

# Electroless Copper Plating on Acrylonitrile Butadiene Styrene Material Surfaces Without Chromic Acid Etching and a Palladium Catalyst

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**ABSTRACT:** Hydrolysis modification of nitrile groups on acrylonitrile butadiene styrene (ABS) plate surfaces into carboxylic acid groups was investigated to find a new recipe for electroless copper plating of ABS plate surfaces without etching reactions using chromic acid and also without a palladium catalyst. Hydrolysis modification of nitrile groups was successfully conducted in an aqueous sodium hydroxide (NaOH) solution (70 wt %) at 80°C for more than 72 h, and nitrile groups were modified into carboxylic acid groups. The hydrolysis modification was accelerated by the addition of dioxane as a supplement to the aqueous NaOH solution. The modification, when an aqueous mixture solution of NaOH (35 wt %) and dioxane (10 wt %) was used as a

reagent, was accomplished at 65°C in 30 min. The hydrolyzed ABS plate surfaces were successfully metalized by electroless copper plating. A silver catalyst, instead of a palladium catalyst, was usable in the electroless copper-plating process. Adhesion between the deposited copper metal and ABS plate surface was perfect for the Scotch tape test. Consequently, we propose a new recipe for an electroless copper-plating process without an etching process using chromic acid and without a palladium catalyst. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1034–1044, 2009

**Key words:** adhesion; ESCA/XPS; FT-IR; metal-polymer complexes; surfaces

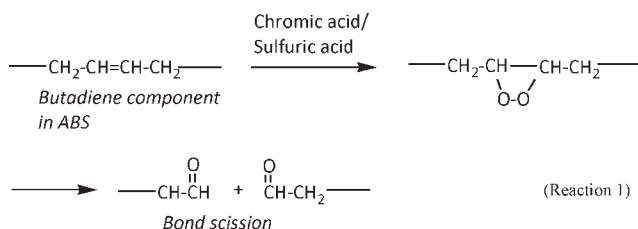
## INTRODUCTION

The copolymer acrylonitrile butadiene styrene (ABS) is an engineering plastic that possesses high impact resistance as well as high strength and colorless transparency, and it is widely used in automobiles (door mirrors, console boxes, front grilles, etc.), electric devices ( housings for televisions, video players, and digital video disc players, enclosures for vacuum cleaners and air conditioners, lighting fixtures, etc.), and office equipment ( housings for laser printers, copiers, personal computers, etc.). Such usage, especially in automobiles, demands a metal-like appearance from the viewpoint of decorativeness. Surfaces of door mirrors and front grilles are already metalized by a combination of electroless plating and electroplating techniques.

Surfaces of fabricated ABS materials are easily copper-metalized by an electroless plating technique. First, ABS surfaces are etched with a mixture of chromic acid and sulfuric acid to roughen the sur-

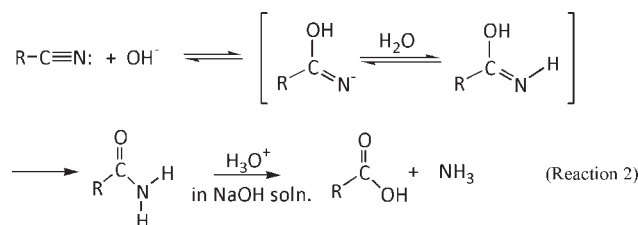
face, and then palladium (Pd) catalysts, used for reduction reactions of  $\text{Cu}^{2+}$  to  $\text{Cu}^0$  with formaldehyde, adsorb onto the roughened surfaces. Afterwards, the Pd-catalyst-containing ABS surfaces are brought into contact with an aqueous mixture solution of copper sulfate, formaldehyde, and sodium hydroxide (NaOH), and then, the electroless copper-plating process initiates spontaneously from the surface of the Pd catalysts.<sup>1</sup> Finally, copper metal deposits on all surfaces of the fabricated ABS materials. Such an electroless-plated ABS surface is electrically conductive, and it is applicable to the conventional electroplating process for the deposition of other metals such as gold, silver (Ag), chromium, and nickel.<sup>1</sup> Therefore, electroless copper plating is a basic process of metallization of ABS material surfaces. In the electroless copper-plating process, important items are (1) how a Pd catalyst can be adsorbed onto ABS material surfaces and (2) what combination of catalyst and reducing reagent is effective in reduction reactions of  $\text{Cu}^{2+}$  to  $\text{Cu}^0$ . In the conventional electroless copper-plating process, ABS surfaces are treated with a mixture of chromic acid and sulfuric acid, and the butadiene component in the ABS material is removed from the ABS material surfaces:

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As a result, the ABS surfaces become rough, and many pits are made on the surfaces. Pd catalysts absorb easily on the roughened surfaces and get into pits on the ABS surfaces. The etching process with a mixture of chromic acid and sulfuric acid is an easy and time-saving process (the etching reactions finish within 15 min);<sup>2</sup> however, the use of chromic acid leads to a new knotty problem, the restriction of the use of certain hazardous substances in electrical and electronic equipment. Because of this demand, a new electroless plating process without an etching process using chromic acid has to be found. Kang and coworkers<sup>3-6</sup> have started a research project in which special functional groups such as vinyl imidazole and vinyl pyridine, which can strongly complex with Pd catalysts, are grafted at the polymer surfaces instead of the etching process. The grafted vinyl imidazole and vinyl pyridine groups complex strongly with Pd catalysts, and Pd catalysts can be fixed at the polymer surfaces without an etching process.

Nitrile groups can be hydrolyzed with hydroxyl ions to be modified into carboxylic acid groups:<sup>7,8</sup>



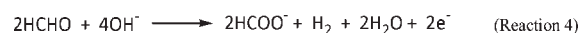
If nitrile groups in the acrylonitrile component of ABS materials are modified into carboxylic acid groups, the carboxylic acid groups can act powerfully as adsorption sites of Pd catalysts. The modified ABS surface is expected to be successful in new metallization without an etching process using chromic acid.

Colloids of Pd/Sn chloride are conventionally used as catalysts for reduction reactions of  $\text{Cu}^{2+}$  to  $\text{Cu}^0$  in the presence of reducing reagents such as formaldehyde in an alkali solution. The use of a Pd catalyst in the electroless copper-plating process also leads to a new and worldwide problem with respect to the availability of precious metals as well as rare earth metals. Therefore, a new catalyst instead of a Pd catalyst is also an emphatic demand of the times.

The electroless copper-plating process involves oxidation-reduction reactions at Pd-catalyst-adsorbed ABS material surfaces. At the cathode surface, copper ions in an electroless plating solution are reduced from  $\text{Cu}^{+2}$  [usually chelated with ethylene diamine tetraacetic acid (EDTA or L) and existing in the form of  $\text{CuL}$  in the solution] to  $\text{Cu}^0$ , and copper metal deposits on the ABS material surfaces:<sup>1</sup>



At the anode surface, formaldehyde, used as a reducing reagent in the electroless plating solution, is oxidized to formic acid:<sup>1</sup>



In the electroless copper-plating process, reactions 3 and 4 occur simultaneously at the surface of the Pd catalyst, copper metal deposits at the Pd catalyst surface, and the copper deposition continues until all surfaces of the Pd catalyst are covered with deposited copper metal. To extend the copper deposition from the area of the Pd-catalyst-adsorbed ABS material surface to that of no-Pd-catalyst-adsorbed ABS material surfaces, it is an essential that the copper metal deposited at the Pd-catalyst-adsorbed ABS material surfaces shows catalytic action in reaction 4 because the Pd catalyst has been already buried under the deposited copper metal and never come into contact with formaldehyde in the electroless plating solution. From this perspective, what reducing reagent is used in reaction 4 is an important factor in the recipe for the electroless copper-plating process. In general, sodium phosphate ( $\text{NaH}_2\text{PO}_2$ ), sodium tetrahydroborate ( $\text{NaBH}_4$ ), dimethylamineborane ( $(\text{CH}_3)_2\text{NHBH}_3$ ), hydrazine ( $\text{NH}_2\text{NH}_2$ ), and formaldehyde ( $\text{HCHO}$ ) are frequently used as reducing reagents in electroless plating, but the other reagents, except for formaldehyde, are ineffective in Cu, Pd, and Ag catalysts.<sup>1</sup> Therefore, formaldehyde is the only reducing reagent for electroless copper plating.

Ag metal, like Pd metal, is applicable as a catalyst in electroless copper-plating reactions. A combination of Ag metal and formaldehyde is expected to be a new recipe for electroless copper plating of ABS materials.

On this basis, we investigated a new recipe for copper electroless plating without chromic acid or a Pd catalyst. The following items were examined:

1. Could nitrile groups of the acrylonitrile component at the ABS material surfaces be hydrolyzed into carboxylic acid groups?
2. What was the important factor for the hydrolysis reactions?

3. Could Ag ions adsorb at sites of carboxylic acid groups hydrolyzed from nitrile groups and initiate reducing reactions of  $\text{Cu}^{+2}$  to  $\text{Cu}^0$  for copper metal deposition?
4. Was there any difference in the adhesion of a deposited copper metal/ABS system between the new process (the hydrolysis of nitrile groups and Ag catalyst) and the conventional process (etching with chromic acid and a Pd catalyst)?

## EXPERIMENTAL

### Materials

ABS (Cyclocac 3001M, UMG ABS, Ltd., Tokyo, Japan) was fabricated into plates ( $50 \times 90 \times 5 \text{ mm}^3$ ) by an injection-molding technique. The plates were washed with ethanol in an ultrasonic washer to remove some contamination from the plate surfaces and were used as specimens for the electroless copper-plating process. An aqueous mixture of copper sulfate, formaldehyde, EDTA, and NaOH was used as an electroless copper-plating solution (OPC-750M-A, OPC-750M-B, and OPC-750M-C, Okuno Chemical Industries Co., Ltd., Osaka, Japan). OPC-80 Catalyst M and OPC-SAL M (Okuno Chemical Industries) were used as Pd catalysts for the electroless copper-plating process.

### Hydrolysis of the ABS material surfaces and electroless copper-plating process

The ABS plates were immersed in an aqueous NaOH solution (7.5–70 wt %) and were hydrolyzed at 65–80°C for 1–96 h. The NaOH solution was stirred with a magnetic stirrer during the hydrolysis process. After the hydrolysis process was finished, the hydrolyzed ABS plates were washed with water to completely remove NaOH from the ABS plate surfaces and then rinsed with a dilute (1M) HCl aqueous solution to exchange Na ions of carboxylate groups for H ions.

The hydrolyzed ABS plates were immersed in an  $\text{AgNO}_3$  aqueous solution (1M) at room temperature for 30 min to adsorb Ag ions at carboxylic acid sites onto the hydrolyzed ABS plate surfaces, and then copper metal deposition started in the electroless copper-plating solution (a mixture of OPC-750M-A, OPC-750M-B, and OPC-750M-C) at room temperature. After the electroless copper-plating process was finished, the ABS plates were rinsed with water, dried, and stored *in vacuo* at room temperature.

### IR spectra of the hydrolyzed ABS material surfaces

Attenuated total reflection (ATR) IR spectra for the hydrolyzed ABS material surfaces were measured in

the ATR mode with a universal ATR attachment with a diamond prism (reflective index = 2.4; Perkin-Elmer, Inc.). A Spectrum One Fourier infrared spectrometer (PerkinElmer Japan Co. Ltd., Yokohama, Japan) was used for the measurement of the IR spectra. The spectra were scanned 64 times in the wave-number range of 4000–680  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ . The analytical depth ( $d_p$ ) for the ATR IR spectra was estimated with eq. (1) to be 0.48–2.97  $\mu\text{m}$  in the wave-number range of 4000–680  $\text{cm}^{-1}$ :

$$d_p = \frac{\lambda}{2\pi[\sin^2 \theta - (n_{21})^2]^{1/2}} \quad (1)$$

where  $\lambda$  is the wavelength of IR light,  $\theta$  is the incident angle of the IR light (45°), and  $n_{12}$  is the reflective index ratio of the diamond prism (reflective index = 2.4) and the hydrolyzed ABS materials (assumed to be 1.55).

### X-ray photoelectron spectroscopy (XPS) and atomic emission spectroscopy (AES) spectra of the hydrolyzed ABS material surfaces

XPS ( $\text{C}_{1s}$ ,  $\text{N}_{1s}$ ,  $\text{O}_{1s}$ , and  $\text{Ag}_{3d}$ ) spectra for the hydrolyzed ABS material surfaces were obtained on an ULVAC-PHI Quantera SXM instrument (ULVAC-PHI, Inc., Chigasaki, Japan) with a monochromatic Al  $K\alpha$  photon source at 400 W and a pressure of  $3.2 \times 10^{-8}$  Pa. To avoid charging of the specimen surface, a neutralizer was operated during the XPS measurements. XPS spectra were recorded at take-off angles of 20 and 45° against the sample surface. The obtained  $\text{C}_{1s}$ ,  $\text{N}_{1s}$ , and  $\text{O}_{1s}$  spectral data were decomposed with a curve-fitting program (PeakFit) supplied by Sea Solve Software, Inc. (Framingham, MA).

AES ( $\text{Ag}_{MNN}$ ) spectra for the hydrolyzed ABS material surfaces also were measured with an Auger JAMP-7810 microprobe (JEOL, Akishima, Japan).

### Contact angles of the hydrolyzed ABS material surfaces

Contact angles of water on the hydrolyzed ABS material surfaces were measured at 20°C with the sessile drop method.<sup>9</sup> A contact-angle meter (model G-1, Erma Co., Ltd., Tokyo, Japan) was used for the measurements. Water used for the measurement was twice-distilled, and the distillation was performed just before the contact-angle measurement.

### Surface topography of the hydrolyzed ABS material surfaces

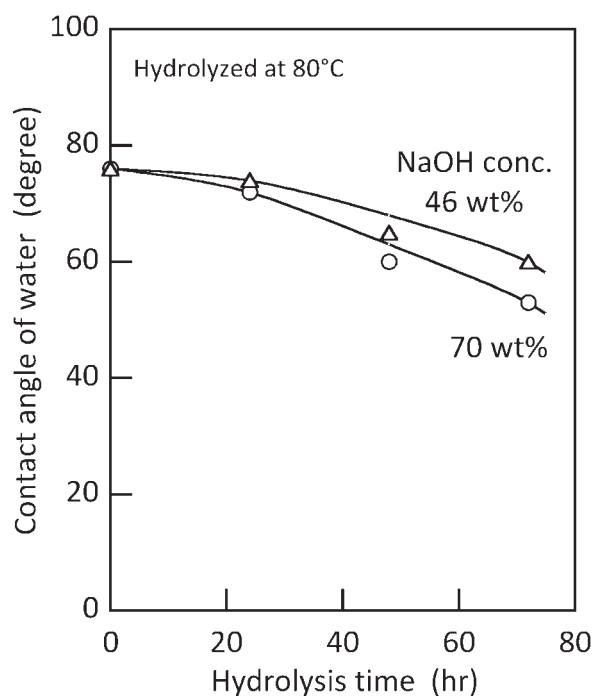
The hydrolyzed ABS material surfaces were scanned with a LEXT OLS3000-IR laser confocal microscope

(Olympus Co., Tokyo, Japan) to evaluate changes in the surface topography. The scanning area was  $1.92 \times 2.56 \text{ mm}^2$ , and two parameters,  $R_a$  and  $R_y$ , which are the average of the surface roughness and the maximum distance between the peak and valley of the roughness, respectively, were estimated from the microscope images.

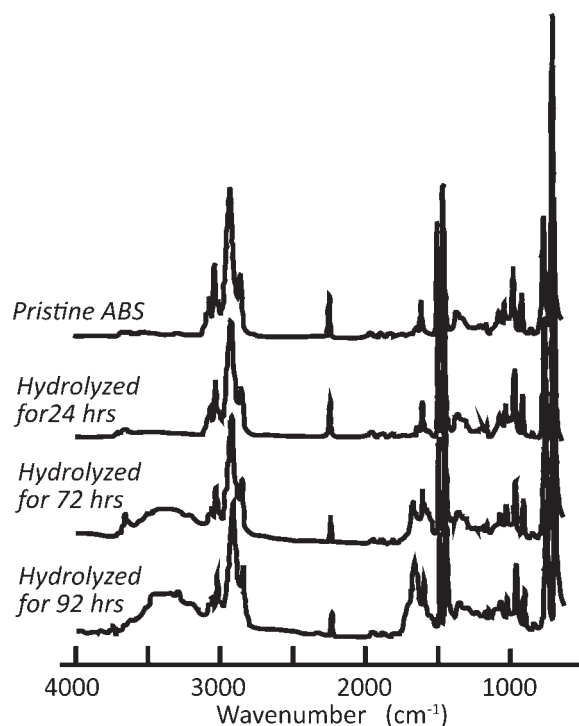
## RESULTS AND DISCUSSION

### Hydrolysis of the ABS material surfaces with an aqueous NaOH solution

The ABS plates were immersed in aqueous NaOH solutions (7.5–70 wt %) at a temperature of 70 or 80°C for 1–96 h to hydrolyze nitrile groups at the ABS plate surfaces. Figure 1 shows typical results for the water contact angle against the ABS plate surfaces hydrolyzed in aqueous NaOH solutions of 46 or 70 wt % at 80°C. As shown in Figure 1, the water contact angle decreased gradually with increasing hydrolysis time. For example, the water contact angle for the ABS plate surface hydrolyzed in an aqueous NaOH solution at 80°C for 72 h decreased from 76 to 53°. Such a decrease in the water contact angle indicates the possibility that some nitrile groups were hydrolyzed into hydrophilic carboxylate and amide groups at the ABS plate surfaces. Figure 2 shows typical ATR IR spectra for the hydrolyzed ABS plate surfaces. The IR spec-



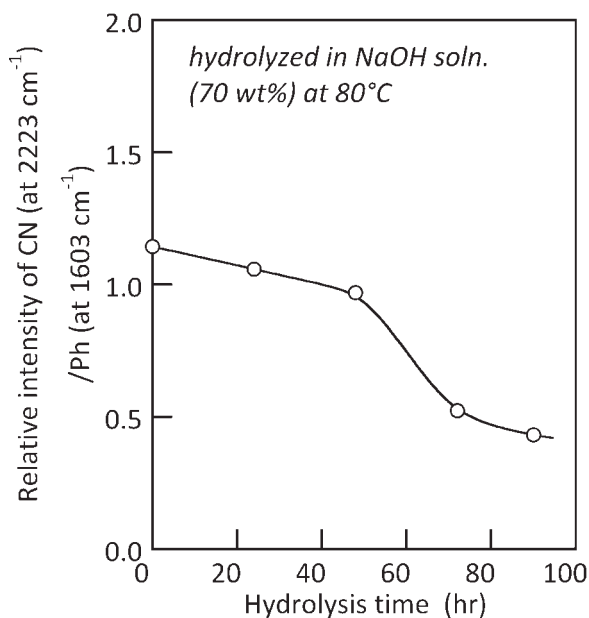
**Figure 1** Contact angle of water on the ABS plate surfaces hydrolyzed in an NaOH (70 wt %) aqueous solution as functions of the hydrolysis temperature and the hydrolysis time.



**Figure 2** ATR IR spectra for the ABS plate surfaces hydrolyzed in NaOH (70 wt %) at 80°C as a function of the hydrolysis time.

trum for the pristine ABS plate surface, as shown in Figure 2, showed intense and characteristic absorptions at 2223, 1450, 1068, and 1028  $\text{cm}^{-1}$  due to the acrylonitrile component, at 3026, 3003, 2927, 967, and 908  $\text{cm}^{-1}$  due to the butadiene component, and at 3026, 3003, 2927, 2850, 1603, 1495, and 1450  $\text{cm}^{-1}$  due to the styrene component.<sup>10,11</sup> For the hydrolyzed ABS plate surfaces, new absorptions appeared at 1666 and 1560  $\text{cm}^{-1}$ , which were assigned C=O stretching vibrations due to C(O)NH<sub>2</sub> and C(O)ONa groups, respectively (Fig. 2). These changes in IR spectra show that nitrile groups were hydrolyzed in an aqueous NaOH solution, and some nitrile groups were modified into amide and carboxylic acid. Figure 3 shows the intensity ratio of the absorptions at 2223 (C≡N groups in the acrylonitrile component) and 1603  $\text{cm}^{-1}$  (phenyl groups in the styrene component) as a function of the hydrolysis time in an NaOH solution (70 wt %) at 80°C. The intensity ratio showed a small decrease until a hydrolysis time of 48 h and afterwards showed a large decrease. The large decrease continued up to a hydrolysis time of 72 h. Therefore, the hydrolysis process of nitrile groups in an aqueous NaOH solution is a time-consuming process, and the hydrolysis modification of ABS plate surfaces needs a long time of at least 72 h.

To investigate what modification in addition to the hydrolysis of nitrile groups occurred at the ABS plate surfaces, C<sub>1s</sub> and N<sub>1s</sub> spectra were scanned at



**Figure 3** Relative intensity ratio of the CN/Ph absorption for the ABS plate surfaces hydrolyzed in NaOH (70 wt %) at 80°C as a function of the hydrolysis time.

take-off angles of 20 and 45° against the ABS specimen faces. Figure 4(a,b) shows the  $C_{1s}$  and  $N_{1s}$  spectra for the pristine ABS plate surface and the ABS plate surface hydrolyzed in an aqueous NaOH solu-

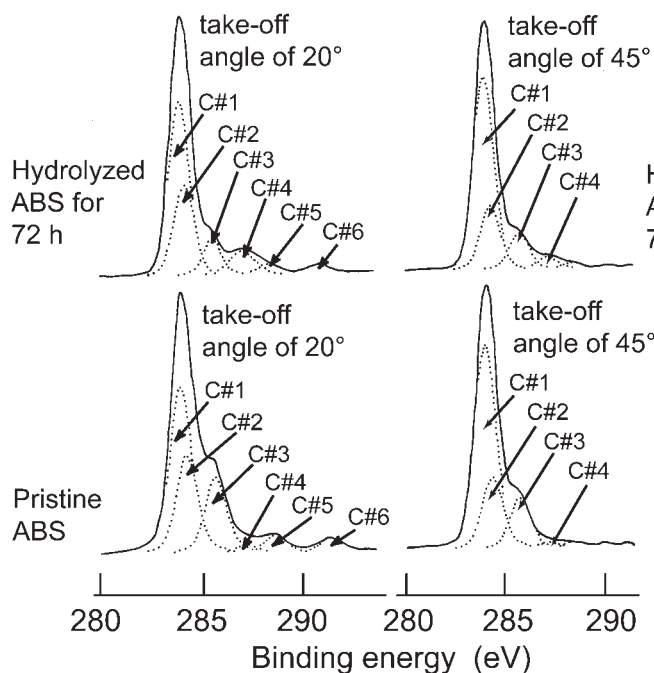
tion of 70 wt % at 80°C for 72 h. The  $C_{1s}$  and  $N_{1s}$  spectra were scanned at different take-off angles of 20 and 45°.  $d_p$  at take-off angle  $\theta$  is shown in the following equation:

$$d_p = 3\lambda \sin \theta \quad (2)$$

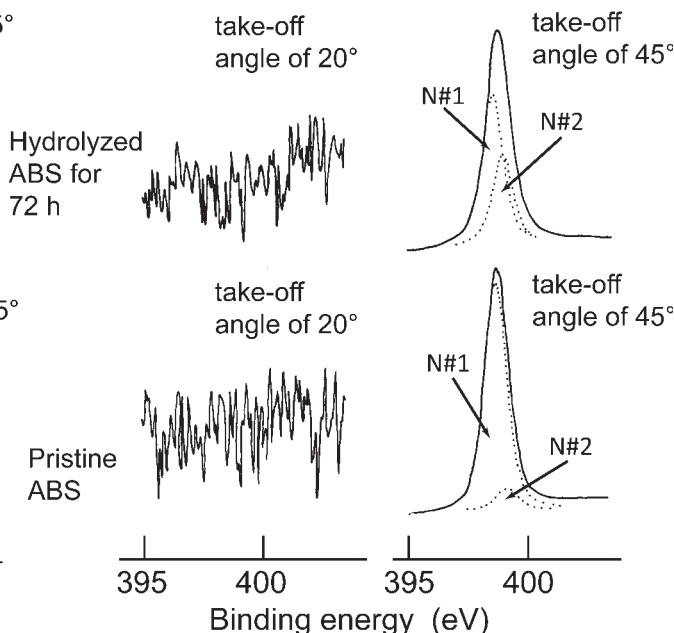
where  $\lambda$  is the inelastic mean free path of the photoelectrons ( $\lambda = 3$  nm for organic polymers). From the estimation at  $\theta$  values of 20 and 45° with eq. (2),  $d_p$  was found to be 3.1 and 6.4 nm, respectively. If the chemical modification occurred at the ABS plate surfaces but did not occur at the inner layer of the ABS plates, the  $C_{1s}$  and  $N_{1s}$  spectra at 20 and 45° would not be the same but would be different. From the comparison of the  $C_{1s}$  and  $N_{1s}$  spectra at 20 and 45°, we can observe how deep the area of the modification was.

The  $C_{1s}$  spectrum at a take-off angle of 20°, as shown in Figure 4(a), was distributed widely from 284 to 292 eV, and the spectrum was decomposed into six  $C_{1s}$  components [at 284.7 eV due to CH groups in aromatic carbons (C#1), at 285.4 eV due to  $CH_2$  and CH groups in aliphatic carbons (C#2), at 286.5 eV due to C—O and C—N groups (C#3), at 287.6 eV due to C=O groups (C#4), at 289.4 eV due to C(O)—O groups (C#5), and at 291.3 eV due to the  $\pi-\pi^*$  shake-up satellite (C#6)].<sup>12-14</sup> On the other hand, the  $C_{1s}$  spectrum at 45°, as shown in

#### $C_{1s}$ spectra



#### $N_{1s}$ spectra



**Figure 4** (a)  $C_{1s}$  spectra (take-off angles = 20 and 45°) for the ABS plate surfaces hydrolyzed in an NaOH (70 wt %) aqueous solution at 80°C for 72 h. (b)  $N_{1s}$  spectra (take-off angles = 20 and 45°) for the ABS plate surfaces hydrolyzed in an NaOH (70 wt %) aqueous solution at 80°C for 72 h.

Figure 4(a), was distributed narrowly, and the spectrum was decomposed into four  $C_{1s}$  components [at 284.7 eV due to CH groups in aromatic carbons (C#1), at 285.4 eV due to  $CH_2$  and CH groups in aliphatic carbons (C#2), at 286.5 eV due to C—O and C—N groups (C#3), and at 287.6 eV due to C=O groups (C#4)].<sup>12–14</sup> Components C#5 and C#6 were not observed on the  $C_{1s}$  spectra at 45°. Similarly, there were remarkable differences between the  $N_{1s}$  spectra observed at take-off angles of 20 and 45°. At a take-off angle of 20°, less  $N_{1s}$  spectrum was observed, but an intense  $N_{1s}$  spectrum was observed at 45°. This discrepancy of the  $N_{1s}$  spectra at 20 and 45° indicates that the ABS plate surfaces were covered with butadiene and styrene components, and the acrylonitrile component never appeared at the topmost layer of the ABS plate. The  $N_{1s}$  spectrum at 45° was composed of a main  $N_{1s}$  component [at 398.7 eV due to  $N\equiv C$  groups (N#1)] and a small  $N_{1s}$  component [at 399.4 eV due to N—C(O) groups (N#2)].<sup>12–14</sup> Even for the pristine ABS plate, some nitrile groups were already hydrolyzed into N—C(O) groups.

The hydrolyzed ABS plate surfaces were different in their atomic composition from the pristine ABS plate surface. The O/C atomic ratios for the hydrolyzed ABS plates were 0.24 and 0.21, which were observed at take-off angles of 20 and 45°. On the other hand, the O/C atomic ratios for the pristine ABS were 0.09 and 0.07 at 20 and 45°, respectively. These large O/C atomic ratios indicate that the ABS plate surfaces were intensely oxidized during the hydrolysis modification. The  $C_{1s}$  spectra for the hydrolyzed ABS plate surfaces, as shown in Figure 4(a), were decomposed into six  $C_{1s}$  components [at 284.7 eV due to CH groups in aromatic carbons (C#1), at 285.4 eV due to  $CH_2$  and CH groups in aliphatic carbons (C#2), at 286.5 eV due to C—O and C—N groups (C#3), at 287.6 eV due to C=O groups (C#4), at 289.4 eV due to C(O)—O groups (C#5), and at 291.3 eV due to the  $\pi-\pi^*$  shake-up satellite (C#6)]. The relative concentration of these  $C_{1s}$  components, especially oxygen-containing components, was different from that for the pristine ABS plate. The C#4 and C#5 components due to C=O and C(O)—O groups,<sup>12–14</sup> respectively, increased from 3 to 6–8%, and the C#3 component due to C—O and C—N groups decreased from 19 to 10%. The  $N_{1s}$  spectrum at 45° for the hydrolyzed ABS plate surfaces, as shown in Figure 4(b), was composed of N#1 and N#2 components at 398.7 eV due to  $N\equiv C$  groups and at 399.2 eV due to NC(O) groups, respectively.<sup>12–14</sup> Their relative concentrations were 59 and 41%. On the other hand, the N#1 and N#2 components for the pristine ABS plate surfaces were 93 and 7%, respectively. This comparison indicates that some nitrile groups were modified into amide groups. An amide group, as shown in reaction 2, is

a precursor of a carboxylic acid group in hydrolysis reactions of nitrile groups.

From the experimental results of ATR IR spectra and XPS spectra for the hydrolyzed ABS plate surfaces, we can conclude that some nitrile groups at the ABS plate surfaces were hydrolyzed in aqueous NaOH solutions into carboxylic acid groups.

### Electroless copper plating on the hydrolyzed ABS material surfaces

The hydrolyzed ABS plate surfaces were immersed in an aqueous  $AgNO_3$  solution, and Ag ions were adsorbed at carboxylate sites at the hydrolyzed ABS plate surfaces. Afterwards, the copper metallization was carried out in an electroless copper-plating solution (a mixture of OPC-750M-A, OPC-750M-B, and OPC-750M-C) at room temperature. Results of the copper metallization are summarized in Table I. Not all of the hydrolyzed ABS plate surfaces, as shown in Table I, succeeded in copper metallization, but some did. The concentration of the NaOH solution and the hydrolysis temperature and time were important factors for success in copper metallization. Hydrolysis modification in aqueous NaOH solutions of 46–70 wt % at 70–80°C for more than 24 h was successful in copper metallization (Table I). Furthermore, adhesion between the deposited copper metal and the ABS plate surfaces was evaluated by the Scotch tape test, and the results are summarized in Table I. The ABS plate surfaces modified in an aqueous NaOH solution of 70 wt % at 80°C for 72 h showed perfect adhesion (shown as +++ in Table I) between the deposited copper metal and ABS plate surface, but the modification in an NaOH solution of less than 70 wt % at 70°C or for a short hydrolysis time of less than 72 h failed to achieve perfect adhesion (Table I). We believe that factors such as the NaOH concentration, hydrolysis temperature, and hydrolysis time may be closely related to the modification of nitrile groups into carboxylic acid groups. Furthermore, how Ag atoms are adsorbed at the modified ABS plate surfaces may be important in copper metallization.

The chemistry of Ag atoms adsorbed at the modified ABS plate surfaces was investigated with XPS and AES spectroscopy. Figure 5(a,b) shows typical  $Ag_{3d}$  XPS and  $Ag_{MNN}$  AES spectra for Ag atoms adsorbed at the ABS plate surfaces. The ABS specimens used for XPS and AES analyses were hydrolyzed in an aqueous NaOH solution of 70 wt % at 80°C for 72 h and then immersed in a 1M aqueous  $AgNO_3$  solution. The XPS spectra showed that the Ag/C atomic ratio was 0.07, and  $Ag_{3d5/2}$  and  $Ag_{3d3/2}$  spectra appeared at 367.4 and 373.1–373.5 eV,<sup>15–18</sup> respectively. The  $Ag_{3d5/2}$  and  $Ag_{3d3/2}$  spectra demonstrated the existence of Ag atoms but did not

**TABLE I**  
**Electroless Copper Plating on the Hydrolyzed ABS Plate Surfaces and the Scotch Tape Test for the Electroless Copper-Plated ABS Plate Surfaces**

Hydrolysis reagent		Hydrolysis condition		Electroless copper plating	Scotch tape test <sup>a</sup>
NaOH concentration (wt %)	Dioxane concentration (wt %)	Hydrolysis temperature (°C)	Hydrolysis time (h)		
7.5	0	70	96	No	
15	0	70	96	No	
23	0	70	96	No	
46	0	70	96	Yes	+
70	0	70	24	Yes	+
70	0	70	48	Yes	+
70	0	70	72	Yes	+
70	0	70	96	Yes	+
7.5	0	80	96	No	
15	0	80	96	No	
23	0	80	96	No	
46	0	80	96	Yes	++
70	0	80	24	Yes	++
70	0	80	48	Yes	++
70	0	80	72	Yes	+++
70	0	80	96	Yes	+++
35	10	65	0.5	Yes	+++
35	10	70	0.5	Yes	+++

<sup>a</sup> Evaluation of the adhesion of copper metal to ABS by the Scotch tape test (number of unremoved cross-hatched squares of  $1 \times 1 \text{ mm}^2/100$  squares). + = 1–50/100; ++ = 51–99/100; +++ = 100/100.

show the chemistry of the absorbed Ag atoms because there was no chemical shift in the binding energy between  $\text{Ag}^0$  and  $\text{Ag}^+$  species.<sup>15–18</sup> On the other hand, the  $\text{Ag}_{\text{MNN}}$  spectrum gave useful information on the chemistry of the absorbed Ag atoms. The  $\text{Ag}_{\text{MNN}}$  spectrum, as shown in Figure 5(b), was distributed widely with two peaks, and the spectrum was decomposed into two components at 353.5 and 357.3 eV, which were assigned to  $\text{Ag}^+$  and  $\text{Ag}^0$  atoms, respectively.<sup>15–18</sup> The relative concentrations of the  $\text{Ag}^+$  and  $\text{Ag}^0$  atoms were 61 and 39%, respectively.

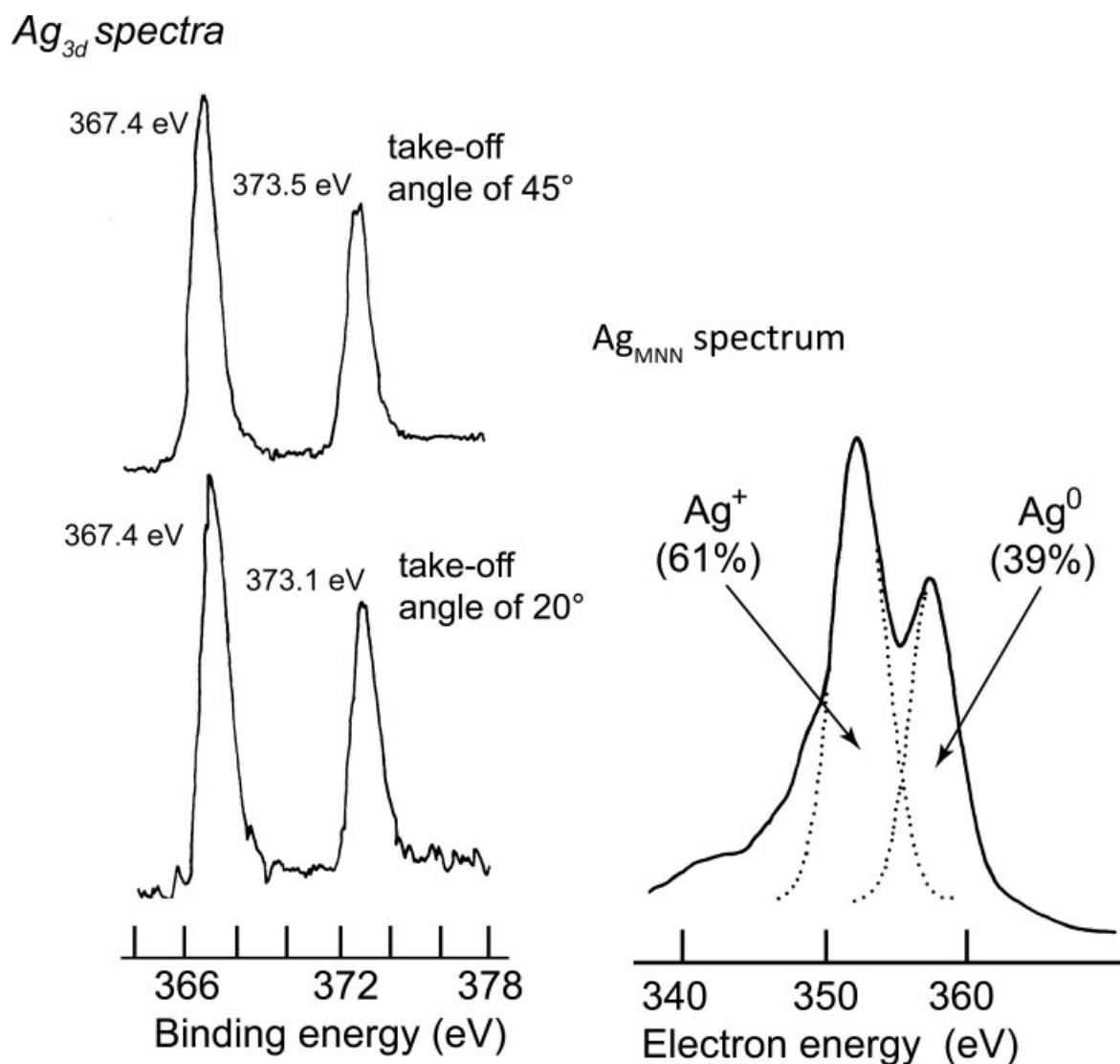
From these experimental results, we can conclude the following:

1. A new surface modification without an etching treatment using chromic acid was proposed for copper metallization of ABS plate surfaces.
2. The modification was accomplished in an aqueous NaOH solution (70 wt %) at 80°C for 72 h.
3. The hydrolyzed ABS plate surfaces were successfully metalized by electroless copper plating.
4. An Ag catalyst instead of a Pd catalyst was proposed for the electroless copper-plating process.
5. Adhesion between the deposited copper metal and ABS plate surface was perfect for the Scotch tape test.

#### Acceleration of the hydrolysis process of the ABS material surfaces

As discussed in the previous section, the hydrolysis modification of ABS plate surfaces in an aqueous NaOH solution was effective in electroless copper plating. Adhesion between the deposited copper metal and ABS plate was perfect and inferior to that for ABS plates metalized by a conventional electroless copper-plating process, which used both an etching process with chromic acid and a Pd catalyst. From this viewpoint, the new electroless copper-plating process, which is a combination of the hydrolysis modification of ABS plate surfaces and an Ag catalyst instead of a Pd catalyst, can be practically applied in the field of metallization of door mirrors, front grilles, and so forth. However, the hydrolysis modification is a time-consuming process and needs a long time for 72 h. We believe that this time-consuming modification may be a large problem for practical applications. The hydrolysis modification of ABS plate surfaces should be accomplished within 1 h for practical applications in the electroless copper-plating process. We have investigated a new process for the hydrolysis modification of ABS plate surfaces.

The  $\text{N}_{1s}$  spectra for the pristine ABS plate surfaces [Fig. 4(b)] indicate an important aspect of the

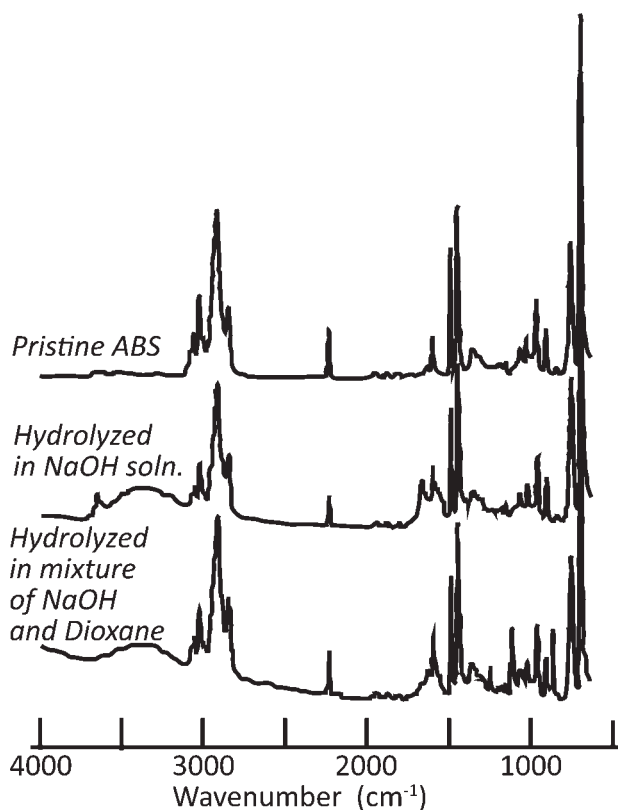


**Figure 5** (a) Ag<sub>3d</sub> spectra (take-off angles = 20 and 45°) for the ABS plate surfaces hydrolyzed in an NaOH (70 wt %) aqueous solution at 80°C for 72 h and immersed in an AgNO<sub>3</sub> (1M) aqueous solution for 30 min. (b) Ag<sub>MNN</sub> spectra for the ABS plate surfaces hydrolyzed in an NaOH (70 wt %) aqueous solution at 80°C for 72 h and immersed in an AgNO<sub>3</sub> (1M) aqueous solution for 30 min.

chemistry of ABS plate surfaces. Less N<sub>1s</sub> spectrum appeared at a take-off angle of 20°, but an intense N<sub>1s</sub> spectrum appeared at 45°.  $d_p$  at 20 and 45° was estimated with eq. (2) to be 3.1 and 6.4 nm, respectively. A comparison of the N<sub>1s</sub> spectra at 20 and 45° indicates that the topmost layer of the ABS surfaces was completely covered with butadiene and styrene components of the ABS plates, and nitrile groups of the acrylonitrile component existed at a depth of 3.1 nm from the face of the ABS surfaces. Therefore, to accelerate hydrolysis reactions of nitrile groups at the ABS plate surfaces, the butadiene and styrene components, which aggregate at the ABS plate surfaces, should be removed from the surfaces, and hydroxyl ions in an aqueous NaOH solution should be able to easily access nitrile groups in the ABS plates. To remove the butadiene and styrene compo-

nents aggregated at the ABS surfaces, dioxane, the solubility parameter of which is similar to those of polybutadiene and polystyrene, was added to the aqueous NaOH solution. The solubility parameters of dioxane, polybutadiene, and polystyrene were 10.0, 8.4–8.6, and 8.56–10.3 cal<sup>1/2</sup>/cm<sup>3/2</sup>,<sup>19</sup> respectively. Aqueous mixtures of 35% NaOH and 5–10% dioxane were used as hydrolysis reagents, and the hydrolysis modification was carried out at 65 and 70°C for 30 min. Figure 6 shows a typical ATR IR spectrum for the ABS plate surfaces, which were hydrolyzed in a mixed aqueous solution of NaOH (35 wt %) and dioxane (10 wt %) at 65°C for 30 min. Intense absorptions appeared at 1666 and 1560 cm<sup>-1</sup> due to C=O stretching vibrations of C(O)NH<sub>2</sub> and C(O)ONa groups,<sup>10,11</sup> respectively, and the absorption at 2223 cm<sup>-1</sup> due to C≡N groups became weak





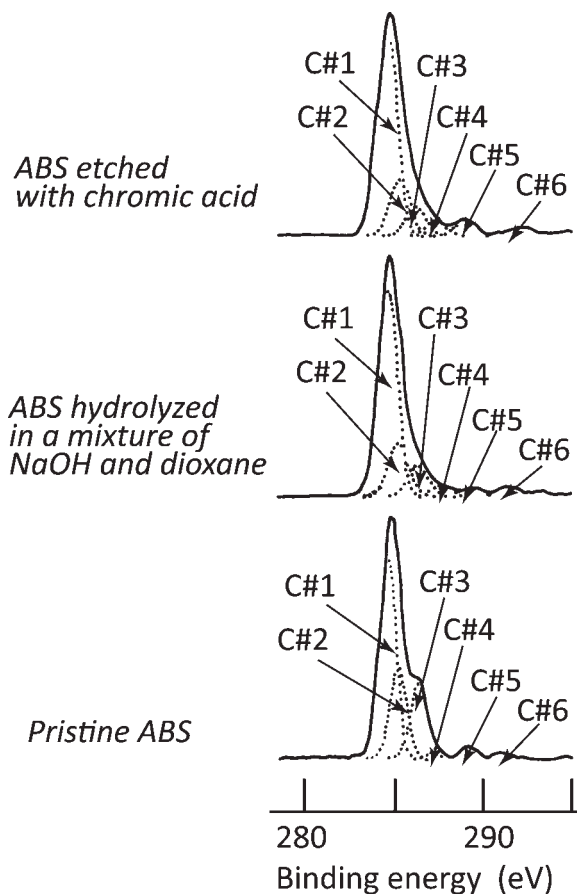
**Figure 6** ATR IR spectra for the ABS plate surfaces hydrolyzed in a mixture of NaOH (35 wt %) and dioxane (10 wt %) at 65°C for 30 min and the ABS surfaces hydrolyzed in an NaOH (70 wt %) aqueous solution at 80°C for 72 h.

in its absorption intensity. These changes in IR absorption are similar to those for the ABS plate surfaces that were hydrolyzed in an aqueous NaOH solution (70 wt %) at 80°C for 72 h (Fig. 6); this indicates that nitrile groups on the ABS plate surface were successfully modified into carboxylate and amide groups when dioxane was used as a supplement reagent, even though the NaOH concentration in the hydrolysis process was lowered from 70 to 35 wt % and the hydrolysis temperature also was dropped from 80 to 65°C. Copper metallization of these hydrolyzed ABS plate surfaces succeeded, and the adhesion between the deposited copper metal and ABS surfaces was perfect (Table I). Therefore, we can conclude that a new hydrolysis process using an aqueous mixture solution of NaOH and dioxane as a hydrolysis reagent is practically applicable.

The ABS plate surfaces, hydrolyzed in an aqueous mixture solution of NaOH and dioxane at 65°C for 30 min, were scanned with XPS to elucidate what modification was carried out in the new hydrolysis process. The  $C_{1s}$  spectra for the ABS plate surfaces hydrolyzed in an aqueous mixture solution of NaOH (35 wt %) and dioxane (10 wt %) at 65°C for 30 min are shown in Figure 7. The  $C_{1s}$  spectrum was

composed of six  $C_{1s}$  components (C#1–C#6), and there were large increases in the C#4 and C#5 components at 287.6 and 289.4 eV due to C=O and C(O)—O groups<sup>12–14</sup> and a decrease in the C#3 component at 286.5 eV due to C—O and C—N groups. These changes are similar to those for the ABS plate surfaces hydrolyzed in an aqueous NaOH solution (70 wt %) at 80°C for 72 h [shown in Fig. 4(a)]. From these spectral results, we can conclude that dioxane contributed to the easy access of hydroxyl ions to nitrile groups and to the accelerated hydrolysis modification of the ABS plate surfaces. Therefore, modification using an aqueous mixture solution of NaOH (35 wt %) and dioxane (10 wt %) at 65°C for 30 min is practically acceptable as a modification process for copper metallization.

Finally, the surface roughness for the hydrolyzed ABS plate surfaces was investigated. The surface roughness is believed to be closely related to adhesion between deposited copper metal and ABS surfaces. In the conventional electroless copper-plating process, ABS surfaces are etched with chromic acid to remove the butadiene component on the ABS



**Figure 7**  $C_{1s}$  spectra for the ABS plate surfaces hydrolyzed in a mixture of NaOH (35 wt %) and dioxane (10 wt %) at 65°C for 30 min and the ABS surfaces etched with chromic acid.

**TABLE II**  
**Surface Roughnesses ( $R_a$  and  $R_y$ ) of the ABS Plate Surfaces Hydrolyzed in an Aqueous Mixture Solution of NaOH and Dioxane and in an NaOH Aqueous Solution and the ABS Surfaces Etched with Chromic Acid**

Modified ABS surfaces	Surface roughness (nm)	
	$R_a$	$R_y$
Pristine ABS	1.69	50
ABS surfaces hydrolyzed in a mixture solution of NaOH (35 wt %) and dioxane (10 wt %) at 65°C for 30 min	1.32	65
ABS surfaces hydrolyzed in an NaOH (70 wt %) aqueous solution at 80°C for 72 h	4.00	71
ABS surfaces etched with a chromic acid solution at 70°C for 15 min	1.59	73

surfaces by oxidation reactions (reaction 1) and to make nanometer-size pores on the ABS surfaces. These nanometer-size pores act as mechanical interlocking sites (anchor effect)<sup>20</sup> of deposited copper metal and also as adsorption sites of Pd catalysts. Therefore, adhesion between the deposited copper metal and ABS surfaces is closely related to how the ABS surfaces are etched.

ABS plate surfaces hydrolyzed in an aqueous mixture of NaOH (35 wt %) and dioxane (10 wt %) at 65°C for 30 min were scanned within an area of  $1.92 \times 2.56 \text{ mm}^2$  with a laser confocal microscope, and the surface roughness, represented by  $R_a$  and  $R_y$  (the average of the surface roughness and the maximum distance between the top and bottom of the nanosize pores, respectively), were compared with those for the ABS plate surface modified with an aqueous NaOH (70 wt %) solution at 80°C for 72 h and the ABS plate surface etched with chromic acid (Table II). The hydrolysis modification using the mixture of NaOH and dioxane led to small changes in  $R_a$  and  $R_y$ :  $R_a$  and  $R_y$  were 1.32 and 65 nm, respectively, and those for the pristine ABS surface were 1.69 and 50 nm, respectively. On the other hand, the hydrolysis modification in the aqueous NaOH (70 wt %) solution alone led to large increases in  $R_a$  and  $R_y$ .  $R_a$  and  $R_y$  were 4.00 and 71 nm, respectively. The etching treatment with chromic acid also made the ABS plate surface rough.  $R_y$  was 73 nm. This comparison indicates that the ABS plate surface modified in the mixture of NaOH and dioxane was not as rough as those modified in the aqueous NaOH (70 wt %) solution or those treated with chromic acid. Therefore, chemical interactions between copper metal and functional groups such as C=O groups at the hydrolyzed ABS plate surface rather than an anchor effect may contribute to good adhesion between the deposited copper metal and ABS plate surface.

## CONCLUSIONS

The hydrolysis modification of nitrile groups at ABS plate surfaces was investigated to find a new recipe for the copper metallization of ABS plate surfaces without an etching treatment using chromic acid and also a new catalyst to replace Pd catalysts. The results can be summarized as follows:

1. The hydrolysis modification of nitrile groups at ABS plate surfaces into carboxylic acid groups was successfully performed in an aqueous NaOH (70 wt %) solution at 80°C for more than 72 h. The hydrolyzed ABS plate surface was able to be metalized by the electroless copper-plating technique.
2. The hydrolysis modification was accelerated by the addition of dioxane as a supplement to the aqueous NaOH solution. The hydrolysis modification was completely performed in an aqueous mixture solution of NaOH (35 wt %) and dioxane (10 wt %) at 65°C for 30 min.
3. The ABS plate surfaces modified in the mixture of NaOH and dioxane succeeded in copper metallization. An Ag catalyst instead of a Pd catalyst was usable in the electroless copper-plating process. Adhesion between the deposited copper metal and ABS plate surface was perfect for the Scotch tape test.
4. The chemistry of Ag atoms adsorbed on the hydrolyzed ABS plate surface was a mixture of  $\text{Ag}^0$  and  $\text{Ag}^+$  species, of which the relative concentrations were 35 and 65%, respectively.  $\text{Ag}^0$  species may act as a catalyst for reducing reactions of  $\text{Cu}^{+2}$  to  $\text{Cu}^0$  for copper metal deposition.

From these experimental results, we can propose a new recipe for the copper metallization of ABS plate surfaces without an etching process using chromic acid and without a Pd catalyst.

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