ELECTROLESSLY NICKEL PLATING ON A NON-METALLIC BASIS MATERIAL

Inventors: Nobuyuki Kamiya, Yokohama-shi; Kiyotaka Funada, Chigasaki-shi; Takashi Shinohara, Yokohama-shi; Hiroko Inoue, Tokyo, all of Japan

Assignee: Nihon Kagaku Kizai Kabushiki Kaisha, Tokyo, Japan

Filed: Dec. 8, 1969

Appl. No.: 883,311

Foreign Application Priority Data
Dec. 6, 1968 Japan...........................................43/89357

U.S. Cl. ..............................................117/47 A, 106/1, 117/47 R, 117/54, 117/160 R

Int. Cl. ..............................................C25B 3/02

Field of Search ..................................117/47 R, 47 A, 54, 160 R; 106/1

References Cited
UNITED STATES PATENTS

Primary Examiner—Alfred L. Leavitt
Assistant Examiner—J. R. Batten, Jr.
Attorney—Stevens, Davis, Miller & Mosher

ABSTRACT

A process for depositing nickel on a non-metallic basis material from a chemical nickel plating bath containing a hypophosphate as a reducing agent to form a nickel coating on the basis material, the coating being indispensable for the practice of the subsequent electroplating, characterized in that the bath contains, as a second reducing agent, a member selected from the group consisting of L-ascorbic acid, its salts, and any substances which will produce L-ascorbic acid when incorporated in the bath as one of the components thereof, thereby to eliminate the sensitizing pre-treatment required for the conventional processes for chemically plating a non-metallic basis material with nickel.

6 Claims, No Drawings
This invention relates to a process for forming a preliminary metallic coating on a non-metallic substrate. In order to electroplate a non-conductive, non-metallic basis material such as synthetic resin, glass, ceramics or the like, it is necessary to form a preliminary metallic coating on the basis material thereby making it electrically conductive for the subsequent electroplating.

Formation of such a preliminary metallic coating has generally been effected either by depositing nickel containing a small proportion of phosphorus on a surface to be coated from a conventional, chemical plating bath comprising nickel and hypophosphite ions, said nickel deposited being obtained by reducing the nickel ion with the hypophosphite ion, or by depositing copper on a surface to be coated from a conventional, chemical plating bath of copper-formalin type, said copper deposited being obtained by reducing copper ion with formalin.

More particularly, a typical conventional process for the formation of a preliminary coating comprises the steps of:

1. etching a basis material, which has previously been subjected to degreasing and other chemical treatments and, as required, mechanical treatments such as liquid honing and the like in order to effect the conditioning of the surface thereof, by immersing it in a mixed solution of chromic and hydrosulfuric acids (a basis material mechanically treated may be passed to the following step without being subjected to this etching step),

2. sensitizing the etched basis material by immersing it in a mixed solution of stannous chloride and hydrochloric acid,

3. activating the sensitized basis material by immersing it in a mixed solution of palladium chloride and hydrochloric acid, and

4. forming a preliminary metallic coating on the activated basis material by immersing it in a chemical plating bath containing nickel or copper ion and depositing the metal thereon from the bath by means of the reduction of the metallic ion, said preliminary metallic coating being useful for the subsequent electroplating because of its electric conductivity.

(It is needless to say that washing with water or with warmed water should be carried out after each of the above-mentioned steps.)

The conventional chemical nickel plating baths, from which nickel may be deposited on a basis material to form a nickel coating thereon necessary to the subsequent electroplating, generally have the following compositions:

<table>
<thead>
<tr>
<th>Alkaline bath</th>
<th>Additive bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sulfate, g/l</td>
<td>30-35 (pref. 25)</td>
</tr>
<tr>
<td>Sodium hypophosphite, g/l</td>
<td>15-25 (pref. 20)</td>
</tr>
<tr>
<td>Glycol, g/l</td>
<td>1-5 (pref. 3)</td>
</tr>
<tr>
<td>Ammonium sulfide, g/l</td>
<td>40-70 (pref. 60)</td>
</tr>
<tr>
<td>Acidified sulfide, g/l</td>
<td>16-20 (pref. 20)</td>
</tr>
<tr>
<td>pH of bath</td>
<td>4-5 (pref. 4.5)</td>
</tr>
<tr>
<td>Temp. of bath, °C</td>
<td>60-80</td>
</tr>
</tbody>
</table>

The nickel sulfate may be substituted by other soluble nickel salts, such as nickel chloride, in the amount equal to that of the sulfate, calculated as nickel.

The conventional process, when practiced, will require lots of experience in controlling the composition of the treating solution, the temperature and the immersing time used in each of the steps. Thus, even if it is carried out by workers considerably skilled in this field, it will tend to give products the metallic coating of which is deficient in tight adhesion to the basis material and uniform deposition of the metal thereon. In particular, if the treatment with a mixed solution of stannous chloride and hydrochloric acid is not conducted properly, the metallic coating to be formed will have a rough surface, no uniform brightness or brilliance and other disadvantages in addition to the previously mentioned deficiencies.

The process of this invention is characterized by the fact that the nickel-hypophosphite type chemical plating bath used contains another specific reducing agent thereby eliminating the sensitizing step and lessening the drawbacks the conventional preliminary metallic coatings have had.

The novel chemical nickel plating bath according to this invention is prepared by adding L-ascorbic acid as a second reducing agent to an aqueous solution comprising nickel ions, hypophosphite ions as a first reducing agent, and an organic acid. A non-metallic basis material which has been subjected to etching and activating treatments, is immersed in said novel bath to deposit thereon nickel containing a small proportion of phosphorus.

In the practice of the conventional, generally used, chemical nickel plating, when a non-metallic basis material with stannous ion adsorbed thereon in the sensitizing step is passed to the next activating step, the stannous ion will reduce palladium ion attached to the basis material in this step to metallic palladium. If, in this case, excess palladium ion is left unreacted on the basis material, it will be removed therefrom by the subsequent washing with water. The metallic palladium attached to the surface of the basis material will be catalytic nuclei in a nickel-reducing reaction, thereby depositing nickel on the basis material in the chemical nickel plating step. Thus, if the basis material be immersed in the plating bath after the activating treatment without the previous sensitizing treatment thereof, palladium ion will partly be carried with the basis material into the plating bath and will act as a catalyst to deposit nickel in fine particle form thereby forming on the basis material a nickel coating having a rough surface or, in some cases, decomposing the plating bath so that it is no longer usable as such. This is the reason why it is inevitable for even those considerably skilled in the art to often produce articles having a defective nickel coating, as previously mentioned.

L-ascorbic acid contained in a chemical plating bath according to this invention is considered to effect the selective reduction of palladium ion therewith prior to the commencement of the reduction of nickel ion with hypophosphite ion, thereby to prevent the palladium ion from diffusing in the plating bath. L-ascorbic acid may be contained in the bath in any desired amounts. However, the ascorbic acid used is in amounts of preferably 3-30 g/l, more preferably 5-20 g/l. The acid may be substituted by its salts or other substances which will produce L-ascorbic acid when added to the bath as one component thereof. The bath may be acidic or alkaline and, however, it is stable when acidic and is advantageously usable when having a pH value of 3-6, preferably 4-5.5. And the use of a bath having a pH value lower than 3 will cause the rate of depositing nickel from the bath to become lowered.

The temperature at which nickel is deposited on the basis material from the bath containing L-ascorbic acid or its equivalent as a second reducing agent, need not be varied owing to the presence of the second reducing agent in the bath and may be the same as that generally used in the conventional baths. Thus, it depends mainly upon the kind of a basis material to be plated and is generally in the range of room temperature to about 60°C, preferably about 40°C to about 50°C.

This invention will be better understood by the following examples in which 10 pieces (100 × 100 mm) of the plate of non-metallic basis material were used as test pieces to be plated.

**Example 1**
Test pieces used were made of ABS (acrylonitrile-butadiene-styrene) (Plating Grade).

The test pieces were subjected to the following successive treatments:

1. Degreasing with a weak alkali,
2. Washing with water,
3. Immersing in a treating solution for 40 minutes, the solution being prepared by adding 30 g of chromic anhydride to every 1 liter of a solution consisting of water and conc. H₂SO₄ in a ratio by volume of 6 to 4 and being heated to 60°C,
4. Washing with water,
3,664,860

5. Immersing, for 2 minutes, in a solution kept at room temperature and prepared by adding 0.1 g of palladium chloride and 0.1 cc of conc. HCl to 1.0 liter water,
6. Washing with water,
7. Immersing, for 5 minutes, in a chemical plating bath at 40° C prepared by incorporating into 1.0 liter of water 20 g of nickel sulfate (heptahydrate), 15 g of sodium hypophosphite (undecahydrate), 10 g of adipic acid and 10 g of sodium l-ascorbate and adjusting the pH value of the resulting solution to 6,
8. Washing with water, in order to obtain the test pieces covered with a nickel layer or coating which is necessary for the subsequent electroplating.

The electroplating generally is the one of copper-nickel-cadmium type. The compositions of baths, temperatures, current densities and the like used in the electroplating of said type are not shown here because they are not novel and can easily be determined by the skilled in the art, as required.

The above-mentioned treatments or steps (1) to (6) are such that the conventional plating processes now in general use comprise them as a part of the steps thereof, although the treating solution used in each of the steps may vary in composition and temperature as desired.

Thus, in each of the following examples, there will be described only the steps in which operational conditions different from those used in Example 1 were used.

EXAMPLE 2

The same procedure as in Example 1 was followed except employing the test pieces made of polypropylene (Plating Grade) and the modified steps of (5') and (7') in each of which operational conditions used were different from those used in the corresponding step of Example 1. The modified steps were as follows:

5'. Immersing in a solution at 40° C, prepared by dissolving 1 gram of disodium palladium tetrachloride (Na₂PdCl₄) in 1 liter of water, for 3 minutes, and
7'. Immersing, for 3 minutes, in a bath at 30° C prepared by adjusting to 8 with sodium carbonate the pH value of a solution comprising 16 g/l of nickel sulfate, 11 g/l of sodium hypophosphite, 6 g/l of citric acid, 2.5 g/l of borax and 3 g/l of l-ascorbic acid.

EXAMPLE 3

The procedure of Example 1 was repeated, but using test pieces of glass as test pieces and substituting the steps (1) and (7) by modified steps (1') and (7''), respectively. These modified steps were as follows:

1'. Slightly roughening the surface of the test pieces by means of liquid honing,
7''. Immersing, for 3 minutes, in a bath at 60° C prepared by adjusting to 4 with sodium hydroxide the pH value of a solution comprising 20 g/l of nickel sulfate, 15 g/l of sodium hypophosphite, 15 g/l of sodium succinate and 30 g/l l-ascorbic acid.

EXAMPLE 4

The same procedure as in Example 1, but using test pieces made of epoxy resin and substituting the steps (1), (5), and (7) by modified ones (1''), (5''), and (7'') respectively. The modified steps were shown below:

1''. Slightly roughening the surface of the test pieces by means of liquid honing,
5''. Immersing in a solution at 40° C comprising 0.3 g/l of palladium chloride and 0.2 cc/l of hydrochloric acid, for 40 minutes, and
7''. Immersing, for 3 minutes, in a bath at 50° C prepared by adjusting to 5 with sodium acetate the pH value of a solution comprising 15 g/l of nickel sulfate, 17 g/l of sodium hypophosphite and 5 g/l of l-ascorbic acid.

EXEMPLARY 5

The procedure of Example 1 was repeated, but using test pieces made of styro resin and replacing the steps (1), (5), and (7) by the modified ones (1'''), (5'''), and (7'''), respectively. The modified steps were as follows:

1'''. Etching in a solution, at 40° C and an adjusted pH of 5.0, comprising 600 g/l of hydrochloric acid, 100 g/l of phosphoric acid, 300 g/l of water and 20 g/l of potassium dichromate, for a time length of 5 minutes,
5'''. Immersing in an activating solution comprising 0.5 g/l of disodium palladium tetrachloride and 0.3 cc/l of hydrochloric acid, at room temperature for 3 minutes, and
7'''. Immersing in a chemical plating bath comprising 30 g/l of nickel chloride (hexahydrate), 10 g/l of sodium hypophosphite (monohydrate), 3 cc/l of lactic acid, 0.3 cc/l of propionic acid and 15 g/l of l-ascorbic acid, said immersion being effected at a temperature of 60° C for 2 minutes.

The 10 nickel-coated test pieces thus obtained in each of the examples, were all satisfactory in uniform coating and brilliance, without surface roughness.

The nickel-coated, ABS and polypropylene test pieces respectively obtained in Examples 1 and 2 were then electroplated with a metal such as nickel or copper. The overall metallic coating thus formed on the resinous test pieces adhered tightly thereto without causing peeling and creating blisters.

What is claimed is:
1. A process for forming a preliminary nickel coating on a non-metallic basis material comprising:
   degreasing a non-metallic basis material with a weak alkali,
   washing the degreased basis material with water,
   etching the surface of the degreased basis material,
   washing the etched basis material,
   activating with a mixed solution of palladium chloride and HCl the etched basis material without previously sensitizing with a mixed solution of stannous chloride and HCl and
   then forming a preliminary nickel coating on the activated basis material by immersing the activated material in a chemical nickel plating bath, characterized in that the bath consists essentially of a second reducing agent selected from the group consisting of l-ascorbic acid and its salts,
   in addition to nickel ions, hypophosphite ions as a first reducing agent, and an organic acid.
2. A process as claimed in claim 1, wherein the bath contains the second reducing agent in an amount of 3-30 g/l, calculated as l-ascorbic acid.
3. A process as claimed in claim 2, wherein the bath is at pH of 3-6.
4. A process as claimed in claim 3, wherein the bath is operated at a temperature of room temperature to about 60° C.
5. A process as claimed in claim 1, wherein the non-metallic basis material is a synthetic resin.
6. A process as claimed in claim 5, wherein the synthetic resin is selected from the group consisting of acrylonitrile-butadiene-styrene and polypropylene.

* * * * *