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ELECTROLESS NICKEL PLATING OF HOLLOW CONTAINERS

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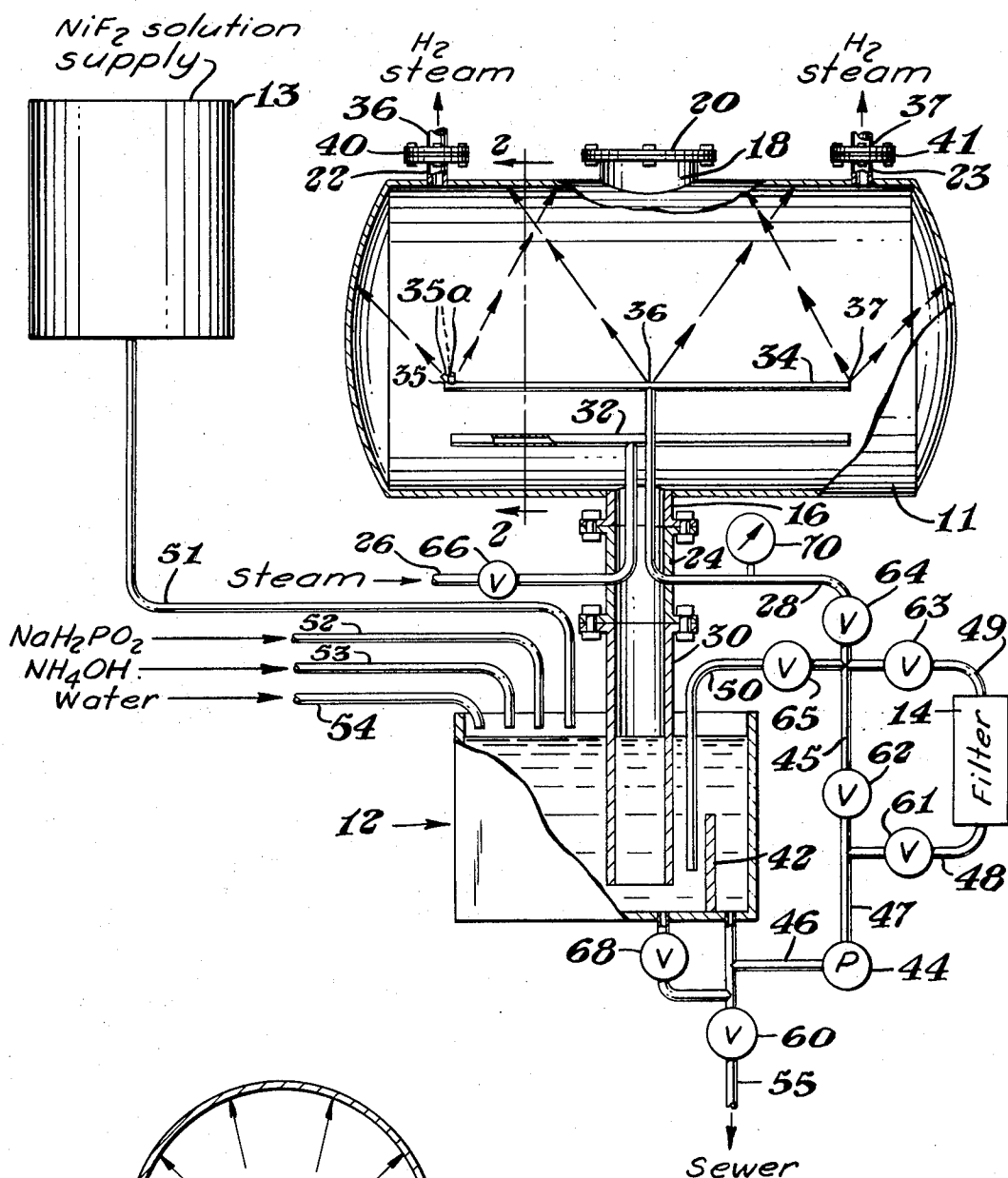


Fig. 1

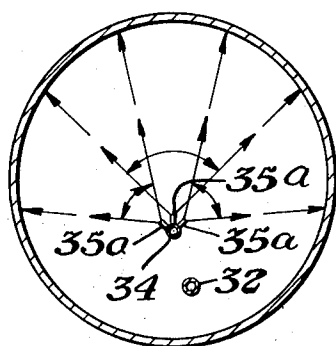


Fig. 2

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1

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ELECTROLESS NICKEL PLATING OF HOLLOW CONTAINERS

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May 31, 1966. This application Aug. 5, 1969, Ser.
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U.S. Cl. 117—50

15 Claims

ABSTRACT OF THE DISCLOSURE

Catalytic metal surfaces are nickel plated from a cation-hypophosphite anion solution. Plating is accomplished by spraying the reactive solutions on the metal surface and heating the surface as by contacting it with steam. Plating solution is recovered, adjusted in pH as necessary to assure satisfactory plating and recycled.

This application is a continuation-in-part of application Ser. No. 554,026 filed May 31, 1966 and now, abandoned.

This invention relates to chemical nickel plating and more particularly is concerned with a novel process for chemically plating a nickel-based coating on the surface of metals and metal coated surfaces of other thermally resistant materials.

There is a need for an improved and more economical method for the application of a corrosion resistant and/or decorative coatings of the nickel-phosphorous type by chemical means, a process well known in the art and hereinafter referred to as electroless nickel plating, to the catalytic surfaces of fabricated metal products, such as tanks, chemical process equipment, etc. Methods usually employed comprise either completely filling a hollow container with an aqueous electroless nickel plating solution, ordinarily of the nickel cation-hypophosphite anion type, or partially filling the container with such a solution and rotating said container about a substantially horizontal axis so as to contact all portions of the surface to be plated with the plating solution.

One embodiment of the latter method well known in the art for thus plating the interior surfaces of large tanks, for example, comprises partially filling the tank with an aqueous chemical plating solution of the nickel cation-hypophosphite anion type and recirculating relatively large volumes of plating solution through a complex cooling, processing, storage and heating system. This embodiment requires large volumes of plating solution relative to the volume of the tank being plated since the solution is repeatedly reused and, therefore, processed so that the composition of the solution recirculated to the tank is substantially constant. In addition to reservoirs required to handle such large volumes of plating solution, other auxiliary equipment is required. For example, a heat exchanger or other cooling device is usually employed to cool the solution leaving the tank to a temperature substantially below the plating temperature maintained within the tank before returning it to a reservoir, and a second heat exchanger means is necessarily employed to heat the solution before returning it from a reservoir to the tank so as to maintain the solution in the tank within a predetermined plating temperature range. Additional equipment also is needed to add chemical reagents to the recirculating solution. Other equipment is ordinarily required to process the relatively large volume of plating solution in order to maintain the concentrations of certain components of the solution within operable ranges; for example, it is usually necessary that phosphite ions formed by the chemical plating reactions be removed from the

2

solution by precipitation and filtration or other means to prevent the formation of a precipitate of nickel phosphite as a source of nickel ions is added to the solution to maintain the nickel ion concentration within a predetermined range. In this method the plating solution as it leaves the tank being plated is usually cooled to a temperature at which excessive "plating-out" of the solution will not occur on catalytic surfaces of auxiliary equipment which it contacts before being reheated to the plating temperature prior to re-entering the tank.

When external surfaces are to be plated such as the external surfaces of pipe and the like or certain fabricated devices which are incapable of holding the plating fluids, they are generally immersed in an enclosed or partially enclosed chamber and the aforementioned procedure followed.

In any method for electroless nickel plating with a plating solution of the nickel cation-hypophosphite anion type, the possibility of spontaneous decomposition, i.e., reduction of nickel ions by hypophosphite reducing agent to form finely divided metallic nickel particles within the body of the solution, always exists. This spontaneous decomposition once initiated is autocatalytic since the large surface area of the metallic nickel particles thus formed catalyzes further reduction of nickel ions to metallic nickel. Should such decomposition occur it is usually necessary to discard the entire volume of plating solution, to completely remove all metallic nickel particles and other insoluble matter both from the article being plated and from all equipment employed in the plating process, and to thoroughly clean and flush the entire system, usually with water, before resuming the plating operation with fresh plating solution. Thus, in the art methods described hereinbefore which usually require large volumes of plating solution in relation to the surface area of the article to be plated, such decomposition of the solution disrupts the plating operation, creates a waste disposal problem, necessitates discarding large quantities of expensive plating solution components, and results in costly and uneconomical operation.

A principal object of the present invention is to provide a method for electroless nickel plating the surfaces of a fabricated article using markedly reduced volumes of plating solution as compared with art methods practiced heretofore. A further object is to provide a method for electroless nickel plating the interior surfaces of hollow containers such as large tanks, chemical process equipment and the like while such containers are "in place" or in normal operating position. Another object is to provide a method for electroless nickel plating the catalytic surfaces of fabricated articles which requires a minimum of auxiliary processing equipment and substantially eliminates the need for large reservoirs, heat-exchangers, plating solution processing equipment and the like.

Other objects and advantages of the present invention will become apparent from the detailed description presented hereinafter when considered in reference to the accompanying drawing.

One embodiment of the present invention is illustrated in the accompanying drawing wherein the same parts in the different views are identified by the same numbers:

FIG. 1 is a side elevation, partly in section, of a tank to be plated and of auxiliary equipment used in the plating operation.

FIG. 2 is a transverse sectional view of the tank taken along line 2—2 of FIG. 1.

The method of the present invention comprises disposing suitable spray apparatus adjacent the surface to be plated, said surface being catalytic to the deposition of a nickel-based coating from a plating solution of the

3

nickel cation-hypophosphite anion type, heating said surface and maintaining said surface within a predetermined plating temperature range, spraying an electroless nickel plating solution of the nickel cation-hypophosphite anion type so that all portions of the surface are contacted with plating solution either by direct impingement of the sprayed solution or by the gravity flow of the solution along the surface. Plating solution is collected from the bottom interior of the enclosing chamber and funneled or pumped into a receiving and recirculating means. The plating solution is recirculated to said spray apparatus, while maintaining the hypophosphite ion concentration and the pH of the solution within predetermined ranges.

It is preferred that a substantially continuous film of plating solution be maintained in contact with all portions of the interior surface by employing spray apparatus which provides a fixed spray pattern. However, a cyclic spray pattern such as that provided, for example, by rotary or oscillating type spray apparatus may be employed so that all portions of the surface to be plated are contacted by plating solution in a cyclic rather than in a continuous manner. For example, it has been found that satisfactory coatings can be deposited by employing such a cyclic spraying operation wherein portions of the surface are contacted with plating solution for a period of about 3 to 4 minutes during a 10 minute spray pattern cycle.

In the practice of the invention, the surface of an article to be plated can first be heated and the plating solution then supplied to the spray apparatus and sprayed onto the heated catalytic surface of the article. Alternatively, the heating of the surface of the article to the predetermined plating temperature and the spraying operation can be carried out simultaneously, for example, steam and the plating solution can each be sprayed on the surface to be coated.

In one embodiment of the present invention for plating a hollow container having one or more outlets disposed near the bottom of said container, plating solution flowing along the interior surfaces of the container toward such bottom outlets is drained from the interior of the container through said outlets into receiving and recirculating means disposed exterior to said container.

In plating other containers the receiving and recirculating means can be positioned either within or outside such containers and the plating solution can be transported by pumping, suction, pressure or other liquid transport means from the bottom interior of the container to said receiving and recirculating means.

The term enclosing chamber as used herein means any container to be interiorly plated, or enclosure in which articles are placed for plating treatment, having walls which define a substantially completely enclosed interior space. This term includes any vessel or container which has openings in said walls in communication with the exterior of said containers, which openings may be temporarily sealed during the plating operation to prevent escape of plating solution from the interior of the container. Although sealing is advantageous, it is not necessary since the entire plating process can be practiced under complete exposure to the atmosphere. The process, however, is particularly suitable for use with hollow containers having at least one outlet disposed at or near the bottom of said containers to facilitate solution removal from the interior of such containers.

The term catalytic surface as used herein means any surface catalytic to the deposition of a nickel-based coating from a plating solution of the nickel cation-hypophosphite anion type. Such surfaces may consist essentially of, for example, one or more metals of the group of iron, cobalt, nickel, copper, aluminum, magnesium, titanium, silver and platinum.

Articles to be coated may be fabricated from such metals or may be made of some other material such as

4

wood or a thermally stable plastic to which has been applied a surface coating of a catalytic metal.

In actually carrying out the method of the present invention, the surface of the article is first prepared for plating by degreasing, mechanically cleaning, light pickling and like operations according to standard practices well known in the art. The surface of the article is then initially heated to a predetermined plating temperature by any suitable means. The surface may be heated by either internal or external contact within any convenient heat source including, for example, hot water, radiant heat, steam or other hot gas. The method of heating will depend on several considerations, including the size, location, the type of container, i.e., jacketed, insulated or uninsulated, as well as the material of construction. For most operations with article having catalytic metal surfaces this plating temperature is in the range of from about 175 to about 200° F. The plating solution is then supplied to spray apparatus disposed adjacent said surfaces as hereinbefore described and the temperature of the interior surface and of the plating solution is maintained within a predetermined plating temperature range by suitable means during the spraying and recirculation of the plating solution.

In one embodiment of the invention, the surface of the article to be plated and the recirculating plating solution are initially heated to the plating temperature simultaneously by the introduction of steam. Such steam may be applied to conduits through which the plating solution travels or to surfaces contacted with the plating solution. In a preferred embodiment the plating solution is heated by being sprayed through the hot vapors as well as by contact with the heated surface to be plated.

It is well understood that necessary precautions must be taken to protect the surface to be plated from any corrosive attack which would detrimentally affect the deposition of a sound, adherent electroless nickel coating while the surface is being heated to the plating temperature and/or before it is contacted with the plating solution. To minimize such a possibility, it may be desirable to carry out simultaneously the steps of heating the surface to be plated and of spraying the plating solution rather than to heat the surface to the plating temperature before contacting it with the plating solution.

In practice of the invention, ordinarily relatively small volumes of plating solution are used in relation to the surface area to be plated. The solution is sprayed and recirculated at a rapid rate to assure that the temperature of the recirculating solution is substantially constant and that the composition of the solution per pass through the container is also substantially constant. Such rapid recirculation also serves to maintain all portions of said surface at a substantially constant temperature to assure deposition of a nickel-based coating of uniform thickness. Preferably solution volume (V)/surface area (A) ratios in the range of from about 0.1 to about 0.5 are used. (V being the volume in gallons of the recirculating plating solution and A being the area in square feet of the surface to be plated.)

The method of the present invention particularly is adapted to the deposition of electroless nickel-phosphorous type coatings of a predetermined desired thickness on the surface of the article by employing a succession of plating cycles, the nickel values being substantially depleted from a relatively small volume of plating solution of the nickel cation-hypophosphite anion type during each cycle after which the depleted solution is discarded and replaced with a quantity of fresh solution.

The initial composition of the plating solution is predetermined so that the nickel values originally contained therein can be substantially depleted during a plating cycle to provide a coating of a predetermined desired thickness. However, the hypophosphite ion concentration, the pH, the concentration of other components of the plating solution, such as buffering agents, chelating agents, etc.,

5

are maintained within predetermined ranges such that a satisfactory rate of plating is assured, the plating solution does not detrimentally degrade, the equipment is not detrimentally attacked by contact with the solution. Ordinarily such ranges are maintained by the addition of predetermined amounts of suitable reagents to the recirculating solution, usually as aqueous solutions, as is well understood by one skilled in the art of electroless nickel plating. For most nickel cation-hypophosphite anion type chemical plating solutions, operable sources of hypophosphite ions are water-soluble salts including, for example, alkali metal hypophosphites such as sodium hypophosphite, ammonium hypophosphite and the like. Suitable bases ordinarily added to control the pH of such solutions to maintain solubility of its ingredients include ammonium hydroxide and alkali metal hydroxides, such as sodium hydroxide, for example.

Electroless nickel plating solutions of the nickel cation-hypophosphite anion type which are stable at the plating temperature employed and from which nickel values can be substantially depleted without the formation of detrimental amounts of insoluble material such as, for example, nickel phosphite, while the concentrations of hypophosphite ions and other plating solution components are maintained within predetermined ranges may be employed in the practice of the present process. For a particular plating solution formulation, the plating temperature and the concentrations of the components of the solution to be employed in the present method will depend on the characteristics of said solution which relate to solution stability, plating rate, and other variables as the nickel values are depleted from the solution, as is well understood by one skilled in the art.

It is well known that such solutions commonly contain various additives and/or components such as nickel complexing agents, chelating agents, buffering agents, stabilizers, exaltants, wetting agents and the like. Insofar as these do not detrimentally degrade or otherwise interfere with the criteria for operability required of a plating solution suitable for use in the present process, solutions containing such additives are operable. The present method, therefore, is not limited to the use of any particular plating solution formulation.

Electroless nickel plating solutions suitable for use in the present method are not to be confused with solutions well known in the art as "spray type" electroless plating solutions, e.g., as set forth in U.S. Pat. 2,956,900, which are normally used to deposit relatively thin coatings on catalytic surfaces by a single contact of converging sprays of both a nickel ion containing solution and reducing agent containing solution from separate spray means upon said surfaces. Reducing agents commonly employed in such two solution spray methods, such as, for example, hydrosulfites, are so highly reactive that they cannot be used in electroless plating solutions suitable for use in the method of the present invention which contain both nickel ions and a hypophosphite reducing agent.

The use of relatively small volumes of plating solution as uniquely practiced in the present process has several unexpected advantages.

One important advantage is that the resulting low V/A ratios permit the rapid heating of the plating solution to the predetermined plating temperature since it is heated both by being sprayed through the hot vapors between its issuing spray orifice and by repeatedly contacting the relatively large heated surface area of the article being plated as the solution is recirculated. The hottest surface contacted by the plating solution, therefore, is the heated surface of the article to be plated, and no other heat exchanger surfaces are necessary. Since the solution is not heated to a temperature higher than the predetermined plating temperature, the possibility that spontaneous decomposition could be initiated by the solution contacting high temperature heat exchanger surfaces substantially is eliminated.

6

Another advantage of the present method is that insoluble foreign matter and small amounts of any precipitates which may form within the plating solution are continuously flushed from the surfaces of the article being plated as the solution is recirculated so that such insoluble material cannot accumulate on portions of such surfaces thereby to interfere with the deposition of a uniform, adherent, imperfection free coating.

A further advantage is that, should spontaneous decomposition of the plating solution occur for any reason, the relatively small volume of solution employed can be discarded much more readily, replaced with a quantity of fresh solution and the system more easily and quickly readied for continued plating, than when using the large solution volumes employed in the art processes practiced heretofore.

Another advantage of the present method resulting from the use of small volumes of plating solution which are discarded after the nickel values have been substantially depleted therefrom as compared to the repeated reuse of relatively large volumes of plating solution, as is commonly practiced in well known methods, is that such large volumes of solution must normally be processed to restore the chemical balance of the solution. For example, phosphite ions formed in the chemical plating reactions as nickel ions are reduced by the hypophosphite reducing agent usually must be removed so as to prevent the precipitation of nickel phosphite as nickel ions are added to the solution to maintain the nickel ion concentration within a range which permits the repeated reuse of such large volumes of plating solution.

An additional advantage of the present method relates to the problem of hydrogen blanketing. In any method for the electroless nickel plating of hollow containers or fabricated articles having cavities which could entrap gas, the blanketing of portions of the interior surface of the container by pockets of the hydrogen gas which is evolved in the chemical plating reactions may prevent the deposition of a nickel-based coating of uniform thickness. This blanketing is particularly likely to occur with those methods which require that the container or fabricated article be completely filled with, or immersed in, plating solution in order to maintain all portions of the surface to be plated in contact with the solution. In the present method such hydrogen gas blanketing readily is avoided by positioning the spray apparatus so that all portions of the surface of the fabricated article, particularly those of irregular shape, are contacted with plating solution. This may be readily accomplished by moving the article to be plated in relation to the spray or moving the spray in relation to the article to be plated.

The following example will serve further to illustrate the present invention but is not meant to limit it thereto.

A 750 gallon capacity cylindrical mild steel tank approximately 6'6" in length, having a diameter of approximately 4'6", and having approximately 120 sq. ft. of internal surface area, was prepared for electroless nickel plating by sand blasting the interior surface of the tank, removing sand and other solid foreign matter from the tank interior by thorough vacuum cleaning. During the elapsed time interval between the preparation of the surface and the initial contact of the prepared surface with plating solution as described hereinafter, necessary precautions were taken to protect the surface from any corrosive attack which would detrimentally affect the deposition of a sound, adherent electroless nickel coating.

Referring to FIG. 1 of the drawing, the tank 11 had a 6" flanged bottom outlet 16 of circular cross-section, an 18" flanged top opening 18 of circular cross-section provided with a fluid tight cover plate closure 20, and two 3" flanged top openings 22 and 23. A conduit 24 of circular cross-section provided with a flange at each end was removably attached to the flanged bottom tank outlet 16 so as to provide a fluid tight seal between the flanged tank outlet 16 and the flanged conduit 24. Both a steam

inlet pipe 26 and a plating solution inlet pipe 28 were arranged to enter into the annular internal space of circular cross-section defined by the interior side walls of the conduit 24 through suitable openings in said side walls, said inlet pipes being permanently and rigidly attached thereto so as to provide a fluid tight seal between the exterior walls of the inlet pipes 26 and 28 and the side walls of conduit 24. Thus conduit 24 and the two inlet pipes 26 and 28 entering into the internal annular space defined by the side walls of conduit 24 constituted a single rigid assembly.

A conduit 30 of circular cross-section provided with a flange at one end was removably attached to the bottom flange of conduit 24 so as to provide a fluid tight seal therewith, said conduit 30 being of sufficient length to extend well below the surface of the plating solution contained in the receiver 12 and to a point near the bottom of said receiver.

Steam inlet pipe 26 extended vertically into the tank interior within the annular space defined by the interior walls of the conduit 24 and the bottom tank outlet 16 and was removably attached to a perforated steam distribution header 32, the longitudinal axis of which was substantially parallel to the longitudinal axis of the tank 11. The plating solution inlet pipe 28 extended vertically into the tank interior within the annular space defined by the interior walls of the conduit 24 and the bottom tank outlet 16 and was removably attached to the spray assembly header 34, the longitudinal axis of which was substantially parallel to the longitudinal axis of the tank 11.

Three (3) commercially available Sprayco No. 6E full-cone spray nozzles 35a were disposed and rigidly attached at each of three (3) points along the length of the spray assembly header 34 in such a manner that the conical spray patterns from the spray nozzles overlapped at the interior surfaces of the tank walls both when viewed from a direction perpendicular to the longitudinal axis of the tank 11 as shown in FIG. 1 and when viewed from a direction parallel to the longitudinal axis of the tank as shown in FIG. 2.

The disposition of the spray assembly header 34 within the tank 11 and the manner in which the nine (9) spray nozzles were disposed and attached to the spray assembly header 34 ensured that all portions of the interior surface of the tank were thoroughly and continuously wet with plating solution during the plating operation either by direct impingement of said solution emitting from said nozzles or by a substantially continuous film of plating solution flowing by gravity towards the bottom tank outlet 16 and out of said outlet through conduits 24 and 30 into the receiver 12.

The two (2) vent lines 36 and 37 were removably attached so as to be sealed fluid tight to the two (2) 3" flanged top tank openings 22 and 23 through which both steam and the hydrogen gas produced in the plating reactions were vented to the atmosphere, and were provided with fine mesh screens 40 and 41 to prevent droplets of sprayed plating solution from escaping through said top tank openings.

A baffle plate 42 was positioned within the receiver 12 so that solution could not leave said receiver and enter pump 44 through line 46 without flowing over the top of said baffle plate in order to minimize the intake of hydrogen gas from the plating solution in the receiver 12 into the pump 44. Receiver 12 was of sufficient capacity to contain the maximum volume of plating solution to be utilized during a plating cycle during the plating operation.

Following the cleaning of the tank as hereinbefore described, and the disposition of the spray assembly header and the steam distribution header within the tank in the desired predetermined positions, about 11.5 gal. of filtered nickel fluoride (NiF_2) solution was run into the receiver 12 from supply tank 13 through line 51. The NiF_2 solution contained in tank 13 had been previously prepared by

first dissolving predetermined quantities of basic nickel carbonate ($2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), 70 percent aqueous hydrofluoric acid, and citric acid ($\text{H}_3\text{C}_6\text{H}_5\text{O}_7$) in water, adjusting the pH of the resulting solution to about 5.0 with 30 percent aqueous ammonia, and then filtering the solution by suitable means to remove any insoluble matter. The concentrations of the above listed ingredients, excluding ammonia, expressed as grams per liter of final solution volume were:

- (1) HF (anhydrous) -----g./l. 63.5
- (2) $\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ -----g./l.¹ 28.4
- (3) $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ -----g./l. 18.4

¹ Equivalent to 12.2 g. Ni/l.

- About 1 gallon of an aqueous solution of sodium hypophosphite containing about one pound of



per gallon was then added to the receiver 12 through line 52. The NiF_2 and $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ solutions were thoroughly mixed by recirculating the mixed solutions from the receiver 12 through the filter 14 and back to the receiver through line 50 by means of pump 44 (valves 61, 63 and 65 open and valves 60, 62, 64 and 68 closed) while adding sufficient 30 percent aqueous ammonia to the receiver through line 53 during mixing to adjust the pH of the final solution to about 6.5.

The initial concentration of nickel ions (Ni^{++}) in this mixed plating solution was about 13.1 g./l. or about 0.22 g. mole/l., and the initial concentration of hypophosphite ions (H_2PO_2^-) was about 5.9 g./l. or about 0.09 g. mole/l., the initial mole ratio $\text{Ni}^{++}/\text{H}_2\text{PO}_2^-$ being about 2.5.

The plating solution was then supplied to the spray assembly header 34 by pumping the solution from the receiver 12 by means of pump 44 through lines 47, 45 and 28 (valves 62 and 64 open and valves 61, 63 and 65 closed) so as to by-pass the filter 14. The pressure in the spray header, as indicated by the pressure gage 70, was maintained at about 25 p.s.i.g. by adjusting valve 62. At this pressure the volume of plating solution being supplied to the spray header 34 was about 20-24 gal./min., or about 2.5 gal./min. per spray nozzle. The solution leaving the tank 11 drained by gravity flow into the receiver 12 and was recirculated to the spray assembly header 34 by means of pump 44.

After the recirculation of the plating solution had been started, steam was admitted through pipe 26 into the steam distribution header 32 until the temperature of the interior surfaces of the tank wall and the recirculating solution reached the predetermined plating temperature of about 185-190° F. The steam flow was then reduced and adjusted by means of valve 66 to maintain the temperature of the interior surfaces of the tank and of the recirculating plating solution within the stated plating temperature range of about 185-190° F. During this initial heating of the tank surface, the plating solution was diluted with about 2 gal. of condensate so that the nickel ion concentration and the hypophosphite ion concentration were approximately 11.3 g./l. and 5.1 g./l., respectively, when the plating temperature was reached. As plating proceeded the pH of the recirculating plating solution was continuously adjusted to about 6.5 by the addition of 30 percent aqueous ammonia through pipe 53, and additional sodium hypophosphite was added to the recirculating solution as an aqueous solution containing about one pound $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ per gallon through pipe 52 so as to maintain the hypophosphite ion concentration at a level necessary to assure the deposition of nickel on the interior surfaces of the tank at a satisfactory rate. The nickel plating solution was continuously recirculated, adjusting the pH and the hypophosphite ion concentration as described directly hereinbefore, until the nickel ion concentration reached a predetermined level of about 0.8-1.0 g. Ni/l. while regulating the flow of steam to the

steam header 32 so as to maintain the interior surface of the tank wall within the stated plating temperature range of 185–190° F. The total volume of plating solution, including the hold-up in the tank 11, was about 18 gallons when the nickel ion concentration had been depleted to the above mentioned range of about 0.8–1.0 g. Ni/l. Upon depletion of the nickel ion concentration to this level, the recirculation of the plating solution was stopped by shutting down pump 44, and valves 60 and 68 were opened to allow the system to drain to the sewer through line 55.

Another portion of about 11.5 gallons of nickel fluoride solution was run into the receiver 12 (valves 60 and 68 closed) and mixed with about one gallon of aqueous sodium hypophosphite solution containing about one pound of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ while adjusting the pH to about 6.5 with aqueous ammonia as previously described. When the mixing of this fresh solution was complete, it was supplied to the spray assembly header 34 (valves 61, 63 and 65 closed and valves 62 and 64 open). Since the temperature of the tank wall was maintained within said predetermined temperature range of 185–190° F. during the preparation of this fresh plating solution there was appreciably no dilution of the solution with condensate as it was rapidly heated to the plating temperature by being sprayed through the hot vapors within the tank and by repeatedly contacting the heated interior tank surfaces. This solution was continuously recirculated from the receiver to the spray assembly header, while continuously adjusting the pH, the hypophosphite ion concentration, and the rate of steam flow to the steam header 32 in the same manner as described for the previous plating cycle until the nickel ion concentration was depleted to the aforementioned level.

A total of nine (9) plating cycles were utilized to deposit a sound, adherent electroless nickel coating having a substantially uniform thickness of about 2.0 mils on the interior surfaces of the tank. Examination of the nickel coating showed it to be free of imperfections and satisfactory in all respects. The total over-all time required to deposit this electroless nickel coating was about 18 hours.

An efficiency of about 85 percent deposition of nickel on the tank wall was achieved, based on the nickel content of the total volume of NiF_2 solution used for the nine (9) plating cycles.

No appreciable amount of precipitate such as either finely divided nickel or nickel phosphite was observed during the plating of the tank as described in this example. It is understood, however, that plating solution from the receiver 12 can be supplied to the spray assembly header through a filter such as 14 as shown in FIG. 1 of the drawing should small amounts of precipitate form during a plating cycle.

In a manner similar to the foregoing procedure, several rolled sheets of mild steel were suspended in an enclosing chamber fitted with means for spraying the plating solution, means for heating the part by spraying it with steam, and a drain at the bottom for recovery of the plating solution. Several aliquots of the previously prepared plating solution were cycled through the apparatus until each aliquot was depleted of nickel ion. Subsequent metallographic examination of the coated plates revealed a non-porous nickel deposit and good adhesion of the individual layers of nickel deposit produced by the individual aliquots of plating solution.

Various modifications can be made in the present process without departing from the spirit or scope thereof for it is understood that we limit ourselves only as defined in the appended claims.

We claim:

1. A method for chemically plating a nickel-based coating on the surface of a fabricated article from a plating solution of the nickel cation-hypophosphite anion type, said surface being catalytic to the deposition of a nickel-

based coating from a plating solution of said type, which comprises:

- (a) heating the surface of said fabricated article to a temperature sufficient to substantially increase the plating rate,
 - (b) spraying a quantity of a single chemical plating solution of the nickel cation-hypophosphite anion type onto the surface to be plated while maintaining said surface of said fabricated article at said temperature, the spray pattern of the sprayed solution being such that all portions of said surface to be plated not contacted directly with the sprayed solution are contacted by said solution flowing towards the bottom of said fabricated article, and
 - (c) recovering said plating solution as it drains from the bottom of said fabricated article.
2. A method as in claim 1 and including the additional step of recirculating said recovered plating solution to said spray apparatus.
3. The method of claim 1 wherein said catalytic interior surface of said fabricated article consists essentially of a ferrous-based metal.
4. The method of claim 1 wherein heating is carried out by contacting the surface to be plated with steam.
5. The method of claim 4 wherein the plating solution is heated by contacting the solution with steam.
6. A method as in claim 1 and including the step of introducing the fabricated articles to be plated into an enclosing chamber thereby to contact repeatedly all portions of said surface of said fabricated article to be plated with the plating solution.
7. The method of claim 6 wherein said enclosing chamber has at least one outlet disposed near the bottom thereof and wherein said plating solution flowing towards the bottom of the container is drained through said outlet into a receiving and recirculating means disposed exterior to said container.
8. The method of claim 7 including the additional step of successively supplying fresh quantities of plating solution to said spray apparatus so as to provide a nickel-based coating on said surface of said fabricated article and substantially deplete nickel values from the plating solution.
9. A method for chemically plating a nickel-based coating on the interior surface of a hollow container from a plating solution of the nickel cation-hypophosphite anion type, which comprises:
- (a) disposing removable spray apparatus adjacent the interior surface of a hollow container, said surface being catalytic to the deposition of a nickel-based coating from a plating solution of said type,
 - (b) heating the interior surface of said hollow container to a temperature sufficient to substantially increase the plating rate,
 - (c) supplying a quantity of chemical plating solution of the nickel cation-hypophosphite anion type to said spray apparatus,
 - (d) spraying a single chemical plating solution directly onto portions of said interior surface of said container to be plated while maintaining said interior surface of said container at said temperature, the spray pattern of the sprayed solution being such that all portions of said interior surface to be plated not contacted directly with the sprayed solution are contacted by said solution flowing towards the bottom of the container,
 - (e) transporting said solution from the bottom interior of said container into a receiving and recirculating means, and
 - (f) recirculating said plating solution from said receiving and recirculating means to said spray apparatus thereby to contact repeatedly all portions of said interior surface of said container to be plated with plating solution.

11

10. The method of claim 9 wherein said hollow container has at least one outlet disposed near the bottom of said container, and wherein said solution flowing towards the bottom of the container is drained through said outlet into a receiving and recirculating means disposed exterior to said container. 5

11. The method of claim 9 wherein said catalytic interior surface of said hollow container consists essentially of a ferrous-based metal.

12. The method of claim 8 wherein said plating solution is recirculated until nickel values are substantially depleted therefrom, and including the step of: 10

(g) removing the depleted solution from said hollow container and from the assembly of said receiver, spray apparatus and recirculating means.

13. The method of claim 12 wherein quantities of fresh plating solution are supplied successively to said spray apparatus so as to provide a nickel-based coating on said interior surface of said hollow container and substantially deplete nickel values from the plating solution. 20

12

14. The method of claim 9 wherein heating is carried out by contacting the surface to be plated with steam.

15. The method of claim 14 wherein the plating solution is heated by contacting the solution with steam.

References Cited

UNITED STATES PATENTS

2,410,626	11/1946	Boudreau	117—105
2,726,968	12/1955	Spaulding	117—102 A
2,955,959	10/1960	Du Rose	117—50
2,956,900	10/1960	Carlson et al.	117—160 R
2,996,406	8/1961	Weinrich	117—160 R
3,010,841	11/1961	Heard et al.	117—160 R

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20 117—47, 102 A, 105, 130 E, 160 R