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## METAL PLATING OF PLASTICS

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15 Claims

### ABSTRACT OF THE DISCLOSURE

Plastic surfaces are prepared to make them susceptible to being plated by chemical plating solutions by treatment with a solution of a noble metal salt, for example, palladium chloride, in an acid etchant for the plastic, followed by treatment with a solution containing amine boranes or ammonia borane. The borane solution may be a chemical plating solution, in which case, the second step of the surface preparation and the plating occurs simultaneously.

This invention relates to the electroless plating of metals on plastics and more particularly to such plating in which the plastic surface to be plated is pretreated to make it susceptible to being plated by a chemical plating bath.

The conventional method of forming a metal plate on plastics by electroless or chemical plating, which plate can then be a base for further electroless plating or for electroplating, utilizes, after cleaning to remove soil and grease, a series of sequential surface conditioning treatments: (1) the surface is etched by dipping in an etchant for the particular plastic to roughen or modify the plastic surface to make it receptive to subsequent treatment, (2) the etched surface is sensitized by dipping in an acid solution of stannous chloride, (3) the sensitized surface is activated by dipping in an acid solution of a noble metal chloride, such as palladium chloride. The thus pretreated plastic is then dipped in a chemical plating bath containing metal ions and a reducing material such as hypophosphites or amine boranes. It is conventional to water rinse the surface between each treatment step.

This invention is based on my discovery that a plastic surface may be conditioned for electroless metal plating by treatment with a single etch-activator solution followed by treatment with a solution containing amine boranes or ammonia borane, hereinafter frequently referred to as the borane solution. The borane solution may be simply an aqueous solution of amine boranes or ammonia borane, in which case the plastic surface is activated so that it is susceptible to plating with any chemical plating bath. In the now preferred embodiment the borane solution is itself an electroless chemical plating bath containing metal ions as well as the borane, in which case, the plastic is directly plated with the metal corresponding to the metal ion or ions in the bath.

The etch-activator bath of this invention is a solution of a noble metal salt, particularly chlorides such as gold chloride, platinum chloride, or preferably, palladium chloride in an etchant for the particular plastic to be treated. The etch-activator solution should contain at least about 0.001 weight percent noble metal salt and preferably to obtain high plating rates between about 0.005 and 0.010 weight percent. The bath may contain higher amounts of noble metal salts, but is generally undesirable because no substantial benefit is realized and the salts are quite expensive. The etchant used, is of course, selected to be effective with the particular plastic to be used and any acid etchant in which the noble metal salts are soluble is satisfactory for use in the etch-activator solutions. Generally, acid etchants are mixtures of oxidizing acid, such as chromic acid and sulfuric acid mixtures formed by dissolving chromic oxide or alkali metal chromates in sul-

furic acid. Phosphoric acids are also commonly used as etchants in admixture with chromic acid and sulfuric acid. The etchants may also contain additives such as, for example, wetting agents. In addition, there are a number of acid proprietary etchants which may also be used in making the pretreatment bath of this invention, provided, of course, that the noble metal salt can be dissolved therein. Any plastic that is etched by acid etchants, such as ABS (acrylonitrile-butadiene-styrene copolymers) and polystyrene, and acetates and polyolefins that are etchable with acid etchants after pretreatment with organic solvents.

The conditions of treatment with the etch-activator solution, such as temperature and time of contact, may be varied widely depending on the particular etchant and plastic used. Conditions at which the etchant alone will satisfactorily etch the plastic are suitable conditions for use of the etch-activator bath. Generally, a slightly elevated temperature, between about 40 and 80° C., and a contact time of about 1 to 10 minutes are used.

Following treatment with the etch-activator, the plastic surface is contacted with a solution containing an amine borane or ammonia borane. This may suitably be essentially a solution of the borane in an inert solvent, suitably water, preferably containing between about 0.01 and 1 mole/liter of amine borane or ammonia borane. Higher concentrations of boranes may be used if desirable without detriment or benefit. The amine borane may be any of the wide variety of amine boranes used in electroless plating baths, such as boranes of primary, secondary and tertiary amines. In such instances the surface is activated so that any metal or alloy electroless plating solution will form an adherent plate on the surface by conventional methods, regardless of the reductant used in the plating baths. For example, nickel plates may be laid down from conventional hypophosphite-nickel plating solutions and copper from conventional formaldehyde-copper plating solutions.

Preferably the borane-containing solution is itself an electroless plating bath. Borane chemical plating baths contain an amine borane or ammonia borane and a soluble metal salt, such as nickel, cobalt, iron or zinc salts, and, if desired, additional solubilizing agents, chelating agents, stabilizers, buffering materials or other additives. A large number of such plating baths are well known, such as those disclosed by Hoke in U.S. Patent 2,990,296, by Zirngiebl and Klein in U.S. Patents 3,140,188 and 3,234,031, by McLeod in U.S. Patent 3,062,666, and by E. I. du Pont de Nemours and Company in British Patent 842,826. Any of the electroless plating baths with an amine borane reductant, such as boranes of primary, secondary or tertiary amines, as well as ammonia borane, may be used in the practice of this invention. The preferred reductant is dimethylamine borane, as baths having this reductant give complete coverage of the surface at a somewhat faster rate than those containing only other amine boranes. Generally, the concentration of amine borane in such plating baths is between about 0.01 mol and 0.1 mol per liter, the concentration of metal ion is between about 0.02 mol and 0.3 mol per liter, and the pH is maintained above about 3.5. When borane plating solutions are so used an adherent continuous metal plate, corresponding to the metal ion in the solution, is formed on the plastic surface under the conditions which the plating bath is ordinarily useable.

The borane solution may be plating solution having primarily another chemical reductant and only a small catalytic amount of amine borane or ammonia borane. For example, a nickel plate is formed when a plastic surface pretreated with etch-activator is contacted with a conventional hypophosphite-nickel bath containing as little as 0.001 mol/liter of amine borane or ammonia borane.

## 3

It should be recognized that the metal plates may be single metals or alloys, depending on the plating bath and conditions used, and frequently will contain minor amounts of boron or phosphorous. This invention is applicable for use with any of the well-known chemical plating baths and such bath compositions or plates produced therefrom constitute no part of my discovery.

The following examples are illustrative of this invention.

## EXAMPLE I

A plaque of ABS plastic Cyclac EP-3510 (Marbon Chemical Company) was cleaned by a dip in an alkaline cleaning solution to remove extraneous dirt and grease. The plaque was then immersed for two minutes at 50° C. in an etch-activator bath containing 100 g. Cr<sub>2</sub>O<sub>3</sub>, 50 ml. of concentrated H<sub>2</sub>SO<sub>4</sub>, 0.0221 g. of PdCl<sub>2</sub> and sufficient water to bring the solution volume to 400 ml. The plaque was then rinsed with water and immersed for 2 minutes at 50° C. in a chemical plating bath having the following composition: NiSO<sub>4</sub>·6H<sub>2</sub>O, 0.13 mol./liter; C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·H<sub>2</sub>O, 0.07 mol./liter; (CH<sub>3</sub>)<sub>2</sub>NBH<sub>3</sub>, 0.04 mol./liter; and NH<sub>4</sub>OH to pH 7.0-7.5. At the end of the treatment, the plaque was covered with a continuous adherent, bright nickel plate.

## EXAMPLE II

Example I was repeated, except the etch-activator was (a) diluted to ½ the original concentration, (b) 25 ml. of concentrated H<sub>2</sub>SO<sub>4</sub> was added to the etch-activator, and (c) 250 ml. of 72 wt. percent H<sub>2</sub>SO<sub>4</sub> was added to the etch-activator, with substantially the same results.

## EXAMPLE III

A clear plaque of Cyclac EP 3510 was immersed for 4 minutes at 60° C. in an etch-activator bath containing 30 g. of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, 200 ml. of concentrated H<sub>2</sub>SO<sub>4</sub>, 0.1096 g. PdCl<sub>2</sub> and 200 ml. of water. After rinsing with water, the plaque was plated with nickel as in Example I.

## EXAMPLE IV

Example I was repeated with the same results, except that the etch-activator contained 0.0067 g. of PdCl<sub>2</sub>.

## EXAMPLE V

Example III was repeated using etch-activator solution to which 10, 20, 30 and 40 ml., respectively, of 85% H<sub>3</sub>PO<sub>4</sub> was added. The plating rate was slightly faster than Example IV in the first three runs and somewhat slower in the fourth run.

## EXAMPLE VI

A plaque of Cyclac EP 3510 was immersed for two minutes at 60° C. in an etch-activator bath containing 200 ml. concentrated H<sub>2</sub>SO<sub>4</sub>, 25 ml. concentrated HCl, 0.1255 g. PdCl<sub>2</sub> and 200 ml. water. After rinsing with water the plaque was nickel plated as in Example I.

## EXAMPLE VII

A number of Cyclac EP 3510 plaques were treated with the etch-activator as in Example IV, rinsed, and then each was nickel plated with various amine borane chemical plating baths. A number of plaques were satisfactorily plated with baths containing dimethylamine borane and nickel sulfate, the concentration of dimethylamine borane ranging from 2.0 g./l. to 3.5 g./l., the pH ranging from 5.0 to 9.0, and with various nickel complexing agents, including citrates, lactates, glycolates and ammonia, at temperatures between about 30° C. and 65° C.

A pretreated plaque was satisfactorily plated at 50° C. with a bath containing 7.5 g. of NiSO<sub>4</sub>·6H<sub>2</sub>O, 5 g. of citric acid dihydrate, 0.3 g. NH<sub>3</sub>BH<sub>3</sub>, water to 250 ml. total volume and NH<sub>4</sub>OH to a pH of 6.5.

Another pretreated plaque was satisfactorily plated at 65° C. with a bath containing 15 g. NiSO<sub>4</sub>·6H<sub>2</sub>O, 10 g. of citric acid dihydrate, 5 g. tributylamine borane, water to 400 ml. total volume, and NH<sub>4</sub>OH to a pH of 5.0.

## 4

## EXAMPLE VIII

To illustrate the unsuitability of plating baths containing only hypophosphite reductants, a plaque pretreated as in Example IV was immersed at 65° C. in a hypophosphite bath containing 8.1 g. NiSO<sub>4</sub>·6H<sub>2</sub>O, 12.8 g. of 85% lactic acid, 4.0 g. succinic acid, 9.6 g. NaH<sub>2</sub>PO<sub>2</sub>, water to 400 ml. total volume, and NaOH to a pH of 5.5. There was negligible nickel deposition, even when plaques had been immersed as long as 60 minutes in the etch-activator bath and in the hypophosphite plating bath. The hypophosphite bath is a typical bath that produced good plates on plastics pretreated by the prior art procedures outlined hereinbefore.

## EXAMPLE IX

Example VIII was repeated except that 0.12 g. of dimethylamine borane was added to the hypophosphite bath and a good nickel plate was produced with an immersion time of two minutes in the etch-activator and 5-10 minutes in the plating bath.

## EXAMPLE X

A plaque pretreated as in Example IV was immersed in a 1 wt. percent aqueous dimethylamine borane solution and rinsed with water. A good nickel plate was formed when the plaque was immersed in the hypophosphite bath of Example VIII.

## EXAMPLE XI

A plaque was pretreated with etch-activator and aqueous dimethylamine borane solution as in Example X. After rinsing, the plaque was rapidly plated with copper on immersion in the proprietary electroless copper-plating solution Q-88 Copper obtained from the Bigelow Metalizing Chemistry Company.

According to the provisions of the patent statutes, I have explained the principle and mode of practice of my invention and have described what I now consider to represent its best embodiment. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

I claim:

1. A method of metal plating a plastic surface comprising the steps of sequentially (1) contacting the surface with an etch-activator solution of a noble metal salt in an acid etchant selected from the group consisting of mixtures of chromic and sulfuric acids and mixtures thereof with phosphoric acid, and (2) rinsing the surface with water, and (3) contacting the surface with a second solution selected from the group consisting of a water solution of an amine borane or ammonia borane and a chemical nickel-plating bath containing an amine borane or ammonia borane.

2. A method according to claim 1 in which the plastic is an acrylonitrile-butadiene-styrene copolymer.

3. A method according to claim 1 in which the etch-activator solution consists essentially of at least about 0.001 weight percent palladium chloride in the etchant.

4. A method according to claim 3 in which the amine borane is dimethylamine borane.

5. A method according to claim 3 in which the second solution is a chemical plating bath consisting essentially of a nickel salt and a reductant selected from the group consisting of amine boranes and ammonia borane.

6. A method according to claim 3 in which the second solution is a hypophosphite-nickel plating bath containing at least about 0.001 mole per liter of amine borane or ammonia borane.

7. A method according to claim 1 in which the noble metal salt is a chloride.

8. A method according to claim 7 in which the etch-activator solution consists essentially of at least about 0.001 weight percent palladium chloride in the etchant.

5

9. A method according to claim 7 in which the second chemical plating bath consisting essentially of nickel salt and a reductant selected from the group consisting of amine boranes and ammonia borane.

10. A method according to claim 9 in which the etch-activator solution consists essentially of at least about 0.001 weight percent palladium chloride in the etchant.

11. A method according to claim 10 in which the amine borane is dimethylamine borane.

12. A method according to claim 7 in which the second solution is a hypophosphite-nickel plating bath containing an amine borane or ammonia borane in at least an amount sufficient to cause the formation of a nickel plate.

13. A method according to claim 12 in which the plating bath contains at least about 0.001 mole per liter of amine borane or ammonia borane.

14. A method according to claim 13 in which the etch-activator solution consists essentially of at least about 0.001 weight percent palladium chloride in the etchant.

15. A method according to claim 13 in which the amine borane is dimethylamine borane.

6

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