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THIN NICKEL COATINGS

Donald J. Levy, Mountain View, Calif., assignor to Lockheed Aircraft Corporation, Burbank, Calif.

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The present invention relates to nickel coatings which possess unique chemical and physical properties and to the processes and baths for producing said nickel coatings. More particularly, it relates to thin nickel coatings which possess certain preferred chemical and magnetic properties and to an autocatalytic chemical reduction process for producing thin nickel coatings which process incorporates solutions of special composition.

Heretofore, it has been the practice to produce nickel coatings by autocatalytic deposition by means of immersing catalytic surfaces in plating baths containing nickel cations and hypophosphite ions. Although the coatings produced have been highly satisfactory for their intended use, they have invariably contained impurities in such quantities that requisite physical and chemical properties for certain applications are seriously affected. In particular, the coatings produced by the prior art contain phosphorus in sufficient quantity to substantially diminish the purity level of the nickel coating and thereby prohibit or restrict the use of these coatings in applications where a high level of nickel purity is essential and especially in applications where the presence of phosphorus cannot be tolerated.

The general purpose of this invention is, therefore, to provide by an autocatalytic plating technique a nickel coating that is substantially free of impurities and exhibits, as a consequence, properties hitherto unobtainable in nickel in thin film condition. To accomplish this result, the present invention contemplates unique plating bath compositions whereby substantially impurity-free coatings of nickel are realized.

It is, therefore, one object of the present invention to provide thin nickel coatings of relatively high purity.

It is another object of the invention to provide a nickel coating which is substantially devoid of the impurity phosphorus.

A still further object of the invention is to provide nickel coatings which possess unusual magnetic properties.

Another object of the invention is the provision of thin nickel coatings of high saturation magnetization.

It is another object of the invention to provide thin nickel coatings which exhibit a hysteresis loop with a high squareness ratio, B_r/B_s .

Still another object is to provide a nickel coating of low coercivity.

Yet another object of the invention is the provision of coatings of uniform thickness whereby homogeneous magnetic characteristics result.

A still further object is the provision of nickel coatings having a range of radiation absorption and emission characteristics which may be selectively varied.

An additional object is the provision of a nickel coating having, as one of its properties, high specularity.

Another object of the invention is to provide a nickel film having high adhesion characteristics whereby excellent film adherence to the substrate is effected.

A further object of the invention is the provision of thin nickel coatings obtainable by autocatalytic deposition.

A still further object of the invention is to provide new and improved chemical nickel plating solutions which are relatively stable and which do not decompose spontaneously during the plating reaction.

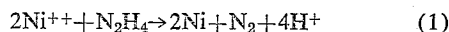
A still further object of the invention is to provide

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nickel plating solutions and processes which do not require elaborate electrical equipment for use in conjunction therewith.

It is another object of the invention to provide nickel coatings which have decorative appeal, improved corrosion resistance, and properties making them exceptionally useful as chemical reaction catalysts.

In the practice of the present invention, it has been found that a reaction takes place between nickel ions and hydrazine such that metallic nickel is deposited. It is believed that the overall chemical reaction can be described by the following equation:



When a vessel is provided with nickel ions and hydrazine in aqueous solution in the proportions and under the conditions specified hereinafter and, subsequently, an article of catalytic material such as copper is immersed into the solution, reaction (1) above is catalyzed and metallic nickel is deposited on the surface of the article. This reduction of nickel cations to metallic nickel occurs without the use of an external power source since the plating bath itself contains a reductant, hydrazine, which provides the necessary electrons to reduce the nickel cations. The newly plated nickel surface, which is itself catalytic, serves as a catalyst for further nickel plating. Therefore, the process is properly referred to as autocatalytic due to its self-sustaining nature whereby reaction continues and nickel metal is deposited on the article until it is withdrawn from solution. Film thickness, consequently, is a linear function of immersion time provided the nickel ions and hydrazine are maintained at a substantially constant concentration in the solution.

BATH COMPOSITION AND OPERATING CONDITIONS

In the plating process as described in this invention, it is, of course, necessary that the constituents listed as reactants in Equation 1 be present in solution and that they be present in the proper proportions. Additional environmental factors such as pH and temperature must also be carefully controlled; the preferred practice of the invention incorporates bath compositions and operating conditions as specified in Table I below.

Table I

Ni ⁺⁺ , g. ions/liter	10 ⁻¹⁰ to 10 ⁻² .
Hydrazine, moles/liter	0.05-3 (preferred).
Temperature, ° C.	70-100 (preferred 90-95).
pH	6.5 min. (preferred 7-11).

The nickel ion referenced in Table I is the free aquo ion, presumably $\text{Ni}(\text{H}_2\text{O})_6^{++}$, and it may be derived from the ionization of any nickel salt of adequate solubility, e.g., nickel chloride, nickel nitrate, nickel sulfate, nickel acetate, nickel sulfamate. Since the Ni^{++} concentration would be rapidly depleted during plating under practical commercial conditions, some means of conveniently adding Ni^{++} at the same rate that they are removed by the plating reaction is desired. One method is to add at an appropriate rate to the solution an excess of a nickel salt whose solubility matches the desired Ni^{++} concentration. A second and preferred method is to add a complexing agent to the solution and complex all Ni^{++} greater than the quantity desired. It is well known in coordination chemistry that metal complexers dissociate in aqueous solution to form and maintain a relatively constant concentration of free metal ion, the concentration of free metal ion depending on the amount and nature of the complexer used. The complexing agents which are suitable for this process are vast in number and character. The donor atom may be oxygen,

nitrogen, or other specie in a ligand (complexer) of mono- or poly-dentate structure. Carboxylates, hydroxycarboxylates, and amines are particularly satisfactory. The various types and the method in which they are employed will become evident in subsequent examples and descriptions of the process. The amount of soluble nickel in the complexed form which is present in the solution is arbitrary and may vary from nil to large amounts limited only by the solubility of the most soluble nickel salt. It is clear, therefore, that the preferred ranges for the total quantities of nickel salt in solution may vary considerably as long as a suitable complexing agent is available to tie up the dissociated nickel salt as a complex ion so that only 10^{-10} to 10^{-2} g. ions/liter of free nickel cations are present in the bath.

Consequently, the concentration of hydrazine used may be varied over wide limits. The plating rate is found to increase with hydrazine concentration up to a saturation value (about 1 molar with one set of conditions) beyond which the rate remains constant irrespective of hydrazine concentration as high as 5 molar. The hydrazine functions as a chemical reductant in the process such that other inorganic and organic functionally substituted hydrazine compounds and their derivatives may be used in place of the parent compound so long as they have adequate solubility. For example, hydrazine sulfate, hydrazine hydrochloride, methyl hydrazine and hydroxyethyl hydrazine are all suitable reductants for the purpose of this invention.

The plating rate increases with temperature so that operating temperatures of 90° – 95° C. are generally preferred. However, higher temperatures can be attained by employing closed pressure vessels in the event significantly greater rate of plating is desired.

It is also observed that the plating rate increases with pH and with the nickel ion activity (concentration). The catalytic reaction (1) proceeds in solutions that are either substantially neutral or alkaline. Suitable sources

decomposition of the solution occurs. For this reason, the following procedure is suggested for making up plating solutions in accordance with the instant invention: First dissolve the nickel-containing salt in a quantity of water to form a first solution. Next dissolve the complexing agent, such as a tartrate, in a quantity of water to form a second solution. Add the first and second solutions together and to the resulting mixture add the hydrazine solution. Finally, add the hydroxide solution and quantity of water required to bring the total up to the necessary composition. Heat the bath to the desired temperature and it is ready for use.

The method of this invention and the desirable properties of the nickel coating will become apparent in the detailed examples which follow.

EXAMPLE I

A plating solution was prepared and mixed in the proper order to comprise 0.05 mole per liter (m.p.l.) of nickel chloride, 0.15 m.p.l. hydrazine, and 0.01 m.p.l. ammonium carbonate. This solution was heated to a temperature of 90° C. and maintained at a pH of 6.8. A glass microscope slide was used as a substrate and was sensitized with palladium by the common and well known technique of cleaning by immersion in hot chromic acid solution, rinsing with water, immersing in stannous chloride solution, again rinsing with water, immersing in palladium chloride solution, and finally water rinsing so as to coat the non-conductive glass with an invisible film of palladium and thus impart to the surface the characteristics of a catalytic metal. The slide thusly prepared was then immersed into the plating solution for 5 minutes, water rinsed, and dried. The slide was found to be coated with a bright film of nickel about 700 Å thick.

In similar fashion, nickel films were deposited on other glass slides using the plating solutions listed in Table II below.

Table II

Bath Composition, moles/liter			Operating Conditions		Plating Rate, mg. Ni/cm. ²	Plating Appearance
NiCl ₂	Complexer	Hydrazine	pH	° C.		
0.02	0.1 mandellate	1.0	10	95	0.90	Dark.
0.02	0.06 glycine	1.0	10	95	0.87	Do.
0.02	0.08 ethylene diamine	1.0	10	95	0.28	Do.
0.02	0.10 maleate	1.0	10	95	0.09	Do.
0.02	0.03 triethylenetetraamine	1.0	10	95	0.06	Bright.
0.02	0.06 cyanide	1.0	10	95	0.02	Do.
0.03	0.03 tartrate	1.0	10	95	0.30	Lt. brown.
0.2	0.2 tartrate	1.0	10	95	0.28	Bright.
0.02	0.02 tartrate	0.65	10	95	0.23	Do.
0.02	0.02 tartrate	2.0	10	95	0.31	Brown.
0.05	0.01 ammonium carbonate	0.15	6.8	90	0.07	Bright.
0.05	0.02 ammonium carbonate plus 0.7 ammonium hydroxide.	0.05	8.3	90	0.23	Do.

of the hydroxyl ion, for alkaline solutions, are LiOH, NaOH, KOH, NH₄OH and other metal hydroxides of adequate solubility.

In practice, it is desirable to have a "stable" solution, that is, one that does not generally decompose by a homogeneous reaction of Equation 1 and deposit finely divided nickel particles throughout the solution. This homogeneous reaction accompanies the plating reaction only when one attempts to obtain too high a plating rate. The situation is easily corrected by reducing the Ni⁺⁺ concentration, pH, or temperature individually or in combination.

The manner in which these new and improved nickel plating solutions are prepared can be quite important in that ingredients placed in the solution in an improper order may very well result in not all of the ingredients becoming dissolved; or else spontaneous homogeneous

EXAMPLE II

Coupons of copper sheet, .040" x 2" x 1", were cleaned by immersion in a dilute solution of nitric acid, water rinsed, and then immersed into the plating solutions as listed in Table III for periods of time sufficient to produce the thicknesses indicated. It was found that the saturation magnetization M_s of these films was unusually high compared to M_s for bulk nickel which is 484 gauss/cm.³. Because of a $\pm 3\%$ instrumental error involved in testing these small samples, several of the average readings ran above the theoretical maximum. For example, in the third sample a value of 500 gauss/cm.³ was recorded, a figure which probably included approximately 16 gauss/cm.³ as an experimental error in the measuring technique. Such a reading indicates that values equal to or extremely close to the theoretical maximum M_s of nickel were in fact achieved by the instant process. By way of contrast

when 10 nickel films were prepared by the prior art teachings utilizing a nickel-anion hypophosphite-cation type solution, 6 samples exhibited no detectable M_s while the other 4 showed values less than 100 gauss/cm.³.

Table III

Solution Composition, m.p.l.			Plating Conditions		Film Properties	
NiCl ₂	Tartrate	Hydrazine	pH	° C.	Thickness, A.	M_s , gauss/cm. ³
0.02	0.02	0.6	10.0	90	120	495
0.02	0.02	0.6	10.0	90	12,400	430
0.2	0.2	1.0	9.5	90	450	500
0.2	0.2	1.0	9.5	90	1,570	475

EXAMPLE III

A coupon of mild iron, .040" x 2" x 1", was cleaned by immersion in a dilute solution of hydrochloric acid, water rinsed, and then immersed into a plating solution composed of 0.02 m.p.l. NiCl₂, 1.0 m.p.l. hydrazine, and 0.04 m.p.l. sodium malonate which was maintained at a temperature of 71° C. and a pH of 9.0. It was found that nickel deposited spontaneously on the iron coupon at the rate of 440 A./min. and that a bright, continuous, and firmly adherent coating was formed.

EXAMPLE IV

A glass microscope slide was cleaned and sensitized as described in Example I. A plating solution was prepared which contained 0.02 m.p.l. NiCl₂, 0.005 sodium malonate, 0.1 m.p.l. hydrazine, and which was adjusted to a pH of 7.5 and heated to 95° C. The sensitized slide was immersed into the plating solution for three minutes after which the plated sample was rinsed and dried. Upon examination of the specimen in a B-H hysteresis loop tester, it was found that the coercivity, H_c , was only 16 oersteds, an unusually low and desirable value and the loop showed good squareness, $B_r/B_s=0.92$.

PROCESS

The plating reaction will initiate spontaneously on all clean surfaces which will function catalytically for hydrogenation-dehydrogenation reactions. It is well known that such catalytic materials include, among others, platinum, palladium, nickel, gold and iron. In the event that it is desired to coat articles composed of substances which are not catalytic, they may be first coated with a thin layer of some catalytic material by such techniques as electroplating, immersion plating, vacuum evaporation, painting with conductive paints, or other appropriate methods. A well known method of "sensitizing" nonconductors with a film of palladium was described in Example I.

The process, as described, consists of immersing the article to be coated into the plating solution. In commercial practice, it is usually desirable to maintain the plating solution at a rather constant composition or within a small composition range. Consequently, one may make additions of the constituents which become depleted because of the plating reaction, evaporation, and drag-out losses. These additions may be made continuously or batch-wise at intervals. The present invention can be readily practiced as a continuous process by well-known techniques whereby pumps, filters and storage tanks are employed to recirculate and regenerate the plating solution.

Whereas the invention has been described by the technique of immersion of an article into a plating solution of specified composition, pH, and temperature, the invention shall not be limited to this type of article-solution contact. Contact may be achieved by flowing the solu-

tion over or spraying solution on the catalytic surface of the article. Also, if desired, simultaneous dual spray application may be performed wherein nickel and hydrazine solutions are maintained separate with the other required

constituents added to one of these solutions, as appropriate.

The thickness of the coating is a direct function of solution-article contact time, other factors remaining constant. Films in the order of 100 A. have been prepared and thinner films are possible. Conversely very thick coatings can be prepared, if required for a specific application, since adhesion is excellent. Furthermore, the process causes the deposition of films of uniform thickness irrespective of the geometrical complexity of the article surface.

In accordance with the present invention, other additives may be added to the plating solution for special purposes without detrimentally affecting the plating action or the purposes of this invention. Since pH control is desirable to stabilize the plating rate, the complexer may be selected to function dually as one half of a pH buffer pair, or alternately, a pH buffer may be added. Likewise, trace quantities of catalyst poisons may be added so as to prevent tiny suspended particulates from precipitating general decomposition of the plating solution. It was found that substances, e.g., malonates, with a great affinity for protons, accelerated the plating rate. Such substances may be added to function separately or dually (as a complexer also). Additional refinements, known in the art of metal deposition from aqueous solutions, may be employed within the scope of the process of this invention.

NICKEL FILM PROPERTIES

In order to determine the compositional impurities in the nickel films, special techniques for analysis had to be employed. Unsupported nickel films of approximately 1,000 angstroms in thickness were examined by elastic scattering of particles emitted from a Van de Graaff accelerator. The principal impurities to be found in the nickel film are hydrogen, nitrogen, and oxygen. The hydrogen content in the nickel film was found to be approximately .1 to 0.2 percent by weight of hydrogen as determined by proton-proton scattering with the Van de Graaff accelerator. Some difficulties were encountered in attempting to determine the oxygen and nitrogen content using 2.3 mev. alpha particles, but in any event it was clearly shown that the nitrogen content is definitely less than 2.5 percent and the oxygen content is likewise less than 2.5 percent. Because of the small quantities of nickel available for analysis, accurate determinations to find out just how low the nitrogen and oxygen content are were not possible. Because of the lack of phosphorus in the plating environment, substantially no phosphorus is to be found in the film.

In order to determine the crystal structure of the nickel film, both electron and X-ray diffraction measurements were employed and it was determined that the structure is predominantly crystalline and possesses the normal face centered cubic lattice of bulk nickel. No preferred ori-

entation of the crystal structure was evident through these analyses.

Saturation magnetization, M_s , was determined by the Guoy method using a permanent magnet with a field strength of 500 gauss per centimeter. It was found that the M_s of the samples varied from between about 80% and 90% of the theoretical maximum for bulk nickel (484 gauss per centimeter³) irrespective of the complexing donor atom species, pH in the range of 7 to 10, film color, or other parameters. However, certain films were found to exhibit M_s values essentially equal to that of bulk nickel, and in some cases exhibited apparent M_s 's at least equal to 484 gauss per centimeter³; the nickel films which exhibited the highest M_s values were those which were plated onto copper sheet. As seen in Example IV the nickel films of the present invention possess desirable square B-H loop characteristics and a majority of the samples exhibited a B_r/B_s of at least 0.80 and moreover, possess desirable low coercivity in the range of from 15-30 oersteds. It is of interest to note that the obtention of a square hysteresis loop by the instant process is an unusual characteristic for nickel. However, just exactly why this effect has been achieved in the practice of the invention is not fully understood at the present time.

In order to effectively use the desirable magnetic characteristics of the nickel film, glass substrates are sensitized with a palladium strike plate in predetermined areas using an appropriate masking device. Immersion of the sensitized ceramic substrate into the preferred solutions of the instant invention will result in the formation of nickel films at these preselected areas which films will represent a multitude of individual memory disks of abovementioned preferred magnetic characteristics substantially as previously described. The same result may be likewise achieved through utilization of chemical resist-coating technique whereby selected areas are coated with a material that resists subsequent etching steps. Other applications of the film will obviously suggest themselves by virtue of the desirable magnetic characteristics which the film possesses as hereinabove pointed out.

From the foregoing description it can be appreciated that the invention provides a commercially practicable chemical nickel plating solution and a resultant nickel film which has unique chemical and physical properties. By means of the invention, relatively thick coatings of nickel may be autocatalytically plated without requiring the use of elaborate and expensive electrical equipment, and yet, any desired thickness of nickel plating can be formed up to a predetermined maximum thickness. Furthermore, the nickel plating may be readily formed on irregularly shaped objects and surfaces, with the assurance that such irregularly shaped surfaces will receive a uniform coating of nickel. Also the invention provides a plating solution and process capable of carrying out the above objects which solution is relatively stable and the process is relatively simple to conduct.

Obviously other modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that changes may be made in the particular embodiments of the invention described which are within the full intended scope of the invention as defined by the appended class.

I claim as my invention:

1. An autocatalytic chemical reduction process for continuously plating nickel on objects having a catalytic metal surface comprising the steps of providing an aqueous solution comprised of free nickel ions in the amount of from 10^{-10} to 10^{-2} gram-ions per liter, and a reductant selected from the group consisting of hydrazine and hydrazine derivatives, maintaining said solution at a temperature of from 70° to 100° C. and at a pH of from 6.5 to 11, immersing into said solution an object with a catalytic surface which will catalyze hydrogenation-dehydrogenation reactions maintaining said object in the solution for a predetermined time until a nickel layer of a preselected

depth has been deposited and finally withdrawing the object from the solution.

2. A bath for the autocatalytic plating of nickel on catalytic metal surfaces comprising an aqueous solution of free nickel ions in the amount of from 10^{-10} to 10^{-2} gram-ions per liter and hydrazine in the amount of from 0.05 to 3 gram moles per liter, said solution having a pH greater than 6.5.

3. An autocatalytic chemical reduction process for plating nickel on objects having a catalytic metal surface, said process comprising the steps of providing an aqueous solution containing from 10^{-10} to 10^{-2} gram-ions per liter of free nickel ions, 0.05 to 3 moles per liter of hydrazine, maintaining said solution at a temperature in the range of from 70° C. to 100° C. and a pH greater than 6.5, immersing the object to be plated in the solution, and continuously plating a nickel film on said object by the autocatalytic reaction of said solution at the catalytic metal surface until the desired film thickness is obtained.

4. An autocatalytic chemical reduction process for continuously plating nickel on objects having a catalytic metal surface, said process comprising the steps of providing an aqueous solution containing from about 0.02 to about 0.2 gram moles per liter of a nickel salt, at least one nickel complexer selected from the group consisting of a ligand having at least one oxygen donor atom, a ligand having at least one nitrogen donor atom, and a ligand having at least one oxygen donor atom and at least one nitrogen donor atom, said complexer being present in the ratio of about 1 to 10 gram moles per gram mole of nickel salt, and about 0.05 to 3 gram moles per liter of hydrazine; maintaining said solution at a temperature of from 70° C. to 100° C. and at a pH of from 6.5 to 11; immersing said object in said solution to plate nickel on said object by the autocatalytic reaction of said solution at the catalytic metal surface, and removing said plated object from said solution.

5. A bath for the autocatalytic plating of nickel on catalytic metal surfaces comprising an aqueous solution of about 0.02 to about 0.2 gram moles per liter of a nickel salt, at least one nickel complexer selected from the group consisting of a ligand having at least one oxygen donor atom, a ligand having at least one nitrogen donor atom, and a ligand having at least one oxygen donor atom and at least one nitrogen donor atom, said complexer being present in the ratio of about 1 to 10 gram moles per gram mole of nickel salt, and about 0.05 to 3 gram moles of hydrazine per liter of solution, said solution having a pH of from 6.5 to 11.

6. An autocatalytic chemical reduction process for continuously plating nickel on objects having a catalytic metal surface, said process comprising the steps of providing an aqueous solution of a nickel salt, a nickel complexing agent in the amount of 1 to 10 moles per mole of nickel salt, and a reductant selected from the group consisting of hydrazine and hydrazine derivatives, maintaining said solution at a temperature of from about 70° C. to about 100° C. and at a pH greater than 6.5, contacting said object with said solution, plating nickel on said object by the autocatalytic reaction of said solution at the catalytic metal surface, and removing said plated object from said solution.

7. A bath for the autocatalytic plating of nickel on catalytic metal surfaces comprising an aqueous solution of a nickel salt selected from the group consisting of nickel chloride, nickel sulfate, nickel acetate, nickel nitrate, and nickel sulfamate, a complexer selected from the group consisting of a ligand having at least one oxygen donor atom, a ligand having at least one nitrogen donor atom, and a ligand having at least one oxygen donor atom and at least one nitrogen donor atom, said complexer being present in the ratio of about 1 to 10 moles per mole of nickel salt,

a reductant selected from the group consisting of hydrazine and hydrazine derivatives, said solution having a pH greater than 6.5.

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