is developing rapidly in recent years in Turkey. There is a lot of importance of the metal-plating on plastics: to be corrosion resistant, increasing the salability of the product with glossy or satin-looking metallic surfaces etc. In most cases, lightweight material characteristic of the plastic provides a major advantage [1 and 2]. New types of plastics are stronger, and some are more heat resistant than others, but the lack of hard is the common feature of all. Therefore, the plating of the plastic surface allows the use of longer period of the material. Electroless plating utilizes a simpler process. The component is treated with chemicals to remove oils and other corrosive elements, and is then activated with an acid etch or proprietary solution [2 and 4].

The application of anti-oxidation chemicals completes the process, rendering the component resistant to corrosion and friction. While electroplating requires complex filtration equipment and possibly dangerous battery applications, electroless plating uses no extra equipment [5 and 6]. Electroless copper deposition using formaldehyde as a reducing agent at 60°C is widely used in commercial printed circuit board industries.

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However, formaldehyde, as a carcinogen, has high potential risk to the environment and the plating operators. Therefore, alternatives to formaldehyde used in electroless copper deposition have been proposed.

The traditional processes mainly include sensitization and activation. The plastic substrate was placed in a sensitizing solution and activation solution during the process. Then the surface adsorbs some discontinuously distributed Sn as the chemical reductant so that noble metals such as Ag and Pd can be further reduced from the activating solution to serve as the catalyst for electroless plating. This process is complicated and involves the use of not only poisonous Sn but also noble metallic elements. And the process also produces waste and contributes to pollution [7 and 10]. Ionic liquids (ILs) are electrically conductive liquids composed exclusively of ions. Room temperature ionic liquids (RTILs) possess a number of interesting and advantageous characteristics, which vary depending on the individual liquid, suited to the purposes of electrochemistry. EMIC, ($C_6H_{11}N_2Cl$, 1-ethyl-3-methyl imidazolium chloride), is now widely employed as a cationic source for low temperature molten salts. The cation consists of a five-membered ring with two nitrogen and three carbon atoms, i.e. a derivative of imidazole, with ethyl and methyl groups substituted at the two nitrogen atoms. Dicyanamide ($C_8H_{11}N_5$) is the ionic liquid which has very low viscosity [11 and 12]. Acrylonitrile butadiene styrene (chemical formula $(C_8H_8)_x \cdot (C_4H_6)_y \cdot (C_3H_3N)_z$) is a common thermoplastic polymer. ABS is amorphous and therefore has no true melting point. ABS is a terpolymer made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. The proportions can vary from 15 to 35% acrylonitrile, 5 to 30% butadiene and 40 to 60% styrene. ABS plastic is an important chemical reagent an engineering material with high thermal stability, high mechanical strength and high resistance. It is widely used for machining pre-production prototypes since it has excellent dimensional stability and is easy to paint and glue. Applications of ABS are housings for vacuum cleaners, kitchen appliances; telephones, toys; the automotive industry, the electrical/electronics segment (primarily in white goods & computer/communication electronics) [13].

2. RESEARCH SIGNIFICANCE

Aim of this study is to investigate the operating conditions of electroless copper plating over ABS plastic and determining the best plating conditions.

3. EXPERIMENTAL METHOD-PROCESS

The experiments consist of four steps: preparing the chemicals and materials, etching, plating and the analysis characterization of samples. The investigated parameters were sandpaper size, plating time, plating temperature, pH and effects of ionic liquid types (RTIL). Initially, 20mmx35mmx1.5mm ABS plastic samples were grounded with the 120-500 grit size sandpapers to increase the surface area for molecular bonding. The samples were placed in a 65°C oven for 4 to 5 h to remove the stress. The samples were taken from oven and placed in a 10g/L NaOH alcoholic solution and NaOH alcoholic solution was placed into in a 35-40°C water bath for 30 min. to dislodge the grease and for a hydrophilic plastic surface. The samples were placed in an aqueous solution with a certain ratio of nitric acid, hydrogen peroxide and ammonium fluoride (Table 1).

It was exposed to ultrasonic wave for 30 min. for non-noble metal activation pretreatment. Then resultant samples were washed with deionized water [14].

For the material pretreatment solution of $CuCl_2$ and ionic liquid were weighed with the molar ratio 2:1 and the samples were immersed in the ionic liquid solution and was left for a week.

The samples were placed at 60-80˚C bath containing the plating solution prepared with the chemicals at Table 2. NaOH was gradually added during the process to ensure the pH. The operating condition of pH of the plating solution was 11-12.

No apparent phenomenon was observed at the initial stage (10 min to 20 min). The reaction then produced numerous bubbles for 50 min to 60 min. After being washed by deionized water, the final copper plating specimen was placed in a 45˚C oven to dry. Finally, the surface morphology and amount of deposit analysis were done by Fischerscope X-Ray XDL-B System, X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM-EDX).

Table 1. Composition of aqueous solution [14]

Chemical	Density(g/cm³)	Mass(g)	Volume(mL/L)
HNO_3	1.51	378.2-453.9	250-300
H_2O_2	1.45	13.6-20.41	9.38-14.08
NH_4F	1.009	2-4	1.98-3.96

Table 2. Composition of the electroless copper plating solution [14]

Chemical	Formula	Concentration(g/L)
Copper Sulfate	$CuSO_4 \cdot 5H_2O$	12-15
EDTA-2Na	$C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$	40-45
2.2-Dipyridyl	$C_{10}H_8N_2$	0.04-0.05
Formalin	CH_2O	20-25

4. FINDINGS AND DISCUSSIONS

In the study, the electroless copper plating was performed with RTIL used as catalyst. The effects of EMIC and DCA ionic liquid types, 120-500 sandpaper sizes and 90-120-150 min. plating times were investigated for the amount of deposit. The plating bath temperature was taken as constant at 60^0C. The plating bath pH was adjusted to 11-12. The samples were analyzed by Fischerscope X-Ray XDL-B System. Plating time effect for DCA and EMIC was illustrated at Figures 1-4. The dependence of plating time on the amount of deposit was investigated for both ionic liquids. According to the results from X-Ray analysis of DCA, when time increased, the amount of deposit increased using 320 grit size sandpaper (Figure 1). But stable increase could not be obtained using 120 grit size sandpaper. When time increased, the amount of deposit increased first from 0.28 to 3.27, and then at 120 min, it was decreased from 3.27 to 1.48 (Figure 2). The maximum amount of the deposit was found as 3.27µm for 120 min by using DCA. According to the results from X-Ray analysis of EMIC, stable increase was obtained with different plating time values (Figures 3 and Figure 4). The amount of deposit increased with increasing plating time of the substrate at constant temperature (60˚C). The maximum amount of the deposit was about 6.67µm for 150 min and 500 grit sizes for EMIC. As a result, it is concluded that EMIC is more suitable ionic liquid then DCA type ionic liquid as catalyst for copper plating on ABS plastic.

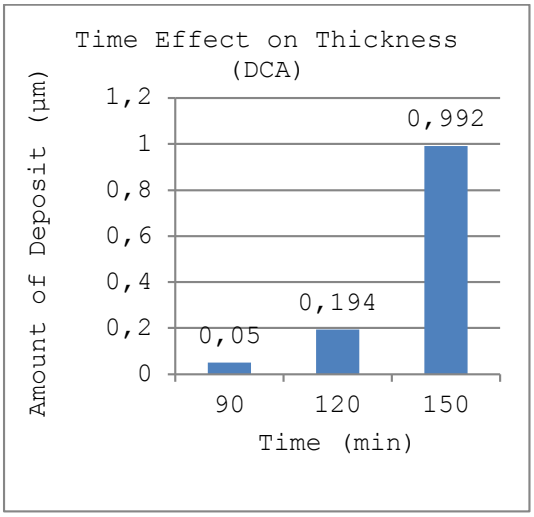

Figure 1. Time effect on amount of deposit for DCA and 320 grit size sandpaper

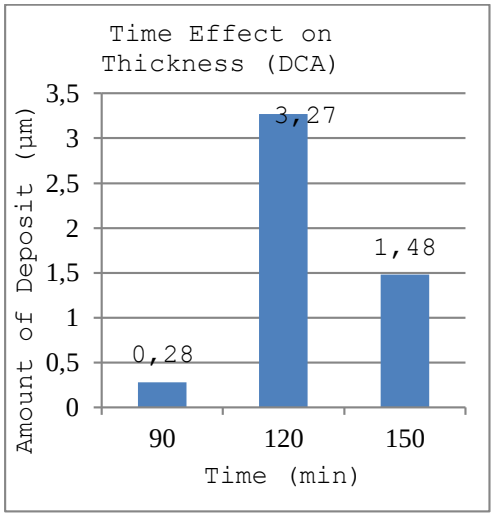

Figure 2. Time effect on amount of deposit for DCA and 120 grit size sandpaper

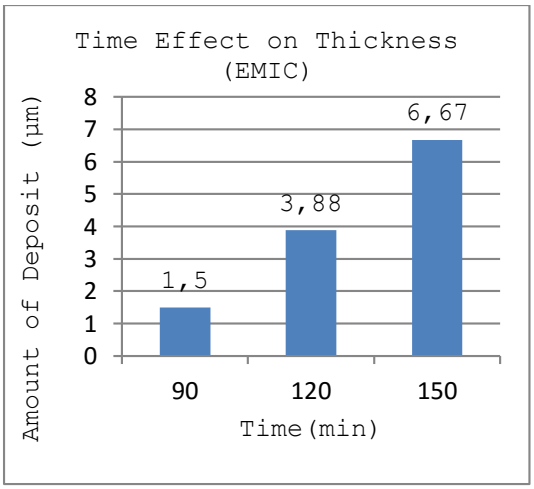

Figure 3. Time effect on amount of deposit for EMIC and 500 grit size sandpaper

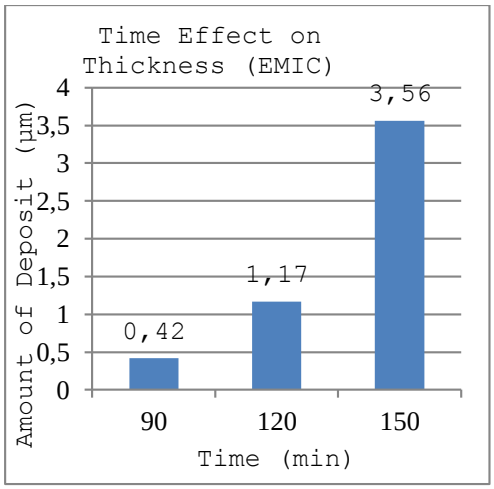

Figure 4. Time effect on amount of deposit for EMIC and 120 grit size sandpaper

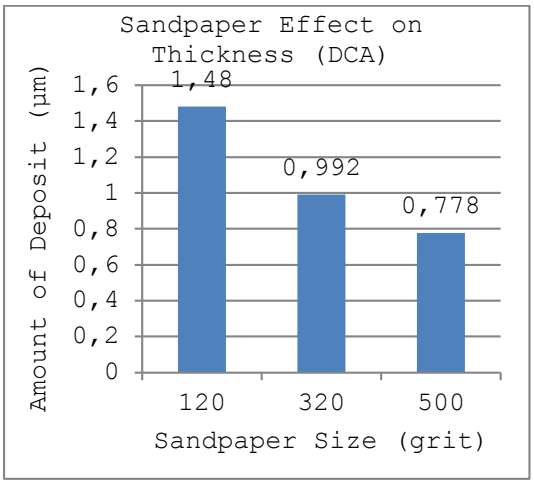

Figure 5. Amount of deposit versus sandpaper size for DCA and 150 minutes

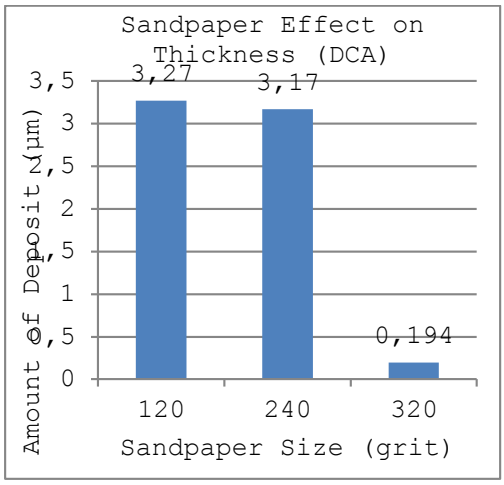

Figure 6. Amount of deposit versus sandpaper size for DCA and 120 minutes

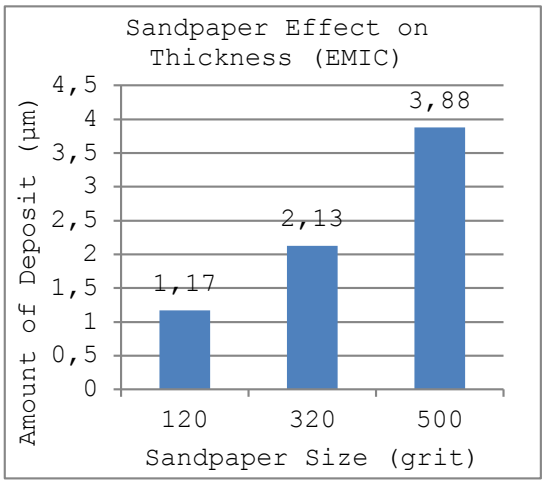

Figure 7. Amount of deposit versus sandpaper size for EMIC and 120 minutes

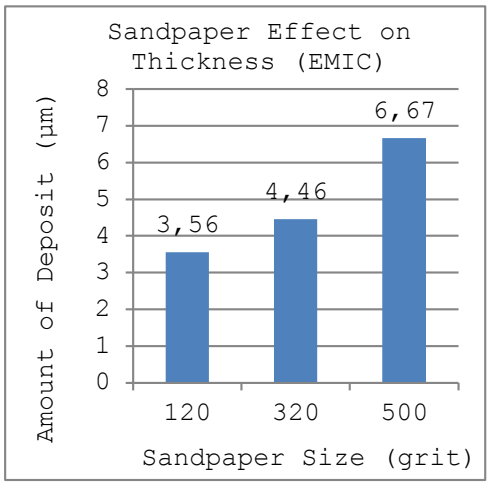

Figure 8. Amount of deposit versus sandpaper size for EMIC and 150 minutes

Sandpaper size effects on plating amount were evaluated and thickness versus sandpaper size graphs was plotted (Figures 5-8). The amount of deposit should be increased when sandpaper size was increased as expected, but the amount of deposit decreased when sandpaper size increased using DCA (Figures 5 and Figure 6). The reason can be ingredients of the activation solution (alcohol solution) or solution that includes nitric acid, hydrogen peroxide and ammonium fluoride. Stable increase was obtained with EMIC, as expected based on the literature [14]. It was shown from Figures 7 and 8 that, the thickness of the copper film increased when sandpaper size increased by using EMIC. The maximum amount of the deposit was about 6.67µm for 500 grit of sand paper. After X-ray measurements, the XRD and SEM analyses were performed for plated samples. Figure 9 shows the XRD patterns of plating, it also reveals the absence of other elements' diffraction peaks, which states that the plating only includes Cu. According to the literature, the results of XRD analysis was obtained as expected. Diffraction peaks was obtained at approximately 45, 50, and 75 degrees [14].

The results of the SEM analysis were shown in the Figures 10 and Figure 12. They were obtained by using EMIC with 120 grit size sandpaper at 60 minutes. The deposit amount was 3.56µm. It was shown from the figures that a crystalline material was deposited on the surface of the substrate and it proved that electroless plating took place. The elemental mapping result by SEM-EDX also indicated that the plating film consisted of mainly copper 80wt%, and the copper was homogeneously distributed on the surface of the film (Table 3).

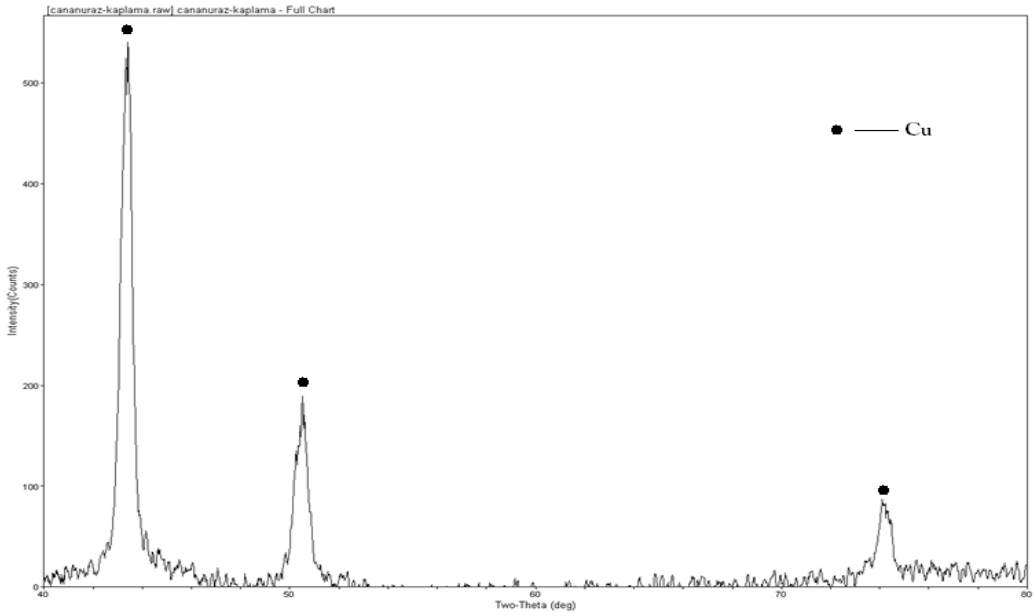

Figure 9. XRD analysis for copper plating with EMIC

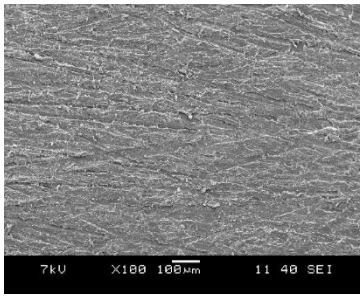

Figure 10. 100 X SEM analysis of sample which obtained by using EMIC with 120 grit size sandpaper at 150 minutes

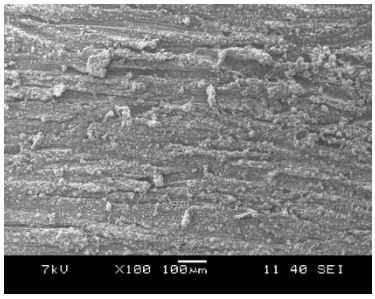

Figure 11. 100 X SEM analysis of sample which obtained by using EMIC with 320 grit size sandpaper at 150 minutes

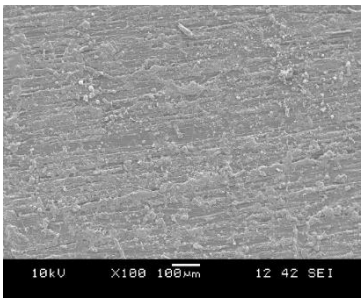

Figure 12. 100 X SEM analysis of sample which obtained by using EMIC with 500 grit size sandpaper at 150 minutes

Table 3. The elemental mapping result using SEM-EDX

Component		Mole Conc.	Conc.	
Cu		50.424	80.157	wt.%
O		49.576	19.483	wt.%
		100.00	100.00	wt.%
Elt.	Line	Intensity(c/s)	Error 2-sig	Conc.
O	Ka	0.60	0.154	19.843
Cu	Ka	1.65	0.257	80.157
				100.00

kV 20
Takeoff Angle 35.0^0
Elapsed Livetime 100.0

5. CONCLUSION

The aim of this study was to investigate and to develop of electroless plating catalyst and activation solution in the electroplating industry. Traditional copper plating steps are

consisting of etching with chromic and sulphuric acids, metallization with hydrochloric acid, palladium and tin, accelerate with accelerator chemicals. These chemicals are hazardous both environment and human. For this purpose, electroless baths was prepared by using environmentally friendly chemicals (EMIC & DCA) instead of the plating operation with hazardous chromic and sulphuric acids, palladium…etc. chemicals. Etching of the ABS was provided by sandpaper. On the contrary of the conventional sensitization and activation steps, palladium-free surface activation process was used to activate ABS plastic. After copper plating, the pretreated plastic surface obtained uniformly distributed coating. It is succeeded in demonstrating the electroless plating of dense, smooth, and pure metal for copper and nickel. XRD results indicated that the deposited film was copper. The elemental mapping results of SEM-EDX also indicated that the plating film consisted of copper only, and it was homogeneously distributed on the surface of the film. In the literature, there was found no electroless copper plating on ABS plastic study with RTIL. There is a new study for the plating industry.

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NOTICE

In this study, Hatay-Turkey held on 26-28 September 2018 at the 15th International Corrosion Symposium (KORSEM'18) was also presented as oral presentations.

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