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2,884,344

NICKEL PLATING

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13 Claims. (Cl. 117—130)

This invention relates to an improved method for chemical plating of nickel on metal surfaces. More particularly, the invention concerns a novel method for inhibiting the reduction of nickel ion in plating baths and to novel inhibited bath compositions for use in chemical plating of nickel.

The chemical plating of nickel on metal surfaces involves methods which have been known for several years, and is generally carried out by means of aqueous baths of the nickel cation-hypophosphite anion type. Plating occurs in the reduction of the bath to metallic nickel by action of the metal being nickel-plated, with corresponding oxidation of the hypophosphite to phosphite. In practical experience with plating solutions of this character, it has been found that after the bath has been in use, even for a comparatively brief period of time, there is a tendency for some of the nickel ion to be randomly reduced in the plating solution, and thus for nickel to be lost to the process. This phenomenon is manifested by the appearance of small flakes of nickel-phosphorus alloy which tend to accumulate on the surface of the metal being plated and thereby to produce rough and nodular nickel plated deposits.

The reduction phenomenon just described is thought to result from limited reduction of nickel ions in the solution itself by hypophosphite ions present. There is also a tendency for this internal reduction to be catalyzed by small amounts of the metal being plated. In any event, the effect is to diminish the efficiency of the plating process both by loss of nickel from the bath, poorer coatings, and particularly in terms of the over-all time required for plating to be completed. Various methods have been proposed for overcoming this defect, including, for example, the addition to the plating bath of trace amounts of buffer additives such as sulfide ions, and of trace amounts of elements such as lead, tin, or bismuth in order to stabilize the baths. Such addition agents have been described in U.S. Patent 2,762,723. Experience has shown, however, that the stabilizing action of these additives is undependable, and, in fact, the aforementioned patent warns that under certain conditions the metal used, such as lead or bismuth, may become a catalytic poison thus considerably reducing the plating rate.

In accordance with the present invention, it has been found that by the incorporation of trace amounts of two or more cations of elements of Group Va of the periodic system in a chemical nickel plating bath of the character described, the nickel hypophosphite plating solution is rendered entirely stable for prolonged periods of time, both in storage, and in contact with a catalytic metal surface, such as the surface of a metal

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to be plated therewith. While, as pointed out previously, metallic ions per se are known to exhibit a limited stabilizing effect upon nickel hypophosphite plating baths, the presence of such ions does not produce a lasting effect. In accordance with the present invention, the surprising and unexpected discovery has been made that the cations of elements of Group Va of the periodic system, which subgroup includes the elements arsenic, antimony, and bismuth, exert a specific action in connection with baths of this type, in that their presence substantially increases the plating rate of the bath, such increase being of the order of magnitude of 20 to 25 percent. Surprisingly, it has been further found, in accordance with this invention, that if two or more of these cations are present in the plating bath at the same time, a synergistic interaction results which creates an extraordinary rise in the plating rate, a rise which substantially doubles the plating rate of a plating bath which contains none of these cations, and which is from 30 to 50 percent higher than the plating rate of a bath which contains only one of the cations of arsenic, antimony or bismuth. The cause of this action is not presently understood, and no explanation therefor is suggested here.

The elements arsenic, antimony and bismuth in cation form may be present in the nickel hypophosphite plating solution in an aggregate concentration ranging approximately between 0.1 and 100 parts per million by weight of the plating solution. In these small amounts, the cations act not only to accelerate the plating process, as has been mentioned, but they also act to stabilize the plating bath against catalytic decomposition by the catalytic action of the metal surface being plated, and also against internal decomposition of the solution on storage. Smooth and bright nickel deposits are obtainable even after long periods of plating, such as 24 hours or more. The spontaneous and random reduction of the nickel in the bath is, for practical purposes, eliminated.

The metal surface being plated may include that of any metal which decomposes, by catalysis or otherwise, the nickel hypophosphite bath, of which examples are given of the following metals: iron, nickel, aluminum, copper, bronze, silver, gold, platinum, and palladium.

The arsenic, antimony or bismuth cations may be either in the pentavalent or the trivalent state. It has been found, however, that best results are obtained when trivalent cations are employed in our novel method. These inhibiting or stabilizing elements may be added to the nickel bath in the form of their water soluble inorganic or organic salts, such as, for example, chlorides, sulfates, nitrates, or acetates. Thus, for example, we may add to the nickel hypophosphite bath, arsenic trichloride, antimony trichloride, or bismuth chloride, or suitable combination thereof.

The practice of my invention may be illustrated with reference to the following type of commercial nickel-hypophosphite plating bath, but it will be understood that the application is not limited thereto, and that the invention is fully effective with any chemical nickel plating bath of this general type:

	Gms. per liter of solution
Sodium hypophosphite ($\text{Na}_2\text{H}_2\text{PO}_3$)	23
Sodium citrate	8
Sodium tartrate	1
Sodium acetate	8
Nickel sulfate, $\text{Ni}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$	25 to 30
Inhibitor (total as cation)	p.p.m. 0.1 to 100

A series of comparative tests was performed using the above nickel plating solution with and without inhibitor additions. The purpose of these tests was to determine the plating rate of the bath with and without the inhibitor cations, measured in mg. per sq. cm. per minute at a temperature of about 95° C., plating upon an aluminum sheet having an area of approximately 20 sq. cm., and using a solution volume of about 70 cc. In each example where inhibitors were used, the arsenic, antimony or bismuth were added as the trichlorides, the amount of As⁺⁺⁺, Sb⁺⁺⁺ or Bi⁺⁺⁺ cations present in the solution, being indicated, in p.p.m.

The effects of the cation additions in comparison with the plating rate of a control solution containing no inhibitor, and the striking synergistic effects of combining cations are set forth in Table 1, which summarizes the results of these tests:

TABLE 1
Comparative nickel plating rates

	Inhibitor, p.p.m.	Plating Rate, mg./sq. cm./min. at 95° C.
1. Control nickel plating solution (no addition)		0.41
2. Nickel plating solution with addition of Sb as SbCl ₃	2	0.53
3. Nickel plating solution with addition of As as AsCl ₃	5	0.51
4. Nickel plating solution with addition of Bi as BiCl ₃	10	0.56
5. Nickel plating solution with addition of 10 p.p.m. Bi and 2 p.p.m. Sb	12	0.84
6. Nickel plating solution with addition of 10 p.p.m. Bi and 5 p.p.m. As	15	0.79
7. Nickel plating solution with addition of 5 p.p.m. As and 2 p.p.m. Sb	7	0.75

It will be seen from Table 1 that the addition of both bismuth and antimony cations produces an accelerated plating rate which is more than 100% higher than the plating rate of the bath containing no additions of these metals. Combinations of bismuth and arsenic, and of arsenic and antimony produce results only slightly less effective.

In combining these metal cations for purposes of addition to the nickel baths, the relative proportions of the metals may be varied to some extent. Thus, where antimony and bismuth combinations are employed, the combined parts per million may range between about 5 and 25 p.p.m., and preferably between about 15 and 20 p.p.m. Within this combined cation content, the ratio of antimony to bismuth may vary from approximately 1 to 5, to 1 to 0.5. When employing these ranges, there can generally be expected plating rates between about 0.70 and 0.85 mg. per sq. cm. per minute, using the above described plating bath, at about 95° C. Similar ranges are found to be advantageous when employing combinations of arsenic and antimony, or of arsenic and bismuth, or all three metals together.

Another series of tests was made to determine the effect of adding the metal cations to the plating bath in terms of their power to inhibit decomposition of the bath. For this purpose, a palladium salt, such as palladium chloride (PdCl₂), was added to the plating bath after it had been heated to 95–96° C. The ability of the plating solution to tolerate various concentrations of PdCl₂ before commencement of spontaneous decomposition is indicative of the stabilizing effect of the additions of arsenic, antimony and bismuth cations. The effect of the latter was evaluated by adding PdCl₂ from a solution containing 1000 p.p.m., to 50 cc. of the plating bath maintained at 95–96° C. The amount of PdCl₂ in p.p.m. needed to decompose spontaneously the plating solution serves as an index for evaluation of the cationic inhibitor. The larger

the amount of PdCl₂ needed, the more effective was the inhibitor. The results of these tests are shown in Table 2:

TABLE 2
Evaluation of inhibitor by PdCl₂ additions

	Inhibitor, p.p.m.	Amt. PdCl ₂ Added, p.p.m.
1. Control nickel plating solution (no addition)		1
2. Nickel plating solution with addition of Sb as SbCl ₃	2	20
3. Nickel plating solution with addition of As as AsCl ₃	5	10
4. Nickel plating solution with addition of Bi as BiCl ₃	10	25
5. Nickel plating solution with addition of 10 p.p.m. Bi and 2 p.p.m. Sb	12	32
6. Nickel plating solution with addition of 10 p.p.m. Bi and 5 p.p.m. As	15	20
7. Nickel plating solution with addition of 5 p.p.m. As and 2 p.p.m. Sb	7	15

It will be seen from Table 2 that an increased amount of PdCl₂ is needed as the result of addition of inhibitor cations, particularly in combinations.

A third series of tests was made to evaluate the length of time nickel plating could be carried on with the above solution before nickel flake appeared in the solution. By plating an aluminum surface of 4 sq. cm. area in a solution of approximately 50 cc., volume, a volume to surface ratio of 12.5 was maintained. Under these conditions the time required to plate out all the nickel ranged from about 4 to 6 hours. Where the plating bath was without an inhibitor, small flakes of nickel collected at the bottom of the bath. With solution maintained at about 95–96°, the time required for nickel flakes to appear was measured. The results of this series of tests is shown in Table 3.

TABLE 3
Time for formation of nickel flake during plating

	Inhibitor, p.p.m.	Time in Hours
1. Control nickel plating solution (no addition)		15 min.
2. Nickel plating solution with addition of Sb as SbCl ₃	2	1 hour.
3. Nickel plating solution with addition of As as AsCl ₃	5	1½ hrs.
4. Nickel plating solution with addition of Bi as BiCl ₃	10	2 hours.
5. Nickel plating solution with addition of 10 p.p.m. Bi and 2 p.p.m. Sb	12	over 3 hours.
6. Nickel plating solution with addition of 10 p.p.m. Bi and 5 p.p.m. As	15	1½ hrs.
7. Nickel plating solution with addition of 5 p.p.m. As and 2 p.p.m. Sb	7	1 hour.

It will be apparent from Table 3 that the presence of combinations of cations markedly increases the time period for formation of flake nickel to a point which eliminates the danger of formation for practical purposes.

I claim:

1. A chemical nickel cation hypophosphite anion plating solution containing an aggregate amount of approximately 0.1 to 100 parts per million by weight of the solution of at least two of the metallic elements of Group Va of the periodic system the two metallic elements being present in ratios ranging from about 1:5 to 1:0.5.
2. A chemical nickel cation hypophosphite anion plating solution containing an aggregate amount of approximately 5 to 25 parts per million by weight of the solution, of bismuth and antimony the ratio of antimony to bismuth ranging from about 1:5 to 1:0.5.
3. A chemical nickel cation hypophosphite anion plating solution containing an aggregate amount of approximately 15 to 20 parts per million by weight of the solution, of bismuth and antimony the ratio of antimony to bismuth being about 1:5.

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4. A chemical nickel cation hypophosphite anion plating solution containing an aggregate amount of approximately 15 to 20 parts per million by weight of the solution, of antimony and bismuth, the ratio of antimony to bismuth ranging from about 1:5 to about 1:0.5.

5. Method for the preparation of a chemical nickel cation hypophosphite anion plating solution which comprises incorporating in said solution an aggregate amount of approximately 0.1 to 100 parts per million by weight of at least two of the metallic elements of Group Va of the periodic system, the two metallic elements being present in ratios ranging from about 1:5 to 1:0.0.

6. Method for the preparation of a chemical nickel cation hypophosphite anion plating solution which comprises incorporating in said solution an aggregate amount of approximately 0.1 to 100 parts per million by weight of at least two elements selected from the group consisting of arsenic, antimony and bismuth, said elements being added in the form of their chlorides and being present in ratios ranging from about 1:5 to 1:0.5.

7. The method of chemical nickel plating on the surface of a metal selected from the group consisting of aluminum, iron, nickel, copper, bronze, silver, gold, platinum, and palladium, which comprises immersing said metal in the plating solution of claim 1.

8. The method of chemical nickel plating on the surface of a metal selected from the group consisting of

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aluminum, iron, nickel, copper, bronze, silver, gold, platinum, and palladium, which comprises immersing said metal in the plating solution of claim 2.

9. The method of chemical nickel plating on the surface of a metal selected from the group consisting of aluminum, iron, nickel, copper, bronze, silver, gold, platinum, and palladium, which comprises immersing said metal in the plating solution of claim 3.

10. The method of chemical nickel plating on the surface of a metal selected from the group consisting of aluminum, iron, nickel, copper, bronze, silver, gold, platinum, and palladium, which comprises immersing said metal in the plating solution of claim 4.

11. The method of chemical nickel plating on the surface of aluminum which comprises immersing the aluminum in the plating solution of claim 2.

12. The method of chemical nickel plating on the surface of aluminum which comprises immersing the aluminum in the plating solution of claim 3.

13. The method of chemical nickel plating on the surface of aluminum which comprises immersing the aluminum in the plating solution of claim 4.

References Cited in the file of this patent

UNITED STATES PATENTS

2,762,723 Talmey et al. ----- Sept. 11, 1956

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,884,344

April 28, 1959

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 12, for "1:5 to 1:0.0" read -- 1:5 to 1:0.5 --.

Signed and sealed this 6th day of September 1960.

(SEAL)

Attest:

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