METHOD FOR APPLYING SEMI-DRY ELECTROPLATING METHOD ON SURFACE OF PLASTIC SUBSTRATE

A method for applying a semi-dry electroplating method on a surface of plastic substrate is related to an electroplating method of plastic, which realizes the surface metallization of plastic materials, simplifies the electroplating procedure, dramatically reduces the amount of waste water, reduces the pollution to environment and expands electroplatable range of plastic substrates, is provided. Water-free cleaning and dust removal are conducted to a plastic substrate; a first-time activated treatment is conducted to the surface of the plastic substrate; a PVD plating metallic base layer, an alloy transition layer and a metallic electrical conductive layer are applied in turn on it, ultrasonic water washing and a second-time activated treatment are conducted on the treated plastic substrate; the treated plastic substrate is directly electroplated with acid copper or is moved to a nickel plating bath, and then complete the final surface treatment according to the actual process requirements.

ABSTRACT

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Electroplated microporous nickel layer and electroplated bright chromium layer

Electroplated fully-bright nickel layer

Electroplated semi-bright nickel layer

Electroplated acid copper layer

Vacuum vapor deposited layer (PVD Cr/CrCu/Cu)

Plastics parent metal
FIG. 1

- electroplated microporous nickel layer and electroplated bright chromium layer
- electroplated fully-bright nickel layer
- electroplated semi-bright nickel layer
- electroplated acid copper layer
- vacuum vapor deposited layer (PVD Cr/CrCu/Cu)

plastics parent metal
METHOD FOR APPLYING SEMI-DRY ELECTROPLATING METHOD ON SURFACE OF PLASTIC SUBSTRATE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is related to an electroplating method, and more particularly to a method for applying a semi-dry electroplating method on a surface of a plastic substrate.

2. Description of Related Art

Since applying metalizing electroplating procedure on a surface of a plastic substrate can achieve anti-corrosive, wear-resisting, scratch-resisting effects and a decoration function with beautiful appearance, the application scope of the plastic substrate thus expands. However, such traditional plastic electroplating procedure has two disadvantages including: (1) electroplatable plastic substrates being limited to ABS, PC/ABS and very few kinds of nylon; (2) pretreatment before electroplating procedure (including each procedure of chemical degreasing and cleaning, roughening, naturalization, sensitization, chemical nickel-plating and so forth) resulting in a large amount of discharging waste water, which is not environmental friendly. Therefore, developing a novel green electroplating procedure with reduced discharge is required. Simultaneously, a novel electroplating procedure, which allows all kinds of plastic to conduct metalizing electroplating is more desired. In this way, more economical benefits can be gained while pollution to environment can be reduced.

For expanding application scope of electroplatable plastic, conventional methods are mainly included as follows:

1) Chinese Patent, CN03104647.9, discloses a method for spraying electrically conductive medium on plastic pieces and cooperating electrolytic plating to conduct electroplating of a plastic surface.

2) Chinese Patent, CN02127419.3, used a method for roughening with dichromic acid content and activation of noble metal to metalize different kinds of plastics.

3) Chinese Patent, CN00410018367.2, used a vacuum sputtering method, which form a thin layer of basic metallic coating by sputtering on a surface of non-metallic material to conduct metalization.

The insufficiency of the foregoing methods 1) and 2) is that using dichromic acid and spraying electrically conductive paint result in serious environmental pollution problem and has higher cost of production. Using metalizing technology with vacuum evaporation coating on a plastic substrate is more environmentally friendly when compared to the foregoing methods 1) and 2). However, such simple way of vacuum evaporation coating leads to poor adhesion between the plastic substrate and PVD metallic layer. After electroplating, abscission layer, foaming or other phenomena would occur between the plastic substrate and PVD metallic layer or the final electroplating products confront failure in the thermal cycling test or other problems.

SUMMARY OF THE INVENTION

The objective of the present invention is, in view of disadvantages and insufficiency existing in the conventional plastic electroplating procedure, to provide a method for applying a semi-dry electroplating method on a surface of a plastic substrate, which realizes surface metallization of plastic materials, simplifies an electroplating procedure, dramatically reduces the amount of waste water, reduces the pollution to environment and expands electroplatable range of a plastic substrate.

The present invention includes the following steps:

1) conducting water-free cleaning and dust removal to a plastic substrate;
2) conducting a first-time activated treatment to the surface of the plastic substrate;
3) applying a PVD plating metallic base layer, an alloy transition layer and a metallic electrical conductive layer in turn on the activated-treated surface of the plastic substrate;
4) conducting an ultrasonic water washing and a second-time activated treatment on the plastic substrate treated in the step 3);
5) directly electroplating the plastic substrate treated in the step 4) with acid copper or moving it to a nickel plating bath to conduct nickel electroplating;
6) moving the plastic substrate treated in the step 5) into a chromium plating bath to conduct a final chromium electroplating or transferring it to a PVD oven to conduct deposition of chromium layer.

In the step 1), said plastic substrate can use a plastic substrate produced by injection molding or extrusion molding. Said plastic substrate can use engineering-plastics, glass fibers or mineral-powder reinforcing plastics or the like. Said engineering-plastics can be selected from one of ABS, PC, PC/ABS blends, PA6, PETG, PBT, PA66, TPU, TPU/ABS blends or the like. Said glass fiber reinforcing plastics can be selected from one of PA6+glass fiber, PBT+glass fiber, PC+glass fiber, PA66+glass fiber, PP+glass fiber or the like. Said mineral-powder reinforcing plastics can be selected from one of PA6+mineral powder, PP+mineral powder or the like. Said water-free cleaning can use the following methods: First, Electrostatic precipitation of the product surface, then wipe the surface of the product with anhydrous alcohol, And then using ion-source glow cleaning or bias glow cleaning in a PVD oven or corona activated treatment, washing with water first to remove oil then drying if the product surface is severely contaminated with greasy dirt. And then using ion-source glow cleaning or bias glow cleaning in a PVD oven or corona activated treatment.

2) conducting a first-time activated treatment to the surface of the plastic substrate:

In the step 2), said first-time activated treatment can use following methods: plasma glow modification using ion-source glow or bias glow mode to conduct the activated treatment, or corona activated treatment.

In the step 3), said metallic base layer can be a metallic base layer or an alloy base layer using chromium, titanium, aluminum, nickel, iron, zirconium or the like. Said metallic base layer can use arc ion plating or magnetron sputter plating to produce the PVD base layer. Said alloy transition layer is an alloy layer with at least one metal selected from chromium, titanium, aluminum, nickel, iron, zirconium, copper or the like and can be produced by arc ion plating or magnetron sputter plating. Said metallic electrically conductive layer can be a metallic electrically conductive layer of copper, nickel or other metal. Said metallic electrically conductive layer can use are ion plating or magnetron sputter plating to produce the PVD base layer.

In the step 4), said ultrasonic water washing comprises transferring the plastic substrate treated in the step 3)
into water galvanization line to conduct the ultrasonic water washing. Activating solution used in said second-time activated treatment can use sulfuric acid solution or the like.

[0023] In the step 5, if the surface of the plastic substrate is not flat, electroplating starts from plating acid copper. Said nickel electroplating can use at least one of semi-bright nickel, fully-bright nickel, microporous nickel or the like. If the surface of the plastic substrate is flat, electroplating directly starts from electroplating a semi-bright nickel layer, then electroplating a fully-bright nickel layer or a microporous nickel layer or the like.

[0024] Since plastics used in conventional electroplating procedure are limited to ABS, PC/ABS and very few PA6, glass fiber reinforced PBT or glass fiber reinforced PC or the like, the electroplating of plastic surfaces suffers from a tremendous limitation. The present invention uses improved PVD surface plating technology to treat the surface of the substrate with the water-free clean, the activated treatment and PVD multilayer technology, to plate the electrically conductive layer on the plastic surface first with physical vapor deposition (PVD), then to transfer the plastic substrate into traditional electroplating procedure to metalize the surface of the plastic material, and to incorporate simplified electroplating to prepare a semi-dry electroplated product with high quality. Pretreatment before electroplating is not required and therefore traditional chemical degreasing, roughening, naturalization, sensitization, chemical nickel-plating and so forth can be ignored. The procedures of electroplating the copper layer, electroplating the nickel layer and electroplating the chromium layer are directly conducted or electroplating chromium can be conducted in a PVD stove. As a result, the semi-dry electroplated product with high quality can be produced. Additionally, the amount of wastewater discharge in the present invention is merely a half of that in the traditional electroplating procedure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] The invention, as well as its many advantages, may be further understood by the following detailed description and drawings in which:

[0026] FIG. 1 is a cross-sectional side view of the product prepared by example 1 of the present invention. In FIG. 1, from the bottom to the top, there are a plastic substrate, a vacuum vapor deposited layer (PVD Cr/CrCu/Cu), an electroplated acid copper layer, an electroplated semi-bright nickel layer, an electroplated fully-bright nickel, an electroplated microporous nickel layer, and a electroplated bright chromium layer.

DETAILED DESCRIPTION OF THE INVENTION

Example 1

Procedure of Semi-Dry Electroplating Method when the Surface of a Plastic Piece is Not Flat

[0027] Applying semi-dry electroplating method on a surface of a car-door handle with PC+ABS plastic substrate has following specific steps:

[0028] Step 1 (injection molding): PC+ABS engineering plastic resin was dried at 80°C for 4 h, then was injection molded to form a plastic piece of car-door handle. The surface of plastic piece was flat.

[0029] Step 2 (cleaning of plastic piece and plasma surface modification): The cleaning (dry cleaning) procedure before plating comprises wiping the surface with anhydrous alcohol and plasma glow cleaning in a PVD stove. Parameters for the plasma glow cleaning comprise: Ar flux being 65 sccm, time for glow cleaning being 5 min, bias voltage being 70V, bias vacuum ratio being 70%, and ion source current being 0.3 A.

[0030] The plastic piece after cleaning was put into a vacuum oven to conduct plasma surface modification. Parameters for the plasma glow surface modification comprise: O2 100 sccm, ion source current being 0.3 A, time for surface modification being 10 min, bias voltage being 70V, and bias vacuum ratio being 70%.

[0031] Step 3 (PVD metallic base layer and alloy transition layer): For PVD metallic base layer, the target was metallic Cr target and arc ion plating was used for plating. Ar flux was 50 sccm, Cr target current was 50 A, bias voltage was 60V, bias vacuum ratio was 75%, time for plating was 5 min, and vacuum pressure for plating was 0.13 Pa. The alloy transition layer was CrCu alloy transition layer using arc Cr target and sputtering Cu target to form a CrCu alloy membrane with arc Cr target current being 50 A, copper target current for magnetron sputter plating from 2 A gradually raised to 8 A, bias voltage being 60V, bias vacuum ratio being 75%, time for plating being 8 min. Ar flux being 130 sccm, and vacuum pressure for plating being 0.3 Pa.

[0032] Step 4 (PVD electrically conductive layer): A magnetic sputter depositing copper target was used for plating with copper target current being 8 A, bias voltage being 70V, bias vacuum ratio being 70%, time for plating being 40 min. Ar gas flux being 130 sccm, and vacuum pressure for plating being 0.3 Pa.

[0033] Step 5 (galvanic plating): The product was transferred to hang on plating racks and was started to be plated from water washing and activation before contacting acid copper. Plated layers in turn comprise acid copper, semi-bright nickel, fully-bright nickel, microporous nickel, and bright chromium.

Example 2

Procedure of Semi-Dry Electroplating Method when the Surface of a Plastic Piece is Flat

[0034] Applying semi-dry electroplating method on a surface of a faucet knob made of polyamide modified engineering plastics has following specific steps:

[0035] Step 1 (injection molding): Polyamide modified engineering plastic powder was dried at 120°C for 4 h, then was injection molded to form a plastic piece of faucet knob. Since the ingredients for modification comprise glass fibers, the surface of plastic piece has little orange peel.

[0036] Step 2 (cleaning of plastic piece and plasma surface modification): The cleaning (dry cleaning) procedure before plating comprises wiping the surface with anhydrous alcohol and plasma glow cleaning in a PVD stove. Parameters for the plasma glow cleaning comprise: Ar flux being 65 sccm, time for glow cleaning being 5 min, ion source current being 0.3 A, bias voltage being 70V, bias vacuum ratio being 70%, and ion source current being 0.3 A. If the surface of the product is contaminated severely, washing with water would be required to remove oil, time for oil-removal and water-washing is 5 min and then the surface of the product would be dried under 120°C.

[0037] The plastic piece after cleaning was put into a vacuum oven to conduct plasma surface modification. Parameters for the plasma glow surface modification comprise: O2
gas flux being 100 sccm, time for surface modification being 10 min, bias voltage being 70V, and bias vacuum ratio being 70%.

**[0038]** Step 3 (PVD metallic base layer and alloy transition layer): For PVD metallic base layer, the target was metallic Cr target and physical sputter plating was used for plating with Ar flux being 130 sccm, Cr target current being 8 A, bias voltage being 60V, bias vacuum ratio being 75%, time for plating being 5 min, and vacuum pressure for plating being 0.29 Pa. The alloy transition layer was CrCu alloy transition layer using medium frequency magnetron sputter plating Cr target and magnetron sputter plating Cu target to form a CrCu alloy membrane. Current of the medium frequency magnetron sputter plating Cr target gradually decreased from 5 A to 0 A, copper target current for magnetron sputter plating gradually raised from 2 A gradually raised to 8 A, bias voltage was 60V, bias vacuum ratio was 75%, time for plating was 8 min, Ar 130 sccm, and vacuum pressure for plating being 0.3 Pa.

**[0039]** Step 4 (PVD electrically conductive layer): A copper target was used and a magnet sputter plating was used for plating with copper target current being 8 A, bias voltage being 60V, bias vacuum ratio being 75%, time for plating being 40 min, Ar 130 sccm, and vacuum pressure for plating being 0.3 Pa.

**[0040]** Step 5 (galvanic plating): The product was transferred to hang on plating racks and was started to be plated from water washing and activation before contacting acid copper. Plated layers in turn comprise acid copper, semi-bright nickel, fully-bright nickel, microporous nickel, and bright chromium.

**Example 3**

**[0041]** Applying semi-dry electroplating method on a plastic substrate surface of a high-density ball head made of polyamide modified engineering plastic has following specific steps

**[0042]** Step 1 (injection molding): Polyamide modified engineering plastic powder was dried at 120°C for 4 h, and then was injection molded to form a plastic piece of high-density ball head. The surface of the plastic piece was flat.

**[0043]** Step 2 (cleaning of plastic piece and surface modification): The dried plastic piece was put into a vacuum oven to conduct plasma glow cleaning and plasma surface modification. Parameters for the plasma glow cleaning comprise: Ar gas flux being 65 sccm, time for glow cleaning being 5 min, ion source current being 0.3 A, bias voltage being 70V, bias vacuum ratio being 70%, and ion source current being 0.3 A. Parameters for the plasma surface modification comprise: O₂ gas flux being 100 sccm, time for gloss surface modification being 10 min, bias voltage being 70V, and bias vacuum ratio being 70%.

**[0044]** Step 3 (PVD metallic base layer and alloy transition layer): For PVD metallic base layer, the target was Cr target and arc ion plating was used for plating with Ar flux being 50 sccm, Cr target current being 50 A, bias voltage being 60V, bias vacuum ratio being 75%, time for plating being 5 min, and vacuum pressure for plating being 0.13 Pa. The alloy transition layer was CrCu alloy transition layer using arc Cr target and sputtering Cu target to form a CrCu alloy membrane with arc Cr target current being 50 A, copper target current for magnetron sputter plating from 2 A gradually raised to 8 A, bias voltage being 60V, bias vacuum ratio being 75%, time for plating being 8 min, Ar flux being 130 sccm, and vacuum pressure for plating being 0.3 Pa.

**[0045]** Step 4 (PVD electrically conductive layer): A copper target was used as the target and a magnetic sputter plating was used for plating with copper target current being 8 A, bias voltage being 60V, bias vacuum ratio being 75%, time for plating being 40 min, Ar 130 sccm, and vacuum pressure for plating being 0.3 Pa.

**[0046]** Step 5 (galvanic plating): The product was transferred to hang on plating racks and was started to be plated from water washing and activation before forming semi-bright nickel. Plated layers in turn comprise semi-bright nickel, fully-bright nickel, microporous nickel, and bright chromium.

**[0047]** The comparison of examples 1–3 is shown in Table 1.

<table>
<thead>
<tr>
<th>Example</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plastic substrate</td>
<td>ABS + PC</td>
<td>PA6 + 30% GF + iron powder CP</td>
<td>PA6 + iron powder CP</td>
</tr>
<tr>
<td>Product</td>
<td>Car handle</td>
<td>Cover of fuse</td>
<td>Ball head</td>
</tr>
<tr>
<td>Appearance of plastic piece</td>
<td>Flat</td>
<td>Little orange peel</td>
<td>Flat</td>
</tr>
<tr>
<td>Surface cleaning</td>
<td>Anhydrous alcohol wipe</td>
<td>Water washing and oil removal</td>
<td>Plasma glow cleaning</td>
</tr>
<tr>
<td>Surface modification</td>
<td>Plasma glow modification</td>
<td>Plasma glow modification</td>
<td>Plasma glow modification</td>
</tr>
<tr>
<td>Metallic base layer</td>
<td>CrCu</td>
<td>CrCu</td>
<td>CrCu</td>
</tr>
<tr>
<td>Alloy transition</td>
<td>Cu 1 μm</td>
<td>Cu 1 μm</td>
<td>Cu 1 μm</td>
</tr>
<tr>
<td>Electrically-conductive layer Acid copper</td>
<td>15–20 μm</td>
<td>15–20 μm</td>
<td>0 μm</td>
</tr>
<tr>
<td>Semi-bright nickel</td>
<td>6 μm</td>
<td>6 μm</td>
<td>6 μm</td>
</tr>
<tr>
<td>Fully-bright nickel</td>
<td>9 μm</td>
<td>9 μm</td>
<td>9 μm</td>
</tr>
<tr>
<td>Microporous nickel</td>
<td>1 μm</td>
<td>1 μm</td>
<td>1 μm</td>
</tr>
<tr>
<td>Bright chromium</td>
<td>0.25 μm</td>
<td>0.25 μm</td>
<td>0.25 μm</td>
</tr>
<tr>
<td>Copper-accelerated acetic acid-salt spray corrosion test 8 h corrosion test</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
</tr>
<tr>
<td>Thermal cycling</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
</tr>
</tbody>
</table>

**[0048]** Many changes and modifications in the above described embodiment of the invention can, of course, be carried out without departing from the scope thereof. Accordingly, to promote the progress in science and the useful arts, the invention is disclosed and is intended to be limited only by the scope of the appended claims.

1. A method for applying semi-dry electroplating method on surface of plastic substrate, characterized in that the method comprises following steps including:
   (a) conducting water-free cleaning and dust removal to a plastic substrate;
   (b) conducting a first-time activated treatment to the surface of the plastic substrate;
   (c) applying a PVD plating metallic base layer, an alloy transition layer and a metallic electrical conductive layer in turn on the activated-treated surface of the plastic substrate;
   (d) conducting ultrasonic water washing and a second-time activated treatment on the plastic substrate treated in the step (c);
(e) directly electroplating the plastic substrate treated in the step (d) with acid copper or moving it to a nickel plating bath to conduct nickel electroplating;
(f) moving the plastic substrate treated in the step (e) into a chromium plating bath to conduct final chromium electroplating or transferring it to a PVD oven to conduct deposition of chromium layer.

2. The method for applying semi-dry electroplating method on surface of plastic substrate as claimed in claim 1, characterized in that in the step (a), said plastic substrate uses a plastic substrate produced by injection molding or extrusion molding; said plastic substrate uses engineering-plastics, glass fibers or mineral-powder reinforcing plastics; said engineering-plastics is selected from one of ABS, PC, PC/ABS, PA6, PETG, PBT, PA66, TPU, TPU/ABS; said glass fiber reinforcing plastics is selected from one of PA6+glass fiber, PBT+glass fiber, PC+glass fiber, PA66+glass fiber, PP+glass fiber; said mineral-powder reinforcing plastics is selected from one of PA6+mineral powder, PP+mineral powder.

3. The method for applying semi-dry electroplating method on surface of plastic substrate as claimed in claim 1, characterized in that in the step (a), said water-free cleaning uses the following methods: (a1) electrostatic cleaning, (a2) anhydrous alcohol wipe, (a3) a using ion-source glow cleaning or bias glow cleaning in a PVD oven, (a4) corona treatment, (a5) washing with water first to remove oil then drying if the product surface is severely contaminated with greasy dirt.

4. The method for applying semi-dry electroplating method on surface of plastic substrate as claimed in claim 1, characterized in that in the step (b), said first-time activated treatment uses following methods: (b1) plasma glow modification using ion-source glow or bias glow mode to conduct the activated treatment, (b2) corona activated treatment.

5. The method for applying semi-dry electroplating method on surface of plastic substrate as claimed in claim 1, characterized in that in the step (c), said metallic base layer is metallic base layer or alloy base layer using chromium, titanium, aluminum, nickel, iron, zirconium.

6. The method for applying semi-dry electroplating method on surface of plastic substrate as claimed in claim 1, characterized in that in the step (c), said metallic base layer uses arc ion plating or magnetron sputter plating to produce PVD base layer; said alloy transition layer is an alloy layer with at least two metals selected from chromium, titanium, aluminum, nickel, iron, zirconium, copper and produced by arc ion plating or magnetron sputter plating.

7. The method for applying semi-dry electroplating method on surface of plastic substrate as claimed in claim 1, characterized in that in the step (c), said metallic electrically conductive layer is a metallic electrically conductive layer of copper, nickel; said metallic electrically conductive layer uses arc ion plating or magnetron sputter plating to produce the PVD base layer.

8. The method for applying semi-dry electroplating method on surface of plastic substrate as claimed in claim 1, characterized in that in the step (d), said ultrasonic water washing comprises transferring the plastic substrate treated in the step (c) into water galvanization line to conduct the ultrasonic water washing.

9. The method for applying semi-dry electroplating method on surface of plastic substrate as claimed in claim 1, characterized in that in the step (d), activating solution used in said second-time activated treatment uses sulfuric acid solution.

10. The method for applying semi-dry electroplating method on surface of plastic substrate as claimed in claim 1, characterized in that in the step (e), if the surface of the plastic substrate is not flat, electroplating starts from plating acid copper; said nickel electroplating uses at least one of semi-bright nickel, fully-bright nickel, microporous nickel; and if the surface of the plastic substrate is flat, electroplating directly starts from electroplating a semi-bright nickel layer, then electroplating a fully-bright nickel layer or a microporous nickel layer.

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