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PROCESS FOR CONTINUOUSLY PRODUCING NICKEL OR NICKEL-GOLD COATED WIRES

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ABSTRACT OF THE DISCLOSURE

The present invention provides novel and useful processes, that is, a process for continuously producing nickel-coated metal wires by using a nickel sulfate bath to which sulfate of cobalt or an alkali metal is added, a process for continuously producing wires coated with double layers of nickel and gold by coating the above nickel-plated wires further with gold, and a process for repeatedly drawing and heat-treating those nickel-plated or nickel-gold-plated wires after the plating operation. Further, this invention is characterized by producing with high efficiency coatings of nickel or gold of a uniform thickness which possess excellent heat resistant adhesive property.

The present invention relates to a process for continuously producing wires coated with a layer of nickel or double layer of nickel and gold.

The primary object of this invention is to provide a process for continuously producing metal wires with nickel coating, uniform in thickness, free from crack on the surface, and excellent in heat-resistant adhesion to the core metal.

Generally nickel coated wire made by electroplating has a serious problem with regard to workability, that is, the wire is very difficult to work because of fragility due to colloidal particles existing in the plating electrolyte, hydrogen fragility due to the pH and the remaining stress.

As a means to solve the problem, the present invention provides a process to obtain an electrodeposition of nickel, which can be mechanically processed with ease, by adding an alkali metal sulfate or cobalt sulfate to the electrolytic bath of nickel sulfate, and makes possible the high-efficiency production of quality nickel-coated wires. More particularly, the effect of adding alkali sulfate to the nickel sulfate bath consists in greatly diminishing the amount of hydrogen deposit during the electrolysis by adding cations of small ionization energy. As a result a thick electrodeposited layer of nickel which is soft and ductile can be obtained.

On the other hand, the effect of adding cobalt sulfate to the nickel sulfate bath consists in obtaining an electrodeposition in which codeposited cobalt ions are microscopically mixed to nickel ions owing to the similarity in the atomic arrangement of the two salts, so that smooth sliding of metal becomes possible during the processing and hence breakdown can be prevented. The cobalt content of the product should be in a certain range and too small or too large a content does not afford a product of good quality to be processed. The suitable range, which is expressed by the concentration of cobalt sulfate to be added to the electrolysis bath, is in the range 0.05–1.0 mol/l.

The present invention relates to a process for continuously producing nickel coated metal wires characterized by plating wires with nickel in a nickel bath containing, as well as nickel sulfate as major constituent, at least one metal sulfate selected from the group consisting of sulfates of cobalt and alkali metals preferably in the concentration of 0.05–1.0 mol/l., and by then drawing and heat-treating the wires.

The present invention also provides a process for nickel plating and an electrolysis bath thereto, by which surfaces of the wires can be coated with a thick layer of soft and ductile electrodeposited nickel.

As is already known, relatively soft nickel platings can be obtained by electroplating in various types of nickel plating baths such as the typical Watts nickel bath and nickel cobalt bath. However, those processes which employ conventional nickel plating baths require, to obtain a plated layer of desired softness, the current density, temperature and pH to be maintained in certain limits. Moreover, the product thus obtained has a fault of easy cracking because it is poor in drawability and flexibility.

The soft electrodeposited nickel obtained from conventional plating baths has the Vickers hardness of approximately 200–230, while the Vickers hardness of electrodeposited nickel generally exceeds 220.

In the process of this invention, the plating bath can be prepared and maintained with ease and can be used for a long period. This plating bath can afford, in a wide range of cathodic current density and the bath temperature, a thick layer of soft and ductile electrodeposited nickel, which has an appreciably smaller hardness and better quality than conventional plated layers of soft nickel.

By employing the nickel plating bath of this invention, a soft and ductile electroplated nickel layer can be obtained in a wide range of cathodic current density around 10 a./dm.^{2} and in varied thicknesses even above 1000μ. The bath temperature can be varied from the room temperature up to about 70° C.

The plating bath employed in the present invention is a nickel sulfate plating bath containing nickel sulfate as major component in which is dissolved the sulfate of an alkali metal selected from the group consisting of sodium, potassium and lithium or cobalt sulfate. The concentration in the bath of the alkali metal sulfate or cobalt sulfate is made 0.05–1.0 mol/l., because the concentration less than 0.05 mol/l. is not effective while the concentration more than 1.0 mol/l. makes the solution difficult to control. The most desirable concentration is in the range 0.2–0.5 mol/l.

The nickel sulfate plating bath referred to in the present invention contains nickel sulfate as major component, of which the concentration is in the range of 0.3–3 mol/l., and the bath is usually acid. The components other than nickel sulfate are not particularly limited, but boric acid and sodium chloride may be added to improve the plating performance and the anodic dissolution.

The nickel layer produced by the above-mentioned process has little internal stress and therefore, even when it is made thick, never cracks and can remain unaffected in the subsequent drawing and heat-treatment.

The processes of drawing and heat-treatment mentioned above are repeated in the air at a temperature of 200–800° C. as often as necessary until a desired wire diameter is reached.

Metal wires to which the nickel coating process of this invention may be applied include not only wires of copper

and copper alloys but wires of iron-nickel alloys and other metals.

Needless to say, it is required prior to the plating process to polish wires with buff to secure surface smoothness, to remove grease in an alkali bath, to remove scales in an alkali cyanide bath and others.

Another object of this invention is to provide wires coated with double layer of nickel and gold, in which the gold coating layer shows good adhesion against heat, lustrous surface, arbitrary controlled uniform thickness and readily controlled mechanical and electrical properties, and, in addition, of high productivity due to the easy adaptation to continuous operation.

The gold plating in general is very sensitive to wire drawing. Especially a lustrous hard gold plating formed in a neutral or acid bath is not suited to drawing or other work. The present invention is characterized by employing an alkaline bath for plating in which potassium cyanide is the major component, pH is above 8.0 and the concentration of gold is 4 g./l. (0.02 mol/l.) In the case of gold plating, a strike plating in a plating bath of low gold concentration should precede the above-mentioned gold plating that ensures good workability. Furthermore, to prevent mutual diffusion of gold and core metal, the nickel plating with good workability under the present invention should be provided before the gold strike plating, by which it is possible to prevent reduction in workability due to alloy formation.

In case the metal to be coated is an iron-nickel alloy instead of copper, a wire of the alloy to be used for glass sealing is plated in the same way as copper because, like copper, it is chemically basic and susceptable to oxidation.

As above, the present invention has been illustrated citing gold and nickel as coating metals and copper, copper alloys and iron-nickel alloys as metals to be coated. The advantages of this invention are that it has overcome the defects of the conventional solid phase adhesion or plating, that it produces better nickel coated wires and nickel-gold coated wires than manufactured by any conventional process, and that it ensures very high productivity because it permits plating on a wire of a large diameter before it is drawn to a desired diameter.

This invention relates to a process for continuously producing wires coated with double layer of nickel and gold, which comprises plating metal wires with nickel, plating gold preliminarily for a short time in a plating bath of a low gold concentration, plating gold in the desired thickness and finally treating the products by alternate drawing and heating.

In the process of this invention, the major plating of gold is performed in an alkaline gold plating bath in which potassium cyanide is the major component with pH of above 8.0 and the gold concentration of over 4 g./l. (0.02 mol/l.).

On the other hand, the plating treatment in a plating bath of a low gold concentration is performed in a cyanide bath of gold 0.05–2 g./l. for 5–60 sec.

The drawing and the heating treatment are conducted in the same manner as for the nickel coated wires.

The following are examples of this invention. They are described only for illustration and not intended to restrict the scope of this invention.

Qualities of the products obtained in Examples 1 through 6 are summarized in Table 1.

EXAMPLE 1

A tough pitch copper wire of 0.9 mm. in diameter was polished by 1μ with a buff, immersed in a 10% aqueous solution of sulfuric acid, then plated with nickel at 50° C. for 50 min. in a plating bath, containing 400 g./l. of $NiSO_4$, 71 g./l. of Na_2SO_4 (or 0.5 mol/l. of sodium sulfate), 10 g./l. of sodium chloride and 20 g./l. of boric acid, with the current density 5 a./dm.^{2}, and the product obtained was drawn to 0.45 mm. in diameter, heated to 600° C. for an hour and again drawn to 0.4 mm. in diameter to obtain a product of a nickel coated wire.

EXAMPLE 2

A brass (Cu 65%, Zn 35%) wire of 2.0 mm. diameter was polished by 2μ with a buff, washed with a 10% sulfuric acid solution to remove scale, then plated with nickel for 20 min. in an electrolytic bath containing 250 g./l. of $NiSO_4$, 15.5 g./l. of $CoSO_4$ (or 0.1 mol/l. of cobalt sulfate) and 30 g./l. of boric acid by a current 5 a./dm.^{2} at 55° C. The resulting wire was drawn to 1.05 mm. in diameter, annealed by the induction heating method and further drawn to 1.0 mm. in diameter to obtain a nickel coated wire.

EXAMPLE 3

An iron-nickel alloy (Fe 48%, Ni 52%) wire of 0.5 mm. diameter was degreased by supersonic waves in an alkali solution, washed for 30 sec. in a 15% aqueous hydrochloric acid solution at 27° C. to remove scale and then plated with nickel at 60° C. by electroplating for 5 min. and at 5 a./dm.^{2} in a plating bath containing 250 g./l. of nickel sulfate, 87 g./l. of potassium sulfate (or 0.5 mol/l. of K_2SO_4) and 10 g./l. of sodium chloride. The resulting wire was drawn to 0.4 mm. in diameter, annealed (500° C., 1 hour) while running and again drawn to 0.3 mm. in diameter to obtain a nickel coated wire.

EXAMPLE 4

An oxygen-free copper wire of 0.6 mm. diameter was degreased with an alkali solution, plated with nickel at 45° C. in a plating bath containing 300 g./l. of nickel sulfate, 31 g./l. of cobalt sulfate (or 0.2 mol/l. of $CoSO_4$) and 25 g./l. of boric acid at a current of 5 a./dm.^{2} for 2 min., then plated with gold by the strike plating at 8 a./dm.^{2} for 10 sec. in a bath containing 0.5 g./l. of Au (0.025 mol/l.) and 10 g./l. of free CN and finally plated with gold in a thickness of 20μ at 50° C. at a current of 0.5 a./dm.^{2} in a bath containing 5 g./l. of Au and 7 g./l. of free CN. The resulting wire was drawn to 0.5 mm. in diameter, annealed at 25° C. for an hour and further drawn to 0.03 mm. in diameter to obtain a wire coated with double layers of nickel and gold.

EXAMPLE 5

A beryllium-copper (Cu 98%, Be 2%) alloy wire of 1.0 mm. diameter was washed for 1 min. with an aqueous solution of sulfuric acid and chromic acid at 60° C., plated with nickel for 10 min. and at a current of 2.5 a./dm.^{2} in a bath containing 345 g./l. of nickel sulfate, 11.4 g./l. of sodium sulfate (or 0.08 mol/l. of Na_2SO_4) and 15 g./l. of boric acid at 30° C., then plated with gold for 15 sec. in a strike plating bath containing 1.0 g./l. of Au and 20 g./l. of free CN at 45° C. at a current of 10 a./dm.^{2}, and finally plated with gold in a gold plating bath containing 10 g./l. (0.05 mol/l.) of Au and 4 g./l. of free CN at 60° C. at a current of 1.0 a./dm.^{2} until a 5μ layer of plated gold was obtained. The resulting wire was drawn to 0.8 mm. in diameter and then aged for 2 hours in a salt bath at 316° C. to obtain a wire coated with double layers of nickel and gold.

EXAMPLE 6

An iron-nickel alloy (Fe 50%, Ni 50%) wire of 0.8 mm. diameter was polished by 1μ with a buff, plated with nickel in the same manner as in Example 5, then plated with gold in a strike plating bath containing 0.2 g./l. of Au and 15 g./l. of free CN at 55° C., for 20 sec., and finally plated with gold in a thickness of 8μ in a gold plating bath containing 12 g./l. (or 0.06 mol/l.) of Au and 8 g./l. of free CN at 50° C. at a current of 0.2 a./dm.^{2}. The resulting wire was drawn to 0.7 mm. in diameter, annealed and then further drawn to 0.5 mm. in diameter to obtain a nickel alloy wire coated by gold.

TABLE 1

Example Number	Tensile strength, kg./mm.²	Elongation percent	Electrical conductivity, percent IACS	Coating thickness, μ	Adhesive property after heated in air for 1 hour at 400° C.
1	35	3	87	Ni 20	Not detached by twisting.
2	42	15	22	Ni 10	Do.
3	85	1	5	Ni 3	Do.
4	60	1	65	Ni 0.1, Au 1	Do.
5	125	5	24	Ni 4, Au 4	Do.
6	87	1	4	Ni 4, Au 5	Do.

EXAMPLE 7

	G./l.
Nickel sulfate	400
Boric acid	40
Potassium sulfate (K_2SO_4)	[1] 87

[1] 0.5 mol/l.

In a nickel plating bath of the above composition, pretreated copper wires were placed together with a nickel plate anode and an electrolysis was conducted with a cathodic current density 6–10 a./dm.² at the bath temperature 50±2° C. until about 200μ layer of nickel was deposited. The Vickers hardness of the coating was 175–190.

This example demonstrates a plating process in an unstirred bath. For a stirred bath, however, a higher cathodic current density can be applied to produce a plated layer of soft nickel.

In an unstirred bath, the cathodic current density was maintained almost constant at 82–95% in the temperature range between the room temperature up to 70° C.

EXAMPLE 8

Nickel sulfate—220–500 g./l., preferably 300–450 g./l.
Boric acid—10–50 g./l., preferably 20–40 g./l.
Potassium sulfate (K_2SO_4)—8.7–174 g./l. (0.05–1.0 mol/l.), preferably 35–87 g./l. (0.2–0.5 mol/l.).

Using a nickel plating bath of the above composition, a process similar to that in Example 7 was followed to obtain a similar result.

EXAMPLE 9

	G./l.
Nickel sulfate	400
Potassium sulfate (K_2SO_4)	[1] 87
Sodium chloride	10

[1] 0.5 mol/l.

Using a nickel plating bath of the above composition, a plating process was followed at the bath temperature 50° C. and with the cathodic current density 5–7 a./dm.². A soft nickel plating similar to the one shown in Example 7 was obtained.

EXAMPLE 10

	G./l.
Nickel sulfate	400
Sodium sulfate (Na_2SO_4)	[1] 71
Sodium chloride	10
Boric acid	20

[1] 0.5 mol/l.

Using a nickel plating bath of the above composition, a plating process was followed at the bath temperature 50° C. and with the cathodic current density 7 a./dm.². A soft nickel plating similar to the one shown in the preceding Example 9 was obtained.

What is claimed is:

1. A process of continuously producing nickel-gold coated wires, consisting essentially of

(a) electroplating nickel coated wire or nickel alloy wire with gold in a first gold-containing plating bath to form a preliminary strike plating of gold, said first plating bath being a cyanide-containing bath containing 0.05–2 g./l. of gold, said electroplating being conducted for 5–60 seconds;

(b) thereafter finish electroplating directly on the preliminary strike plating of gold with gold in a second gold-containing plating bath, said second plating bath being an alkaline plating bath in which potassium cyanide is the major component, the concentration of gold being larger than 0.02 mol/l.; and

(c) then subjecting the wire to alternate drawing and heating.

2. A process as claimed in claim 1, wherein the heating is effected after the drawing.

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