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METHOD OF PRODUCING DULL ELECTRONICKEL

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This invention relates to an improvement in the technique of producing hard, ductile nickel by electrolytic deposition, and specifically relates to the production of a new form of electrolytic nickel characterized as having compressive rather than contractile stress, as having a dull rather than a bright surface, and as being harder than known forms of such nickel as produced by conventional processes. More specifically defined, the invention relates particularly to a novel form of electrolyte for use in the electrolytic cell for producing such improved form of metallic nickel and to the resulting electronickel.

An object of the invention is to provide an improved and simplified electrolytic process for rapidly depositing a thick, hard nickel plate which is ductile and thus non-brittle, free of residual contractile stress, cracks or pits and which is particularly characterized in that it has a high residual internal compressive stress.

The invention is concerned primarily with an additional agent used in the electrolyte in the electrodeposition of metallic nickel and specifically contemplates the addition of orthoformylbenzenedisulfonic acid to the aqueous acid solution forming the electrolyte. The electrolyte otherwise comprises essentially a modified form of a Watts bath in that it contains the sulfate or chloride or both of a nickel salt together with a buffer, such as boric acid. The ortho-formylbenzenedisulfonic acid acts primarily as a hardening agent but also contributes to the formation of the desired internal compressive stress, maintains the nickel ductile, and prevents pitting and treeing of the deposited metallic nickel.

It is recalled that a regular Watts bath contains nickel sulfate, nickel chloride and boric acid in the proportions of:

	Grams per liter
Nickel sulfate ($6H_2O$)	278
Nickel chloride ($6H_2O$)	60
Boric acid	38

It is suggested in the patent to Freed, No. 2,409,119, October 8, 1946, directed to the production of bright nickel, that a brightening agent may be added to the conventional electrolytic bath in the form of a compound broadly described as a sulfonated aromatic aldehyde. As stated in that patent, the non-alkylated compound (ortho-formylbenzenesulfonic acid) includes ortho-sulfobenzaldehyde (ortho-formylbenzenemonosulfonic acid) and disulfobenzaldehyde (ortho-formylbenzenedisulfonic acid). This brightening agent is added in amount corresponding to the 3.7 grams per liter or about one percent of the solids present in the electroplated bath.

According to this patent, when this modified Watts bath was electrolyzed at a current density of 5 to 75 amperes per square foot, at a temperature of 110–130° F., with a pH of 3–5, there was produced a brilliant nickel deposit. In distinction from what is produced by following this Freed patent, the present invention relates to the production of what is herein called dull or dull-surfaced nickel.

To obtain this dull nickel the present disclosure modifies the regular Watts bath primarily by reducing the percentage therein of its nickel chloride; by increasing the

percentage of boric acid content; and by using ortho-formylbenzenedisulfonic acid, preferably as its sodium salt, and in an amount less than one percent by weight of the solids present in those cases where the nickel salt used is in the form of its sulfate. When the bath so modified is operated under conditions where the current density is high, 15 to 140 amperes per square foot, the above-identified desired hard, dull-surfaced electronickel characterized by high-residual internal compressive stress is obtained.

DEFINITIONS

"Dull" surfaced electronickel as used in this disclosure means a surface of the electrodeposited nickel which has a dull-gray, mottled, uniform satiny finish, is not image reflective, and has a surface roughness RMS of materially more than two microinches.

"Hard" electronickel as herein used means nickel possessing high hardness values, say, between 440 and 710 Vickers.

"High internal compressive stress" as used herein is intended to cover the range of 2400 pounds to 5200 pounds per square inch.

"Ductile" electronickel means a non-brittle nickel capable of being elongated under a load which may be either compressive tensile or impact without fracture.

"Thick electronickel plate" as herein used means an electrodeposited nickel plate having a thickness of the order of 0.001 inch or greater and thus thicker than what may be called a flash deposit.

It has been found experimentally that the concentration of ortho-formylbenzenedisulfonic acid required to give the hardness sought in the electrodeposited nickel may vary about from two-tenths (0.2) of a gram to ten (10) grams per liter of the electrolyte. Concentrations materially greater or less than this range fail to produce satisfactory deposits for the purpose of this invention but within this range a variation therefrom of up to plus or minus 5 percent causes no marked effect on the hardness, so that precise control of the addition agent is eliminated.

The other constituents of the plating solution, namely, the nickel sulfate, nickel chloride, and boric acid, in the Watts bath, or the nickel sulfamate hereinafter suggested in Example 3, serve their usual purpose in this type of plating solution to provide a source of nickel ions, to improve anode corrosion, and to prevent wide fluctuations in the hydrogen ion concentration.

The nickel sulfate concentration may vary from 190 grams per liter up to 350 grams per liter, although the lower limits are preferred in order to reduce losses by dragout. The nickel sulfamate can be used to replace the nickel sulfate and can be used in concentrations up to saturation. The nickel chloride concentration may vary from 20 grams per liter up to 60 grams per liter, but best results are obtained at the lower concentrations because of the tendency of chlorides to counteract the internal compressive stress produced by the addition agent. It is particularly noted that the boric acid concentration must be higher than the concentration of 38 grams per liter of the regular Watts bath, and it may vary from 50 grams per liter up to 60 grams per liter. Best results are obtained at the higher concentrations.

It is also important to the success of this invention that the maximum concentrations of metallic impurities in the plating solution be limited to those permissible in solutions not containing the addition agent herein featured, namely, iron 0.15 gram per liter; copper 0.04 gram per liter; zinc 0.05 gram per liter; and lead 0.002 gram per liter, since the presence of these impurities has a deleterious effect upon the appearance, ductility and stress produced in the nickel deposit.

Another advantage of the process featured in the pres-

ent invention is the wide permissible range of hydrogen ion concentration over which nickel may be plated with the desired hardness, the range being from as low as pH 2.0 up to pH 5.5, measured electrometrically. The hardness of the resulting nickel deposits is higher at the higher pH values, but a variation of as much as plus or minus 0.5 pH unit has no appreciable effect upon the hardness over a period of several plating cycles, thus eliminating the need for close supervision of the process with regard to the pH.

The electroplating solution may be electrolyzed over a wide temperature range, from as low as 100° F. or even at room temperature, to about 150° F. or more, although a preferred operating range is between 120° and 150° F. However, a temperature variation of plus or minus 5° F. during a plating cycle has no marked effect upon the hardness of the nickel deposit. However, when higher current densities are employed it is desirable to operate the bath near the upper end of this temperature range to prevent excessive polarization and burning.

A wide range of current densities may be used to deposit a sound nickel plate according to the present invention, the permissible range being from 10 amperes per square foot to as high as 200 amperes per square foot. An important advantage of this plating process is that the current density may vary by as much as fourfold without a marked variation in hardness of the deposit, thereby making it possible to plate irregular objects such as aeroplane propeller blades with a nickel coating of variable thickness, but which is essentially uniform in hardness over its entire surface.

An important and most desirable feature of the process is that the electronickel deposits are obtained with a residual internal compressive stress at current densities up to 200 amperes per square foot or even higher. Where hard electronickel as herein featured is applied to basis metals such as steel it has been found that the fatigue endurance limit is greatly increased if the nickel coating has an internal compressive stress. For this reason, the present invention is suited to situations wherein the basis metal is subjected to conditions normally causing failure by cracking, as in aeroplane propeller blades. Also, due to its internal compressive stress the nickel electrodeposited as herein featured is ideal for coating both conductive and non-conductive surfaces where the adhesion is not good since the tendency of the plate to lift or curl is eliminated and intimate contact is achieved permanently, or at least for a long period of time.

An additional advantage of the present invention is that the desired high degree of ductility of the electrodeposit is attained even at high current densities and this makes it possible for the nickel plate to withstand severe impacts without cracking. It is possible to strike the deposit with sufficient force to dent the basis metal on which the nickel is formed without cracking the nickel. Thus, the present process is well suited for use in situations wherein the plated surface is subjected to sudden severe impacts.

Because of its high degree of hardness, the nickel deposit has a resistance to abrasion and gouging and is ideally suited to situations in which the plated surface is subjected in use to excessive wear or scratching.

For an illustration of one example of an electrolyte which has given entire satisfaction in obtaining the hard, dull-surfaced nickel desired, the following has been used with success, operating under the conditions listed:

Example 1

Electrolyte:	Grams per liter
Nickel sulfate ($7H_2O$)	300.
Nickel chloride ($6H_2O$)	25.
Boric acid	50.
Ortho - formylbenzenedisulfonic acid, Na salt	0.85 (i. e. 0.22% of the solids present).
Water to make up 1 liter.	

Operating conditions:

Temperature	130° F.
pH	4.2.
Current density, amperes per square foot	15.

The plating under these conditions was continued for a period of 360 minutes and at the end of this time a plate having a thickness of 0.004 inch was obtained.

The nickel plate electrodeposited from this solution was smooth, ductile, pit-free, and had a hardness of 439–453 Vickers as measured with a 1 kilogram load.

In the several examples herein listed the anode was formed of electronickel, but any suitable form of anode may be used. In general the usual approved practices for electrodeposition of metals such as agitation and maintenance of concentration of the reagents were followed.

For another and preferred example:

Example 2

Electrolyte:	Grams per liter
Nickel sulfate ($7H_2O$)	250.
Nickel chloride ($6H_2O$)	25.
Boric acid	50.
Ortho - formylbenzenedisulfonic acid, Na salt	1.5–2.5 (i. e., 0.50%–0.83% of the solids present).
Water to make up 1 liter.	

Operating conditions:

Temperature	130° F.
pH	5.0.
Current density, amperes per square foot	35–140.

The plating under these conditions was continued for a period of 360 minutes and at the end of this time a plate of 0.008 to 0.040 inch was obtained.

The nickel electrodeposited according to this example resembled in general that produced in Example 1. In this case the nickel was plated onto an irregular object, specifically, an aeroplane propeller blade having rounded edges and at the edges was plated at a current density of about four times that at the center of the object. The hardness of the smooth, dull, ductile, pit-free resulting nickel was 515–613 Vickers as measured with a 1 kilogram load, and withstood a hammer blow sufficient to dent the basis metal without developing a crack in the deposit. The rounded edges of the blade were nickel plated to a thickness of about 0.040 inch, while the center of the plate along the camber surfaces had a thickness of 0.008 inch.

For still another example with a nickel containing material where other than nickel sulfate was used:

Example 3

Electrolyte:	Grams per liter
Nickel sulfamate	360.
Nickel chloride ($6H_2O$)	20.
Boric acid	50.
Ortho-formylbenzenedisulfonic acid, Na salt	10 (i. e. 2.2% of the solids present).
Water to make 1 liter.	

Operating conditions:

Temperature	130° F.
pH	4.5.
Current density, amperes per square foot	30.

The plating under these conditions was continued for a period of 240 minutes and at the end of this time a plate of 0.006 inch was obtained.

The nickel electrodeposited from this solution was

smooth, dull, pit-free, and had a hardness of 713 Vickers as measured with a 1 kilogram load. Although this deposit lacked the ductility found in the other examples, it is cited to illustrate the extent to which hard nickel may be plated according to this invention, using a relatively high percentage of the sodium salt of ortho-formylbenzenedisulfonic acid and with the nickel sulfamate used as a substitute for nickel sulfate.

As an indication of the magnitude of the compressive stress in the nickel electrodeposit formed by following the process herein featured, a measurement was made at a current density of 200 amperes per square foot in the solution cited in Example 2, using a Brenner Spiral Contractometer and the nickel plate had a thickness of 0.0004 inch, and the internal compressive stress was calculated to be 2800 pounds per square inch. At lower current densities the compressive stress of the deposited nickel increased to almost double this figure, being 5200 pounds per square inch at a current density of 90 amperes per square foot, the maximum compressive stress found. At current densities somewhere well above 300 amperes per square foot the stress changes from compressive to contractile. It might be noted that in some instances the contractile stress as developed in electronickel produced by known processes is sufficient to cause spontaneous cracking of the nickel deposit, particularly at the high current density areas. In the absence of the ortho-formylbenzenedisulfonic acid from the above-listed formulae, the nickel deposit was found to have a high contractile stress, so that, in addition to functioning as a hardening agent, this additional material, even in the smallest amounts herein suggested, acted to defeat the formation of contractile stress and to enhance the formation of compressive stresses.

This application is a continuation of parent application Serial Number 435,069, filed June 7, 1954, now abandoned.

I claim:

1. An aqueous, acid, electroplating bath which comprises in the aqueous medium a nickel ion yielding material together with a reagent selected from the group which consists of ortho-formylbenzenesulfonic acid having not more than two sulfonate groups in the benzene ring and the salts of ortho-formylbenzenesulfonic acid added in an amount less than 1% by weight of the solids present in the electrolyte and sufficient to obtain upon electrolyzing of the bath at a temperature of about 130° F. and at current densities extending simultaneously over a fourfold range of the order of 35 to 140 amperes per square foot a dull nickel deposit with residual compressive stress and a hardness ranging from 440–710 Vickers as measured with a 1 kilogram load with a surface having a dull, satiny finish and a roughness RMS of materially more than two microinches.

2. An aqueous, acid electroplating bath which comprises in the aqueous medium a metal ion yielding material consisting of a material selected from the group consisting of nickel sulfate, nickel chloride, a mixture of nickel sulfate and nickel chloride, nickel sulfamate, a mixture of nickel sulfamate and nickel chloride, and a mixture of nickel sulfamate, nickel sulfate and nickel chloride, together with the sodium salt of ortho-formylbenzenesulfonic acid having not more than two sulfonate groups in the benzene ring added in an amount less than 1 percent by weight of the solids present in the electrolyte and sufficient to obtain upon the electrolyzing of the bath at a temperature of about 130° F., and at current densities extending simultaneously over a fourfold range of the order of 35 to 140 amperes per square foot a dull cathodic deposit of the metal with a residual compressive stress and with a hardness ranging from 440–710 Vickers as measured with a one kilogram load and with a surface having a dull, satiny finish with a surface roughness RMS of materially more than two microinches.

3. The process of depositing hard, ductile, dull nickel having internal compressive stress, which process comprises passing an electric current from an anode to an irregularly shaped cathode at a current density of 15 to 150 amperes per square foot through an aqueous acid electroplating bath maintained at a temperature of about 130° F. and containing a nickel ion producing material and between 0.85 and 3.25 grams per liter of a reagent selected from the group consisting of orthoformylbenzenesulfonic acid having not more than two sulfonate groups in the benzene ring and the salts of orthoformylbenzenesulfonic acid and continuing the action until a hard, ductile layer of substantially pure nickel to a thickness in excess of 0.001 inch has been formed.

4. The process of depositing a dull electrodeposit of nickel which comprises electrolyzing an aqueous acid bath containing a nickel ion yielding material and between 0.85 and 3.25 grams per liter of an additive taken from the group consisting of ortho-formylbenzenesulfonic acid having not more than two sulfonate groups in the benzene ring and salts of ortho-formylbenzenesulfonic acid at a temperature of about 130° F. and with current densities extending over a range of the order of 35 to 140 amperes per square foot and continuing the action until a hard layer of substantially pure dull nickel to a thickness in excess of 0.001 inch has been formed, free of residual contractile stress, cracks or pits and which has a residual compressive stress.

5. In the art of electroplating irregularly shaped articles, requiring current densities varying as much as fourfold, with a thick, ductile, dull nickel deposit having substantially uniform hardness and high residual compressive stress throughout, the process which comprises passing an electric current from an anode to the article through an aqueous acid electrolyte containing a nickel ion yielding material and between 0.2 percent and 1.0 percent by weight of the solids in the electrolyte of a reagent selected from the group which consists of ortho-formylbenzenesulfonic acid having not more than two sulfonate groups in the benzene ring and salts of ortho-formylbenzenesulfonic acid, maintaining the electrolyte at a temperature of approximately 130° F., and controlling said current to plate nickel on the article at current densities extending over a range of the order of 35 to 140 amperes per square foot.

6. In the art of forming hard, ductile, dull nickel having a residual compressive stress, the process which consists in electrolyzing an aqueous acid bath containing a nickel ion yielding material, boric acid and a reagent selected from the group which consists of ortho-formylbenzenesulfonic acid having not more than two sulfonate groups in the benzene ring and its salts, the reagent being present in about 0.85–3.25 grams per liter, and wherein the process is performed at a temperature of about 130° F., at current densities extending simultaneously over a fourfold range of the order of 35 to 140 amperes per square foot and with a pH of 2–5.

7. In the electrodeposition of a hard nickel, the process which consists in electrolyzing an aqueous acid bath containing a nickel ion producing material, boric acid in an amount 50–60 grams per liter and less than 1 percent by weight of solids in the bath of an additional agent taken from the group consisting of ortho-formylbenzenesulfonic acid having not more than two sulfonate groups in the benzene ring and its sodium salts at a temperature of about 130° F., and at a current density of 15–150 amperes per square foot and continuing the operation until there is formed a plate having a thickness materially greater than 0.001 inch.

References Cited in the file of this patent

UNITED STATES PATENTS

2,409,119 Freed ---------- Oct. 8, 1946