

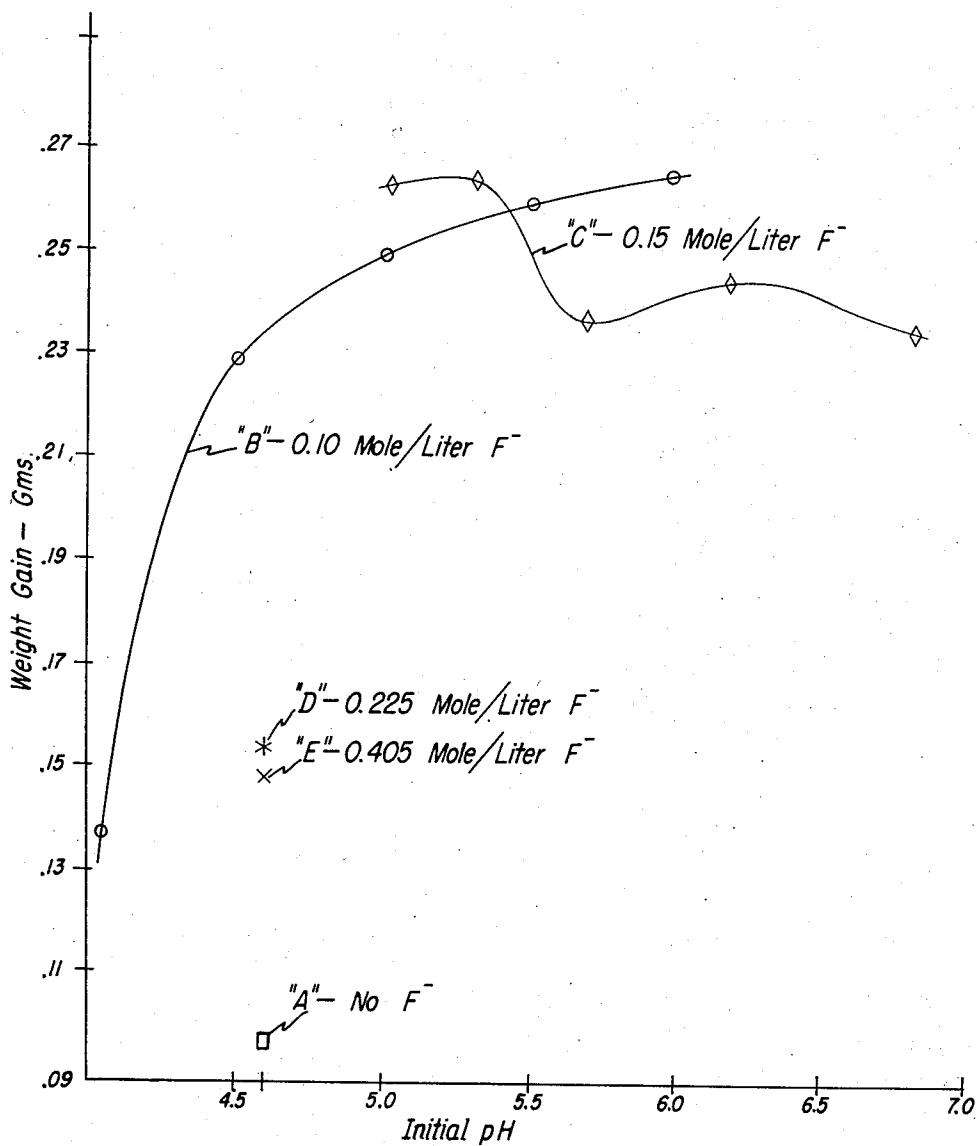
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PROCESSES OF CHEMICAL NICKEL PLATING AND BATHS THEREFOR

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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 employed in such processes.

The chemical nickel plating of a catalytic material employing an aqueous acid 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 bath, and the exterior surface of the body of catalytic material is coated with nickel. The following elements are examples of catalytic materials which may be nickel-plated: copper, silver, gold, beryllium, boron, germanium, aluminum, thallium, silicon, carbon, vanadium, molybdenum, tungsten, chromium, selenium, tellurium, titanium, iron, cobalt, nickel, palladium and platinum; and the following elements are examples of non-catalytic materials which ordinarily may not be nickel-plated: bismuth, cadmium, tin, lead and manganese. The activity of these catalytic materials varies considerably; and the following elements are particularly good catalysts in the chemical nickel plating bath: aluminum, copper, chromium, cobalt, iron, 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 both catalytic; and the reduction of the nickel cations to metallic nickel in the 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 bath combine with the hydrogen cations to form an acid, which, in turn, lowers the pH of the bath, tending to dissolve the nickel deposit. Also the reducing power of the hypophosphite anions is decreased as the pH value of the bath decreases. Moreover, there is a tendency for the bath, as the pH value thereof is decreased, to become unstable with the formation of a "black precipitate" that comprises a random chemical non-catalytic reduction of the nickel cations; which formation of the "black precipitate" is also favored by a high absolute concentration of hypophosphite anions in the bath. Of course, this formation of "black precipitate" comprises a decomposition of the bath; and is further objectionable in that it causes the nickel deposit to be coarse and rough.

For the dual purposes of increasing the stability of the bath (preventing 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 that serve either as buffers or as exaltants. For example, 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, there is disclosed a chemical nickel plating bath of the nickel cation-hypophosphite anion type that contains as an additive a buffer in the form of a salt of an organic acid, and specifically sodium acetate; and in the

Ramirez, Serial No. 204,424, filed January 4, 1951, now Patent No. 2,658,842, granted November 10, 1953, there is disclosed a chemical nickel plating bath of the nickel cation-hypophosphite anion type that contains as an additive an exaltant in the form of a simple short chain saturated aliphatic dicarboxylic acid, and specifically sodium succinate.

The present invention involves the discovery that the plating rate of a bath of the nickel cation-hypophosphite anion type may be greatly increased without rendering the bath unstable by employing as an additive a small amount of a soluble fluoride; which additive may be employed either in lieu of, or in conjunction with, an additive of the character of that employed in the baths mentioned above. It is postulated that the fluoride anions form heteropoly-acid anions with the hypophosphite anions and that the reducing power of these complex anions is much greater than that of the simple hypophosphite anions or that of the complex anions produced by the organic acids mentioned. These complex anions seem to be fluoro-hypophosphite anions; and in any case, the phenomenon of "exaltation" is achieved; whereby the increase in the rate of catalytic oxidation of the hypophosphite anions to phosphite anions can be measured experimentally by determining the amount of hydrogen gas evolved per unit of time, with and without the addition of the fluoride anions, with all other conditions in the bath remaining the same.

It is, therefore, the primary object of the present invention to provide an improved catalytic nickel plating process of the character described, in which the reaction involved is carried out more efficiently, rapidly and perfectly than heretofore, thereby rendering the process more desirable from a commercial standpoint.

A further object of the invention is to provide an improved process of the character described that employs a bath of the nickel cation-hypophosphite anion type containing as an additive fluoride anions.

Another object of the invention is to provide an improved aqueous acid bath of the nickel cation-hypophosphite anion type containing fluoride anions.

A further object of the invention is to provide an improved process of chemical nickel plating employing a bath of the nickel cation-hypophosphite anion type, which includes as "exaltants," both a soluble salt of a simple short chain saturated aliphatic dicarboxylic acid and a soluble fluoride.

These and other objects and advantages of the present invention will be understood from the foregoing and the following description, taken with the accompanying drawing, in which the single figure shows the variations in the weight of the nickel plating deposited upon standard test samples with changes in the initial pH of the bath and with different absolute concentrations of the fluoride anions therein.

In accordance with the process of the present invention, the article to be nickel plated, and normally formed of a catalytic material, is properly prepared by mechanically cleaning, degreasing and light pickling, according to the standard practice 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 fluoride anions, the pH of the bath having been, if necessary, adjusted to an optimum value by the addition of a suitable agent, 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 phosphorus). 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 stops, or until it is determined that the required thickness of the nickel coating has been deposited upon the steel object. Of course, the steel object is then

removed from the bath and rinsed off with water, and is then ready for use. In general, best chemical nickel plating results are obtained when the ratio (V/A) between the volume of the bath (cm^3) and the surface area of the object being plated (cm^2) is below 10.

With respect to the composition of the bath, it essentially comprises an aqueous acid solution containing nickel cations, hypophosphite anions, and fluoride anions, and may be formed by dissolving in a suitable acid-water solution, a soluble nickel salt, a soluble hypophosphite, and a soluble fluoride. For example, the nickel cations may be derived from nickel chloride (commercial grade); the hypophosphite anions may be derived from sodium, potassium, lithium, calcium, magnesium, strontium, barium, etc., hypophosphites, or various combinations thereof; and the fluoride anions may be derived from sodium, potassium, etc., fluorides. In passing, it is noted that certain alkaline cations that may be thus introduced in the bath appear to retard in the process the rate of nickel deposition with respect to other cations; for example, barium cations appear to retard the rate of nickel deposition with respect to sodium and potassium cations. Specifically, a suitable bath may be formed in an exceedingly simple manner by dissolving in a hydrochloric acid-water solution commercial nickel chloride, sodium hypophosphite and sodium fluoride. The desired pH of the bath is established by the introduction therein of additional hydrochloric acid, and is appropriately adjusted by the addition thereto of a weak alkali, preferably sodium bicarbonate. Also, it will be understood that the fluoride anions and some of the hydrogen cations may be derived by introducing hydrofluoric acid, instead of sodium fluoride, into the bath; although ordinarily hydrofluoric acid is more troublesome to handle than hydrochloric acid.

The terms "cation," "anion" and "ion" as employed herein include the total quantity of the corresponding elements that are present in the 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 bath.

For the purpose of demonstrating the exalting effect, with reference to the increase in the plating rate, of the fluoride anion additive, a series of comparative plating tests were conducted. In the first of these plating tests a steel sample was plated for 10 minutes in a simple aqueous acid bath of the nickel cation-hypophosphite anion type maintained at a temperature of 98°C . The bath employed in this first plating test comprised no buffer or exaltant and consisted essentially of nickel cations (0.09 mole/liter) derived from commercial nickel chloride, hypophosphite anions (0.225 mole/liter) derived from sodium hypophosphite, and enough water to produce a liter of solution, the initial pH of the bath being adjusted with hydrochloric acid to approximately 4.5. In this first plating test, the plating rate, expressed in $\text{gm./cm}^2/\text{min.}$, was 0.585×10^{-4} .

A second plating test was conducted under conditions identical to the first plating test, except that the bath was modified by the addition of fluoride anions (0.10 mole/liter) derived from sodium fluoride. In this second plating test, the plating rate, expressed in $\text{gm./cm}^2/\text{min.}$, was 3.58×10^{-4} . Accordingly, in the second plating test, the plating rate was increased, with respect to that of the first plating test, by over 500%; which circumstance clearly demonstrates the exalting effect of the fluoride anions; and moreover, the first and second plating tests clearly demonstrate that the exalting effect of the fluoride anions is not a result of interaction with organic additives (buffers and other exaltants), since the bath employed in the second plating test contained no organic additives.

A third plating test was conducted employing a steel sample for a time interval of 120 minutes and utilizing a bath identical to that of the second plating test, except that a small amount of an organic exaltant, sodium succinate (0.02 mole/liter) was added thereto. The plating rate obtained in the third plating test, expressed in $\text{gm./cm}^2/\text{min.}$, was 5.35×10^{-4} , which represents an increase of about 815% in the plating rate over that obtained in the first plating test, and a considerable increase in the plating rate over that obtained in the second plating test. Thus a comparison of the second and third plating tests demonstrates that the combination of the

fluoride anion and the succinate anion additives are productive of a composite exalting effect.

A fourth plating test was conducted upon a steel sample for ten minutes employing a bath maintained at a temperature of 98°C . This bath was substantially identical to that of the first plating test, except that it was modified by employing as an additive a buffer in the form of sodium citrate and a slightly different pH. More particularly, the bath included citrate anions (0.03 mole/liter) derived from sodium citrate; and the initial pH of the bath was 4.6 obtained by hydrochloric acid. In this fourth plating test, the plating rate, expressed in $\text{gms./cm}^2/\text{min.}$, was 1.32×10^{-4} . A fifth plating test identical to the fourth plating test was conducted, except that the bath was modified by the addition of fluoride anions (0.10 mole/liter) derived from sodium fluoride. In this fifth plating test, the plating rate, expressed in $\text{gms./cm}^2/\text{min.}$, was 3.18×10^{-4} . A comparison of the fifth plating test with the fourth plating test demonstrates that the exalting effect of the fluoride anion additive to the citrate bath was productive of an increase of 140% in the plating rate.

In order to demonstrate the increased plating rates that are obtained by employing the fluoride anion additive in a nickel cation-hypophosphite anion bath of the character of that disclosed in the Gutzeit and Krieg application, previously mentioned, two series of comparative plating tests were conducted, first without and then with the additive mentioned, and with variable initial pH. In each of these plating tests, a steel sample having an area of 20 cm^2 was plated for 60 minutes in 50 cc. of the bath at a temperature of 98°C . In the first series of these plating tests, the bath contained nickel cations (0.0704 mole/liter) derived from commercial nickel chloride; hypophosphite anions (0.225 mole/liter) derived from sodium hypophosphite; and acetate anions (0.120 mole/liter) derived from sodium acetate. In four of these plating tests of this first series, the initial pH were respectively: 5.01, 5.38, 5.79 and 6.33; and the respective weight gains, expressed in gm., were: 0.1832, 0.1952, 0.2064 and 0.2063. In the second series of these plating tests, the principal composition of the baths was identical to that of the baths employed in the first series of plating tests, except that each of the baths contained the fluoride anion additive (0.10 mole/liter) derived from sodium fluoride. In four of these plating tests of this second series, the initial pH were respectively: 4.53, 4.93, 5.34 and 6.35; and the respective weight gains, expressed in gm., were: 0.2262, 0.2486, 0.2645 and 0.2544. Accordingly, these two series of plating tests demonstrate that the combination of the fluoride anion additive and the acetate anion buffer are productive of a composite exaltation of the plating rate in a bath of the nickel cation-hypophosphite anion type. For example, in a bath of the character noted, at a pH of about 5.35, the weight gains of test samples were 0.1952 gm. of nickel without the fluoride anion addition, and 0.2685 gm. of nickel with the fluoride anion addition in the amount of only 0.10 mole/liter of fluoride anion, representing roughly 35% improvement in the nickel plating rate.

In order to demonstrate the increased plating rates that are obtained by employing the fluoride anion additive in a bath of the general character of that disclosed in the Gutzeit and Ramirez application previously mentioned, a further series of plating tests No. 1 to No. 13, inclusive, were conducted, employing certain variables in the compositions of the baths, as explained more fully hereinafter, and as set forth in the table appearing subsequently. First, it is noted that in plating test No. 1, the bath contained as an exaltant only the anions of the simple short chain saturated aliphatic dicarboxylic acid mentioned; whereas in plating tests Nos. 2 to 13, inclusive, the corresponding baths contained as exaltants not only the anions of the simple short chain saturated dicarboxylic acid mentioned but also fluoride anions. In each of plating tests Nos. 1 to 13, inclusive, 50 cc. of the plating bath was employed, and the nickel plating was deposited upon a steel sample having an area of 20 cm^2 during a test time interval of 60 or 66 minutes, as indicated in the table mentioned. Also, in each test, the V/A ratio between the volume of the plating bath in cm^3 and the surface area of the steel sample in cm^2 was 2.5. Further, in each test, the bath comprised 0.09 mole/liter of nickel cations derived

from commercial nickel chloride, 0.225 mole/liter of hypophosphite anions derived from sodium hypophosphite, and 0.06 mole/liter of succinate anions derived from sodium succinate. In the various baths, the principal variants were the contents of fluoride anions derived from sodium fluoride and the initial pH values thereof, as illustrated in the table:

Test No.-----	1	2	3	4	5	6	7	8	9	10	11	12	13
Mole/liter F ⁻ -----	None	0.10	0.10	0.10	0.10	0.10	0.15	0.15	0.15	0.15	0.15	0.225	0.405
Initial pH-----	4.60	4.06	4.50	5.00	5.50	5.94	5.01	5.32	5.68	6.18	6.82	4.60	4.60
Duration of test (mins.)-----	60	60	60	60	60	60	66	66	66	66	66	60	68
Weight gain (gms.)-----	0.0975	0.1387	0.2297	0.2495	0.2599	0.2643	0.2621	0.2625	0.2374	0.2445	0.2354	0.1544	0.1480
Sample appearance-----	(1)	(1)	(1)	(1)	(1)	(1)	(2)	(2)	(2)	(2)	(2)	(1)	(1)
Time to black prec. (mins.)-----	(4)	(4)	(4)	(4)	(4)	(4)	26	27	45	44	45	34	34

¹ Bright and smooth.

² Slightly rough.

³ Semi-bright.

⁴ Satin.

⁵ No. B. P.

In the drawing, the results of test No. 1 are plotted as the point "A"; the results of plating tests Nos. 2 to 6, inclusive, are plotted as the curve "B"; the results of plating tests Nos. 7 to 11, inclusive, are plotted as the curve "C"; and the results of plating tests Nos. 12 and 13 are respectively plotted as the points "D" and "E." In each case, the weight gain in grams of the standard test sample is plotted as the ordinate, and the initial pH of the bath is plotted as the abscissa. A comparison of the curve "B" with the point "A" dramatically illustrates that the addition of the exaltant comprising the fluoride anions to the otherwise identical bath produces the very remarkable increases in nickel plating rates. For instance, a comparison of plating tests Nos. 1 and 6 reveals that the nickel plating rate of the bath of plating test No. 6 comprises a 271% increase over the nickel plating rate of the bath of plating test No. 1, due substantially entirely to the addition of the fluoride anions in the small amount of 0.10 mole/liter in conjunction with the more favorable initial pH value of the bath. Also the curve "B" illustrates that the optimum value of the pH of the bath falls within the relatively narrow range 5.5 to 6.0. In each of plating tests Nos. 1 to 7, inclusive, it is noted that the nickel coating deposited upon the test sample was bright and smooth in appearance, and was otherwise highly satisfactory, as indicated by the table.

From the curve "C," it will be observed that while increased nickel plating rates were obtained in plating tests Nos. 7 to 11, inclusive, with respect to the point "A," corresponding to plating test No. 1, when the corresponding baths contained as an exaltant 0.15 mole/liter of fluoride anions, the corresponding nickel deposits were slightly rough, or at least only semi-bright; whereby the nickel deposits were not considered to be altogether satisfactory. In passing, it is noted when the nickel deposit upon the test sample is even slightly rough, the corresponding measurement of the weight of the deposit is considered to be unfavorably high by virtue of the small amounts of trapped "black precipitate." Accordingly, the curve "C" indicates that there is a definite upper limit to the maximum amount of exaltant in the form of fluoride anions that may be advantageously introduced into the plating bath. Specifically, when the plating bath contains the exaltant in the form of the fluoride anions in an amount somewhat in excess of 0.12 mole/liter, the stability of the plating bath is adversely affected, as indicated by the early formation of the "black precipitate" and the consequent production of slightly rough nickel deposits upon the test samples, as clearly indicated by plating tests Nos. 7 to 11, inclusive. Finally, plating tests Nos. 12 and 13, the results of which are respectively plotted at the points "D" and "E," demonstrate that when the amount of exaltant in the form of the fluoride anions in the baths is substantially increased above the content noted above, bright and smooth nickel deposits may still be obtained employing lower pH values of the baths, but that in these cases, the increase in the nickel plating rate is relatively small with respect to test No. 1, plotted as the point "A." Accordingly, it may be stated that an excess of the exaltant in the form of the fluoride anions in the bath above the content of about 0.12 mole/liter is detrimental as the excess either impairs the stability of the bath, as indicated by plating tests Nos. 7 to 11, inclu-

sive, or the excess contributes little to increase the nickel plating rate, as indicated by plating tests Nos. 12 and 13.

In plating according to the present invention, the exaltant in the form of the succinate anions is not "used up" in the plating operation, but forms slightly dissociated succinic acid, and likewise the exaltant in the form of the fluoride anion is not "used up" in the plating operation,

but forms strongly dissociated hydrofluoric acid so that an exhausted plating bath can be regenerated by readjusting the nickel cation content and the hypophosphite anion content and by neutralizing the acids to the proper pH value by means of a weak alkali, such as sodium bicarbonate. Accordingly, this technique has the advantage that a brighter nickel coating at a greatly increased plating rate may be produced, whereby the time interval required to produce a nickel coating of a predetermined thickness upon a catalytic object is greatly minimized.

In view of the foregoing, it is apparent that there has been provided an improved process of plating a catalytic material with nickel and an improved bath of the nickel cation-hypophosphite anion type for use in the process, wherein the plating rate of the process is greatly increased with respect to prior processes of this character, by virtue of the incorporation in the bath of the exaltant in the form of a small quantity of soluble fluoride.

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. The process of chemically plating with nickel a solid body essentially comprising an element selected from the group consisting of copper, silver, gold, aluminum, iron, cobalt, nickel, palladium and platinum, which comprises contacting said body with a bath consisting essentially of an aqueous solution of a nickel salt and a hypophosphite and a salt of a simple short chain saturated aliphatic dicarboxylic acid and a fluoride, wherein the absolute concentration of fluoride ions in said bath expressed in mole/liter is between 0.01 and 0.12.

2. The process set forth in claim 1, wherein the ratio between nickel ions and hypophosphite ions in said bath expressed in molar concentrations is between 0.25 and 1.60, wherein the absolute concentration of hypophosphite ions in said bath expressed in mole/liter is between 0.15 and 1.20, and wherein the absolute concentration of dicarboxylic ions in said bath is at least two carboxyl groups for every nickel ion that can be deposited.

3. The process set forth in claim 2, wherein the initial pH of said bath is in the approximate range 4.5 to 6.5.

4. The process of chemically plating with nickel a solid body essentially comprising an element selected from the group consisting of copper, silver, gold, aluminum, iron, cobalt, nickel, palladium and platinum, which comprises contacting said body with a bath consisting essentially of an aqueous solution of a nickel salt and a hypophosphite and a succinate and a fluoride, wherein the absolute concentration of fluoride ions in said bath expressed in mole/liter is between 0.01 and 0.12.

5. The process set forth in claim 4, wherein the ratio between nickel ions and hypophosphite ions in said bath expressed in molar concentrations is between 0.25 and 1.60, wherein the absolute concentration of hypophosphite ions in said bath expressed in mole-liter is between 0.15 and 1.20, and wherein the absolute concentration of succinate ions in said bath expressed in mole/liter is at least 0.05.

6. A bath for the chemical plating of a catalytic material with nickel consisting essentially of an aqueous solu-

tion of a nickel salt and a hypophosphite and a salt of a simple short chain saturated dicarboxylic acid and a fluoride, wherein the absolute concentration of fluoride ions in said bath expressed in mole/liter is between 0.01 and 0.12.

7. The bath set forth in claim 6, wherein the ratio between nickel ions and hypophosphite ions in said bath expressed in molar concentrations is between 0.25 and 1.60, wherein the absolute concentration of hypophosphite ions in said bath expressed in mole/liter is between 0.15 and 1.20, and wherein the absolute concentration of dicarboxylic ions in said bath is at least two carboxyl groups for every nickel ion that can be deposited.

8. The bath set forth in claim 7, wherein the initial pH of said bath is in the approximate range 4.5 to 6.5.

9. A bath for the chemical plating of a catalytic material with nickel consisting essentially of an aqueous acid solution of nickel chloride, sodium hypophosphite, sodium succinate and sodium fluoride, wherein the absolute concentration of fluoride ions in said bath expressed in mole/liter is between 0.01 and 0.12, and wherein the initial pH of said bath is in the approximate range 4.5 to 6.5.

10. The process of chemically plating with nickel a solid body essentially comprising an element selected from the group consisting of copper, silver, gold, aluminum, iron, cobalt, nickel, palladium and platinum, which comprises contacting said body with a bath consisting essentially of an aqueous solution of a nickel salt and a hypophosphite and a fluoride, wherein the absolute concentra-

tion of fluoride ions in said bath expressed in mole/liter is between 0.01 and 0.12.

11. A bath for the chemical plating of a catalytic material with nickel consisting essentially of an aqueous solution of a nickel salt and a hypophosphite and a fluoride, the absolute concentration of fluoride ions in said bath expressed in mole/liter being between 0.01 and 0.12.

12. A bath for the chemical plating of a catalytic material with nickel consisting essentially of an aqueous solution of a nickel salt and a hypophosphite and a buffer in the form of a salt of an organic acid and an exaltant in the form of a fluoride, wherein the absolute concentration of fluoride ions in said bath expressed in mole/liter is between 0.01 and 0.12.

13. A bath for the chemical plating of a catalytic material with nickel consisting essentially of an aqueous solution of a nickel salt and a hypophosphite and an exaltant, said exaltant consisting essentially of a salt of an organic acid and a fluoride, wherein the absolute concentration of fluoride ions in said bath expressed in mole/liter is between 0.01 and 0.12.

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