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3,597,267

BATH AND PROCESS FOR CHEMICAL METAL PLATING

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No Drawing. Continuation-in-part of application Ser. No. 468,921, July 1, 1965, and a continuation of application Ser. No. 661,218, Aug. 17, 1967. This application Feb. 26, 1969, Ser. No. 804,369

Int. Cl. C23c 3/02

U.S. Cl. 117—130

2 Claims

ABSTRACT OF THE DISCLOSURE

A bath and process for the electroless (chemical) plating of nickel, cobalt, iron and chromium on other materials such as metals and plastics. The bath utilizes a reducing agent to which is added a nickel, cobalt, iron or chromium coordination compound as the source of the plating metal. Other constituents also normally added to the bath are complexing agents and buffering agents. Utilization of metal-coordination compounds as the starting plating material source greatly enhances the operating characteristics of the bath and makes possible the plating of materials heretofore not susceptible to electroless plating.

CROSS REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of application Ser. No. 468,921, filed July 1, 1965, now abandoned, and a continuation of application Ser. No. 661,218, filed Aug. 17, 1967, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to plating of a material by chemical deposition and, in particular, to the electroless plating of a metal on the surface of the material from a plating bath employing a nickel, cobalt, iron or chromium coordination compound as the source of plating materials.

A number of processes for plating certain catalytic materials with nickel and other transition metals by means of an electroless plating bath are now quite well known. In general, the technique depends on the use of a plating bath containing a supply of the metal ions and a hypophosphite reducing agent. By properly preparing the material to be plated, e.g., by galvanic initiation where this is necessary, plating is begun and sustained by the catalytic action which the prepared material has on an aqueous solution containing the metal and hypophosphite ions and certain other supporting agents. The process is frequently referred to as the catalytic deposition of the metal by virtue of the fact that the object to be plated is itself the catalyst which triggers the plating reaction.

A typical electroless plating bath contains the following elements: a source of nickel, cobalt or iron cations, a source of hypophosphite anions, an organic complexing agent, and means for regulating the pH of the bath. The source of metal cations is normally a salt of the metal, e.g., a sulfate or chloride. The source of hypophosphite ions is generally sodium hypophosphite but can be any salt of hypophosphoric acid. The organic complexing agent is usually an organic hydroxycarboxylic acid and both acid and alkali materials are used as pH regulators depending on whether the bath is to be acid or alkaline in condition.

In the prior art, electroless plating solutions have been limited to deposition on metals that are directly catalytic to reaction or to metals that can be plated through galvanic initiation. Metals in the former category include iron, cobalt, nickel, ruthenium, rhodium, palladium,

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osmium, iridium and platinum. Metals in the latter category include gold, copper, silver, beryllium, germanium, aluminum, carbon, vanadium, molybdenum, tungsten, chromium, selenium, titanium and uranium.

As disclosed in British Pat. 821,763 and U.S. Pats. 2,935,425 and 2,766,138, and numerous other technical publications relating to this area of technology, prior art electroless plating solutions have been incapable of depositing plating materials on bismuth, cadmium, tin, lead and zinc. By utilization of the plating solution of the present invention and in particular use of a plating metal-coordination compound as one of the starting materials for formulating the plating solution, all of the aforementioned materials which could be plated in the prior art as well as cadmium, tin, zinc, lead, bismuth and combinations of these metals can now be plated electrolessly.

There are several factors of importance in producing a bath suitable for commercial production processes regardless of the material to be plated. In particular, it is desirable to provide a stable bath, that is, one in which the bath is provided with some means whereby the plating metal is prevented or retarded from being hydrolyzed or being subjected to other solvolytic effects which would cause it to be precipitated out rather than reduced to the elemental metal and deposited in a satisfactory manner on the object to be plated. Furthermore, since the plating process is a relatively slow one, steps are taken, where possible, to speed the plating rate. Both acid and alkaline baths are used. Although alkaline baths are generally conceded to produce a more desirable finished product, heretofore there have been certain problems attendant on the use of an alkaline bath which have caused most commercial producers to resort to acid baths.

The present invention is concerned with both alkaline and acid baths. In the alkaline condition the various disadvantages normally associated with this type of bath are eliminated while retaining its positive features, such as relaxation of the problem of control of the pH of the bath and improved quality of the metal plating. Some of the most pronounced disadvantages of typical alkaline baths which are now eliminated are their inconvenience and cost due to the use of ammonia. They are costly because of the rapid loss of ammonia due to its volatility, especially at high temperatures. This loss results in poor pH regulation, bath instability and the need for constant replenishment of ammonia in the bath. They are inconvenient because ammonia is a noxious substance with which to work and special provisions must usually be made to vent the ammonia fumes.

In addition to providing an improved alkaline bath, the bath of the present invention can also be operated in the acid condition. Operation of the bath in this manner is frequently important where the hardness of the plating is a paramount consideration. The choice of an alkaline or acidic bath according to this invention depends on the nature of the constituents selected for use in the bath, the metals in the coordination compound and the particular type of plating desired.

The present invention provides a bath for plating a material with a transition metal selected from the class consisting of nickel, cobalt, iron and chromium by chemical deposition. It comprises an aqueous solution of a transition metal reducing agent for the class to which is added a coordination compound of a substituted short chain carboxylic acid and one of the transition metals of the class. The coordination compound is formed by reacting nickel, iron, cobalt and chromium and compounds of these metals with the carboxylic acid prior to its addition to the plating bath. A ligand complexing agent and a buffering agent for adjusting the pH to a predetermined value in the range of from about one to about fourteen can also be added to the bath. Care is taken to limit the

presence of extraneous anions in the solution to an amount less than 3400 parts per million parts of solution. To obtain plating, the material or article to be plated is placed in the bath, the temperature of the bath is adjusted to a suitable level, and the article is retained therein until the metal in the desired thickness has been plated thereon.

The present invention is characterized by several outstanding capabilities. Primary among these is the heretofore unattainable objective of electroless plating of bismuth, cadmium, lead, tin and zinc. Among others are substantially greater stability than the presently known electroless plating baths. This stability is thought to result from a shift in the reduction potential of the metal and is believed to be due to the fact that an increased number of the coordination positions of the plating metal atom are now filled by bonds to atoms of the ligand with which it is compounded and the ligand complexing agent in the bath in comparison to the number of filled coordination positions in the plating metal complexes of the prior art.

This is to be contrasted with conventional nickel plating baths which are produced by the method of dissolving a metal salt, e.g., nickel chloride, nickel sulfate, in an aqueous solution of an organic material in the plating bath itself. In these conventional baths the chloride and sulfate anions of the salts are not completely removed from the coordination sphere of the metal ion but rather are in equilibrium competition with the organic complexing agent molecules and solvent molecules for the coordination positions of the metal ions. As the alkalinity of such baths is increased, the aquo-metal ions tend to hydrolyze to yield metal hydroxides which precipitate out of solution. In baths of the present invention, by the use of plating metal-coordination compounds and limitation of the amount of simple salt anions such as chloride and sulfate anions present in the bath it is thought that all but one of the coordination positions of the metal ion are filled by organic ligands or polydentate inorganic ligands, e.g., pyrophosphate anions, thus drastically reducing the tendency of the metal ion to hydrolyze.

This increased stability of the bath means that it is possible to use higher concentrations of the reducing agent, thereby increasing the plating rate. Further it has been found that the ammonium ion is no longer needed as a complexing agent for such a bath when it is operated in the alkaline condition, and hence the invention lends itself to adaptation to a commercial alkaline plating bath with the advantages inherent therein.

Finally, the present invention provides a bath which can be operated at lower temperatures than that at which conventional baths are presently operated while yielding the same plating rate. These and other features of the invention will be more readily apparent by reference to the following detailed discussion.

In describing the formation of complexes such as metal complexes in chemical plating baths, it is frequently useful to describe metal compounds formed in the baths in terms of coordination compounds and coordination positions of the metal ion. The term coordination compound refers to a type of association between an anion and cation. A metal cation is said to have a number of coordination positions which are filled by bonds to anions. An ion capable of forming one or more such coordinate bonds with another ion is a ligand. A ligand forming a ring type compound with a metal anion is defined as a chelate. Plating metals of the present invention, i.e., nickel, cobalt, iron and chromium, have four to six coordination positions, nickel, cobalt and iron having four or six coordination positions depending on the species employed, and chromium having six. According to the theory of the invention the nature of the cations or ligands forming coordinate bonds with the metal ion and the number of coordinate bonds made (or put another way, the number of coordination positions of the metal which are filled) in a complex are thought to be of significance with respect to plating metal baths of the present invention.

The nature of the ligands is important because some ligands, e.g., sulfate and chloride anions, have a greater tendency to allow metal hydrolysis than do organic or inorganic polydentate ligands and if present in significant amounts, i.e., in excess of 3400 parts per million parts of bath by weight in baths of the present invention, compete with the latter types of ligands for the coordination positions of the metal, allowing formation of insoluble precipitates with the metal ions which deposit on the article to be plated, degrading the quality of the plating and, when present in sufficient quantity, preventing a plating reaction from taking place. According to the present invention then, the number of extraneous anions, e.g., chloride and sulfate anions, in the plating baths of the invention are to be limited to an amount less than 3400 parts per million.

The number of metal-coordination positions which are filled by bonds to ligands as opposed to bonds to solvent molecules are also important with respect to the stability of the bath and the types of materials which can be plated. By utilizing a compound referred to herein as a plating metal-coordination compound as the source of plating metal for the bath of the present invention, limiting the number of extraneous anions in the bath to a number less than 3400 parts per million and providing a ligand complexing agent of an organic or inorganic polydentate nature, it is believed that all but one of the coordination positions of the plating metal ion in the bath are filled by bonds to ligands of an organic and inorganic polydentate nature thereby providing the improved plating metal baths of the present invention. The ligand complexing agent is added to the bath in amount sufficient to fill all of the coordination positions of the metal ion, although one less than all of the coordination positions may actually be filled. The improved bath of the present invention can be achieved if all but one of the coordination positions are filled. A preferred embodiment of the bath is one in which all of the coordination positions are filled with bonds to organic or inorganic polydentate ligands.

In conventional electroless nickel plating baths, the usual sources of nickel ions are salts of nickel, such as nickel chloride and nickel sulfate. To obtain a plating bath, these salts are dissolved in a water solution to which an organic compound had been added. It has been found that when the nickel salts are reacted with an organic material in this manner, the stability of the reaction product is less than satisfactory and to combat this problem stabilizers, such as thiourea, sodium ethylxanthate, lead sulfide and tin sulfide, are provided. Where stabilizers are not used, it is customary to supply an ammonium compound in sufficient quantity such that the ammonium ions complex with the nickel ions to prevent them from entering into other solvolytic reactions and precipitating out as an insoluble precipitate. In either case, whether it be the provision of stabilizers or the use of an excess of ammonium compound to complex the nickel ions, the stability of the bath is still unsatisfactory.

In most instances, alkaline electroless nickel plating solutions employ ammonium hydroxide, ammonium chloride, ammonium sulfate and the like to supply the excess of complexing ammonium ion. This excess of complexing ammonium ion hinders the tendency of the bath to form nickel hydroxide which precipitates out of the solution and quickly renders the bath inoperable. The ammonium compound also serves the function of maintaining the pH of the bath in the alkaline range. However, as indicated previously, the use of these materials involves several disadvantages, viz, volatility and inconvenience due to noxious ammonia fumes. Because of volatility, ammonium ions have to be periodically resupplied to the bath. By virtue of providing a bath operable with complexing agents other than ammonium hydroxide or chloride, the present invention eliminates the source of the two problems which heretofore have most seriously militated against the use of alkaline plating baths.

We have now found that by the use of nickel, cobalt, iron, and chromium coordination compounds, i.e., compounds of a plating metal selected from the class consisting of nickel, cobalt, iron and chromium and a substituted short chain carboxylic acid as the starting ingredient added to a solution of a plating metal reducing agent to serve as the source of the metal ion for the plating operations, the plating bath is made substantially more stable. When a plating metal compound is produced in the conventional manner (e.g., addition of simple nickel salt to a water solution of an organic compound with which the salt is to be reacted), a more limited number (between two and four depending on the plating metal being compounded) of the coordination positions of the metal atom are filled by bonds to the organic molecule. Since the number of filled positions is limited, the stability of the plating metal in the plating bath is also limited.

On the other hand, a plating metal-coordination compound as the term is used herein, e.g., one which is produced by reacting nickel carbonate, nickel oxide, or nickel powder with a mono- or di-carboxylic acid prior to introduction into the plating bath produces a substantially improved nickel plating material when used as the starting material for the plating bath. The substantial improvement resides in the enhanced stability of a plating system using such compounds to systems using conventional plating compounds. The improvement in stability is due to the fact that in this system all but one of the coordination positions of the plating metal atom are filled by orbital overlap bonds to the atoms of the primary or secondary ligand and are not subject to competition from extraneous inorganic anions for any of the coordination positions. This more complete filling of the coordination positions of the plating atom with organic ligands or polydentate inorganic ligands is manifested by a shift in the reduction potential of a plating metal complex according to the present invention when compared with the potential of conventional complexes, thereby resulting in baths having substantially improved resistance to deleterious effects such as hydrolysis. For ease of reference, metal plating compounds formed by the reaction of carbonates, oxides, and the like of the metals and a carboxylic acid having one or more substituted groups will be designated herein as plating metal-coordination compounds to distinguish them from simple plating metal salts such as nickel chloride and nickel sulfate.

Plating baths utilizing plating metal-coordination compounds are operable in either the acid or alkaline condition, the choice depending on the particular plating characteristic of paramount importance. For example, where the hardness of the nickel plate is important, an acid bath is used since the greater amount of phosphorus deposited with the nickel in an acid bath produces a substantially harder plate than an alkaline bath. Where the speed of plating is paramount, an alkaline bath is used. The higher plating rate of an alkaline bath prevents the deposition of amounts of phosphorus comparable to acid baths and the hardness of the plate is diminished. Regardless of the pH of the bath, other reducing agents besides salts of hypophosphorous acid, e.g., sodium, ammonium, potassium and lithium hypophosphite, can be used without any significant deterioration in results. Suitable substitutes for such salts include water soluble boranes including amine boranes such as morpholine borane, dimethylamine borane and various hydrazine compounds such as hydrazine sulfate.

When operated in the alkaline condition, the invention makes possible the substitution of non-ammonium complexing agents thereby eliminating the disadvantages attendant upon the use of ammonia compounds. Moreover, in addition to eliminating a problem, the substituted materials also produce distinct advantages in that in baths utilizing them the rate of plating metal deposition is increased and the pH of the solution does not vary during

the plating operation. Because of their effect in accelerating the plating rate for an equivalent amount of reducing agent (relative to prior art baths), these agents will be referred to herein as accelerating agents. These accelerating agents are carbonate compounds such as, for example, alkali metal carbonates and organic carbonates. In most baths such agents also serve as secondary buffering agents and to some extent as complexing agents. Specific examples of these carbonates include potassium, lithium and sodium carbonate and choline carbonate. Further advantage of the use of these non-ammonium carbonates has been found to be that a solution utilizing them can be operated at a lower temperature while still obtaining comparable rates of deposition compared to the prior art. Though less desirable than non-ammonium carbonates, it is also possible to use ammonium carbonate in this capacity since it is the carbonate anion which produces the accelerating action independent of any contribution from the cationic portion of the accelerating agent molecule. While reintroducing the undesirable feature of ammonia, such a substance retains the positive features characteristic of carbonates in general and has the added factor of being one of the most economical of the carbonates obtainable. In certain instances it is foreseeable that the economic factor may outweigh the inconvenience of the ammonia.

Although the theory is not completely understood, the stability of the bath of the present invention is thought to be due to the displacement of solvent and extraneous molecules from the coordination sphere of the plating metal ion by the complexing effect of the ligands used. In addition, the plating bath must be substantially free of extraneous inorganic anions which will compete with the ligand complexing agents for one or more of coordinating positions of the plating metal atom. Secondary ligand complexing agents are added to keep the nickel ion in solution preparatory to plating out on the material to be plated. If chloride or sulfate anions are present in the bath in the amounts specified previously, e.g., when such simple salts are added as in the prior art baths as the source of the plating metal or are present by virtue of other reagents used in the bath, the secondary ligand complexing agent is displaced from one or more of the coordination positions of the metal, and the stability of the bath is reduced to at least the point where bismuth, cadmium, lead, tin, and zinc can no longer be plated.

The selection of complexing agents for use with the baths of the present invention is made from a selection of constituents capable of acting as ligands for the plating metal ion used in the bath. Among the suitable constituents are carboxylic acids such as glycolic acid, lactic acid, beta-hydroxybutyric acid, glyceric acid, gluconic acid, malic acid, tartaric acid, citric acid, salicylic acid, 5-sulfosalicylic acid, 5-aminosalicylic acid, mercaptoacetic acid, dithiotartaric acid, ascorbic acid, erythorbic acid, beta-D-thiogluconic acid, 1-thio sorbitol, iminodiacetic acid, and ethylenediaminetetraacetate acid, and amino acids such as adenosine phosphate, amino acid cystine, methionine, serine, lysine, arginine, orthithine, valine, glycine, leucine, isoleucine, phenylalanine, tyrosine, aspartic acid, glutamic acid, histidine, proline. In preferred embodiments of the bath, where a metal compound of a monodentate ligand, such as nickel acetate and cobaltous acetate is used, it has been found that polydentate ligands such as potassium citrate, glycine, cyanoacetic acid, malonic acid, and betalanine are preferred as complexing agents in the bath. Where the source of metal ions is a metal compound of polydentate organic or inorganic ligands such as nickel pyrophosphate, nickel malonate, nickel citrate, cobaltous citrate, ferrous gluconate, the secondary complexing agent may be a monodentate ligand such as sodium propionate, formic acid, and potassium acetate, or it may also be a polydentate ligand such as glycine, potassium citrate, potassium lactate and potassium glycolate.

When the primary and secondary ligands are polydentate, the preferred choice of secondary ligands are those

that form loose coordination bonds to prevent the constituents of the complex from being so strongly bonded that the nickel cannot be reduced to its elemental state. Control of the quantities of the secondary ligand used provides another means by which the strength of the overlap bonds can be controlled. In the preferred embodiments, the amount of secondary ligand added is sufficient to fill the coordination positions of the metallic complex in the solution.

Examples of typical formulations in accordance with the invention follow.

BATH NO. 1

	Preferred	Range
Element, grams/liter:		
Nickel added as nickel cyanoacetate.....	10	1-30
Sodium hypophosphite.....	20	10-100

The preceding bath which consists of a nickel coordination compound and a reducing agent will plate a catalytic material and is illustrative of the essential constituents of a plating bath according to this invention. The pH of the bath can be either acid or alkaline depending on the condition desired and the buffering agent selected. Plating is obtained in the temperature range from ambient to boiling.

BATH NO. 2

	Preferred	Range
Element, grams/liter:		
Nickel pyrophosphate.....	18	6-50
Potassium citrate.....	40	10-120
Sodium hypophosphite.....	18	10-60
Sodium carbonate.....	30	10-50
pH.....	10.3	9.7-10.5
Temperature, ° F.....	140	65-160

BATH NO. 3

	Preferred	Range
Element, grams/liter:		
Cobaltous citrate.....	25	12-60
Potassium citrate.....	60	30-150
Potassium hydroxide.....	2.3	2.3-5
Sodium hypophosphite.....	20	10-40
pH.....	10.3	9.7-10.5
Temperature, ° F.....	170	150-180

BATH NO. 4

	Preferred	Range
Element, grams/liter:		
Nickel added as nickel glycolate.....	7.5	1-30
Glycine.....	10	1-50
Sodium hypophosphite.....	10	1-100

To enhance the operation of a bath containing the above constituents, there can be added accelerating agents such as the carbonate agents specified previously. The pH is adjusted with a buffering agent such as sodium or potassium hydroxide to the desired alkalinity, the preferred pH for the above formula being 9.0.

A bath for plating cobalt, iron or chromium is obtained by substituting a cobalt, iron or chromium coordination compound for the nickel coordination compound such as that used in Bath No. 2. The formulation above is changed only in that 7.5 grams per liter of cobalt, iron or chromium is added as, for example, cobalt, iron or chromium glycolate in place of nickel glycolate. Again the permissible range of the metal is 1 to 30 grams per liter. When plating these latter three substances, the pH of the bath is maintained in the alkaline range, 7-14, in order to obtain plating. Other alkaline formulations for

plating metals such as nickel, cobalt, iron or chromium follow.

BATH NO. 5

	Preferred	Range
Element, grams/liter:		
Cobaltous citrate.....	22.5	15-40
Potassium lactate.....	40	15-60
Sodium hypophosphite.....	30	10-50
Sodium carbonate.....	30	7.5-40
pH.....	10.5	9.7-10.6
Temperature, ° F.....	180	160-210

BATH NO. 6

	Preferred	Range
Element, grams/liter:		
Ferrous gluconate.....	60	30-80
Potassium glycolate.....	40	10-60
Sodium hypophosphite.....	10	10-30
pH.....	9.5	9.0-10.1
Temperature, ° F.....	185	165-185

BATH NO. 7

	Preferred	Range
Element, grams/liter:		
Chromium acetate.....	20	10-40
Potassium gluconate.....	50	20-80
Potassium carbonate.....	20	10-30
Potassium citrate.....	30	10-80
Sodium hypophosphite.....	25	10-40
pH.....	9.2	8.0-10.0
Temperature, ° F.....	195	190-210

BATH NO. 8

	Preferred	Range
Element, grams/liter:		
Nickel added as nickel cyanoacetate.....	7.5	1-30
Sodium or potassium glycolate.....	30	0-100
Glycine.....	10	1-50
Cyanoacetic acid.....	10	0-50
Sodium hypophosphite.....	10	1-100
Potassium carbonate.....	20	10-50
pH.....	10.1	8.7-10.5
Temperature, ° F.....	170	140-180

To a bath containing the above constituents is added an accelerating agent such as potassium carbonate, sodium carbonate or an organic carbonate. The pH is adjusted with sodium or potassium hydroxide. The bath is operable over the temperature range indicated with the plating rate increasing as the temperature of the bath is increased.

BATH NO. 9

	Preferred	Range
Element, grams/liter:		
Nickel added as nickel citrate.....	7.5	1-30
Sodium or potassium citrate.....	25	0-100
Glycine.....	10	1-50
Cyanoacetic acid.....	10	0-50
Sodium hypophosphite.....	10	1-100

In this bath the pH is again adjusted to between 8.0 and 9.5 with a buffering system or buffering agent such as sodium or potassium hydroxide. This solution is also operable over the temperature range from ambient to the boiling point, the plating rate again increasing with increasing temperature.

BATH NO. 10

	Preferred	Range
Element, grams/liter:		
Nickel added as nickel citrate.....	7.5	1-30
Sodium or potassium citrate.....	25	0-100
Glycine.....	10	1-50
Cyanoacetic acid.....	10	0-50
Dimethylamine borane.....	10	0.5-30

In addition to dimethylamine borane, other reducing agents such as morpholine borane, potassium, ammonium

and lithium hypophosphite may be substituted in the various baths including Bath No. 5.

BATH NO. 11

	Preferred	Range
Element, grams/liter:		
Nickel added as nickel glycolate or nickel ammonium citrate.....	7.5	1-30
Potassium citrate.....	60	10-100
Sodium hypophosphite.....	10	1-100
Chlorine carbonate.....	20	10-50

To this bath is added a sufficient additional amount of choline carbonate to adjust the pH to between 8.0 and 9.5. The bath is operable over the same temperature range as Bath No. 4.

BATH NO. 12

	Preferred	Range
Element, grams/liter:		
Nickel added as nickel ammonium glycolate..	7.5	1-30
Potassium citrate.....	10	5-30
Potassium carbonate.....	30	10-75
Sodium hypophosphite.....	25	10-100

The preferred pH of the solution is 8.0 but depending upon the amount of potassium carbonate added is operable over the pH range of 7.5 to 9.0. The operable temperature range again extends from ambient to just below the boiling point of the solution.

BATH NO. 13

	Preferred	Range
Element, grams/liter:		
Nickel added as nickel glycolate.....	7.5	1-30
Sodium propionate.....	10	5-30
Potassium carbonate.....	30	10-75
Sodium hypophosphite.....	25	10-100

The pH is preferable adjusted to 8.0 but is operable at other values in the alkaline range.

BATH NO. 14

	Preferred	Range
Element, grams/liter:		
Nickel added as nickel acetate.....	7.5	1-30
Carboxypimelic acid.....	10	1-50
Sodium hypophosphite.....	10	1-100

The pH is adjusted with a suitable buffering agent such as sodium or potassium hydroxide to a value in the range from about 7.0 to 8.5. A carbonate accelerating agent can be added to increase the plating rate if desired.

BATH NO. 15

	Preferred	Range
Element, grams/liter:		
Cobaltous acetate.....	25.5	18-40
Potassium carbonate.....	30.0	10-50
Potassium citrate.....	60.0	20-80
Ammonium hydroxide.....	25.0	7-30
Sodium hypophosphite.....	18.0	10-30
pH.....	10.5	9.6-10.7
Temperature, ° F.....	200	190-210

BATH NO. 16

	Preferred	Range
Element, grams/liter:		
Ferrous lactate.....	40	20-50
Potassium citrate.....	75	30-90
Sodium hypophosphite.....	10	10-30
Potassium carbonate.....	30	15-40
pH.....	9.5	9.5-10.2
Temperature, ° F.....	195	165-210

BATH NO. 17

	Preferred	Range
Element, grams/liter:		
Cobalt citrate.....	25	10-35
Nickel citrate.....	25	10-35
Potassium lactate.....	50	20.5-100
Potassium hydroxide.....	15	7.5-18
Sodium hypophosphite.....	18	10-30
pH.....	10.5	9.6-10.7
Temperature, ° F.....	200	170-210

As the formulation of Bath No. 17 indicates, a bath containing two metal complexes is operative.

As indicated previously, the present invention includes acid as well as alkaline solutions of the bath. Examples of acid baths are as follows:

BATH NO. 1

	Preferred	Range
Element, grams/liter:		
Nickel added as nickel glycolate.....	7.5	1-30
Potassium citrate.....	30	5-40
Glycine.....	10	1-20
Morpholine borane.....	10	0.5-50

This bath is operative over the pH range from about 2 to about 7 with the preferred value being 2.0. Adjustment to this pH figure is obtained by adding citric acid to the bath. The operable temperature range extends from ambient to the boiling point of the bath.

BATH NO. 2

	Preferred	Range
Element, grams/liter:		
Nickel malonate.....	40	10-40
Potassium acetate.....	15	7.5-50
Sodium hypophosphite.....	10	10-30
pH.....	5.0	4.3-6.0
Temperature, ° F.....	200	160-210

BATH NO. 3

	Preferred	Range
Element, grams/liter:		
Nickel added as nickel glycolate.....	7.5	1-30
Potassium citrate.....	30	5-49
Glycine.....	10	1-20
Dimethylamine borane.....	10	0.5-50

This bath is operative over the pH range from about 2 to about 7 with the preferred value being 3.5. Adjustment to this pH figure is obtained by adding citric acid to the bath. The operable temperature range extends from ambient to the boiling point of the bath.

BATH NO. 4

	Preferred	Range
Element, grams/liter:		
Nickel added as nickel acetate.....	7.5	1-30
Cyanoacetic acid.....	10	5-30
Sodium hypophosphite.....	10	1-100

This bath is operative in the pH range from about 3.0 to 7.0. The preferred pH of the solution is 4.8 and adjustment of the pH of the bath is accomplished with citric acid. The operative temperature range is ambient to boiling.

BATH NO. 5

	Preferred	Range
Element, grams/liter:		
Nickel added as nickel glycolate.....	7.5	1-30
Formic acid.....	10	1-20
Sodium hypophosphite.....	10	5-50

The pH is adjusted with a suitable acidic buffering such as citric acid to a value in the range from 3.0 to 7.0.

BATH NO. 6

	Preferred	Range
Element, grams/liter:		
Nickel glycolate.....	25	15-40
Malonic acid.....	50	20-60
Potassium hydroxide.....	35	12-40
Potassium hypophosphite.....	10	10-30
pH.....	5.3	4.2-6.0
Temperature, ° F.....	210	160-211

BATH NO. 7

	Preferred	Range
Element, grams/liter:		
Nickel added as nickel formate.....	7.5	1-30
Glycine.....	10	1-20
Morpholine borane.....	10	5-50

The pH of this bath is likewise adjusted to a value in the range from about 3.0 to 7.0.

Whereas electroless plating has heretofore been limited to the plating of materials which are catalytic to reaction or to metals that can be plated through the galvanic initiation, the present invention provides a plating metal bath in which it is now possible to plate such metals as cadmium, bismuth, tin, lead and zinc, heretofore designated as non-catalytic materials which could not be plated electrolessly. By utilizing plating metal-coordination compounds as the starting material and source of plating metal in a bath with a secondary ligand complexing agent added in an amount sufficient to fill the coordination positions of the metallic complex in solution, the five preceding metals now lend themselves to a process of electroless plating with the advantages attendant therein. The presence of extraneous anions is of greater significance in baths for plating cadmium, bismuth, etc. For satisfactory plating it has been found that the amount of such ion should be limited to an amount not in excess of 1000 parts per million of bath by weight. Examples of plating solutions for accomplishing the plating of bismuth, cadmium, zinc, tin, lead and combinations of these metals include:

BATH NO. 1

	Preferred	Range
Element:		
Nickel citrate, grams/liter.....	30	15-60
Ammonium hydroxide, percent by volume...	15	10-20
Sodium hydroxide, grams/liter.....	2	1-5
Potassium carbonate, grams/liter.....	30	10-60
Sodium hypophosphite, grams/liter.....	25	10-60
pH.....	9.7	8.9-11.0
Temperature, °F.....	175	120-200

BATH NO. 2

	Preferred	Range
Element:		
Nickel ammonium glycolate, grams/liter.....	40	15-60
Ammonium hydroxide, percent by volume...	15	10-20
Sodium hydroxide, gram/liter.....	1	0.1-5
Potassium carbonate, grams/liter.....	30	10-60
Potassium pyrophosphate, grams/liter.....	30	15-60
Sodium hypophosphite, grams/liter.....	18	10-60
pH.....	9.7	8.9-11.0
Temperature, °F.....	175	120-200

BATH NO. 3

	Preferred	Range
Element:		
Nickel ammonium lactate, grams/liter.....	45	15-60
Ammonium hydroxide, percent by volume...	15	10-20
Sodium hydroxide, grams/liter.....	2	0.5-5
Potassium carbonate, grams/liter.....	30	10-60
Sodium hypophosphite, grams/liter.....	18	10-60
pH.....	9.5	8.0-10.3
Temperature, °F.....	175	120-200

BATH NO. 4

	Preferred	Range
Element:		
Nickel malonate, grams/liter.....	25	15-60
Ammonium hydroxide, percent by volume...	15	10-20
Sodium hydroxide, gram/liter.....	1	0.5-5
Potassium carbonate, grams/liter.....	30	10-60
Sodium hypophosphite, grams/liter.....	18	10-60
pH.....	9.7	8.0-10.3
Temperature, °F.....	175	120-200

BATH NO. 5

	Preferred	Range
Element:		
Nickel succinate, grams/liter.....	30	15-60
Ammonium hydroxide, percent by volume...	15	10-20
Sodium hydroxide, gram/liter.....	1	0.5-5
Potassium carbonate, gram/liter.....	30	10-60
Sodium hypophosphite grams/liter.....	18	10-60
pH.....	9.7	8.0-10.3
Temperature, °F.....	180	120-200

BATH NO. 6

	Preferred	Range
Element:		
Nickel formate, grams/liter.....	25	15-60
Ammonium hydroxide, percent by volume...	15	10-20
Sodium hydroxide, gram/liter.....	1	0.1-5
Potassium carbonate, grams/liter.....	30	10-60
Potassium pyrophosphate, grams/liter.....	30	10-60
Sodium hypophosphite, grams/liter.....	18	10-60
pH.....	10.1	8.0-10.3
Temperature, °F.....	150	120-200

BATH NO. 7

	Preferred	Range
Element, grams/liter:		
Cobaltous glycolate.....	36	15-50
Potassium citrate.....	40	20-100
Potassium pyrophosphate.....	30	7.5-60
Sodium hydroxide.....	3	1-4
Sodium hypophosphite.....	30	10-60
pH.....	10.2	9.3-10.5
Temperature, °F.....	150	65-180

BATH NO. 8

	Preferred	Range
Element, grams/liter:		
Chromous acetate.....	20	10-25
Potassium citrate.....	30	15-50
Potassium pyrophosphate.....	30	7.5-60
Sodium erythorbate.....	15	3.0-25
Sodium hypophosphite.....	20	10-50
pH.....	9.5	9.1-10.3
Temperature, °F.....	150	65-180

Sodium ascorbate can be substituted for sodium erythorbate, both compounds serving in the function of reducing agents and secondarily as complexing agents.

BATH NO. 9

	Preferred	Range
Element, grams/liter:		
Ferrous gluconate.....	60	30-80
Potassium heptagluconate.....	25	10-50
Sodium hypophosphite.....	15	10-30
pH.....	9.1	8.0-10.0
Temperature, °F.....	180	150-210

BATH NO. 10

	Preferred	Range
Element, grams/liter:		
Chromic oxalate.....	12	8-20
Potassium glycolate.....	15	10-30
Ascorbic acid.....	7.5	2-15
Sodium hypophosphite.....	18	10-30
pH.....	5.5	4-10
Temperature, °F.....	200	180-210

To further enhance the deposition rate of plating metal and to improve the quality of the deposit in terms of brightness it has been found that the addition of pyrophosphates to baths which plate on cadmium, bismuth, zinc, tin, and lead is particularly useful. By adding sodium or potassium pyrophosphate in an amount of from 10 to 60 grams per liter, the rate of plating increases substantially and at the same time produces a better quality deposit of plating metal.

In terms of practical results, the plating baths of the present invention are capable of achieving a plating rate of 3 mils per hour. In our copending application, Ser. No. 481,944, filed Aug. 23, 1965 and assigned to the assignee of the instant application the method of adapting the baths of the present invention to the plating of non-catalytic materials such as plastics is described.

We have disclosed a bath and a process for plating catalytic materials with transition metals such as nickel, iron, cobalt and chromium by means of an electroless plating bath and in particular a bath for chemically plating metals including cadmium, bismuth, tin, zinc and lead.

The outstanding advantages of such a bath and process are that they provide a hard, bright, adherent plating not subject to flaking or other deformation due to machining of fabricating of the plated material. In addition, the bath and process also possess advantages such as greater ease and convenience of operation, operability at low tem-

perature, greater bath stability and higher plating rates.

What is claimed is:

1. A process for plating a material selected from the group consisting of bismuth, cadmium, tin, lead and zinc with a transition metal selected from the class consisting of nickel, cobalt, iron and chromium by chemical deposition comprising the steps of

(1) forming a transition metal-organic complex from

(a) a member selected from the class consisting of the transition metal in powder form, transition metal oxide or a transition metal carbonate and

(b) a short chain carboxylic acid selected from the group consisting of formic, acetic, oxalic, glycolic, malonic, lactic, succinic and gluconic acids;

(2) adding the transition metal-organic complex formed in (1) to an aqueous solution of

(c) a ligand complexing agent present in an amount ranging between 1-150 grams per liter of the total, said ligand complexing agent being selected from the class consisting of

(i) a carboxylic acid selected from the class consisting of glycolic, lactic, beta-hydroxybutyric, glyceric, gluconic, malic, tartaric, citric, salicylic, 5-sulfosalicylic, 5-amino-salicylic, mercaptoacetic, dithiotartaric, cyanoacetic, malonic, formic, propionic, erythorbic, iminodiacetic, aspartic, glutamic, ethylenediaminetriacetic, ascorbic and carboxypimelic acids;

(ii) an amino acid selected from the class consisting of amino acid dystine, methionine, serine, lysine, arginine, ornithine, valine, glycine, leucine, isoleucine, phenylalanine, tyrosine, histidine and proline; and

(iii) a salt selected from the class consisting of potassium citrate, potassium glycolate, potassium lactate, potassium acetate, potassium gluconate, potassium pyrophosphate, potassium heptagluconate, potassium pro-

pionate, sodium propionate and sodium glycolate;

(d) a transition metal reducing agent present in an amount ranging between 1-100 grams of the total and selected from the class consisting of sodium, potassium, lithium and ammonium hypophosphites, dimethylamine, morpholine borane and hydrazine sulfate; and

(e) a buffering agent in amounts sufficient to maintain the pH of the resulting mixture from about 1-14, said transition metal-organic complex being added to the aqueous solution in amounts sufficient to provide in the resulting bath between 1-80 grams per liter of said transition metal wherein the amount of chloride and sulfate anions present in said mixture is less than 1000 parts per million;

(3) placing said material to be plated in said bath to initiate the plating reaction; and

(4) allowing said material to be plated to remain in said bath until the transition metal has been deposited thereon to the depth desired.

2. The process of claim 1 wherein the bath is maintained at a temperature ranging from 65°-210° F.

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U.S. Cl. X.R.