May 12, 1959 N. L. DUVALL 2,886,452

PROCESSES OF REGENERATING CHEMICAL NICKEL PLATING SOLUTIONS

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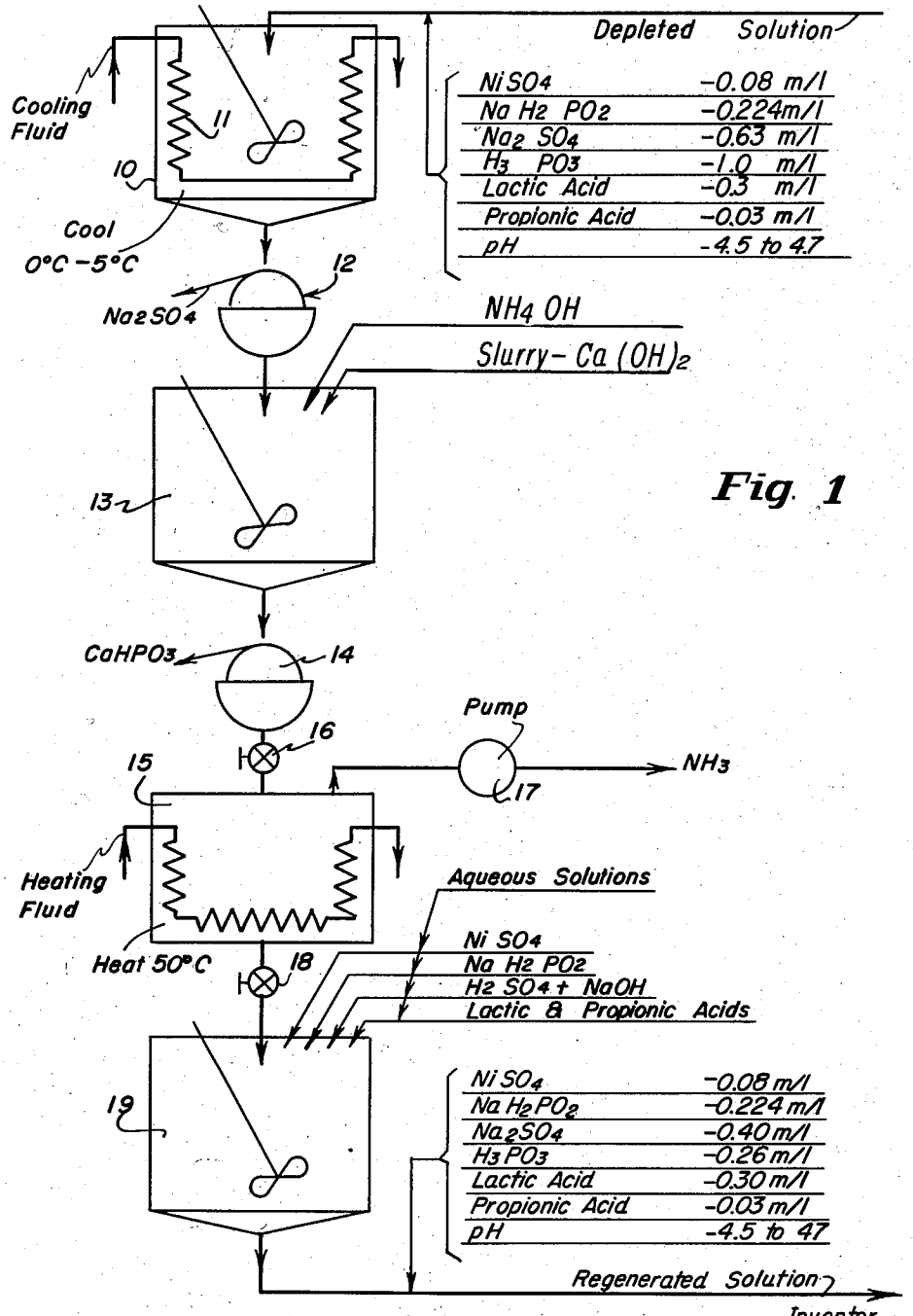


Fig. 1

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Fig. 2

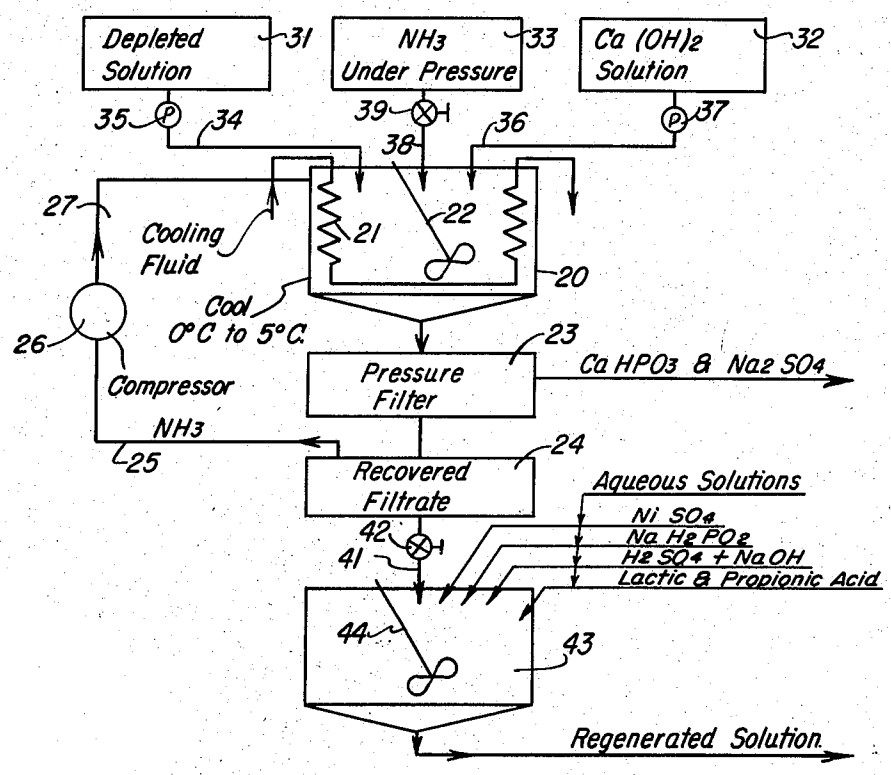
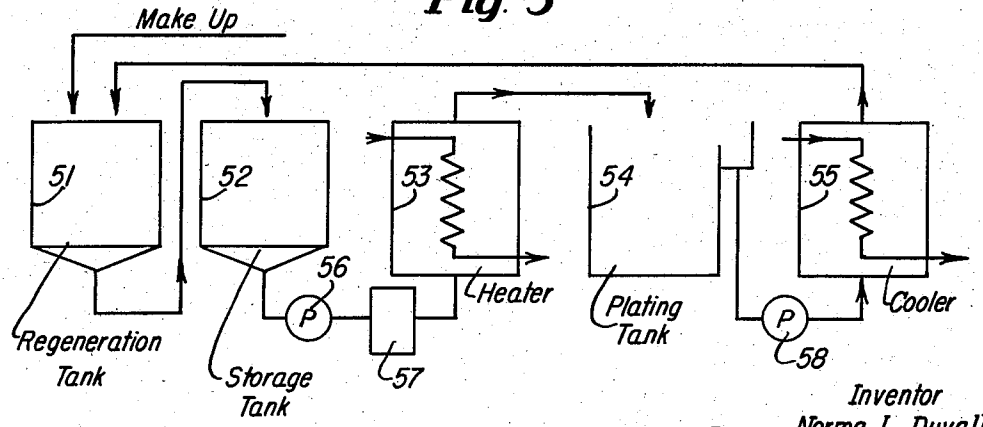


Fig. 3



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United States Patent Office 2,886,452 Patented May 12, 1959

2,886,452

PROCESSES OF REGENERATING CHEMICAL NICKEL PLATING SOLUTIONS

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Application January 17, 1958, Serial No. 709,690

11 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 hyphophosphite 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 of 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 reduc-

tion-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 process 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 im-

proved 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.

Another object of the invention is to provide an improved process of the character noted, wherein the nickel cations are completely complexed in the solution undergoing treatment, so that the precipitation of an alkaline earth phosphite therein does not effect the coprecipitation of nickel phosphite therein even though the pH of the solution is well above 8.

A further object of the invention is to provide an improved process of the character noted, that involves the utilization of ammonia as the complexing agent to prevent the coprecipitation of nickel phosphite with the alkaline earth phosphite from the solution undergoing treatment.

A further object of the invention is to provide an improved process of the character noted, wherein the nickel cations are completely complexed with ammonia and the phosphite anions are precipitated as calcium phosphite.

A further object of the invention is to provide an improved process of the character noted, wherein the complete complexing of the nickel cations is achieved in a pressurized treatment system employing gaseous ammonia.

A still further object of the invention is to provide an improved process of the character noted, wherein undesirable phosphite anions and sulfate anions and sodium cations are simultaneously removed from the treated solution, without the removal of desirable nickel cations and hypophosphite anions, wherein the ions mentioned are removed by the coprecipitation of alkaline earth phosphite and sodium sulfate.

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;

Fig. 2 is a diagrammatic illustration of the steps involved in a modified form of the present process; and

Fig. 3 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-hydrophosphite anion type, the undesirable phosphite anions may be selectively precipitated in the presence of the desirable nickel cations and hypophosphite anions, without the co-precipitation of either the nickel cations or the hypophosphite anions, when the nickel cations are completely complexed, during the precipitation of an alkaline earth phosphite in the plating solution. In accordance with the arrangement, the required ammonia is supplied to the depleted plating solution by the addition of ammonium hydroxide, gaseous ammonia, or a suitable ammonium salt, and the required alkaline earth cations are supplied to the depeleted plating solution by the addition of the corresponding hydroxide. In any case, the required ammonia is provided in the depleted plating solution, so as completely to complex all of the nickel cations therein, prior to the calcium hydroxide addition for the purpose of precipitating the phosphite as calcium phosphite.

For example, when the plating solution is initially composed employing nickel sulfate and sodium hypophosphite, calcium hydroxide may be advantageously employed, together with ammonium hydroxide. In this case, sodium sulfate is first stripped from the depleted plating solution by crystallization at low temperature and filtration, and then an ammoniacal solution is produced of the resulting solution in which all of the nickel cations therein are in the form of a nickel-ammonia complex, and raising the pH thereof somewhat above 8, and then calcium hydroxide is added to the ammoniacal solution so as to effect the precipitation therein of calcium phosphite, without the co-precipitation of calcium hypophosphite or any nickel compound. After separation of the calcium phosphite, the resulting solution is treated to break the nickel-ammonia complex, with the evolution of ammonia gas; and thereafter the resulting solution is reconstituted to provide a regenerated chemical nickel plating solution of desired composition.

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:

$NiSO_4$	m./l.	0.08
NaH_2PO_2	m./l.	0.224
Na_2SO_4	m./l.	0.65
H_3PO_3	m./l.	1.0
Lactic acid	m./l.	0.3
Propionic acid	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 sodium sulfate is crystallized out therein. 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**. Into the tank **13**, there is added first ammonium hydroxide, and then calcium hydroxide, in order to supply ammonia and Ca^{++}, so as to increase the pH above about 8 and to precipitate calcium phosphite, without any substantial precipitation of calcium hypophosphite or any nickel salt. Now, of course, it will be understood that all of the nickel cations in the solution in the tank **13** are completely complexed, so that they are not co-precipitated as nickel hydroxide or nickel phosphite. In this step, the calcium hydroxide addition should normally comprise the stoichiometric amount of calcium cations to effect precipitation of all of the phosphite anions, while the ammonium hydroxide addition should normally comprise several times the stoichiometric amount of ammonia, so as positively to insure that all of the nickel cations in the solution are in the nickel-ammonia complex.

The resulting suspension is delivered to an associated filter **14**, whereby the calcium phosphite is separated therefrom, and the resulting filtrate is delivered to a closed tank **15** via a conduit including a valve **16**. In the tank **15**, the solution is heated to a temperature of about 50° C., while being subjected to a subatmospheric pressure by a pump **17** connected to the tank **15**, whereby the nickel-ammonia complex is broken, with the liberation of gaseous ammonia that is discharged to the exterior. The solution is then delivered from the tank **15** via a conduit including a valve **18** to a tank **19**. In carrying out the process the valve **16** is closed after a

quantity of the filtrate is delivered into the tank **15**, and then operation of the pump **17** is initiated for the purpose explained. After the nickel-ammonia complex has been broken, operation of the pump **17** is arrested, and the valve **18** is opened to admit air into the tank **15** and to cause the solution to flow from the tank **15** into the tank **19**, as noted above.

In the tank **19**, the filtrate is reconstituted by the addition thereto of nickel sulfate and sodium hypophosphite, lactic acid, propionic acid and sulfuric acid and sodium hydroxide, so as to produce a regenerated plating solution. At this time, the regenerated plating solution has substantially the composition of the initially formulated solution and is returned to the continuous plating system for further plating use; and specifically, the composition of the regenerated plating solution may be as follows:

$NiSO_4$	m./l.	0.08
NaH_2PO_2	m./l.	0.224
Na_2SO_4	m./l.	0.40
H_3PO_3	m./l.	0.26
Lactic acid	m./l.	0.30
Propionic acid	m./l.	0.03
pH		4.5 to 4.7

In the foregoing process of regenerating the depleted plating solution, it will be appreciated that the complete complexing of the nickel cations in the tank **13**, under these controlled conditions, accommodates precipitation of calcium phosphite, without any substantial precipitation of calcium hypophosphite or any nickel salt. Subsequently, following the removal of the calcium phosphite, the nickel-ammonia complex is boken in the tank **15**, by the combination of the heating and the subatmospheric pressure, whereby the liberated ammonia gas is discharged to the exterior. Also, it is pointed out that, when the sodium sulfate is crystallized out, it carries therewith from 46% to 67%, by weight, of water of crystallization, and when the calcium phosphite is precipitated, it carries therewith 18%, by weight, of water of crystallization; whereby the process actually effects a concentration of the depleted solution, notwithstanding the utilization of the aqueous slurry in the tank **13**.

The foregoing regeneration procedure will be best illustrated from the following example, wherein and aqueous chemical nickel plating solution of the nickel cation-hypophosphite anion type was composed having a volume of 36 liters and having the following composition:

$NiSO_4$	m./l.	0.08
NaH_2PO_2	m./l.	0.224
Lactic acid	m./l.	0.30
Propionic acid	m./l.	0.03
pH (adjusted with NaOH)		4.5 to 4.7

This plating solution was employed in the continuous chemical nickel plating system with the consequent depletion thereof and with periodic partial regeneration thereof by the addition of nickel sulfate, sodium hypophosphite and sodium hydroxide for an appropriate time interval; whereby the same was determined to be depleted. At this time, the depleted plating bath contained the following components:

	G./l.
Ni^{++}	4.4
NaH_2PO_2	24.8
Na_2HPO_3	131.7
Ca^{++}	Trace
H_2SO_4	32

This depleted plating solution was first subjected to the previously described treatment in the tank **10** of Fig. 1, whereby the sodium sulfate was crystallized out and subsequently removed in the filter **12**. In the tank **13** (which was open to the atmosphere in this run) there were added to the filtrate first 3.2 m./l. of NH_3 (derived from 7.2 liters of aqueous NH_4OH solution) and then the slurry containing 1.5 m./l. of $Ca(OH)_2$. In the treated solution, there was precipitated calcium phosphite; and the calcium phosphite was removed by the filter **14**. Thereafter, the filtrate was treated in the tank **15**, and the resulting solution was delivered to the tank **19**. A sample of this resulting solution was analyzed and was found to contain the following components:

	G./l.
Ni^{++}	3.4
NaH_2PO_2	16.7
Na_2HPO_3	33.7
Ca^{++}	None
H_2SO_4	27

Accordingly, in this salvaged filtrate 77% of the desirable nickel cations were saved, the loss being substantially entirely due to lack of complete complexing of the Ni^{++} in the open tank **13** in this run; and substantially 74% of the undesirable phosphite anions were removed by the calcium phosphite precipitation. Furthermore, in the calcium phosphite precipitation step, the molar ratio between the NH_3 and Ni^{++}, in this example, was 40, which is equivalent to 670% of the amount of NH_3 required theoretically to complex 100% of the nickel cations in the solution, the great excess of NH_3 being employed in order absolutely to guarantee complete complexing of all of the nickel cations in the solution during the precipitation of the calcium phosphite.

The salvaged filtrate was delivered to the tank **16** and was reconstituted by the addition of the aqueous make-up solutions, and the resulting regenerated plating solution having substantially the initial composition set forth was returned to the continuous plating system for further use; and bright, smooth nickel coatings were produced on the work-pieces therewith that were in every respect identical to the coatings produced upon the original work-pieces with the initially composed plating solution.

Referring now to Fig. 2, a modified form of the process is illustrated which is carried out in a pressurized system including a reaction tank **20** that is provided with a cooling coil **21** together with an agitator **22**. The reaction tank **20** is connected to a pressure filter **23** that, in turn, is connected to a recovery tank **24**. In turn, the recovery tank **24** is connected by a conduit **25** to the inlet of an associated compressor **26**, the outlet of the compressor **26** being connected by a conduit **27** to the reaction tank **20**. Also the system comprises a tank **31** in which the depleted plating solution is stored, and a tank **32** in which an aqueous solution of calcium hydroxide is stored, as well as a bottle or tank **33** containing ammonia gas under pressure. The tank **31** is connected to the reaction tank **20** by a conduit **34** in which there is arranged a pump **35**; and the tank **32** is connected to the reaction tank **20** by a conduit **36** in which there is arranged a pump **37**. The pressure bottle **33** is connected to the reaction tank **20** by a conduit **38** in which a valve **39** is arranged. Furthermore, the recovery tank **24** is provided with an outlet conduit **41**, including a valve **42**; which outlet conduit **41** communicates with a regeneration tank **43** provided with an agitator **44**.

In this arrangement, the depleted plating solution is pumped from the storage tank **31** into the reaction tank **20** by the associated pump **35**, and likewise the aqueous solution of calcium hydroxide is pumped from the tank **32** into the reaction tank **20** by the pump **37**. Also the ammonia gas contained in the pressure bottle **33** is admitted into the reaction tank **20** by control of the valve **39**. In this case, the ammonia gas admitted into the reaction tank **20** brings about the formation of the nickel-ammonia complex in the treated solution, with the small resulting heating; however, cooling of the solution undergoing the reaction is effected by the cooling coil **21**; whereby the temperature of the reacted solution is maintained within the general range 0° C. to 5° C. In this

case, the ammonia gas is first admitted into the tank **20**, and then the slurry is pumped thereinto so that the calcium phosphite is precipitated concurrently with the crystallizing out of the sodium sulfate; whereby in the pressure filter **23**, both the calcium phosphite precipitate and the sodium sulfate crystals are removed and the resulting filtrate is delivered to the recovery tank **24**. In this arrangement, the compressor **26** exerts a suction upon the filtrate in the recovery tank **24** in order to insure the removal of gaseous ammonia therefrom and complete breaking of the nickel-ammonia complex. The filtrate is delivered from the recovery tank **24** into the regeneration tank **42**; whereby the addition of the aqueous make-up solutions thereto restores the filtrate to produce the regenerated plating solution of the desired composition in the manner previously explained.

This arrangement of the steps of the present process is very advantageous, as there is substantially no loss of gaseous ammonia from the system and complete complexing of the nickel in the solution undergoing treatment in the reaction tank **20** can be readily insured by maintaining the required pressure head of ammonia gas thereover; which can be accomplished in a ready manner by operation of the compressor **26** and by the control of the valve **39**. In passing, it is noted that the ammonia in the bottle **33** is normally in the liquid state and is flashed into the gaseous state at the valve **39** incident to opening thereof.

Referring now to Fig. 3, a conventional continuous chemical nickel plating system is diagrammatically illustrated as comprising a regeneration tank **51**, a storage tank **52**, a heater **53**, a plating tank **54** and a cooler **55**, arranged in tandem relation in the order named, together with a pump **56** and a filter **57** arranged in series relation between the storage tank **52** and the heater **53**, and a pump **58** arranged between the plating tank **54** and the cooler **55**.

In the operation of the continuous plating system, the plating solution is regenerated in the regeneration tank **51** (which may correspond in fact to the tank **19** of Fig. 1 or the tank **43** of Fig. 2), and while the plating solution is cool and at a temperature of about 60° C. From the regeneration tank **51**, the plating solution is delivered to the storage tank **52** from which it is pumped by the pump **56** through the filter **57** and thence through the heater **53** and delivered to the plating tank **54**. In the heater **53**, the plating solution is heated to an effective plating temperature in the general range 85° C. to 95° C. From the plating tank **54**, the plating solution is pumped by the pump **58** through the cooler **55** and returned to the regeneration tank **51**. In the cooler **55**, 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 **51**. Of course, the work-pieces to be plated are immersed in the plating solution in the plating tank **54** 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, manganese, 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 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 **55** to the regeneration equipment, followed by the present treatment and then the return thereof to the regeneration tank **51**.

In the foregoing description of the present process, the regeneration of the depleted plating solution was set forth in conjunction with the removal of calcium phosphite utilizing calcium hydroxide as the precipitating agent, and this alkaline earth hydroxide is preferred as a matter of simplicity and economy. However, other alkaline earth hydroxides may be employed to precipitate the corresponding alkaline earth phosphites, 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 hydroxide may be barium hydroxide, strontium hydroxide, or calcium hydroxide.

The procedure utilizing the other alkaline earth hydroxides is identical to that previously described, as it will be understood that it is the complexing of the nickel cations that prevents the precipitation of the various nickel salts. Also, it is mentioned that the various alkaline earth hydroxides are substantially equally effective to bring about the precipitation of the corresponding alkaline earth phosphite 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 calcium hydroxide, since it will be immediately apparent that the utilization of barium or strontium hydroxides would be primarily effective to bring about the precipitation of the corresponding barium or strontium sulfates and secondarily effective to bring about the precipitation 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 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.

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 for 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 aqueous 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, comprising treating the depleted plating solution to produce an ammoniacal solution thereof in which all of the nickel cations therein are in the nickel-ammonia complex, then adding to the ammoniacal solution alkaline earth hydroxide so as to precipitate therein alkaline earth phosphite without precipitating therein any substantial amounts of alkaline earth hypophosphite or of any nickel compound, said alkaline earth hydroxide addition to said ammoniacal solution being sufficient to effect the removal therefrom of a substantial proportion of the phosphite anions therein, removing the precipitated alkaline earth phosphite from the resulting solution, then removing ammonia from the resulting solution to break the nickel-ammonia complex therein, and then adding to the resulting solution the required nickel cations and hypophospite 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, comprising treating the depleted plating solution with ammonia under pressure so as to produce an ammoniacal solution thereof in which all of the nickel cations therein are in the nickel-ammonia complex, then adding to the ammoniacal solution while it is under ammonia pressure alkaline earth hydroxide so as to precipitate therein alkaline earth phosphite without precipitating therein any substantial amounts of alkaline earth hypophosphite or of any nickel compound, said alkaline earth hydroxide addition to said ammoniacal solution being sufficient to effect the removal therefrom of a substantial proportion of the phosphite anions therein, removing the precipitated alkaline earth phosphite from the treated solution while it is under ammonia pressure, then relieving the ammonia pressure and removing ammonia from the resulting solution to break the nickel-ammonia complex therein, 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, comprising adding to the depleted solution sufficient ammonium hydroxide completely to complex all of the nickel cations therein, then treating the resulting solution with alkaline earth hydroxide so as to precipitate therein alkaline earth phosphite without precipitating therein any substantial amounts of alkaline earth hypophosphite or of any nickel compound, said alkaline earth hydroxide addition to said ammoniacal solution being sufficient to effect the removal therefrom of a substantial proportion of the phosphite anions therein, removing the precipitated alkaline earth phospite from the treated solution, then removing ammonia from the resulting solution to break the nickel-ammonia complex therein, 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 of regenerating a depleted aqueous chemical nickel plating solution containing desirable nickel cations and hypophosphite anions and undesirable phosphite anions, comprising adding to the depleted solution sufficient ammonium hydroxide completely to complex all of the nickel cations therein, then treating the resulting solution with calcium hydroxide so as to precipitate therein calcium phosphite without precipitating therein any substantial amounts of calcium hypophosphite or of any nickel compound, said calcium hydroxide addition to said ammoniacal solution being sufficient to effect the removal therefrom of a substantial proportion of the phosphite anions therein, removing the precipitated calcium phosphite from the treated solution, then removing ammonia from the resulting solution to break the nickel-ammonia complex therein, 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.

5. The process of regenerating a depleted aqueous chemical nickel plating solution containing desirable nickel cations and hypophosphite anions and undesirable sodium cations and phosphite anions and sulfate anions, comprising cooling the depleted solution to a temperature at least as low as 5° C. so as to crystallize out sodium sulfate therein, removing the sodium sulfate from the cooled solution, treating the resulting solution to produce an ammoniacal solution thereof in which all of the nickel cations therein are in the nickel-ammonia complex, then adding to the ammoniacal solution alkaline earth hydroxide so as to precipitate therein alkaline earth phosphite without precipitating therein any substantial amounts of alkaline earth hypophosphite or of any nickel compound, said alkaline earth hydroxide addition to said ammoniacal solution being sufficient to effect the removal therefrom of a substantial proportion of the phosphite anions therein, removing the precipitated alkaline earth phosphite from the resulting solution, then removing ammonia from the resulting solution to break the nickel-ammonia complex therein, and then adding to the resulting solution the required amounts of nickel sulfate and sodium hypophosphite and hydrogen ions to produce a plating solution of desired composition.

6. The process of regenerating a depleted aqueous chemical nickel plating solution containing desirable nickel cations and hypophosphite anions and undesirable sodium cations and phosphite anions and sulfate anions, comprising cooling the depleted solution to a temperature at least as low as 5° C. so as to crystallize out sodium sulfate therein, removing the sodium sulfate from the cooled solution, treating the resulting solution to produce an ammoniacal solution thereof in which all of the nickel cations therein are in the nickel-ammonia complex, then adding to the ammoniacal solution calcium hydroxide so as to precipitate therein calcium phosphite without precipitating therein any substantial amounts of calcium hypophosphite or of any nickel compound, said calcium hydroxide addition to said ammoniacal solution being sufficient to effect the removal therefrom of a substantial proportion of the phosphite anions therein, removing the precipitated calcium phosphite from the resulting solution, then removing ammonia from the resulting solution to break the nickel-ammonia complex therein, and then adding to the resulting solution the required amounts of nickel sulfate and sodium hypophosphite and hydrogen ions to produce a plating solution of desired composition.

7. The process of regenerating a depleted aqueous chemical nickel plating solution containing desirable nickel cations and hypophosphite anions and undesirable sodium cations and phosphite anions and sulfate anions, comprising cooling the depleted plating solution to a temperature at least as low as 5° C. so as to crystallize out sodium sulfate therein, removing the sodium sulfate from the cooled solution, adding to the resulting solution sufficient ammonium hydroxide completely to complex all of the nickel cations therein, then treating the resulting solution with calcium hydroxide so as to precipitate therein calcium phosphite without precipitating therein any substantial amounts of calcium hypophosphite or of any nickel compound, said calcium hydroxide addition to said ammoniacal solution being sufficient to effect the removal therefrom of a substantial proportion of the phosphite anions therein, removing the precipitated calcium phosphite from the treated solution, then removing ammonia from the resulting solution to break up nickel-ammonia complex therein, and then adding to the resulting solu-

tion the required amounts of nickel sulfate and sodium hypophosphite and hydrogen ions to produce a plating solution of desired composition.

8. The process of regenerating a depleted aqueous chemical nickel plating solution containing desirable nickel cations and hypophosphite anions and undesirable sodium cations and phosphite anions and sulfate anions, comprising cooling the depleted plating solution to a temperature in the range 0° C. to 5° C. while subjecting the same to a head pressure of ammonia and while adding thereto calcium hydroxide so as to crystallize out therein sodium sulfate and so as to produce an ammoniacal solution thereof in which all of the nickel cations therein are in the nickel-ammonia complex and so as to precipitate therein calcium phosphite without precipitating therein any substantial amounts of calcium hypophosphite or of any nickel compound, said calcium hydroxide addition to said ammoniacal solution being sufficient to effect the removal therefrom of a substantial proportion of the phosphite anions therein, removing simultaneously the sodium sulfate and the calcium phosphite from the cooled solution while it is under ammonia

pressure, then relieving the ammonia pressure and removing ammonia from the resulting solution to break the nickel-ammonia complex therein, 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.

9. The process set forth in claim 1, wherein said alkaline earth hydroxide is calcium hydroxide.

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

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

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