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3,684,572

**ELECTROLESS NICKEL PLATING PROCESS  
FOR NONCONDUCTORS**

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6 Claims

**ABSTRACT OF THE DISCLOSURE**

The use of a quaternary amine surfactant solution in an electroless metal plating process produces a uniform coating on a nonconductor surface and excellent surface coverage.

**BACKGROUND OF THE INVENTION****(1) Field of the invention**

This invention relates to an electroless metal plating process for a nonconductor and more particularly to a process wherein a uniform metal coating is obtained on the surface of a nonconductor by treatment of the surface with a solution of a quaternary amine surfactant during the process.

**(2) Description of the prior art**

In the process of metalizing a nonconductor surface such as polypropylene, acrylonitrile-butadiene-styrene or other plastics, the surface is first etched or conditioned usually by immersion in an oxidizing solution to make the surface hydrophilic. After the oxidizing treatment, the surface is then rinsed with water to remove excess oxidizing solution and then immersed in a catalyst solution. After treatment with the catalyst solution, the surface is rinsed with water to remove excess catalyst solution and then immersed in a reducing solution to reduce the catalyst to metallic form after which the surface is rinsed with water and immersed in an electroless metal plating bath to metalize the part.

Frequently, it is found that the nonconductor surface is not completely covered with a uniform coating of metal. There may be voids or discontinuities in the metal coating on the nonconductor. Further, the metal coating may be rough rather than smooth and the thickness of the coating variable.

**SUMMARY OF THE INVENTION**

An electroless metal plating process, which gives excellent surface coverage of a nonconductor has been found. The process produces uniform metal coating on a part molded from a nonconductor such as polypropylene (PP), acrylonitrile-butadiene-styrene (ABS) or the like. Improved results are attributed to treatment of the surface of the nonconductor during the process with a solution of a quaternary amine surfactant where one radical is an alkyl having from about 10 to about 20 carbon atoms and a second radical is an alkyl having about 10 to about 20 carbon atoms, benzyl or an alkyl benzyl radical.

It is an object of this invention to provide a surfactant solution for improving the coverage of a nonconductor when plated by an electroless nickel plating process. Another object of this invention is to provide an electroless plating process. A further object is to provide an improved electroless plating process wherein the surface of the nonconductor is treated with a quaternary amine surfactant after etching and before catalyzing the surface to obtain a uniform metal coating. A further object is to provide uniform coverage of nonconductor surface with metal. Other objects will become apparent from the detailed

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description given hereinafter. It is intended that this description and specific examples merely indicate preferred embodiments and are not given to limit this invention since various changes and modifications within the scope of this invention will become apparent to those skilled in the art.

**DESCRIPTION OF THE PREFERRED  
EMBODIMENTS**

10 The surface of a nonconductor is treated with a dilute solution of a quaternary amine surfactant, after etching and before catalyzing. Useful surfactants include N-alkyl (C<sub>12</sub>—40%, C<sub>14</sub>—50%, C<sub>15</sub>—10%) dimethyl benzyl ammonium chloride such as Hyamine 3500 (Rohm and Haas Co., Philadelphia, Pennsylvania), n-alkyl (C<sub>12</sub>—C<sub>18</sub>) dimethyl ethylbenzyl ammonium cyclohexyl sulfamate such as Onyxide 172 (Onyx Chemical Co., Jersey City, N.J.), dilauryl dimethyl ammonium chloride such as Aliquat 204 (General Mills, Kankakee, Ill.), cetyl dimethyl benzyl ammonium chloride such as Ammonyx T (Onyx Chemical Co., Jersey City, N.J.). The above surfactants are used to prepare dilute aqueous solutions containing from about 0.01 to about 0.1% by volume of active surfactant. These surfactant solutions can then be used to treat the surface of the nonconductor after etching and before catalyzing in the electroless plating process. Or they may be used in other steps of the process.

Advantages of the process of this invention include faster deposition of metal, more uniform deposition of metal, reduced operating temperatures in the oxidizing solution bath and electroless nickel bath. Further, use of the surfactant solution does not appear to adversely affect other steps in the process. Life tests on a plating line did not show any evidence of contamination or other adverse effects that might be attributed to the surfactant solution or its use. The surfactant can also be dissolved in the reducing solution and the resulting solution of surfactant and reducing agent can be used as the reducing solution. If desired, use of a surfactant solution after etching and before catalyzing the surface can be omitted when a solution of surfactant and reducing agent is used. However, further improvements in plating results can be obtained using both a surfactant solution and a reducing solution containing a surfactant and reducing agent in this process.

40 In the process of metalizing a nonconductor surface, for example, polypropylene (PP), acrylonitrile-butadiene-styrene (ABS) or other polymeric material, the surface is first etched or conditioned, usually by immersion in an oxidizing solution to make the surface hydrophilic. U.S. Pat. 3,471,313, Saubestre et al., patented Oct. 7, 1969 discloses numerous oxidizing solutions useful for this purpose. There are also numerous commercial oxidizing solutions offered under proprietary names for this purpose.

45 After thorough rinsing with water, the surface of the substrate is then immersed in one of the dilute solutions of cationic surfactants described above and then rinsed thoroughly with water. The substrate surface is then catalyzed by being immersed in a catalyst solution of a catalytic metal ion usually palladium ions obtained by dissolving a palladium salt in a solution of acid. Various concentrations of a palladium salt and hydrochloric acid can be used. A typical catalyst solution has the following composition:

50 Palladium chloride—0.1 g./l.—0.3 g./l.

Hydrochloric acid—10 ml./l.—50 ml./l.

Water to make 1 l.

55 (Reference: Goldie, William, Metallic Coating of Plastics, Middlesex, England: Electrochemical Publications Limited, 1968, pp. 39—52.) The following solution designated as catalyst solution A has been used to catalyze ABS and PP surfaces for metalizing.

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## Catalyst solution A

	G./l.
Palladium chloride	0.2
Hydrochloric acid	0.2
Water to make 1 l.	

The catalyst solution can be the palladium catalyst solution described in copending U.S. patent application, Ser. No. 54,571. After removal from the catalyst solution, the nonconductor surface is rinsed with water and immersed in a reducing agent solution. A typical reducing agent solution has the following composition:

	G./l.
Dimethylamine borane	5
Water to make 1 l.	

After removal from the reducing solution, the substrate surface is rinsed with water and then immersed in an electroless metal plating bath.

Typical electroless metal plating baths have the following compositions:

## Electroless nickel bath A

	G./l.
Nickel sulfate hexahydrate	31.3
Sodium acetate	3
Citric acid	20
Sodium hypophosphite monohydrate	20
Water to make 1 l.	

For use at a temperature of 75° to 85° F. and a pH of 8.5 to 8.7.

## Electroless nickel bath B

	G./l.
Nickel sulfate hexahydrate	26.3
Ammonium chloride	53.5
Sodium hypophosphite monohydrate	21.2
Water to make 1 l.	

For use at room temperature, pH adjusted to 9 with NaOH.

Electroless nickel bath B is from U.S. Pat. 3,488,166, Kovac et al., patented Jan. 6, 1970. There are also numerous commercial electroless nickel baths offered under proprietary names for this use.

If desired, from about 0.01 to about 1.0% by weight of one of the above quaternary amine surfactants can be dissolved in the above reducing solution and used in conjunction with the surfactant solution in the above described process or the surfactant solution omitted from the process and the solution of surfactant and reducing agent used alone.

The ease with which extruded or molded plastic nonconductor surfaces are metalized varies from part to part or even from batch to batch. Reasons for this variation are not really known but have been attributed to variations such as mold design, gate size, mold temperature, melt temperature, etc. These variations are readily overcome by use of the process of this invention.

While the common practice is to refer to the deposits from the above hypophosphite containing electroless nickel bath as "nickel," it is well known that the deposits are really a nickel phosphorus alloy. The term "nickel" as used herein is understood to refer to this nickel phosphorus alloy.

Since the solutions used in the above plating sequences are generally not compatible with each other, the surface of the substrate should be rinsed with water between each treatment step to avoid contaminating the solutions used in the next and subsequent steps with the active ingredients of the preceding solution.

For a fuller understanding of the nature and objects of this invention, reference may be made to the following examples. These examples are given merely to illustrate the invention and are not to be construed in a limit-

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ing sense. All references to temperature are ° F. unless otherwise indicated.

## EXAMPLE 1

To demonstrate the increased rate of metal deposition and the greater uniformity of the metal deposit obtained by the use of these quaternary amine surfactants in the process of metallizing nonconductors, a number of pieces of injection molded acrylonitrile-butadiene-styrene (ABS) and polypropylene (PP) polymers which had been etched were metallized with and without the use of the surfactants and after 45 seconds immersion in the electroless nickel metallizing bath, the pieces were removed and the percent of the surface of the nonconductor which was covered by the electroless nickel deposit was determined by visual observation.

After etching in a chromic acid-sulfuric acid etching solution, the following sequences were used to metallize the surfaces. These sequences show type of solution used in treatment, temperature of treatment and time period of treatment. Surfaces of the pieces were rinsed with water between each step in the sequences.

## Sequence 1

25 Catalyst solution A, room temperature, 2 min.  
Reducingg solution, room temperature, 1 min.  
Nickel bath A or B, room temperature, 45 sec.

## Sequence 2

30 Surfactant solution, room temperature, 2 min.  
Catalyst solution A, room temperature, 2 min.  
Reducing solution, room temperature, 1 min.  
Nickel bath A or B, room temperature, 45 sec.

## Sequence 3

35 Catalyst solution A, room temperature, 2 min.  
Reducing solution, room temperature, 1 min.  
Catalyst solution A, room temperature, 1 min.  
Reducing solution, room temperature, 1 min.  
Nickel bath A or B, room temperature, 45 sec.

## Sequence 4

40 Surfactant solution, room temperature, 2 min.  
Catalyst solution A, room temperature, 2 min.  
45 Reducing solution and surfactant, room temperature, 1 min.  
Catalyst solution A, room temperature, 1 min.  
Reducing solution and surfactant, room temperature, 1 min.  
50 Nickel bath A or B, room temperature, 45 sec.

Where surfactant solution is shown in the sequence above, the solution was prepared by dissolving sufficient commercial quaternary amine surfactant in water to obtain a solution containing the percent by volume of active surfactant which is shown in the column under this heading in Tables 1 and 2. In sequence 4, where use of reducing solution and surfactant is shown, this solution was prepared by adding an equivalent amount of the same surfactant to the reducing solution as was used to prepare the surfactant solution. When Ammonyx T is used, the solution can be prepared more easily if the surfactant is first dissolved using 1 volume to 2 volumes of ethanol and then added to either the reducing solution or to water to make up the surfactant solution. Sequences 1 and 2 were used to plate ABS polymers and sequences 3 and 4 were used to plate PP polymers. Table 1 shows the percentage of the surface covered with nickel when nickel bath A was used to metallize the surface of the polymer as well as the type and concentration of surfactant used, the plating sequence used and the polymer which was metallized. Table 2 shows the same information for those examples where nickel bath B was used to metallize the surface of the polymer.

TABLE 1.—PERCENT OF SURFACE COVERED WITH ELECTROLESS NICKEL DEPOSIT AFTER 45 SEC. WHEN NICKEL BATH A WAS USED TO METALIZE THE SURFACE

Surfactant used	Percent by volume of active surfactant	Metaling sequence used	Polymer	Percent of surface covered with metal
None		1	ABS	5
Hyamine 3500	0.05	2	ABS	100
None		1	ABS	None
Hyamine 3500	0.05	2	ABS	100
None		3	PP	None
Hyamine 3500	0.05	4	PP	100
None		1	ABS	10
Aliquat 204	0.075	2	ABS	100
None		1	ABS	10
Onyxide 172	0.8	2	ABS	90
None		1	ABS	10
Ammonyx T	0.25	2	ABS	90

TABLE 2.—PERCENT OF SURFACE COVERED WITH ELECTROLESS NICKEL DEPOSIT AFTER 45 SEC. WHEN NICKEL BATH B WAS USED TO METALIZE THE SURFACE

Surfactant used	Percent by volume of active surfactant	Metaling sequence used	Polymer	Percent of surface covered with metal
None		1	ABS	None
Hyamine 3500	0.05	2	ABS	95
None		3	PP	None
Hyamine 3500	0.05	4	PP	100
None		1	ABS	10
Aliquat 204	0.075	2	ABS	80
None		1	ABS	10
Onyxide 172	0.8	2	ABS	90
None		1	ABS	10
Ammonyx T	0.25	2	ABS	90
None		3	PP	25
Onyxide 172	0.7	4	PP	100
None		3	PP	25
Ammonyx T	0.25	4	PP	100
None		3	PP	25
Aliquat 204	0.075	4	PP	100

## EXAMPLE 2

The quaternary amine surfactant solutions listed below were used in conjunction with a commercial system for plating on ABS plastic to plate ABS panels. The following plating sequence was used:

Etching solution, 135–145° F., 6 min.

Surfactant solution, room temperature, 1–3 min.

Catalyst solution, 140° F., 1–3 min.

Reducing solution, room temperature, 1–2 min.

Electroless nickel bath, 70–85° F., 1 min.

Surfaces of the panels were rinsed with water between each step in the sequence. When the surfactant solution step was omitted, only 10% of the surface was covered with nickel. When the surfactant step was included in the sequence, the following results were obtained:

Surfactant used	Percent by volume of active surfactant	Percent of surface covered with nickel in 1 min.
Onyxide 172	0.8	100
Ammonyx T	0.25	80–95
Hyamine 3500	0.05	95–100
Aliquat 204	0.75	95

## EXAMPLE 3

A 0.05% by volume surfactant solution of Hyamine 3500 was used in conjunction with a commercial system for plating polypropylene to plate injection molded PP chips and plaques. The sequence used to plate these parts was as follows:

Etching solution, 175–185° F., 10–15 min.

Surfactant solution, room temperature, 1–3 min.

Catalyst solution, room temperature, 1–2 min.

Reducing solution, room temperature, 1 min.

Catalyst solution, room temperature, 1 min.

Electroless nickel bath, 70–85° F., 6 min.

Surfaces of the parts were rinsed with water between each step in the sequence. When the surfactant solution was omitted from the above sequence, the nickel deposit did not completely cover the surface of the plastic and parts were unsuitable for subsequent electroplating. When the surfactant solution was included in the above sequence, the surface of plastic parts was completely covered with electroless nickel and the parts were suitable for subsequent electroplating.

What is claimed is:

1. In an electroless nickel plating process for a nonconductor wherein the nonconductor substrate surface is oxidized to convert the surface to a hydrophilic state followed by water rinsing, the process which then comprises the steps of:

(a) treating the surface in an aqueous surfactant solution comprising from 0.01 to 0.1% by volume of a quaternary amine surfactant where one radical is an alkyl having from about 10 to about 20 carbon atoms and a second radical is selected from the group consisting of an alkyl having from about 10 to about 20 carbon atoms, benzyl and an alkyl benzyl radical, then

(b) rinsing the surface with water to remove excess surfactant solution, thereafter

(c) treating the surface in a palladium salt catalyst solution, then

(d) rinsing the surface with water to remove excess catalyst solution, thereafter

(e) treating the surface in a reducing solution, thereafter

(f) rinsing the surface to remove excess reducing solution, and then

(g) treating the surface in an electroless nickel plating bath to deposit nickel from the bath onto the surface.

2. The process of claim 1 wherein the nonconductor is a polypropylene polymeric material.

3. The process of claim 1 wherein the nonconductor is an acrylonitrile-butadiene-styrene polymeric material.

4. The process of claim 1 wherein the nonconductor is immersed in an electroless nickel plating bath at a temperature of about 65° to about 140° F.

5. The process of claim 1 wherein from 0.01 to 0.1% by volume of the surfactant used in step (a) is also added to the reducing solution in step (e).

6. The process of claim 1 wherein from 0.01 to 0.1% by volume of the surfactant used in step (a) is added to the reducing solution in step (e) and steps (a) and (b) are omitted.

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