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ELECTROLESS NICKEL SOLUTION

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10 Claims

ABSTRACT OF THE DISCLOSURE

The invention relates to electroless nickel solutions characterized by the addition of a small but effective amount of a source of iodate ions for increased bath stability. It is known in the art that solutions for electroless nickel plating are unstable and tend to decompose with use. It is also known that decomposition can be retarded and the useful life of a plating solution increased by the addition of various additives, frequently catalytic poisons, in very small concentrations. In accordance with the present invention, it has been found that the stability of an electroless nickel plating solution can be substantially increased by the addition of a source of cuprous ions.

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part to U.S. patent application Ser. No. 65,301 filed Aug. 19, 1970, which application is a division of U.S. patent application Ser. No. 785,350 filed Dec. 19, 1968 and both now abandoned.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to nickel depositing compositions and more particularly, to electroless nickel plating solutions having extended life and temperature tolerance and characterized by the addition of iodate ions as a stabilizer.

(2) Description of the prior art

Electroless nickel deposition refers to the chemical plating of nickel or its alloys over an active surface by chemical reduction in the absence of the external electric current. Processes and compositions useful therefore are described in numerous publications. For example, compositions for depositing electroless nickel, are described in U.S. Pat. Nos. 2,690,401; 2,690,402; 2,762,723; 2,935,425; 2,929,742; and 3,338,726. Other useful compositions for depositing nickel and its alloys are disclosed in the 35th Annual Edition of the Metal Finishing Guidebook for 1967, Metal and Plastics Publications, Inc., Westwood, N.J., pages 483 to 486. Each of the foregoing publications are included herein by reference.

Known electroless nickel deposition solutions generally comprise at least four ingredients dissolved in a solvent, typically water. They are (1) a source of the nickel ions, (2) a reducing agent such as a hypophosphite or an amine borane, (3) an acid or hydroxide pH adjustor to provide required pH and (4) a complexing agent for metal ions sufficient to prevent their precipitation in solution. A large number of suitable complexing agents for electroless nickel solutions are described in the above noted publications. In some formulations, the complexing agents are helpful but not a necessity.

Although electroless nickel solutions have been used for many years, the commercially used formulations have not been satisfactory for several reasons. Among these are relatively slow deposition rates and bath instability. It has

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been found that plating rate is dependent to some extent, upon the concentration of the reducing agent or the nickel ion in the plating solution as well as solution pH, and that increased concentration of either generally results in an increased rate of deposition. However, increased concentration of reducing agent and/or nickel, also results in decreased bath stability. This is evidenced by a decrease in the time in which the plating solution will undergo uncontrollable deposition (trigger).

It is known in the art that certain additives or inhibitors added to an electroless nickel solution in properly controlled trace quantities act as stabilizers and retard the rate of bath decomposition. Generally speaking, these stabilizers are catalytic poisons and their concentration in solution is usually critical. Trace quantities, typically in the range of a few parts per million parts of solution provide stability. An excess of stabilizer will partially or totally stop deposition of the electroless metal.

One such stabilizer which is also a catalytic poison is disclosed in U.S. Pat. No. 2,762,723. This patent teaches an acid nickel plating solution stabilized with a source of sulfide ions and a "sulfide ion controller" which combines with the sulfide ions to prevent their liberation from a hot or boiling solution. Such sulfide ion controllers are lead, bismuth, tin, selenium, tellurium, tungsten, thorium, titanium, copper, zinc, manganese and rhenium. The sulfide ions, which comprises the active portion of the stabilizing combination, are catalytic poisons and as such, depress plating rate in trace quantities and prevent plating in larger quantities.

STATEMENT OF THE INVENTION

The present invention is predicated upon the discovery that the addition of a small but effective amount of a source of iodate ions to substantially any electroless nickel or nickel alloy solution improves stability without significantly retarding the rate of deposition. Accordingly, the present invention provides an electroless nickel deposition solution comprising (1) a source of nickel ions, (2) a reducing agent therefore, (3) a pH adjustor, (4) a complexing agent for the nickel ions sufficient to prevent their precipitation from solution where necessary, and (5) a source of iodate ions as a stabilizer for the solution.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As noted above, the iodate ions are believed to be responsible for increased bath stability, corrosion resistance and brightness. Substantially, any iodate compound sufficiently soluble in the electroless nickel plating solution and free of an interfering anion is suitable for purposes of the present invention. Typical examples of iodate compounds include ammonium iodate, calcium iodate, cobaltous iodate, magnesium iodate, nickel iodate, potassium iodate and sodium iodate.

Since the iodate ion is not believed to be a catalytic poison, its concentration is not critical and it may be added in an amount as low as one part per million parts of solution with some improvement in stability up to an amount in excess of 1000 parts per million parts of solution, though it is preferred to add the iodate compound in an amount of from 5 to 100 parts per million parts of solution.

The particular iodate compound selected from purposes of the present invention is not critical provided it yields sufficient iodate ions in solution and provided further that the anion of the compound is not harmful to the plating solution.

Electroless nickel plating solutions stabilized with an iodate compound in accordance with the invention are used to deposit nickel in the same manner as any prior art electroless nickel solution. The surface of the part to

be plated should be free of grease and contaminating material. Where a non-metallic surface is to be plated, a surface area to receive the deposit must first be sensitized to render it catalytic to the reception of the electroless nickel as by the well known treatment with an acidic aqueous solution of stannous chloride followed by treatment with a dilute aqueous acidic solution of palladium chloride. Alternatively, extremely good sensitization of non-metallic surfaces is achieved by contact with a colloid of a precious metal having a protective stannic acid colloid and formed by the admixture of stannous chloride and a precious metal chloride, preferably palladium chloride, the stannous chloride being present in stoichiometric excess based upon the amount of precious metal chloride.

The invention will be better understood by reference to the following examples where stability of a solution was measured by the time it takes a bath to spontaneously decompose (trigger) when plating either catalyzed cloth or activated aluminum. The catalyzed cloth was prepared by treating a cotton fabric according to the following sequence of steps:

(1) Rinse cloth in a 20% (by weight) ammonium hydroxide solution maintained at room temperature for five minutes. Rinse in cold water.

(2) Rinse for five minutes in 20% acetic acid solution maintained at room temperature. Rinse in cold water.

(3) Immerse for some twenty to forty seconds in a sensitizing solution of palladium colloid having a protective stannic acid colloid (catalyst 6F) maintained at room temperature. Rinse in cold water.

(4) Immerse for one to three minutes in a dilute hydrochloric acid solution maintained at room temperature. Rinse in cold water.

(5) Dry cloth and cut to size.

The activated aluminum used as a 2024 alloy activated by immersion in 30% hydrochloric acid for two minutes.

In all examples, to determine stability, one square foot of either the catalyzed cloth or the activated aluminum per gallon of solution was used to initiate deposition and triggering. Also, reagent grade chemicals and distilled water were used to avoid contamination by impurities.

EXAMPLE 1

Nickel sulphate tetrahydrate -----grams--	35
Sodium hypophosphite	
monohydrate -----do-----	15
Sodium acetate -----do-----	15
Water -----liters--	To 1
Temperature -----° F--	195 to 205
pH -----	5 (approx.)

The activated aluminum caused triggering of the above bath in 12 minutes with heavy side wall deposition occurring in about 8 minutes. When 15 parts per million parts of solution of iodate ion as potassium iodate were added to the bath, it did not trigger within 40 minutes.

EXAMPLE 2

Nickel chloride -----grams--	30
Sodium hypophosphite	
monohydrate -----do-----	10
Ammonium chloride -----do-----	100
Ammonium hydroxide -----pH--	To about 9
Water -----liters--	To 1
Temperature -----° F--	195 to 205

The following bath triggered in about 20 minutes using activated aluminum. With the addition of 15 parts per million parts of solution of iodate ion as sodium iodate,

triggering did not occur for approximately 40 to 45 minutes.

EXAMPLE 3

Nickel chloride -----grams--	30
5 Sodium hypophosphite	
monohydrate -----do-----	10
Ammonium chloride -----do-----	25
Ammonium hydroxide -----pH--	To about 8.5
10 Water -----liters--	To 1
Temperature -----° F--	About 180

Addition of catalyzed cloth to the above solution resulted in triggering within about 1 to 2 minutes. With the addition of about 10 parts per million parts of iodate ion as potassium iodate, triggering did not occur for about 12 minutes. When the iodate ion content was increased to 20 parts per million parts of solution, triggering did not occur for about 20 minutes. Increase of the iodate ion content to 50 parts per million parts of solution resulted in triggering in about 30 minutes. Finally, when the iodate ion content was increased to 100 parts per million parts of solution, triggering did not occur within 40 minutes.

We claim:

1. In an aqueous electroless nickel plating solution comprising a source of nickel ions, a reducing agent therefore, a pH adjustor to provide required solution pH and a complexing agent for said nickel ions, the improvement comprising iodate ion in solution in a small but effective amount capable of providing increased bath stability, said iodate ion being derived from a salt having a cationic portion non-interfering with said plating solution.

2. The solution of claim 1 where the reducing agent is a hypophosphite.

3. The solution of claim 2 where the iodate ions are in solution in an amount up to about 1000 parts per million parts of solution.

4. The solution of claim 2 where the iodate ions are in solution in an amount varying from about 5 to 100 parts per million parts of solution.

5. The solution of claim 2 where the source of the iodate ions is an alkali metal iodate.

6. The solution of claim 2 where the nickel plating solution is an acidic solution.

7. The solution of claim 2 where the nickel plating solution is an alkaline solution.

8. In an acidic aqueous electroless nickel plating solution comprising a source of nickel ions, hypophosphite as a reducing agent for said nickel ions, a pH adjustor to provide required solution pH and a complexing agent for said nickel ions, the improvement comprising a small but effective amount of iodate ions in solution capable of providing increased bath stability, said iodate ion being derived from a salt having a cationic portion non-interfering with said plating solution.

9. The solution of claim 8 where the iodate ions are in solution in an amount varying from about 5 to 100 parts per million parts of solution.

10. The solution of claim 8 where the source of iodate ions is an alkali metal iodate.

References Cited

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65 LORENZO B. HAYES,	Primary Examiner		

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