Oct. 11, 1960 A. H. DU ROSE 2,955,959

CHEMICAL NICKEL PLATING

Filed Sept. 22, 1958

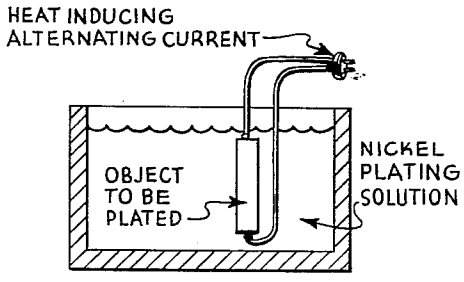


FIG. 1

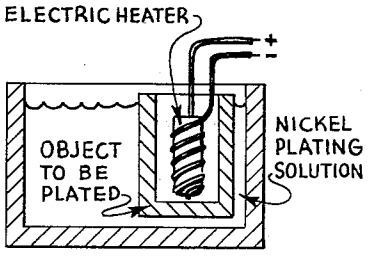


FIG. 2

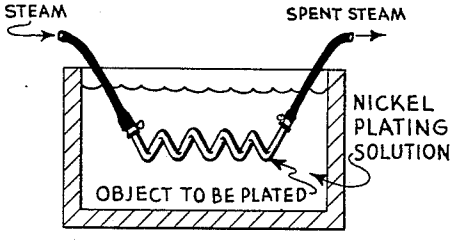


FIG. 3

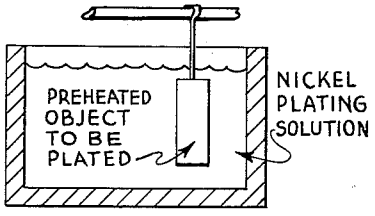


FIG. 4

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United States Patent Office 2,955,959
Patented Oct. 11, 1960

2,955,959

CHEMICAL NICKEL PLATING

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Filed Sept. 22, 1958, Ser. No. 762,249

8 Claims. (Cl. 117—113)

The present invention relates to processes of chemical nickel plating.

Methods of nickel plating which do not depend upon the passage of an electric current through the plating solution have been known for many years. Such processes are described, for example, in U.S. Patent No. 455,230, issued in 1891, and in U.S. Patent No. 1,207,218, issued in 1916. More recently, such processes have come into commercial use and particularly those of the type described in U.S. Patent No. 2,658,839.

In these commercial processes, the usual mode of operation is to maintain a chemical plating solution at an elevated temperature, close to the boiling point of the solution, and to immerse the object to be coated in the solution for a period of time which is suitable for the thickness of deposit desired, ranging up to several hours. The process depends upon the reduction of nickel cations by hypophosphite anions in the presence of a catalyst, at temperatures near the boiling point of water. As is understood in the art, the catalyst is usually the object to be plated, though in some instances a non-catalytic object may be plated by initiating the plating reaction in various ways as discussed below. These commercial processes are usually of a continuous-flow type, wherein the plating bath is a small, heated container, and the reserve solution is contained in a reservoir of larger capacity at a lower temperature. Additional reagent may be added during processing to the reservoir, to replenish the active agents in the solution which are used up during plating.

This two-tank system is used largely to overcome the difficulty encountered with undesired plating which tends to take place within the process equipment wherever the plating solution is present at elevated temperatures. Nevertheless, simply keeping the major part of the solution in the reservoir at a depressed temperature, does not completely overcome the problem, and the additional expedient of using tanks, conduits, and other equipment of non-catalytic material, such as plastic, or which is glass-lined, also has been necessary. Even so, the plating reaction frequently is initiated on the non-catalytic materials used in the system, by specks of catalytic material, and once nickel plating begins, it continues, nickel being itself catalytic for the process. Thus, the problem has remained a serious one.

I have found that if the temperatures of the solutions used are kept below a certain critical point (about 185° F. in the case of the solutions which I have utilized), and if the workpiece itself is heated above such critical point, but its surface is kept below the boiling point of the solution, an excellent coating on the workpiece can be obtained while at the same time the problem of deposition of metal from the nickel solution onto the process equipment is largely avoided. This is because of the fact that in my process the major portion of the solution, all except a thin layer adjacent to the workpiece, may be kept below the critical temperature at which nickel deposition takes place at an appreciable rate, a temperature

which I refer to herein as the critical point or the precipitation temperature.

While my process is chiefly useful in those instances where the workpiece can be heated while in the solution, or can be repeatedly heated and dipped, it can, nevertheless, be used in an important number of industrial applications. For example, it may be used to plate the interior surfaces of tubing, a problem which was formerly very difficult, and it may be used to plate hollow bodies of highly irregular shape, either externally or internally; and it has other uses which will be apparent from the following description.

In one method of practicing my invention I may use a glass tank containing the plating solution, and heat the solution in the tank by means of an external heating source. Two formulations of plating solution which may be used are as follows:

Component	Formulation A, g./l.	Formulation B, g./l.
Nickel Chloride	30	30
Sodium Citrate	10	
Sodium Hypophosphite	10	10
Sodium Hydroxyacetate		10
pH	5	5.5

The quantities of reagents may, of course, be varied, within limits. Thus, satisfactory results could be obtained with nickel chloride present within the range of about 15 to 75 grams per liter and sodium hypophosphite present within the range of about 5 to 50 grams per liter, while sodium citrate or sodium hydroxyacetate present in amounts from 5 to 60 grams per liter would be permissible. However, the preferred ranges for these substances are: nickel chloride 25 to 35 grams per liter, sodium hypophosphite 8 to 15 grams per liter, and sodium citrate or sodium hydroxyacetate 5 to 15 grams per liter. The pH may vary from about 3.5 to 6 with a pH of around 4.5 to 5.5 being the most satisfactory.

As is well known in the art, other salts may be used to make up a plating bath containing nickel cations and hypophosphite anions, which would give similar results. Moreover, as is known in the art, the concentration of the various ingredients, within broad limits, has but little effect on the reaction, except perhaps for the speed at which it takes place, and except also that too high a concentration of hypophosphite tends to cause spontaneous decomposition to take place more readily.

With these solutions, the plating reaction which takes place is the following:

$$NiCl_2+NaH_2PO_2+H_2O \xrightarrow{cat} Ni+2HCl+NaH_2PO_3$$

The reaction does not take place spontaneously, but only upon certain surfaces, which are, or can be made catalytic for the reaction. Such surfaces are copper, silver, gold, beryllium, boron, germanium, aluminum, thallium, silicon, carbon, vanadium, molybdenum, tungsten, chromium, selenium, tellurium, titanium, iron, cobalt, nickel, palladium, platinum and alloys thereof such as steel, brass and bronze. I will refer to such materials herein as basis materials. Nickel itself is a catalyst, so that the process is not self-limiting like the displacement method of plating and the thickness of the deposit is not limited.

There are various ways of inducing deposition on non-catalytic surfaces. Thus, Brenner and Riddell in Research Paper R.P. 1835, volume 39, November 1947 of the U.S. Department of Commerce, National Bureau of Standards, discuss various ways of obtaining deposition on usually non-catalytic metal surfaces by changing the composition of the plating solution, by making contact with a more electronegative metal, or by the deposition

of a thin layer of catalytic material on the surface of the non-catalytic material.

Talmey, U.S. Patent No. 2,658,839, states that some materials, non-catalytic by themselves, can be plated by the use of iron as an initiator. For example, he states that copper can be used as a basis material by contacting it with an iron wire to initiate the plating reaction, after which the wire is removed. In this connection, it is of interest to note that I have found that copper is a catalytic material if the solution is hot enough, and particularly if the amount of hypophosphite is increased somewhat.

Brenner, in U.S. Patent No. 2,532,283, states that brass and bronze may be plated by a chemical process if they are "given additional preplating treatment in the form of a momentary "bright" acid dip followed by a dip for about one minute in a solution of 0.02 gram of palladium chloride ($PdCl_2$) and 20.0 grams of hydrochloric acid per liter of solution. The concentration and length of the palladium dip can be varied inversely and when the solution is heated, can be decreased." He states that "objects of platinum and silver, when immersed in the plating bath require momentary contact with aluminum to initiate the plating operation." Thus, it may be seen that my process is suitable for use on materials upon which the chemical plating reaction may be initiated by means which are known in the art.

Using the solutions which I have mentioned, as the reaction proceeds the pH tends to drop, and for continued rapid deposition, additions of a dilute sodium hydroxide solution must be made. Sodium hypophosphite is added only when needed, since a varying amount of loss of hypophosphite takes place in the presence of nickel salts by the following reaction:

$$NaH_2PO_2+H_2O\rightarrow NaH_2PO_3+H_2\uparrow$$

To make the process continuous, both reducting agent and nickel salts must be replenished from time to time.

The following plating operations using the above solutions will serve as examples of the operation of my improved method:

Example I

A length of steel wire (in this instance 35.5 mils in diameter) was immersed in a tank of solution A, the solution being held at 180° F. for 30 minutes. No discernible nickel deposit was produced. However, when a 15 ampere current was passed through the wire from an alternating current source, thereby heating the wire, a coating of nickel 0.5 mil in thickness was deposited on the wire in about 35 minutes.

Example II

An electric heater was inserted into the open end of a hollow steel cylinder, which was closed at the opposite end. The cylinder was immersed in solution A while the solution was maintained at 160° F. for a period of one hour. Nickel did not deposit out of the solution at any appreciable rate when the heater was not energized, but when the current was turned on and the cylinder was heated, a nickel deposit formed at a rate of about one mil per hour on the external surface of the cylinder.

Example III

A coil of steel tubing having ¼" outside diameter and a .03" wall thickness was immersed in solution B for one hour, during which time the solution was maintained at 164° F. A deposit of 0.12 mils in thickness resulted. With steam at 232° F. passing through the tubing, a deposit 0.92 mil thick resulted, after one hour, on the external surface of the tubing. In this case, it may be noted that although the steam within the tubing was well above the boiling point of the plating solution, the solution did not boil because of the rapid convection which takes place during the process.

Example IV

A tank of solution A was placed in an induction furnace with a steel bar suspended in it. The solution was maintained at an average temperature of 130° F. for two hours, and no measurable amount of nickel was deposited. However, when the bar was heated by the induction effect of the induction furnace for one hour, a 0.25 mil thickness of nickel was deposited on the steel bar.

The drawing is further illustrative of the foregoing examples, each figure of the drawing corresponding to its respectively numbered example.

Figure 1 illustrates the process performed in Example 1.

Figure 2 illustrates the process performed in Example 2.

Figure 3 illustrates the process performed in Example 3.

Figure 4 illustrates the process performed in Example 4.

My proposed method is suitable for nickel plating the interior of tubing or pipes. The tubing, either in a coil, or in the form of numerous straight courses connected by U-bends, and having an inlet and an outlet end, can be enclosed in a heating chamber and plating solution passed through the tubing. Plating can then be accomplished by maintaining the heating chamber temperature near the boiling point of the solution for the appropriate length of time for the thickness of plating desired. After plating, the tubes or pipes can be further processed, as by bending, or cutting to the desired lengths.

Similarly, by introducing plating solution into a hollow body which is heated externally, the body may be internally plated.

Massive bodies also can be plated by my method, by heating them, as in a furnace, then dipping into the solution, with repeated applications of heat, to restore heat lost to the solution, and repeated dipping, to the extent necessary, until the proper thickness of nickel is deposited.

I have found that the optimum workpiece temperature, in all cases, is a temperature just below that at which the solution in contact with the workpiece begins to boil. If the temperature is too high, the solution will boil, and the workpiece will then be bathed with both liquid and vapor alternately, producing a very unsatisfactory plating result. It also appeared from my tests, that if the solution could be kept below about 185° F., the deposit of undesired nickel plating could be largely eliminated.

My method is readily applicable to the type of industrial process in which the solution used is replenished continuously as it becomes depleted. This type of process has the advantage that, by providing for the regeneration of the solution, a high quality nickel plating of any reasonable desired thickness may be obtained. Such processes usually embody a small plating tank and a larger solution reservoir, with means for heating the solution in the small plating tank, and frequently, means for cooling the solution as it goes to the large reservoir. Such systems usually also include various pumps, filters, valves, etc. It is in this type of system that the problem of unwanted metal deposits is particularly serious, and necessitates the complex apparatus providing for repeated heating and cooling of solution as it flows through the system, and embodying glass-lined or plastic tanks, pipes, etc. By the application of my improved method, however, these expensive glass-lined and plastic systems may, in many cases, be dispensed with. It still is desirable, although not absolutely necessary, to have a system comprising a small plating tank and a larger reservoir, since it is desirable to maintain the plating solution at a temperature above room temperature in the plating tank. Actually, the process would work even if the main body of the solution were kept appreciably below room temperature, but there is no apparent economic reason for operating the system in this way.

What I claim is:

1. A process comprising subjecting a surface of a workpiece to be coated with nickel to a body of chemical nickel plating solution comprising nickel cations and hypophosphite anions for time sufficient to produce a coating of desired thickness, said solution, except essentially a thin layer thereof closely adjacent to said workpiece surface being maintained at temperatures below the precipitating temperature thereof, said surface of said workpiece being maintained at temperatures above the precipitating temperature of said solution and below the boiling point thereof whereby a thin layer of solution adjacent said surface is at a temperature above the precipitating temperature of said solution and below the boiling point thereof, said surface of said workpiece being composed of a substance of the class consisting of copper, silver, gold, beryllium, boron, germanium, aluminum, thallium, silicon, carbon, vanadium, molybdenum, tungsten, chromium, selenium, tellurium, titanium, iron, cobalt, nickel, palladium, platinum and alloys thereof.

2. The process set forth in claim 1 werein said chemical nickel plating solution is an aqueous solution comprising a nickel salt within the range from about 15 grams per liter to about 75 grams per liter and sodium hypophosphite within the range from about 5 grams per liter to about 50 grams per liter, and the pH of said solution is maintained within the range from about 3.5 to 6.0.

3. The process set forth in claim 1 wherein said body of chemical nickel plating solution is maintained at a temperature below 185° F. except a thin layer adjacent to said workpiece surface.

4. The process set forth in claim 1 wherein the said body of chemical nickel plating solution is maintained within a temperature range below 185° F. and the said solution is an aqueous solution comprising nickel chloride within the range from about 15 grams per liter to about 75 grams per liter, and sodium hypophosphite within the range from about 5 grams per liter to about 50 grams per liter, and the pH of said solution is maintained within the range from about 3.5 to 6.0.

5. In a nickel plating process of the chemical type, in which metallic nickel is deposited on a workpiece surface out of an aqueous chemical nickel plating solution near its boiling point, said solution comprising nickel cations and hypophospite anions, the process comprising the steps of immersing a workpiece of the class consisting of copper, silver, gold, beryllium, boron, germanium, aluminum, thallium, silicon, carbon, vanadium, molybdenum, tungsten, chromium, selenium, tellurium, titanium, iron, cobalt, nickel, palladium and platinum, and alloys thereof, in a body of said nickel cation-hypophosphite anion solution, the major part of said body of solution being maintained at a temperature below the precipitating temperature of said solution, heating the said workpiece surface to a temperature such that the portion of the said solution immediately adjacent said workpiece surface is slightly below the boiling point of said solution, and continuing said immersion and heating for a period of time required to produce the thickness of nickel plating desired, whereby nickel plating conditions occur in said body of solution substantially only at said workpiece surface.

6. The process set forth in claim 5 wherein said chemical nickel plating solution is an aqueous solution comprising a nickel salt within the range from about 15 grams per liter to about 75 grams per liter, and sodium hypophosphite within the range from about 5 grams per liter to about 50 grams per liter, and the pH of said solution is maintained within the range from about 3.5 to 6.0.

7. The process set forth in claim 5 wherein the said body of chemical nickel plating solution is maintained within a temperature range below 185° F. and the said solution is an aqueous solution comprising nickel chloride within the range from about 15 grams per liter to about 75 grams per liter, and sodium hypophosphite within the range from about 5 grams per liter to about 50 grams per liter, and the pH of said solution is maintained within the range from about 3.5 to 6.0.

8. Heating a surface of a workpiece to be nickel-coated while said surface is immersed in a body of chemical nickel plating solution comprising nickel cations and hypophosphite anions which is at a temperature below its precipitating temperature, said surface being at a temperature between the precipitating temperature of said solution and its boiling point, said workpiece surface being metallic and catalytic toward said solution, thereby to produce a deposit of nickel on said surface while said solution remains at a temperature below its precipitation temperature except for essentially thin layer closely adjacent to said workpiece surface.

References Cited in the file of this patent

UNITED STATES PATENTS

97,838	Walker	Dec. 14, 1869
2,532,283	Brenner et al.	Dec. 5, 1950

UNITED STATES PATENT OFFICE

CERTIFICATION OF CORRECTION

Patent No. 2,955,959 October 11, 1960

Arthur H. Du Rose

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the grant, lines 1, 2 and 3, for "Arthur H. Du Rose, of Euclid, Ohio," read -- Arthur H. Du Rose, of Euclid, Ohio, assignor to The Harshaw Chemical Company, of Cleveland, Ohio, a corporation of Ohio, --; line 12, for "Arthur H. Du Rose, his heirs" read -- The Harshaw Chemical Company, its successors --; in the heading to the printed specification, line 3, for "Arthur H. Du Rose, 107 E. 202 St., Euclid 23, Ohio" read -- Arthur H. Du Rose, Euclid, Ohio, assignor to The Harshaw Chemical Company, Cleveland, Ohio, a corporation of Ohio --.

Signed and sealed this 9th day of May 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents