Chromic Acid Etching-free Plating Process Using ABS Alloy Resin

Toshimitsu Nagao, Kazuya Satoh, Toshihiro Tai[*]*, Weihong Gu*[**] *and Hitomi Omae*[**]
Main Research Laboratory, Okuno Chemical Industries Co., Ltd., Osaka, Japan.
[*] *Department of Development, Daicel Polymer Ltd., Osaka, Japan*
[**] *Analysis Service Center, Daicel Chemical Industries, Ltd., Hyogo, Japan*

Chromic acid-sulfuric acid etching solution has been applying in the plating process on ABS resin which has been used most commonly as plastics plating. By applying PA/ABS resin which has excellent mechanical properties, we developed chromic acid etching-free plating process. This plating process gives high plating adhesion, and one rack treatment is applicable.

So at first, we wish to introduce this plating process, and report our research for plating deposition mechanism and adhesion mechanism in one rack system mainly.

For more information, contact;
Toshimitsu Nagao
1-10-25, Hanaten-Higashi,
Tsurumi-ku, Osaka, 538-0044
JAPAN
Phone-81-6-6965-4114
Fax-81-6-6963-0740
E-mail: t-nagao01@okuno.co.jp

1. Introduction

The decorative plating on plastics has been applying to various fields such as the exterior parts for automotives, electric home appliances and others, as it gives metallic glossy appearance with light weight. ABS resin (acrylonitrile-butadiene-styrene) which has excellent workability, affinity to surface treatment and low price has the most highest general versatility. In plating on ABS resin, etching step by mixed solution of chromic acid and sulfuric acid is essential. This etching solution has the following advantages. ① Dissolves butadiene component on the resin surface and makes the resin surface rough (we call this state as "Anchor"), and gives good adhesion between resin and plating film. ② Adsorbs chromium on the jig surface (*), and protects jig from deposition of electroless plating because this adsorbed chromium acts as catalytic poison. For this reason, we can use same jig at both electroless plating process and electrolytic plating process (one rack).

(*) Jig for Plating: Jig for plating is coated by sol-coating (applying PVC sol in general) on metal bar, and metal at only racking points with resin exposes

However, the hexa-valent chromium contained in the etching solution is one kind of carcinogen and harmful to human body, the work environment of etching step is poor and the waste solution may induce serious environmental contamination problem. And also, the waste water regulation standard for chromic acid is severe and it takes large costs and load for the waste water treatment. Recently, the subject for environmental protection has been taking up widely, and ELV Directive and RoHS Directive in Europe restrict usage of hazardous substances strictly. In plastics plating, lead-free electroless nickel plating or direct acid copper plating to plastics have been applying in the actual lines as environmental friendly plating process. However, with reference to the studies[1),2)] of the substitution technology for chromic acids etching, they have been progressing considerably, but have not been practiced yet.

We applied plating on the plating grade of PA/ABS resin developed by Daicel Polymer Ltd. without applying of chromic acid etching. The gained plating film has high adhesion and one rack plating process is applicable. In this paper, we wish to introduce the mechanism of its plating process.

2. Experimental

2-1. Features and Physical Properties of PA/ABS Resin

As our test specimens, we used PA/ABS resin made by Daicel Polymer Ltd. PA/ABS resin is the polymer alloy of PA (Poly Amide) resin which is normally

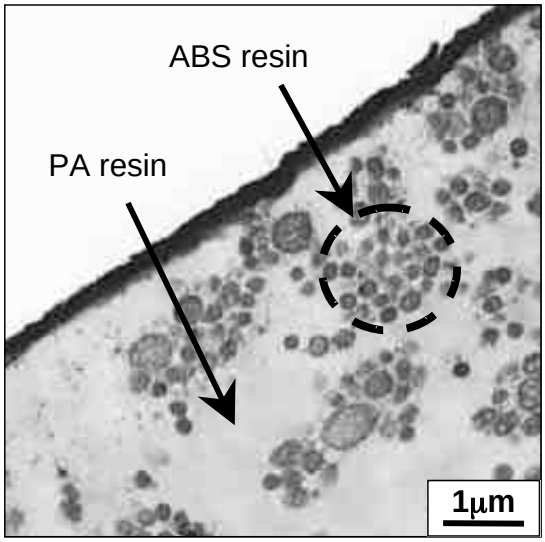


Fig.1 Cross sectional TEM image of PA/ABS resin

non-compatible and ABS resin by their compound technology with compatibility agent. So this alloy resin has advantages of both PA resin and ABS resin. Fig. 1 shows the cross sectional TEM (Transmission Electron Microscope) image of PA/ABS resin. In PA/ABS resin, PA resin exists as matrix and ABS resin disperses uniformly in it. Table 1 shows the physical properties of PA/ABS resin. PA/ABS resin has the properties of good heat-resistance by matrix phase and high impact resistance by dispersed ABS resin phase. Compared with PA resin, PA/ABS resin has smaller change in physical properties at absorption of moisture, and has good molding effect and dimension stability. The plating grade of PA/ABS resin which we used in this test was improved its plating adhesion and stability by adding plating effect improver and selecting the special ABS resin component.

Table 1 Physical properties of PA/ABS resin before and after plating

	ABS resin		PA/ABS resin	
	substance	after plating	substance	after plating
Tensile Strength 【MPa】	46	48	45	45
Flexural Strength 【MPa】	68	84	70	90
Flexural Modulus 【GPa】	2.4	4.9	1.9	10
Charpy IS 【kJ/m²】	26	16	30	25
DTUL (1.8MPa)【℃】	82	94	70	220

2-2. Plating Process

Fig. 2 shows plating process on PA/ABS resin. We eliminated the description of "Water Rinsing" at between each step in this process sheet. In this plating process on PA/ABS resin does not contain etching step by chromic acid. We treated the test specimens by hydrochloric acid type etching solution, and applied 2 steps of catalyzing.

Catalyzing Ⅰ is hydrochloric acid solution containing palladium-tin colloid. Catalyzing Ⅱ is palladium ion aqueous solution. At conducting step, the conducting film was gained on the resin surface. The film gained in this conducting bath is copper plating film. This conducting bath does not contain any phosphorus components, nitrogen compounds and strong chelating agent such as EDTA and reducing agent such as formalin. The conducting bath in this plating process is electroless copper plating solution which contains reducing agent having a trace of reducing effect. As this conducting bath has less formation of wasted materials, after making-up fresh bath, we can apply it for almost semi-permanently by replenishment. Furthermore, the solution is stable, and the phenomenon of no-deposition or loss of plating control by balance-out of the bath composition does not occur. After conducting treatment, thick film type direct acid copper plating following to water rinsing is applicable, and strike plating and acid activity step before and after of it are not required.

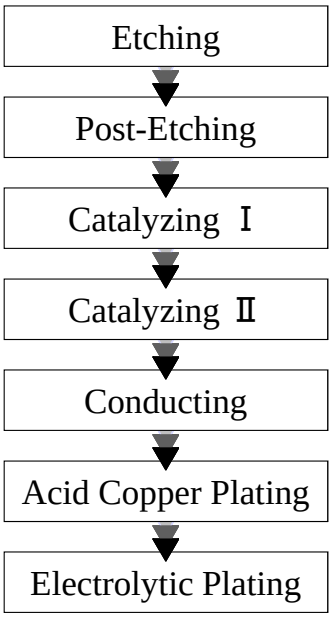


Fig.2 Chromic acid etching-free plating process of PA/ABS resin

3. Results and Discussion

3-1. Deposition Effect of Plating and Physical Properties of Plating Film

Fig. 3 shows behavior of plating deposition by changing of acid copper plating time. In applying of plating on PA/ABS resin according to the treatment process stated in Fig.2, acid copper plating did not deposit on the jigs, but deposited on only resin surface. The acid copper plating film gained by this process deposited gradually from the jigging points. After about 120 seconds, the whole surface of the test specimen covered by plating film completely, and we could gain good plating appearance. Even we prolonged the plating time, the plating did not deposit on the jigs. In case that we eliminated the Catalyzing Ⅱ step in this plating process, acid copper plating could deposit on the resin surface partially.

The peeling strength of the plating film gained by this process was 0.7 ~ 0.9 kgf/cm. After applying electrolytic plating (copper－semi-bright nickel—bright nickel—chromium plating) on resin molding, we applied thermal cycle test. The resin appearance after thermal cycle test was good appearance with no blisters and cracks.

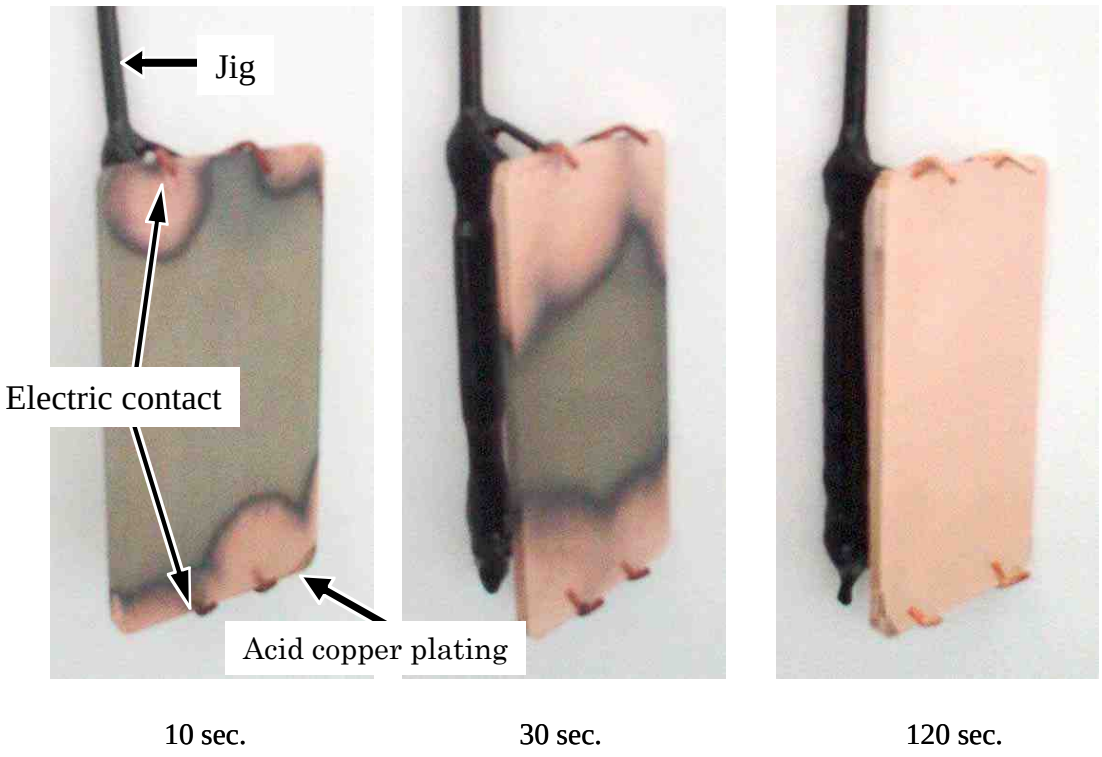
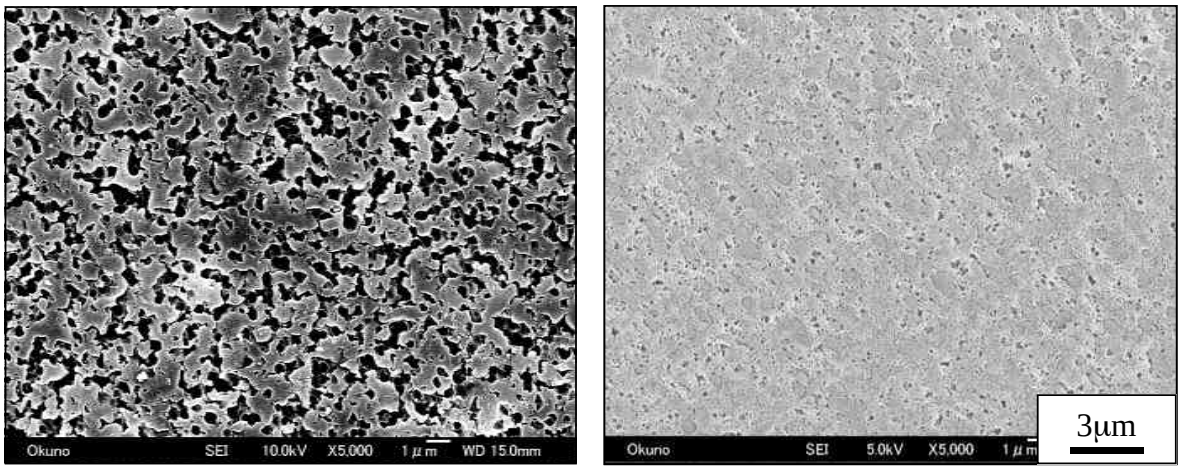


Fig.3 Deposition behavior of acid copper plating at changing the plating time

3-2. Adhesion Mechanism of Plating

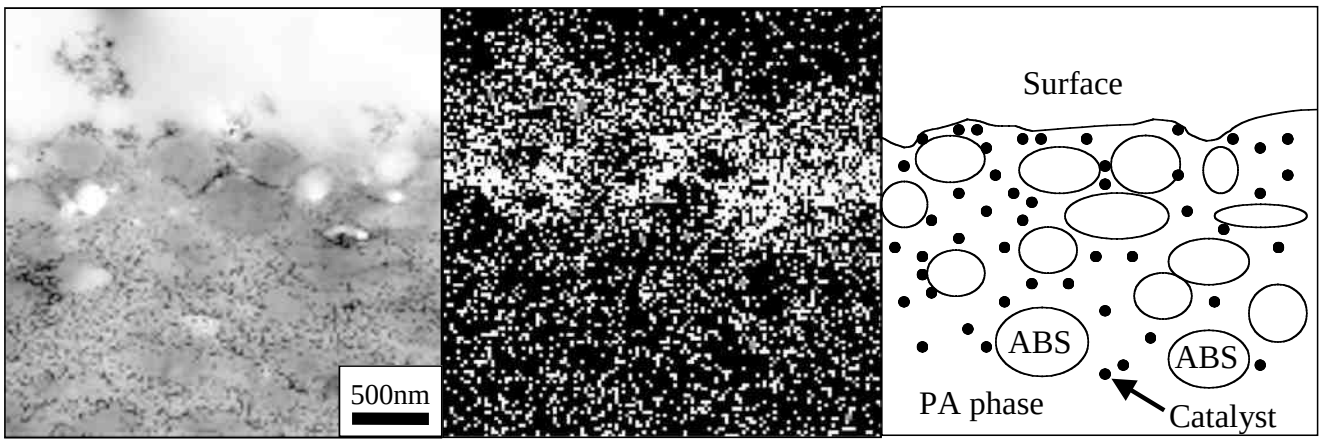
Fig. 4 shows SEM (Scanning Electron Microscope) image of PA/ABS resin surface after etching (right side image). As comparison, we shows SEM image of ABS resin after chromic acid-sulfuric acid etching (left side image). Compared with ABS resin, PA/ABS resin has smaller roughness. This roughness is considered to be formed by dissolution of PA resin and elimination of ABS resin particles.

Fig. 5 shows TEM image at the around surface of PA/ABS resin after catalyzing step and palladium mapping image. Palladium-tin colloid penetrates and adsorbs into PA



ABS resin *PA/ABS resin*

Fig.4 SEM images of PA/ABS and ABS resin after etching treatment



TEM image *Pd mapping image*

Fig.5 Cross sectional TEM image and Palladium mapping image of PA/ABS resin after catalyzing I

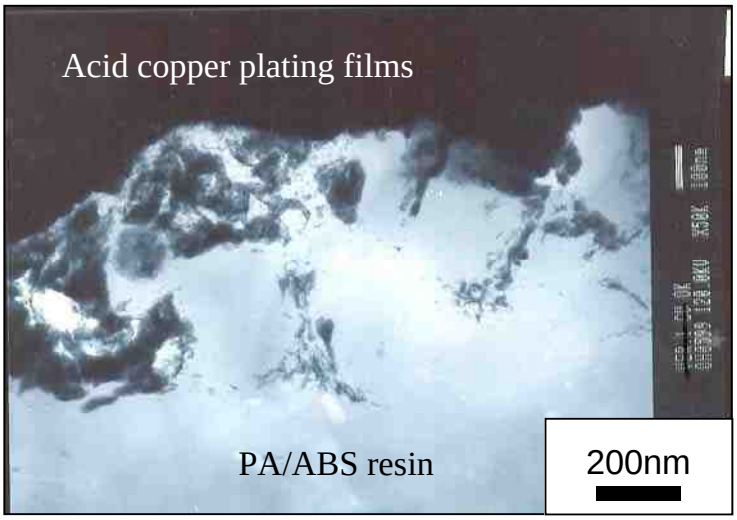


Fig.6 Cross sectional TEM image of PA/ABS resin after acid copper plating

phase by escaping from ABS phase. PA/ABS resin is combined PA resin having strong hydrophilic property with ABS resin having weak hydrophilic property. The role of PA compound is swelling by acid at catalyzing step and fixing the dispersion structure of resin/catalyst. Fig.6 shows cross sectional TEM image of resin after acid copper plating. We found that copper plating film having blackish contrast deposited in the inside of resin in net-like structure. This structure was just like root of tree penetrating into the ground. For this reason, we think that this phenomenon came from the penetration of palladium-tin colloid at catalyzing step into the inside of resin.

Therefore, we suppose that high adhesion of plating was induced by synergism of surface roughness of resin and deposition of plating into the inside of resin.

3-3. Deposition Mechanism of Plating and One Racking System

The conventional electroless plating method can deposit electroless plating film for about 0.5 μm by applying of palladium catalyst. Furthermore, as chromium which is catalytic poison remains on the jig surface, one rack treatment can be applied. On the other hand, in case of chromic acid etching-free process, as chromium of catalytic poison does not exist on the jig surface, electroless plating will deposit on the jig surface. In case that electroless plating deposits on the jig, it leads poor appearance of plating film. In general, it is required to exchange the jigs between electroless plating process and electrolytic plating process. However, this exchange of jigs reduces work efficiency and increases plating costs.

The deposition mechanism of this plating process is plating by formation of

conductive film. Along with the conductive film composed by palladium, tin and copper for the thickness of several tens of nm, copper plating starts deposition from the racking points. In case of non-continuous conductive film, copper plating will not deposit.

Fig. 7 shows the adsorption amount of catalyst adsorbed on the resin surface and jigs. By applying of 2 steps of catalyzing step, palladium catalyst adsorbed on resin surface increased. From cross sectional TEM image, we can observe the formation of thick catalyst layer on the resin surface. On the other hand, the adsorption amount of palladium on the jig was extremely low compared with that on PA/ABS resin surface. This difference in the adsorption amounts gave big influence to the following steps. The surface resistance value at PA/ABS resin surface after conducting step was 18.5 k Ω. On the other hand, we could not measure the surface resistance value at the jig surface. This matter means that conductive film will form on resin surface, but will not form on jig surface. Even if palladium adsorbs on the jig surface, plating by one rack system can be applied as continuous conductive film does not form.

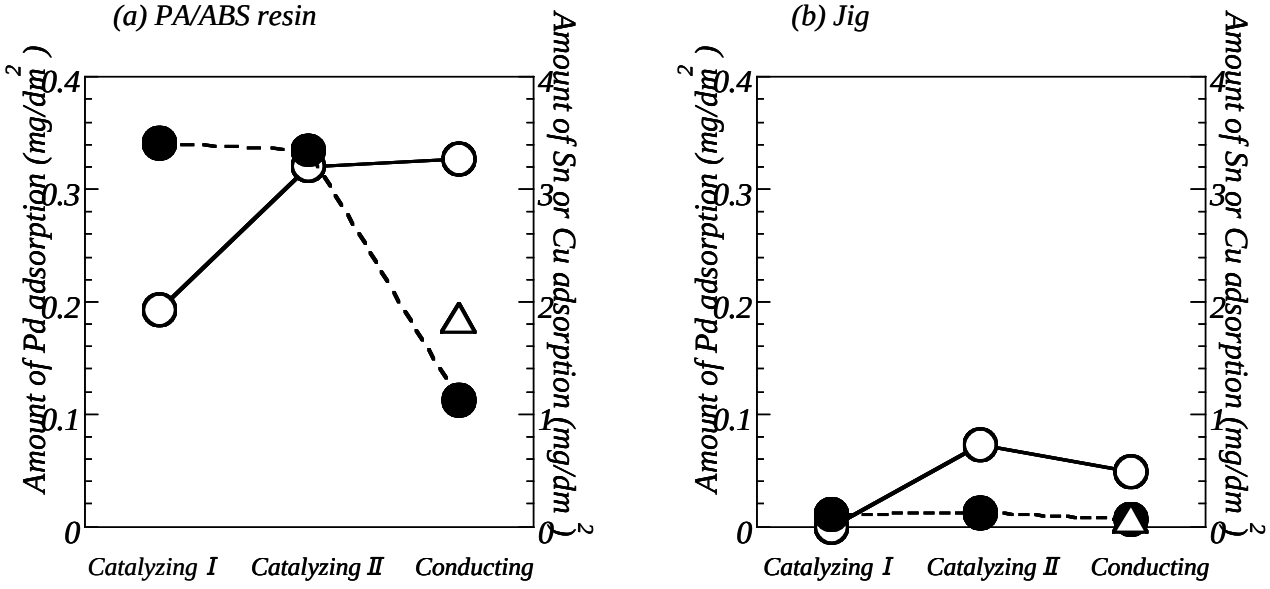


Fig.7 Catalyst adsorption amount adsorbed on PA/ABS resin (a) and jig (b)
(○: Palladium, ●: Tin, △: Copper)

4. Conclusion

We developed plating process having high plating adhesion by one rack system on PA/ABS resin having excellent mechanical properties without using chromic acid etching step. The feature of this plating process is as below.

① 2 steps of catalyzing step induces adsorption of palladium catalyst for much amount and accelerates formation of continuous conductive film. So acid copper plating will deposit on the whole surface of PA/ABS resin.

② By surface roughness of the resin surface by dissolution of PA component at etching step and deposition of electroless plating into the inside of resin by penetration of palladium-tin colloid into the inside of resin at catalyzing step, high plating adhesion can be gained.

③ As the adsorption amount of palladium to jig surface is extremely lower than that to resin surface, conductive film will not form on the jig surface. So plating by one racking system can be applied.

We can say that this plating process is environmental friendly plating process which does not contain hazardous substances and industrialization is possible. Compared with the conventional process using chromic acid etching step, by applying of this process, the work environment can be improves and load to environment is low. And also, as chromic acid etching step and the conventional electroless plating step can be eliminated, the treatment process can be shorten by about 30% and work efficiency can be improved. We can expect to apply this plating process on not only ABS resin, but also PC/ABS resin, PA resin and modified PPO resin as substitution technology.

Reference :

1) Y. Fumitaka et al., *2005 SAE World Congress*, 2005-01-0618, (2005).

2) K. Tashiro et al., *J. Japan Institute of Electronics Packaging*, **8**, 427 (2005).

