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3,148,072

ELECTROLESS DEPOSITION OF NICKEL

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The present invention relates to the electroless plating of metals, and particularly to an improved process and bath for the plating of metallic surfaces with a coating of nickel by autocatalytic chemical reduction reaction.

The chemical nickel plating of a catalytic material employing an aqueous bath of the nickel cation-hypophosphite anion type is based upon the catalytic reduction of nickel cations to metallic nickel and the corresponding oxidation of hypophosphite anions to the phosphite anions with the evolution of hydrogen gas at the catalytic surface.

The reactions take place when the body of catalytic material is immersed in the plating bath, and the exterior surface of the body of catalytic material is coated with nickel.

Metallic elements that are catalytic for the oxidation of hypophosphite ions include iron, cobalt, nickel, platinum, rhodium, palladium, and the like. These metallic elements can be directly nickel plated.

Metallic elements that can be nickel plated by virtue of the initial displacement deposition of nickel thereon either directly or through a galvanic effect include copper, silver, gold, beryllium, germanium, aluminum, carbon, vanadium, molybdenum, tungsten, chromium, titanium, uranium and the like.

Materials that are non-catalytic and cannot be nickel plated by catalytic reduction of nickel cations to metallic nickel include bismuth, cadmium, tin, lead, and zinc.

Certain non-metallic members such as wood, glass, and plastic can be nickel plated by first activating the surface thereof with an activator such as palladium chloride. Other activators are known in the art.

Details concerning electroless nickel deposition can be found in U.S. Patent No. 2,532,283, issued to Brenner et al., and in the following references: N.B.S. Journal of Research 37, pp. 1-4, 1946; Proceedings of the Electroplaters Society 33, 16, 1946; N.B.S. Journal of Research 39, pp. 385-395, 1947; Proceedings of American Electroplaters 34, p. 156, 1947; Metal Finishing, November-December, 1954.

For a complete understanding of the nature of this invention, reference is made to the following detailed description.

The present invention is predicated upon the discovery that plating baths of the nickel cation-hypophosphite anion type can be improved substantially by increasing substantially the amount of nickel cation present in the bath, and increasing substantially the nickel ion-hypophosphite ion ratio.

In addition, it has been discovered that the nickel deposited will have superior resistance to corrosion if there is included in the bath a small amount of chromium ion. Further, the chromium ion addition provides a nickel coating that is hard and has less tendency to discolor.

The basic ingredients of the prior art baths include nickel cations and hypophosphite anions, which is the active chemical reducing agent. A complexing agent such as ammonium ions which form various molecular complexes with the nickel ions depending upon the molar ratio therebetween in the plating bath is often employed in the bath. The complexing agent serves two primary purposes in that (1) it keeps the nickel ion in the solu-

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tion in the form of soluble complexes as the pH goes up, and (2) it serves also as a buffer to keep the pH of the bath from changing too rapidly during the plating operation. Other complexing agents are well known in the art.

The plating bath of this invention comprises hypophosphite ions in the range of from about .05 to .10 mole per liter of plating bath and nickel ions. The ratio between nickel ions and hypophosphite ions in the bath is in the range of from 20:1 to 40:1. The concentration of the chromium ions in the bath will be within the range of from about .005 to .075 mole per liter.

In the plating bath of this invention the nickel ions can be derived from any suitable nickel salt such, for example, as nickel chloride, nickel sulfate, and nickel hypophosphite.

The hypophosphite ions can be derived from any suitable hypophosphite such, for example, as sodium hypophosphite, nickel hypophosphite, ammonium hypophosphite, and potassium hypophosphite. Ammonium ions can be present in the bath as a complexing agent, which complexes with the nickel ion depending on the molar ratio therebetween in the plating bath. Ammonium ions can be derived from any suitable ammonium compound, such for example, as ammonium hydroxide, ammonium chloride, ammonium sulfate, ammonium hypophosphite.

The chromium ion can be derived from any suitable soluble chromium salts such, for example, as chromium acetate, chromium chloride, chromium phosphide, chromium oxalate, and chromium sulfate.

The pH of the bath of this invention can be varied between from about 2 to 11. The pH can be controlled by known methods. An acid bath is obtained by employing nickel salts of a strong acid such as sulfuric or hydrochloric acid, or by the addition of an organic or inorganic acid to the bath. An alkaline bath can be prepared by employing ammonium hydroxide, or an alkali metal hydroxide.

Known addition agents can be employed in the bath of this invention if desired. Thus, for example, an exalting additive can be employed in the bath to effect a substantial increase in the plating rate thereof. Examples of exaltants include xylic acid, tropic acid, toleric acid, tiglic acid, quinic acid, formic acid, valeric acid, and malonic acid.

The following examples are illustrative of plating baths of this invention.

Example I

Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	grams per liter	460
Ammonium hypophosphite	do	10
Ammonium citrate	do	20
Ammonium chloride	do	10
pH		8 to 11
Temperature	° F.	170 to 212

Example II

Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	grams per liter	460
Ammonium hypophosphite	do	10
Ammonium citrate	do	20
Ammonium chloride	do	10
Chromium acetate	do	1
pH		8 to 11
Temperature	° F.	170 to 212

Example III

Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	grams per liter	460
Sodium hypophosphite	do	10
Sodium citrate	do	20
Sodium chloride	do	5
Ammonium chloride	do	10
pH		4 to 7
Temperature	° F.	170 to 212

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Example IV

Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	grams per liter	460
Sodium hypophosphite	do	10
Sodium citrate	do	20
Sodium chloride	do	5
Ammonium chloride	do	10
Chromium acetate	do	1
pH		4 to 7
Temperature	$^{\circ}\text{F}$	170 to 212

Example V

Nickel chloride	grams per liter	460
Sodium hypophosphite	do	10
Sodium citrate	do	20
Sodium chloride	do	5
Ammonium chloride	do	10
pH		4 to 6
Temperature	$^{\circ}\text{F}$	170 to 212

Example VI

Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	grams per liter	460
Sodium hypophosphite	do	10
Sodium citrate	do	20
Sodium chloride	do	5
Ammonium chloride	do	10
Hydroxylamine hydrochloride	do	0.05
pH		4 to 7
Temperature	$^{\circ}\text{F}$	170 to 212

Example VII

Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	grams per liter	460
Sodium hypophosphite	do	10
Sodium citrate	do	20
Sodium chloride	do	5
Ammonium chloride	do	10
Hydroxylamine hydrochloride	do	0.05
Chromium sulfate	do	1
pH		4 to 7
Temperature	$^{\circ}\text{F}$	170 to 212

In accordance with the process of this invention, the article to be nickel plated and normally having a catalytic surface is properly prepared by mechanical cleaning, degreasing, and light pickling substantially in accordance with standard practices in electroplating processes. For example, in nickel plating a steel member it is customary to clean the rust and scale from the object, to degrease the object and then lightly pickle the object in a suitable acid, such as hydrochloric acid. The object is then immersed in a suitable volume of the bath containing the proper proportions of the ingredients of the bath of this invention, the pH of the bath having been, if necessary, adjusted to the optimum value by the addition of an appropriate acid or base, and the bath having been heated to a tempera-

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ture just below its boiling point, such as about 195°F ., at atmospheric pressure. Almost immediately hydrogen bubbles are formed on the catalytic surface of the steel object and escape in a steady stream from the bath; a surface of the steel object is slowly coated with the metallic nickel which contains some phosphorus. The steel object is ultimately removed from the bath after an appropriate time interval corresponding to the required thickness of the nickel coating deposit thereon that is desired. Ultimately the steel object is rinsed off with water, and is then ready for use.

The metallic deposit secured by following the teachings of this invention is high in nickel and low in phosphorus. The deposit or plate is ductile and shows substantially no signs of oxidation. The deposit or plate can be heat-treated to provide a substantially non-porous electroless nickel deposit.

It is to be understood that the above description of the invention is illustrative thereof and not in limitation thereof.

We claim as our invention:

1. A bath for the chemical plating of a catalytic material with nickel comprising an aqueous solution of an ionized nickel salt, hypophosphite, a complexing agent and chromium salt, the chromium ions being present in an amount of from about 0.005 to 0.075 mole per liter of plating bath, the hypophosphite ions being present in an amount of from about 0.05 to 0.10 mole per liter of plating bath, and the ratio of the nickel ions to the hypophosphite ions being in the range of from about 20:1 to 40:1.

2. A process for chemically plating a body of a catalytic material with nickel which comprises contacting said body with an aqueous bath comprising nickel ions, hypophosphite ions, a complexing agent and chromium ions, the chromium ions being present in an amount of from about 0.005 to 0.075 mole per liter of plating bath, the hypophosphite ions being present in an amount of from about 0.05 to 0.10 mole per liter of plating bath, and the ratio of the nickel ions to the hypophosphite ions being in the range of from about 20:1 to 40:1.

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