Conventional methods in electroless plating of resin involve surface modification to generate carboxylate moieties that enhance palladium catalyst adsorption. To further enhance palladium adsorption, a variety of Pd(II) amino acid complexes were synthesized, which bear a cationic pendant group with affinity for the carboxylate generated on the resin surface. As a result, an electroless plating catalyst was fabricated. The Pd(II) complexes were characterized using UV-vis spectroscopy, revealing chelation of the amine and carboxylate groups of amino acids to Pd(II). For the Pd(II) complexes of Arginine or Lysine, affinity of the cationic pendant groups to resin surface carboxylate groups was suggested by enhanced Pd adsorption, ca. 80 fold increase compared to complexes without cationic moieties. Furthermore, even under mild surface modification conditions with 0.5 mol/dm$^3$ KOH, the Pd(II) complexed with Arginine or Lysine displayed performance as a electroless Ni catalyst, allowing for electroless copper plated laminates of 1 kN/m adhesion strength.

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Electroless Plating Catalyst Performance of a Cationic Moiety Bearing Palladium Complex

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Experimental

Synthesis of the Pd(II)-bisamino acid complexes.— Palladium(II) chloride (0.01 mol) was dissolved in hydrochloric acid (0.02 mol) at 70 °C, then diluted with 0.9 dm$^3$ deionized water. Then amino acid (0.022 mol) was added and following, the pH was adjusted to 7–8 with potassium hydroxide before dilution with deionized water to give 1 dm$^3$ solution of Pd (II)-amino acid complex. Amino acids used were glycine (Gly), L-alanine (Ala), L-serine (Ser), L-histidine (His), L-cysteine (Cys), L-monosodium glutamate monohydrate (Glu), L-arginine hydrochloride (Arg), and L-lysine (Lys).

Characterization of the Pd (II)-bisamino acid complexes.— The coordination geometry of the Pd(II)-bisamino acid complexes were verified by UV-vis spectroscopy. UV-vis and near-infrared spectra of 2 mmol/dm$^3$ samples in 1 cm quartz cells were attained using a Shimadzu Co. SolidSpec-3700 spectrophotometer.

Polyimide film surface modification methods.— Control of the modified layer depth and amount of generated carboxylate groups on polyimide (PI) film surfaces by cleavage of the imide rings giving with hydroxide ions to form polyamide carboxyl groups (Fig. 2) has been demonstrated. Immersion of PI film (Toray-Du Pont, Kapton 150EN-C) in aqueous 0.5 mol/dm$^3$ or 5.0 mol/dm$^3$ potassium hydroxide (KOH) solution at 50 °C for 2 min was performed for preparation the two types of modified surface. Surface modification was verified by Fourier transform infrared spectrophotometry (FT-IR) on a JASCO Co. FT/IR-6100 using the one-time attenuated total reflection method (ATR). Germanium was used as the ATR crystal, and measurements were taken at an incidence angle of 45°.

Surface modification of acrylonitrile, butadiene, and styrene copolymer (ABS) resin (UMG ABS Co. 3001 M series) was carried out by treatment in a solution of potassium permanganate (2 g/L) and 85% phosphoric acid (0.7 dm$^3$) at 35 °C for 10 min. Formation of the modified layer was verified using scanning X-ray photoelectron spectrophotometry (XPS) on an ULVAC-PHI Co. PHI Quantera SXM spectrophotometer.

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Electroless plating using the Pd (II) complexes as the plating catalyst.— Surface modified PI film was plated using the electroless nickel plating bath and sequential process specified in Table I. Surface modified ABS substrate was plated using the electroless nickel plating bath and sequential process specified in Table II. Plating performance was verified by visual inspection. Using the Pd(II)-Arg2 complex, plating selectivity was confirmed by comparison to PI and ABS samples that had not been modified.

**Evaluation of the plating adhesion.**— Electroless nickel plated PI or ABS film samples, which were dried at 150°C for 2 min, were then subsequentially treated with 10 wt% sulfuric acid at 25°C for 30 min to activate the nickel surface before electrolytic plating of a 20 μm copper film using the standard commercially available JCU Co. CUBRITE RF plating bath. 10 mm wide patterns were then formed by etching the plated samples with ferric chloride solution, for which the 90° peel strength in accordance with JIS C 6471 were measured.

**Measurement of the amount of palladium adsorbed.**— Pd was adsorbed onto surface modified PI film samples by immersion in the Pd(II) complex solutions at 50°C for 5 min. Next, adsorbed Pd was extracted with aqua regia (conc. hydrochloric acid : conc. nitric acid = 3 : 1), and the amount of Pd in each extract was measured using a Shimadzu Co. high frequency plasma spectrometer.

**Adsorption conditions of the Pd(II)-amino acid complexes.**— To study the adsorption mechanism of the Pd(II)-amino acid complexes onto surfaces modified by treatment in 5 mol/dm³ potassium hydroxide at 50°C for 15 min. (immerged in the water solution of a range of Pd (II)-amino acid complex of 1 mmol/dm³ at 50°C for 1 h)

The setting of the surface modification treatment time at 15 min was intended to obtain a clear FTIR-ATR spectra of the Pd (II) complex in a modified layer (Fig. 3). Longer surface modification time than 15 min was verified to cause C=O symmetric stretching vibration (1776 cm⁻¹), which derives from the imide ring of PI, and C=O antisymmetric stretching vibration (1718 cm⁻¹) to disappear completely, instead allowing COO symmetric stretching vibration (1410 cm⁻¹), which derives from the carboxylate group of polyamic acid resulting from modification, and COO antisymmetric stretching vibration (1576 cm⁻¹) to appear, thus making it possible to obtain the spectrum of polyamic acid only. This will much help assessing the adsorbed condition of polyamic acid and various Pd (II)-amino acid complexes.9,10

**Results and Discussion**

**Characterization of the Pd(II)-bisamino acid complexes.**— Pd(II)-bisamino acid complexes were prepared and coordination structure identified by UV-vis spectroscopy. The resulting UV-vis spectra are as

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**Table I. Plating process of the Polyimide film.**

| Process                      | Solution composition | Concentration | Temperature | Time |
|------------------------------|----------------------|---------------|-------------|------|
| Surface modification         | Potassium hydroxide  | 0.5, 5 mol/dm³ | 50°C        | 2 min. |
| Catalyzing                   | Amino acid Pd (II) complex | 1 mmol/dm³ | 50°C        | 2 min. |
| Reduction                    | Sodium borohydride   | 50 mmol/dm³   | 40°C        | 2 min. |
| Electroless nickel plating   | Nickel sulfate hexahydrate | 0.1 mol/dm³ | 40°C        | 5 min. |
|                             | Ammonium citrate tribasic | 0.1 mol/dm³ |             |      |
|                             | Sodium hypophosphite monohydrate | 0.2 mol/dm³ |             |      |
|                             | Sodium hydroxide     | Adjusted to pH = 8 |             |      |

**Table II. ABS resin plating process.**

| Process                      | Solution composition | Concentration | Temperature | Time |
|------------------------------|----------------------|---------------|-------------|------|
| Surface modification         | Potassium permanganate | 2 g/dm³     | 35°C        | 10 min. |
|                             | 85% phosphoric acid  | 0.7dm³/dm³   |             |      |
| Catalyzing                   | Amino acid Pd (II) complex | 1 mmol/dm³ | 50°C        | 2 min. |
| Reduction                    | Sodium borohydride   | 50 mmol/dm³   | 40°C        | 2 min. |
| Electroless nickel plating   | Nickel sulfate hexahydrate | 0.1 mol/dm³ | 40°C        | 5 min. |
|                             | Ammonium citrate tribasic | 0.1 mol/dm³ |             |      |
|                             | Sodium hypophosphite monohydrate | 0.2 mol/dm³ |             |      |
|                             | Sodium hydroxide     | Adjusted to pH = 8 |             |      |
shown in Fig. 4, and the wavelengths of maximum absorption, $\lambda_{\text{max}}$, are listed in Table III. Aqueous solutions of the Pd(II) complexes of Gly, Ala, Ser, Glu, Arg, and Lys were transparent, light yellow in color and had similar absorption spectra with a $\lambda_{\text{max}}$ of about 320 nm. Ohata, Yamauchi and others have reported the molecular structure and $\lambda_{\text{max}}$ for the Pd(II)-Arg$_2$ complex.\textsuperscript{7,8} A N$_2$O$_2$ type tetra-coordinated square planner geometry where the amino and carboxylate moieties of Arg were coordinated to the Pd(II) center had been proven. As the value of $\lambda_{\text{max}}$ depends on the electronic environment of Pd(II) center, the coordination geometry of all the Pd(II) complexes prepared here should also have the same geometry. In contrast, the Pd(II)-Cys$_2$ complex solution was orange and the Pd(II)-Cys$_2$ and Pd(II)-His$_2$ complexes differed in $\lambda_{\text{max}}$. This suggested that these two complexes possessed a different structure, possibly where the Pd(II) center was coordinated by the thiol or imidazole moiety, respectively. If the chelation effect is involved, it can be assumed that His has a square planner geometry of the N$_4$ type, where the amino and imidazole groups coordinate to Pd(II) and that Cys had an N$_2$S$_2$ type coordination. In both cases, the carboxylate group may have been free. Although His is one of the basic amino acids, it has been found not to form a geometry as the design guideline dictates. The proposed structures of the Pd(II) complexes is illustrated in Fig. 5. The neutral free pendant groups of Gly-Ala-Ser should not coordinate with Pd(II) ions. The amino acids,
His, Cys and Glu bear anionic pendant groups, and Arg and Lys bear cationic pendant groups.

**Surface modification of substrate materials.**—The surface of PI film was modified with KOH under mild or strong conditions as to obtain substrate materials having two varied amounts of carboxylate moieties. FTIR-ATR spectra of PI film before and after the surface modification treatments are shown in Fig. 6, and differential variation due to the modification treatments in Fig. 7. As can be seen in Fig. 6 and 7, the spectrum of PI treated with 0.5 mol/dm$^3$ KOH was proportionally less altered in the vicinity of 1500 to 1700 cm$^{-1}$ and 2500 to 3500 cm$^{-1}$ than that of PI treated with 5.0 mol/dm$^3$ KOH. The symmetric stretching vibrations of imide rings at 1776 cm$^{-1}$ and 1714 cm$^{-1}$ were attenuated. The absorption of amides I and II attributed to polyamic acid at 1640 cm$^{-1}$ and 1556 cm$^{-1}$, respectively, and the absorption of anti-symmetric stretching vibration and symmetric stretching vibration of carboxylate groups at 1580 cm$^{-1}$ and 1409 cm$^{-1}$, respectively, were intensified. These spectral alterations suggested that treatment even with 0.5 mol/dm$^3$, KOH led to formation of polyamic acid. We also experimented ABS resin, its surface with a permanganate-phosphoric acid mixture solution to produce carboxylate groups. Fig. 8 shows the XPS spectrum (C1s) of ABS resin surface after modification treatment. Attenuation of the ABS C-C bond peaks at 289.0 eV of ABS resin and intensification of carbonyl peaks at 287.6 eV and carboxylate peaks at 289.0 eV due to modification was confirmed.

**Performance of the palladium complexes as a catalyst for plating.**—The Pd(II)-amino acid complexes were evaluated as a catalyst source for the electroless nickel plating process. Images of samples are shown in Table IV. With the strong modification condition, catalyst adsorption from the neutral and cationic pendent bearing complex solutions resulted in autocatalytic deposition, while under the mild modification condition, only catalyst adsorption from the cationic pendent bearing complex solutions did. The amount of palladium adsorbed by modified PI from each complex solution, shown

| Surface modification | Neutral pendant group | Anionic pendant group | Cationic pendant group |
|----------------------|-----------------------|-----------------------|------------------------|
|                      | Gly   | Ala | Ser | Cys | Glu | His | Arg | Lys |
| 0.5 mol/dm$^3$-KOH   | ![Image] | ![Image] | ![Image] | ![Image] | ![Image] | ![Image] | ![Image] | ![Image] |
| 5.0 mol/dm$^3$-KOH   | ![Image] | ![Image] | ![Image] | ![Image] | ![Image] | ![Image] | ![Image] | ![Image] |
Table V. Palladium adsorbed amount on the modified PI film.

| Ligand | Palladium adsorbed amount |     |
|--------|---------------------------|-----|
| Gly    | 0.005 mg/dm²              |     |
| Ala    | 0.004 mg/dm²              |     |
| Ser    | 0.005 mg/dm²              |     |
| Cys    | Undetectable              |     |
| Glu    | Undetectable              |     |
| His    | Undetectable              |     |
| Arg    | 0.458 mg/dm²              |     |
| Lys    | 0.351 mg/dm²              |     |

in Table V, corresponds to the electroless Ni plating results, showing increased Pd adsorption from cationic, less from neutral, and negligible Pd adsorption from anionic pendant bearing complex solutions. The correlations of catalytic activity and palladium adsorption to the anionic-neutral-cationic gradient supported the proposed concept of attractive and repulsive electronic interactions between catalyst and surface, and illustrated the ability to tune palladium adsorption and therefore catalytic activity based on the interaction.

Next, the PI samples on which nickel deposition occurred, 20 μm thick copper films were electrolytically deposited and 90° peeling strengths measured for which results are displayed in Table VI. Under the strong modification condition with 5.0 mol/dm³ KOH, were all c.a. 0.7 kN/m and c.a. 1 kN/m under the mild modification condition with 0.5 mol/dm³ KOH, thus no noticeable relation to electronic nature of the Pd complex and adhesion was observed. Adhesion strength was found to be more influenced by the modification condition. This dependency can be attributed to modified surface structure, the imide ring cleaved polyamate material was not as tough as the PI material, breakage would occur more easily in the modified material. Therefore, the ability to plate on a mildly treated surface, made possible by the electronic interaction between the cationic Pd complex and anionic carboxylate surface groups, allowed stronger adhesion.

Plating selectivity has an impact on industrial process productivity. High affinity of cationic pendant bearing Pd-complex for modified anionic surfaces was found found to improve selectivity. The selectivity of Pd(II)-Lys₂ is illustrated in Fig. 9, where no plating was observed on the untreated surface. ABS resin is a common base material for automobile parts and faucets. However as can be observed in Fig. 10, deposition on the jig was circumvented by taking advantage of the cationic-anionic affinity.

Adsorbed condition of the Pd (II)-amino acid complex on a modified surface.—To verify the adsorption of various Pd (II)-amino acid complexes on a modified surface, samples after catalyzing process were measured by FTIR-ATR, and was illustrated in Fig. 11. Differential spectra as compared with PI spectra after modifying surfaces on which no Pd (II)-amino acid complex adsorbed are shown in Fig. 12. Those samples which exhibited a difference from the
Figure 12. Differential spectra of Pd (II) spectra adsorbing on a PI film. (a) Gly, (b) Ala, (C) Ser, (d) Cys, (e) Glu, (f) His, (g) Arg, (h) Lys.

spectra of surface-modified PI were Arg and Lys having cationic pendant groups. In these samples, great increase of absorbance in the vicinity of 1622 cm$^{-1}$ was identified. This difference was particularly noticeable in the differential spectra. The FTIR-ATR spectrum of Pd (II)-Lys$_2$ complex water solution is shown in Fig. 13. The spectral patterns of the differential spectrum and the spectrum of the complex water solution practically agree with each other. The peaks of their C-N stretching vibration at 1622 cm$^{-1}$ deriving from amino groups with the greatest adsorbance completely agreed with each other. These facts verify that the Pd (II) complex of Arg and Lys having cationic pendant groups is taken into the modified layer as a complex. Another finding that no change in the spectral pattern was identified in other Pd (II) complexes indicate that anionic Pd (II)-amino acid complexes whose pendant group is neutral or anionic are not taken into a modified layer as a complex.

**Adsorption mechanism of the Pd (II)-amino complex.**—Our proposed adhesion mechanism of Pd (II) complexes to modified surface having carboxylate was illustrated on Fig. 14.
FTIR-ATR spectra of Pd (II) complexes with the neutral pendant group was not observed into the modified layer after catalyzing. However, in the modified surface in which many carboxylates were formed, adsorption of a little Pd was observed and electrolessly Nickel deposited. From this result, Pd (II) complexes with the neutral pendant group penetrated into the modified layer, then a little Pd (II) complexes coordinated to carboxylate of modified layer. Thus, only the amino acid which coordinated to Pd center was removed outside the modified layer.

FTIR-ATR spectra of Pd (II) complexes with the anionic pendant group was not observed into the modified layer after catalyzing. Moreover, in the modified surface in which many carboxylates were formed, Pd adsorption was not observed, and electrolessly nickel was not deposited. From this result, negative charge of anionic pendant group and negative charge of carboxylate on the modified surface caused electrostatic repulsion. Therefore, Pd (II) complexes with the anionic pendant group was not able to penetrate into the modified layer.

FTIR-ATR spectra of Pd (II) complexes with the cationic pendant group was observed into the modified layer after catalyzing. These Pd (II) complexes had the excellent performance of Pd adsorption and electroless plating depositability. We thought this is the interaction between positive charge of cationic pendant group and negative charge of carboxylate on the modified surface. As a result, the Pd (II) complexes penetrated inside of the modified layer effectively.

For the modified layer with a negative charge, it was manifested that the electric charge of the pendant group of the Pd (II) complex had a big influence for the adsorption of the catalyst.

Conclusions

We took notice the capability of anionic carboxylate group which are formed by various resin surface modification method. Then, to verify the characteristic of catalyst in electroless plating, synthesized and Pd (II) complexes [Pd^{II}(L-arg)_2]^{2+} and [Pd^{II}(L-lys)_2]^{2+} comprising basic amino acid which having cationic functional groups that can interact with carboxylate groups.

These two types of Pd (II) complex were found to be able to provide superior depositability in electroless nickel plating even on those mild modified resin surface. Said superior depositability brought about a plated coat boasting of high adhesive strength, which helps minimize the brittleness of the surface-modified resin. Furthermore, the two types of Pd (II) complex provide selective adsorption to the carboxylate groups, which made us succeeded in selectively depositing electrolessly plated nickel. From the results of FTIR-ATR spectral measurement, of the adsorption mechanism of the Pd (II)-basic amino acid complex, Pd (II) ions are taken into a surface-modified layer as a Pd (II)-basic amino acid complex. This is considered to be as anionic carboxylate groups in a surface-modified layer interact with the amino and guanidyl groups of the cationic pendant groups of the Pd (II)-amino acid complex based on the design guideline dictates. Thus, it has been revealed that Pd (II) complexes [Pd^{II}(L-arg)_2]^{2+} and [Pd^{II}(L-lys)_2]^{2+} are very effective electroless plating catalysts on a surface having anionic groups like carboxylate groups. we could successfully demonstrate that the effect of electric charge of pendant groups of a palladium catalyst is critical in designing a catalyst.

Acknowledgments

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