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(54) **Coating method for molded resin.**

(57) This invention provides a coating method for a molded resin that is effective for achieving satisfactory adhesion of the coating material, good contact properties ; inexpensive production ; and good coating appearance. The method comprises forming an electroless plating film to provide a specific surface resistance on the surface of a molded resin then applying a top coat without applying a conductive primer. The coating method of this invention is suitable for any type of molded resin, especially for a molded resin containing a polyamide resin and polyphenylene ether resin or polypropylene resin.

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This invention is concerned with a coating method for a molded resin which is effective for the production of a molded resin having both good coating contact properties and the high conductivity required for electrostatic coating.

When a molded resin was electrostatically coated, an undercoat which was called a conductive primer was usually used to achieve good contact properties with the top coat and good adhesion by means of electrostatic coating.

The conductive primer had to contain either a conductive filler or a conductive additive such as a surfactant at the time of coating in order to achieve conductivity. Examples of conductive fillers include the following: nonmetallic fillers such as carbon powder or graphite metallic fillers such as silver, copper, nickel, tin, zinc, titanium, palladium, aluminum; composite fillers made by plating fine particles of the following, e.g., glass, mica, plastic, carbon, with either copper or silver.

The paint for the above-mentioned conductive primer was expensive. As the film had to be very thick in order to achieve a satisfactory conductivity for the electrostatic coating, the cost for the complete process was very high. As automatic coating by an electrostatic coating apparatus was difficult to implement, the process had to be done by hand, which caused an increase in cost.

A molded product that was conductive could be made by molding a mixture of conductive filler and resin. However, in order to achieve high conductivity, a very large amount of filler was required; this resulted in a poor appearance of the coating. As the conductive filler was expensive, the cost was high.

The inventors described coating methods for polyamide resins in both Japanese Kokai Patent Application Nos. 1-242637 and Hei 2[1990]-181174. Satisfactory coating contact properties could be achieved by the techniques of both inventions; on the other hand, it was found that a satisfactory conductivity required for electrostatic coating could not be achieved in the case of coating with a metal.

This invention provides a coating method for a molded resin with none of the above-mentioned problems which conventional techniques had and that is effective for achieving the following, e.g., satisfactory adhesion of the coating material, contact properties; inexpensive production; good coating appearance.

The problems can be solved by using the following method, e.g., forming an electroless plating film to obtain a specific surface resistance in the surface of a molded resin containing a polyamide resin, then applying a top coat without applying a conductive primer. The coating method of this invention's is suitable for any type of molded resin. The method is especially suitable for a molded resin containing a polyamide resin. A resin composition chiefly containing both polyphenylene ether resin and polyamide resin, used for either the outer flat plate of a car or a bumper, is preferred. A resin composition chiefly containing a polyamide resin and a polypropylene resin is also preferred.

Any conventional polyphenylene ether can be used. Examples include the following: poly(2,6-dimethyl-1,4-phenylene) ether, poly(2,6-diethyl-1,4-phenylene) ether, poly(2-methyl-6-ethyl-1,4-phenylene) ether, poly(2-methyl-6-propyl-1,4-phenylene) ether, poly(2,6-dipropyl-1,4-phenylene) ether, poly(2-ethyl-6-propyl-1,4-phenylene) ether, copolymer of styrene and the example ethers.

A conventional polyamide can be used for this case; examples include the following: polycapramide (nylon 6), polyhexamethylene adipamide (nylon 66), polyhexamethylene sebacamide (nylon 6 10), polyundecanamide (nylon 11), polydecanamide (nylon 12), amorphous nylon, their copolymers.

Examples of polypropylene resins include the following: isotactic propylene monomers that show crystallinity, ethylene/propylene random copolymer consisting of either a copolymer made of an ethylene/ethylene/propylene random copolymer containing minimal amounts of the ethylene unit, or a homopolymer made of a propylene monomer and comparatively large amounts of the ethylene unit. Besides a crystalline resin, an amorphous polypropylene may be suitable. The type of polypropylene is not specifically restricted.

The molded resin is etched after being washed in the coating method of this invention. The following mineral acids, e.g., hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid, chromic acid, can be used for etching. Examples of organic acids include the following: organic carboxylic acids such as formic acid, acetic acid, or citric acid.

In particular, hydrochloric acid containing 10-400 mL/L (36% HCL) is preferable. The resin surface is dissolved with the mineral acid, which results in formation of projections and indentations on the resin that may be brought into contact with the electroless plating film (coated) at the molded resin surface.

An etching solution containing the following surfactants, e.g., cationic, nonionic, anionic, amphoteric, is preferable. The following concentrations are desirable, e.g., 0.01-50 g/L for the cationic surfactant; 0.01-50 g/L for the cationic surfactant + 0.01-50 g/L for the nonionic surfactant. A suitable surface roughness for good contact with an electroless plating film can be achieved by soaking in an etching solution at 10-60°C for 1-30 min.

Furthermore, the adsorption of palladium, which becomes an electroless plating catalyst nucleus in the later work unit is promoted by the resin. Furthermore, the etching solution is allowed to contain an inorganic salt to promote the effects of the surfactants. The concentration is preferably in a range of 1-1000 gL. The surface roughness suitable for providing an electroless plating film (coating) with good adhesion is carried out by dipping in this etching solution at 10-60°C for 1-30 min.

The material is sensitized and activated after etching. The following methods which are usually used for plating plastics, e.g., a catalyst-accelerator method, a sensitizer-activator method, soaking in a palladium solution-reduction solution which is used for either a polyamide resin or a through-hole substrate, can be used.

Satisfactory conductivity can be achieved by sensitization and activation, however, electroless plating is done to improve the conductivity. The following, e.g., Ni-P, Ni-Co-P, Ni-Zn-P, Ni-Sn-P, Ni-Pd-P, Ni-Cu-P, Ni-B, Cu, can be used for electroless plating. Either an alkali, neutral or an acid solution can be used. The following total metal concentration in the electroless nickel plating solution is desirable, e.g., 0.1-10 g/L, especially 0.5-5 g/L. An alkali solution is preferable.

The material is desirably soaked in the electroless nickel plating solution at 20-90°C, preferably at 30-50°C, for 10 sec to 20 min, preferably for 10 sec to 10 min.

The molded product in the above-mentioned process has a surface with high conductivity. A metal having a low electrical resistance can be adhered to the electroless plated film. The following metals, e.g., Ni, Cu, Pd, Pt, Au, Ag, can be used. Either electroless plating deposition or substitution deposition may be used. A molded resin having a surface with the improved conductivity can be made by the above-mentioned process.

The molded resin treated by electroless plating in the above-mentioned process can be either naturally dried at normal temperature or dried by heating after electroless plating at 50-150°C for 3 min to 20 h.

As the molded resin has a value of 107 W·cm or less for the surface resistance, electrostatic coating with either a middle coating material or a top coating material can be done without applying any conductive primer for coating. Any top coating material can be used in this case. A suitable coating material such as a melamine crosslinking polyester polyol resin coat, or an acrylic urethane coat, can be applied.

EXAMPLES

In the following, the details of this invention are described. A test sample made by molding GTX6006 (base material, brand: made by Nippon G.E. Plastic K.K., a resin composition containing both polyphenylene ether resin and polyamide resin) was used for both Application Examples 1 and 2.

Application example 1

The above-mentioned test sample was etched with the following etching solution at 30°C for 10 min.

Etching solution

hydrochloric acid (35%HCL)	270 mL/L
EP-Etching GL	400 mL/L (brand: Kizai K.K.)
water	rest

The sample was then soaked at normal temperature for 1 min in 35% hydrochloric acid (50 mL/L), then washed with water, then sensitized by soaking at 30°C for 3 min in the following sensitizing solution.

Sensitizing solution

EP-Akuchi [transliteration] GL	Solution A 100 mL/L (brand: Kizai K.K.)
EP-Akuchi GL	Solution A 100 mL/L (brand: Kizai K.K.)

After washing with water, activation was done with the following activating solution.

Activating solution

EP-Akuse [transliteration] GL	100 mL/L (brand: Kizai K.K.)

After the above-mentioned treating solution was washed off with water, an electroless nickel plated film was made by soaking in an electroless nickel plating solution at 40°C for the specific time shown in Table I (10, 20, 30 sec).

Electroless nickel plating solution

EP-Naiko GL Solution A	100 mL/L (brand: Kizai K.K.)

EP-Naiko GL Solution B 100 mL/L (brand: Kizai K.K.)

The treated sample was dried at 120°C for 10 min with hot air.

The following tests were done with the sample to verify effects.

(1) Surface resistance

The surface resistance of the test sample was measured by JIS K6911, "The Conventional Test Method for Thermosetting Plastic". After electroplating, the test sample was repeatedly baked at 160°C in a hot-air oven to measure the surface resistance in each baking process. The results are shown in Table I.

(2) Coating contact property, coating appearance, coating thickness

Haiepiko [transliteration] #100 (brand: made by Nippon Yushi K.K., middle coating material) was applied as a coating material using electrostatic coating, then left for 10 min, then baked for 30 min at 140°C in a hot-air oven, then removed from the oven, and left at normal temperature for 30 min. Then, Neoamirak [transliteration] (brand: made by Kansai Paint K.K., top coating material) was applied for coating by the electrostatic coating, then left for 10 min, then baked at 140°C for 30 min, then removed from the oven, then left at normal temperature for 24 h; the following evaluation was then done.

(1) Primary contact property

Crosshatch test (100 crosshatches, 1 mm [x 1 mm]) based on JIS K5400, was used for tape exfoliation. The numbers of residual coated film out of 100 crosshatches were counted.

(2) Secondary contact property test

After soaking a test piece in hot water (at 40°C) for 10 days, the same test performed in the above-mentioned primary contact test was done.

(3) Coating appearance

The appearance of the coated film surface was evaluated by visual observation.

(4) Coated film thickness

The cross section of the coated film was observed with an electron microscope to measure the film thickness.

The test results are shown in Table I.

Table I Results for application example 1

1	2 (Ω · cm)			6	7	8	9 (μm)
		160℃	160℃				
	3	4	5				
1 0	$4x10^7$	$4x10^7$	$4x10^7$	100	100	10	5 1
2 0	$7x10^5$	$6x10^5$	$6x10^5$	100	100	10	6 5
3 0	130	147	153	100	100	10	7 0

Key:
1 Time (seconds) required for soaking in the electroless nickel plating solution
2 Surface resistance
3 First time
4 Baked once
5 Baked twice
6 Primary contact property
7 Secondary contact property
8 Coating appearance
9 Coated film thickness
10 Satisfactory

Comparative Example 1

Except for electroplating for 5 sec, and for 60 sec, the same test performed in Application Example 1 was done. The results are shown in Table II.

Table II Results of Comparative Example 1

1	2 (Ω · c m) 160℃ 160℃ 3 4 5			6	7	8	9 (μm)
5	4x10¹²	4x10¹⁴	4x10¹⁴	100	100	10	3 6 12
6 0	0.5	0.5	0.5	4	0	11	7 3

Key:
1 Time (seconds) required for soaking in the electroless nickel plating solution
2 Surface resistance
3 First time
4 Baked once
5 Baked twice
6 Primary contact property
7 Secondary contact property
8 Coated film appearance
9 Coated film thickness
10 Satisfactory
11 Unsatisfactory
12 Shortage

Application Example 2

The following processes, e.g., etching; sensitization; activation, which were done in Application Example 1, were performed with the above-mentioned test sample, then after washing with water, the sample was soaked in the following electroless copper plating solution at 25 °C for the specific time shown in Table II. An electroless copper plated film was obtained.

Electroless plating solution CP-CU 305 (brand: Kizai K.K.)

Solution A	100 mL/L
Solution B	100 mL/L
Solution C	20 mL/L

The product test sample was dried at 120°C for 10 min. After washing with water, the sample was activated with the following activating solution, which was done in Application Example 1.

Activating solution

EP-Akuse GL 100 mL/L (brand: Kizai K.K.)

After washing to remove the above-mentioned treating solution, the sample was soaked in the following electroless nickel plating solution at 40°C for the specific time shown in Table I (10, 20, 30 seconds). An electroless nickel plated film was obtained.

Electroless nickel plating solution		
EP-Naiko GL	Solution A	100 mL/L (brand: Kizai K.K.)
EP-Naiko GL	Solution B	100 mL/L (brand: Kizai K.K.)

The sample was dried for 10 min at 120°C.
The following test was done with the sample to verify the effects.

(1) Surface resistance

The surface resistance of the test sample was measured by JIS K6911, "Conventional Test Method for Thermoset Plastics". The test sample was repeatedly baked in a hot-air oven at 160°C after electroplating, then the surface resistance was measured each time the sample was baked. The results are shown in Table I.

(2) Coating contact property, coating appearance, coated film thickness

Haiepiko #100 (brand: made by Nippon Yushi K.K., middle coating material) was applied as a coating by the electrostatic coating method, then left for 10 min, then baked for 30 min at 140°C in a hot-air oven, then taken out, then left at normal temperature for 30 min. Then, Neoamirakku (brand: made by Kansai Paint K.K., top coating, material) was applied as a coating, left for 10 min, baked at 140 °C for 30 min, taken out, then left for 24 h at normal temperature. The following evaluation was done.

(1) Primary contact property

A crosshatch (100 crosshatch, 1 mm square) based on JIS K5400, was done for tape exfoliation, and the residual coated film out of 100 crosshatch was counted.

(2) Secondary contact property test

After soaking the sample in hot water at 40°C for 10 days, the same contact property test as used for the primary contact property test was done.

(3) Coating appearance

The coated surface appearance was evaluated by visual observation.

(4) Coated film thickness

The cross section of the coated film was observed with an electron microscope to measure the film thickness. The test results are shown in Table III.

Table III Test results from Application Example 2

1	2 (Ω · cm)			6	7	8	9
	3	160℃ 4	160℃ 5				(μm)
60	$2x10^2$	$7x10^3$	$3x10^4$	100	100	10	66
180	3	24	56	100	100	10	73

Key:
1 Time (seconds) required for soaking in the electroless copper plating solution
2 Surface resistance
3 First time
4 Baked once
5 Baked twice
6 Primary contact property
7 Secondary contact property
8 Coating appearance
9 Coated film thickness
10 Satisfactory

Comparative example 1

Except for electroplating for 10 sec, the same test used for Application Example 2 was done. The results are shown in Table IV.

Table IV Results for Comparative Example [2]

1	2 (Ω · cm)			6	7	8	9
	--	160℃	160℃				(μm)
	3	4	5				
1 0	$6x10^9$	$1x10^{11}$	$4x10^{12}$	100	100	10	2 4

Key:
1 Time (seconds) required for soaking the electroless copper plating solution
2 Surface resistance
3 First time
4 Baked once
5 Baked twice
6 Primary contact property
7 Secondary contact property
8 Coated film appearance
9 Coated film thickness
10 Satisfactory
11 Unsatisfactory

Better conductivity can be obtained by using the coating method of this invention for a molded resin than by using a conventional coating method that includes a conductive primer coating process. The cost of the following, e.g., coating materials, coating, and baking, can be reduced.

A ground is required for the specific electric potential between the material to be coated and the coating material in the case of electrostatic coating. A conductive coating material was sprayed on the back surface of the product to form a conductive ground region. As electroless plated films can be formed on both the front and back surfaces of the product by electroless plating, the ground can be connected to any desired location on the back surface, which means no special treatment is required.

In the case of a molded resin having both projections and indentations, the coating material could not be applied to the entire surface of the resin using the conductive primer coating method; this resulted in uneven coating. In the case of a molded resin having both the projections and indentations, an even film can be formed and even coating can be achieved using this invention's electroless plating method.

Claims

1. A coating method for a molded resin characterized by including formation of an electroless plating film to result in a specific surface resistance prior to coating using a coating method for a molded resin containing a polyamide resin.

2. The coating method for a molded resin described in Claim 1 and characterized by sequentially etching, sensitizing and activating, and electroless plating a molded resin prior to coating.

3. The coating method for a molded resin, including the following, e.g., sequentially etching, sensitizing and activating, and electroless plating the molded resin, adhering a metal having a low electrical resistance

to the electroless plating film.

4. The coating method for a molded resin described in one of Claims 1-3, and using a mineral acid and/or an organic acid as the etching solution for the above-mentioned etching process.

5. The coating method for a molded resin described in Claim 4, and using the above-mentioned etching solution including a surfactant and/or an inorganic acid.

6. The coating method for a molded resin described in Claims 1-5, and characterized by coating a metal which is chosen from the following: Ni, Cu, Pd, Pt, Au, Ag, on an electroless plate.