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 **A method for coating a molded resin product.**

 In coating a molded resin product containing a polyamide resin, prior to the application of the coating material, an electroless plating film that provides surface resistance values with a specified range is formed, and coating with the desired coating material is then carried out. This provides a coating method that is both economical and can provide good coating adhesion with respect to molded resin products.

The present invention concerns a method for coating a resin molded product that is capable of simultaneously endowing the resin molded product with good coating adhesion and with the conductivity needed for electrostatic coating.

Electrostatic coating is often utilized in the coating of molded resin products. In order to perform electrostatic coating on the surface of such molded resin products, undercoating materials referred to as "conductive primers" have generally been applied as a pretreatment to attain the objective of good adhesion to the overcoat and to obtain good throwing power in the electrostatic coating.

In order to render the surface of a nonconductor conductive, a conductive filler is added to the material in this primer, or a conductive additive such as a surfactant is added to it. Examples of conductive fillers which can be used include nonmetallic fillers such as carbon black and graphite, metallic fillers such as silver, copper, nickel, tin, zinc, titanium, palladium, and aluminum, and composite fillers obtained by plating fine particles of materials such as glass, mica, plastic, and carbon with materials such as copper or silver.

Because the materials in these conductive primers are costly, when attempts are made to achieve the conductivity needed for coating, the coating must be applied to a sufficient thickness, leading to the problem of increases in the overall processing costs. Moreover, because the electrostatic coating must include a grounding treatment to ensure a specified potential difference between the object to be coated and the coating material, a ground connection must be formed on the back surface. However, because such treatment is difficult to carry out with devices such as automatic electrostatic coating devices, human labor must be used, leading to a further increase in the coating costs.

It is also possible to impart conductivity to the molded product itself by molding a product in which a conductive filler has been mixed into the resin beforehand. However, to obtain sufficiently great conductivity, it is necessary to add large amounts of this filler, making it difficult to obtain a good coating appearance. Moreover, the aforementioned high cost of the aforementioned filler has an effect on the costs.

In the past, the inventors disclosed methods for coating polyamide resins in Japanese Kokai Patent Application Nos. Hei 1[1989]-242637 and Hei 2[1990]-181174. In the technology pertaining to these applications, although it was possible to obtain sufficient coating adhesion, it later became clear that the high conductivity needed for electrostatic coating was not sufficiently present when simultaneous coating with metals was performed.

The present invention concerns a method for coating a molded resin product that solves such problems in the prior art as described above, simultaneously provides sufficient material throwing power and material adhesion in the electrostatic coating of molded resin products, and imparts a good coating appearance.

The above objectives are achieved by a method for coating a molded resin product in which a metal film is applied to the surface of a molded resin product for the purpose of obtaining a specified surface resistance, after which electrostatic coating is carried out without applying a conductive primer. In such cases, it is desirable that the process for applying the metal component be an electroless plating method. Moreover, it is desirable that the surface resistance of the molded resin product possessing a film of metal component formed in the aforementioned manner be on the order of $1\ \Omega\text{-cm}$ or above and $10^7\ \Omega\text{-cm}$ or less.

In the present invention, a surface resistance suitable for electrostatic coating is achieved by applying a metal component film of a suitable variety and thickness to the surface of the resin product. As a result, good coating adhesion is obtained, and good throwing power is imparted to the material at the same time. Specifically, the present invention has been conceived upon noting that the surface resistance which is necessary and adequate in practical terms for electrostatic coating is obtained according to the state of the applied film of metal component, in consideration of the fact that, when sufficient surface resistance is obtained by applying a sufficient amount of metal film to the surface of the resin, the coating process is easily performed, but the coating adhesion is reduced by the complete metallization, as well as the fact that, if an insufficient amount of metal component is applied, when the surface resistance is high, the electrical field formed on the side to which the coating has been applied loses uniformity, and the electrostatic coating cannot be carried out evenly.

While the application of the metal in the present invention can be implemented by any appropriate means, it is possible to form the film by electroless plating. In so doing, the electroless plating film can be obtained by various known methods depending on the variety of the resin, but is not limited thereto.

Ordinarily, to obtain an electroless plating film on the surface of the resin molded product, a washing process, a surface roughening process (chemical etching), a catalyst addition process needed for the initial deposition of the electroless plating, and an electroless plating process are carried out; however, the processes are not limited to this particular sequence. Although a catalytic layer containing a material such as Pd, Ag, Au, or Pt is selected at this time, Pd is often used in the interests of economy.

Additionally, examples of the type of metal used in the electroless plating film include nickel, copper, gold, silver, and tin, but are not limited to these. Each of these processes can include, or have performed before

and after it, a process such as washing. Moreover, they can also contain processes such as drying.

Examples of the type of resin used include various polymer materials, such as ABS, PA6, PA66, PBT, PET, PC, PA6/PPE alloy, PA6/noncrystalline PP alloy, noncrystalline PA, and/or fillers that are suitable in these resins. However, they are not limited thereto.

Because the aforementioned type of electroless plating film is ordinarily necessary in performing electroless plating of nonconductive materials, it is held to be indispensable in the plating of plastic surfaces. Generally, in order to perform electroless plating, a surface resistance of $1\ \Omega\cdot\text{cm}$ or less is necessary. It is indicated that when the surface resistance of the pertinent material is higher than this, the application of the metal plating layer becomes nonuniform, and its adhesion strength also decreases.

However, when an electroless plating with a surface resistance of $1\ \Omega\cdot\text{cm}$ or less is applied and this surface is coated, the metal film covers the entire surface of the molded resin product, completely metallizing it. This makes it difficult to obtain adhesion of the coating. Accordingly, because differences in the coating adhesion occur depending on the location, a surface resistance of preferably $1\ \Omega\cdot\text{cm}$ or less is preferable. In contrast, when the surface resistance is $10^7\ \Omega\cdot\text{cm}$ or above, although coating adhesion is obtained, the electrical field formed at the surface to be coated becomes nonuniform, making it impossible to obtain sufficient throwing power of the coating material during electrostatic coating.

In light of the above, an electroless plating film that gives a resistance in the range of $1\ \Omega\cdot\text{cm}$ or above and $10^7\ \Omega\cdot\text{cm}$ or less is suitable as the surface resistance of the molded resin product.

In the present invention, an electroless plating film providing the above desired surface resistances is formed on the surface of the molded resin product, after which electrostatic coating is carried out without applying a conductive primer. As the coating material for carrying out the electrostatic coating, any material can be used, e.g., melamine-crosslinked polyester polyol resin coating materials and acrylic urethane coating materials. However, the coating material is not limited to these.

When the coating method pertaining to the present invention is implemented, in comparison to situations where a conductive primer is applied, the desired conductivity is obtained by electroless plating. As a result, the application of an electroless plating as a pretreatment for electrostatic coating makes it easy to obtain the uniform electrical field needed for electrostatic coating. Moreover, the grounding treatment needed in the electrostatic coating process for rendering the back surface conductive is also facilitated. Accordingly, the costs relating to the coating material and the coating operation can be reduced.

EXAMPLES

Application Example 1

The substance of the present invention will be explained in detail below by means of application examples. The test pieces used in the application examples were obtained using Noryl GTX6006 (a trademark; product of GE Plastics Japan, Inc.; a resin composition containing polyphenylene ether resin and polyamide resin).

The aforementioned test pieces were subjected to the following type of etching treatment for surface roughening with an etching treatment solution and water washing. The treatment temperature and treatment time were 10 min [treatment temperature omitted].

Etching treatment solution:

Hydrochloric acid (35% HCl)	270 mL/L
EP ethylene glycol GL	400 mL/L (trademark; product of Kizai Corp.)
water	remainder

The aforementioned etched test pieces were washed with water, after which they were subjected to a 3 min, 30°C sensitizing treatment process for the purpose of adding a catalyst.

Solution for catalyst addition sensitizing treatment

EP Acti GL	Solution A	100 mL/L (trademark; product of Kizai Corp.)
EP Acti GL	Solution B	100 mL/L (trademark; product of Kizai Corp.)

After washing, a 30°C , 3 min activation treatment process was carried out with the activation treatment solution shown below.

Activation treatment solution

EP Acti GL 100 mL/L (trademark; product of Kizai Corp.)

After washing with the aforementioned treatment solution, immersion was performed in the electroless nickel plating solution at 40°C for the duration shown in Table I, and an electroless nickel plating film was obtained.

Electroless nickel plating solution		
EP Naico GL	Solution A	100 mL/L (trademark; product of Kizai Corp.)
EP Naico GL	Solution B	100 mL/L (trademark; product of Kizai Corp.)

The specimen obtained by the above-mentioned application example was dried at 120°C for 10 min with hot air.

The test samples obtained in the aforementioned application example were subjected to the following kind of test to confirm the effect of the present invention.

(1) Surface resistance

The surface resistances of the test pieces were measured in accordance with JIS K 6911, "General Test Method for Thermosetting Plastics." Here, test pieces that had been subjected to electroless plating treatment were subjected to a treatment of repeated baking in a 160°C hot blast oven, and the surface resistance at each baking was measured. The results were as shown in Table I.

(2) Coating adhesion, coating appearance and coating film thickness

Haiepico [transliteration] No. 100 (trademark; product of Nihon Yushi K.K., intermediate coat) was applied as the coating material by means of electrostatic coating, and the test pieces were allowed to stand for 10 min, after which they were baked for 30 min in a 140°C hot blast oven. They were then removed and allowed to stand for 30 min. Subsequently, Neoamilac [transliteration] (trademark; product of Kansei Paint K.K., overcoat) was applied by electrostatic coating, and the test pieces were allowed to stand for 10 min. They were then baked for 30 min at 140°C and removed, after which they were allowed to stand for 24 h at room temperature, and subjected to the following evaluation.

(1) Initial adhesion

Tape peeling was carried out in a condition conforming to a checkerboard test (using 100 1-mm squares) according to JIS K 5400, and the number of coating films remaining from the 100 was measured.

(2) Secondary adhesion test

The test pieces were immersed in 40°C warm water for ten days, after which they were tested in the same manner as in the aforementioned initial adhesion test.

(3) Coating appearance

The appearance of the coating surface was evaluated visually.

(4) Coating film thickness

The cross section of the coating film was observed by electron microscope, and the film thickness was measured.

Comparative Example 1

Testing was carried out in the same manner as in Application Example 1, with the exception that the duration of the electroless plating treatment was changed. Results were as shown in Table I.

Table I. Results of testing by
the processes in Application Example 1

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	3	4	5	6	7	8
	(S)	$\Omega \cdot \text{cm}$				(μm)
1	2 0	3×10^7	1 0 0	1 0 0	9	5 3
	3 0	7×10^4	1 0 0	1 0 0	9	6 3
	4 0	3 6	1 0 0	1 0 0	9	7 5
2	1 0	4×10^{12}	1 0 0	1 0 0	9	2 1
	9 0	0 . 0 6	2 4	3	10	9 0

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Key: 1 Application Example 1
 2 Comparative example
 3 Electroless plating immersion time
 4 Surface resistance
 5 Initial adhesion
 6 Secondary adhesion
 7 Coating appearance
 8 Coating thickness
 9 Good
 10 Poor

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Application Example 2

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Application Example 2 was carried out in the same manner as in Application Example 1, with the exception that an electroless copper plating film was formed in place of the nickel in the electroless plating. In this application example as well, the test pieces used were formed from Noryl GTX6006 (trademark; product of GE Plastics Japan; resin composition containing polyphenylene ether resin and polyamide resin) in the same manner as in Application Example 1.

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The aforementioned test pieces were subjected to the following type of etching treatment for surface roughening with an etching treatment solution and water washing. The treatment temperature and treatment time were 40°C and 10 min.

Etching treatment solution:

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Hydrochloric acid (36% HCl)	300 mL/L
GX Etchant	200 mL/L (trademark; product of Okuno Seiyaku K.K.)
water	Remainder

The aforementioned etched test pieces were washed with water and subjected to a neutralizing treatment, after which they were subjected to a 3 min, 40°C sensitizing treatment process for the purpose of adding a catalyst.

5 Solution for catalyst addition sensitizing treatment

Catalyst C 30 mL/L (trademark; product of Okuno Seiyaku K.K.)
 Hydrochloric acid (36% HCl) 50 mL/L
 TN Catalyst 180 mL/L (trademark; product of Okuno Seiyaku K.K.)

10 After washing and sulfuric acid acceleration, a 40°C, 5 min postacceleration treatment process was carried out with the activation treatment solution shown below.

Activation treatment solution

15 Sodium hydroxide 15 g/L
 TN postaccelerator 15 mL/L (trademark; product of Okuno Seiyaku K.K.)

After washing with the aforementioned treatment solution, immersion was performed in the 40°C electroless nickel plating solution shown below for the duration shown in Table I, and an electroless nickel plating film was obtained.

20	Electroless nickel plating solution		
25	TMP Chemical Nickel	Solution A	160 mL/L (trademark; product of Okuno Seiyaku K.K.)
		Solution B	160 mL/L (trademark; product of Okuno Seiyaku K.K.)

Comparative Example 2

30 Testing was carried out in the same manner as in Application Example 2, with the exception that the duration of the electroless plating treatment was changed. Results were as shown in Table II.

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Table II. Results of testing by the processes in Application Example 2

	3	4	5	6	7	8
	(S)	$\Omega \cdot \text{cm}$				(μm)
1	2 0	3×10^5	1 0 0	1 0 0	9	4 2
	3 0	7×10^3	1 0 0	1 0 0	9	5 6
	4 0	3 6	1 0 0	1 0 0	9	6 4
2	1 0	4×10^{12}	1 0 0	1 0 0	9	2 6
	6 0	0 . 0 6	2 4	3	10	9 0

Key: 1 Application Example 2
 2 Comparative example
 3 Electroless plating immersion time
 4 Surface resistance
 5 Initial adhesion
 6 Secondary adhesion
 7 Coating appearance
 8 Coating thickness
 9 Good
 10 Poor

Application Example 3

As Application Example 3, the following electroless plating treatment, in which only the final stage differed from Application Example 2, was carried out. The treatment was performed at a temperature of 23°C, for the durations shown in Table III. An electroless copper film was obtained.

Electroless copper plating solution

TMP Chemical Copper Mekkyu [transliteration]-100 (trademark; Okuno Seiyaku K.K.)

Solution A 160 mL/L

Solution B 160 mL/L

Solution C 25 mL/L

The test pieces obtained in Application Example 3 as shown above were subjected to the same tests as in Application Example 1 for the purpose of confirming the effect of the present invention.

Comparative Example 3

Testing was carried out in the same manner as in Application Example 1 [sic; possibly, 3], with the exception that the duration of the electroless plating treatment was changed. Results were as shown in Table III.

Table III. Results of testing by the processes in Application Example 3

	3	4	5	6	7	8
	(S)	$\Omega \cdot \text{cm}$				(μm)
1	3 0	$\times 10^7$	1 0 0	1 0 0	9	4 2
	4 0	$\times 10^4$	1 0 0	1 0 0	9	5 6
	1 8 0	3	1 0 0	1 0 0	9	6 4
2	2 0	$\times 10^{12}$	1 0 0	1 0 0	9	2 4
	6 0 0	0 . 0 1	2 4	3	10	9 0

Key: 1 Application Example 3
 2 Comparative example
 3 Electroless plating immersion time
 4 Surface resistance
 5 Initial adhesion
 6 Secondary adhesion
 7 Coating appearance
 8 Coating thickness
 9 Good
 10 Poor

When the method for coating a molded resin product pertaining to the present invention is implemented, it is possible to obtain higher conductivity than in conventional coating methods that include a process of applying a conductive primer, and it is also possible to reduce the costs relating to the coating material and the coating operation.

Additionally, a ground is required in implementing electrostatic coating; conventionally, it has normally been necessary to spray a grounding coating material onto the back surface of the molded product to form a conductive area for use as a ground. However, in electroless plating, the formation of an electroless plating film on the entire back surface of the molded product eliminates the need to subject the molded resin product that is coated to a special treatment.

Also, when a conductive primer is applied, if a complex configuration incorporating the molded resin product is formed, wraparound of the coating material sufficient to apply the coating material will be difficult. However, when the method pertaining to the present invention for forming an electroless plating film is used, a uniform film can be formed even with complex configurations.

Claims

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1. A method for coating a molded resin product, characterized in that a metal film for the purpose of obtaining a desired resistance is formed on the surface of a resin molded product, after which electrostatic coating is carried out without applying a conductive primer.
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2. The method for coating a molded resin product described in Claim 1, characterized in that the process for forming the aforementioned metal film is a method for forming an electroless plating film.
3. The method for coating a molded resin product described in Claim 2, wherein the surface resistance of the molded resin product upon which the aforementioned metal film has been formed is in the range of $10^7 \Omega \cdot \text{cm}$ or less.

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