

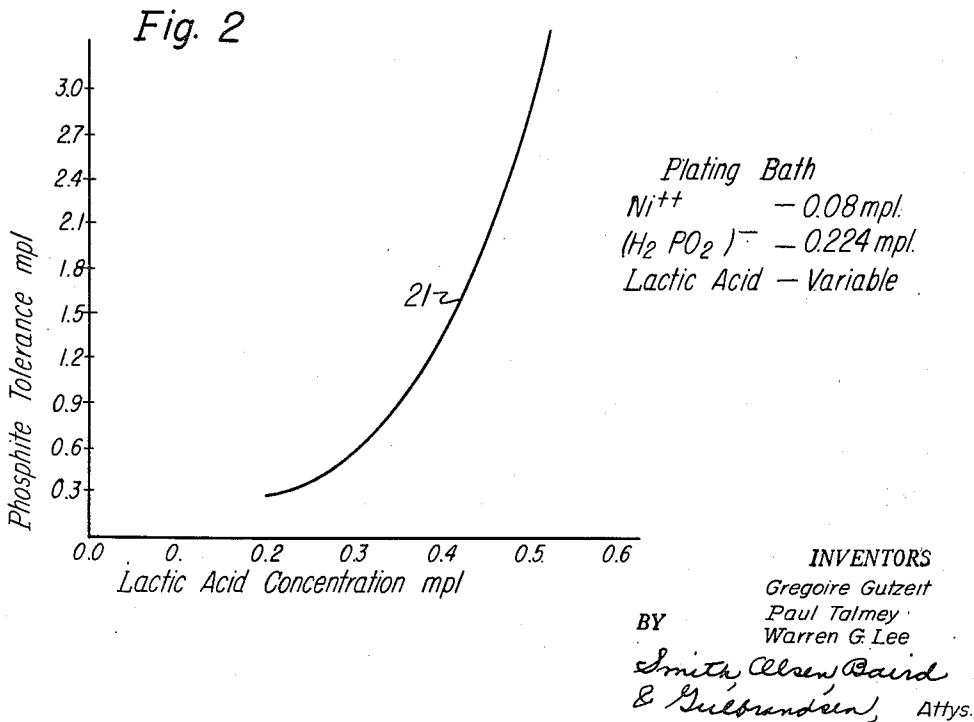
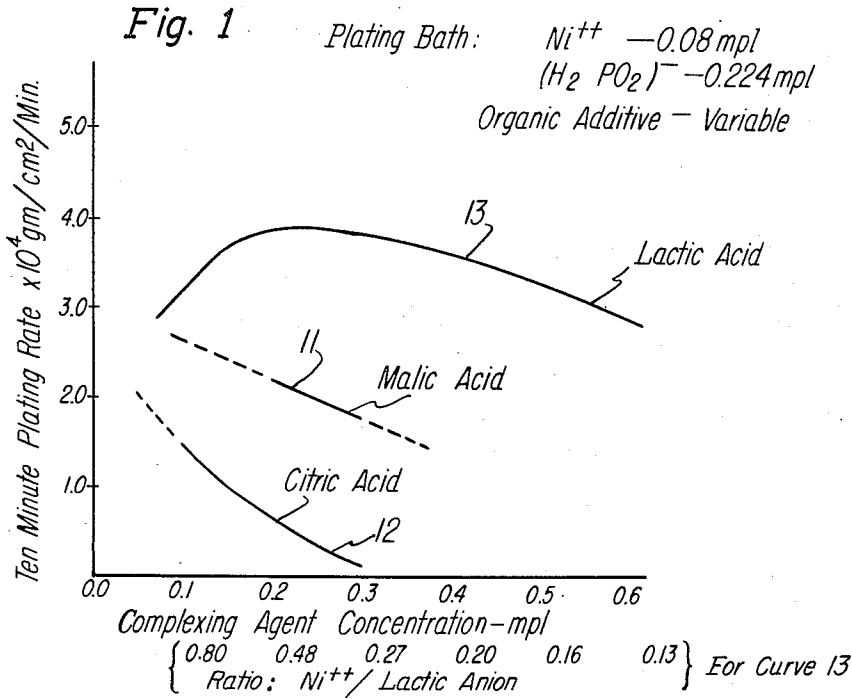
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G. GUTZEIT ET AL

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CHEMICAL NICKEL PLATING PROCESSES AND BATHS THEREFOR

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CHEMICAL NICKEL PLATING PROCESSES AND BATHS THEREFOR

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7 Claims. (Cl. 117—130)

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 more particularly to such processes and baths involving a continuous system of the character of that disclosed in U. S. Patent No. 2,658,839, granted on November 10, 1953, to Paul Talmey and William J. Crehan. This application is a continuation-in-part of the copending application of Gregoire Gutzeit, Paul Talmey and Warren G. Lee, Serial No. 478,492, filed December 29, 1954; and the last-mentioned application is, in turn, a continuation-in-part of the abandoned application of Gregoire Gutzeit, Paul Talmey and Warren G. Lee, Serial No. 376,968, filed August 27, 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 ions, in the presence of an excess of nickel cations.

In a batch plating process, 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.

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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. Any fine solid particles suspended in the plating bath, or adhering to the walls of the plating vessel, at the plating temperature, initiate the formation of the black precipitate by acting as nuclei.

In a continuous plating process the reactions are maintained substantially at their initial rates by the regeneration of the plating bath, i. e., by the adding thereto of soluble nickel-containing and hypophosphite-containing reagents, as well as an alkali for pH control; however, the problem of preventing the formation of black precipitate in the plating bath and the consequent decomposition thereof is the same as that previously mentioned. Moreover, another practical difficulty is encountered in the continuous plating process that is not encountered in the batch plating process in that there is a considerable build-up of the by-product phosphite therein as time proceeds and as a consequence of the cycling of the bath. More particularly, while nickel hypophosphite is readily soluble in an aqueous solution, nickel phosphite is much less soluble in an aqueous solution; whereby there is a tendency, as the phosphite concentration of the plating bath builds-up, for nickel phosphite to be precipitated therein, and thereby provide the solid particles that serve as nuclei for the formation of the black precipitate therein, previously mentioned. In passing, it is noted that the initiation of the precipitation of nickel phosphite in the plating bath is indicated by turbidity thereof, visible in a "Tyndall beam."

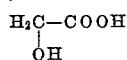
In carrying out the chemical nickel plating process on a commercial scale, the continuous system disclosed in the Talmey and Crehan patent may be employed; which system involves periodic or continuous regeneration of the plating bath by the addition thereto of appropriate ingredients for the purpose of maintaining substantially constant the composition of the bath, as previously noted. More specifically in this system, there are provided a plating chamber and a reservoir; preferably one portion of the plating solution is stored at a relatively low temperature well below the boiling point thereof in the reservoir; and preferably 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 such time interval soluble reagents are added to the solution in the reservoir to maintain in the bath in the plating chamber during such 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 consists essentially of adding thereto appropriate amounts of

soluble nickel-containing and hypophosphite-containing reagents, as well as an alkali for pH control, as previously noted.

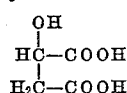
In a plating bath of the nickel cation-hypophosphite anion type, the threshold of precipitation of the insoluble nickel phosphite begins when the $(\text{HPO}_3)^-$ concentration attains a value above the solubility of its simple nickel salt or its double nickel-alkali salt; i. e., above 0.03 to 0.07 m. p. l.; and in order to obviate this defect, there are disclosed in the previously mentioned abandoned application of Gregoire Gutzeit, Paul Talmey and Warren G. Lee, Serial No. 376,968, filed August 27, 1953, modified plating baths of the nickel cation-hypophosphite anion type containing both complexing agents and exalting additives. In these plating baths, the complexing agents serve to "tie-up" the nickel ions, thereby preventing precipitation of nickel phosphite until a high concentration of phosphite ions (about 1.0 m. p. l.) is reached in the plating bath in the continuous plating system; and the exalting additives serve to increase the normally low plating rates of these baths containing the complexed nickel ions. Among the complexing agents disclosed, those forming water-soluble chelates are most efficient; and, within that group, the hydroxycarboxylic acids have several practical advantages, such as: ready availability, low price and high buffering capacity.

More particularly, it is apparent that if the nickel ions are very strongly "tied-up" (i. e., if the chelate is very stable), they are actually removed from the plating process, and no longer available for deposition; whereas, if the complex bond energy is at a lower level, an equilibrium is reached between the dissociation rate of the nickel complex ion and the deposition rate of metallic nickel. The stability of nickel chelates with various hydroxycarboxylic acid additives is not only a function of the number of hydroxyl and carboxyl groups in the acid molecule, but also of molecular structure and steric factors, as may be better appreciated from a consideration of the structure of the more common of these acids:

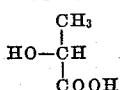
Glycollic acid (hydroxyacetic acid)



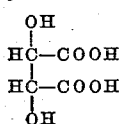
Malic acid (monohydroxysuccinic acid)



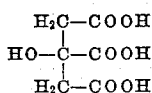
Lactic acid (alpha-hydroxypropionic acid)



Tartaric acid (dihydroxysuccinic acid)



Citric acid



It is obvious that tartaric acid having two hydroxyl and two carboxyl groups will give the most stable complex; and it is also normal that glycollic and lactic acid complexes will show the least stability, both being monohydroxy-monocarboxylic acids. On the other hand, the lactic chelate of nickel is less stable than the glycollic complex; and this is due to a structural factor, i. e., the presence of an additional methyl group (CH_3). Moreover, chelate stability is also determined by the number of carboxyl groups in the molecule so that the nickel-

malic acid complex (a monohydroxy-dicarboxylic compound) is more stable than the corresponding chelates of both glycollic and lactic acids (monohydroxy-monocarboxylic acids), while the citric acid complex is the most stable of all.

Generally, if hydroxycarboxylic acids instead of a non-chelating buffer) are added to a chemical plating bath of the nickel cation-hypophosphite anion type in continuous operation, the resulting plating rate will be an inverse function of chelate stability; however, on the other hand, the more stable the nickel complex, the higher a phosphite ion concentration can be built-up before precipitation of nickel phosphite occurs.

For the above reasons, the plating baths disclosed in the Gutzeit, Talmey and Lee application, Serial No. 478,492 comprise relatively stable complexing agents in combination with powerful exalting additives dicarboxylic acids, aminocarboxylic acids and certain monocarboxylic acids) to increase the normally low plating rates of these baths.

The present invention is predicated upon the discovery that in a plating bath of the nickel cation-hypophosphite anion type described, while the nickel chelating function of lactic acid is directly proportional to the concentration thereof in the bath, the effect thereof upon the plating rate of the bath is not inversely proportional to the concentration thereof as is the general case with the other hydroxycarboxylic acids); rather within a given range of concentration, lactic acid is a definite exaltant in the bath, substantially increasing the plating rate thereof. The mechanism of this exalting effect is not fully understood, but the effect is very pronounced; and it is most unusual and entirely unexpected that lactic acid unlike the other common hydroxy-carboxylic acids) should possess this particular characteristic.

The general composition of a plating bath in accordance with the present invention essentially comprises an aqueous solution of a nickel salt, a hypophosphite, and lactic acid or a salt thereof; wherein the absolute concentration of hypophosphite anions in the bath is in the range 0.15 to 1.20 m. p. l., the ratio between nickel cations and hypophosphite anions in the bath expressed in molar concentrations is within the range 0.25 to 1.60, and the ratio between nickel cations and lactic ions in the bath expressed in molar concentrations is within the range 0.15 to 0.35. The pH of the bath is normally in the range 4.0 to 5.6; and the bath is employed in the plating chamber of the continuous plating system at a temperature above 90°C ., ordinarily slightly below the boiling point thereof and at about 97° to 99°C . The bath has a nickel plating rate of at least 1 mil/hour (0.001"/hour), or expressed in c. g. s. units of at least 3.5×10^{-4} gm./cm.²/min.; and no precipitation of nickel phosphite takes place therein even at a phosphite ion concentration in some cases very close to 1.0 m. p. l. Further, the plating appearance on both metals and non-metals is excellent (bright, smooth and non-porous); and adhesion of the nickel plating on both metallic and non-metallic bodies is excellent (no flaking of the nickel coating in bending, abrading and shock tests).

In accordance with the process of the present invention, the plating bath of the composition specified is preferably employed in the continuous plating system of the character previously described, whereby the lactic acid additive is present therein in the optimum range specified so that it serves both the complexing or chelating function with respect to the nickel ions and also the function of increasing the otherwise relatively low plating rate of the bath. This complexing of the nickel cations in the plating bath prevents the formation of precipitated phosphite therein, thereby rendering the bath of exceedingly long life in spite of the build-up of phosphite ions therein to a concentration even in excess of one molar. This complex of nickel in the plating bath is water-soluble and of medium stability resulting in a bond strong enough

to prevent the nickel cations from forming insoluble nickel compounds, but having a stability constant low enough to release the nickel cations required for the nickel plating operation to effect a plating rate of the bath of at least 3.5×10^{-4} gm./cm.²/min., as previously explained.

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 (clarity of solution) than heretofore, thereby rendering the process more desirable from a commercial standpoint.

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

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-hypophosphite anion type of the character specified, wherein the lactic acid substantially completely complexes all of the nickel cations in the bath and substantially increases the plating rate thereof to at least 3.5×10^{-4} gm./cm.²/min.

A further object of the invention is to provide an improved nickel plating process of the continuous type involving an improved plating bath of the nickel cation-hypophosphite anion type, so that the useful life of the bath is greatly extended in that it remains clear, notwithstanding the presence therein of a phosphite anion concentration approaching one molar.

A still further object of the invention is to provide an improved nickel plating bath of the character described that involves a novel range of lactic ion addition.

These and other objects and advantages of the invention pertain to the particular arrangement of the steps of the plating process and of the composition of the plating bath, as will be understood from the foregoing and following description, taken in connection with the accompanying drawing, in which:

Figure 1 is a series of curves illustrating the relationship between the plating rates of a number of plating baths of the nickel cation-hypophosphite anion type and the concentrations of several common hydroxy-carboxylic acids contained therein; and

Fig. 2 is a curve illustrating the relationship between phosphite tolerance of a plating bath of the type mentioned and the concentration of lactic acid contained therein.

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 mechanical cleaning, degreasing and light pickling substantially in accordance with standard practices in electroplating processes. For example, in the nickel plating of a steel article, it is customary to clean the rust and mill scale from the article, to degrease the article and then lightly to pickle the article in a suitable acid, such as hydrochloric acid. The article is then immersed in a suitable volume of the plating bath containing the proper proportions of nickel cations, hypophosphite anions and lactic ions, 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 article and escape in a steady stream from the plating bath, while the surface of the steel article is slowly coated with metallic nickel (containing some phosphorus). The steel article is subsequently removed from the bath after an appropriate time interval corresponding to the required thickness of the nickel coating deposited thereon that

is desired; and ultimately the steel article is rinsed off with water, so that it is ready for use.

In the plating bath, the nickel cations may be derived from nickel chloride, nickel sulfate, etc., or various combinations thereof; the hypophosphite anions may be derived from sodium hypophosphite, potassium hypophosphite, etc., or various combinations thereof; and the lactic ions may be derived from lactic acid, or various lactates, or various combinations thereof. The desired pH of the bath is established by the eventual introduction thereto of hydrochloric acid or an alkali, such as sodium hydroxide, sodium carbonate or 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.

In order to demonstrate the remarkable advantages of the plating bath of the present invention, first and second series of reference plating tests (10 minute rate tests) were conducted employing standard steel samples that had been given a standard pretreatment. More particularly, steel samples (Dayton Rodgers) of 20 cm.² total area were vapor degreased, cleaned by an alkaline soak and lightly pickled in 1:1 hydrochloric acid. The steel samples thus prepared were then plated at $98 \pm 1^\circ$ C. in 50 cc. of different plating baths each containing nickel cations (as nickel sulfate) 0.08 m. p. l. hypophosphite anions (as sodium hypophosphite) 0.224 m. p. l. and the indicated amounts of organic additives (acetate ions or hydroxycarboxylic ions), the latter being equivalent with respect to their hydroxyl groups, and the pH being adjusted with NaOH to about 4.7.

The results of the first series of reference plating tests employing sodium acetate are shown in the table below:

TABLE I

Acetic anions, m. p. l.	0.16	0.30
Weight gain (gm.)	0.0993	0.1018
Plating rate, $R \times 10^4$ gm./cm. ² /min.	4.97	5.09
Initial pH	4.67	4.70
Final pH	4.00	4.31
Bath appearance	(1)	(1)
Plating appearance	(2)	(2)

¹ Clear.

² Smooth and dull.

The results of the second series of reference plating tests employing various hydroxycarboxylic acids, and one without an organic additive for reference purposes are shown in the table below:

TABLE II

Hydroxycarboxylic Anions..	Glycollic	Malic	Tartaric	Citric	None
Hydroxyl groups	1	1	2	1	-----
Concentration, m. p. l.	0.3	0.3	0.15	0.3	-----
Weight gain (gm.)	0.0502	0.0357	0.0305	0.0032	0.0245
Plating rate, $R \times 10^4$ gm./cm. ² /min.	2.51	1.79	1.53	0.16	1.22
Initial pH	4.68	4.68	4.72	4.67	4.70
Final pH	4.23	4.55	4.28	4.67	2.80
Bath appearance	(1)	(1)	(1)	(1)	(1)
Plating appearance	(2)	(2)	(2)	(2)	(2)

¹ Clear.

² Smooth and bright.

From a comparison of the last plating bath in Table II (the bath containing no organic additive) with the two plating baths in Table I (the baths containing sodium acetate), it will be appreciated that the acetate anions in the baths serve as an exaltant; however, it is noted that the acetic anion is not a very satisfactory additive since the boiling point of acetic acid is 118.1° C., whereby its vapor tension at plating temperatures is very high with the resulting rapid loss due particularly to "steam volatilization."

7 zation" (steam entrainment). Moreover, in these 10-minute rate tests, the plating rates are much higher than in comparable 1-hour rate tests, but they are valid for dynamic (or cyclic operation), in which the bath is continuously circulated and regenerated. While the plating baths of Table I have high plating rates, these baths are totally unsuitable for continuous operation in that they lack stability, black precipitate being formed therein when the phosphite concentration reaches a value as low as 0.03 m. p. l. in the baths.

Referring now to the first four plating baths of Table II (the baths respectively containing glycollic, malic, tartaric and citric anions), it will be appreciated that the plating rates thereof are very low, particularly with malic, tartaric and citric anions, the citrate being the best buffer (no pH change in 10-minutes). The low plating rate of the fifth plating bath of Table II (the bath containing no organic additive) is, of course, due to the rapid rise in hydrogen ion concentration (reduction in pH), there being no buffering action so that the reducing efficiency of the hypophosphite is rapidly decreased, plating stopping altogether at a pH below about 3.0.

Then a third series of reference plating tests were conducted under conditions identical to the second series of reference plating tests described above, except that in the plating baths the amounts of the hydroxycarboxylic acid additives were selected so that they were equivalent with respect to the carboxyl groups. The results of this third series of reference plating tests are shown in the table below:

TABLE III

Hydroxycarboxylic Anions	Glycollic	Malic	Tartaric	Citric
Carboxyl groups.....	1	2	2	3
Concentration, m. p. l.....	0.3	0.15	0.15	0.1
Weight gain (gm.).....	0.0502	0.0470	0.0305	0.0309
Plating rate, $R \times 10^4$ gm./cm. ² /min.....	2.51	2.35	1.53	1.55
Initial pH.....	4.68	4.71	4.72	4.68
Final pH.....	4.23	4.35	4.28	4.42
Plating appearance.....	(1)	(1)	(1)	(1)

¹ Smooth and bright.

From a comparison of Tables II and III, it will be observed that the results of the second and third series of reference plating tests were substantially identical.

Then a fourth series of reference plating tests were conducted under conditions identical to the second and third series of reference plating tests described above, except that in the plating baths only the chelating agents, malic acid and citric acid, were involved and the con-

centration thereof was varied in the different baths. The results of this fourth series of reference plating tests are shown in the table below:

TABLE IV

Hydroxycarboxylic Anions	Malic		Citric		
	0.15	0.30	0.1	0.2	0.3
Concentration, m. p. l.....	0.0470	0.0357	0.0309	0.0125	0.032
Weight gain (gm.).....	2.35	1.79	1.55	0.63	0.16
Plating rate, $R \times 10^4$ gm./cm. ² /min.....					

8 An examination of Table IV reveals that an increase in the concentration of chelating agent (hydroxycarboxylic acid) decreases the plating rate almost as a linear function of reagent concentration and complex stability; which relationship is graphically illustrated by the curves 11 and 12 in Fig. 1, respectively corresponding to malic acid and citric acid.

In this connection, it is noted that for complete stoichiometric complexing, each mole of nickel requires at least two carboxyl groups and at least one hydroxyl group. Thus two moles of glycollic acid or lactic acid are necessary per mole of nickel, while one mole of tartaric acid or malic acid will chelate one mole of nickel. On the other hand, two moles of citric acid will complex three moles of nickel. Accordingly, in these plating baths of the nickel cation-hypophosphite anion type, the amounts of hydroxycarboxylic acids sufficient to achieve complete stoichiometric complexing of the nickel are set forth in the table below:

TABLE V

Hydroxycarboxylic Anions	Glycollic	Lactic	Malic	Tartaric	Citric
Carboxyl groups.....	1	1	2	2	3
Mol/l. needed to complex 0.08 m. p. l. Ni.....	0.16	0.16	0.08	0.08	0.053

As disclosed in the previously-mentioned application of Gutzeit, Talmey and Lee, Serial No. 478,492, plating baths containing hydroxycarboxylic acids in the concentrations indicated in Table V above give continuous plating rates (without the addition of exaltants) of only about 1.80×10^{-4} gm./cm.²/min.

Now it has been discovered that by increasing the proportion of lactic acid in these plating baths of the nickel cation-hypophosphite anion type (or more precisely a ratio between nickel cations and lactic acid anions of about 1:4), there results both a relatively high phosphite tolerance (almost one molar) and a plating rate in excess of 3.5×10^{-4} gm./cm.²/min. (corresponding to 1 mil/hour).

In another plating test, conducted under conditions identical to the second and third series of reference plating tests described above, a plating bath containing lactic acid in the concentration noted immediately above was employed; and the results of this plating test, together with a recapitulation of the results of the tests of the second and third series of reference plating tests are set forth in the table below:

TABLE VI

Hydroxycarboxylic Anions	Glycollic	Malic	Tartaric	Citric	Lactic	
Concentration, m. p. l.....	0.30	0.15	0.30	0.15	0.10	0.30
Weight gain (gm.).....	0.0502	0.0470	0.0357	0.0305	0.0309	0.0032
Plating rate, $R \times 10^4$ gm./cm. ² /min.....	2.51	2.35	1.79	1.53	1.55	0.16
Initial pH.....	4.68	4.71	4.68	4.72	4.68	4.67
Final pH.....	4.23	4.35	4.55	4.28	4.42	4.67
Bath appearance.....	(1)	(1)	(1)	(1)	(1)	(1)
Plating appearance.....	(2)	(2)	(2)	(2)	(2)	(2)

¹ Clear.

² Smooth and bright.

Accordingly, from Table VI, it will be observed that lactic acid (a weak chelating agent) has the advantages inherent to all hydroxycarboxylic anions as far as preventing phosphite precipitation is concerned, and in addition thereto the function of an exaltant. Further, the alkali salts of lactic acid (the lactates) are good buffers in the proper pH range.

A further series of plating tests were conducted under conditions identical to the second and third series of reference plating tests described above, except that in the plating baths variable concentrations of lactic acid anions

were employed. The results of these plating tests are set forth in the table below:

TABLE VII

Lactic anion concentration, m. p. l.	0.08	0.16	0.24	0.30	0.40	0.60
Weight gain (gm.)	0.0563	0.0759	0.0791	0.0706	0.0692	0.0602
Plating rate, $R \times 10^4$ gm./cm. ² /min.	2.82	3.80	3.96	3.53	3.46	3.01
Initial pH	4.67	4.69	4.63	4.73	4.68	4.65
Final pH	3.32	3.63	3.87	4.02	4.17	4.37
Bath appearance	(¹)	(¹)	(¹)	(¹)	(¹)	(¹)
Plating appearance	(²)	(²)	(²)	(²)	(²)	(²)
Phosphite tolerance in m. p. l.	0.18	0.35	0.55	1.40	0.20	0.13
Ni ⁺⁺ /lactic ion	1.00	0.50	0.33	0.27	0.20	0.13

¹ Clear.

² Smooth and bright.

The results of these plating tests are represented graphically by the curve 13 in Fig. 1, employing the data of Table VII above; whereby the relationship between the plating rate and the concentration of lactic acid is unique in that there is a definite maximum plating rate with Ni⁺⁺/lactic ion ratios at about 1:3.

ing rate is exalted by an increased concentration of lactic acid in the plating bath.

As is usual with chemical nickel plating baths of the buffered nickel cation-hypophosphite type, the plating rate is a function of pH; and in order to demonstrate this characteristic, still another series of plating tests were conducted employing steel samples (Dayton Rodgers Shimstock) of 20 cm.² total area that had been vapor degreased, electrocleaned and lightly pickled in dilute hydrochloric acid. These plating tests were run for ten and sixty minutes at 98° C. $\pm 1^\circ$ C. in 50 cc. of the plating bath having the following fundamental composition:

Nickel ion	0.08 m. p. l. (NiSO ₄ ·6H ₂ O).
Hypophosphite ion	0.225 m. p. l. (NaH ₂ PO ₂).
Lactic acid	0.40 m. p. l. (lactic acid).

In these baths, the relatively high concentration of lactic ions is necessary for stability (prevention of formation of black precipitate) at elevated pH values employed in the plating tests; and in the plating tests, the pH of the baths were adjusted with NaOH. The results of these plating tests are shown in the table below:

TABLE VIII

Duration of test, min.	10					60				
	Initial pH	4.5	5.0	5.5	6.0	6.5	4.5	5.0	5.5	6.0
Final pH	4.0	4.0	4.1	4.1	4.1	3.8	3.9	3.95	4.0	4.0
Weight gain (gm.)	0.0699	0.0762	0.0826	0.0832	0.0851	0.1862	0.1920	0.1928	0.1939	0.1844
Plating rate, $R \times 10^4$ gm./cm. ² /min.	3.5	3.81	4.13	4.12	4.26	(¹)	(¹)	(¹)	(¹)	(¹)
Plating appearance	(¹)	(¹)	(¹)	(¹)	(¹)	(¹)	(¹)	(¹)	(¹)	(¹)

¹ Bright and smooth.

Furthermore, the phosphite tolerances in m. p. l. of these plating baths of Table VII are illustrated graphically by the curve 21 in Fig. 2; whereby it is apparent that the phosphite tolerance thereof increases disproportionately with an increase in the lactic acid concentration therein.

Also in this connection, it is pointed out that a substantially identical plating bath containing 0.30 m. p. l. of acetic anions has a phosphite tolerance of only 0.05 m. p. l.; whereas a substantially identical plating bath containing as little as 0.10 m. p. l. of citric acid has a phosphite tolerance in excess of 2.0 m. p. l.

Accordingly, it will be appreciated from a study of the data of Table VII, together with the curve 13 of Fig. 1 and the curve 21 of Fig. 2, that the maximum plating rate is obtained when all of the nickel has been complexed and enough additional lactic anion is present to form a mono-heteropolyacid with the hypophosphite radical (i. e., one additional mole), while the phosphite tolerance is strictly a function of available excess of chelating agent. However, in order to obtain optimum overall results in a continuous plating system, it is not possible to take advantage of the maximum plating rate (which occurs when the Ni⁺⁺/lactic ion ratio is about 1:3), but a compromised value for the Ni⁺⁺/lactic ion ratio has to be chosen so that the plating rate remains above 3.5×10^{-4} gm./cm.²/min., while the phosphite tolerance is as high as possible. This optimum region, based upon both of the considerations mentioned immediately above, is around a Ni⁺⁺/lactic ion ratio of about 1:(5 \pm 1), or expressed numerically about 0.15 to 0.25. However, the bath may contain lactic anions in the approximate range 0.25 to 0.60 m. p. l.

The mechanism of the combination complexing and exalting effects of lactic acid in the plating bath is not altogether understood as it is entirely different from that of any other hydroxycarboxylic acid with reference to the plating rate. In other words, instead of depressing the plating rate directly in proportion to concentration, as is the normal characteristic of other common hydroxycarboxylic acids, there is a definite optimum range in which the plat-

From Table VIII, it will be observed that a maximum plating rate is obtained around a pH of 6.0; however, in a continuous plating operation, phosphite precipitation takes place at a lower concentration of (HPO₃)⁻⁻⁻ at lower hydrogen ion concentrations; and moreover adhesion to the base metals is very superior at pH values below 5.0. For these particular reasons, the preferred pH is between 4.4 and 5.6 despite a lower plating rate. However, the bath is useful over the relatively wide approximate pH range 4.0 to 5.6.

In these plating baths, it is, of course, permissible to vary the nickel cation and hypophosphite anion concentrations within limits, provided the Ni⁺⁺/lactic anion ratio remains within the indicated optimum range of about 1:(5 \pm 1); the absolute concentration of hypophosphite ions in the bath, expressed in mole/liter, may be within the range 0.15 to 1.20; and the ratio between nickel ions and hypophosphite ions in the bath, expressed in molar concentrations, may be within the range 0.25 to 1.60.

In order further to illustrate the practical range of the Ni⁺⁺/lactic anion ratio, companion plating tests were conducted under conditions identical to those previously described in 10-minute rate tests employing two baths as follows:

Bath I

Nickel ion	0.0675 m. p. l.
Hypophosphite ion	0.225 m. p. l.
Lactic acid	0.300 m. p. l.
pH	4.80 (NaOH).
Ni ⁺⁺ /lactic ion	0.24

Bath II

Nickel ion	0.0675 m. p. l.
Hypophosphite ion	0.225 m. p. l.
Lactic acid	0.400 m. p. l.
pH	4.75 (NaOH).
Ni ⁺⁺ /lactic ion	0.17.

In these companion plating tests, the respective plating rates were 4.21 for Bath I and 3.84 for Bath II (expressed

in $R \times 10^{-4}$ gm./cm.²/min.); and the phosphite tolerance (using C. P. $\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$) was better than 0.9 m. p. l. of $(\text{HPO}_3)^-$ — for Bath I.

In a continuous plating system, a plating test was performed involving a number of steel samples prepared in the manner previously explained and utilizing a similar plating bath having the following initial composition:

Bath III

Nickel ion..... 0.07 m. p. l. (as nickel sulfate).
Hypophosphite ion..... 0.225 m. p. l. (as sodium hypophosphite).
Lactic ion..... 0.300 m. p. l. (as lactic acid).

The initial pH of Bath III was adjusted to 4.55 with caustic soda; and at the conclusion of the dynamic run, it was determined that the average plating rate upon the samples was 0.9 mil./hour, that the hypophosphite utilization was the usual 33.33%, and that the phosphite tolerance was 0.953 m. p. l. The plating was analyzed as 90.5% nickel and 9.2% phosphorus; the hardness of the plating was from 500 to 600 Vickers number, with 70% of the samples being 537 V.

Then in the continuous plating system, a similar plating test was performed involving a number of cycles of circulation of the body of plating solution and including periodic regeneration of the plating bath in the reservoir exteriorly of the plating chamber, as disclosed in the previously mentioned Talmey and Crehan patent. In this plating test, a number of cold rolled steel samples (1 $\frac{3}{4}$ " x 6" x 14 ga.) were employed that had been subjected to a pretreatment including vapor degreasing, alkaline soaking and pickling in 2:1 hydrochloric acid. In this plating test, the initial composition of the plating bath was as follows:

Bath IV

Nickel ion..... 0.08 m. p. l. (as nickel sulfate).
Hypophosphite ion..... 0.23 m. p. l. (as sodium hypophosphite).
Lactic ion..... 0.30 m. p. l. (as lactic acid).

The initial pH of plating Bath IV, was adjusted to 4.50 with caustic soda; and the specific results of this continuous plating test are set forth in the table below:

TABLE IX

Cycle No.....	1	2	3	4	5	6	7	8	9	10
Total weight gain (gm.).....	5.0	5.0	4.7	4.0	3.6	2.6	2.6	2.80	2.95	3.00
Plating rate, $R \times 10^4$ (gm./cm. ² /min.).....	3.08	3.13	2.95	2.71	2.44	3.90	3.90	3.45	3.70	3.76
Plating rate (mil./hr.).....	0.88	0.89	0.84	0.77	0.70	1.11	1.11	0.99	1.06	1.07
Soln. flow rate (cc./min.).....	105	105	105	105	105	105	105	105	105	105
Plating time (min.).....	56	55	55	51	51	46	46	56	55	55
Initial pH.....	4.50	4.51	4.50	4.50	4.51	4.50	4.50	4.50	4.50	4.50
Ni added (gm.) (as $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$).....	4.65	4.65	4.37	3.72	3.24	2.40	2.40	2.60	2.79	2.79
NaH_2PO_3 added (gm.).....	24	24	23.6	20.0	17.3	15.6	15.6	14.0	14.5	14.5
NaOH added (gm.).....	6.3	6.3	5.9	5.0	4.3	3.9	3.9	3.1	3.6	3.6
Additive (p. p. m.) Pb^{++}	1.0	0.5	0.5	0	0.5	0	0	0.5	0	0
Ni turnover (mol./liter).....	0.0132	0.0264	0.0388	0.0494	0.0586	0.0659	0.0723	0.0796	0.0875	0.0981
Plating appearance.....	(¹)	(¹)	(¹)	(¹)	(¹)	(¹)	(¹)	(¹)	(¹)	(¹)

¹ All samples semi-bright and smooth.

In cycles 1 to 5, inclusive, of this plating test, two of the panels specified having a total area of 290 cm.² were plated; whereas in cycles 6 to 10, inclusive, of this plating test, only one panel specified having a total area of 145 cm.² was plated. Furthermore, at the beginning of cycle 8 of this plating test, an extra 4.0 gm. of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was added, as an analysis showed that the nickel content of the plating bath was low. Also, the plating rates obtained in cycles 6 and 7 of this plating test were clearly indicative of the circumstance that the total content of Ni^{++} was running lower than that desired.

In plating operations involving plating baths of the nickel cation-hypophosphite anion type containing lactic ion as the complexing and exalting agent, as disclosed

above, it is desirable to add a separate and independent exaltant, because in continuous operation the complexing action of the lactic acid predominates; and while exaltants of the character disclosed in U. S. Patent No. 2,658,842, granted on November 10, 1953, to Gregoire Gutzeit and Ernest J. Ramirez (simple short chain saturated aliphatic dicarboxylic acids and salts thereof) are highly satisfactory, it is economically advantageous to employ as an exaltant a simple short chain saturated monocarboxylic acid (acetic, propionic, butyric and valeric), particularly in view of the solubility of their calcium salts, as will be shown below.

More specifically, in the operation of the continuous plating system, after a relatively long time interval of production plating, the phosphite concentration builds-up to a point where a slight excess of $(\text{HPO}_3)^-$, despite the presence of a complexing agent, will result in nickel phosphite precipitation; in other words, a threshold is reached where the solubility of nickel phosphite, even in the presence of a nickel chelating agent, is exceeded. At this time, it becomes necessary to remove, by some method, the excess phosphite ion, as well as the excess sodium and sulfate ions that have accumulated as a result of regeneration. A simple and economical method of achieving this objective is disclosed in the copending application of Paul Talmey, Gregoire Gutzeit and Donald Metheny, Serial No. 479,040, filed December 31, 1954, now abandoned, and involving the addition to the "spent" plating bath of a slight excess of calcium hydroxide, resulting in the precipitation of nickel phosphite, calcium phosphite and calcium sulfate; whereby, for practical reasons, it is highly desirable to employ in these plating baths a simple short chain saturated aliphatic monocarboxylic acid as an exaltant, which is not removed in the above described process, because its calcium salt is soluble. Also it is noted that the calcium salts of lactic acid are soluble, while most common hydroxycarboxylic acids form insoluble calcium compounds (malic, citric, tartaric, etc.).

The process and the bath comprising both lactic acid and a separate and independent exalting additive selected from the group consisting of propionic acid, butyric acid and valeric acid is disclosed and claimed in the copend-

ing application of Gregoire Gutzeit, Paul Talmey and Warren G. Lee, Serial No. 569,815, filed March 6, 1956.

In this connection, it is pointed out that as the phosphite concentration builds-up in a plating bath of this type, as the plating bath is used in the continuous plating system, the plating rate of the bath declines. Accordingly, it will be appreciated that the level of concentration of the phosphite in a plating bath of this type must be maintained as low as possible by employing continuous regeneration thereof during use, as disclosed in the previously-mentioned copending application of Paul Talmey, Gregoire Gutzeit and Donald E. Metheny. Otherwise, the plating bath must be discarded for further use, when about one-half to three-fourth of the phosphite tolerance thereof is reached, thereby to insure that in the plating

operation there is no formation of black precipitate in the plating bath.

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 and also containing as a combination complexing agent and exalting additive a predetermined range of lactic acid.

Further, these baths may advantageously contain as a separate and independent exalting additive a simple short chain saturated aliphatic monocarboxylic acid, preferably propionic acid, as disclosed in the previously mentioned copending divisional application of Gutzeit, Talmei and Lee. These plating baths are particularly well-adapted for use in a continuous plating system, as they exhibit a fast plating rate, have an exceedingly long life, are productive of entirely satisfactory plating quality, and maintain nickel phosphite in solution in concentrations approaching one molar.

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 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 a bath consisting essentially of an aqueous solution of nickel ions, hypophosphite ions, and a complexing agent selected from the group consisting of lactic acid 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 ratio between nickel ions and hypophosphite ions in said bath expressed in molar concentrations is within the range 0.25 to 1.60, the absolute concentration of lactic ions in said bath expressed in mole/liter is within the range 0.25 to 0.60, and the initial pH of said bath is within the approximate range 4.0 to 5.6.

2. 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 a bath consisting essentially of an aqueous solution of a nickel salt, an alkaline hypophosphite, and a complexing agent selected from the group consisting of lactic acid 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 ratio between nickel ions and hypophosphite ions in said bath expressed in molar concentrations is within the range 0.25 to 1.60, the absolute concentration of lactic ions in said bath expressed in mole/liter is within the range 0.25 to 0.60, and the initial pH of said bath is within the approximate range 4.0 to 5.6.

3. A bath for the chemical plating of a catalytic material with nickel consisting essentially of an aqueous solution of a nickel salt, a hypophosphite, and a complexing agent selected from the group consisting of lactic acid 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 ratio between nickel ions and hypophosphite ions in said bath expressed in molar concentrations is within the range 0.25 to 1.60, the absolute concentration of lactic ions in said bath expressed in mole/liter is within the range 0.25 to 0.60, and the pH of said bath is within the approximate range 4.0 to 5.6.

4. 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 a bath consisting essentially of an aqueous solution of nickel ions, hypophosphite ions, and a complexing agent selected from the group consisting of lactic acid 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 ratio between nickel ions and hypophosphite ions in said bath expressed in molar concentrations is within the range 0.25 to 1.60, the absolute concentration of lactic ions in said bath expressed in mole/liter is within the range 0.25 to 0.45, and the initial pH of said bath is within the approximate range 4.4 to 5.6.

5. A bath for the chemical plating of a catalytic material with nickel consisting essentially of an aqueous solution of a nickel salt, a hypophosphite, and a complexing agent selected from the group consisting of lactic acid 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 ratio between nickel ions and hypophosphite ions in said bath expressed in molar concentrations is within the range 0.25 to 1.60, the absolute concentration of lactic ions in said bath expressed in mole/liter is within the range 0.25 to 0.45, and the pH of said bath is within the approximate range 4.4 to 5.6.

6. 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 a bath consisting essentially of an aqueous solution of nickel ions, hypophosphite ions and lactic ions, wherein the absolute concentration of hypophosphite ions in said bath expressed in mole/liter is within the range 0.15 to 1.20, the ratio between nickel ions and hypophosphite ions in said bath expressed in molar concentrations is within the range 0.25 to 1.60, and the absolute concentration of lactic ions in said bath expressed in mole/liter is within the range 0.25 to 0.60.

7. A bath for the chemical plating of a catalytic material with nickel consisting essentially of an aqueous solution of a nickel salt, a hypophosphite and a lactate, wherein the absolute concentration of hypophosphite ions in said bath expressed in mole/liter is within the range 0.15 to 1.20, the ratio between nickel ions and hypophosphite ions in said bath expressed in molar concentrations is within the range 0.25 to 1.60, and the absolute concentration of lactic ions in said bath expressed in mole/liter is within the range 0.25 to 0.60.

References Cited in the file of this patent

UNITED STATES PATENTS

2,532,283	Brenner et al.	Dec. 5, 1950
2,658,842	Gutzeit et al.	Nov. 10, 1953