

Electroless Nickel Plating on ABS Plastics from Nickel Chloride and Nickel Sulfate Baths

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Summary: Aqueous acid nickel chloride and alkaline nickel sulphate bath were studied for electroless nickel plating on acrylonitrile-butadiene-styrene (ABS) plastic. Before electroless nickel plating, specimens were etched, sensitized and activated. Effects of sodium hypophosphite and sodium citrate concentrations on the electroless nickel plating thickness were discussed. Aqueous acid nickel chloride bath comprising, nickel chloride 10 g/L, sodium hypophosphite 40 g/L, sodium citrate 40 g/L at pH 5.5, temperature 85°C and density of 1 Be' for thirty minutes gave best coating thickness in micrometer. It was found that acid nickel chloride bath had a greater stability, wide operating range and better coating thickness results than alkaline nickel sulphate bath. Acid nickel chloride bath gave better coating thickness than alkaline nickel sulfate bath.

Introduction

An adherent bright metallic coating was applied to plastic articles by pretreating the surface, depositing a primary electroless copper underlayer, then depositing a bright secondary electroless metallic overlayer, with elimination of any subsequent electroplating process. The coating can be limited to selected surface areas by mechanical removing a portion of the primary copper prior to immersion in the secondary bath. Thus, ABS copolymer [9003-56-9] radio knobs were etched five minutes at 65-70°C in a conventional chromic acid-sulphuric acid solution, rinsed in water, neutralized, rinsed in water, activated fifteen minutes at 40°C with a cuprous chloride-hydrochloric acid solution, rinsed in hot water, accelerated ten minutes at 30°C with a sodium borohydride-sodium hydroxide-surfactant solution, rinsed in water, immersed thirty to sixty minutes at 25-30°C and pH 12.0 to 12.5 in a primary bath comprising copper sulphate 20, nitrilotriacetic acid trisodium salt 50, sodium hydroxide 20, sodium cyanide 0.01-0.02, and 37% formaldehyde 30 g/L, and immersed twenty to thirty minutes at 70-90°C and pH 4.5 to 5.5 in a secondary bath comprising nickel sulphate 20, 80% lactic acid 30, propionic acid 2, lead acetate 0.001, and sodium hypophosphite 25 g/L. The overlayer had reflectivity 80-90% [1].

Electroless nickel coatings on ABS plastics were obtained from ammonium hydroxide solution with small amounts of sodium hypophosphite at a

coating rate of 4-5 µm/h. The stability of the solution was increased by decreasing its temperature without addition of stabilizers. The electroless layer is defect-free and can be used as an interlayer for electrochemical nickel plating [2].

The development of electroless nickel-phosphorous composite coatings was reviewed. It highlights the method of formation, mechanism of particle incorporation, factors influencing particle incorporation, effect of particle incorporation on the structure, hardness, friction, wear and abrasion resistance, corrosion resistance, high temperature oxidation resistance of electroless nickel-phosphorous composite coatings as well as their applications. The improvement in surface properties offered by such composite coatings will have a significant impact on numerous industrial applications and in the future they will secure a more prominent place in the surface engineering of metals and alloys [3].

The electroless deposition of nickel-tungsten-phosphorous alloy coatings onto metal substrates using $H_2PO_2^-$ as reducing agent from solutions containing nickel sulfate, sodium tungstate, sodium citrate, ammonium sulfate and other additives was studied. At most temperatures (60-80°C) and pHs (7-11) investigated, bright and coherent coatings uniform in appearance were produced. Phosphorous and tungsten contents ranging from 3.5 to 8 wt % and

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0.5 to 6 wt %, respectively, were obtained depending upon solution temperature and pH. Trends such as the effects of pH and temperature on average metal deposition rate and the phosphorous content in the alloy are similar to that reported previously for the nickel-phosphorous system. Correlation of open-circuit potentials with events occurring at the electrode surface in different solutions and polarization curves provide strong evidence that Ni^{2+} ions participate in tungsten and phosphorous deposition, hydrogen evolution and H_2PO_2^- oxidation and that H_2PO_2^- ions participate in cathodic reduction. This indicates that the partial reactions for the nickel-tungsten-phosphorous system do not occur independently of one another [4].

The mechanism of electroless nickel plating on ceramic in a bath containing nickel chloride 7.5, sodium hypophosphite 7.5, ammonium chloride 8.75, and sodium citrate 6.25 g/L at $80 \pm 2^\circ\text{C}$ and $\text{pH} = 5.4$ was discussed. The existence of phosphate ions in bath after several depositions was, presumably, due to the oxidizing of phosphite ions by divalent nickel ions [5].

Results and Discussion

Electroless nickel plating on ABS plastic specimens was carried out. Two types of electroless nickel plating baths were studied: (1) acid nickel chloride bath, (2) alkaline nickel sulphate bath.

Effect of sodium citrate and sodium hypophosphite: Effect of sodium citrate and sodium hypophosphite on coating thickness of electroless nickel coating from acid chloride bath was investigated. Results obtained are shown in figure 1. The concentration of sodium chloride was maintained at 10 g/L in this set of experiments. The electroless nickel coating was carried at temperature 85°C , $\text{pH} 5.5$, and solution density 1 Be^l . The plating conditions were kept constant in all sets of experiments.

Figure 1 shows that the maximum coating thickness was obtained when sodium citrate/sodium hypophosphite ratio was 1:1. Also by increasing the concentration of both sodium citrate and sodium hypophosphite, keeping the ratio 1:1, the coating thickness of electroless nickel coating was also increased, figure 1.

The effect of nickel chloride concentration on coating thickness is shown in figure 2. It was seen that, figure 2, nickel chloride 10 g/L, gave the maximum thickness in all cases of sodium citrate/

sodium hypophosphite, 5/5, 10/10, 20/20, 30/30, 40/40 g/L. The bath comprising, nickel chloride 10 g/L, sodium hypophosphite 40 g/L, sodium citrate 40 g/L at $\text{pH} 5.5$, temperature 85°C and density of 1 Be^l for thirty minutes gave best coating thickness in micrometer, 18 microns, figure 2. Acid nickel chloride bath gave better coating thickness (16 μm /thirty minutes) than alkaline nickel sulphate bath (10 μm /thirty minutes). The stability of the solution is very important for the solution to operate properly. The stability of the solution was maintained by removing the residual metallic nickel in the solution.

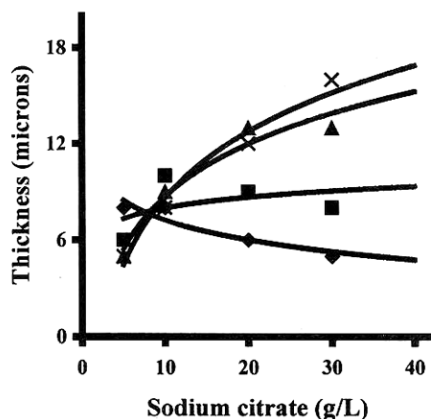


Fig. 1: Effect of concentration of sodium citrate and sodium hypophosphite on thickness of electroless nickel plating from nickel chloride bath. Nickel chloride 10 g/L. 1- Sodium hypophosphite 5 g/L, 2-sodium hypophosphite 10 g/L, 3-sodium hypophosphite 20 g/L, 4- sodium hypophosphite 30 g/L

Electroless nickel coating was also carried out from alkaline nickel sulfate bath. The effect of nickel sulfate's concentration on thickness of electroless nickel coating is shown in figure 3. The effect was studied at different concentrations of sodium citrate and sodium hypophosphite but their ratio was kept 1:1. The electroless nickel plating was carried out at temperature $40-45^\circ\text{C}$, $\text{pH} 9$, density 5 Be^l and deposition time thirty minutes. The plating conditions were kept constant in all the experiments. At nickel sulfate 30 g/L, maximum coating thickness was obtained in all cases; at sodium citrate/sodium hypophosphite 5/5, 10/10, 20/20, 30/30, 40/40 g/L, figure 3.

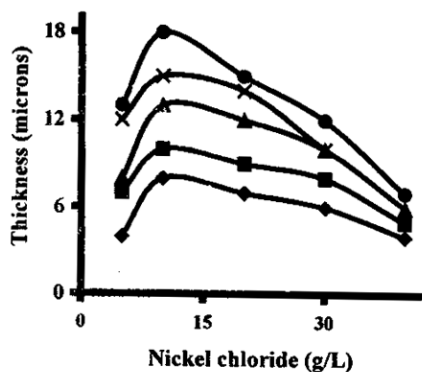


Fig. 2: Effect of concentration of nickel chloride on thickness of electroless nickel plating from nickel chloride bath. 1-Sodium citrate/sodium hypophosphite 5/5 g/L, 2-sodium citrate/sodium hypophosphite 10/10 g/L, 3-sodium citrate/sodium hypophosphite 20/20 g/L, 4-sodium citrate/sodium hypophosphite 30/30 g/L, 5-sodium citrate/sodium hypophosphite 40/40 g/L

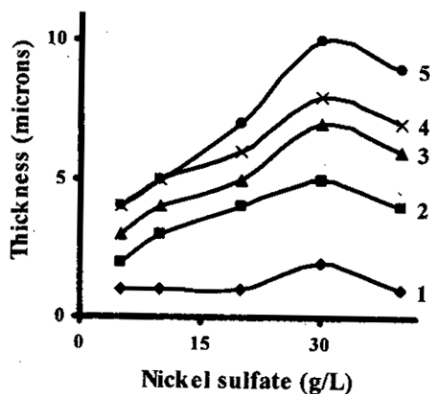


Fig. 3: Effect of concentration of nickel sulfate on thickness of electroless nickel plating from nickel sulfate bath. 1-Sodium citrate/sodium hypophosphite 5/5 g/L, 2-Sodium citrate/sodium hypophosphite 10/10 g/L, 3- Sodium citrate/sodium hypophosphite 20/20 g/L, 4-Sodium citrate/sodium hypophosphite 30/30 g/L, 5-Sodium citrate/sodium hypophosphite 40/40 g/L

Alkaline nickel sulphate bath containing nickel sulphate 30 g/L, sodium hypophosphite 40 g/L, sodium citrate 40 g/L at pH 9, temperature 50°C

and density of 5 Be' gave good coating thickness, 10 microns, figure 3. At pH < 7, electroless nickel sulphate bath was not operated properly because hydrogen ions are a by-product, and the pH of the electroless nickel bath decreases during operation. The pH of the bath was maintained by the addition of ammonium hydroxide and sodium carbonate. Acid nickel chloride bath had a greater stability, wide operating range and better coating thickness results than alkaline nickel sulphate bath. The acid nickel chloride bath gave better coating thickness than alkaline nickel sulfate electroless nickel bath.

The saw test

The metallic nickel layer was not peeled off during sawing across the electroless nickel plated ABS component.

Appearance test

It was seen that electroless nickel deposit was grey in color with smooth surface. Bright deposits were obtained at higher nickel concentration. The nickel coatings have satin finish.

Experimental

Chemicals

Nickel sulphate, NiSO₄.6H₂O, INCO, Canada; nickel chloride, NiCl₂.6H₂O, INCO, Canada; chromium trioxide, CrO₃, OXYCHEM, USA; sulphuric acid, BDH, England; stannous chloride, SnCl₂, BDH, England; palladium chloride, PdCl₂, Johnson & Mathe, England. Other chemicals, sodium hypophosphite monohydrate, sodium citrate dihydrate, sodium hydroxide, sodium carbonate, ammonium hydroxide, hydrochloric acid, were of laboratory grade or better and were used as received.

ABS plastic specimens

ABS plastic sheet having smooth surface was cut into small strips of various shapes. These strips were used as a base material for electroless nickel plating process. Before electroless nickel plating ABS surface was rinsed with 10% common detergent solution in order to remove greasy materials.

Etching

Then thoroughly washed with distilled water and etched in chromic plus sulphuric acid solution; chromium trioxide 300 g/L, sulphuric acid 200 ml/L, density 24 Be', at temperature 65-70°C and immer-

sion time ten minutes. Specimens were immersed in acid solution for one minute at temperature 30°C to remove any traces of chromic acid etch solution left on the surface

Sensitization

Aqueous acidic colloidal stannous chloride solution was used to sensitize the previously etched ABS specimens. Sensitization was carried out from solution, stannous chloride 3 g/L, hydrochloric acid (10%) 20 ml/L, at temperature 40°C for immersion time five minutes.

Activation

For activation the specimen were immersed in palladium chloride solution, palladium chloride 0.3 g/L, hydrochloric acid (10%) 20 ml/L, at temperature 40°C for five minutes. The pH of the solution was 2.9.

Accelerating

Acceleration of palladium activated ABS specimens was done in an aqueous sulphuric acid (20%, volume/volume) solution at temperature 40°C, for three to five minutes.

Electroless nickel plating

Electroless nickel was plated on previously activated ABS specimens from aqueous solutions of nickel chloride/nickel sulphate, sodium hypophosphite and sodium citrate.

Electroless nickel chloride bath

Nickel chloride bath for electroless nickel plating was prepared from nickel chloride, sodium citrate and sodium hypophosphite. The concentration of each substituent was varied from 5 to 40 g/L and their effect was studied. In all the experiments the solutions were prepared in distilled water. The plating conditions were, temperature 85°C, pH 5.5, density 1 Be' and deposition time thirty minutes. The pH of the bath was maintained by the addition of ammonium hydroxide. The plating conditions were kept constant in all the experiments.

Electroless nickel sulfate bath

Nickel sulfate bath for electroless nickel plating was prepared from nickel sulfate, sodium citrate and sodium hypophosphite. The concentration of each substituent was varied from 5 to 40 g/L and their effect was studied. In all the experiments the

solutions were prepared in distilled water. The plating conditions were, temperature 40-455°C, pH 9, density 5 Be' and deposition time thirty minutes. The pH of the bath was maintained by the addition of ammonium hydroxide and sodium carbonate. The plating conditions were kept constant in all the experiments.

Drying

After electroless nickel coating, ABS specimens were immersed in warm water for one minute to wipe out completely traces of chemicals left on the finished surface. Double water rinsing was done before drying the finished ABS plastics.

Thickness measurement

The thickness of electroless nickel coating was measured by difference in thickness of nickel coated and uncoated ABS component automatically in five seconds and recorded by (Echometer, an ultrasonic thickness gauge) a hand-held instrument. A few drops of fluid (for example, grease, water or glycerine) were applied to the location on the work-piece where the measurement was to be made. The probe was attached and thickness was recorded [6].

Conclusions

Effect of nickel chloride, sodium hypophosphite and sodium citrate concentrations for aqueous acid nickel chloride bath and effect of nickel sulphate concentrations in alkaline nickel sulphate bath was studied for electroless nickel plating process on ABS plastic. It was found that acid nickel chloride bath had a greater stability, wide operating range and better coating thickness results than alkaline nickel sulphate bath. Best nickel chloride concentration was found 10 g/L and that of nickel sulphate 30 g/L. Concentrations of sodium hypophosphite 40 g/L and sodium citrate 40 g/L gave best coating thickness results for each bath. The electroless nickel coatings were bright, have satin finish and good adhesion.

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