METAL FINISHING ALLOY OF NICKEL-COPPER-PHOSPHORUS

Filed June 21, 1973 3 Sheets-Sheet 1

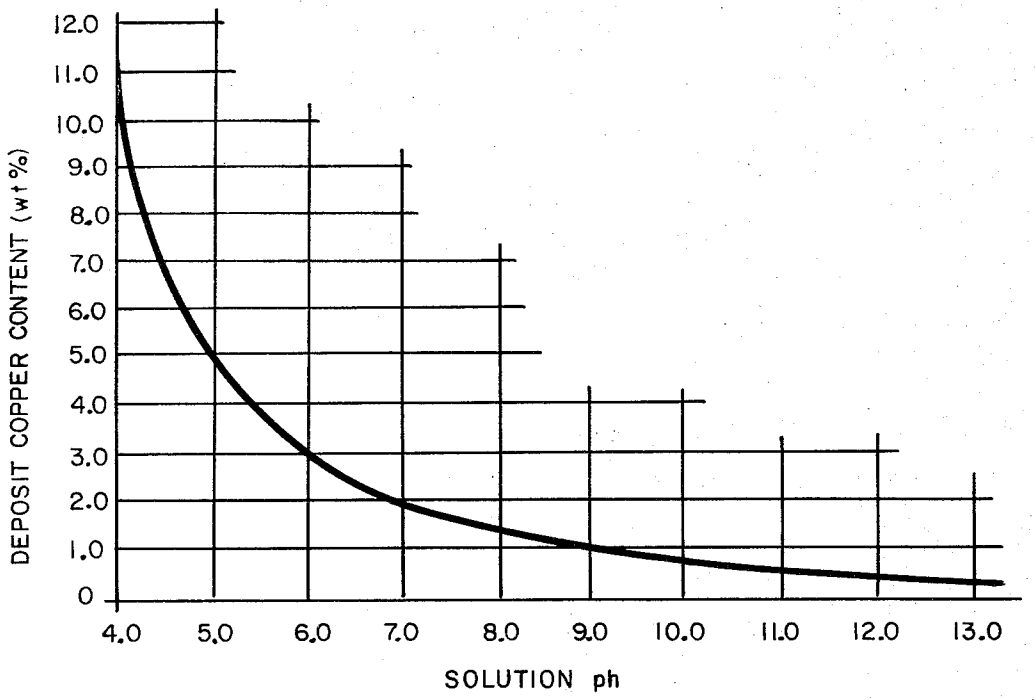


FIG. 1

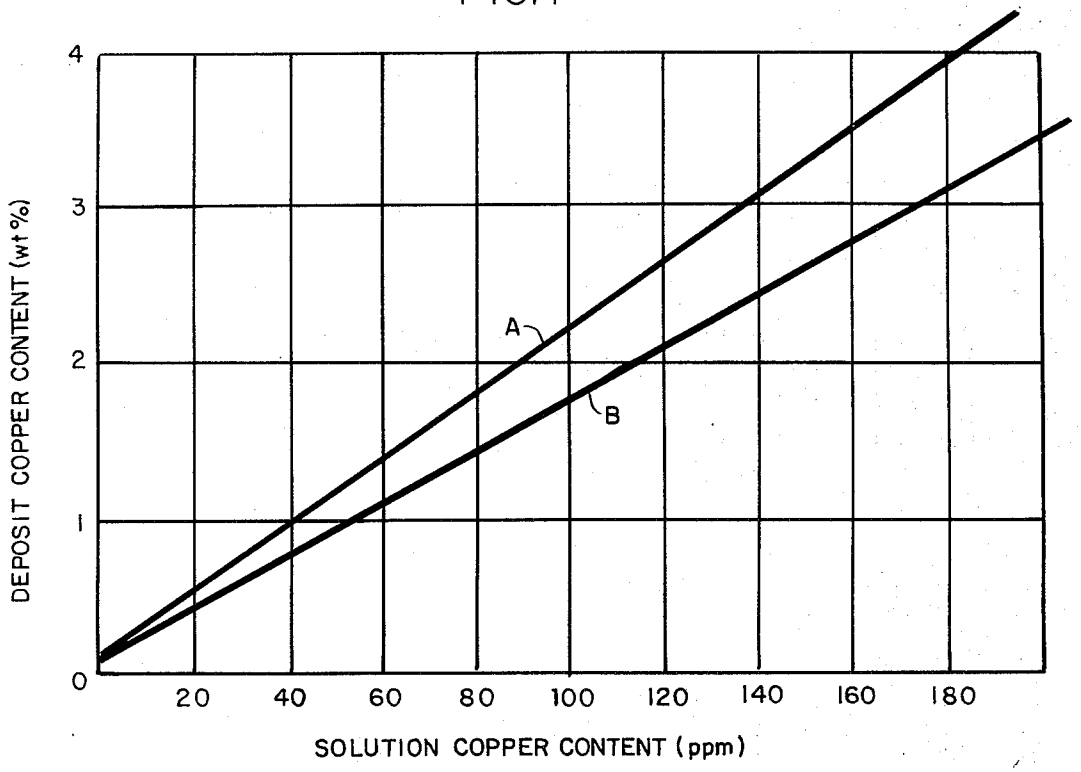


FIG. 2

METAL FINISHING ALLOY OF NICKEL-COPPER-PHOSPHORUS

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FIG. 3A

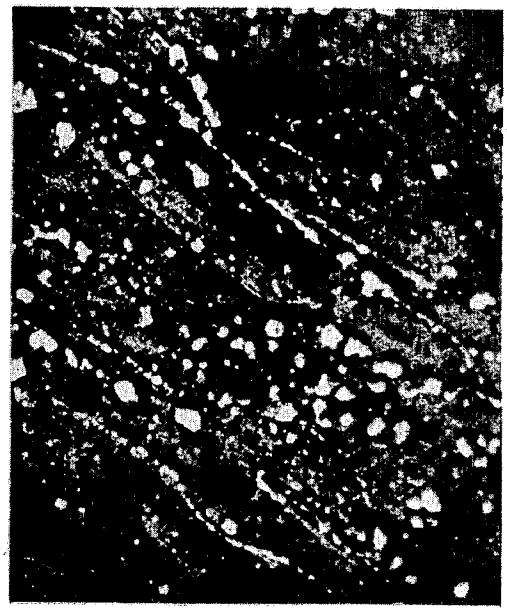


FIG. 3B

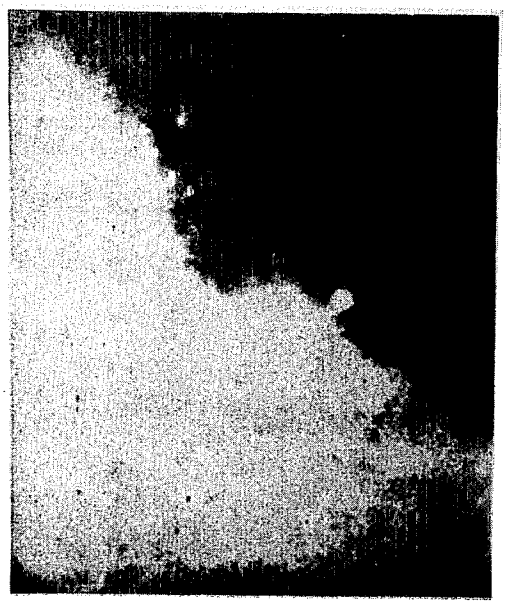


FIG. 3C

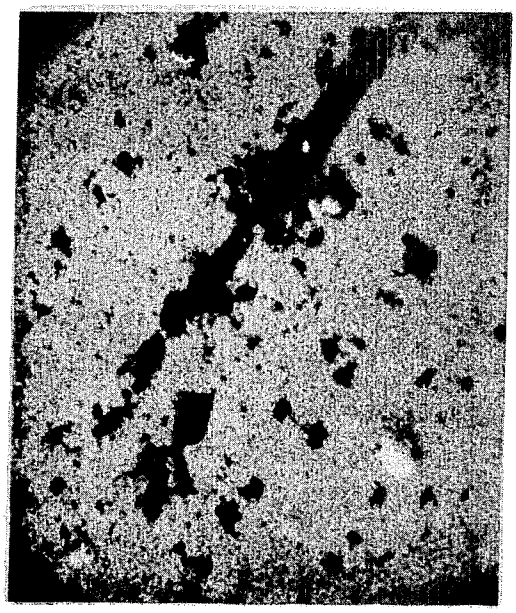


FIG. 3D

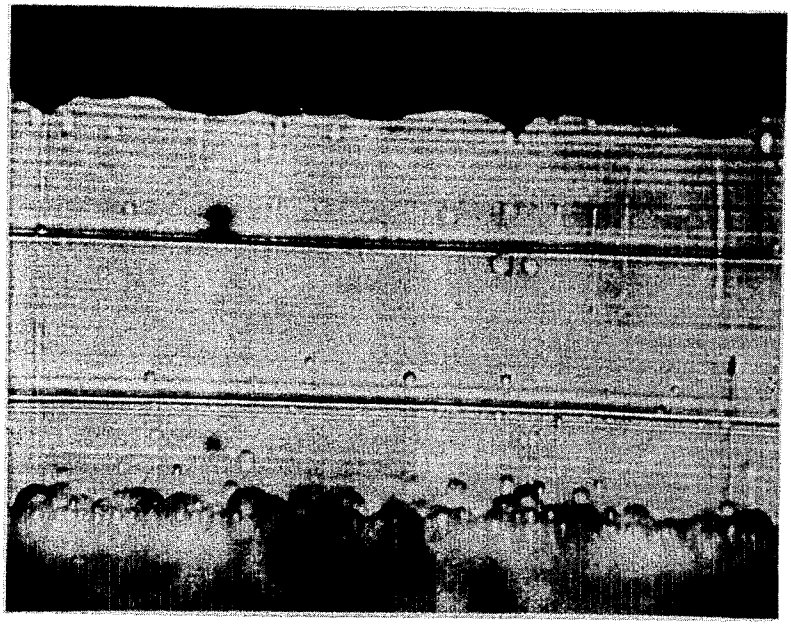


FIG. 4A

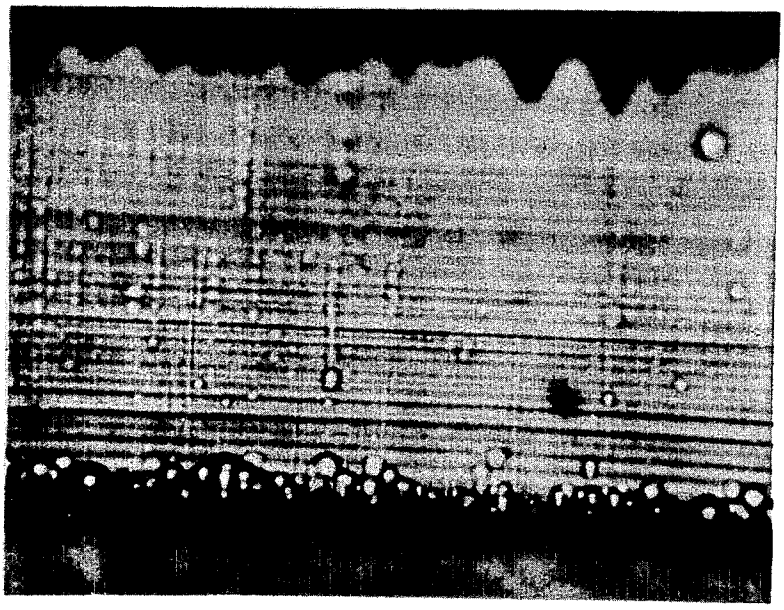


FIG. 4B

United States Patent Office 3,832,168
Patented Aug. 27, 1974

3,832,168

METAL FINISHING ALLOY OF NICKEL-COPPER-PHOSPHORUS

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Continuation-in-part of abandoned application Ser. No. 207,697, Dec. 13, 1971, which is a division of abandoned application Ser. No. 119,661, Mar. 1, 1971. This application June 21, 1973, Ser. No. 372,430
Int. Cl. C22c *19/00*
U.S. Cl. 75—170 6 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to a new metal coating useful as a protective and decorative finish which finish also has unusual functional properties and to a metal plating solution capable of depositing said coating. The coating is an electroless nickel copper-phosphorus alloy substantially free of co-deposited sulfur which coating is deposited from an electroless nickel solution characterized by the presence of a small amount of copper ions. The copper ions provide an extremely smooth deposit resulting in a lustrous surface appearance. Moreover, copper ions in the monovalent cuprous state, added to the electroless nickel solution, provide the secondary advantages of stabilizing the plating solution and substantially improving corrosion resistance of the deposit. Copper ions in either the monovalent cuprous state or the divalent cupric state added to the electroless nickel solution co-deposit with the nickel providing the electroless alloy deposit of nickel, phosphorus and copper.

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part application of co-pending U.S. Patent Application Ser. No. 207,697, filed Dec. 13, 1971, now abandoned, which latter application was a divisional of U.S. application Ser. No. 119,661, filed Mar. 1, 1971, now abandoned.

BACKGROUND OF THE INVENTION

(1) Field of the Invention

This invention relates to electroless depositing compositions and electroless alloy deposits formed therefrom and more particularly, to electroless nickel alloy plating solutions having extended life and temperature tolerance and to new metal finishes comprising nickel-copper-phosphorus alloy deposits characterized by improved appearance.

(2) Description of the Prior Art

Electroless nickel deposition refers to the chemical plating of nickel or its alloys over an active surface by chemical reduction in the absence of an external electric current. Processes and compositions useful therefor are described in numerous publications. For example, compositions for depositing electroless nickel are described in U.S. Pats. Nos. 2,690,401; 2,690,402; 2,762,723; 2,925,425; 2,929,742; and 3,338,726. Other useful compositions for depositing nickel and its alloys are disclosed in the *35th Annual Edition of the Metal Finishing Handbook for 1967*, Metal and Plastics Publications, Inc., Westwood, N.J., pages 483 to 486. Each of the foregoing publications are included herein by reference.

Known electroless nickel deposition solutions generally comprise at least four ingredients dissolved in a solvent, typically water. They are (1) a source of nickel ions, (2) a reducing agent such as hypophosphite, (3) an acid or hydroxide pH adjustor to provide required pH and (4) a complexing agent for metal ions sufficient to prevent their precipitation from solution. A large number of suitable complexing agents for electroless nickel solutions are

described in the above noted publications. In some formulations, the complexing agents are helpful but not a necessity.

Although some attempts have been made in the prior art to use electroless nickel deposits as a decorative metal finish, it has not generally been accepted for such purposes for several reasons. Firstly, the prior art electroless nickel does not possess the bright, mirror-like appearance required of a decorative metal finish. Secondly, of those electroless nickels termed bright, within a short period of time, a yellowish haze forms over the electroless nickel which is a corrosion product resulting from exposure to air. Finally, a decorative metal finish should also be corrosion resistant. The electroless nickels of the prior art, though possessing good corrosion resistance, do not possess the corrosion resistance required for a decorative or protective metal finish.

STATEMENT OF THE INVENTION

The present invention is predicated upon the discovery that the addition of a small but effective amount of a source of cuprous ions to an electroless nickel solution free of sulfur compounds to the extent that the deposit obtained thereon is substantially free of co-deposited sulfur results in deposition of an electroless nickel-copper-phosphorus alloy which alloy is exceptionally smooth, pore free and substantially free of imperfections. As a result, the electroless alloy deposit of the invention is characterized by a lustrous surface appearance which does not tarnish and exceptional corrosion resistance. With these properties, the alloy deposit can be characterized as a new protective and decorative metal finish.

It is a further discovery of this invention that the addition of cuprous ions to the metal depositing solutions also results in substantial improvement in stability of the solution without significantly retarding the rate of deposition. Thus, as a secondary aspect of the invention, there is provided a new solution stabilizer for electroless nickel solutions which is not a solution poison.

Another discovery of this invention is that the addition of copper ions in the cupric form also substantially improves deposit appearance though not to the same extent as cuprous ions. Though somewhat unexpectedly, the cuprous ions have little effect on solution stability and deposit corrosion resistance.

An electroless nickel-copper-phosphorus alloy depositing solution in accordance with the invention would comprise (1) a source of nickel ions, (2) hypophosphite reducing agent for said nickel ions (3) a pH adjustor, (4) a complexing agent for the nickel ions sufficient to prevent their precipitation from solution where necessary and (5) a source of copper ions which are preferably in the monovalent cuprous form.

DESCRIPTION OF THE DRAWINGS

In the drawings, FIG. 1 graphically represents concentration of copper in a nickel deposit as a function of pH of the electroless nickel plating solution from which the deposit is obtained;

FIG. 2 graphically represents concentration of copper in a nickel deposit as a function of copper ion concentration in the electroless nickel plating solution;

FIG. 3 comprises photomicrographs of the surface of various nickel alloy deposits with and without copper and/or sulphur compounds contained in the metal depositing solutions; and

FIG. 4 comprises photomicrographs of the crosssection of two nickel deposits formed in accordance with the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As noted above, cuprous ions are believed to be responsible for increased bath stability, deposit corrosion resistance and deposit appearance and copper ions in the cupric form provide a deposit of improved appearance. Consequently, the addition of both cuprous and cupric compounds to a nickel depositing electroless solution is contemplated though the cuprous compounds are preferred.

Both simple and complex copper compounds soluble in the electroless nickel plating solution are suitable as a source of the copper ions for purposes of the present invention. Typical examples of such compounds include cuprous acetate, cupric acetate, cuprous benzoate, cupric benzoate, cuprous bromide, cupric bromide, cuprous carbonate, cupric carbonate, cuprous chloride, cupric chloride, cuprous fluoride, cupric fluoride, cupric nitrate, cuprous hydroxide, cupric sulphate, cuprous ammonium chloride and cupric ammonium chloride.

The copper compound may also be added in a complexed form such as in the form of cuprous maleate, propionate or the like provided the dissociation constant and rate of dissociation of the complex are sufficient to provide the copper in solution in an amount as required.

With respect to the cuprous compound, it should be noted that many such compounds are not fully soluble in aqueous solution and some are considered insoluble. However, the cuprous compound, for purposes of the present invention, is required in an amount capable of yielding cuprous ions in concentrations of only parts per million. Consequently, cuprous compounds considered essentially insoluble in aqueous solution may be soluble to the extent that they yield cuprous ions in a concentration sufficient for purposes of the invention. The cuprous compounds most soluble are preferred.

In use, as the metal deposits from the plating solution, copper codeposits with nickel to form a nickel-copper-phosphorus alloy. There are several factors relating to the amount of codeposited copper in the electroless alloy. One such factor is solution pH, it having been found that a low pH, particularly below 4.5, favors a higher concentration of codeposited copper. The relationship between solution pH and the concentration of codeposited copper is depicted in FIG. 1 of the drawings where for purposes of illustration, the electroless solution of Example 1 under the conditions listed was used to which 200 p.p.m. of cuprous ion (in the form of cuprous chloride) were added. The pH was adjusted by the addition of ammonium hydroxide. From FIG. 1, it can be seen that copper codeposition increases significantly as pH drops below 5.0.

Another factor affecting copper concentration in the deposit is copper concentration in the plating solution. This relationship is depicted in FIG. 2 where Curve A illustrates the relationship between cuprous ion content in solution and copper content in the resulting nickel deposit and Curve B represents cupric content in solution versus copper content in the deposit. The base electroless depositing solution is that of Example 1 below using the conditions listed.

A third factor that appears to affect copper concentration in the deposit is the operating temperature of the solution. It has been found that as the solution temperature drops below about 190° F., the concentration of the copper in the deposit increases substantially.

From the above, it may be seen that copper content in the deposit is relatively high compared to copper content in solution, especially where the solution is operated at low pH, low solution temperature or both. This indicates that copper deposition might be preferential to nickel deposition and frequent replenishment with a copper salt may be necessary and is usually preferred. Typically, copper concentration in the deposit varies from 0.05 to 25% by weight, preferably does not exceed 12% by weight, more preferably varies between 1 and 8% by weight for some usage and between 0.25 and 2% by weight for other usage.

The numerical value for copper concentration in the deposit as depicted in the drawings may be somewhat misleading. Though not wishing to be bound by theory, it is believed that on a highly activated surface, as an initial deposit, there is plate-out of copper before nickel. Then nickel begins to plate-out with the copper at an increasingly rapid rate. Thus there is believed formed a first layer essentially of copper followed by an alloy layer becoming increasingly rich in nickel. This is believed to be especially true at the low solution pH and temperature. Consequently, the resultant full thickness deposit is believed to comprise an interface in contact with the coated substrate having the highest concentration of codeposited copper and the surface farthest from the substrate having the lowest copper concentration, there exisiting a gradient in copper concentration between the two. Furthermore, should the solution be replenished with copper during plating of a particular substrate, then a structure would be formed where the copper concentration is high at that portion of the deposit formed at the time of replenishment with a new gradient being formed going from high copper concentration to low copper concentration as the replenished copper plates out. This is illustrated in FIGS. 4A and 4B which are cross-sections of deposits, that in FIG. 4A being replenished twice during plating while that of 4B not be replenished. The layered structure is clearly visible in FIG. 4A.

Since it is desired to form a nickel-copper-phosphorus alloy, it is desirable to frequently replenish the plating solution with copper. If a layered structure is not desired, then it is desirable to make frequent replenishments with small amounts of copper rather than infrequent addition of large amounts of copper.

The amount of copper tolerable in solution is dependent upon several factors. For example, alteration of the base solution such as change in complexing agent, change in nickel or hypophosphite content and the like changes the maximum amount of copper tolerable in solution. In addition, operating conditions such as pH and temperature are factors relating to the maximum copper content in solution. In this respect, under preferred operating conditions, with a fresh bath copper ion content in solution is preferably maintained between 5 and 200 parts per million parts of solution (expressed as copper metal) and more preferably, between about 40 and 100 parts per million parts of solution. With a used bath, where nickel is depleted and residual products formed as a result of the plating reaction, the copper ion concentration is preferably decreased substantially, desirably down to from ½ to 20 parts per million parts of solution and preferably from 1 to 5 parts per million parts of solution. This is especially true where the solution has been used for more than ½ plating cycle. Preferred operating conditions are defined herein as pH approximately at least 4.0 and more preferably, pH 4.5 to 7.0 and a solution operating temperature of about 190° F. or greater. Under these conditions, at relatively large concentrations of copper in solution, e.g., in excess of about 200 parts per million parts of solution, for reasons not fully understood, deposits are obtained having a dull, rather than bright appearance and a spongy structure. It should be noted that the copper ion concentration ranges stated herein are guidelines only and most desirably, the copper ion concentration in solution is maintained at a level sufficient to achieve the stated objective of improved corrosion resistance and appearance while avoiding spongy, dull deposits.

As noted above, when the copper in solution is in the form of the cuprous ion, increased bath stability is obtained. It is well known that though electroless nickel solutions have been used for many years, the commercially used formulations frequently suffer from relatively slow

deposition rate and bath instability. It has been found in the prior art that plating rate is depedent to some extent upon the concentration of the reducing agent or the nickel ion in the plating solution and that increased concentration generally results in an increased rate of deposition. However, increased concentration of reducing agent and/or nickel also results in decreased bath stability. This is evidenced by a decrease in the time in which the plating solution will undergo uncontrollable decomposition (trigger).

It is well known in the art that certain additives or inhibitors added to an electroless nickel solution in properly controlled trace quantities act as stabilizers and retard the rate of bath decomposition. Generally speaking, these stabilizers are catalytic poisons and their concentration in solution is usually critical. Trace quantities, typically in the range of a few parts per million parts of solution provide stability dependent upon the particular stabilizer used and the particular solution to which it is added. An excess of stabilizer will partially or totally stop deposition of the electroless metal.

One such stabilizer which is also a catalytic poison is disclosed in U.S. Pat. No. 2,762,723 of Talmey et al. This patent teaches an acid nickel plating solution stabilized with a source of sulfide ions and a "sulfide ion controller" which combines with the sulfide ions to prevent their liberation from a hot or boiling solution. Such sulfide ion controllers are lead, bismuth, tin, selenium, tellurium, tungsten, thorium, titanium, copper, zinc, manganese and rhenium. The sulfide ions, which comprise the active portion of the stabilizing combination, are catalytic poisons and as such, depress plating rate in trace quantities and prevent plating in larger quantities. In accordance with this invention, substantially improved stability is used with small amounts of cuprous ion and only negligible effect on plating rate is observed because the cuprous ion is not a catalytic poison.

With respect to the use of the sulfide ion as a stabilizer, as disclosed in the forementioned Talmey et al. patent, it is also a discovery of this invention that the presence of the sulfide ion or for that matter, any other sulphur compound that codeposits with the electroless alloy at least in part and/or dissociates to yield free sulphur in solution such as in the form of the sulfide or sulfhydro ion, is detrimental to deposit appearance as well as other properties such as corrosion resistance. Thus, though the addition of copper to the solution provides an electroless nickel copper-phosphorus alloy deposit that is smooth and dense and therefore lustrous in appearance and corrosion resistant, these beneficial properties are impaired when there is also free sulfur in the plating solution. Sulfur compounds that have limited tolerance in solution are those that are covalently bonded with carbon atoms thus preventing the introduction of free sulphur into solution. Though these compounds are detrimental, they are not as harmful as those that dissociate. Consequently, the preferred compositions of this invention are free of sulfur compounds that dissociate in solution to yield free sulfur and more preferably free of all sulfur compounds.

It should be noted with regard to the above that analytical techniques are not now available for measuring sulfur content in parts per billion as reported in the Talmey et al. patent and it cannot be assured that the solutions in the most preferred embodiment of this invention are absolutely free of sulfur. However, it is a discovery of this invention that where sulfur content is present in a stabilizing quantity such that an initially unstable solution will not decompose within a time interval of 60 minutes, the sulfur content is too high for purposes of this invention and the improved deposit properties are lost. As sulfur content decreases below a stabilizing quantitity, properties continue to improve until no sulfur is in solution (as determined by carefully eliminating all possible sources of sulfur from solution such as by use of pure chemicals and distilled water and/or by holding the solution at elevated temperature to volatize the sulfur as hydrogen sulfide). Thus, the invention contemplates solutions having less than a stabilizing quantity of sulfur where stabilizing quantity is defined above, preferably less than fifty percent of a stabilizing quantity and most preferably no sulfur. The amount of sulfur necessary to provide stabilization is dependent upon the particular solution used.

In one embodiment of the invention, sulfur may be initially present in solution, but with use of the solution for plating or where "dummied" out by plating at elevated temperature, the sulfur is lost by volatilization. If not replenished, the resultant solutions are then within the scope of the invention.

The effects of sulfur in solution are readily shown in FIG. 3 of the drawings wherein four photomicrographs are set forth illustrating the surfaces of four nickel deposits at a magnification of five thousand. Photomicrograph A illustrates a deposit from a nickel-hypophosphite solution free of both copper and sulfur containing compounds. It can be seen that the deposit has a rough, irregular appearance. Photomicrograph B is a deposit from the same formulation, but the formulation contained 10 parts of thiourea per one million parts of the formulation. Little difference can be seen between the deposits of photomicrographs A and B. Photomicrograph C was of the same formulation as A, but contained 100 parts of cuprous chloride per million parts of solution. A comparison of photomicrograph C with photomicrographs A and B shows sharp contrast in that no imperfections whatsoever can be seen on the surface of the deposit depicted in photomicrograph C. Photomicrograph D is of a deposit from the same formulation as that from photomicrograph C, but 100 parts of thiourea per million parts of the depositing formulation were added. It can be seen that the deposit has a roughened surface only slightly improved over that of the deposits depicted in photomicrographs A and B.

The particular copper compound selected as the source of copper ions for purposes of the invention is not critical provided it yields sufficient copper ions and provided further that the anion of the copper compound is not detrimental to the plating solution. In this respect, it is well known in the art that certain anions in sufficiently large quantities such as cyanide are detrimental to plating solutions and salts containing these anions or other anions known to be harmful should be avoided.

The nickel solutions of this invention contemplate the use of hypophosphite as a reducing agent. As is well known in the art, the resulting deposit will contain phosphorus as an alloying element where the phosphorus content typically ranges between about 5 and 15% by weight dependent upon numerous factors such as the ratio of hypophosphite to nickel in the plating solution, solution pH and the like. The most usual range of such deposits using ordinary prior art procedures varies between about 5 and 10% though the higher phosphorus contents ranging between 10 and 15% are obtainable if desired.

Electroless nickel alloy plating solutions prepared in accordance with the invention are used to deposit nickel in the same way prior art electroless nickel solutions are used. The surface of the part to be plated should be free of grease and contaminating material. Where a non-metallic surface is to be plated, a surface area to receive the deposit must first be sensitized to render it catalytic to the reception of the electroless nickel alloy as by the well known treatment with an acidic aqueous solution of stannous chloride followed by treatment with a dilute aqueous solution of palladium chloride. Alternatively, extremely good sensitization of non-metallic surfaces is achieved by contact with a colloid of a precious metal having a protective stannic acid colloid and formed by the admixture of stannous chloride and a precious metal chloride, preferably palladium chloride, the stannous chloride being present in stoichiometric excess based upon the amount of precious metal chloride.

The invention will be better understood by reference to the following examples where stability of a solution was measured by the time it takes a bath to spontaneously decompose (trigger) when plating catalyzed cloth or activated aluminum and deposit properties were measured by plating a chromated base steel. The catalyzed cloth was prepared by treating a cotton fabric according to the following sequence of steps:

(1) Rinse cloth in a 20% (by weight) ammonium hydroxide solution maintained at room temperature for five minutes. Rinse in cold water.

(2) Rinse for five minutes in 20% acetic acid solution maintained at room temperature. Rinse in cold water.

(3) Immerse for some twenty to forty seconds in a sensitizing solution of palladium colloid having a protective stannic acid colloid (catalytic 6F) maintained at room temperature. Rinse in cold water.

(4) Immerse for one to three minutes in a dilute hydrochloric acid solution maintained at room temperature. Rinse in cold water.

(5) Dry cloth and cut to size.

The activated aluminum used is a 2024 alloy activated by immersion in 37% hydrochloric acid for two minutes.

In all examples, to determine stability, one square foot of either the catalyzed cloth or the activated aluminum per gallon of solution was used to initiate deposition and triggering. Also, chemically pure chemicals and distilled water were used to avoid contamination by impurities.

EXAMPLE 1

Nickel sulphate tetrahydrate	35 grams.
Sodium hypophosphite monohydrate	15 grams.
Sodium acetate	Do.
Water	To 1 liter.
Temperature	195 to 205° F.
pH	5.0 (approx.).

The activated aluminum caused triggering of the above bath in 12 minutes with heavy side wall deposition occurring in about 8 minutes. When 50 parts per million parts of solution of cuprous ion (as cuprous chloride) were added to the bath, it did not trigger within 60 minutes.

EXAMPLE 2

Nickel chloride	30 grams.
Sodium hypophosphite monohydrate	10 grams.
Ammonium chloride	100 grams.
Ammonium hydroxide	To pH about 9.
Water	To 1 liter.
Temperature	195 to 205° F.

The above bath triggered in about 20 minutes using activated aluminum. With the addition of 50 parts per million parts of solution of cuprous ion (as cuprous chloride), triggering did not occur for approximately 40 to 45 minutes indicating that improvement occurred, but the bath was not stable within the terms of the aforesaid definition of stability.

EXAMPLE 3

Nickel chloride	30 grams.
Sodium hypophosphite monohydrate	10 grams.
Ammonium chloride	25 grams.
Ammonium hydroxide	To pH about 8.5.
Water	To 1 liter.
Temperature	About 180° F.

Addition of catalyzed cloth to the above solution resulted in triggering within about 1 to 2 minutes. With the addition of about 25 parts per million parts of cuprous ion as cuprous chloride, triggering did not occur for about 4 minutes. When the cuprous ion content was increased to 40 parts per million parts of solution, triggering did not occur for about 7 to 8 minutes. Increase of the cuprous ion content to 50 parts per million parts of solution resulted in triggering in about 10 to 12 minutes. Though the bath was not stable where stability is as above defined as capable of standing 60 minutes without triggering, improvement in deposit properties were obtained such as improved corrosion resistance of the deposit and appearance. Thus, if a non-sulfur stabilizer were added to the formulation, such as iodate, the bath would be stable and provide a deposit of excellent chemical and appearance properties. Finally, when the cuprous ion content was increased to 200 parts per million parts of solution, triggering did not occur within 12 to 15 minutes, but the appearance of the deposited nickel was dull and a spongy structure was observed.

From the above, it can be seen that the cuprous ion stabilizer is more effective with acid nickel baths than with alkaline baths but some improvement is realized with the latter.

EXAMPLES 4–10

Nickel sulphate tetrahydrate	35 grams.
Sodium hypophosphite monohydrate	15 grams.
Sodium acetate	Do.
Sulfur stabilizer [1]	5 p.p.m.
Water	To 1 liter.
Temperature	195–205° F.
pH	5.0 (approx.).

[1] Added as thiourea.

Cuprous ions were added as cuprous chloride and catalyzed cloth was used to determine stability in the manner described above. Also, brightness and corrosion resistance were determined with results as follows:

Ex. No.[1]	Cuprous content (p.p.m.)	Brightness [2]	Corrosion resistance [3]	Stability (min.)
4	0	1	Heavy gassing in 30 seconds. Immediate black smut formation.	>60
5	5	1	Gassing in 3½ minutes. Black streaks in 1 minute.	>60
6	25	3	Gassing in 40 minutes. Black streaks in 14½ minutes.	>60
7	50	4	No gassing or streaking in 8 hours	>60
8	0		Sample unavailable for evaluation due to insufficient plating time.	2
9	25	5	No gassing or streaking in 72 hours	>60
10	50	5	No gassing or streaking in 150 hours	>60

[1] Examples 8, 9 and 10 were of formulations from which the thiourea was omitted.

[2] An arbitrary scale determined by observation with the numeral 1 indicating a dull, non-reflective surface and the numeral 5 indicating a bright, mirror-like surface. The numerals between 1 and 5 represent gradations in reflectivity.

[3] Determined by immersion of plated part in 6N hydrochloric acid at 100° F.

From the above table, it can be seen that the thiourea is an effective stabilizer, but provides no improvement in corrosion resistance or brightness of the deposit, in fact, is detrimental thereto and destroys the improvements due to the presence of cuprous ions. Cuprous ions without the thiourea significantly improves brightness and corrosion resistance of the deposit and stability of the solution. Consequently, electroless nickel solutions free of sulfur containing compounds of the type described above are preferred for purposes of this invention as it is believed that codeposition of sulfur results in inclusions within the deposit interfering with deposit properties.

EXAMPLES 11–16

Cupric chloride in varying amounts was added to the formulation of Example 1 and the resultant formulation was used to plate chromated steel. Thereafter, the deposits so formed were peeled from the substrate and each was analyzed for copper content. The amount of copper added to the solution and the amount of copper found

in the deposit for each plated part are set forth in the following table:

Example No.	Cupric content in solution (p.p.m.)	Copper content in deposit (wt. percent)
11	0	0.01
12	20	0.36
13	40	0.68
14	80	1.28
15	100	1.50
16	200	3.44

The deposits from Examples 12 through 15 were lustrous in appearance and no gassing or streaking was observed when the foils of deposited alloys were immersed in 6N hydrochloric acid at 100° F. The deposit of Example 16 was dull in appearance and spongy in structure.

EXAMPLES 17–22

The procedure of Examples 11 to 16 was repeated substituting cuprous chloride for the cupric chloride. The results obtained are set forth in the following table:

Example No.	Cuprous content in solution (p.p.m.)	Copper content in deposit (wt. percent)
17	0	0.01
18	20	0.39
19	40	0.76
20	80	1.40
21	100	1.90
22	200	3.90

The results of these Examples 11 through 22 are set forth in the drawings, FIG. 2, wherein curve A represents the curve for the cuprous addition and curve B represents the curve for the cupric addition. It can be seen that the two curves closely parallel each other.

EXAMPLE 23

Nickel sulphate tetrahydrate	35 grams.
Sodium hypophosphite monohydrate	15 grams.
Sodium acetate	Do.
Thiodiethyleneglycol	25 p.p.m.
Cuprous chloride	100 p.p.m.
Water	To 1 liter.
Temperature	195 to 205° F.
pH	5.0 (approx.).

An electroless nickel-copper-phosphorus alloy was deposited from the above formulation. It had a lustrous, bright appearance. No gassing or streaking was observed when the foil of the alloy was immersed in 6N hydrochloric acid at 100° F. This illustrates that certain types of sulphur compounds can be tolerated in the solution without adverse affect to the deposit with improvement in stability of the plating solution.

EXAMPLE 24

Nickel sulphate tetrahydrate	35 grams.
Hydroxyacetic acid	30 grams.
Sodium hypophosphite monohydrate	15 grams.
Sodium acetate	Do.
Cuprous chloride	75 p.p.m.
Water	To 1 liter.
Temperature	200° F.
pH	5.0 (approx.).

A bright, corrosion resistant deposit was obtained from the above formulation having about 3.0% by weight co-deposited copper in a sample one mil in thickness. It had the following properties:

Specific gravity	Approx. 8.20.
Melting point, °C.	Approx. 1000.
Hardness (as plated), Vickers	600.
Max. hardness by heat treatment (Vickers)	1100.
Hydrogen content, p.p.m.	30–50.
Magnetics	Non-magnetic.[1]
Resistivity, microhm-cm.	150 cm.

[1] Magnetic moment=1/1000 of pure Ni.

Corrosion resistances of deposits of varying thickness are as follows:

SALT SPRAY TEST (ASTM B–17–57T)

Thickness over steel, mil:	Exposure time
1	At least 240 hours.[1]
0.5	At least 500 hours.[1]
0.3	At least 96 hours.[1]
0.2	Aa least 48 hours.[1]

[1] After exposure to 5% salt spray no detectable rust or discoloration could be observed on surfaces.

The provision for a new decorative metal finish in accordance with the invention is a significant advance in the art. At the present time, the most commonly used decorative metal finishing is chromium which is electroplated onto a substrate. Many steps are involved in a process for depositing chromium such as the provision for leveling layers, corrosion resistant layers, and where over a non-conductor such as a plastic is to be plated, provision for a conductive layer. By using the electroless plating formulation of the subject invention, a decorative metal finish can be provided by electroless deposition solely from the metallizing solution of the invention with deposition proceeding to full thickness.

By virtue of the unusual properties of the electroless nickel alloy deposits of the invention, they are useful for many new commercial purposes. For example, though having a mirror-like appearance, their appearance can be improved further by a flash coating of chromium to provide a blue-white surface appearance characteristic of a chrome plated surface. Also, it has been discovered that the alloy deposit lends itself to soldering, brazing, ultrasonic bonding, and other metal to metal bonding methods known in the art. Because the phosphorus content can consistently be maintained above 8 and typically above 10%, the alloy deposit has non-magnetic properties making the alloy useful for a metal base for subsequent deposition of magnetic coatings. This is especially so in view of the fact that the alloy has an extremely smooth surface which permits a uniform distribution of the magnetic coating material over the non-magnetic alloy base. An additional desirable property is the hardness of the alloy which makes the same useful for wear resistant surfaces. Finally, the alloy is characterized by a high degree of flexural ductility which is surprising in view of the high phosphorus content associated in the prior art with brittleness. Therefore, the alloy deposit can be used in application where there is movement of either the alloy itself or the combination of the alloy and the substrate upon which it is plated. In this respect, the alloy can be used alone without a substrate such as in the manufacture of metal bellows. The ductility is maintained even when the alloy is subjected to high temperatures in use or heat treatment at temperatures as high as 500° F. for periods of time up to 100 minutes. The ductility may be attributable to a low hydrogen content which typically does not exceed

100 p.p.m. and usually varies between about 20 and 60 p.p.m.

What is claimed is:

1. An electroless alloy consisting essentially of from 0.05 to 25% by weight copper, 5 to 15% by weight phosphorus and the remainder nickel, said alloy being substantially free of sulphur.

2. The electroless alloy of claim 1 wherein the copper concentration varies between 0.25 and 12% by weight.

3. The alloy of claim 2 where the copper concentration varies between 1 and 8% by weight.

4. The alloy of claim 2 where the copper concentration varies between 0.25 and 2% by weight.

5. The alloy of claim 2 where the phosphorus content varies between about 5 and 15% by weight.

6. The alloy of claim 2 where the phosphorus content varies between about 10 and 15% by weight.

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