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NICKEL CHEMICAL REDUCTION PLATING BATH AND METHOD OF USING SAME

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2 Claims. (Cl. 117—130)

This invention relates to improvements in the chemical reduction plating of metals.

There has been some prior use of chemical reduction type metal plating employing as a plating bath, an aqueous solution of a reducing agent and a metal salt. In the ensuing chemical reaction, the dissolved metal salt is reduced to the free metal and is deposited as a metallic coating on the immersed article. Up to the present time, nickel has been deposited on metallic articles by immersing the article to be plated into an aqueous solution of sodium hypophosphite and nickel chloride.

Chemical type plating offers certain advantages over conventional electroplating. For example, it permits the deposition of metal evenly over irregularly shaped surfaces and permits plating deeply recessed structures which would be extremely difficult to electroplate. Additionally, since no electric current is employed, the attendant difficulties inherent in electroplating operations are avoided. Up to the present time, however, it has been found that as a chemical plating bath, for example, the aforementioned nickel chloride bath, is used, the deposited metal becomes increasingly dull and rough. This depreciation of the quality of the deposited metal coating has been attributed to the gradual precipitation in the solution of insoluble metallic salts. For proper plating, it has been found desirable to provide in solution a relatively large amount of dissolved metal salt. Accordingly, because the dissolved metal salt is usually highly ionized, there is a large number of metallic ions in solution, greatly in excess of the number needed at any one time for proper plating. These ions readily combine and form insoluble precipitates with basic materials which are either initially present in the bath, or are frequently added to control the pH and/or the products of the reaction.

Accordingly, the principal object of this invention is the provision of an improved chemical reduction plating bath and plating process in which an improved metal deposit is obtained and the formation of undesirable reaction products is minimized. A further object is to provide an improved chemical reduction plating solution having an improved stability. A still further object is the provision of an electroless plating solution adapted to regulate the availability of metallic ions therein.

We have now discovered that a greatly improved metallic deposit can be obtained in chemical reduction plating by providing in the bath a reagent which reduces the availability of the metallic ions in solution thus precluding the build-up of any undesirable metallic salt precipitates to impair the quality of the deposited coating. We have found that excellent results are obtained by employing a chemical reduction bath comprising an aqueous solution of at least one metallic salt, a chemical reducing agent and an additive to control the ionization of the dissolved metal salt. Using such a bath, only a relatively small concentration of metallic ions exists in the bath at a given time and there is little tendency for precipitation of metallic salts, the metallic ions being consumed in the plating reaction substantially as they become available in the solution.

We have found that superior results are obtained by employing as an additive, various chelating agents which complex the dissolved metallic salts to preclude the formation of undesirable precipitates during the oxidation-reduction plating reaction. Moreover, we have found that the presence in the bath of a small amount of such a chelating agent serves to change the surface tension of the bath, thus facilitating smooth metallic deposits. In addition to complexing the dissolved metallic salts, it has been observed that many impurities in the plating bath, which otherwise would impair the quality of the deposited metal, also are rendered harmless by the chelating agent.

Although the selection of a chelating agent and the amount to employ for a particular chemical plating bath will, of course, depend upon the metal to be deposited, the characteristics of the dissolved metallic salts, as well as the bath temperature, and the compatibility of the various bath ingredients, we have found that in many instances, extremely beneficial results have been obtained by using as an addition agent the alkali metal salts of ethylene diamine tetra acetic acid, and preferably the tetra sodium salt of ethylene diamine tetra acetic acid. At times the mono, di, and tri sodium salts of ethylene diamine tetra acetic acid also may be used. It will be understood, of course, that corresponding potassium, or ammonium salts or, salts of other noninterfering cations including, for example, a salt of the metal to be deposited, may be used instead of the sodium salts. By the expression "chelating agent" as used herein is meant a compound which inactivates a metallic ion by forming an inner ring structure within the chelating compound molecule, the metallic ion to be complexed or inactivated, becoming a part of the ring. In certain chemical plating solutions a sequestering agent may be used together with, or in lieu of, a chelating compound. As used in this specification a "sequestering agent" includes any complexing compound which forms a water soluble metal complex compound. Hence, at times the term "sequestering agent" actually includes "chelating agent," the chelating agents generally being organic compounds, while the sequestering agents are inorganic compounds. While various salts of ethylene diamine tetra acetic acid have been set forth as preferred chelating agents, it is to be understood that the invention is not solely restricted to the use of these compounds, but that other chelating or sequestering agents may be used. Examples of these are sodium beta-phosphate, sodium pyrophosphate, tetra sodium pyrophosphate, sodium tetra phosphate, and sodium tripolyphosphate, as well as derivatives of beta-diketones such as benzoyl acetone and its derivatives.

In a chemical reduction plating bath embodying the present invention it is possible to incorporate an amount of the dissolved metal salt greatly in excess of the amount which otherwise could be used since the addition agent will not permit all of the dissolved salt to ionize, but will maintain it in reserve until needed. Since the addition agents of the present invention do not chemically plate out of solution, only a relatively small amount must be added periodically to replace that carried out by mechanical dragout. The addition agents of the present inven-

tion generally may be incorporated in various chemical reduction plating baths in any desired amount. Excellent results, in many instances, have been obtained by employing the addition agent in amounts sufficient to complex about 5% to 30% of the metallic ion although in particular applications it may be desirable to increase the amount of addition agent used, the maximum amount depending largely on the particular metallic ions to be complexed and the bath operating conditions. Up to the present time, most satisfactory results have been obtained by employing the addition agent in an acid type chemical plating bath as used typically in the plating of nickel.

In the deposition of nickel from baths embodying the invention, any soluble nickel salt may be used as a source of nickel. For example, nickel chloride, nickel acetate, nickel sulphate, etc., may be used. It will be understood, of course, that these are illustrative only of some of the soluble nickel salts and that in certain applications other soluble nickel salts may be used as well. Some nickel salts which are relatively insoluble in water may be used in a bath embodying the present invention because of the increased solubility provided by the complexing action of the addition agent.

The chemical reducing agent preferably employed is the hypophosphite radical, generally provided by the addition to the bath of hypophosphorous acid, sodium hypophosphite, potassium hypophosphite, ammonium hypoposphite, etc.

In most instances it is advantageous to add to the bath an alpha hydroxy carboxylic acid or a salt of such an acid. Examples of alpha hydroxy carboxylic acids which can be used are glycollic acid, lactic acid, tartaric acid and citric acid.

Excellent results in the practice of this invention have been obtained by employing chemical plating baths within the following composition range where the quantities are expressed in moles per liter of solution.

Nickel	.01 to 2
Reducing agent	.01 to 1.5
Alpha hydroxy carboxylic acid or salt thereof	.1 to 2
Addition agent	.01 to 1.5

The following are illustrative examples of acid type plating baths for the deposition of smooth adherent nickel coatings where the quantities expressed are per liter of solution.

Example 1

	Grams
Nickel chloride hexahydrate	30
Sodium hypophosphite	30
Glycollic acid	35
Tetra sodium salt of ethylene diamine tetra acetic acid	20

Example 2

	Grams
Nickel chloride hexahydrate	45
Nickel acetate	20
Sodium hypophosphite	25
Glycollic acid	35
Tetra potassium salt of ethylene diamine tetra acetic acid	150

Example 3

	Grams
Nickel acetate	50
Sodium hypophosphite	50
Glycolic acid	42
Tetra sodium salt of ethylene diamine tetra acetic acid	29

Example 4

	Grams
Nickel chloride hexahydrate	100
Sodium hypophosphite	65
Lactic acid	180
Tetra sodium salt of ethylene diamine tetra acetic acid	200

Example 5

	Grams
Nickel chloride hexahydrate	20
Sodium hypophosphite	10
Tartaric acid	20
Tetra sodium salt of ethylene diamine tetra acetic acid	25

Superior results are obtained by replenishing the bath ingredients as they are consumed in operation. Utilizing baths of the type set forth in the preceding examples, typical hourly replenishment quantities per liter of solution are: 5 grams nickel salt of 7–10 grams of sodium hypophosphite.

Baths having compositions as set forth above are operated successfuly at a temperature within the range from approximately 100° F. to 212° F., 180° F.–210° F. preferred at present. A preferred pH range is between 4.0 and 5.0, although the aforementioned baths will operate successfully over a somewhat wider range of pH values, typically from pH values of about 3.0 to 6.5. The pH may be adjusted by additions of sodium hydroxide, potassium hydroxide, ammonium hydroxide, etc.

Typical rates of deposition of nickel from chemical reduction plating baths embodying the invention are within the range of approximately .0002 to .0015 inch per hour. The rate of deposition in any particular case depending on several variables, the exact interdependence of which is not clearly understood at present.

Using baths embodying the present invention, a variety of base metals such as iron, steel, platinum, silver, nickel, aluminum, palladium, copper, and various alloys thereof may be coated.

For optimum results, the metallic article to be plated should be thoroughly cleaned before immersion in the bath. A typical cleaning procedure includes an initial cathodic alkali cleaning, a water rinse, an acid dip, and a final water rinse. In some instances, a sand blasting of the surface is desirable.

The following is an illustrative example of the preparation of a reduction type nickel plating bath embodying the invention, and the deposition of nickel therefrom. A chemical reduction plating bath is prepared by adding 30 grams of nickel chloride to 500 milliliters of water, thereafter dissolving in the nickel chloride solution 35 grams of glycollic acid. To this solution are then added 32 grams of the tetra sodium salt of ethylene diamine tetra acetic acid which is sufficient to complex about 25% of the nickel ions. The pH is adjusted with sodium hydroxide to a pH value within the range of 5.0 to 5.2, and 10 grams of sodium hypophosphite added. The bath thereafter is diluted with water to one liter and heated to a temperature of approximately 190° F. A thoroughly cleansed SAE 1010 steel panel to be coated with nickel is then immersed in the bath for a time sufficient to deposit the thickness of nickel desired. The herein described bath is quite stable and may be operated for extended periods of time with proper maintenance. In the plating operation, no precipitate is formed in solution to impair the surface quality of the nickel. Moreover, the deposition rate of nickel and the appearance of the deposited coating are greatly improved.

Various changes and modifications of the embodiments of the invention described herein may be made by those skilled in the art without departing from the spirit and principles of the invention.

What is claimed is:

1. A chemical reduction process for the deposition of nickel on a metallic article, said process comprising the steps of providing an aqueous solution of about .01 to 2 moles per liter dissolved nickel, about .01 to 1.5 moles per liter of a hypophosphite reducing agent, about .1 to

2 moles per liter alpha hydroxy carboxylic acid radical, and about .01 to 1.5 moles per liter of a salt of ethylene diamine tetra acetic acid, said bath having a pH of about 3 to 6.5 and being maintained at a temperature of about 100° F. to 212° F., and immersing said metallic article in said solution until the desired thickness of nickel is deposited thereon.

2. A chemical reduction plating bath comprising an aqueous solution of approximately .01 to 2 moles per liter dissolved nickel, .01 to 1.5 moles per liter of a hypophosphite reducing agent, .1 to 2 moles per liter of a material selected from the group which consists of alpha hydroxy carboxylic acids, salts of alpha hydroxy carboxylic acids, and mixtures thereof, and .01 to 1.5 moles per liter of a salt of ethylene diamine tetra acetic acid, said bath having a pH of from 3 to 6.5 and a temperature of from 100° F. to 212° F.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,024,134 March 6, 1962

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

Column 1, line 42, for "frequently" read -- subsequently --; column 4, line 16, for "of", first occurrence, read -- or --.

Signed and sealed this 19th day of June 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents