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ELECTROLESS PLATING OF NICKEL VIA DECOMPOSITION OF NICKEL ZERO COMPLEXES IN SOLUTION


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14 Claims

The present invention relates to electroleless plating of nickel, and more particularly to a process for nickel plating by thermally decomposing nickel zero phosphites.

Nickel plating has been accomplished by electrolytic, vapometallurgical and chemical techniques. Nickel is most extensively plated by well known electroplating processes. Although electroleplating processes have many advantages, the chief disadvantage is the difficulty encountered when attempting to apply a plating of uniform thickness on geometrically irregular shapes. Furthermore, a nickel plate of 0.4 mil, electroplated from a Watts bath, can contain as many as 166 pores per square centimeter. Most vapometallurgical processes of plating nickel rely on the thermal decomposition of nickel carbonyl. Since nickel carbonyl present shipping difficulties, such processes have not been widely employed because their use generally entails additional capital costs of providing apparatus to generate nickel carbonyl at the plating site. Nickel can also be plated by electroleless chemical techniques, but the nickel plate is often characterized by impurity contents up to about 8%. Although attempts were made to overcome the foregoing difficulties and other difficulties, none, as far as we are aware, was entirely successful when carried into practice commercially on an industrial scale.

It has now been discovered that nickel can be electrolessly plated from tetrakis-(triorganophosphite)nickel (0) compounds without unduly contaminating the nickel deposit.

It is an object of the present invention to provide an electroleless process for plating nickel.

Another object of the invention is to provide an electroleless process for nickel plating employing tetrakis-(triorganophosphite)nickel (0) compounds.

Other objects and advantages will become apparent from the following description taken in conjunction with the accompanying drawing wherein there is shown an elevational view partly in section of an embodiment of apparatus in which the novel electroless nickel plating process provided by the present invention can be carried into practice.

Generally speaking, the present invention contemplates an electroless process for nickel plating a substrate in a non-aqueous solution of a tetrakis-(triorganophosphite)-nickel (0) compound which is heat decomposable to metallic nickel. Once the solution is established, a substrate heated to at least the decomposition temperature of the compound is contacted with the solution to deposit nickel upon the solution-exposed surfaces of the substrate. The solution is maintained at a substantially uniform temperature at least about 90°C below the decomposition temperature of the compound.

The tetrakis-(triorganophosphite)nickel (0) compounds which can be employed in accordance with the process of the present invention can be prepared by reacting hydrated nickel bromide with triorganophosphites and then reducing the resulting nickel-containing reaction product to the zerovalent state. For example, nickel bromide dihydrate is slurried with acetonitrile and then about six moles of trimethylphosphite for each mole of nickel bromide dihydrate is added to the slurry while maintaining the slurry at a temperature of about -15°C to about -20°C and in a state of vigorous agitation. Under the same conditions, approximately two moles of diethylamine for each mole of nickel bromide are added to the reaction mixture to reduce the nickel compound to the zerovalent state. Tetrakis-(trimethylphosphite)nickel (0) is then isolated by removing the solvent through a reduced pressure treatment at a temperature between about 30°C and 35°C, and is purified by washing and recrystallization techniques. Alternatively, the tetrakis-(triorganophosphite)nickel (0) compound can be produced by reacting one mole of nickel carbonyl with four moles of a triorganophosphite compound. For example, a solution of nickel tetracarbonyl and at least four moles of trimethylphosphite for each mole of nickel tetracarbonyl is established at about room temperature. When the evolution of carbon monoxide, the solution can be heated to elevated temperatures to complete the stepwise substitution of trimethylphosphite for carbon monoxide.

Examples of tetrakis-(triorganophosphite)nickel (0) which can be employed are tetrakis-(triethylphosphite)-nickel (0) compounds such as tetrakis-(trimethylphosphite)nickel (0), tetrakis-(tripropylphosphite)nickel (0) and tetrakis-(triisopropylphosphite)nickel (0), and tetrakis-(triethylphosphite)nickel (0), and tetrakis-(triethylphosphite)nickel (0) compounds such as tetrakis-(trimethylphosphite)nickel (0) and tetrakis-(triethylphosphite)nickel (0) which are advantageously employed in practicing the process of the present invention and tetrakis-(trimethylphosphite)nickel (0) has been found to be particularly advantageous since it imparts the greatest solubility in the non-aqueous solvents.

Electroless nickel plating with the aforementioned compounds is effected from a solution made by dissolving the compounds in a non-aqueous solvent. The non-aqueous solvents which can be employed are characterized by their chemical inertness to the zerovalent nickel compounds, to the deposited nickel and to the other products of reaction such as the triorganophosphites released by the decomposition of the nickel zerovalent compounds, by melting points lower than the temperature at which the bath is maintained and by boiling points above the temperature to which the plating solution is subjected in the plating operation. Examples of suitable solvents are above about 280°C or even above about 300°C, esters of dicarboxylic acids such as diethyl sebacate and dibutyl adipate and esters such as bis-(4-methylbenzyl) ether and benzyl ether, liquid paraffins such as nujol, dinitriles such as adiponitrile and higher molecular weight esters of phthalic acid such as diocyl phthalate and dibutyl phthalate. The concentration of zerovalent nickel...
3 compounds dissolved in the solvent is maintained between about 0.1 molar and 1.5 molar and advantageously be-between about 0.2 molar and 0.3 molar, although lower concentrations of the zerovalent nickel compound can be used, it is advantageous to employ concentration of at least about 0.1 molar since more dilute solutions result in insufficient plating rates. High concentrations of the zerovalent nickel compound, i.e., above about 1.5 molar, result in crystallization of the zerovalent nickel compounds in the cooler parts of the bath.

Nickel plating from the aforementioned solution is accomplished by immersing a heated substrate into the aforesaid describe solutions of zerovalent nickel compounds or by heating the substrate while immersed therein. In order to ensure adherence of the plating to the surface of the substrate can, before plating, be treated by well known processes to free the surface of grease and/or surface oxides. For example, steel surfaces can be pickled with hydrochloric acid solutions. The substrate, after any surface treatment, is heated to at least the decomposition temperature of the tetrakis-(triorganophosphite)nickel (0) compound being employed, e.g., the substrate is heated to at least about 190°C. Advantageously, the substrate is heated to a temperature between about 200°C and 250°C. In order to provide commercially feasible plating rates while avoiding boiling of the solvent which may occur at temperatures above about 300°C. At these temperatures the zerovalent compounds decompose to metallic nickel which is deposited on the liquid exposed surfaces of the heated substrates and to triorganophosphites which can be recovered to prepare additional zerovalent nickel compounds for further utilization.

In order to avoid undesirable side reaction and possible contamination of the nickel plate, the solution containing the zerovalent nickel compound is maintained at a temperature at least about 90°C below the decomposition temperature of the zerovalent compound. For example, the temperature of the solution can be maintained at about 100°C to 120°C below the decomposition temperature of the zerovalent compound or, in absolute terms, at a temperature of about 100°C to 130°C. The plating process is advantageously conducted in the apparatus illustrated in the drawing so that the proper temperature differential between the substrate and the solution can be maintained. As shown in the drawing, a vessel or container 10 of a suitable material is provided with a gas-tight top or lid 11 which has gas inlet and outlet conduits 12 and 13, respectively, so that an inert gas such as nitrogen can be flowed over the surface of the solution in order to avoid oxidation of the air-sensitive zerovalent nickel compounds. The vessel 10 is also equipped with cooling means such as cooling coils 14 which are arranged within the vessel so that they are in heat exchangeable contact with the zerovalent-nickel-containing solution. Vessel 10 is also provided with a rotary agitator 15 which is driven by shaft 16 when shaft 16 is rotated by a power source not shown in the drawing. As shown in the drawing the substrate is mounted on the shaft 16 but it is to be understood that the substrate 18 can be placed in the vessel in an independent manner so long as the agitator 15agitates the solution in the vicinity of the liquid-exposed surfaces of the substrate sufficiently to insure a substantially uniform temperature of the solution throughout the vessel. In order to heat the substrate 18 to above the decomposition of the zerovalent nickel compound, the vessel is provided with heating means such as the induction heater 17 shown in the drawing. It will be apparent to those skilled in the art that when an induction heater is employed the vessel 11 should be made of a non-conductive material such as glass or ceramic in order to avoid heating the vessel itself. The substrate can also be heated by other means such as resistance heating. When the substrate is non-conductive, non-electrical heating means are employed or the substrate is preheated before immersing it in the zerovalent nickel solution.

For the purpose of giving those skilled in the art a better understanding of the invention and/or a better appreciation of the advantages of the invention, the following illustrative example is given:

A diethyl sebacate solution containing 12.5 weight percent tetrakis(dimethylphosphite) nickel zero was placed in a reactor as illustrated in the drawing. The substrate material cylinder made of mild steel, the surface of which was deliberately made non-adherent by chemical polishing so that the plate could be conveniently stripped off for chemical analysis, was attached to the agitator shaft and the thermostats indicating solution and substrate temperature were attached. By means of an induction heater the substrate metal was brought to a temperature of 200°C. The agitation was adjusted to maintain this temperature, while the solution was being cooled by a copper heat exchange coil. The entire system was purged and blanketed with an atmosphere of nitrogen. Heating and stirring were continued for 15 minutes. A temperature spread of 90°C between solution temperature and skin metal (substrate) temperature was effected through manipulation of the agitator speed, the cooling coil temperature, and the radio frequency input of the induction heating system. At the close of the heating period the solution temperature was brought to 20°C and an atmosphere of nitrogen, the reactor was dismantled. The coated steel tube was removed and washed with acetone, dried and finally weighed. A weight increase of 138 mg. was observed which corresponded to 0.2 ml increase for the surface area of 29 cm². The tube was sawed in half down its length and one half was flattened and the nickel stripped off. Analysis for nickel and phosphorus are as follows:

Percent nickel: 99.98; gravimetric, dimethylglyoxime method.

Percent phosphorus: 0.06; colorimetric, phosphomolybdate method. It will be noted that at phosphorus levels as low as 0.06% or lower the colorimetric analysis is not entirely precise and the overall analysis of the plate exceeds 100%.

Steel tubes were nickel plated with different plate thicknesses in accordance with the process of the invention and the porosity of each nickel plate was compared with an electrolytic plate of the same thickness. The porosity of each specimen was determined by submerging the plated tubes in an aqueous solution having a pH value of 6.5 for one hour while maintaining the aqueous solution at a temperature of 180°F. Such a treatment results in the staining of the nickel plate by oxidized iron through any pores and the porosity of a sample can be determined by counting the number of stains per surface area unit.

The results as tabulated in Table I confirm that electroless nickel plating in accordance with the process of the present invention produces a nickel plate which is substantially less porous than a nickel plate produced by electrolytic techniques.

<table>
<thead>
<tr>
<th>Specimen plated</th>
<th>Plate-plated standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness, mil</td>
<td>Pores/cm²</td>
</tr>
<tr>
<td>0.2</td>
<td>300</td>
</tr>
<tr>
<td>0.5</td>
<td>200</td>
</tr>
<tr>
<td>0.4</td>
<td>250</td>
</tr>
<tr>
<td>0.3</td>
<td>300</td>
</tr>
<tr>
<td>0.2</td>
<td>350</td>
</tr>
</tbody>
</table>

1 Test conditions: pH 6.5, 180°F, 1 hr.
2 Many (95% failure of coating)

In addition to the test shown in the specific example, results from other tests employing tetrakis(dimethylphosphite)nickel (0) dissolved in diethyl sebacate are tabulated in Table II. Table II shows the concentration of the zerovalent nickel compound, the temperature of the substrate (the zerovalent nickel solution was maintained at a temperature of about 100°C below the substrate temperature), the thickness of the plate, the plating rate, the
It is to be observed that the present invention provides an electroless nickel plating process in which tetrakis-
(triorganophosphite)nickel (0) compounds are thermally
decomposed in non-aqueous solutions to deposit nickel on
substrates heated to at least the decomposition temperature
of said compounds while maintaining said solution at a
temperature of at least about 90° C. below said decomposition
temperature.

The process in accordance with the present invention can be utilized for plating nickel or any substrate which can be heated to the decomposition temperature of the tetrakis-
(triorganophosphite)nickel (0) compounds employed. However, the process of the present invention is particularly useful in plating irregular objects and interior surfaces such as those of pipes.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A non-aqueous electroless process for depositing nickel on a substrate which comprises establishing a non-
aqueous solution containing a tetrakis-(triorganophos-
phite)nickel (0) compound which is heat decomposable
to metallic nickel and contacting the substrate heated to
at least the decomposition temperature of the tetrakis-
(triorganophosphite)nickel (0) compound with the non-
aqueous solution while maintaining the non-aqueous solution
at a temperature of at least about 90° C. below the
decomposition temperature of the tetrakis-(triorganophos-
phite)nickel (0) compound to deposit nickel upon the
solution exposed surfaces of the substrate.

2. A process as described in claim 1 wherein the non-
aqueous solution containing tetrakis-(triorganophos-
phite)nickel (0) compounds is agitated to maintain a
substantially constant concentration of the tetrakis-(tri-
organophosphite)nickel (0) compound throughout the
entire solution and to maintain the solution at a substan-
tially constant temperature.