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2,999,770

PROCESSES OF CHEMICAL NICKEL PLATING AND BATHS THEREFOR

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The present invention relates to improved processes of chemical nickel plating of catalytic materials employing baths of the nickel cation-hypophosphite anion type and to improved baths therefor; and the invention is an improvement upon that disclosed in the copending application of Gregoire Gutzeit and Abraham Krieg, Serial No. 194,656, filed November 8, 1950, now Patent No. 2,658,841, granted November 10, 1953.

The chemical nickel plating of a catalytic material employing an aqueous bath of the nickel cation-hypophosphite anion type is based upon the catalytic reduction of nickel cations to metallic nickel and the corresponding oxidation of hypophosphite anions to phosphite anions with the evolution of hydrogen gas at the catalytic surface. The reactions take place when the body of catalytic material is immersed in the plating bath, and the exterior surface of the body of catalytic material is coated with nickel. The following elements are catalytic for the oxidation of hypophosphite anions and thus may be directly nickel plated; iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum. The following elements are examples of materials which may be nickel plated by virtue of the initial displacement deposition of nickel thereon either directly or through a galvanic effect: copper, silver, gold, beryllium, germanium, aluminum, carbon, vanadium, molybdenum, tungsten, chromium, selenium, titanium and uranium. The following elements are examples of non-catalytic materials which ordinarily may not be nickel plated: bismuth, cadmium, tin, lead and zinc. The activity of the catalytic materials varies considerably; and the following elements are particularly good catalysts in the chemical nickel plating bath: iron, cobalt, nickel and palladium. The chemical nickel plating process is autocatalytic since both the original surface of the body being plated and the nickel metal that is deposited on the surface thereof are catalytic; and the reduction of the nickel cations to metallic nickel in the plating bath proceeds until all of the nickel cations have been reduced to metallic nickel, in the presence of an excess of hypophosphite anions, or until all of the hypophosphite anions have been oxidized to phosphite anions, in the presence of an excess of nickel cations. Actually the reactions are slowed-down rather rapidly as time proceeds because the anions, as contrasted with the cations, of the nickel salt that is dissolved in the plating bath combine with the hydrogen cations to form an acid, which, in turn, lowers the pH of the bath, and the reducing power of the hypophosphite anions is decreased as the pH value of the bath decreases. Moreover, there is a tendency for the early formation in the plating bath of a "black precipitate" that comprises a random chemical reduction of the nickel cations. Of course, this formation of the black precipitate comprises a decomposition of the plating bath, and is particularly objectionable in that it causes the nickel deposit to be coarse, rough and frequently porous.

For the dual purposes of retarding the formation of the black precipitate mentioned and of increasing the normal plating rate of the bath, various baths of the present type have been suggested employing different additives. For example, in the previously-mentioned Gutzeit and Krieg patent, there is disclosed a chemical nickel plating bath of this type that contains, as an additive, a buffer in the form of a soluble salt of an organic acid,

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and specifically sodium acetate. A typical chemical nickel plating bath of the character of that disclosed in the Gutzeit and Krieg patent essentially comprises an aqueous acid solution of a nickel salt and a hypophosphite and a buffer in the form of an alkaline acetate; the initial pH of the bath being within the approximate range 4.5 to 5.6, the absolute concentration of hypophosphite ions in the bath being in the range 0.15 to 0.35 mole/liter, the ratio between nickel ions and hypophosphite ions in the bath being in the range 0.25 to 0.60, and the absolute concentration of acetate ions in the bath being approximately 0.120 mole/liter.

In carrying out the chemical nickel plating process on a commercial scale employing a plating bath of the type mentioned, there may be utilized a continuous system of the character of that disclosed in the copending application of Paul Talmey and William J. Crehan, Serial No. 222,222, filed April 21, 1951, now Patent No. 2,658,839, granted November 10, 1953; which system involves periodic or continuous regeneration of the plating bath by the addition thereto of appropriate ingredients for the purpose of maintaining substantially constant the composition of the bath. More specifically in this system, there are provided a plating chamber and a reservoir; one portion of the plating solution is stored at a relatively low temperature well below the boiling point thereof in the reservoir; and another portion of the plating solution is held as a bath at a relatively high temperature slightly below the boiling point thereof in the plating chamber. The solution is continuously circulated at a low rate from the reservoir to the plating chamber and then back to the reservoir, the solution being heated substantially to the relatively high temperature after withdrawal thereof from the reservoir and before introduction thereof into the plating chamber, and the solution being cooled substantially to the relatively low temperature after withdrawal thereof from the plating chamber and before return thereof to the reservoir. The body that is to be nickel plated is immersed in the bath in the plating chamber, and is subsequently withdrawn from the bath in the plating chamber after a time interval corresponding to the thickness of the nickel plating thereon that is desired; and during the time interval soluble reagents are added to the solution in the reservoir to maintain in the bath in the plating chamber during the time interval substantially the predetermined composition of the bath previously mentioned, so as to compensate for the ingredients of the bath that are exhausted during the time interval in the plating chamber; this regeneration of the solution in the reservoir consisting essentially of adding thereto appropriate amounts of soluble nickel-containing and hypophosphite-containing reagents, as well as a weak alkali for pH control.

In carrying out the chemical nickel plating process, particularly in a continuous system of the character described, it has been discovered that after some use, and notwithstanding the presence of a buffer, the bath decomposes with the formation of the previously-mentioned black precipitate. Moreover, it has been found that the plating rate of a bath of the character described is not as high as is desirable and that the utilization of a plating bath having an optimum pH as low as that mentioned is not always desirable.

The present invention is predicated upon the discovery that in plating baths of the nickel cation-hypophosphite anion type mentioned, the formation of black precipitate may be retarded and the plating rates thereof may be substantially increased by the addition thereto of a compound selected from the group consisting of short chain aliphatic aminocarboxylic acids and the salts thereof; which compounds function to produce an "exaltation" phenomenon. Moreover, in the bath these compounds

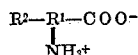
are amphoteric, producing "zwitterions," and thereby forming stable, water-soluble chelate complexes with nickel so that the useful pH range of the bath can be substantially extended to embrace the neutral and near alkaline regions, without resulting in precipitation of insoluble basic nickel salts. Further, these compounds are stable at elevated temperatures, i.e. near the boiling point of the plating bath, so that no reagent loss occurs in the neutral and alkaline zones where purer deposits are obtained. Finally, these compounds, by forming stable, water-soluble chelate complexes with the nickel ions, retard precipitation of nickel phosphite, which is the normal by-product of the chemical nickel plating process resulting from the oxidation of the hypophosphite anions. The last-mentioned feature is particularly important in continuous nickel plating operation in a system of the character disclosed in the Talmey and Crehan patent in view of the fact that in such a continuous system the phosphite anion concentration soon builds-up, after a number of cycles, to a point where the solubility of nickel phosphite is exceeded, with the resultant formation of nickel phosphite as a precipitate, and the consequent rough nickel plating.

In order to be of utility for the present purpose, the compounds mentioned must, of course, be water-soluble; and moreover, for the purpose of chelate formation with the nickel ions the amino group should be either in the alpha or beta position with relation to the carboxyl group, so that either five- or six-membered rings will result.

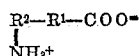
Specifically, the zwitterions of the general formula



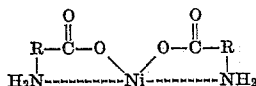
should have the specific structures:



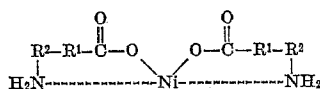
or



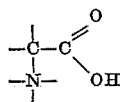
so that the resulting nickel chelates have the specific structures:



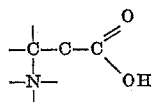
or



The hydrogen atoms of the amino group can, of course, be substituted, as the nitrogen atom alone is necessary for ring closure. Water-soluble salts of amino acids, alpha or beta-polyamino acids, monoaminopolycarboxylic acids and polyaminopolycarboxylic acids are suitable for the purpose. In other words, the water-soluble compounds should have the reactive groups:



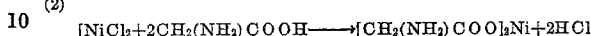
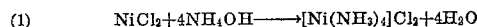
or



It is noted that the chelate complexes (also called "inner complexes") are particularly stable since all primary valences as well as the secondary valences of the bound metal atom are satisfied. While, in an ordinary inorganic cation complex, the coordinated molecules

form a first zone around the central cation, which then becomes a new complex ion, this is not the case in chelates; rather in chelates the whole structure represents a new, very slightly dissociated, neutral molecule.

- 5 A comparison between an ammonia complex of nickel and an amino-acid complex of nickel immediately shows this difference:



In view of the foregoing, it is the primary object of the present invention to provide an improved nickel plating process of the character described in which the reactions involved are carried out more efficiently and under more stable conditions than heretofore, thereby rendering the process more desirable from a commercial standpoint.

- 20 Another object of the invention is to provide an improved aqueous chemical nickel plating bath which may be employed with advantage in the practice of the improved process.

- 25 Another object of the invention is to provide an improved nickel plating process of the character described that employs a plating bath of the nickel cation-hypophosphate anion type containing as an exaltant a compound selected from the group consisting of short chain aliphatic aminocarboxylic acids and salts thereof.

- 30 A still further object of the invention is to provide an improved aqueous nickel plating bath of the character described that contains nickel ions, hypophosphite ions and zwitterions.

- 35 These and other objects and advantages of the invention pertain to the particular arrangement of the steps of the method and of the composition of the plating bath, and will be understood from the foregoing and following description.

- In accordance with the process of the present invention, the article to be nickel plated and normally having a catalytic surface is properly prepared by mechanically cleaning, degreasing and light pickling, substantially in accordance with standard practices in electroplating processes. For example, in the nickel plating of a steel object, it is customary mechanically to clean the rust and mill scale from the object, to degrease the object, and then lightly to pickle the object in a suitable acid, such as hydrochloric acid. The article is then immersed in a suitable volume of the bath containing the proper proportions of nickel cations, hypophosphite anions and amino-

- 50 acid anions, the pH of the bath having been, if necessary, adjusted to an optimum value by the addition of an appropriate acid or base, and the bath having been heated to a temperature just below its boiling point, such as 99° C. at atmospheric pressure. Almost immediately hydrogen bubbles are formed on the catalytic surface of the steel object and escape in a steady stream from the bath while the surface of the steel object is slowly coated with metallic nickel (containing some phosphorous). The reaction is continued until the color of the bath (green at the start) shows the absence of nickel, or until the evolution of hydrogen gas stops, or until it is determined that the required thickness of the nickel coating has been deposited on the steel object. Of course the steel object is

- 55 then removed from the bath and rinsed off with water, and is then ready for use.
- 60 Instead of using a batch plating process, as described above, the steel object may be plated in the plating chamber of the continuous system, previously described, by the immersion thereof in the plating chamber for an appropriate time interval. Thereafter, the steel object is removed from the plating chamber, and is rinsed off with water and is then ready for use.

- 65 With respect to the composition of the bath, it essentially comprises an aqueous solution containing nickel

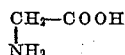
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cations, hypophosphite anions and zwitterions. For example, the nickel cations may be derived from nickel chloride; the hypophosphite anions may be derived from sodium, potassium, etc., hypophosphites or various combinations thereof; and the zwitterions may be derived from a compound selected from the group consisting of short chain aliphatic aminocarboxylic acids and the salts thereof. Specifically, a suitable bath may be formed in an exceedingly simple manner by dissolving in water, nickel chloride, sodium hypophosphite and sodium aminoacetate. The desired pH of the bath is established by the eventual introduction thereto of hydrochloric acid or by the addition thereto of a weak alkali, preferably sodium bicarbonate.

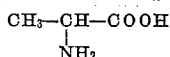
The terms "cation," anion" and "ion," as employed herein, except where specifically noted, include the total quantity of the corresponding elements that are present in the plating bath, i.e. both undissociated and dissociated material. In other words, 100% dissociation is assumed when the terms noted are used in connection with molar ratios and concentrations in the plating bath. Also hereinafter the expression "percent exaltation" is employed with the arbitrary definition as the percent increase in the rate of hydrogen evolution with reference to a given hypophosphite solution resulting from the addition thereto of the exaltation agent.

Turning now more particularly to the introduction of the zwitterions into the bath, the following examples of short chain aliphatic amino-acids have been found to be particularly suitable:

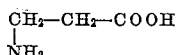
Aminoacetic acid (glycine)



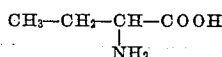
Alpha-aminopropionic acid (alpha-alanine)



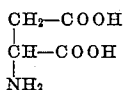
Beta-aminopropionic acid (beta-alanine)



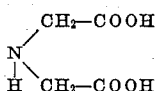
Alpha-aminobutyric acid



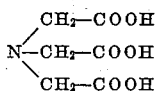
Aminosuccinic acid (aspartic acid)



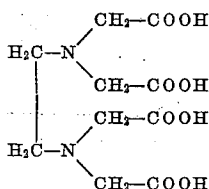
Iminodiacetic acid



Iminotriacetic acid



Ethylenediaminetetraacetic acid



As a matter of convenience, the zwitterions may be introduced into the plating bath by dissolving therein, the salts, particularly the alkali salts, of the short chain aliphatic aminocarboxylic acids mentioned. This is partic-

ularly convenient, since the alkali salts of these aminocarboxylic acids are usually more readily obtainable upon the market. For example, the tetrasodium salt of ethylenediaminetetraacetic acid is available in the market under the various trade names: "Versene," "Nullapon," and "Sequestrene."

For the purpose of studying the increase of the hydrogen gas evolution due to exaltation with the use of different additives including those involved in the discovery of the present invention, i.e. short chain aliphatic aminocarboxylic acids, and other additives which have been used or suggested for chemical nickel plating baths, tests were made with test solutions of 50 cc. and containing sodium hypophosphite at a concentration of 0.225 mole/liter (to which a trace of a nickel salt, i.e. 0.024 mole/liter was added to initiate the reaction at a vigorous rate).

Pickled pieces of mild steel, 20 cm.² in area, were introduced for periods of 30 minutes each. The different test solutions respectively contained no additive, and additives in the form of salts of the following acids: acetic, citric, lactic, succinic, aminoacetic and aspartic. Specifically, the additives, when used, were employed as the sodium salts of the corresponding acids in a concentration of 0.125 mole/liter of the anion, and the hydrogen gas evolved was collected and its volume measured by usual methods. The results of these exaltation tests were:

30.	Additive (anion) 0.125 m/l.	H ₂ evolved in 30 min. from 50 cc. solution at 0.225 m/l. sodium hypo- phosphite	Percent exaltation
35.	None..... Acetic..... Citric..... Lactic..... Succinic..... Aminoacetic..... dl-Aspartic.....	80 155 130 145 220 180 250	0 94 63 81 175 125 213

By comparison of the unsubstituted, and the amino-substituted carboxylic acids, it will be observed that a remarkable increase in percentage exaltation is produced by the substitution in the organic radical of one amino group for one hydrogen atom. Specifically, the exaltation figure for acetic anion is 94; whereas that for aminoacetic anion is 125 (a positive difference of 31). Similarly, the exaltation figure for succinic anion is 175; whereas that for monoaminosuccinic anion (dl-aspartic) is 213 (a positive difference of 38). The hydroxy-substituted acids are in this connection inferior to the unsubstituted carboxylic acids. In conjunction with these tests, it is noted that exaltation is independent of buffering efficiency and of the capability of the organic compound to complex the nickel ions with the formation of chelates. In other words, the short chain aliphatic aminocarboxylic acids, and the salts thereof, have the three unrelated properties of exalting, buffering and chelating; all of which are highly advantageous in the nickel plating process.

In the use of short chain aliphatic aminocarboxylic acids for chemical nickel plating exaltation, it is believed that this phenomenon results from the formation of a heteropoly-acid between the organic additive and the hypophosphite anions, which competes with inner-complex (chelate) formation between the nickel ions and the amino-acid radical. If the nickel amino-acid chelate is too stable, insufficient nickel cations are available for deposition, and the plating rate becomes low despite the exalting effect produced by the organic additive.

In actual plating tests employing plating baths containing short chain aliphatic aminocarboxylic acids and water-soluble salts thereof, it has been found that the pH variations have less influence on plating rates, in the optimum nickel and hypophosphite ion concentration

ranges, than is the case with other organic additives. This is unquestionably due to the amphoteric character of the zwitterions. For example, with aminoacetic ions (glycine) there are three optimum, although not particularly marked, pH regions, i.e. at about 5.5, 6.5 and 8.5; and in any case, the useful pH range of the plating bath is clearly extended with reference to plating baths buffered with salts of simple, unsubstituted carboxylic acids of the character disclosed in the previously-mentioned Gutzeit and Krieg patent.

On the other hand, in the case of short chain aliphatic amino-acid salts (as opposed to ordinary buffers) added to the plating bath, best plating results are obtained when the ratio between the amino group and the nickel ion is above 1.5; in other words, when the amount of amino acid ions is sufficient to complex most or substantially all of the nickel ions contained in the plating bath. In this connection, it is pointed out that substantial exaltation is achieved in the plating bath when the amount of amino radical is such that the ratio mentioned is above about 0.5 and that substantially all of the nickel ions are complexed to form chelates when the amount of amino radical is such that the ratio mentioned is 2 or above.

Again referring to the composition of the aqueous plating bath, the following concentrations of ingredients have been found to be optimum: the absolute hypophosphite ion concentration should be in the range 0.15 to 1.20 mole/liter; the nickel ion/hypophosphite anion ratio should be in the range 0.25 to 1.60; the ratio between the amino group and the nickel ions should be in the range 0.5 to 6.0; and the pH should be in the approximate range 4.5 to 9.0.

The exalting and other characteristics of the various short chain aliphatic aminocarboxylic acids in the plating baths were established by a series of plating tests that were made employing a series of test plating baths of the general character of that previously described and as explained more particularly hereinafter.

In the various plating tests appearing hereinafter weights of nickel plating deposited are reported in gms., and plating rates are usually reported in gm./cm.²/min., although occasionally plating rates are reported in mils/hour, (i.e. 0.001"/hour).

In a first series of these plating tests, an amino-acetate plating bath was employed that had the following composition:

Sodium hypophosphite.....m./l.....	0.225
Nickel chloride.....m./l.....	0.075
Sodium aminoacetate.....m./l.....	0.125
Ratio: Ni ⁺⁺ /hypo ⁻	0.33
Ratio: Amino/Ni ⁺⁺	1.67

In 50 cc. of this plating bath properly cleaned steel samples of 20 cm.² area were plated for 10 minutes, the temperature of the bath being 96° C.-98° C. and the pH thereof having been adjusted with sodium bicarbonate, with the following results:

Initial pH	Weight deposited 10 min. (gm.)	Rate (mils/hour)
6.5 (as prepared).....	0.0996	1.3
8.5 (as adjusted).....	0.1030	1.4

In a second series of these plating tests, an amino-acetate bath was employed that had the following composition:

Sodium hypophosphite.....m./l.....	0.225
Nickel chloride.....m./l.....	0.09
Sodium aminoacetate.....m./l.....	0.120
Ratio: Ni ⁺⁺ /hypo ⁻	0.40
Ratio: Amino/Ni ⁺⁺	1.32

In 50 cc. of this plating bath, properly cleaned steel samples of 5 cm.² area (16 gauge) were plated for 60 minutes, the temperature of the bath being 97° C.-98° C. and the pH having been adjusted with sodium bicarbonate, with the following results in duplicate tests:

Initial pH	Weight deposited 60 min. (gm.)	Black precipitate	Sample appearance
5.75 (as prepared)....	0.1198, 0.1229	None	Medium bright, smooth.
8.00 (as adjusted)....	0.1282, 0.1273	do	Dull.

These first and second series of plating tests clearly demonstrate that the present plating baths are satisfactory in the near neutral and basic regions of the pH range.

In a third series of these plating tests, an amino acetate bath was employed that had the following composition:

Sodium hypophosphite.....m./l.....	0.225
Nickel chloride.....m./l.....	0.1125
Sodium aminoacetate.....	Variable
Ratio: Ni ⁺⁺ /hypo ⁻	0.5

In 50 cc. of this plating bath properly cleaned steel samples of 20 cm.² area were plated for 10 minutes, the temperature of the bath being 97° C.-98° C. and the pH thereof having been adjusted with acetic acid and/or caustic soda. In this plating bath, the plating rate, without the addition of aminoacetate at pH 6.4 was only 0.84×10⁻⁴ gm./cm.²/min. and with the aminoacetate additive, the plating was bright and smooth. The specific results in these tests were as follows (averages of duplicate tests being given):

Sodium aminoacetate.....m./l.....	0.06
Ratio: Amino/Ni ⁺⁺	0.53

Test.....	1	2	3
Initial pH.....	6.01	6.49	6.70
Plating rate, R×10 ⁴	2.70	2.91	2.98

Sodium aminoacetate.....m./l.....	0.12
Ratio: Amino/Ni ⁺⁺	1.067

Test.....	1	2	3
Initial pH.....	6.00	6.78	7.02
Plating rate, R×10 ⁴	3.66	3.36	3.42

Sodium aminoacetate.....m./l.....	0.18
Ratio: Amino/Ni.....	1.60

Test.....	1	2	3	4
Initial pH.....	5.98	6.20	6.39	6.62
Plating rate, R×10 ⁴	4.44	4.99	4.31	4.89

The above plating tests illustrate that best plating rates are obtained when the ratio of the amino-nickel ions is above about 1.50.

In a fourth series of these plating tests, an amino-acetate bath was employed that had the following composition:

Sodium hypophosphite.....m./l.....	0.225
Nickel chloride.....m./l.....	0.0675
Sodium aminoacetate.....	Variable
Ratio: Ni ⁺⁺ /hypo ⁻	0.3

In 50 cc. of this plating bath, properly cleaned steel samples of 20 cm.² area were plated for 10 minutes, the temperature of the bath being substantially 96° C. and the pH having been adjusted with acetic acid and/or

caustic soda. In these plating tests, the plating was bright and smooth, and the specific results were as follows:

Sodium aminoacetate.....m./l. 0.0675
Ratio: Amino/Ni⁺⁺..... 1.0

Test.....	1	2	3	4
Initial pH.....	5.92	6.35	6.65	6.90
Plating rate, R×10 ⁴	2.22	2.225	2.18	2.535

Sodium aminoacetate.....m./l. 0.1013
Ratio: Amino/Ni⁺⁺..... 1.5

Test.....	1	2	3	4
Initial pH.....	6.0	6.29	6.60	6.94
Plating rate, R×10 ⁴	3.225	3.98	4.03	4.22

Sodium aminoacetate.....m./l. 0.135
Ratio: Amino/Ni⁺⁺..... 2.0

Test.....	1	2	3	4
Initial pH.....	6.0	6.22	6.58	6.95
Plating rate, R×10 ⁴	4.30	4.465	4.92	4.73

In both the third and fourth of plating tests, it will be observed that when the Ni⁺⁺/hypophosphite ion ratio is either 0.5 or 0.3, increased plating rates are obtained with increased ratios of amino/Ni⁺⁺.

In a fifth series of these plating tests an amino-acetate bath was employed that had the following composition:

Sodium hypophosphite.....m./l. 0.225
Nickel chloride.....m./l. 0.0675
Sodium aminoacetate..... Variable
Ratio: Ni⁺⁺/hypo⁻..... 0.3

In 50 cc. of this plating bath properly cleaned steel samples of 20 cm.² area were plated for 10 minutes, the temperature of the bath being 97° C. (±1° C.) and the pH having been adjusted with NaOH and HCl. In these plating tests, the plating was bright and smooth. The specific results in these tests were as follows (averages of triplicate tests being given):

Ratio: Amino/Ni ⁺⁺	2.0	3.0	4.0
Initial pH.....	6.64	6.70	6.68
Final pH.....	5.58	5.82	5.88
Weight gain.....	0.0907	0.0984	0.1030
Rate, R×10 ⁴	4.54	4.65	5.15

From the fifth series of plating tests, it will be observed that the greatest weight gains were achieved with this plating bath when the amino/Ni⁺⁺ ratio was 4.0.

In a sixth series of these plating tests, an aminoacetate bath was employed that had the following composition:

Sodium hypophosphite.....m./l. 0.225
Nickel chloride.....m./l. 0.0675
Sodium aminoacetate..... Variable
Ratio: Ni⁺⁺/hypo⁻..... 0.3

In 50 cc. of this plating bath, properly cleaned steel samples of 20 cm.² area were plated for 60 minutes, the temperature of the bath being substantially 96° C. and the pH having been adjusted with acetic acid and/or caustic soda. In these plating tests, the plating was bright and smooth. The specific results in these tests were as follows (averages of duplicate tests being given):

Sodium aminoacetate.....m./l. 0.0675
Ratio: Amino/Ni⁺⁺..... 1.0

Test.....	1	2	3	4
Initial pH.....	5.92	6.35	6.65	6.90
Final pH.....	2.90	2.88	2.73	2.81
Weight gain.....	0.1015	0.1090	0.1110	0.1186

Sodium aminoacetate.....m./l. 0.1013
Ratio Amino/Ni⁺⁺..... 1.5

Test.....	1	2	3	4
Initial pH.....	6.0	6.29		
Final pH.....	3.25	3.49		
Weight gain.....	0.1698	0.1728		

Sodium aminoacetate.....m./l. 0.135
Ratio Amino/Ni⁺⁺..... 2.0

Test.....	1	2	3	4
Initial pH.....	6.0	6.22	6.58	6.95
Final pH.....	3.37	3.67	4.12	4.72
Weight gain.....	0.1871	0.1956	0.2114	0.2141

In a seventh series of these plating tests, an aminoacetate bath was employed that had the following composition:

Sodium hypophosphite.....m./l. 0.225
Nickel chloride.....m./l. 0.1125
Sodium aminoacetate..... Variable
Ratio: Ni⁺⁺/hypo⁻..... 0.5

In 50 cc. of this plating bath, properly cleaned steel samples of 20 cm.² area were plated for 60 minutes, the temperature of the bath being substantially at 98° C. In these plating tests, the plating was bright and smooth and the specific results were as follows:

Aminoacetate ion mole/l.....	0	0.06	0.12	0.18	0.24	0.30
Amino/Ni ⁺⁺		0.53	1.067	1.60	2.135	2.67
Initial pH.....	6.38	6.42	6.39	6.38	6.43	6.41
Final pH.....	5.10	2.92	3.15	3.35	4.55	4.92
Weight gain.....	0.0434	0.1460	0.2282	0.2532	0.2562	0.2593

From these sixth and seventh series of plating tests, it will be observed that over the time interval of 60 minutes, the weight gains of plating increase with increasing pH and with increasing aminoacetate concentrations.

From this seventh series of plating tests, it will be observed that the weight gains in plating increase rapidly up to an aminoacetate concentration of 0.18 mole/liter, and from thereon, at a much slower rate. Moreover, it will be observed that the differences between the initial and final pH values become smaller as the aminoacetate concentration is increased due to buffering action in the bath.

In an eighth series of these plating tests where the Ni⁺⁺/hypo⁻ ratio was varied, an aminoacetate bath was employed that had the following composition:

Sodium hypophosphite.....m./l. 0.225
Nickel chloride..... Variable
Sodium aminoacetate.....m./l. 0.12

In 50 cc. of this plating bath, properly cleaned steel samples of 20 cm.² area were plated for 10 minutes and 60 minutes, the temperature of the bath being substantially at 98° C. and the pH having been adjusted with ammonium hydroxide to an initial value within the range

6.4 to 6.6. In these plating tests, the plating was bright and smooth and the specific results were as follows:

10 MINUTE TESTS

Ni ⁺⁺ /hypo-----	0.128	0.26	0.36	0.512	0.575	0.647
NiCl ₂ m./l.-----	0.0288	0.0585	0.0810	0.1152	0.1293	0.1456
Final pH-----	5.35	5.42	4.94	5.00	4.88	4.86
Rate, R×10 ⁴ -----	3.61	4.54	5.10	5.23	5.63	5.59

Ni ⁺⁺ /hypo-----	0.705	0.769	1.026	1.282	1.538	
NiCl ₂ m./l.-----	0.1586	0.1730	0.2308	0.2884	0.3460	
Final pH-----	4.80	4.72	4.32	4.27	4.28	
Rate, R×10 ⁴ -----	5.42	4.80	4.29	3.99	4.08	

60 MINUTE TESTS

Ni ⁺⁺ /hypo-----	0.128	0.26	0.36	0.512	0.575	0.647
Final pH-----	5.04	3.37	3.18	3.17	3.17	2.90
Weight gain-----	0.0914	0.1702	0.1896	0.2282	0.2317	0.2300

Ni ⁺⁺ /hypo-----	0.705	0.769	1.026	1.282	1.538	
Final pH-----	3.08	3.12	2.95	2.80	2.88	
Weight gain-----	0.2234	0.1912	0.2066	0.2031	0.2113	

This eighth series of plating tests shows that there is a definite optimum ratio of Ni⁺⁺/hypophosphite ions in plating baths due to the inclusion in the commercial reagents employed in the production of the plating bath of stabilizing impurities (particularly lead) with the con-

plating solution in the reservoir in excess of 24 cycles (as contrasted with a few cycles of regeneration employing prior baths of the character of that disclosed in the Gutzeit and Krieg patent) before there is an intolerable build-up in the plating bath of the by-product phosphite. As a matter of interest, the plating rate of the plating bath in the subsequent cycles of the continuous plating system is increased over the initial cycles thereof; which phenomenon is not exactly understood.

10 In the continuous plating system, a plating bath was employed having the following composition:

Sodium hypophosphite-----m./l-----	0.225
Nickel chloride-----m./l-----	0.1125
Sodium aminoacetate-----m./l-----	0.225
Ratio: Ni ⁺⁺ /hypo-----	0.5
Ratio: Amino/Ni ⁺⁺ -----	2.20
Trace ion stabilizer Pb ⁺⁺ -----p.p.m-----	1
Initial pH adjusted with 0.18 m./l. NaOH-----	6.5

20 The trace of Pb⁺⁺ was added to the plating bath to increase the stability thereof as disclosed in the previously mentioned Talmey and Gutzeit application.

In the continuous plating system, 6 liters of the plating bath were used, the plating solution being flowed by gravity through a heating coil and then through the plating chamber having a capacity of about 300 cm.³ so that the temperature of the plating bath in the plating chamber was maintained at 99° C. (±1° C.). The plating solution was regenerated in the reservoir exteriorly of the plating chamber after each cycle by adding thereto the necessary re-agents, and four steel samples of 20 cm.² area each (80 cm.² total area) were plated in the plating chamber with the following results:

Cycle No.-----	1	2	3	4	5	6	7	8
Initial pH-----	6.62	6.62	6.60	6.48	6.57	6.56	6.51	6.50
Final pH-----		6.22	6.19	6.29	6.15	6.16	6.29	6.28
Duration (min.)-----	115	90	100	89	98	264	101	106
Soln. flow rate cc./min-----	49	63	57	64	58	22	56	54
Weight gain (gms.)-----	3.80	2.51	3.34	2.81	3.06	3.57	7.66	4.16
Plating rate, R×10 ⁴ -----	4.13	3.49	4.17	3.95	3.90	4.52	4.91	4.80
Depletion percent-----	9.0	6.0	7.9	6.7	7.7	18.0	8.7	9.9
Cumulative deplet. percent-----	9.0	15.0	22.9	29.6	37.3	55.3	64.0	73.9

Cycle No.-----	9	10	11	12	13	14	15	16
Initial pH-----	6.46	6.45	6.49	6.51	6.49	6.48	6.48	6.47
Final pH-----	6.01	6.19	6.31	6.31	6.35	6.32	6.30	6.14
Duration (min.)-----	126	114	116	110	90	103	106	147
Soln. flow rate cc./min-----	45	50	49	52	57	55	54	39
Weight gain (gms.)-----	4.83	4.52	4.69	4.52	4.22	4.56	4.87	6.75
Plating rate, R×10 ⁴ -----	4.80	4.96	5.05	5.14	5.21	5.54	5.75	5.74
Depletion percent-----	11.5	10.7	11.7	10.7	10.1	10.7	11.6	16.0
Cumulative deplet. percent-----	85.4	96.1	107.2	117.9	128.0	138.7	150.3	166.3

Cycle No.-----	17	18	19	20	21	22	23	24
Initial pH-----	6.49	6.50	6.48	6.45	6.52	6.46	6.52	6.52
Final pH-----	6.23	6.25	6.32	6.33	6.32	6.35	6.39	6.42
Duration (min.)-----	136	141	162	136	119	145	136	128
Soln. flow rate cc./min-----	42	40	35	42	48	39	42	44
Weight gain (gms.)-----	6.24	6.58	7.14	7.41	5.87	7.50	6.65	6.55
Plating rate, R×10 ⁴ -----	5.73	5.83	5.70	6.81	6.17	6.45	6.22	6.40
Depletion percent-----	14.8	15.6	16.9	17.6	13.9	17.7	15.8	16.5
Cumulative deplet. percent-----	181.1	196.7	213.6	231.2	245.1	262.8	278.6	295.1

sequent inclusion in the bath of a trace of amount of sulfide ion controller as disclosed in the copending application of Paul Talmey and Gregoire Gutzeit, Serial No. 359,428, filed June 3, 1953. Specifically, the optimum ratio of Ni⁺⁺/hypophosphite ions in plating baths containing amino-acids is between 0.575 and 0.650, due to the circumstance noted.

In the foregoing series of plating tests, a batch plating process was involved; however, baths of the present type are even more advantageous when employed in a continuous plating system as disclosed in the Talmey and Crehan patent. Specifically, these baths have a fast plating rate and are stable permitting regeneration of the

This test was stopped after 24 cycles without reaching the point where nickel phosphite precipitated in the plating solution, whereby a total weight of 123.81 gms. of nickel was plated from the 6 liters of plating solution without phosphite removal, the volume of the plating solution being kept constant by adding some water as the rate of evaporation was greater than the volume of reagent solution added for regeneration. The percent of depletion is an arbitrary indication of the amount of nickel taken out, as a deposit, from the original solution.

In these plating baths, the nickel ion may be supplied by nickel salts other than the chloride, such, for instance, as the sulfate; and in the following plating tests employ-

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ing the continuous plating system, the following plating bath composition was used:

Ni ⁺⁺ as nickel sulfate	m./l.	0.1125
Sodium hypophosphite	m./l.	0.225
Sodium aminoacetate	m./l.	0.225
Ratio: Ni ⁺⁺ /hypo		0.5
Ratio: Amino/Ni ⁺⁺		2.0
Initial pH adjusted with 0.18 m./l. caustic soda	(About)	6.50
Trace ion stabilizers:		
Pb ⁺⁺	p.p.m.	1
Te ⁺⁺	p.p.m.	1

In the plating system, the conditions were the same as previously described with reference to the preceding plating test and the following results were obtained:

Cycle No.	1	2	3	4	5
Initial pH	6.38	6.49	6.54	6.48	6.50
Final pH	5.96	6.19	6.20	6.07	6.27
Duration (min.)	117	97	115	155	114
Soln. flow rate cc./min.	49	59	49	37	50
Weight gain	4.66	3.61	4.05	5.39	4.14
Plating rate, R $\times 10^4$	4.98	4.53	4.40	4.34	4.53
Depletion percent	11.1	8.3	9.6	12.8	9.8
Cumulative depl. percent	11.1	19.4	29.0	41.8	51.6

Cycle No.	6	7	8	9	10
Initial pH	6.49	6.52	6.52	6.47	6.50
Final pH	6.18	6.29	6.19	6.19	6.32
Duration (min.)	101	134	133	127	111
Soln. flow rate cc./min.	56	42	43	45	51
Weight gain	3.76	4.91	5.03	4.94	4.44
Plating rate, R $\times 10^4$	4.65	4.58	4.71	4.87	5.00
Depletion percent	8.9	11.7	12.1	11.7	10.5
Cumulative depl. percent	60.5	72.2	84.3	96.0	106.5

In all of the foregoing plating tests, steel was used as the plating base material; however, it should be understood that other materials, such as, aluminum, brass, bronze, plastic (Bakelite), etc., may be plated with very good results using these plating baths. In the plating of aluminum bodies a bath of the general character of that disclosed in the copending application of Raymond R. Reschan and Abraham Krieg, Serial No. 309,939, filed September 16, 1952, now Patent No. 2,694,017, granted November 9, 1954, is recommended and a plating bath of this character was used in plating tests and having the following composition:

Sodium hypophosphite	m./l.	0.225
Nickel nitrate	m./l.	0.1125
Sodium aminoacetate	m./l.	0.18
Initial pH (adjusted with NaOH)		6.5
Ratio: Ni ⁺⁺ /hypo		0.5
Ratio: Amino/Ni ⁺⁺		1.6

In 50 cc. of this plating bath a sample of steel and a sample of 2S aluminum each of 20 cm.² area were separately plated for 11 minutes at a temperature of about 98° C., with the following results:

Base material	Steel	2S aluminum
Initial pH	6.41	6.41
Weight gain	0.092	0.128
Plating rate, R $\times 10^4$	4.26	5.82

The plating on the S2 aluminum sample showed excellent adhesion; and these results were verified in a companion 60 minutes test.

In other plating tests a bath of the general character of that disclosed in the Reschan and Krieg patent was employed that had the following composition:

Sodium hypophosphite	m./l.	0.225
Nickel chloride	m./l.	0.1125
Sodium aminoacetate	m./l.	0.18
Sodium fluoride	m./l.	0.01

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Sodium nitrate	m./l.	0.20
Initial pH, adjusted with NaOH		6.5
Ratio: Ni ⁺⁺ /hypo		0.5
Ratio: Amino/Ni ⁺⁺		1.6

In 50 cc. of this plating bath a sample of steel and a sample of S2 aluminum each of 20 cm.² area were separately plated for 10 minutes, the temperature of the bath being about 98° C., with the following results:

	Steel	Aluminum
Weight gain	0.0969	0.0984
Rate, R $\times 10^4$	4.85	5.29
Appearance	Bright, smooth	Very bright, smooth.
Adhesion	Good	Excellent.

In another plating test three ½" brass faucets were plated to 0.4 mil thickness in a bath having the following composition:

Sodium hypophosphite	m./l.	0.225
Nickel chloride	m./l.	0.09
Sodium aminoacetate		0.18
Initial pH adjusted with NaOH		6.5

Trace ion stabilizers:

Pb ⁺⁺	p.p.m.	1
Te ⁺⁺	p.p.m.	1
Ratio: Ni ⁺⁺ /hypo		0.4
Ratio: Amino/Ni ⁺⁺		2.0

In this plating bath the plating rate was 1 mil per 50 minutes and the appearance of the faucets after plating was unusually good.

In another plating test, a sample of general purpose "Bakelite" was plated in a bath having the following composition:

Sodium hypophosphite	m./l.	0.225
Nickel chloride	m./l.	0.1125
Sodium aminoacetate	m./l.	0.18
Pb ⁺⁺ added as stabilizing ion	p.p.m.	5

Prior to plating, the sample of "Bakelite" was prepared in accordance with the methods disclosed in the copending applications of Gregoire Gutzeit, William J. Crehan and Abraham Krieg, Serial No. 230,352, filed June 7, 1951, now Patent No. 2,690,401, granted September 28, 1954, and of William J. Crehan, Serial No. 279,945, filed April 1, 1952, now Patent No. 2,690,402, granted September 28, 1954. Specifically, the outer layer of skin of the "Bakelite" sample was removed mechanically with fine emery cloth; and then it was soaked in an aqueous solution containing 35 p.p.m. of palladium chloride for 72 hours. The sample was then thoroughly rinsed in warm water, dried, and the palladium chloride was reduced to metallic palladium in a hot aqueous solution of sodium hypophosphite (0.335 m./l.) until bubbling subsided. The plating was initiated instantaneously upon immersion of the prepared "Bakelite" sample into the plating bath at a temperature of 92° C.; and the plating was carried out for a time interval of 90 minutes in 50 cc. of the plating bath. The plating appearance was excellent and the adhesion thereof was good. In the plating test the bath remained stable and very clear.

In passing, it is noted that further plating tests showed that a soaking for 3 hours in the aqueous palladium chloride solution is optimum for coating adhesion although a soaking time as short as 5 minutes is adequate to obtain initiation of the nickel plating.

In succeeding plating tests, the same technique was applied in the preparation of other plastic materials including fiberglass reinforced polyester plastic, neoprene and phenolic plastic (Hycar). These plating tests were also highly successful in that the plating appearance was excellent and the adhesion was good.

A plating test upon a "Bakelite" sample was con-

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ducted employing the continuous plating system previously described and utilizing a plating bath having the following composition:

Sodium hypophosphite	m./l.	0.225
Nickel sulfate	m./l.	0.1125
Sodium aminoacetate	m./l.	0.225
Ratio: Ni ⁺⁺ /hypo ⁻		0.5
Ratio: Amino/Ni ⁺⁺		2.0
Stabilizing ion Pb ⁺⁺	p.p.m.	4
Initial pH adjusted with NaOH		6.40-6.50

In this plating test, the bath had a volume of 4.5 liters and the "Bakelite" sample was pretreated substantially in the manner previously described. Specifically, the pretreatment of the "Bakelite" sample consisted of the removal of the skin thereon on a sanding belt, followed by the soaking thereof for about 15 minutes in an aqueous solution of palladium chloride (35 p.p.m.) at a temperature in the range 60° C.-80° C. Thereafter the "Bakelite" sample was rinsed in hot water, and then immersed in a hot aqueous solution of sodium hypophosphite (0.225 m./l.) until bubbling subsided. Thereafter the "Bakelite" sample was rinsed in hot water and transferred to the plating chamber in the continuous plating system; whereby it was plated therein with the following results:

Cycle No.	1	2	3	4	5	6	7
Initial pH	6.44	6.51	6.50	6.47	6.45	6.48	6.47
Final pH	5.91	6.15	6.35	6.26	6.17	6.19	6.20
Soln. flow rate cc./min.	38	40	38	37	43	40	43
Weight gain, gms.	3.7475	3.4591	3.2524	4.1670	3.0849	3.9216	4.7550
Cumulative depletion, percent	12.6	24.2	35.2	49.2	63.0	76.4	91.6

In the foregoing series of plating tests, the short chain aliphatic aminocarboxylic acid additive in the plating bath consisted of aminoacetic acid (glycine) or the alkali salt thereof, fundamentally due to the practical circumstance that these compounds are both cheap and readily available in large quantities in the commercial market. Moreover, it has been verified that the other short chain aliphatic aminocarboxylic acids do not have any particular advantage over glycine and they are considerably more expensive and only available in small quantities in the market. Accordingly, from a practical standpoint, it is recommended that the short chain aliphatic aminocarboxylic acid additive in the plating bath take the form of glycine or sodium aminoacetate. However, the other short chain aliphatic aminocarboxylic acids and their salts are entirely satisfactory as additives in the plating bath as indicated by the various series of plating tests reported hereinafter.

In a series of these plating tests, an alpha-alanine (dl-alpha-aminopropionic acid) plating bath was employed that had the following composition:

Sodium hypophosphite	m./l.	0.225
Nickel chloride	m./l.	0.09
Alpha-alanine	m./l.	0.18
Ratio: Ni ⁺⁺ /hypo ⁻		0.4
Ratio: Amino/Ni ⁺⁺		2.0
Initial pH adjusted with NaOH		6.1

In 50 cc. of this plating bath, properly cleaned steel samples of 20 cm.² area were plated, the temperature of the bath being 97° C. $\pm$ 1° C. In these plating tests, the plating was bright and smooth and the specific results were as follows:

Duration of test	10 minutes	60 minutes
Initial pH	6.10	6.10
Final pH	5.10	3.10
Weight gain	0.1050	0.2231
Rate, R $\times$ 10 ⁴	5.25	

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In another series of these plating tests, an alpha-alanine plating bath was employed that had the following composition:

Sodium hypophosphite	m./l.	0.225
Nickel chloride	m./l.	0.1125
Alpha-alanine	m./l.	0.225
Ratio: Ni ⁺⁺ /hypo ⁻		0.5
Ratio: Amino/Ni ⁺⁺		2.0
pH, adjusted with NaOH		Variable

In 50 cc. of this plating bath, properly cleaned steel samples of 20 cm.² area were plated, the temperature of the bath being about 97° C. In these plating tests, the plating was bright and smooth in the acid bath, semi-bright in the substantially neutral baths, and dull in the alkaline baths, and the specific results were as follows:

(a) Rate tests—10 minutes

Initial pH	5.54	6.01	6.52	7.01	7.53	7.99	8.53	9.00
Weight gain	0.0696	0.0923	0.0862	0.0789	0.0847	0.0802	0.0839	0.0831
Rate, R $\times$ 10 ⁴	3.48	4.62	4.31	3.94	4.424	4.01	4.40	4.16

(b) Plating tests—60 minutes

Initial pH	5.54	6.01	6.52	7.01	7.53	7.99	7.53	9.00
Weight gain	0.2045	0.2373	0.2544	0.2558	0.2595	0.2325	0.2252	0.2044

In a series of these plating tests, a beta-alanine (dl-beta-aminopropionic acid) plating bath was employed that had the following composition:

Sodium hypophosphite	m./l.	0.225
Nickel chloride	m./l.	0.1125
Beta-alanine	m./l.	0.225
Ratio: Ni ⁺⁺ /hypo ⁻		0.5
Ratio: Amino/Ni ⁺⁺		2.0
Initial pH adjusted with NaOH		

In 50 cc. of this plating bath, properly cleaned steel samples of 20 cm.² area were plated, the temperature of the bath being 97° C. $\pm$ 1° C. In these plating tests, the plating was bright and smooth, and the specific results were as follows:

Duration of test	10 minutes			60 minutes		
Initial pH	6.05	7.58	8.61	6.05	7.58	8.61
Weight gain	0.0523	0.0727	0.0820	0.1294	0.1378	0.1639
Rate, R $\times$ 10 ⁴	2.61	3.64	4.10			

From a comparison of the two last-mentioned series of plating tests, it will be observed that the plating rates of the short chain aliphatic beta-aminocarboxylic acid plating baths are slower than the short chain aliphatic alpha-aminocarboxylic acid plating baths; which is, of course, expected as the complex formation is more difficult due to the steric factor. Furthermore, it will be observed that the optimum plating rates occur in the alkaline range of the plating baths.

In a series of these plating tests, an alpha-aminobutyric acid (dl-alpha-amino-n-butyric acid) plating bath was employed that had the following composition:

Sodium hypophosphite	m./l.	0.225
Nickel chloride	m./l.	0.09
Alpha-aminobutyric acid	m./l.	0.18
Ratio: Ni ⁺⁺ /hypo ⁻		0.4
Ratio: Amino/Ni ⁺⁺		2.0
Initial pH adjusted with NaOH		6.5

In 50 cc. of this plating bath, properly cleaned steel samples of 20 cm.² area were plated, the temperature of the bath being 97° C. $\pm$ 1° C. In these plating tests, the

plating was bright and smooth and the specific results were as follows:

Duration of tests.....	10 minutes	60 minutes
Initial pH.....	6.50	6.50
Final pH.....	5.80	3.60
Weight gain.....	0.0740	0.2401
Rate, $R \times 10^4$	3.70	

In another series of these plating tests, an alpha-aminobutyric acid plating bath was employed that had the following composition:

Sodium hypophosphite.....	m./l.	0.225
Nickel chloride.....	m./l.	0.1125
Alpha-aminobutyric acid.....	m./l.	0.225
Ratio: $Ni^{++}/hypo^-$		0.5
Ratio: Amino/ Ni^{++}		2.0
pH adjusted with NaOH.....		Variable

In 50 cc. of this plating bath, properly cleaned steel samples of 20 cm.² area were plated, the temperature of the bath being about 97° C. In these plating tests, the plating was bright and smooth in the acid baths, dull in the substantially neutral baths, and semi-bright in the alkaline baths, and the specific results were as follows:

(a) Rate tests—10 minutes

Initial pH.....	5.52	6.05	6.53	7.00	7.56	8.62	9.10
Weight gain.....	0.0733	0.0684	0.0533	0.0480	0.0464	0.0608	0.0576
Rate, $R \times 10^4$	3.66	3.42	2.66	2.40	2.32	3.04	2.88

(b) Plating tests—60 minutes

Initial pH.....	5.53	6.05	6.53	7.00	7.56	8.08	8.62	9.10
Weight gain.....	0.1902	0.2356	0.2463	0.2465	0.2321	0.2310	0.2224	0.2000

In connection with the alpha-aminobutyric acid baths, it is pointed out that while the 10 minute rates are low, the 60 minute rates compare very well with those obtained in the aminoacetic acid bath; which circumstance indicates a long initiation period, possibly due to the fact that a longer time is needed for reaching a complexation equilibrium.

In the continuous plating system, an aminosuccinic acid (aspartic acid) plating bath was employed having the following composition:

Sodium hypophosphite.....	m./l.	0.225
Nickel chloride.....	m./l.	0.09
Aspartic acid.....	m./l.	0.18
Ratio: $Ni^{++}/hypo^-$		0.4
Ratio: Amino/ Ni^{++}		2.0
Initial pH adjusted with $NaHCO_3$		6.60–7.00
Stabilizing ion Pb^{++}	p.p.m.	4

In the plating system, the conditions were substantially the same as previously described with reference to the prior plating tests involving the continuous plating system, except that only 4 liters of the bath were employed and the total area of the steel samples was 60 cm.², the temperature of the bath being about 99° C., and the following results were obtained:

Cycle No.....	1	2	3
Initial pH.....	7.00	6.70	6.60
Final pH.....	6.40	6.20	6.30
Weight gain (gms.).....	1.4009	1.1415	1.5655
Rate, $R \times 10^4$	3.81	3.73	3.89
Duration of cycle (min.).....	72	51	67
Soln. flow rate cc./min.....	51.4	78.4	59.6

In this aspartic acid bath, the plating was bright and smooth.

In a series of these plating tests, an ethylenediaminetetraacetic acid plating bath was employed that was

formed from the tetrasodium salt thereof (Versene) and that had the following composition:

Sodium hypophosphite.....	m./l.	0.225
Nickel chloride.....	m./l.	0.09
Ethylenediaminetetraacetic acid (tetrasodium salt thereof).....	m./l.	0.04
Ratio: $Ni^{++}/hypo^-$		0.4
Ratio: Amino/ Ni^{++}		0.9
Initial pH adjusted with acetic acid or NaOH.....		

In 50 cc. of this plating bath, properly cleaned steel samples of 5 cm.² area (shimstock) were plated for 10 minutes, the temperature of the bath being 97° C. $\pm 1^\circ$ C. In these plating tests, the plating was bright and smooth and the specific results were as follows:

Initial pH.....	6.0	7.0	8.0
Final pH.....	3.5	3.5	4.9
Weight gain (gms.).....	0.0345	0.0367	0.0679

In passing, it is noted that Versene is chemically identical to Nullapon and Sequestrene that have also been employed with identical results. In these tests, the weight gains should be multiplied by four for comparison purposes with the other plating tests (because the area of the steel sample was 5 cm.² instead of 20 cm.² as previously); and it will be observed that this additive (ethylenediaminetetraacetic acid) produces optimum results in the alkaline range where this complexing agent is most effective.

In connection with Versene-Fe-Sp (an acid sodium salt of ethylenediaminetetraacetic acid), it is pointed out that the optimum results are obtained in the near acid range and the following bath composition is recommended:

Sodium hypophosphite.....	M./l.	0.225
Nickel chloride.....		0.09
"Versene-Fe-Sp".....		0.04

In 50 cc. of this plating bath, properly cleaned steel samples of 5 cm.² area (shimstock) were plated, the temperature of the bath being 97° C. $\pm 1^\circ$ C. In these plating tests, the plating was bright and smooth and the specific results were as follows:

Initial pH.....	5.0	6.0
Final pH.....	4.3	4.1
Weight gain (gms.).....	0.0458	0.0530

Again it is noted that in these plating tests the weight gains should be multiplied by four for comparison purposes with the other plating tests.

As previously noted, the utilization of an short chain aliphatic aminocarboxylic acid additive in a plating bath of the character of that disclosed in the Gutzeit and Krieg patent is advantageous and a plating bath of this character of the following composition is recommended:

Magnesium hypophosphite.....	0.156 m./l.
Nickel acetate.....	0.086 m./l.
Versene (38% soln.).....	Variable (0.2% and 1% corresponding to about 0.0027 and 0.0135 m./l.).

Initial pH adjusted with acetic acid..... 5.69

In 50 cc. of this plating bath, properly cleaned steel samples of 20 cm.² were plated for 60 minutes, the temperature of the bath being about 97° C. and the following results were obtained:

Versene	None	0.2%	1.0%	None	1%
Duration of test—min.....	10	10	10	29	90
Weight gain.....	0.1106	0.1168	0.1246	0.2286	0.2426
Stability (min.).....	Stable	Stable	Stable	20	Stable

It is noted that this bath is an acetate buffered bath and that the Versene additive results in increased plating rate and has a stabilizing action at a concentration of 1% (0.0135 m./l.).

In passing, it is noted that in similar tests "Bakelite" samples, prepared in the manner previously explained, were plated, and it was found that the initiation period was shortened from about 9 minutes to about 3 minutes, again indicating the advantage of utilizing the short chain aliphatic aminocarboxylic acid additive in an acetate buffered bath of the character of that disclosed in the Gutzeit and Krieg patent.

In a further series of plating tests, several short chain aliphatic aminocarboxylic acid additives were employed in each bath, and it was discovered that their actions were accumulative and good results were obtained. In these plating tests, the following four baths were utilized respectively designed as I, II, III and IV, and having the receptive compositions:

BATH I

	M./l.
Sodium hypophosphite.....	0.225
Nickel chloride.....	0.09
Sodium aminoacetate.....	0.120

BATH II

Sodium hypophosphite.....	0.225
Nickel chloride.....	0.09
Sodium aminoacetate.....	0.120
Versene	0.04

BATH III

Sodium hypophosphite.....	0.225
Nickel chloride.....	0.09
Sodium aminoacetate.....	0.120
Versene Fe-Sp.....	0.04

BATH IV

Sodium hypophosphite.....	0.225
Nickel chloride.....	0.09
Sodium aspartate.....	0.120
Versene	0.04

In 50 cc. of these plating baths, properly cleaned steel samples of 5 cm.² area were plated for 60 minutes, the temperature of the baths being 98° C. ± 1° C., with the following results:

Bath No.....	I	II	III	IV
Initial pH.....	5.75	6.0	6.0	6.0
Final pH.....	5.0	4.3	4.4	3.8
Weight gain (gms.).....	0.1214	0.1563	0.1506	0.1584

In view of the foregoing, it is apparent that there has been provided an improved process of chemical nickel plating, as well as improved plating baths therefor, wherein the baths are of the nickel cation-hypophosphite anion type containing as an additive a compound selected from the group consisting of short chain aliphatic aminocarboxylic acids and salts thereof. The additives mentioned are very advantageous in the plating bath in that they function both as exaltants and as to the plating rate and as retarders as to the formation of black precipitate. Moreover, in the arrangement, the nickel plating may take place within a wide pH range (from about 4.5 to about 9.0), being most useful around neutrality, where the base metal is least attacked by the plating bath and where plating equipment corrosion is minimized. Furthermore, when these additives are used in the optimum proportion (amino/Ni⁺⁺ about 2.0) they keep the nickel phosphite from precipitating after many cycles in the continuous plating system, rendering it possible to reach a phosphite concentration of about 1 molar (instead of the usual 0.07 m./l.) before precipitation starts in the plating bath.

While there has been described what is at present considered to be the preferred embodiment of the invention,

it will be understood that various modifications may be made therein, and it is intended to cover in the appended claims all such modifications as fall within the true spirit and scope of the invention.

What is claimed is:

1. A method of depositing nickel from a chemical reduction plating bath, said method comprising immersing a catalytic article to be coated in a solution of nickel ion and a hypophosphite reducing agent capable of reducing the nickel in solution, said solution having a nickel ion concentration of about 7 grams per liter, a hypophosphite ion concentration of about 15 grams per liter, a relatively high plating temperature that is disposed near the boiling point thereof, and an initial pH within the range from about 5.5 to 9.1, and allowing said article to remain in said solution until a nickel coating of desired thickness is deposited thereon.

2. A method of depositing nickel from a chemical reduction plating bath, said method comprising immersing a catalytic article to be coated in a solution of nickel ion and a hypophosphite reducing agent capable of reducing the nickel in solution, said solution containing an initial quantity of nickel ion of about 7 grams per liter and an initial quantity of hypophosphite ion of about 15 grams per liter and having an initial pH within the range from about 5.5 to 9.1, said solution having a relatively high plating temperature that is disposed near the boiling point thereof, and allowing said article to remain in said solution for a time interval sufficient to reduce said initial quantity of nickel ion therefrom.

3. The method set forth in claim 2, and further comprising regenerating said solution during said time interval by adding thereto soluble ingredients supplying thereto nickel ion and hypophosphite ion and hydroxyl ion in order to maintain during said time interval in said solution substantially said initial quantity of nickel ion and substantially said initial quantity of hypophosphite ion and substantially said initial pH thereof, and so that the total reduction of nickel ion from said solution during said time interval is in excess of said initial quantity of nickel ion therein.

4. A method of depositing nickel from a chemical reduction plating bath, said method comprising immersing a catalytic article to be coated in a solution of nickel ion and a hypophosphite reducing agent capable of reducing the nickel in solution, said solution having a nickel ion concentration of about 7 grams per liter, a hypophosphite ion concentration of about 15 grams per liter, a relatively high plating temperature that is disposed near the boiling point thereof, and an initial pH within the range from about 5.5 to 9.1, and allowing said article to remain in said solution until the nickel is substantially completely reduced as evidenced by the solution turning from green to colorless.

5. A method of depositing nickel on a catalytic surface by chemical reduction plating, said method comprising immersing the article to be coated in an aqueous solution of nickel acetate and an alkaline hypophosphite, the nickel ion concentration of said solution being about 5 grams per liter and the hypophosphite ion concentration being about 10 grams per liter, said solution having an initial pH within the range of about 5.5 to 9.1 and being maintained at a relatively high plating temperature that is disposed near the boiling point thereof, and maintaining said article in such solution for a time sufficient to reduce substantially all of the nickel in solution as evidenced by the solution turning from green to colorless.

6. A method of depositing nickel from a chemical reduction plating solution which comprises immersing the articles to be plated in an aqueous solution containing nickel ion, acetate ion and hypophosphite ion, and having an initial pH from about 5.5 to 9.1, the nickel ion concentration being about 5 grams per liter, the hypophosphite ion concentration being about 10 grams per liter and the ratio of acetate ion to nickel ion being about 2 to 1, main-

taining said solution at a relatively high plating temperature that is disposed near the boiling point thereof, and allowing said articles to remain in said solution for a time sufficient to reduce substantially all the nickel in the solution.

7. A method of depositing nickel from a chemical reduction plating solution which comprises immersing the articles to be plated in an aqueous solution of nickel chloride, an alkali metal hypophosphite and a soluble acetate, and having an initial pH from about 5.5 to 9.1, the nickel ion concentration being about 5 grams per liter, the hypophosphite ion concentration being about 10 grams per liter and the acetate ion being sufficient to exert a buffering action, maintaining said solution at a relatively high plating temperature that is disposed near the boiling point thereof, and allowing said articles to remain in said solution for a time sufficient to reduce substantially all the nickel in the solution.

8. The process of chemically plating with nickel a body essentially comprising an element selected from the group consisting of iron, cobalt, nickel, aluminum, copper, silver, gold, palladium and platinum; which comprises contacting said body with an aqueous bath comprising nickel ions and hypophosphite ions and a dissolved compound selected from the group consisting of short chain aliphatic aminocarboxylic acids and salts thereof, wherein the absolute concentration of hypophosphite ions in said bath expressed in mole/liter is within the range 0.15 to 1.20, the molar ratio between nickel ions and hypophosphite ions in said bath is within the range 0.25 to 1.60, the numerical ratio between amino ions and nickel ions in said bath is within the range 0.5 to 6.0, and the initial pH of said bath is within the approximate range 4.5 to 9.0.

9. The process set forth in claim 8, wherein the molecule of said compound comprises from 2 to 10 carbon atoms.

10. The process set forth in claim 8, wherein said compound is selected from the group consisting of alpha-aminocarboxylic acids and salts thereof.

11. The process set forth in claim 10, wherein said alpha-aminocarboxylic acid is alpha-aminopropionic acid.

12. The process set forth in claim 8, wherein said compound is selected from the group consisting of beta-aminocarboxylic acids and salts thereof.

13. The process set forth in claim 12, wherein said beta-aminocarboxylic acid is beta-aminopropionic acid.

14. The process set forth in claim 8, wherein said compound is selected from the group consisting of polyaminocarboxylic acids and salts thereof.

15. The process set forth in claim 8, wherein said compound is selected from the group consisting of aminopolycarboxylic acids and salts thereof.

16. The process set forth in claim 8, wherein said compound is selected from the group consisting of polyaminopolycarboxylic acids and salts thereof.

17. The process set forth in claim 8, wherein said compound is selected from the group consisting of ethylenediaminetetraacetic acid and salts thereof.

18. The process set forth in claim 8, wherein said compound is selected from the group consisting of aminoacetic acid and salts thereof.

19. The process set forth in claim 8, wherein said compound is selected from the group consisting of aminosuccinic acid and salts thereof.

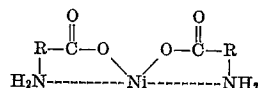
20. The process of chemically plating with nickel a body essentially comprising an element selected from the group consisting of iron, cobalt, nickel, aluminum, copper, silver, gold, palladium and platinum; which comprises contacting said body with an aqueous bath comprising nickel ions and hypophosphite ions and short chain aliphatic zwitterions of the general formula:



where R is an alkyl radical, wherein the absolute concentration of hypophosphite ions in said bath expressed in mole/liter is within the range 0.15 to 1.20, the molar ratio between nickel ions and hypophosphite ions in said bath is within the range 0.25 to 1.60, the numerical ratio between zwitterions and nickel ions in said bath is within the range 0.5 to 6.0, and the initial pH of said bath is in the approximate range 4.5 to 9.0.

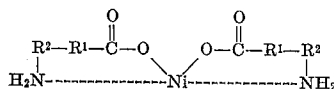
21. The process set forth in claim 20, wherein the numerical ratio between zwitterions and nickel ions in said bath is at least 2 so that substantially all of the nickel ions in said bath are chelated.

22. The process set forth in claim 20, wherein the resulting chelate is of the general structure:



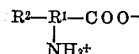
where R is an alkyl radical.

23. The process set forth in claim 20, wherein the resulting chelate is of the general structure:



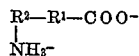
where R¹ and R² are alkyl radicals.

24. The process of chemically plating with nickel a body essentially comprising an element selected from the group consisting of iron, cobalt, nickel, aluminum, copper, silver, gold, palladium and platinum; which comprises contacting said body with an aqueous bath comprising nickel ions and hypophosphite ions and short chain aliphatic zwitterions of the general formula:



where R¹ and R² are alkyl radicals, wherein the absolute concentration of hypophosphite ions in said bath expressed in mole/liter is within the range 0.15 to 1.20, the molar ratio between nickel ions and hypophosphite ions in said bath is within the range 0.25 to 1.60, the numerical ratio between zwitterions and nickel ions in said bath is within the range 0.5 to 6.0, and the initial pH of said bath is in the approximate range 4.5 to 9.0.

25. The process of chemically plating with nickel a body essentially comprising an element selected from the group consisting of iron, cobalt, nickel, aluminum, copper, silver, gold, palladium and platinum; which comprises contacting said body with an aqueous bath comprising nickel ions and hypophosphite ions and short chain aliphatic zwitterions of the general formula:



where R² and R¹ are alkyl radicals, wherein the absolute concentration of hypophosphite ions in said bath expressed in mole/liter is within the range 0.15 to 1.20, the molar ratio between nickel ions and hypophosphite ions in said bath is within the range 0.25 to 1.60, the numerical ratio between zwitterions and nickel ions in said bath is within the range 0.5 to 6.0, and the initial pH of said bath is in the approximate range 4.5 to 9.0.

26. The process of chemically plating with nickel a body essentially comprising an element selected from the group consisting of iron, cobalt, nickel, aluminum, copper, silver, gold, palladium and platinum; which comprises contacting said body with an aqueous bath comprising nickel ions and hypophosphite ions and a dissolved compound selected from the group consisting of short chain aliphatic aminocarboxylic acids and salts thereof, said bath having a hypophosphite ion concentration in the range 10 to 80 grams per liter, the molar ratio between nickel ions and hypophosphite ions in said bath being within the range 0.25 to 1.60, the numerical ratio

between amino ions and nickel ions in said bath being within the range 0.5 to 6.0, and the initial pH of said bath being in the approximate range 4.5 to 9.0.

27. A bath for the chemical plating of a catalytic material with nickel comprising an aqueous solution of a nickel salt and a hypophosphite and a compound selected from the group consisting of short chain aliphatic amino-carboxylic acids and salts thereof, wherein the absolute concentration of hypophosphite ions in said bath expressed in mole/liter is within the range 0.15 to 1.20, the molar ratio between nickel ions and hypophosphite ions in said bath is within the range 0.25 to 1.60, the numerical ratio between amino ions and nickel ions in said bath is within the range 0.5 to 6.0, and the pH of said solution is in the approximate range 4.5 to 9.0.

28. A bath for the chemical plating of a catalytic material with nickel comprising an aqueous solution of nickel ions and hypophosphite ions and short chain aliphatic zwitterions of the general formula:



where R is an alkyl radical, wherein the absolute concentration of hypophosphite ions in said bath expressed in mole/liter is within the range 0.15 to 1.20, the molar ratio between nickel ions and hypophosphite ions in said bath is within the range 0.25 to 1.60, the numerical ratio between zwitterions and nickel ions in said bath is within the range 0.5 to 6.0, and the pH of said bath is in the approximate range 4.5 to 9.0.

29. The bath set forth in claim 28, wherein the numerical ratio between zwitterions and nickel ions is at least 2 so that substantially all of the nickel ions are chelated.

30. A bath for the chemical plating of a catalytic material with nickel comprising an aqueous solution of a

nickel salt and a hypophosphite and a compound selected from the group consisting of short chain aliphatic amino-carboxylic acids and salts thereof, said bath having a hypophosphite ion concentration in the range 10 to 80 grams per liter, the molar ratio between nickel ions and the hypophosphite ions in said bath being within the range 0.25 to 1.60, the numerical ratio between amino ions and nickel ions in said bath being within the range 0.5 to 6.0, and the pH of said bath being in the approximate range 4.5 to 9.0.

31. The process of chemically plating with nickel a body essentially comprising an element selected from the group consisting of iron, cobalt, nickel, aluminum, copper, silver, gold, palladium and platinum, which comprises contacting said body with an aqueous bath comprising about 0.15 to 1.20 moles per liter of hypophosphite ions, about .04-2 moles per liter of nickel ions and about .02-1.5 moles per liter of a salt of ethylene diamine tetra acetic acid, said bath having a pH of about 4.5-6.5.

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