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CHEMICAL REDUCTION PLATING PROCESS AND BATH

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This invention relates to chemical plating and more particularly it relates to novel chemical plating processes wherein nickel-boron and cobalt-boron alloys are plated from new aqueous chemical plating baths.

This application is a continuation-in-part of application Ser. No. 694,097, filed Nov. 4, 1957, and now abandoned.

Plates of the aforementioned alloys have particularly desirable properties as metal plates or coatings and are bright, hard and uniform in thickness. They also have excellent wear and corrosion resistance.

These plates may be formed through the use of a borohydride as a reducing agent as disclosed in my copending applications filed of even date herewith and identified as P.C. 2839-C, Ser. No. 766,170, now Patent 3,045,334, and P.C. 2839-D, Ser. No. 765,017, now Patent 3,096,182.

The inventions disclosed in the aforementioned applications relate to a process wherein metallic surfaces and other catalytic surfaces in general are contacted with an aqueous alkaline plating solution containing nickel or cobalt salts, a borohydride and a complexing agent and to plates obtained using the process. The use of alkaline plating solutions is necessary since the oxidation of borohydride ions by water is very rapid in acid and neutral solutions. Due to the alkalinity of the solution, a complexing agent must be included in order to prevent the precipitation of nickel or cobalt hydroxide.

The present invention is directed to processes using simple aqueous plating solutions containing nickel and cobalt ions and to the production of nickel-boron and cobalt-boron alloy plates having the excellent characteristics noted above. An essential feature of the present invention is the use of amine-boranes as a reducing agent and as a source of boron, preferably in acidic plating solutions, eliminating the necessity of including a sequestering or complexing agent for the nickel and cobalt ions being reduced upon contacting the catalytic surface. Amine-boranes, however, function as excellent reducing agents and as sources of boron over a wide pH range and may be included in highly alkaline plating solutions. It is necessary, however, to employ a sequestering or complexing agent in the event an alkaline plating solution is selected as the plating medium in order to form nickel and cobalt complex ions, preventing the formation of the insoluble hydroxides of nickel and cobalt.

It is an object of this invention to provide a novel chemical plating process for the deposition of nickel and cobalt in the form of their boron-containing alloys from an aqueous solution on the surface of an object, which surface catalyzes the plating or deposition of the nickel or cobalt alloy from the solution.

It is another object of this invention to provide new aqueous chemical plating solutions which are stable, easily formed and which may be readily controlled to plate nickel-boron and cobalt-boron alloys on a catalytic surface at a fast plating rate.

It is still another object of this invention to provide new aqueous chemical plating solutions from which hard, adherent, corrosion- and wear-resistant coatings of nickel-boron and cobalt-boron alloys can be chemically deposited on catalytic surfaces.

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Other objects of the invention will become apparent from the following detailed description of the invention.

Plating is accomplished by initially forming an aqueous plating solution having a pH 3.5–14 which contains simple or complex nickel or cobalt ions and an amine-borane. Nickel-boron and cobalt-boron alloys may then be chemically deposited in uniform layers from such plating solutions on articles which have catalytic surfaces. There are preferred concentrations of the components taking part in the plating process in addition to temperature and pH ranges and other factors which lead to optimum plating conditions. However, it is to be understood that nickel-boron and cobalt-boron alloys may be plated chemically from simple aqueous solutions by reducing nickel and cobalt ions on a catalytic surface where such reduction is fostered by an amine-borane. The reaction is carried out in an aqueous solution at a pH that does not rapidly decompose the amine-borane until it comes into contact with a catalytic surface.

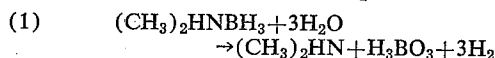
The term "catalytic surface" as used in connection with my chemical plating process refers to the surface of any article which contains, either in whole or in part, a material which promotes on its surface the reduction of nickel or cobalt ions. Such reduction is believed to be preceded by the decomposition of the amine-borane with the formation of atomic hydrogen at the catalytic surface.

Surfaces of glass and various plastics are, in general, noncatalytic. However, these surfaces can be sensitized to be catalytic by producing a film of one of the catalytic materials on these surfaces. This can be accomplished by a variety of techniques known to those skilled in the art. A preferred procedure involves dipping articles of glass or plastic in a solution of stannous chloride and then contacting the treated surface with a solution of palladium chloride. A monolayer of palladium is thus produced. The article can then be chemically plated with nickel-boron or cobalt-boron alloys by the process of this invention.

Those surfaces which are known to promote and catalyze such reduction are essentially the same surfaces disclosed in my copending applications filed of even date and include nickel, cobalt, iron, steel, aluminum, zinc, palladium, platinum, copper, brass, manganese, chromium, molybdenum, tungsten, titanium, tin, silver, carbon, graphite and the like.

Amine-boranes are generally prepared by reacting a primary, secondary or tertiary amine with diborane (B_2H_6) in stoichiometric amounts. Many of these compounds that are known are water soluble. Those amine-boranes which are sparingly soluble may have their solubilities augmented by the addition of hydroxyl or other highly polar groups to the amine substituent in accordance with conventional practices.

It is known that amine-boranes are decomposed by oxidation in aqueous solution to yield the amine, boric acid and hydrogen gas. In the instance of dimethylamine-borane, the following reaction takes place:



The rate of this reaction, which is typical of amineboranes, depends on several factors including temperature and hydrogen ion concentration. Increases of temperature and concentration of hydrogen ion increases the decomposition of amine-boranes, but the rate of decomposition, even at a pH as low as 3.5, is still slow enough to find application in the instant process.

Generally, all amine-boranes possess sufficient stability to resist rapid decomposition in pH>3 solutions. The presence of a catalytic surface accelerates the rate of decomposition. Tertiary amine-boranes possess good stabil-

ity and may be efficiently employed in my process, using a plating solution with a relatively high temperature.

Boranes with BH_3 attached to the nitrogen atom of a heterocyclic compound, such as pyridine and analogs thereof, generally behave and are referred to herein as tertiary amine-boranes.

Secondary amine-boranes appear to possess sufficient stability to be used in acidic solutions having a $\text{pH} > 3$ and yet decompose readily on a catalytic surface at an efficient rate. Some of the amine-boranes are not as suitable as others but still decompose on catalytic surfaces at slow rates and hence are operative.

The nomenclature of many of the amine-borane compounds, which may be successfully employed in my process, has not been fully appraised. However, it is a common characteristic of those compounds, wherein the borane substituent (BH_3) is attached to the nitrogen atom of an amine, to decompose and operate as an effective reducing agent under the conditions outlined herein.

The concentration of the amine-borane in aqueous solutions is important to the rate of plating, but not determinative as to operativeness since the presence of even minute amounts of amine-boranes permits the plating of alloys. High concentrations of amine-boranes, including saturated aqueous solutions of those very soluble amine-boranes, likewise admit plating. As a practical matter, concentrations where the amine-borane is present within the range of 0.015 to about 0.2 g. mole/liter are preferred.

Nickel and cobalt ions may be introduced in aqueous solutions by simply adding an appropriate amount of a water-soluble salt such as the sulfate, chloride, acetate, formate, etc., salts of nickel and cobalt. Salts of strong oxidizing acids and those which include anions such as sulfide, cyanides and thiocyanates should not be used since they tend to interfere with the reduction process. The latter-mentioned antagonistic salts, however, are not normally employed as sources of nickel and cobalt ions.

Additional ways of introducing nickel and cobalt ions will occur to those skilled in the art. For instance, nickel oxide in the presence of small amounts of hydrochloric or sulfuric acid is a common method employed to that end.

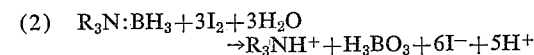
The concentration of nickel and cobalt ions in solution is not in any way critical and may vary over a wide range. The rate of plating is slightly increased with increases in the concentration of nickel and cobalt ions. An initial concentration of from 0.02 to 0.5 g. mole/liter of salt is preferred.

The nickel or cobalt complexing or sequestering agents suitable for use in accordance with this invention include ammonia and organic complex-forming agents containing one or more of the following functional groups: primary amino group ($-\text{NH}_2$), secondary amino group ($>\text{NH}$), tertiary amino group ($>\text{N}-$), imino group ($=\text{NH}$), carboxy group ($-\text{COOH}$), and hydroxy group ($-\text{OH}$). Preferred agents include ethylenediamine, diethylenetriamine, triethylenetetramine, ethylenediaminetetraacetic acid, citric acid, tartaric acid, lactic acid and ammonia. Related polyamines and N-carboxymethyl derivatives thereof may also be used.

In carrying out the plating process, the surface to be plated, normally formed of a metallic catalytic material, may be prepared by mechanical cleaning, degreasing and acid pickling, according to standard practice in electroplating processes. The cleaned surface is then immersed in a suitable volume of the aqueous plating solution. Almost immediately, hydrogen bubbles can be observed forming on the catalytic surface of the article and escaping in a steady stream from the bath, while the surface of the article becomes slowly coated with a metallic plate. Plating is continued until the metal ions are depleted from solution, or until the evolution of hydrogen gas stops, indicating that all the amine-borane is consumed in the plating process.

A method for the quantitative determination of amine-

boranes has been devised. This comparatively simple method can be carried out to determine the amount of amine-borane in plating solutions; the addition agents that are ordinarily in plating solutions do not interfere with the analysis. This method is based on the knowledge that amine-boranes are easily oxidized by iodine in weak acidic solutions. By buffering a solution containing an amine-borane with sodium acetate and acetic acid, a rapid analysis may be carried out with the addition of starch followed by titration with iodine (I_2) solution. The end points in the titration are sharp; the reaction proceeds rapidly and quantitatively as indicated in the following equation:



Quantitative determinations by the iodine titration method closely approximate those results obtained by the convention hydrogen evolution method. The latter-referred-to method, based on hydrolysis of amine-boranes to boric acid and hydrogen, is often unsatisfactory for analyzing plating solutions.

If there were no metal ions being reduced, substantially all of the hydrogen would be in molecular form (H_2) as indicated in Equation 1 above and the pH would increase somewhat because of the free amine. As the nickel or cobalt ions are reduced, electron transfer occurs at the catalytic surface with the formation of hydrogen ions and the pH is lowered. In order to maintain the pH of the bath within the desired range, a buffering system can be advantageously included. Such a system will sustain a substantially constant plating rate and assist to preserve the stability of the bath.

Unlike electroplating processes which necessitate the use of plating solutions that contain a very restricted variety of components, the present invention is relatively free from those limitations imposed by ion migration and anode contamination and practically any buffering system may be used.

Those buffering systems which contain acids and acid salts having cyanide, thiocyanate and sulfide radicals are antagonistic to the plating process for the reasons noted above. However, buffering systems normally do not contain radicals antagonistic to the process disclosed herein and virtually any system may be used.

Both acidic and alkaline buffering systems are operative in general including the common carboxylic acids such as acetic, propionic, etc. When an acidic pH is to be maintained, an acid with a $\text{pK} > 3$ should be selected. The solution may be buffered by adding a weak acid and adjusting the pH with a base, or both the weak acid and its salt may be added in the desired amounts. Another way is to add the salt of a weak acid and a strong acid. This method is not preferred inasmuch as the acid anion and salt cation will be present in solution.

Many of the components included in the buffering systems are capable of forming complex ions with nickel and cobalt ions in the plating solutions. However, the formation of complex ions is in no way detrimental to the process. In fact, the formation of nickel or cobalt complex ions is necessary and beneficial in the event the plating solution is alkaline.

The particular buffering system employed may require the addition of sodium hydroxide or hydrochloric acid to adjust the pH within a certain desired range. Such adjustments are well known to those in the field and one skilled in the art can readily determine the amounts of the various reagents required to adjust the pH.

The rate of plating is an important consideration when devising a commercially feasible plating process. It is influenced by many factors including (1) pH of the plating solution, (2) concentration of amine borane, (3) temperature of plating bath, (4) concentration of nickel or cobalt ions, (5) ratio of volume of bath cm^3/area

plated cm.², (6) presence of soluble fluoride salts and (7) presence of wetting agent and/or agitation.

In general, the rate of plating increases as the pH value is increased. Plating may be done in solutions at a pH 3.5 to 14 although a pH > 10 is often impractical. An increase in the concentration of amineborane also increases the rate of plating. At a constant pH, the rate is approximately proportional to the amineborane concentration. As the temperature increases, the rate of plating increases. As a practical matter, most plating processes will be carried out above 40° C. and preferably at a temperature of at least 60° C. up to the boiling point of water.

It has been found that the addition of soluble fluoride salts, such as sodium fluoride, increases the rate of plating. In addition to sodium fluoride, other soluble fluoride salts may be used providing that the action is inert with respect to the other ingredients in the plating solution. Soluble fluoride salts may be used in the amount of a trace to substantially larger concentrations.

The above four factors have the most important influences on the rate of plating which may be readily adjusted according to the needs of the particular process employed.

An increase in the concentration of nickel or cobalt ions only slightly increases the rate of plating. The larger the ratio of the volume of plating bath (cm.³) to the area of the surface being plated (cm.²), the higher will be the rate of plating since nickel or cobalt ions and the amine-borane reducing agent are depleted slowly. The above ratio preferably has a value of 1 to 10.

The chemical plating of nickel-boron or cobalt-boron by chemical reduction with amine-boranes is accompanied by the evolution of hydrogen gas according to Equation 1 noted above.

The presence of a gas bubble on the surface interferes with the contact between the plating solution and the particular spot where the bubble is being formed. This obviously leads to lower rates of plating and sometimes also to the formation of a pit in the plate. Difficulties of this nature, which are also frequently encountered in the conventional electroplating, can be eliminated by reducing the contact time between the gas bubble and the surface by proper stirring of the bath and/or by adding wetting agents to decrease the surface tension of the plating solution, preferentially below 50 dynes per cm. The use of wetting agents is recommended when plating is done at lower temperatures. Wetting agents such as sodium lauryl sulfate and the like are suitable.

The plating operation may be maintained by continuously or intermittently adding amine-borane, a salt source of nickel or cobalt ions, and the other ingredients consumed. When a buffering system is employed, it can be maintained by the addition of a base. Generally, the molar ratio of the ingredients used in a buffering system and as a complexing or sequestering agent to the salt source of the nickel or cobalt ions should be between 4.0 and 0.2.

The initiation of the plating process can be speeded up, particularly when working at temperatures below about 70° C., by contacting the surface of the material to be plated with a more electro-negative metal such as aluminum, while in contact with the plating solution. Since nickel and cobalt and their alloys with boron are good catalysts for the reduction of the nickel or cobalt ions to metallic nickel or cobalt in the presence of amineboranes, once the initial deposit of these metals is obtained upon a surface, the plating will continue as long as the solution remains workable.

The plating solution is preferably contained in glass or plastic vessels since their surfaces are generally non-catalytic and will not initiate the deposition of nickel- or cobalt-boron alloys when contacted with the plating solutions.

The efficiency of the bath is often impaired to some

extent by contamination with impurities. Those impurities which act as minute catalytic surfaces should be rigorously excluded. In the event impurities of this nature exist and begin to increase in size with deposits of the plating alloy, the solution should be filtered or purified by activated charcoal.

Frequently, the addition of small amounts of some organo sulfur compound or lead salts (1-50 parts/million) will render inert those impurities that are present in the plating bath. Such sulfur compounds as thiourea and xanthates are well-known for this purpose as are various lead salts and may be used when necessary.

Plates of nickel- or cobalt-boron alloys are essentially the same plates obtained by the process disclosed in my aforementioned copending applications. While the plates are difficult to analyze, it has been recently determined, through X-ray diffraction and X-ray microscopy techniques, that the boron is imbedded in an amorphous matrix of the metal placed in both nickel- or cobalt-boron plating processes. The matrix metal is essentially amorphous to X-rays (CuK_α radiation, e.g.) showing only about 5-10% crystalline nickel or cobalt.

All alloy plates that are prepared in accordance with the present invention contain about 92-99% of nickel or cobalt and about 1-8% boron. Approximately 5-10% of the metal is present as crystalline nickel or cobalt; the remainder of the metal is structurally unorganized and noncrystalline. The boron and crystalline metal are uniformly dispersed and distributed throughout the matrix.

After heat treatment for one hour at 600° C., the X-ray diffraction patterns of nickel-boron plates show the presence of crystalline Ni₃B and additional crystalline nickel, indicating that boron and nickel have chemically reacted and that the small amount (5-10%) of crystalline nickel originally present has grown.

It has been further found that the amount of crystalline nickel present in the amorphous matrix is as high as about 10% of the total nickel content present and possibly higher. The amount of crystalline cobalt present in the amorphous matrix of cobalt is frequently lower, sometimes comprising less than 5%.

The addition to the bath of buffers, complexing agents and the like will generally reduce the amount of boron deposited in the plate, especially in the instance of cobalt-boron plates. Under varying conditions in cobalt-boron plating baths, the amount of boron in the plate may be as low as about 1%. All of the plates obtained through the practice of the herein-disclosed invention, however, will contain about 1-8% by weight of boron. Nickel-boron plates containing about 3-7% boron are produced by preferred methods and have shown excellent qualities.

Plate containing both nickel and cobalt in addition to boron may be obtained using a plating solution containing a mixture of nickel and cobalt salts. When equivalent amounts of nickel and cobalt salts are used in the same plating bath, cobalt ions are preferentially reduced, and nickel-boron alloy plates so produced contain a higher percentage of cobalt than nickel. Although nickel is preferred for economic reasons, cobalt and nickel are considered to closely approximate one another for the purposes of the present invention.

In addition to the excellent qualities noted above, plates produced as disclosed herein are useful as ornamental designs, since a non-catalytic surface may be selectively activated by the use of stannous chloride and palladium chloride as described above. Similarly, these metal plates may be deposited in predetermined patterns that serve as electrical conductors. Circuit patterns may thus be selectively plated on the activated areas of an inexpensive sheet of material that is normally non-catalytic.

Examples illustrating various plating baths and conditions under which the process may be carried out follow.

Example 1

Using nickel chloride as a source of nickel ions and dimethylamine-borane, steel samples were plated at varying temperatures.

	G. mole/liter
NiCl ₂ -----	0.1
(CH ₃) ₂ HNBH ₃ -----	0.06

The ratio of the volume of plating bath to area of surface being plated was 1.5. The rate of plating was determined from weight increase.

Temperature, ° C.	Rate of Plating, mg./cm. ² , in 15 min.	Percent of 100 ° C.
100	2.2	100
90	1.8	82
80	1.3	59
70	0.8	36
60	0.5	23
50	0.3	14

Using cobalt chloride instead of nickel chloride and isopropyl amine-borane (C₃H₇)₂NBH₃ in equimolar amounts, the rate of plating cobalt-boron alloy on steel likewise markedly decreases as the temperature is lowered.

In addition to dimethylamine-borane and isopropyl amine-borane at the above concentration of 0.06 g. mole/liter, ethylamine-borane and tertiary propylamine-borane are used at the same concentration in plating baths, together with 0.1 g. mole/liter of NiCl₂. Decreasing the temperature also decreases the plating rate.

Example 2

Excellent results are obtained plating copper, steel or other catalytic surfaces using aqueous plating solutions containing

NiCl ₂ -----	g. mole/liter--	0.1-0.2
(CH ₃) ₂ HNBH ₃ -----	do-----	0.05-0.08
CH ₃ COOH+CH ₃ COONa -----	do-----	0.15-0.30
pH -----		5.0-5.5
Temp. -----	° C.--	70-75
Volume (cm. ³)/area (cm. ²) -----		5-10
Rate of plating -----	mil/hr. ¹ --	0.8-1.0

¹ 1 mil/hr. approximates 22 mg./cm.² per hr.

This preferred plating solution gives the same excellent results when either succinic acid, lactic or tartaric acid is used instead of acetic acid in the same amounts and the pH is adjusted to the above range with NaOH.

Example 3

Using a plating bath (50 cm.³) containing 0.1 g. mole/liter of NiCl₂ and 0.075 g. mole/liter of (CH₃)₂HNBH₃, clean steel samples (33 cm.²) were plated in this solution at 60° C. for 15 minutes. The rate of plating is 1.2 mg./cm.². The same solution containing 0.1% by weight of sodium lauryl sulfate as a wetting agent plates at a rate of 1.9 mg./cm.² under the same conditions.

Example 4

A plating solution of the following composition was used to plate copper and steel surfaces:

	G. mole/liter
NiCl ₂ -----	0.1
(CH ₃) ₂ HNBH ₃ -----	0.06
Mixture of tartaric acid and conc. ammonium hydroxide to give tartrate conc. of 0.2 g. mole/liter and pH of 8.	
Temp. -----	50° C.
Volume (cm. ³) } -----	1.35
Area (cm. ²) }	
Rate of plating -----	1.8 mg./cm. ² in 30 min.

Example 5

NiCl ₂ -----	g. mole/liter--	0.1
(CH ₃) ₂ HNBH ₃ -----	do-----	0.06
Ethylenediamine -----	do-----	0.4
pH -----		11.0
Temp. -----	° C--	70
Volume (cm. ³) }		
Area (cm. ²) }		1.35
Rate of plating on copper or steel is about 0.3 mg./cm. ² in 15 min. Cobalt chloride in the same amount plates in the same alkaline bath.		

Example 6

CoSO ₄ -----	g. mole/liter--	0.05
(CH ₃) ₂ HNBH ₃ -----	do-----	0.075
CH ₃ COOH+CH ₃ COONa -----	do-----	0.25
pH -----		5.2
Temp. -----	° C--	75
Volume (cm. ³) }		
Area (cm. ²) }		1.35
Rate of plating on copper surface was 0.8 mg./cm. ² in 30 minutes.		

Example 7

NiCl ₂ -----	g. mole/liter--	0.1
Na ₃ citrate -----	do-----	0.25
Pyridine-borane (C ₅ H ₅ NBH ₃) -----	do-----	0.25
pH -----		6.5
Temp. -----	° C--	98-99
Volume (cm. ³) }		
Area (cm. ²) }		1.35
Rate of plating on copper is 0.3 mg./cm. ² in 30 min. The rate of plating on steel is comparable with that of copper. Other catalytic surfaces can also be plated using a plating solution containing the above components in the amounts set forth and they may be plated with either cobalt-boron or nickel-boron alloys.		

Example 8

Initial Composition of Plating Solutions in g. mole/liter		Rate of Plating, mg./cm. ² , in 15 min.
NiCl ₂	(CH ₃) ₂ HNBH ₃	
0.1 M	0.015 M	0.57
0.1 M	0.030 M	1.1
0.1 M	0.045 M	1.7
0.1 M	0.060 M	2.2
0.1 M	0.075 M	2.7
0.2 M	0.060 M	2.4
0.1 M	0.060 M	2.2
0.05 M	0.060 M	2.1

Temperature: 98-99° C.

Material of samples plated: copper

Volume of plating solution (cm. ³)	
Area of the sample (cm. ²)	=1.35

Substituting equal amounts of methylethylamine-borane and diethylamine-borane for dimethylamine-borane, plating baths are prepared having the same concentrations of NiCl₂ and temperatures of 98-99° C. Increasing concentrations of these amine-boranes also increases the rate of plating on copper surfaces. The ratio of plating solution volume/area is about 5.

Example 9

Initial Composition of Plating Solutions in g. mole/liter			Rate of Plating, mg./cm. ² , in 15 min.
NiCl ₂	(CH ₃) ₂ HNBH ₃	NaF	
0.1 M	0.060 M	-----	2.2
0.1 M	0.060 M	0.01 M	2.7
0.1 M	0.060 M	0.025 M	2.9
0.1 M	0.060 M	0.05 M	3.4

Other conditions are the same as in Example 8. Other alkali metal fluoride salts when used in the same concentrations as NaF, likewise increase the rate of plating, as does NiF_2 , NH_4F and the like.

Example 10

Initial Composition of Plating Solutions in g. mole/liter		pH	Rate of Plating, mg./cm. ² , in 15 min.
NiCl_2	$(\text{CH}_3)_2\text{HNBH}_3$		
0.1 M	0.030 M	(1)	1.1
0.1 M	0.030 M	4.0	1.4
0.1 M	0.030 M	4.6	1.6
0.1 M	0.030 M	5.3	1.9
0.1 M	0.030 M	5.6	2.1
0.1 M	0.015 M	5.3	1.0
0.1 M	0.030 M	5.3	1.9
0.1 M	0.060 M	5.3	3.8
0.1 M	0.090 M	5.3	5.2
0.2 M	0.060 M	5.3	3.8
0.1 M	0.060 M	5.3	3.8
0.05 M	0.060 M	5.3	3.0
0.025 M	0.060 M	5.3	2.0

¹ Without buffer.

The plating solutions were made 0.35 molar in acetic acid, and the pH was adjusted to the above values with sodium hydroxide. Other conditions are the same as in Example 8. Using CoSO_4 in amounts which yield cobalt ions in concentrations equal to nickel ion concentrations above, an increase in the pH of the plating bath likewise increases the rate of plating.

Example 11

Clean copper surfaces having different areas were plated in separate 50 ml. baths for 1 hr. The composition of the bath was

NiCl_2 -----	g. mole/liter--	0.1
$(\text{CH}_3)_2\text{HNBH}_3$ -----	do-----	0.17
$\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ -----	do-----	0.27
Sodium lauryl sulfate -----	percent--	¹ 0.1
pH -----		5.5
Temperature -----	° C--	60

¹ By weight of the bath.

Variances in the ratio of volume (cm. ³)/area (cm. ²):	Rate of plating mg./cm. ² in hr.
1.35 -----	6.9
3 -----	9.0
5 -----	11.1
10 -----	12.0
20 -----	12.5
40 -----	13.2

When the ratio has a value of about 10, the rate of plating is seen to be relatively efficient as compared to higher ratio values.

Ammonia borane H_3NBH_3 , prepared by reacting lithium borohydride with ammonium chloride in diethyl ether, is substituted for dimethylamine-borane in the same amount in this plating bath. Increasing the ratio of

$$\frac{\text{volume (cm.³)}}{\text{area (cm.²)}}$$

likewise increases the rate of plating.

Certain theories relating to the disclosed process have been advanced, but it is to be understood that I do not intend to be limited to such theories. They have been advanced to assist those skilled in the art. Modifications and adaptations of the herein disclosed invention will occur to those skilled in the art, but it is to be further understood that I do not wish to be limited except as indicated in the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A chemical plating bath comprising an aqueous solution having a pH of at least 3.5, said solution containing

an amine-borane and a cation selected from the group consisting of nickel and cobalt ions.

2. A chemical plating bath comprising an aqueous acidic solution having a pH within the range of 3.5 to about 7, said solution containing an amine-borane and a cation selected from the group consisting of nickel and cobalt ions.

3. A chemical plating bath comprising a buffered aqueous acidic solution having a pH within the range of 3.5 to about 7, said solution containing an amine-borane and a cation selected from the group consisting of nickel and cobalt ions.

4. A chemical plating solution comprising an aqueous alkaline solution, said solution containing an amine-borane, a cation selected from the group consisting of nickel and cobalt ions and a metal sequestering agent, said cation being in the form of a complex ion.

5. The process of chemically plating a catalytic surface with an alloy selected from the group consisting of nickel-boron and cobalt-boron alloys comprising contacting said surface with an aqueous solution having a pH of at least 3.5, said solution containing an amine-borane and a cation selected from the group consisting of nickel and cobalt ions.

6. The process of chemically plating a catalytic surface with an alloy selected from the group consisting of nickel-boron and cobalt-boron alloys comprising contacting said surface with an aqueous solution having a pH of at least 3.5, said solution containing an amine-borane, a cation selected from the group consisting of nickel and cobalt ions and a soluble fluoride salt.

7. The process of chemically plating a catalytic surface with an alloy selected from the group consisting of nickel-boron and cobalt-boron alloys comprising contacting said surface with an aqueous solution having a pH of at least 3.5 and a temperature within the range of 60° to about 100° C., said solution containing an amine-borane and a cation selected from the group consisting of nickel and cobalt ions.

8. The process of chemically plating a catalytic surface with an alloy selected from the group consisting of nickel-boron and cobalt-boron alloys comprising contacting said surface with a plating solution of claim 1.

9. The process of chemically plating a catalytic surface with an alloy selected from the group consisting of nickel-boron and cobalt-boron alloys comprising contacting said surface with a plating solution of claim 3.

10. An aqueous chemical plating solution containing as essential components (1) a compound selected from the group consisting of secondary and tertiary amine boranes, and (2) a compound selected from the group consisting of soluble salts of nickel and cobalt, the proportions of each component being such that the concentration of borane radical is between 0.021 to 0.276 wt. percent, and the concentration of metal ion is between 0.12 to 2.94 wt. percent.

11. A method of plating metal-boron alloys on metal objects which comprises the step of contacting the object to be plated with an aqueous plating solution containing as essential components (1) a compound selected from the group consisting of secondary and tertiary amine boranes, and (2) a compound selected from the group consisting of soluble salts of nickel and cobalt, the proportions of each component being such that the concentration of borane radical is between 0.021 to 0.276 wt. percent and the concentration of metal ion is between about 0.12 to 2.94 wt. percent.

12. A method according to claim 11 in which the amine borane is dimethylamine borane.

13. A method according to claim 11 in which the pH of the plating solution is maintained between 3.5 and about 7.

14. A method according to claim 13 in which the pH is maintained by buffering the solution with a weak non-oxidizing acid.

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15. A method according to claim 11 in which the borane radical concentration is maintained by the periodic addition of amine borane.

16. A method according to claim 11 in which the metal ion concentration is maintained by the periodic addition of a soluble metal salt. 5

17. A bath for plating by chemical deposition consisting essentially of an aqueous solution containing a metal salt selected from the group of water soluble salts of nickel and cobalt, and isopropylamine borane in a molar ratio between about 2 to 1 and 3.3 to 1 wherein the concentration of said isopropylamine borane in said solution is about 1 to 2 grams per liter.

18. A bath for plating by chemical deposition as claimed by claim 17 wherein the metal salt and the isopropylamine borane are present in said solution in the molar ratio of about 3 to 1.

19. A bath for plating by chemical deposition as claimed by claim 17 wherein the metal salt is nickel chloride.

20. A bath for plating by chemical deposition as claimed by claim 18 wherein the metal salt is nickel chloride.

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