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PROCESSES OF REGENERATING CHEMICAL NICKEL PLATING SOLUTIONS

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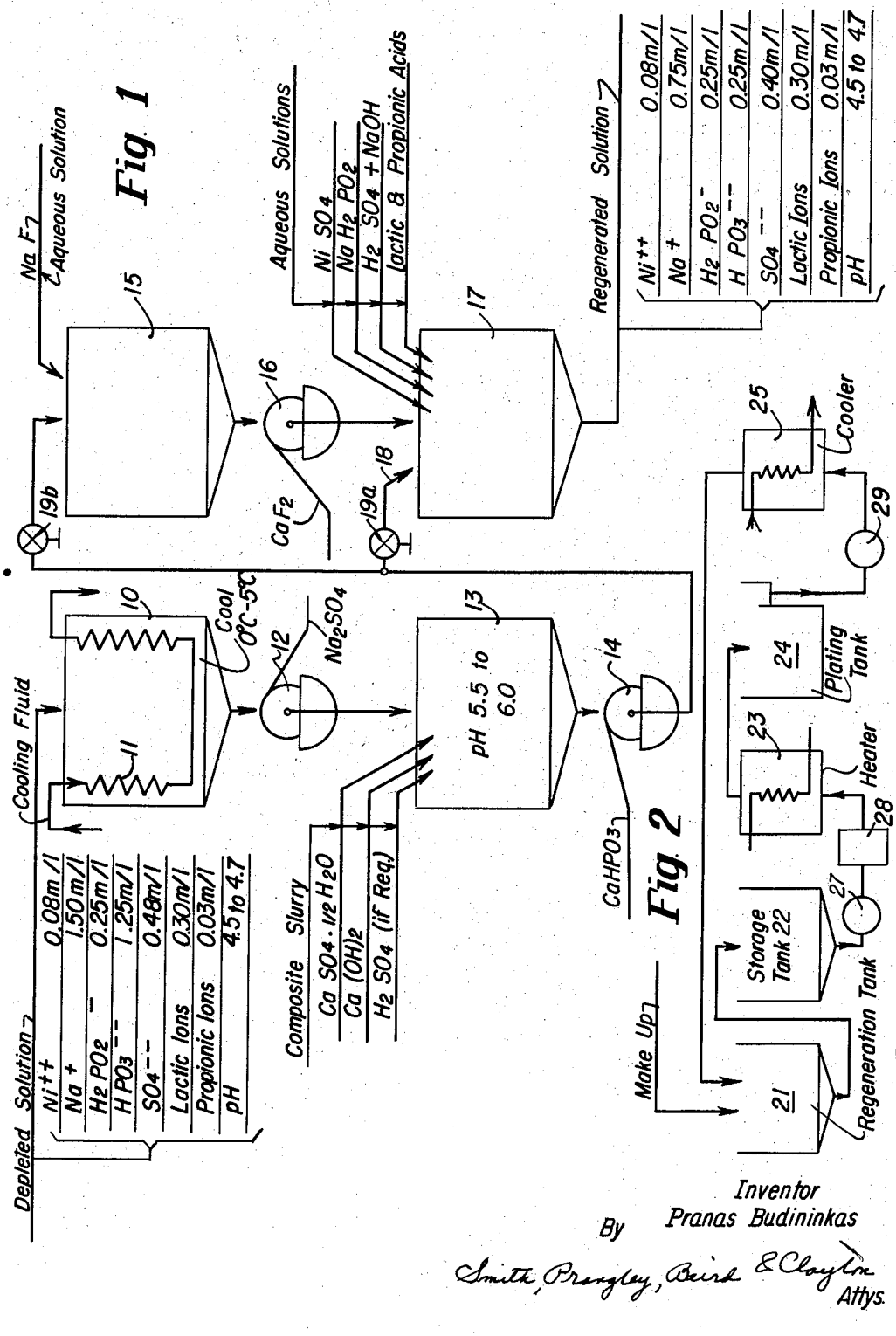

Fig. 2

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PROCESSES OF REGENERATING CHEMICAL NICKEL PLATING SOLUTIONS

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12 Claims. (Cl. 106—1)

The present invention relates to processes of regenerating aqueous chemical nickel plating solutions of the nickel cation-hypophosphite anion type, and particularly to such plating solutions employed in continuous nickel plating systems of the general character of that disclosed in U.S. Patent No. 2,717,218, granted on September 6, 1955, to Paul Talmey and William J. Crehan.

A number of suitable plating solutions are available for the present purpose, as disclosed in U.S. Patent No. 2,532,283, granted on December 5, 1950, to Abner Brenner and Grace E. Riddell; in U.S. Patent No. 2,658,841, granted on November 10, 1953, to Gregoire Gutzeit and Abraham Krieg; and in U.S. Patent No. 2,658,842, granted on November 10, 1953, to Gregoire Gutzeit and Ernest J. Ramirez, as well as in the copending application of Gregoire Gutzeit, Serial No. 376,977, filed August 27, 1953, the copending application of Gregoire Gutzeit, Paul Talmey and Warren G. Lee, Serial No. 478,492, filed December 29, 1954, and in the copending application of Gregoire Gutzeit, Paul Talmey and Warren G. Lee, Serial No. 569,815, filed March 6, 1956, now U.S. Patent No. 2,822,294.

A chemical nickel plating solution of this type essentially comprises an aqueous solution of nickel cations and hypophosphite anions, the nickel cations being derived from nickel sulfate, nickel chloride, nickel hypophosphite, etc., and the hypophosphite anions being derived from hypophosphorous acid, sodium hypophosphite, potassium hypophosphite, nickel hypophosphite, etc. Preferably, such a plating solution comprises an absolute concentration of hypophosphite anions within the range 0.15 to 1.20 moles/liter, a ratio between nickel cations and hypophosphite anions expressed in molar concentrations within the range 0.25 to 1.60, and a pH in the range 4.5 to 11. The plating solution disclosed in the Gutzeit, Talmey and Lee application Serial No. 569,815 is particularly advantageous and comprises, in addition to the nickel cations and the hypophosphite anions, lactic anions and propionic anions, and having a pH in the acid range 4.4 to 5.6; and specifically this plating bath comprises an absolute concentration of hypophosphite anions within the range 0.15 to 1.20 moles/liter, a ratio between nickel cations and hypophosphite anions expressed in molar concentrations within the range 0.25 to 1.60, an absolute concentration of lactic anions within the range 0.25 to 0.60 mole/liter and an absolute concentration of propionic ions within the range 0.025 to 0.060. A typical plating solution of this type has the following composition:

Nickel ion (as nickel sulfate) ----------m.p.l--	0.08
Hypophosphite ion (as sodium hypophosphite) m.p.l--	0.225
Lactic ion (as lactic acid) ----------m.p.l--	0.30
Propionic ion (as propionic acid) ---------m.p.l--	0.03
pH (adjusted with H_2SO_4 and NaOH) -------	4.5 to 4.7

In the continuous plating system, as the nickel reduction-hypophosphite oxidation reaction proceeds, the nickel cations and hypophosphite anions are depleted with the

formation of hydrogen ions; and in order to preserve substantially the initial composition of the plating solution, the same is partially regenerated, either periodically or continuously, by the addition of nickel cations, hypophosphite anions and hydroxyl anions; however, as this partial regeneration proceeds, there is a build-up in the plating solution of phosphite anions, the anions of the nickel salt employed and the cations of the hypophosphite employed. Assuming that the plating solution is initially composed, and is regenerated, employing nickel sulfate, sodium hypophosphite and sodium hydroxide, it is apparent that phosphite anions, sulfate anions and sodium cations build-up in the plating solution, as a result of the use and regeneration mentioned.

The build-up of substantial phosphite anions in the plating solution is particularly undesirable, since ultimately nickel phosphite will be precipitated therein, the tolerance of the plating solution to the presence of phosphite anions therein being dependent upon the particular composition of the plating solution, the plating solution of the composition specified above having a phosphite anion tolerance in excess of about one molar.

Nevertheless, the presence of the phosphite anions in the plating solution is objectionable, whereby there is disclosed in the copending application of Paul Talmey, Gregoire Gutzeit and Donald E. Metheny, Serial No. 576,931, filed April 9, 1956, a process for completely regenerating such a chemical nickel plating solution involving the removal therefrom of the phosphite anions (as well as the sodium cations and the sulfate anions in the case where the bath is composed and regenerated employing nickel sulfate and sodium hypophosphite), together with the additions of nickel cations, hypophosphite anions and hydroxyl ions. This process of Talmey, Gutzeit and Metheny is very advantageous in view of the fact that a regenerated chemical plating solution is brought back substantially to the initial composition thereof with no resulting build-up therein of phosphite anions, and the other ions mentioned. In accordance with the fundamental principle of this process, the depleted chemical nickel plating solution is first contacted by a cation exchange resin, so as to bring about the extraction therefrom of the nickel cations; then the effluent is subjected to calcium hydroxide treatment, wherein the pH of the solution is increased well into the base range bringing about the precipitation of calcium phosphite. The resulting solution is then filtered to remove the precipitated calcium phosphite therein; and the filtrate is cooled to a temperature within the general range 0° C. to 5° C., bringing about the crystallization therein of sodium sulfate. This solution is then filtered to remove the sodium sulfate therefrom; and the resulting filtrate is reconstituted by the addition thereto of nickel sulfate, sodium hypophosphite and sulfuric acid.

While this process is entirely satisfactory for the purpose of completely regenerating the depleted plating solution, it is subject to the criticism that it involves a larger number of individual steps than are desirable, as it is emphatic in carrying out the proces that the nickel cations must be removed from the depleted plating solution prior to the treatment thereof with calcium hydroxide in the substantial base range, as otherwise nickel phosphite will be coprecipitated with calcium phosphite.

Accordingly, it is a general object of the present invention to provide an improved process of completely regenerating a chemical nickel plating solution of the nickel cation-hypophosphite anion type that involves a greatly minimized number of individual steps.

Another object of the invention is to provide an improved process of removing phosphite anions from a depleted chemical nickel plating solution of the type noted, without the prior removal of nickel cations from

the solution, and without precipitation of the nickel cations in the solution.

Another object of the invention is to provide an improved process of the character noted, wherein the phosphite anions in the plating solution are precipitated therein as an alkaline earth phosphite in the presence of nickel cations therein, and without the coprecipitation of nickel phosphite.

A further object of the invention is to provide in a process of the character noted, an improved step of precipitating calcium phosphite, without the precipitation of either nickel phosphite or calcium hypophosphite, that involves an improved control of the pH of the solution during the precipitation mentioned.

A still further object of the invention is to provide an improved process of regenerating completely a chemical nickel plating solution of the nickel cation-hypophosphite anion type that is simple and economical to carry out.

Further features of the invention pertain to the particular arrangement of the steps of the process, whereby the above-outlined and additional operating features thereof are attained.

The invention, both as to its organization and principle of operation, together with further objects and advantages thereof, will best be understood by reference to the following specification taken in connection with the accompanying drawings, in which:

Figure 1 is a diagrammatic illustration of the steps involved in the complete regeneration of a chemical nickel plating solution of the nickel cation-hypophosphite anion type, in accordance with the process of the present invention; and

Fig. 2 is a diagrammatic illustration of a continuous nickel plating system in which the plating solution mentioned may be employed.

The present invention is predicated upon the discovery that in a depleted aqueous chemical nickel plating solution of the nickel cation-hypophosphite anion type, the undesirable phosphite anions may be selectively precipitated in the presence of the desirable nickel cations and hypophosphite anions, without the coprecipitation of either the nickel cations or the hypophosphite anions, by alkaline earth cations, when the pH of the solution is properly controlled and maintained within the range 5.5 to 7.0, during the precipitation of the alkaline earth phosphite. In accordance with the arrangement, the required alkaline earth cations are supplied jointly by the corresponding soluble salt and by the corresponding hydroxide.

For example, when the plating solution is initially composed employing nickel sulfate and sodium hypophosphite, calcium may be advantageously employed, the salt (calcium sulfate) and the hydroxide (calcium hydroxide) being employed jointly to supply the required calcium cations and to obtain the desired pH.

Referring now to Fig. 1, a depleted aqueous chemical nickel plating solution of the nickel cation-hypophosphite anion type, derived from a continuous plating system may essentially comprise:

Ni^{++}	m./l. 0.08
Na^{+}	m./l. 1.50
$H_2PO_2^{-}$	m./l. 0.25
HPO_3^{--}	m./l. 1.25
SO_4^{--}	m./l. 0.48
Lactic ions	m./l. 0.30
Propionic ions	m./l. 0.03
pH	4.5 to 4.7

In accordance with the present process, this depleted plating solution is introduced into a tank **10** and cooled therein by an associated cooling coil **11**, while being agitated, to a temperature in the range 0° C. to 5° C., whereby there is crystallized out therein sodium sulfate. The resulting suspension is delivered to an associated filter **12**, whereby the sodium sulfate is removed therefrom, and the resulting filtrate is delivered to an associated tank **13**. In the tank **13**, the filtrate is treated with a composite aqueous slurry of calcium sulfate (gypsum) and calcium hydroxide, the filtrate in the tank **13** being agitated, and the addition of the calcium hydroxide being controlled so that the pH thereof is elevated into the general range 5.5 to 6.0; and particularly the pH is maintained below 7.0, so as positively to prevent the precipitation therein of nickel phosphite. Under the controlled conditions mentioned, calcium phosphite is precipitated, without any substantial precipitation of calcium hypophosphite or any nickel salt. Preferably, the total addition of calcium ion is at least 20% less than the stoichiometric amount thereof required to precipitate all of the phosphite anions in order to avoid the presence of calcium ions in the regenerated plating solution.

The resulting suspension is delivered to an associated filter **14**, whereby the calcium phosphite is separated therefrom, and the resulting filtrate is delivered to an associated tank **15**. In the tank **15**, while the solution is agitated, an aqueous solution of sodium fluoride is added for the purpose of precipitating calcium fluoride. This step is altogether optional, as the amount of excess calcium ions in the filtrate delivered to the tank **15** is very small, or negligible, if the total addition of calcium ions in the tank **13** has been properly controlled, as described. Moreover, this small quantity of calcium ions is not objectionable in the plating solution. However, the calcium ions may be removed, if desired, by the fluoride precipitation, if an excess thereof has been added. As illustrated, the resulting suspension is delivered to an associated filter **16**, whereby the calcium fluoride is separated therefrom, and the resulting filtrate is delivered to an associated tank **17**. The filtrate delivered to the tank **17** contains substantially all of the nickel cations and all of the hypophosphite anions of the initial depleted plating solution, aside from certain small losses that are substantially entirely mechanical in character; however, this filtrate contains only about 10% to 25% of the phosphite anion concentration of the initial depleted plating solution, which phosphite anion content is in no way objectionable. Moreover, during the treatment, there is substantially no loss from the initial depleted plating solution of the lactic anions and propionic anions therein, except for the small quantities thereof that are lost mechanically, as previously noted.

In the tank **17**, the filtrate is reconstituted by the addition thereto of nickel sulfate, sodium hypophosphite and sulfuric acid, together with sodium hydroxide, to obtain the desired pH of about 4.7 in this illustrative bath. Also, small additions of lactic acid and propionic acid are made in order to reconstitute the plating bath with respect to these ingredients. At this time, the regenerated plating solution has substantially the composition of the initially formulated plating solution and is returned to the continuous plating system for further plating use.

In the process, the calcium hydroxide is employed in conjunction with the calcium sulfate so as to provide substantially the required amount of calcium ions to precipitate the calcium phosphite, and to bring the solution to the optimum pH range, as noted above. Also, it is emphasized that the matter of removing the small excess of calcium ions from the filtrate from the filter **14** is optional, whereby a by-pass **18** is illustrated that extends directly from the filter **14** to the tank **17**. A valve **19***a* is arranged in the by-pass **18**, and a valve **19***b* is arranged in the direct conduit to the tank **15**, so that all, or any part, of the filtrate from the filter **14** may be diverted directly to the tank **17**.

Referring now to Fig. 2, a conventional continuous chemical nickel plating system is diagrammatically illustrated as comprising a regeneration tank **21**, a storage tank **22**, a heater **23**, a plating tank **24**, and a cooler **25**, arranged in tandem relation in the order named, together with a pump **27** and a filter **28** arranged in series relation between the storage tank **22** and the heater **23**, and a

pump 29 arranged between the plating tank 24 and the cooler 25.

In the operation of the continuous plating system, the plating solution is regenerated in the regeneration tank 21 (which may correspond in fact to the tank 17 described in conjunction with Fig. 1), and while the plating solution is cool and at a temperature of about 60° C. From the regeneration tank 21, the plating solution is delivered to the storage tank 22, from which it is pumped by the pump 27 through the filter 28 and thence through the heater 23 and delivered to the plating tank 24. In the heater 23, the plating solution is heated to an effective plating temperature in the general range 85° C. to 95° C. From the plating tank 24, the plating solution is pumped by the pump 29 through the cooler 25 and returned to the regeneration tank 21. In the cooler 25, the plating solution is cooled so that the temperature thereof is returned substantially back to about 60° C., prior to the return of the plating solution to the regeneration tank 21. Of course, the work-pieces to be plated are immersed in the plating solution in the plating tank 24 in the usual manner; which work-pieces must necessarily have a catalytic surface so that the plating reaction may proceed. In this connection, it is mentioned that the catalytic elements are: cobalt, nickel, palladium, rhodium and ruthenium. However, a large group of other elements can be rendered catalytic, either by displacement or by galvanic initiation in the plating solution, so that the autocatalytic plating reaction may proceed. This group of elements includes aluminum, carbon, copper, iron, magnesium, titanium and uranium (as well as silver and gold), and the various alloys thereof. Also, insulators can be satisfactorily nickel plated when the surfaces thereof are suitably activated with one of the catalytic elements named.

In the continuous chemical nickel plating system a plating solution that has been regenerated in accordance with the present process is equally effective as an initially composed plating solution in the production of bright, smooth coatings upon the work-pieces, that are intimately bonded thereto, and with a high plating rate. Specifically, in the present example, the plating rate is normally in the range of 0.9 to 1.0 mil/hour of nickel plating upon the work-pieces.

In applying the present process of regeneration to the continuous plating system, the whole body of plating solution may be regenerated after several passes thereof through the system, or a fractional part thereof may be by-passed continuously from the cooler 25 to the regeneration equipment, followed by the present treatment and then the return thereof to the regeneration tank 21.

The following procedure is illustrative of repeated regenerations of an aqueous chemical nickel plating solution of the nickel cation-hypophosphite anion type. Specifically, an initial plating solution of this type was provided and after utilization thereof in the continuous plating system, it became depleted, at which time it had the following composition with respect to the important ions:

	M./l.
Ni^{++}	0.093
$H_2PO_3^-$	0.23
HPO_3^{--}	1.23
SO_4^{--}	0.36

This depleted plating solution was regenerated in accordance with the previously described process; whereby it was first cooled to a temperature of 5° C. to effect the crystallization of sodium sulfate therein. The solution was then filtered to remove the sodium sulfate; and thereafter to the filtrate there was added an aqueous slurry of 0.35 m./l. $CaSO_4.\frac{1}{2}H_2O$ and 0.65 m./l. $Ca(OH)_2$, so as to effect the precipitation of calcium phosphite therein. The suspension was then filtered to remove the precipitated calcium phosphite therefrom; whereby the filtrate had the following composition with respect to the important ions:

	M./l.
Ni^{++}	0.062
$H_2PO_2^-$	0.198
HPO_3^{--}	0.27
SO_4^{--}	0.39
Ca^{++}	0.005

The filtrate was then reconstituted to provide a regenerated plating solution of substantially the initial composition, and after utilization thereof in the continuous plating system, it again became depleted; at which time it had the following composition with respect to the important ions:

	M./l.
Ni^{++}	0.116
$H_2PO_2^-$	0.284
HPO_3^{--}	1.03
SO_4^{--}	0.69

This depleted plating solution was regenerated in accordance with the previously described process; whereby it was first cooled to a temperature of 5° C. to effect the crystallization of sodium sulfate therein. The suspension was then filtered to remove the sodium sulfate; and thereafter to the filtrate there was added an aqueous slurry of 0.35 m./l. of $CaSO_4.\frac{1}{2}H_2O$ and 0.65 m./l. CaO, so as to effect the precipitation of calcium phosphite therein. The suspension was then filtered to remove the precipitated calcium phosphite therefrom; and to the filtrate there was added 0.04 m./l. of NaF, so as to effect the precipitation of calcium fluoride therein. The suspension was then filtered to remove the precipitated calcium fluoride therefrom; whereby the filtrate had the following composition with respect to the important ions:

	M./l.
Ni^{++}	0.088
$H_2PO_2^-$	0.252
HPO_3^{--}	0.22
SO_4^{--}	0.43
Ca^{++}	Negligible

The filtrate was then reconstituted to provide a regenerated plating solution of substantially initial composition and returned to the continuous plating system for further use.

In the foregoing example, the initial plating solution, and each of the reconstituted plating solutions, contained about 0.09 m./l. of nickel cations (as nickel sulfate) and about 0.25 m./l. of hypophosphite anions (as sodium hypophosphite); and in each case, the pH was established at about 4.7 employing H_2SO_4 and NaOH.

Also, in conjunction with the foregoing regenerations, it is noted that in the first case, calcium hydroxide was employed; whereas in the second case, calcium oxide was employed; and it will be understood that the utilization of these two compounds is interchangeable, as each provides calcium cations and effects the desired increase in the pH of the solution. Further it is mentioned that in the second regeneration set forth, sodium fluoride was employed in order to remove the residual calcium cations, as calcium fluoride, as previously explained.

In the foregoing examples of the present process, it is mentioned that about 75% to 95% of the phosphite anions are removed by the calcium phosphite precipitation; and also about 20% of the nickel cations and about 10% of the hypophosphite anions are removed substantially entirely mechanically, rather than by chemical precipitation, as there is no precipitation of any nickel salt. Specifically, the loss of nickel cations and hypophosphite anions is accounted for largely by mechanical trapping and the consequent removal along with the sodium sulfate, the calcium phosphite and the calcium fluoride. Also, it is pointed out that, when the sodium sulfate is crystallized out, it carries from 7 to 10 molecules of water

of crystallization therewith, and when the calcium phosphite is precipitated, it carries 3 molecules of water of crystallization therewith; whereby the process actually effects a concentration of the depleted solution notwithstanding the utilization of the aqueous slurry in the tank 13.

In the foregoing description of the present process, the regeneration of a plating solution has been described in conjunction with the removal of calcium phosphite utilizing calcium sulfate and calcium hydroxide, and this alkaline earth salt and alkaline earth hydroxide are preferred as a matter of simplicity and economy. However, other alkaline earth salts and alkaline earth hydroxides may be employed to precipitate the corresponding alkaline earth phosphite, when the plating solution is initially composed with a nickel salt, other than nickel sulfate. For example, the plating solution may be initially composed utilizing nickel chloride and sodium hypophosphite; whereby in this case, the alkaline earth salt may be barium sulfate, barium chloride, etc., strontium sulfate, strontium chloride, etc., as well as calcium sulfate, calcium chloride, etc.; and likewise, the alkaline earth hydroxide may be barium hydroxide, strontium hydroxide or calcium hydroxide.

The procedure utilizing the other alkaline earth salts and alkaline earth hydroxides is identical to that previously described; and it is preferable that the optimum range of pH 5.5 to 6.0 be employed, as it is this pH range that prevents the precipitation of nickel phosphite. Also, in this connection, it is mentioned that the various alkaline earth hydroxides are substantially equally effective to bring about the precipitation of the corresponding alkaline earth phosphites, without the precipitation of the corresponding alkaline earth hypophosphites.

It is reiterated that when the bath is initially composed with nickel sulfate, then the regeneration must take place with a calcium salt and calcium hydroxide, since it will be immediately apparent that the utilization of barium or strontium salts and hydroxides would be primarily effective to bring about the precipitation of the corresponding barium or strontium sulfates and secondarily effective to bring about the precepitation of the corresponding barium or strontium phosphites. In other words, barium sulfate is far less soluble than barium phosphite, and strontium sulfate is far less soluble than strontium phosphite. However, this is not true of other barium salts (barium chloride) and of other strontium salts (strontium chloride). On the other hand, calcium is unique, as the sulfate thereof is relatively soluble, and so is the chloride; whereby the regeneration procedure using calcium salts and calcium hydroxide has universal application to these plating solutions.

Another consideration is of importance in the regeneration of these plating solutions, as a practical matter, in that it is highly desirable to prevent the introduction of anions that are foreign to those already present therein. By way of illustration: calcium sulfate is employed when the plating solution is composed with nickel sulfate; alkaline earth chloride is employed when the plating solution is composed with nickel chloride; etc.

Furthermore, it will be understood that while the description has proceeded in terms of the utilization of alkaline earth sulfates and alkaline earth chlorides, the other soluble alkaline earth salts are equally effective. Moreover, while the description has proceeded in terms of the utilization of alkaline earth hydroxides, the corresponding alkaline earth oxides and carbonates are equally effective.

In view of the foregoing, it is apparent that there has been provided an improved process of regenerating a depleted aqueous chemical nickel plating solution of the nickel cation-hypophosphite anion type, wherein the desirable nickel cations and hypophosphite anions are maintained in the solution, while the undesirable phosphite anions are removed therefrom; whereby the treated solution comprises an adequate and appropriate basis for the reconstitution of a chemical nickel plating solution having substantially the initially formulated composition.

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 regenerating a depleted aqueous chemical nickel plating solution containing desirable nickel cations and hypophosphite anions and undesirable phosphite anions and having a pH below about 5.5, comprising adding to the depleted plating solution both an alkaline earth hydroxide and an alkaline earth salt of a mineral acid, said addition supplying sufficient hydroxyl ions to the resulting solution to increase the pH thereof into the range 5.5 to 7.0, but not above, so as to precipitate therein alkaline earth phosphite, without precipitating therein any substantial amounts of alkaline earth hypophosphite or of any nickel compound, said addition supplying sufficient alkaline earth cations to the resulting solution to effect the removal therefrom of a substantial proportion of the phosphite anions therein, removing the precipitated alkaline earth phosphite from the resulting solution, and then adding to the resulting solution the required nickel cations and hypophosphite anions and hydrogen ions to produce a plating solution of desired composition.

2. The process of regenerating a depleted aqueous chemical nickel plating solution containing desirable nickel cations and hypophosphite anions and undesirable phosphite anions and having a pH below about 5.5, comprising adding to the depleted plating solution both calcium hydroxide and a calcium salt of a mineral acid, said addition supplying sufficient hydroxyl ions to the resulting solution to increase the pH thereof into the range 5.5 to 6.0, but not above, so as to precipitate therein calcium phosphite, without precipitating therein any substantial amounts of calcium hypophosphite or of any nickel compound, said addition supplying sufficient calcium cations to the resulting solution to effect the removal therefrom of a substantial proportion of the phosphite anions therein, removing the precipitated calcium phosphite from the resulting solution, and then adding to the resulting solution the required nickel cations and hypophosphite anions and hydrogen ions to produce a plating solution of desired composition.

3. The process of regenerating a depleted aqueous chemical nickel plating solution containing desirable nickel cations and hypophosphite anions and undesirable phosphite anions and having a pH below about 5.5, comprising adding to the depleted plating solution both calcium hydroxide and calcium sulfate, said addition supplying sufficient hydroxyl ions to the resulting solution to increase the pH thereof into the range 5.5 to 6.0, but not above, so as to precipitate therein calcium phosphite, without precipitating therein any substantial amounts of calcium hypophosphite or of any nickel compound, said addition supplying sufficient calcium cations to the resulting solution to effect the removal therefrom of a substantial proportion of the phosphite anions therein, removing the precipitated calcium phosphite from the resulting solution, and then adding to the resulting solution the required nickel cations and hypophosphite anions and hydrogen ions to produce a plating solution of desired composition.

4. The process set forth in claim 3, wherein the total amount of calcium cations added to the depleted solution is not in excess of about 80% of the stoichiometric amount thereof required to precipitate all of the phosphite therein.

5. The process of regenerating a depleted aqueous chemical nickel plating solution containing desirable

nickel cations and hypophosphite anions and undesirable phosphite anions and having a pH below about 5.5, comprising adding to the depleted plating solution both calcium hydroxide and calcium sulfate, said addition supplying sufficient hydroxyl ions to the resulting solution to increase the pH thereof into the range of 5.5 to 6.0, but not above, so as to precipitate therein calcium phosphite, without precipitating therein any substantial amounts of calcium hypophosphite or of any nickel compound, said addition supplying sufficient calcium cations to the resulting solution to effect the removal therefrom of a substantial proportion of the phosphite anions therein, removing the precipitated calcium phosphite from the resulting solution, adding to the resulting solution sodium fluoride so as to precipitate therein calcium fluoride, removing the precipitated calcium fluoride from the resulting solution, and then adding to the resulting solution the required nickel cations and hypophosphite anions and hydrogen ions to produce a plating solution of desired composition.

6. The process of regenerating a depleted aqueous chemical nickel plating solution containing sulfate anions, and desirable nickel cations and hypophosphite anions and undesirable sodium cations and phosphite anions and having a pH below about 5.5, comprising stripping from the depleted plating solution a substantial amount of the sodium cations and the sulfate anions therein as sodium sulfate, adding to the resulting solution both calcium hydroxide and calcium sulfate, said addition supplying sufficient hydroxyl ions to the resulting solution to increase the pH thereof into the range 5.5 to 7.0, but not above, so as to precipitate therein substantially only calcium phosphite, said addition supplying sufficient calcium cations to the resulting solution to effect the removal therefrom of a substantial proportion of the phosphite anions therein, removing the precipitated calcium phosphite from the resulting solution, and then adding to the resulting solution the required nickel sulfate and sodium hypophosphite and hydrogen ions to produce a plating solution of desired composition.

7. The process set forth in claim 1, wherein said alkaline earth hydroxide is barium hydroxide.

8. The process set forth in claim 1, wherein said alkaline earth salt is calcium salt.

9. The process set forth in claim 1, wherein said alkaline earth salt is barium salt.

10. The process set forth in claim 1, wherein said alkaline earth salt is calcium sulfate.

11. The process set forth in claim 1, wherein said alkaline earth hydroxide is strontium hydroxide.

12. The process set forth in claim 1, wherein said alkaline earth salt is strontium salt.

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