United States Patent Office 3,060,059 Patented Oct. 23, 1962

3,060,059

ELECTROLESS NICKEL-PHOSPHOROUS ALLOY PLATING BATH AND METHOD

Ralph E. Sickles, Canton, Ohio, assignor to Goodyear Aircraft Corporation, Akron, Ohio, a corporation of Delaware

No Drawing. Filed May 19, 1961, Ser. No. 111,170
8 Claims. (Cl. 117—130)

This invention relates to nickel alloy plating by the so-called electroless action involving chemical reduction, to the bath and plating methods used for such action, and to the plating produced upon the receiving surface, the alloy composition of which is within the percentage range set forth hereinafter.

Various commercial processes for nickel alloy plating have been proposed. 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 cations of the dissolved salt are reduced to metal in the presence of an excess of anions from the dissolved catalyst, the other agent in the autocatalytic process being the surface upon which metal is deposited. This surface may be catalytic in nature or may be made so by various sensitizing procedures used to initiate the plating reaction. These commercial processes are usually of a continuous flow type, wherein the plating bath is heated in a container, and the reserve solution is contained in a reservoir. Additional reagent may be added to the reservoir during processing to replenish the active agents in the solution which are used up during plating.

Heretofore in the electroless plating of various base materials with nickel alloy, it has been very difficult, if not impossible to obtain uniform coverage of a ductile, but hard, bright plated finish on the desired article.

Some previous patents have suggested the use of various materials for obtaining hard, smooth and bright coatings by a nickel plating action, and one of such patents is U.S. Patent No. 2,774,688 which uses boric acid and ammonium chloride in a plating bath for obtaining a nickel deposit which can be easily buffed to have a high luster. The ammonium chloride and boric acid are supposed to produce a low stress, adherent electroless deposited plate.

Another result desired in these plating actions is to obtain a leveling action on irregular base sheets when given a nickel alloy coating. Some commercial organic brighteners and leveling agents have been provided heretofore, but such organic agents function normally to produce a plate coating deposit in which the particles are deposited with tensional forces therebetween and consequently such deposits normally have poor ductility and adhesion both in the deposited material and to the base sheet or member used. One of such organic type nickel plating processes and baths is disclosed in Patent No. 2,819,187.

The general object of the present invention is to provide a novel and improved plating bath for the electroless plating of nickel alloy and where the plating bath and process are characterized by the provision of improved brightness, ductility, adhesion and continuity in the plated finish obtained.

Yet another object of the invention is to use an ammonium nickel salt in association with nickel sulfate for obtaining an improved plating bath and plating method, and where additional buffering agents are present in the bath to provide to the plating solution a correlated reducing buffering action in the presence of a catalyst, or catalysts.

A further object of the invention is to provide an electroless nickel plating bath and method where the initial deposit obtained is a hard, bright plate, which plate can be improved in hardness by ordinary heat treating operations and where conventional precipitation hardening action is obtained.

Yet a further object of the invention is to provide a stress-free, continuous, non-porous nickel plate by an improved process using nickel ammonium sulfate.

The foregoing and other objects and advantages of the invention will be made more apparent as the specification proceeds.

Nickel-phosphorous alloy plating will be deposited from the bath, depending on specific bath makeup, heat, pH and regularity of additions, at a rate within the thickness range of about .00045 to about .00052 inch per hour of immersion time.

The theories of operation of the plating bath and the method of the invention are given heretofore, and tests of the plating baths are set forth hereinafter have given very desirable, improved results in the type of bond secured between the coating and the base sheet. The ductility, and brightness of the deposit have been improved greatly in relation to other known processes, and a substantially stress-free, adherent deposit has been obtained.

One example of a leveling action is that a liquid honed surface, which had an initial 25 microinches of surface roughness was reduced to 18 microinches of surface roughness by a chemical deposit of nickel alloy of between 2 and 2.5 thousandths of an inch.

Another example of a test indicating the very desirable and unusual hardness obtained by use of the chemical plating method of the invention is that a typical soft brass sample with a matt finish was nickel alloy plated in accordance with the invention. Thereafter, it was heat treated for approximately 2 hours at a temperature of 450° F. This sample, after its initial nickel plating, had a Rockwell hardness of C 50, which, after the heat treating, had increased to C 56. This additional hardness is obtained because of a conventional precipitation hardening action. However, the hardness of C 50 on the inital plated sample gave such original soft material a very desirable shiny, hard finish. Initially the unplated sample had not appreciable reading on the Rockwell C scale. In another test, a plated brass part has no appreciable hardness reading before plating, and a reading of C 57 after plating. The test plating was approximately .0005" thick, and had good adhesion and flexibility through bends up to 90°.

The ductility of the plate obtained in accordance with the invention is shown, for example, by the fact that copper foil of a thickness of .0014 inch, and weighing 1 oz. to the square foot was nickel alloy plated by the method of the invention. This nickel alloy plate was of a thickness between .0008 to .001 inch. Thereafter this copper foil plate was bent and creased over 180° many times in different directions with no indication of cracking, flaking, or peeling of the nickel alloy deposit. In other tests, the copper foil has failed before the plate deposit. A plated round bar has been bent around a member of the same diameter without any cracking or failure of the nickel plate.

It is believed by the use of the composition or bath of the invention, and particularly by the use of ammonium nickel salts, I am able to control the reducing action of the hypophosphite ion in the bath. This consequently retards the rapid and random reduction of the dissolved

plating salt or salts and affords a controlled plating action. It is believed that the nickel ammonium sulfate used in the reaction functions both as a buffer ingredient and in combination with the sodium acetate, aids in imparting brightening and leveling characteristics to the bath. In using the plating baths of the invention, it will be understood that the baths are continuously filtered to remove any precipitates forming therein.

It is an important feature of the present invention that the addition of the nickel ammonium sulfate to the bath, where a continuous plating action is to be obtained, is through some type of a liquid communication system only, preferably from a reserve supply tank or container. Such a supply container is provided and is connected to the plating bath for intermittent flow of renewal constituents thereto. The solid nickel ammonium sulfate is added to the supply container, as by through a filter, so that only the soluble portion of such nickel ammonium sulfate passes from the original supply barrel, or container into the plating bath. The plating baths are maintained, for example, by hourly, or more frequent additions of nickel sulfate, nickel ammonium sulfate, sodium hypophosphite and buffering salts as needed, from the supply container that contains plating bath ingredients corresponding to the rates of depletion of such materials in the plating action. Distilled water, preferably preheated to about 190° F., may be directly added to maintain the plating bath level.

In practice of the invention, it is very desirable and necessary to control the pH of the solution within the limits of 4.8 to about 5.4.

In working with the plating bath of the invention, it has been found that the following compositions stated provide a specific bath composition, the preferred range, and the maximum range of deviation or variation in mixing quantities of the components listed and still obtain the improved plating action described:

Plating Bath

	Specific Example, grams/liter	Preferred Range, grams/liter	Maximum Range grams/liter
Nickel Sulfate	35	35–45	30–50
Nickel Ammonium Sulfate	17.5	15–25	10–30
Sodium Citrate	10	10–15	5–20
Sodium Acetate	7	7–14	5–20
Sodium Hypophosphite	10	9–15	5–20

pH of 4.8 to 5.4.
Temperature 185° F. to 195° F.

In varying the amounts of the ingredients used in the plating bath, the amounts for all ingredients should be varied substantially proportionally. That is, for 45 grams/liter of nickel sulfate, 25 grams/liter of nickel ammonium sulfate, 15 grams per liter of sodium citrate, etc. or 30 grams/liter of nickel sulfate, 10 grams/liter of nickel ammonium sulfate, etc.

Sodium citrate is needed in the solution because of its function as a primary buffer. The sodium acetate is used to reduce stresses in the nickel alloy deposit and to promote ductility and uniformity of plating, but in our bath, a novel function of this salt is attained by its combination with nickel ammonium sulfate and sodium citrate, which combination produces a grain refinement, ductility, uniformity and brightness not ordinarily found in prior formulations.

In making up the baths of the invention, the potassium salts may be substituted for the sodium salts listed hereinbefore.

The process of the invention may at least be used for nickel plating iron, steel, aluminum and its alloys, copper and copper base alloys, and on nickel and nickel alloys, as well as on other metal and alloys, or plated surfaces where the metal surfaces are or can be made catalytic for the nickel reduction and reaction by known activating procedures.

The deposited alloy has been analyzed and shows fall within the following range, by weight:

	Percent
Nickel	91 to 93
Phosphorous	7 to 8.9
Carbon	.02 to 1.0
Iron	.02 to .10

Plus traces of aluminum, copper, silicon and/or other elements discharged into the bath from plating salts, catalysts, buffers, or surfaces being plate.

Use of nickel sulfate alone as a nickel source provides a dull, weak deposit, and use of nickel ammonium sulfate alone provides a brittle, alloy deposit. Only by use of both such materials in accord with this invention is the new and improved alloy deposit obtained.

While a certain representative embodiment and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in the art that various changes and modifications may be made therein without departing from the spirit or scope of the invention.

What is claimed is:

1. A bath for use in electroless nickel alloy plating and comprising between about 30 to 50 grams/liter of nickel sulfate, about 10 to 30 grams/liter of nickel ammonium sulfate, about 5 to 20 grams/liter of sodium citrate, about 5 to 20 grams/liter of sodium acetate, and about 5 to 20 grams/liter of sodium hypophosphite, the amounts of the materials used being all substantially proportionally varied within the limits stated.

2. A bath for use in electrloess nickel alloy plating and comprising between about 35 grams/liter of nickel sulfate, about 17.5 grams/liter of nickel ammonium sulfate, about 10 grams/liter of sodium citrate, about 7 grams/liter of sodium acetate, and about 10 grams/liter of sodium hypophosphite.

3. A method of nickel alloy plating a metal by chemical reduction comprising the steps of forming a bath from about 30 to 50 grams/liter of nickel sulfate, about 10 to 30 grams/liter of nickel ammonium sulfate, about 5 to 20 grams/liter of sodium citrate, about 5 to 20 grams/liter of sodium acetate, and about 9 to 15 grams/liter of sodium hypophosphite, and immersing an article made from the group of metals consisting of iron, steel, aluminum and its alloys, copper and its alloys, and nickel and its alloys into the bath, the bath being maintained at a pH of between about 4.8 and 5.4 and at a temperature of about 185° F. to 195° F., the amounts of the materials used being substantially proportionately varied within the limits stated.

4. A method of nickel alloy plating a metal by chemical reduction comprising the steps of forming a bath from about 35 to 45 grams/liter of nickel sulfate, about 15 to 25 grams/liter of nickel ammonium sulfate, about 10 to 15 grams/liter of sodium citrate, about 7 to 14 grams/liter of sodium acetate, and about 9 to 15 grams/liter of sodium hypophosphite, and immersing a metal article into the bath, the bath being maintained at a pH of between about 4.8 to 5.4 and at a temperature of about 185° F. to 195° F.

5. A method of nickel plating a metal by chemical reduction comprising the steps of forming a bath from about 35 to 45 grams/liter of nickel sulfate, about 15 to 25 grams/liter of nickel ammonium sulfate, about 10 to 15 grams/liter of material of the group consisting of potassium citrate and sodium citrate, about 10 to 15 grams/liter of materials of the group consisting of potassium acetate and sodium acetate, and about 9 to 15 grams/liter of material of the group consisting of potassium hypophosphite and sodium hypophosphite, and immersing a

metal article into the bath while heated until a nickel plating is obtained on the article.

6. A method of nickel alloy plating a metal by chemical reduction comprising the steps of forming a bath from about 30 to 50 grams/liter of nickel sulfate, about 10 to 30 grams/liter of nickel ammonium sulfate, about 5 to 20 grams/liter of sodium citrate, about 5 to 20 grams/liter of a material from the group of potassium acetate and sodium acetate, and about 9 to 15 grams/liter of a material from the group consisting of potassium hyposulfite and sodium hypophosphite, and immersing an article made from the group of metals consisting of iron, steel, aluminum and its alloys, copper and its alloys, and nickel and its alloys into the bath, the bath being maintained at a pH of between about 4.8 to 5.4 and at a temperature of about 185° F. to 195° F.

7. A method of nickel alloy plating a metal by chemical reduction comprising the steps of forming a bath from about 35 to 45 grams/liter of nickel sulfate, about 15 to 25 grams/liter of nickel ammonium sulfate, about 10 to 15 grams/liter of sodium citrate, about 7 to 14 grams/liter of sodium acetate, and about 9 to 15 grams/liter of sodium hypophosphite, and immersing a metal article into the bath, the bath being maintained at a pH of between about 4.8 and 5.4 and at a temperature of about 185° F. to 195° F. to obtain a plating within the following ranges by weight: nickel—91 to 93%, phosphorus—7 to 8.9%, carbon—.02 to 1.0%, iron .02 to .10% and only traces of other materials.

8. A method of nickel plating a metal by chemical reduction comprising the steps of forming a bath from about 35 to 45 grams/liter of nickel sulfate, about 15 to 25 grams/liter of nickel ammonium sulfate, about 10 to 15 grams/liter of material of the group consisting of potassium citrate and sodium citrate, about 10 to 15 grams/liter of materials of the group consisting of potassium acetate and sodium acetate, and about 9 to 15 grams/liter of material of the group consisting of potassium hypophosphite and sodium hypophosphite, immersing a metal article into the bath until a nickel plating is obtained on the article, and replenishing the bath from a supply of the bath ingredients in solution form.

References Cited in the file of this patent

UNITED STATES PATENTS

2,819,187 Gutzeit et al. ---------- Jan. 7, 1958

FOREIGN PATENTS

607,615 Canada ---------- Oct. 25, 1960

OTHER REFERENCES

"Metal Finishing Guidebook 1960," published by Metals & Plastics Publications, Inc. (November 23, 1959, page 453 relied on).