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3,531,301

PLATING PROCESS

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No Drawing. Filed Aug. 26, 1968, Ser. No. 755,377

Int. Cl. C23c 3/02

U.S. Cl. 106—1

10 Claims

ABSTRACT OF THE DISCLOSURE

The present invention relates to compositions and processes for chemical nickel plating. More particularly this invention relates to novel plating baths and to processes for the plating of solid substrates of either a conductive or non-conductive nature and, in particular, such solid substrates which require low temperature plating conditions.

BACKGROUND OF THE INVENTION

Chemical nickel plating, commonly referred to as "electroless nickel plating," is a well known technique highly useful in depositing uniform nickel surfaces upon solid substrates. In general the technique involves contacting the substrate with a bath containing nickel ions, hypophosphite ions and a buffer. The technique is applicable to plating substrates of a conductive, e.g., metals, or non-conductive nature such as, for example, plastics, rubber, wood or ceramics. In the latter case, however, it is necessary first to prepare or condition the substrate surface prior to contact with the plating bath.

These plating compositions and methods for their use are described in greater detail in, for example, U.S. Pats. 2,532,283; 2,658,841; 2,658,842; 2,690,401; 2,690,402 and 2,690,403 and are well known in the art. With these prior art plating baths, temperatures upwards of 90° C. are generally employed during the plating operation to achieve satisfactory results. This restricts the utilization of the process to substrates which are stable at such temperatures. Furthermore, when it has been sought to utilize these prior art plating baths at lower temperatures, it has been found that rates of deposition are not satisfactory. Moreover, these prior art baths at such low temperature yield unsatisfactory deposits, and also may result in spontaneous decomposition and contamination of the plating bath itself.

BRIEF DESCRIPTION OF THE INVENTION

I have found that conventional chemical nickel plating baths of the type described above can be adapted to low temperature plating operations by the addition thereto of an alkali metal lignosulfonate. I have found these plating compositions to be useful for the plating of both conductive and non-conductive materials, and they are particularly useful in the chemical nickel plating of non-conductive materials at low temperatures. The presence of the lignosulfonate results in increased deposition rate which is particularly important in low temperature applications. This formulation yields a brighter deposit than normally obtained from electroless nickel baths and is less sensitive to spontaneous decomposition and contamination than many of the baths presently being marketed.

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DETAILED DESCRIPTION OF THE INVENTION

My chemical nickel plating compositions comprise aqueous solutions of a nickel salt, an alkali metal hypophosphite, a buffer in the form of a salt of an organic acid and an alkali metal lignosulfonate. Preferably the lignosulfonate has a molecular weight ranging from about 1,000 to about 20,000. Illustrative of such a composition and forming an especially preferred embodiment of my invention is an electroless nickel bath composition comprising 0.095 mole per liter (m./l.) nickel sulfate, 0.236 m./l. sodium hypophosphite, 0.127 m./l. succinic acid, and 0.036 m./l. trisodium salt of nitrilotriacetic acid monohydrate and 0.1% sodium lignosulfonate having a molecular weight of 1,000 to 20,000. In the last mentioned plating composition the nickel ion to hypophosphite ion ratio is 0.4. The term "ion" as employed herein includes the total quantity of element or radical present in the bath; that is, both on the associated and disassociated material. Thus, 100% association is assumed when the term "ion" is used in connection with molar ratios and concentrations in the bath.

The lignosulfonates useful in my compositions are those alkali metal sulfonate salts made from the lignin of sulfite pulp-mill liquors selected from the group consisting of sodium and potassium. They are a light tan to dark brown powder having no pronounced odor and which are stable in dry form and relatively stable in aqueous solution. It is preferred to use the de-sugared alkali metal lignosulfonates. The products are commercially available. The compositions have an average molecular weight in the range of 1,000 to 20,000 and have a bulk density of 20–50 lbs./cubic foot. The practical solubility limit is 100 grams/100 cc. of water.

In general the advantages of my invention are realized by the addition of the lignosulfonates to conventional chemical nickel plating baths. Such baths are characterized by a nickel to hypophosphite ion ratio, expressed as molar concentrations, falling within the range of from about 0.25 to about 1.60. The absolute concentration of hypophosphite ions in the bath expressed in mole/liter is within the range from about 0.15 to about 1.20 and the absolute concentration of the buffer is approximately equal to 2 carboxyl groups of any nickel ion that can be deposited. Thus, in the case of succinic acid or salts thereof, at least 0.05 mole per liter of succinate ion and, in the case of acetic acid or salts thereof, 0.120 mole per liter of acetate ion, can be employed. The initial pH of the bath is within the approximate range of from about 3.3 to about 6.8, preferably 4.0 to 5.0, a pH of 4.75 being especially preferred. In general, the buffer employed in the system can be a soluble salt of a simple short chain aliphatic mono-, or dicarboxylic acid. For example, acetic acid, butyric acid, propionic acid, malonic acid, succinic acid, glutaric acid and the like, as well as their salts can be employed. In addition the bath can contain, and in the baths of my invention preferably does contain, additional buffers which also serve as chelating or complexing agent, to prevent the precipitation of undesirable metal compounds. Exemplary of such agents are nitrilotriacetic acid, ethylene diamine tetraacetic acid, and the like known complexing agents or their salts. The term "buffer" as used herein encompasses such agents. These baths and methods for their use are described in greater detail in the U.S. patents already

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specified and are well-known in the art, and thus, shall not be further generally detailed here.

The following examples illustrate the preparation of a plating composition of my invention.

Example 1

A bath is formulated by mixing the following compositions with distilled or deionized water:

	Grams/liter
NiSO ₄ ·6H ₂ O	25
Sodium lignosulfonate ¹	1.0
NaH ₂ PO ₂ ·H ₂ O	25
HOOC—CH ₂ CH ₂ —COOH	20
NTA·Na ₃ ·H ₂ O	7.5
Remainder H ₂ O to make 1 liter.	

¹ Sold as "Lignosol SFX" by Lignosol Chemicals Ltd., Quebec, Canada.

Example 2

The bath described in Example 1 is prepared in a suitable container and the pH adjusted to 4.75 with sodium hydroxide. The bath temperature is brought within the preferred operating range of 120–210° F., the particular temperature chosen dependent on the specific application. For instance properly prepared thermoplastic polymers can be plated in the range of 120–140° F. to avoid heat distortion. Metallic substrates can be plated at any temperature within the preferred operating range without the close temperature control required by most electroless nickel processes to obtain satisfactory deposits and deposition rates. A bright deposit is obtained with this bath at any temperature within the range cited above.

Example 3

The rate of deposition of nickel on a metal substrate using the bath of Example 1 was compared to the deposition rate of a bath containing all the components of Example 1 except the sodium lignosulfonate. The results are as follows:

TABLE 1

Temperature	Bath of Example 1, rate-mils/hour	Bath of Example 1 but without sodium lignosulfonate
130.	0.09	0.02
140.	0.15	0.05
150.	0.23	0.10
160.	0.30	0.17
170.	0.38	0.25
180.	0.45	0.33

As is apparent from the above data, there is an unexpected increase in rate of deposition of nickel when using the bath of the present invention.

Example 4

The bath of Example 1 was altered by using NiCl₂·6H₂O in lieu of the NiSO₄·6H₂O and tested in the same manner as Example 3. The results achieved paralleled the results of Example 3.

Example 5

The stability of the bath of Example 1 was compared to

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a bath containing no sodium lignosulfonate. The bath without sodium lignosulfonate was observed to decompose after two days while the bath with sodium lignosulfonate did not decompose after three months.

What is claimed is:

1. In a chemical nickel plating bath having an acidic pH and which comprises an aqueous solution of a nickel salt, an alkali metal hypophosphite, a buffer in the form of an organic acid selected from the group consisting of aliphatic monocarboxylic and aliphatic dicarboxylic acids and salts thereof, the improvement which comprises the presence in said bath of an alkali metal lignosulfonate in an amount effective to permit the use of said bath for low temperature operations.

2. The composition of claim 1 wherein said nickel salt can be selected from the group consisting of nickel sulfate and nickel chloride and mixtures thereof.

3. The composition of claim 2, wherein said hypophosphite is sodium hypophosphite.

4. The composition of claim 3, wherein said buffer is succinic acid and the trisodium salt of nitrilotriacetic acid monohydrate.

5. The composition of claim 4, wherein said alkali metal lignosulfonate can be selected from the group consisting of sodium lignosulfonate, potassium lignosulfonate and mixtures thereof.

6. In the process of chemically nickel plating a solid substrate, in form suitable for nickel plating, which comprises contacting said substrate with a bath having an acidic pH and comprising an aqueous solution of a nickel salt, an alkali metal hypophosphite, a buffer in the form of an organic acid, selected from the group consisting of aliphatic monocarboxylic and aliphatic dicarboxylic acids and salts thereof, the improvement which comprises the introduction into said bath of an alkali metal lignosulfonate in an amount effective to permit said process to be conducted at low temperatures.

7. The process of claim 6, wherein said nickel salt can be selected from the group consisting of nickel sulfate and nickel chloride and mixtures thereof.

8. The process of claim 7, wherein said hypophosphite is sodium hypophosphite.

9. The process of claim 8, wherein said buffer is succinic acid and the trisodium salt of nitrilotriacetic acid monohydrate.

10. The process of claim 9, wherein said alkali metal lignosulfonate can be selected from the group consisting of sodium lignosulfonate, potassium lignosulfonate and mixtures thereof.

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U.S. Cl. X.R.

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