The present invention relates to a method of nickel plating metallic surfaces by chemical reduction and, more particularly, to a novel bath solution and accelerant useful therefor.

Brenner and Riddell of the National Bureau of Standards observed that by chemically reducing nickel salts, such as NiCl₂ and nickel sulfate, with a hypophosphite, e.g., sodium hypophosphite, in the presence of a catalyst (usually the surface to be plated) a uniform coating of nickel deposits on the surface without any need for electrodes. The general equation proposed by Brenner and Riddell is:

\[ \text{NiCl}_2 + \text{Na}_2\text{HPO}_3 \rightarrow \text{H}_2\text{O} \quad \text{Ni}^{++} + 2\text{HCl} + \text{Na}_2\text{HPO}_3 \]

As buffers for the reaction they used sodium citrate, sodium hydroxyacetate or Rochelle salt.

According to the present invention, a significant improvement in the electroless plating method of Brenner and Riddell has been discovered. It has been found, according to the present invention, that substantial reduction of the nickel salt concentration generally required in both solutions of the type disclosed by Brenner and Riddell, that significant increases in plating rates and that pronounced broadening of the pH operating range typical of both these bath solutions may be effected by incorporating into the plating bath an alkali tetraborate, such as sodium tetraborate \( \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \) as an accelerant.

Reduction of the nickel salt concentration hereofore required has several important advantages, among which are faster rates of deposition, increased bath stability and reduced plating cost. The reduction in plating cost is due to the higher rate of utilization of the nickel salt with a smaller initial concentration. These advantages are, indeed, significant.

By using sodium tetraborate according to the instant invention, for instance, 15 grams per liter NiCl₂ in the bath solution gives platings comparable to the platings previously acquired using twice as much NiCl₂ or more. Such a reduction of concentration proved unsuccessful when using sodium fluoride, for example, a known accelerant.

Very desirable results are obtained by using sodium tetraborate \( \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \) concentrations ranging from about 1 to 10 grams per liter of the bath solution, preferably about 3 grams per liter, since the plating rate gradually decreases at gradually lower concentrations. At concentrations above 10 grams per liter more buffering of the solution is required and the stability of a bath gradually decreases.

Although excellent results are obtained using sodium tetraborate, other alkali tetraborates may be employed, such as potassium tetraborate, ammonium tetraborate. They may be either in the anhydrous or in the hydrated form.

The novel nickel bath of the present invention has exceptional properties, for instance, in its use in plating metallic surfaces to be exposed to strong chemicals, such as alkali metal hydroxides and the like. Not only has the novel accelerant of the present invention afforded significant reductions in plating costs and equally significant increased rates of plate deposition, for instance, as clearly defined above, but it has afforded improved nickel plates which are more resistant to corrosive chemicals, as will be seen hereinafter.

While the nickel plate deposited by the methods described by Brenner and Riddell, for example, exhibited cracking and peeling when used on containers employed for the concentration of alkali metal hydroxides, such as caustic potash, the nickel plate liner of the present invention exhibited high resistance to corrosive attack. Hydrated caustic potash, for instance, which was dehydrated in cast iron vessels lined by means of the novel bath solution of the present invention contained substantially no iron impurities as a result of corrosive attack of the potash upon the vessel walls.

A typical efficacious bath useful in the present invention, for example, for chemically plating a cast iron vessel to be used in concentrating caustic potash comprises:

<table>
<thead>
<tr>
<th>Component</th>
<th>Grams per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NiCl}_2 \cdot 6\text{H}_2\text{O} )</td>
<td>15.0</td>
</tr>
<tr>
<td>( \text{Na}_2\text{HPO}_3 \cdot \text{H}_2\text{O} )</td>
<td>10.0</td>
</tr>
<tr>
<td>Sodium citrate</td>
<td>10.0</td>
</tr>
<tr>
<td>( \text{CoCl}_2 )</td>
<td>0.5</td>
</tr>
<tr>
<td>( \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} )</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Generally nickel salts are supplied in amounts to provide a nickel ion concentration in the bath sufficient to produce a nickel plate when reduced by the alkali hypophosphite reductant.

While 15 grams per liter nickel chloride is recited, it is but a preferred amount, since 1 to 30 grams per liter, preferably 11 to 20 grams per liter, may be employed successfully.

The quantity of hypophosphite reductant employed varies depending upon the nickel ion concentration of the bath employed. Generally the amount employed is that amount which is sufficient to cause the nickel ions present in the bath solution to plate out. Utilizing sodium hypophosphite as the reductant in a bath solution, for example, concentrations ranging between about 8 to 30 grams of sodium hypophosphite per liter of solution are conveniently employed. Other hypophosphites, such as potassium and ammonium hypophosphite, may be used in lieu of \( \text{Na}_2\text{HPO}_3 \cdot \text{H}_2\text{O} \).

Although the bath solution recited above calls for 10 grams of sodium citrate per liter, up to 30 and 40 grams per liter or more may be used with equal success, providing the \( \text{pH} \) of the bath, as will be seen hereinafter, is controlled. It is also possible to operate the bath efficiently with no sodium citrate present, providing proper control of the \( \text{pH} \) is maintained to avoid instability of the bath. Other buffers within the scope of the present invention are any organic acid salts, usually the salt of a strong base and a weak acid, such as the oxalates and succinates of potassium and sodium, and so forth.

Up to about 7 grams or more per liter of a cobalt salt and as little as about 0.3 gram per liter thereof may be employed with practically equal success. Nickel-cobalt plates produced with 3 grams per liter cobalt chloride and 0.5 gram per liter cobalt chloride appeared to have equal resistance to caustic potash, for instance; higher concentrations of cobalt in solution produced inferior plates as far as resistance to caustic potash is concerned, although in plating titanium metal, for instance, about 6 grams per liter of a cobalt salt is preferred.

The cobalt salt is not a necessary part of the present invention, although it affords unexpected properties in the treatment of caustic potash at elevated temperatures (as stated above). Nickel plating without the cobalt constituent have diversified utility, particularly those prepared by the novel bath solution and accelerant of the present invention. The instant specific embodiment showing the use of nickel-cobalt liners prepared from the
novel bath solutions of the present invention is but exemplary, and the scope of the disclosure should not be limited thereby.

Although nickel chloride is the preferred salt in the present invention other nickel salts, such as nickel sulfate, nickel nitrate, may also be employed. Whenever a cobalt-containing nickel plate is desired, cobalt chloride may be used, and, while it is the preferred cobalt salt, other salts of cobalt may be used, such as cobalt sulfate, and cobalt nitrate.

It can be seen, therefore, that the improved plating bath and accelerator of the present invention are novel and produce superior results in their application. The nickel-cobalt plate defined above, for instance, and used to line metallic containers employed for handling KOH, may be applied to the containers in any convenient manner. The interior of a cast iron pot, for instance, may be plated by introducing the bath into the pot and maintaining the temperature of the bath between 80°C. and 100°C., preferably between 90°C. and 98°C., until the desired plating thickness on the interior surfaces of the container has been realized.

For better corrosion resistance the casted metal may then be heated to a temperature of about 385°C. to 410°C. This heat treatment may also be accomplished by heating in any convenient manner. For instance, when the interior of a vessel has been lined as described above, heat treatment may be realized by heating the outside of a vessel directly with a gas flame. Care must be taken, however, to avoid oxidation of the nickel.

Change in color of the plate while heating is used to determine the extent of the heat treatment. When the plate reaches a temperature of 200°C., it will turn brown and appear to be charred and burned. The brown color will gradually change to blue and then a gray-white. A uniform blue-gray color over the entire plated surface indicates that the heat treatment is complete.

Surfaces to be plated should first be thoroughly cleaned and free from rust and grease. Sandblasting is the best method found for preparing the surface of cast iron for plating, although acids, such as HCl, have been employed to clean titanium metal surfaces, for instance, with good success. The plating action is slow in starting but after the reaction starts it will proceed until the chemicals in the bath are consumed, if the pH of the solution is controlled. The optimum pH of a chemical plating bath is dependent upon composition of the bath and the type of plates desired.

For a bath of the composition recited in the table above, a pH between 4.5 and 6.8 is preferred. A pH ranging from about 3 to 9 may be employed, however, taking into consideration the ingredient concentrations and their effect on pH.

The pH of a plating bath is controlled by the addition of sodium bicarbonate. Bath pH will drop as the plating reaction progresses because of the formation of hydrochloric acid. Sodium bicarbonate may be added slowly to prevent localized precipitation of nickel. Hypophosphate and nickel salt are added from time to time to keep the bath plating at its optimum rate.

The amount of hypophosphate and nickel to be added to a plating bath can be determined by testing the bath for hypophosphate concentration. The weight of sodium hypophosphate required to deposit one gram of nickel is approximately 4.5 grams; therefore, by determining the amount of hypophosphate that has been consumed in the bath, the amount of nickel used is also determined.

A very convenient method of determining the hypophosphate may be found described by Brenner in "Metal Finishing," December 1954, page 68.

The thickness of the plate deposited is dependent on optimum plating time, volume to area ratio of a bath and surface to be plated. Optimum plating conditions are attained when the volume to area ratio is between 4 to 8 cubic centimeters per square centimeter.

The following is a specific illustration of a preferred method of applying a nickel-cobalt plate to the interior surfaces of a cast iron vessel according to the present invention:

Example I

A plating bath solution prepared as shown in the table above was placed in an 80-gallon cast iron pot whose interior surfaces had been cleaned by sandblasting. Enough solution was added to fill the pot. The bath was then heated to a temperature of about 95°C. for a period of 3 hours. During this plating operation the pH of the bath was maintained between 4.5 and 6.8 by the slow addition of sodium bicarbonate.

Enough sodium hypophosphate and nickel chloride were added from time to time to maintain the bath plating at its optimum rate, approximately 0.36 gram per hour plate weight, as measured on a cast iron coupon having a surface area of 22 square centimeters.

After 3 hours the bath was removed from the vessel and the empty vessel was fired from the outside with a gas flame. When the plate reached about 200°C., it turned brown, and appeared to be burned or charred. As heating continued and the temperature increased to about 392°C., the plate turned blue. Heating was continued at about this temperature until a uniform blue-gray color appeared over the entire plated surface. Analysis of the plate showed it contained 90.28-90.98 percent by weight nickel and less than .001 cobalt.

Example II

The 80-gallon vessel plated as in Example I, supra, was then cleaned and washed free of impurities caused by dust and fumes. The plate was then stripped away by extensive heating and evaporation by heating slowly to 200°C. to avoid spattering, and then to about 360°C. until the potash was anhydrous. Analysis of the product showed it to be white and containing only about .0003 percent by weight iron. The nickel-cobalt plate remained in good condition.

It can be seen, therefore, that high quality alkali metal compounds, for instance, can be prepared in vessels lined by means of the novel bath and accelerator of the present invention. Among the many and unexpected properties of the present invention, for instance, is the fact that the nickel-cobalt plate prepared as in Example I and employed as in Example II manifested superior characteristics, such as high corrosion resistance, when contacted with strong caustics. Because of the novel bath solution and the novel accelerator contained therein, these highly beneficial results are made possible.

Heretofore, when caustic potash was concentrated to an anhydrous state in a metal container by means of heat, the anhydrous product generally contained a high concentration of impurities resulting from corrosion of the metal surfaces. In using cast iron pots, for example, the anhydrous caustic potash produced generally had a high iron content which seriously affected the color of the product. Colors ranging from yellow to dark green indicated an impure product.

Since attempts to remove the iron impurity were met with virtually no success, methods have been attempted to prevent its occurrence in the anhydrous material. Among the methods attempted to prelude corrosion impurities was electrolytic nickel plating of the surfaces to be placed in direct contact with strong chemicals. This proved unsuccessful. Efforts to electrolytically plate the iron with copper and subsequently electrolytically surface the copper with nickel were equally unsuccessful.

The resulting electrolytic nickel plate was porous and the copper subplate was quickly attacked by chemicals. Obviously, therefore, these methods were highly impractical.

According to the present invention, however, the above difficulties have been overcome. In addition to providing a highly improved plating bath solution having a novel
accelerant which increases plating rates, broadens the pH operating range and permits reduction of the nickel salt concentration generally required in baths of this type, there has been found a novel method of plating surfaces to be coated with strong chemicals whereby corrosion of the surfaces by the chemicals has been substantially eliminated. The impurities which previously found their way into the materials contacting unplated surfaces or surfaces plated by methods heretofore known have been substantially eliminated.

While the present invention has been described with great particularity as to specific embodiments thereof, such as the bath concentrations recited in the table, above, such as the concentration of caustic potash in a cast iron vessel lined by means of the bath solution in the table, it is not intended that the invention be so limited, since numerous other applications and modifications will be evident to a skilled chemist. The metal surfaces so treated may be of iron, as stated hereinabove, or of titanium, copper, cobalt, chromium, vanadium, manganese, or the like. Where a reaction vessel is treated with a bath solution of the present invention, the vessel may be used in handling chemicals other than caustic potash, such as caustic soda, alkaline earth metal hydroxides and carbonates, and the like.

In conclusion, therefore, it is not intended that the scope of the present invention be limited, except insofar as the appended claims impose limitations thereon, even though the invention has been described with particularity as to specific embodiments thereof.

This application is a continuation-in-part of my co-pending application Serial No. 592,753 filed June 21, 1956, now abandoned.

I claim:
1. A bath for plating by chemical reduction comprising 1 to 30 grams per liter of a nickel salt, about 8 to 30 grams per liter of a hypophosphite salt, a buffer and 1 to 10 grams per liter of alkali tetraborate.
2. The bath of claim 1 wherein the alkali tetraborate is sodium tetraborate.
3. The bath of claim 1 wherein the buffer is sodium citrate.
4. A bath for nickel-cobalt plating by chemical reduction bath comprising about 15 grams per liter of nickel salt, about 10 grams per liter of a hypophosphite salt, about 0.5 gram per liter of cobalt salt, a buffer and 3.0 grams per liter of alkali tetraborate.
5. The bath of claim 4 wherein the alkali tetraborate is sodium tetraborate.
6. The bath of claim 4 wherein the buffer is 10 grams per liter sodium citrate.
7. A method of chemical plating by chemical reduction which comprises contacting a metal surface with a plating bath comprising 1 to 30 grams per liter of a nickel salt, about 8 to 30 grams per liter of a hypophosphite salt, a buffer and 1 to 10 grams per liter of alkali tetraborate, maintaining the bath at a temperature between 80° C. and 100° C. and at a pH between 3 and 9 until a desired plating thickness on said metal surface is realized.
8. The process of claim 7 wherein the alkali tetraborate is sodium tetraborate.
9. The process of claim 7 in which the resulting plated surface is treated by heating to a temperature of about 385° C. to 410° C.
10. The process of claim 7 in which the metal surface is cast iron.
11. A method of plating by chemical reduction which comprises contacting a metal surface with a nickel-cobalt plating bath comprising 15 grams per liter of a nickel salt, about 10 grams per liter of a hypophosphite salt, 0.5 gram per liter of a cobalt salt, a buffer and 3.0 grams per liter of sodium tetraborate, maintaining the bath at a temperature between 90° C. and 98° C. and at a pH between 4.5 and 6.8 until a desired plating thickness on said metal surface is realized.
12. The process of claim 11 in which the resulting plated surface is treated by heating to a temperature of about 385° C. to 410° C.
13. The process of claim 11 in which the metal surface is cast iron.
14. The plating bath of claim 1 in which up to about 7 grams per liter of cobalt salt is present.
15. A method of plating according to claim 7 in which up to about 7 grams per liter of a cobalt salt is present.
16. A bath for nickel-cobalt plating by chemical reduction containing nickel ions, cobalt ions, an alkali hypophosphite reductant, and an alkali tetra borate accelerator.
17. A bath for nickel plating by chemical reduction containing nickel ions, an alkali hypophosphite reductant, and an alkali tetraborate accelerator.
18. In a process for nickel plating by chemical reduction from a nickel plating solution using an alkali hypophosphite reductant the improvement comprising accelerating the chemical reduction with an alkali tetra borate.
19. In a process for nickel-cobalt plating by chemical reduction from a nickel-cobalt plating solution using an alkali hypophosphite reductant the improvement comprising accelerating the chemical reduction with an alkali tetraborate.
20. A method of preparing anhydrous alkali metal hydroxides which comprises heating an aqueous alkali metal hydroxide in contact with a metal surface consisting essentially of a plating composed of nickel and cobalt chemically reduced with an alkali metal hypophosphite in the presence of an alkali metal tetraborate, said plating containing between 0.00001 and less than about 0.08 percent by weight cobalt.
21. The method of claim 20 wherein said plating contains between 0.001 and 0.00001 percent by weight cobalt.

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