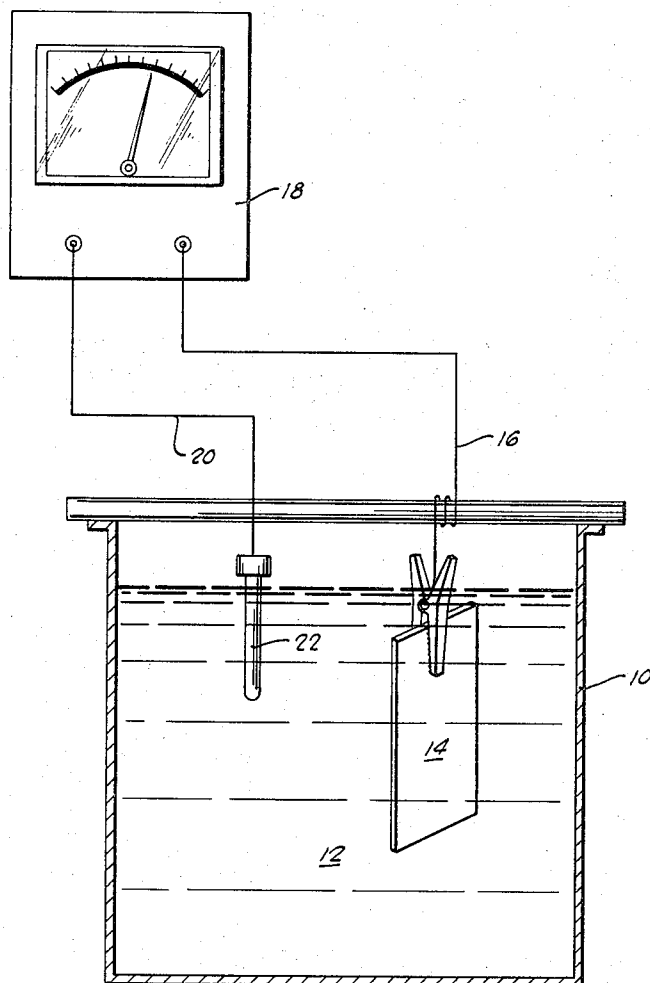


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METHOD OF CONFIRMING THE OCCURRENCE OF PLATING
IN ELECTROLESS NICKEL-PLATING
Filed May 28, 1964



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METHOD OF CONFIRMING THE OCCURRENCE OF PLATING IN ELECTROLESS NICKEL-PLATING

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ABSTRACT OF THE DISCLOSURE

A method of confirming the occurrence of plating in electroless nickel-plating wherein the bath contains hypophosphite anions comprising adjusting the pH to between about 4.0 and about 6.0 and measuring the potential difference between the material being plated and a reference electrode in electrochemical communication with the plating bath.

This invention relates to improvements in the process of non-electrolytic nickel plating. More particularly, the invention relates to a method for detecting the occurrence of the plating reaction by which thin, amorphous, nickel-phosphorus alloy is deposited upon a metallic body by controlled catalytic reduction of nickel ions at the surface of such metallic body.

It is known that, in addition to electroplating of nickel upon various metallic substrates, this metal may also be plated by catalytic chemical methods which are often termed "electroless" plating methods. Electroless plating of nickel is characterized by the selective reduction of the nickel ions at the surface of a catalytic substrate immersed in aqueous solution, and the continued deposition of the nickel on that substrate through the catalytic action of the deposit itself. The most widely used reducing agents employed for effecting the deposition of nickel from an aqueous solution are hypophosphite salts. The reduction is effected at elevated temperatures of from about 175° F. to about 215° F. The deposited coating is amorphous in character and generally contains from about 85 percent by weight to about 95 percent by weight nickel, and from about 3 percent by weight to about 15 percent by weight phosphorus.

In some applications electroless nickel-plating is more desirable than, and presents certain advantages over, nickel coating the substrate by electroplating procedures. For example, the plating deposited by catalytic chemical methods is of uniform thickness in all areas of the solid part regardless of its shape or geometry. Also, coatings which are properly applied by the chemical method are dense and virtually nonporous. Moreover, by reason of the alloying of the nickel with phosphorus in the coating, the coating usually exhibits higher corrosion resistance and is capable of being further hardened by heat treatment.

One of the difficulties which has been experienced in electroless catalytic nickel-plating is the difficulty experienced by operators of the plating bath in determining when the plating reaction is actually occurring so as to result in firm adhesion of the amorphous coating to the surface of the part to be plated. This is particularly true when a plurality of parts to be plated are simultaneously immersed in the bath. Visual inspection has been the method generally used for confirming the occurrence of the plating reaction, with the inspector basing his conclusion relative to plating upon the observed evolution of hydrogen gas at the surface of the part to be plated. This technique has not always been an accurate criterion for making this evaluation since impurities in the bath may result in some gas evolution, and since agitation of the bath in continuous processes may result in some

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entrainment of air, the escape of which may be confused with hydrogen evolution. As previously indicated, the visual determination of the occurrence of the plating reaction is particularly difficult where several work pieces are being plated simultaneously since some of the work pieces may evolve hydrogen gas and others may fail to evolve hydrogen gas, yet due to the close proximity to the parts undergoing plating, give the appearance of yielding hydrogen gas.

The present invention comprises a method for accurately detecting the occurrence of plating in catalytic chemical nickel-plating of the type hereinbefore described. Broadly, the invention comprises measuring the potential difference between the item being plated and a reference electrode in electrochemical communication with the electrolyte plating solution and, from such measurement, identifying the occurrence or non-occurrence of the plating reaction.

The apparatus required for the practice of the invention is relatively simple and can be easily utilized by personnel having little or no technical skill. The apparatus is generally similar to that which is shown in Vann Yuen U.S. Patent 3,034,050 and comprises a reference electrode of relatively constant potential which is placed in electrochemical communication with the nickel-plating bath, a vacuum tube voltmeter or other suitable voltage indicating device and electrical leads for connection between the voltmeter and the work piece which is undergoing plating, and also the reference electrode.

The invention is based upon the principle which we have observed to be characteristic of electroless nickel-plating processes that positive plating of a nickel coating on a metal substrate commences to occur at a threshold potential and continues as long as the potential of the work piece relative to the plating solution remains above such threshold potential, and ceases when the potential shifts in the opposite direction to a value on the opposite side of the threshold potential. The threshold potential at which plating commences to occur will vary for various types of metallic substrates and, to some extent, will be dependent upon the type of plating bath which is employed and the temperature at which the plating reaction is carried out. Nevertheless, it appears that in the use of the catalytic chemical method of nickel-plating in which a hypophosphite salt is used as the reducing agent and a metallic material is the base upon which the nickel is to be plated, the phenomena of the threshold plating potential can be universally observed.

From the foregoing description of the invention, it will be apparent that the process of the invention provides a simple and highly useful technique for ascertaining the point at which a plating reaction positively occurs in a process for plating metals with nickel using an electroless or catalytic chemical method of plating.

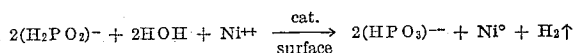
Another object of the invention is to provide a more accurate method for determining the occurrence of the plating reaction in non-electrolytic nickel-plating processes which depend upon catalytic reduction of nickel ions for depositing a nickel-phosphorus coating upon metallic substrates.

In addition to these objects, other objects and advantages will become apparent as the following detailed description of the invention is read in conjunction with the accompanying drawing which schematically illustrates the manner in which the invention is practiced.

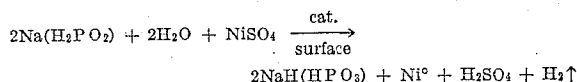
Before referring specifically to the accompanying drawing which illustrates the apparatus used in practicing this invention, a brief description of the electroless or chemical nickel-plating procedure in which the present invention is used will be helpful in understanding the invention. In general, chemical nickel-plating involves the use of a catalytic material which is suspended in an aqueous bath

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containing nickel cations and hypophosphite anions with the plating reaction being based upon the catalytic reduction of the nickel cations to metallic nickel, and the concurrent oxidation of the hypophosphite anions to phosphite anions with the evolution of hydrogen gas at the catalytic surface. This reaction may be expressed in ionic form as follows:



For instance, using nickel sulfate to provide the nickel ion and sodium hypophosphite to provide the hypophosphite ion:



The described reactions take place when the body of catalytic material is immersed in the plating bath and the exterior surface of the body is coated with nickel. Metallic elements which are catalytic for the oxidation of the hypophosphite anions and thus may be directly nickel-plated include iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, uranium and platinum. Other metallic elements which are examples of materials which may be nickel-plated by virtue of the initial displacement deposition of nickel thereon, either directly or through a galvanic effect, are copper, silver, gold, beryllium, germanium, aluminum, carbon, vanadium, molybdenum, tungsten, chromium, selenium and titanium. Non-catalytic materials which ordinarily cannot be nickel-plated are bismuth, cadmium, tin, lead and zinc. The activity of the various catalytic materials varies considerably and the following elements are particularly good catalysts in the chemical nickel-plating bath: iron, cobalt, nickel and palladium.

The chemical or electroless nickel-plating process in which the present invention is used is autocatalytic since most of the original surface of the body being plated and also the nickel metal that is deposited on the surface thereof are catalytic. The reduction of the nickel cations to metallic nickel in the plating bath proceeds until all the nickel cations have been reduced to metallic nickel in the presence of an excess of hypophosphite anions, or until all of the hypophosphite anions have been oxidized to phosphite ions in the presence of an excess of nickel cations.

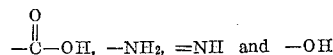
In addition to the presence of nickel cations and hypophosphite anions in the plating bath, certain other additives are usually employed in the bath for purposes of increasing the stability of the plating bath, increasing the normal plating rate of the bath and maintaining the pH within a given range. Soluble salts of simple short chain aliphatic monocarboxylic acids with an ionization constant, pKa, greater than 4.7 are frequently included for their buffering action. Exaltant compounds which further enhance the stability of the bath and increase the plating rate are also sometimes added to the bath, and are generally simple short chain saturated aliphatic dicarboxylic acids, such as sodium succinate. The ionization constant of these exaltant compounds preferably exceeds 5.4. A small amount of a soluble fluoride is also sometimes added to the bath for the purpose of increasing the rate of catalytic oxidation of the hypophosphite anions to phosphite anions. Finally, there is frequently added to electroless nickel-plating baths, a nickel chelating agent selected from the group of compounds having the general formula:



where R is an aliphatic radical, X is a functional group

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containing a dissociable hydrogen atom and selected from the class consisting of:



and Y is a functional group containing a negative atom acting as a center of coordination and selected from the class consisting of:



and wherein the functional groups X and Y are in alpha or beta positions to each other. Such chelating agents include saturated aliphatic hydroxycarboxylic acids and salts thereof, aminoalcohols, polyalcohols, aliphatic keto acids and salts thereof, aliphatic polyamines, aminocarboxylic acids and salts thereof, and short chain aliphatic aminocarboxylic acids and salts thereof.

The plating baths used in electroless nickel-plating generally contain an absolute concentration of hypophosphite anions in the range of from about 0.15 to about 1.2 moles per liter. The ratio between the nickel cations and the hypophosphite anions in the bath is in the range of about 0.25 to about 1.60. Where a chelating agent is employed in the bath, it is generally desirable to maintain a concentration of the chelating agent sufficient to chelate at least 100 percent of the nickel cations in the bath. The absolute concentration of the exalting agents present when these materials are used is at least 0.04 moles per liter. The buffer concentration in the bath should be equivalent to two carboxyl groups for every nickel ion that can be deposited. The pH of the bath is in the general range of from about 4.0 to about 11.0, depending upon the particular ingredients of the bath. The temperature of the bath may range from just below its boiling point (usually about 99° C.) to as low as about 85° C. From about 95° C. to 99° C. is the preferred temperature range. The optimum ratio of the solution volume of the bath to the area of the catalytic material to be plated is below 10.

Additional information relative to the bath and conditions used in electroless or chemical nickel-plating can be found in an article by Brenner and Riddell in the Journal of Research, National Bureau of Standards, volume 37, July 1946, and volume 39, November 1947; Gutzeit et al. U.S. Patents 2,658,841; 2,935,425; 2,694,019; 2,822,293; 2,822,294; and 2,690,401; and Talmey et al. U.S. Patents 2,941,902; 2,847,327 and 2,762,723. Examples of typical electroless nickel-plating bath compositions can also be found in the article entitled, "Catalytic Chemical Methods," at p. 464 of Electroplating Engineering Handbook—2nd edition, published in 1962. Insofar as all of the foregoing publications and patents refer to methods and compositions used in electroless or chemical nickel-plating, they are incorporated by reference in the present application, and it is to be understood that the method of positively determining the occurrence of the nickel-plating reaction as set forth in this application is applicable in principle to each of the electroless nickel-plating techniques therein described.

For convenience, and to promote further understanding of the present invention, a typical aqueous chemical nickel-plating solution has the following composition and the pH.

	Moles per liter
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----	0.08
NaH_2PO_2 -----	0.225
Lactic anion -----	0.30
Propionic anion -----	0.03
pH -----	4.6

The lactic anion may be derived from lactic acid, sodium lactate, etc., while the propionic anion may be derived from propionic acid, sodium propionate, etc.

The absolute concentration of hypophosphite anions in

the bath is within the previously described approximate range of 0.15 to 1.20 moles per liter; the ratio between the nickel cations and the hypophosphite anions in the bath is within the approximate range of 0.25 to 1.60; the absolute concentration of lactic anions in the bath is within the approximate range of 0.25 to 0.60 moles per liter. The absolute concentration of propionic anions in the bath is within the approximate range of 0.025 to 0.060 moles per liter, and the initial pH of the bath is adjusted to within the approximate range of from about 4.0 to about 5.6 employing H_2SO_4 or NaOH , as required.

The plating of a metallic substrate by the described chemical nickel-plating techniques can be carried out as a batch process, or can be carried out on a continuous basis with continuous regeneration of the plating bath being effected by the addition thereto of appropriate ingredients for the purpose of maintaining substantially constant the composition of the bath.

The metallic substrate of catalytic material is properly prepared by mechanically cleaning, degreasing and light pickling substantially in accordance with standard practices well-known in the currently used electro-plating and electroless nickel-plating processes. For example, in the nickel-plating of a steel object, it is customary to mechanically clean the rust and mill scale from the object, to degrease the object and then to lightly pickle the object in a suitable acid, such as hydrochloric acid. The article is then immersed in a suitable volume of the bath containing the proper proportions of nickel cations, hypophosphite anions, buffer and/or exaltant, and stabilizing agent. The pH of the bath is adjusted to an optimum value by the addition of an appropriate acid or base, and the bath is heated to a temperature which is preferably just below its boiling point, such as 95° – 99° C. at atmospheric pressure.

As hereinbefore indicated, the present invention comprises a method for determining electrically and in a positive fashion, the time at which the nickel-plating commences to occur at the surface to be plated. This is accomplished by measuring the potential difference developed between the catalytic metallic substrate being plated and a reference electrode of substantially constant electrical potential which is placed in electrical communication with the plating bath. An apparatus for carrying out the method of the invention is illustrated in the accompanying drawing. In the drawing, the container which holds the plating bath is designated by reference character 10, and the plating bath by reference character 12. The workpiece or metallic substrate to be plated 14, is selected from one of the catalytic materials hereinbefore described, and is suspended by any suitable means in the plating bath.

As schematically illustrated in the accompanying drawing, the workpiece 14 to be plated is electrically connected by an insulated electrical lead 16 to one terminal of a suitable potential indicating device, such as a vacuum tube voltmeter 18. The other terminal of the vacuum tube voltmeter 18 is connected via a suitable insulated electrical lead 20 to a reference electrode 22 which is in electrical communication with the plating bath 12. The reference electrode 22 can be any suitable type of electrode which exhibits a relatively constant electrical potential despite some fluctuation in the chemical composition and temperature of the bath 12. Examples of this type of electrode are a silver-silver chloride electrode and a calomel electrode. Though the electrode is illustrated schematically as immersed in the plating bath 12, it will be recognized by those skilled in the art that where a liquid electrode such as a calomel half-cell is employed, it will be desirable in most instances to provide a suitable salt bridge between the electrode and the bath solution to prevent malfunction of the electrode by contamination thereof by the chemical solution of the bath.

The method of the present invention is based upon my

observation that there is a threshold potential difference value which is developed between the workpiece 14 and the reference electrode 22 at the time that nickel-phosphorus alloy is being deposited upon the workpiece by virtue of the positive occurrence of the desired nickel-plating reaction. This value will vary to some extent depending upon the temperature at which the plating bath 12 is maintained, and the composition of the bath, as well as upon the particular substrate or catalyst workpiece 14 which is used.

As an example of the practice of the invention, a plating bath was made up consisting essentially of one part by weight nickel sulfate in the form of the hexahydrate, three parts sodium hypophosphite, about two parts each of lactic acid and tartaric acid, and about 0.3 parts by weight of propionic acid. A small amount of caustic was added to adjust the pH of the bath to between 4.0 and 6. The temperature of the bath was 95° C. Both stainless steel and mild steel coupons were prepared for plating in the manner hereinbefore described and were immersed at different times in a bath of the described composition. In both instances, a positive plating reaction was perceived to occur at about +400 millivolts. Repetition of the tests indicated that this value for commencement of plating was accurate within ± 200 millivolts, and that in every instance, the plating reaction definitely occurred when a value more noble or positive than 600 millivolts was indicated by the vacuum tube voltmeter.

From the foregoing description of the invention, it will be perceived that this invention provides a simple, inexpensive and accurate method for positively determining the commencement of the occurrence of the nickel-plating reaction in autocatalytic nickel-plating systems. The uncertainties of determinations based on visual observation of hydrogen gas evolution are thus obviated, and the expenditure of time required for replating or the uneconomical necessity to discard undesirably high quantities of rejects is eliminated.

Although the invention has been described with reference made to a specific example of its practice, the basic principles upon which the invention is founded have been clearly set forth and should be relied upon in defining the limits of the spirit and scope of the present invention. Insofar as such basic principles are included in any practice of chemical autocatalytic nickel-plating involving the use of nickel cations and hypophosphite anions, it is intended that such practices be considered within the scope of the present invention except as such scope may be necessarily limited by the appended claims or reasonable equivalents thereof.

What is claimed is:

1. The method for monitoring the occurrence of nickelplating in a system including a catalytic metallic substrate to be plated in a plating solution containing nickel cations and hypophosphite anions, said method comprising:

adjusting the pH of said solution to between about 4.0 and about 6.0,

connecting in a series potential indicating electrical circuit, the metallic substrate, a potential metering device, and a reference electrode of substantially constant electrical potential;

placing the reference electrode in electrochemical communication with said plating solution; and

starting prior to the commencement of said nickel plating continuously measure on said potential metering device the potential difference developed between said metallic substrate and said reference electrode until after said commencement.

2. The method for positively determining the occurrence of the plating reaction at the surface of a metallic work piece in the course of autocatalytic chemical nickel-plating using a plating bath containing nickel cations and hypophosphite anions, said method comprising:

adjusting the pH of said bath to between about 4.0 and about 6.0, initially, in a pilot test, predetermining the electrical potential which is developed between a specimen of the particular metal to be plated and a reference electrode of substantially constant electrical potential when both are in electrical contact with said plating bath and when said plating reaction first commences to occur; then starting prior to the commencement of said nickel plating continuously measure until after said commencement the potential difference developed between the work piece actually to be plated and said reference electrode when both are in electrical contact with said plating bath whereby the occurrence

of said plating reaction is reflected by said measured potential difference.

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