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ELECTRO-ELECTROLESS PLATING METHOD

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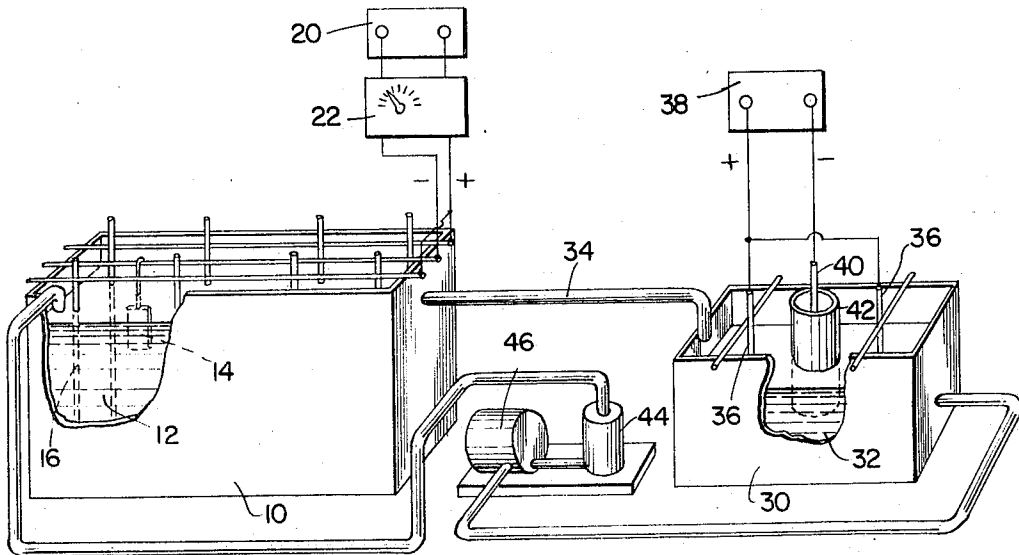


FIG. 1

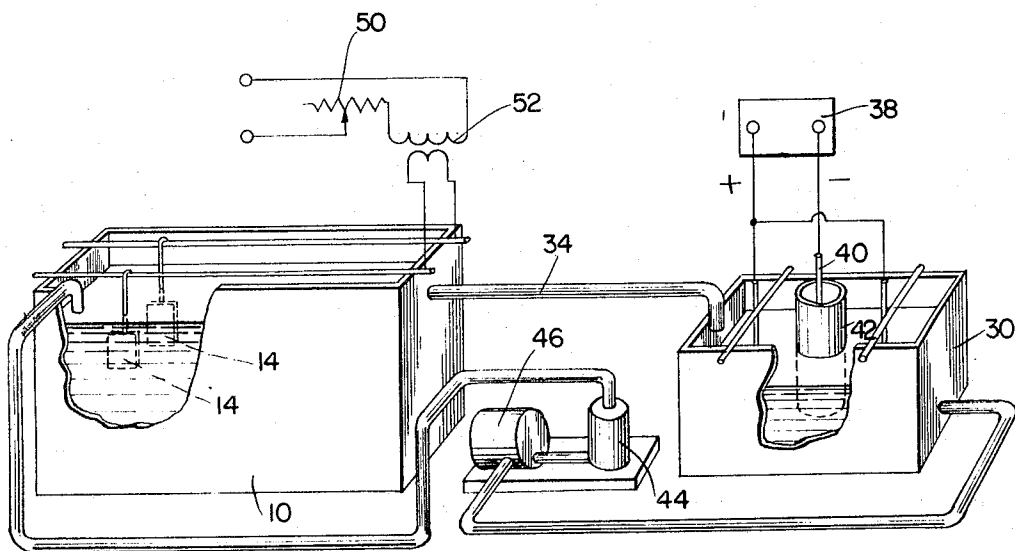


FIG. 2

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ELECTRO-ELECTROLESS PLATING METHOD

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This invention relates to an improved method of depositing on a metal or metal-coated object a brilliant plating of nickel or nickel-phosphorus alloy, this being obtained without the use of "brighteners" or leveling agents such as pyrophosphate, phosphonic acid or phosphinic acid. The art of electro-plating metal articles by immersing the work-piece in a solution of a salt of the plating metal and sending an electric current through the solution from an anode preferably consisting of the plating metal is old and well-known. The art of "electroless" plating by immersing a metal object in a bath containing a salt of the metal to be deposited and an alkaline hypophosphite with no impressed electric current from an outside source is described in U.S. Patent No. 1,207,218 granted to Roux on December 5, 1916, and in several later patents. For example, Patent No. 2,532,283 describes an autocatalytic chemical reduction process by which pure nickel is deposited on a metal work-piece immersed in a bath containing in solution a nickel salt and a relatively low concentration of hypophosphite (sodium, ammonium or potassium).

According to the present invention a small electric current, which may be either direct or alternating, is employed to speed up the depositing of nickel or nickel-phosphorus alloy on a metal work-piece immersed in a bath containing a nickel salt and a hypophosphite, preferably sodium hypophosphite. Since an electric current is employed, though far too small for plating in the usual manner, this process can be termed an "electro-electroless" process. Deposits produced by the electro-electroless process are crystalline in character whereas those produced by the electroless process are believed to be amorphous. The electro-electroless coating is less porous and more resistant to tarnishing than the electroless coating. An important feature of the small current used in the electro-electroless process is that it extends the working life of the solution and has a deterrent effect in restraining sodium hypophosphite from causing spontaneous decomposition of the bath.

If the directions given hereinafter are followed, a brilliant plating results, the thickness of which is remarkably uniform in partially enclosed surfaces such as deep crevices or the interiors of tubes.

Since the depositing of nickel or nickel-phosphorus alloy on the work-pieces results in depletion of the nickel salt and hypophosphite in the bath, reconstitution of the solution is necessary either by periodic additions of a nickel compound and a hypophosphite, or by recirculation of the electrolyte through an auxiliary tank by means of apparatus illustrated on the drawing, of which

FIGURE 1 is a diagrammatic view of apparatus for use with an impressed direct electric current; and

FIGURE 2 is a similar view of apparatus for use with an alternating current.

The apparatus shown in FIGURE 1 comprises a main working tank 10 containing a pool 12 of electrolyte in which is immersed one or more cathode work-pieces 14 and one or more nickel anodes 16. A suitable source of direct current, such as a battery 20, is connected to the anodes and cathodes in the tank 10, preferably through an automatic switching means 22 to turn the current on and off periodically. For example, the switch can be set to turn the current on for 30 seconds and then off for 30 seconds, or can be set to give on and off periods of dif-

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ferent duration. The wetted areas of the work pieces should be much greater than those of the anodes, e.g. ten to one, so as to have a relatively high current density at the anodes.

An auxiliary tank 30 is provided to keep the electrolyte in the tank 10 up to strength. Electrolyte from the main tank 10 flows by gravity into a pool 32 in the tank 30 through a pipe 34. Nickel anodes 36 are dissolved in the pool 32 to reinforce the nickel content therein, the dissolving of the nickel being promoted by direct electric current from a suitable source such as a battery 38 the terminals of which are connected respectively to the nickel anodes 36 and a copper cathode 40 immersed in a 10% solution of sulphuric or hydrochloric acid in a porous pot 42. The enriched electrolyte in the pool 32 is pumped back to the main tank 10 through a filter 44 and connecting pipes by a pump 46 driven by any suitable means (not shown). The nickel anodes 36 in the auxiliary tank constantly replenish the nickel constituent of the plating bath. To replenish the hypophosphite as it is consumed, a fresh solution of hypophosphite can be added to the pool 32 at intervals.

When alternating current is used, as hereinafter described, work-pieces 14 are used as both electrodes, the work-pieces being selected so that the wetted areas of the two electrodes are substantially equal to each other. This results in substantial uniformity of deposits of metal on the electrodes. A rheostat 50 and a transformer 52 may be employed to control the current supplied to the plating bath.

In practicing the present invention, the following ingredients for the bath are essential:

At least one nickel salt (e.g. the sulphate and/or chloride);

A hypophosphite (preferably sodium);

A citrate salt (e.g. sodium citrate) to hold the nickel salt in solution.

For example, the following "electroless" formula can be employed:

	Oz. per gal. of water
Nickel sulphate (and/or chloride) -----	4
Sodium citrate -----	4
Sodium hypophosphite -----	2

The metal salt, the citrate and the hypophosphite are thus in the proportion of 2:2:1 by weight.

If a low-tension electric current is sent through the electrolyte (0.7 amp. to 3 amps. per square foot of cathode surface) the operation is effective for temperatures of the electrolyte as low as 120° F. A nickel anode should be used, having a surface area not more than one-tenth of the surface area of the cathode, the relatively high anode current density serving to prevent nickel from being deposited on the anode from the solution.

Currents lower than 0.7 amps. per square foot of cathode surface will have some effect on the rate and quality of deposited metal, but the benefit to be derived from the use of a current density of less than 0.7 amps. is negligible. The effective range of current densities for the practice of this invention is from 0.7 to 3 amps. per square foot of cathode surface, a current of about 2 amps. being optimum.

One of the factors which determines the current density in any instance is the voltage impressed on the electrodes. It has been found that an impressed voltage of about 1.5 volts is required to overcome the electric potential which is existent in the "electroless" plating cell.

EXPERIMENT

To demonstrate the effectiveness of a low-tension electric current on an autocatalytic bath at a temperature of 120° F. two solutions were prepared according to the

above formula except that in one of them the hypophosphite ingredient was omitted. A direct current of 0.7 amp. per square foot of cathode surface was used. The results were as follows:

Solution	Current	Result
Without hypophosphite	0.7 amp.	No deposit.
With hypophosphite	None	Do.
Do.	0.7 amp.	Bright continuous coat.

Similar results were obtained by the use of *alternating* current of 0.7 amp., both the anode and cathode in this case being work-pieces.

It appears from these experiments that the process is not one of electroplating (as that term is used in the trade) but rather is one in which desirable results are available at the *threshold* of conditions necessary for electroplating. The small applied current (D.C. or A.C.) apparently supplements the galvanic potential of the hypophosphite and excites it to do work which it could not do without such supplementary energy.

The evenness or uniformity of thickness of the plating deposited on a work-piece having deep recesses is improved by periodic interruptions of the applied current. For example, the current can be turned on and off at intervals of a few seconds, and the "on" periods do not have to be equal to the "off" periods. For example, by using an intermittent current of 3.0 amps. per square foot of cathode surface at a temperature of about 180° F. a 6-foot length of one-fourth inch brass tube was plated with a sound, brilliant nickel coating both inside and outside without the use of an internal electrode. The tube was first cleaned in the usual manner with an alkaline cleaner, followed by a fresh water rinse, a brief immersion in acid (1 part nitric, 2 parts sulphuric) and a second rinse. The tube was then suspended by copper wires in an electroless bath and was given a D.C. current of 3 amps. for a few minutes, followed by an interrupted current (2 seconds on, 2 seconds off) for one hour. A bright continuous coating of nickel or nickel-phosphorous was deposited on the entire inner and outer surfaces of the tube. If a heavier interior coating is desired, a flow of electrolyte should be promoted through the tube to sweep out spent electrolyte and thus ensure evenness of deposit.

The effectiveness of interrupting the current may be explained on the theory that the cathode, anode and electrolyte form a cell which may be charged with extra electrical energy by the impressed current. This extra accumulated charge of energy is rapidly discharged when the current from the outside is cut off.

The specific substances hereinbefore mentioned are usually to be preferred because of their commercial availability, but other substances can be effectively used with or instead of those mentioned. Thus, nickel ammonium sulphate, nickel citrate or nickel acetate are effective in practicing the invention. Similar salts of cobalt (including the chloride and sulphate) can be substituted wholly or in part for the nickel salts hereinbefore mentioned. If a cobalt salt is mixed with a nickel salt, the deposited metal will be a nickel-cobalt-phosphorus alloy.

Sodium hypophosphite is the most commercially available hypophosphite, but the electro-electroless process can be practiced if this salt is partly or wholly replaced by ammonium hypophosphite, potassium hypophosphite, calcium hypophosphite, barium hypophosphite or phosphorous acid, but care must be taken to see that the ratio of nickel ions to hypophosphite ions is kept substantially constant.

The concentration of the electrolyte bath described in the foregoing example is not critical but the bath is effective if concentrated (e.g. by evaporation of the

solvent) to several times the strength described or if diluted to half of its original strength.

The "electro-electroless" process herein described produces brilliant nickel coatings without the aid of chemical "brighteners" and with no bath instability as is common with "electroless" methods. It is furthermore not sensitive to specific conditions but can be used at temperatures from 120° F. to the boiling point and with a pH anywhere from 2.0 to 9.0, the preferred value being about 4.5. The process is inexpensive and easy to control, and deposits coatings which are very adherent and are brilliant, continuous and evenly distributed, on bases of any metal, including aluminum or alloys thereof, but excluding zinc, or cadmium or magnesium alloys.

I claim:

1. A process of depositing nickel on an article having metal surfaces, which comprises immersing said surfaces as a cathode in an electrolyte consisting of a solution of nickel sulphate and chloride, sodium citrate and sodium hypophosphite in the approximate proportion of 4 oz. nickel sulphate and chloride, 4 oz. sodium citrate and 2 oz. sodium hypophosphite in each gallon of water, immersing an anode in said electrolyte, and passing a direct electric current of from 0.7 ampere to 3 amperes per square foot of wetted cathode surface through the electrolyte and electrodes.

2. A process as described in claim 1, the wetted surface of said anode being about one tenth that of said cathode.

3. A process as described in claim 1, said current being interrupted at frequent intervals.

4. A process as described in claim 1, said current being a direct current.

5. A process as described in claim 1, said current being an alternating current, said anode and cathode having approximately equal areas of wetted surface.

6. A process of depositing a coating on a metal surface which comprises immersing said surface as a cathode in an electrolyte consisting of an aqueous solution of at least one nickel salt from the class consisting of nickel sulphate, nickel chloride, nickel ammonium sulphate, nickel citrate and nickel acetate, at least one hypophosphite from the class consisting of sodium hypophosphite, ammonium hypophosphite, potassium hypophosphite, calcium hypophosphite and barium hypophosphite, and sodium citrate, said nickel salt, citrate, and hypophosphite being in the approximate proportions of 2:2:1 by weight, immersing an anode in said electrolyte, and passing a direct electric current of from 0.7 to 3.0 amperes per square foot of wetted cathode surface through said electrolyte and electrodes.

7. A process of depositing a coating on a metal surface which comprises immersing said surface as a cathode in an electrolyte consisting of an aqueous solution of at least one metal salt from the class consisting of nickel sulphate, cobalt sulphate, nickel chloride and cobalt chloride, sodium citrate, and sodium hypophosphite, said metal salt, citrate and hypophosphite being in the approximate proportion of 2:2:1 by weight, immersing an anode in said electrolyte, and passing a current of from 0.7 to 3.0 amperes per square foot through said electrolyte and electrodes.

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