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COMPOSITIONS AND PROCESSES FOR ELECTROLESS NICKEL PLATING

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ABSTRACT OF THE DISCLOSURE

An electroless nickel plating composition characterized by the addition of hydroxy-propane sulfonic acid or a salt of hydroxy-propane sulfonic acid. The additive suppresses side reactions consumptive of hypophosphite, provides a more constant ratio of consumption of hypophosphite ions relative to nickel ions in storage and in use and suppresses gas generation and evolution in the body of the composition other than at the catalytic surface being plated.

This invention relates to improved processes of electroless nickel plating of catalytic surfaces employing baths of the nickel cation-hypophosphite anion type, the nickel ions being reduced to metal by the hypophosphite ions. Electroless plating refers to plating by chemical reduction in the absence of an external electric source.

Electroless nickel deposition of the above type is well known and is disclosed for example in United States Patents Nos. 2,532,283; 2,762,723; 2,935,425; and 2,999,770, which disclose suitable materials, concentrations, operating temperatures, pH conditions and various additives such as buffers, complexing agents for the nickel ions, and stabilizers. Deposition occurs in the presence of a catalytic surface, generally a variety of metals as disclosed in the above patents. Also, non-catalytic surfaces, such as plastics, ceramics, or other dielectrics, may be sensitized with catalysts as disclosed in the above patents and as also disclosed in United States Patent No. 3,011,920.

As recognized in the above patents, stability of such nickel compositions in extended deposition and storage is a continuing problem. Plating compositions are employed typically for several cycles by replenishment or addition of consumed ingredients during use to maintain approximately initial concentrations. One cycle represents one complete consumption and replenishment of the amount of nickel initially present.

Replenishment on a satisfactory basis of compositions of the above type require extensive and careful analysis. Consumption of ingredients has not been reasonably predictable based upon the amount of nickel plated, especially with respect to the reducing agent, hypophosphite. A number of side reactions occur, even in storage, and it has been found necessary normally to analyze for hypophosphite as well as for nickel or other ingredients. Replenishment from a standard replenishment mixture is difficult where the relative consumption of ingredients is not reasonably constant.

It is the principal object of the present invention to provide improved electroless plating compositions, and methods employing the same. Further objects include suppression of side reactions consumptive of hypophosphite, provision of a more constant ratio of consumption of hypophosphite ions relative to nickel ion in storage and use, and suppression of gas generation and evolution in the body of the composition other than at the catalytic surface being plated. Extraneous gas evolution of the above type is thought to be evidence of undesired decomposition in the bath and a potential source of instability. Suppression of hypophosphite consumption in side reaction also suppresses production of phosphite ions, a known source of instability, the hypophosphite ions being oxidized to phosphite.

In accordance with this invention, it has been found that the addition of hydroxy propane sulfonic acid, or the compatible solution-soluble salts thereof, generally alkali-metal salts, to electroless nickel compositions of the nickel cation-hypophosphite anion type has the above stated advantages of suppressing hypophosphite consumption, of rendering it relatively constant with respect to nickel ion consumption, and in suppressing decomposition in the body of the solutions evidenced by evolution of gas.

The amounts of the hydroxy propane sulfonic acid addition is not critical, small amounts providing some advantage and large amounts being tolerable. Generally, amounts as small as 0.25 gram per liter up to about 70 grams per liter or greater are useful. Preferred amounts are between about 1 and 20 grams per liter with about 5 grams per liter being most preferred as illustrated below. Addition of the sulfonic acid additive does not significantly alter the nature or concentrations of the materials useful as heretofore known, or the pH or temperature conditions of operation all of which are known and are illustrated in the above-mentioned patents. Such compositions require a source of nickel ions in an amount sufficient to provide a useful deposit, a source of hypophosphite ion as reducing agent therefor, and acid or base to provide the desired pH which may generally be in the range of about 3 to about 11, but which is more preferably on the mildly acid side. In addition, buffers, complexing or chelating agents for the nickel ions and stabilizers such as a source of trace quantities of sulfide ion, are preferred.

The present invention is illustrated by the following examples.

Ingredient	Ex. 1	Ex. 2
$NiSO—6H_2O$ (g./l.)	20	20
$NaH_2PO_2—H_2O$ (g./l.)	30	30
Hydroxy-acetic acid (100%) (g./l.)	28	28
Propane Sultone* (g./l.)		5
NH_4OH, to pH	4. 5–5. 0	4. 5–5. 0
Water, to make (liter)	1	1

*3-hydroxy-1-propane-sulfonic acid (hydrolysis product).

The above compositions were plated hot, for example at 190–200° F., over a steel surface. As the stabilizer, 1 part per million of lead was added as lead chloride to stabilize the above composition in accordance with the disclosure of United States Patent No. 2,762,723. During plating, the concentration of hypophosphite and nickel was maintained by addition thereto of hypophosphite and nickel salts in the ratio of 3 to 1 molar. Additional lead stabilizer was added in the amount of ½ part per million per cycle of nickel consumption.

Each of Examples 1 and 2 above were plated through four complete cycles of nickel consumption without undue instability and without evidence of gas evolution other than at the surface being plated. At the end of four cycles, each example was analyzed for hypophosphite salt content which was determined to be 28 grams per liter for Example 1, and 32 grams per liter for Example 2, a 14% decrease in hypophosphite consumption. In these tests, deposition was accomplished in approximately twelve hours of bath operation and the losses in the hypophosphite in the case of Example 1 would have been far greater with more extended storage and deposition.

It was also found that the consumption of hypophosphite relative to nickel was relatively constant at the ratio of about 2.85 to 1 so that replenishment needs could be satisfactorily calculated on the basis of nickel concentration analysis without the necessity of frequent hypophosphite analysis.

The hydroxy propane sulfonic acid employed in the above tests was propane sultone obtained from the Shell Chemical Company and is fully described in its publication PD–145 in which it is noted that the propane sultone hydrolyzes in water to form the sulfonic acid.

In the above examples the nickel sulfate is the source of nickel ions, the sodium hypophosphite is the source of hypophosphite ions, and the hydroxy-acetic acid is a known chelating agent for the nickel ions.

It should be understood that the above examples are for the purpose of illustration and that the invention includes all modifications within the scope of the appended claims.

I claim:

1. In an aqueous electroless nickel composition comprising a source of nickel ions in an amount sufficient to provide a useful deposit and a source of hypophosphite ions in an amount sufficient to serve as a reducing agent therefor, the improvement comprising the addition of a member selected from the group consisting of hydroxy propane sulfonic acid and salts thereof soluble in said aqueous electroless nickel composition.

2. A composition according to claim **1**, wherein said hydroxy propane sulfonic acid, or salts thereof, are present in an amount sufficient to suppress consumption of hypophosphite ions in use and storage.

3. An electroless nickel composition according to claim **1** wherein said hydroxy propane sulfonic acid, or salts thereof, are present in an amount between about 0.25 and about 70 grams per liter.

4. A composition according to claim **1**, wherein said hydroxy-propane sulfonic acid is present in an amount between about 1 and 20 grams per liter.

5. A composition according to claim **2**, having a pH between about 3 and 11.

6. A process for electroless plating of nickel comprising contacting a catalytic surface with a composition according to claim **1** for a time sufficient to plate nickel, and removing said surface from contact with said composition.

7. A process for electroless plating of nickel comprising contacting a catalytic surface with a composition according to claim **2** for a time sufficient to plate nickel, and removing said surface from contact with said composition.

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