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ELECTROLYTIC NICKEL PLATING BATH

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The present invention relates to a novel electrolytic nickel plating bath which allows the production of electro-nickel deposits which are without discontinuity and are very pure, containing neither boron nor carbon. Such plating baths are particularly valuable for the coating of uranium bars for use in nuclear reactors.

Electrolytic nickel plating has usually been effected up to the present by placing the parts to be treated as the cathodes in baths of which the principal constituent is a nickel salt, the sulphate being most often used. Other nickel salts also employed are the chloride, fluoborate and sulphamate. Nickel-ammonium double salts are also used, but to a lesser extent.

To this principal constituent of known nickel plating baths, generally of sulphate, there is generally added a chloride intended to ensure anodic attack and to facilitate continuity of the electrolysis; this chloride is generally nickel chloride or sodium chloride, more rarely ammonium chloride. To render the bath sufficiently conductive of electricity, a high concentration of nickel salt is usually used, which allows the employment of high current densities and increase of the speed of deposition of the metal. When this means is not used, a conductive salt such as sodium sulphate, can be added in quantities which can be quite large.

It is also necessary to add to these materials a buffering agent which allows the pH to be maintained within selected optimum limits which depend on the composition and conditions of operation of the bath. The buffer most often used is boric acid.

Since it is of advantage to increase as much as possible the concentration of the nickel in the bath and to diminish the concentration of chlorides, which tend to produce pitting in the deposits, the following type of composition is normally used for most standard nickel plating baths:

	G./l.
Nickel sulphate ($NiSO_4$—$7H_2O$)	240–340
Nickel chloride ($NiCl_2$—$6H_2O$)	20–40
Boric acid (H_3BO_3)	20–40

To these constituents, there is also added very frequently a product for lowering the surface tension, to eliminate porosity and pitting and also to ensure continuity of the deposit over all the surface of the object to be plated. Numerous products can be utilized for this purpose, the one most frequently used being sodium lauryl sulphate $(C_{12}H_{25})SO_4Na$, i.e. the sodium salt of sulphonated lauryl alcohol, which is used in an amount of from 0.1 to 0.5 g./l. Such baths when correctly used allow the production of excellent nickel deposits which are perfectly continuous.

However, it is also known to utilize as the buffer, soluble aluminium salts which hydrolyze in aqueous solution.

In the latter case, it is necessary to act on the cathode by introducing high concentrations of chloride (greater than 30 g. of chlorine ions per liter) into the bath.

All the preceding known techniques for nickel plating lead to deposits of good quality, but which also contain

according to the circumstances more or less substantial amounts of boron and/or carbon.

In certain applications, particularly the covering or sheathing of the uranium bars in nuclear reactors, the presence of these elements even in trace form is undesirable. The elimination of boron alone has already been envisaged by replacing boric acid by another buffer. The buffers most often employed for this purpose are ammonium salts, which should only be used in baths containing a product which decreases the surface tension, since they favor the formation of pits and thus of discontinuities in the deposit; there have also been used mixtures of acetic acid and sodium acetate or other acids such as citric acid and tartaric acid. Nickel plating baths comprising such buffers and surface tension depressants can produce nickel deposits which do not contain boron.

However, even in this case most of the buffering agents and materials for lowering the surface tension mentioned above contain carbon or can only be utilized in conjunction with products which contain carbon; part of this carbon passes into the deposited nickel.

It is therefore an object of the present invention to provide an electrolytic nickel plating bath which allows the deposit of very pure nickel coverings without discontinuity and containing neither boron nor carbon.

According to the invention, an electrolytic nickel plating bath comprises, in aqueous solution, a nickel salt, and an aluminium alum at a concentration of at least 15 g./liter of crystallised salt. The bath may also contain up to 15 g./liter of chlorine ions.

The alum utilised in carrying out the invention, is preferably potassium alum, $K_2Al_2(SO_4)_4 \cdot 24H_2O$, and the nickel salt is the sulphate, $NiSO_4 \cdot 7H_2O$. The use of potassium alum has the following advantages which have not been encountered up to he present with the use of a single product:

The alum acts as a buffer by the action of the aluminium salts which it contains;

The alum operates so as to eliminate pitting by the action of the potassium salts which it contains;

The alum is available in a crystalline non-hygroscopic soluble form and is hence easily handled;

The alum does not contain carbon nor boron and consequently can be utilized for covering uranium bars.

It is within the scope of the invention to utilize other aluminium alums, such as sodium alum. The quantities of the alum utilized must be at least equal to 15 g./liter of crystallized salt; the alum can also be used in greater amounts up to the limits of solubility of the particular alum utilized under the conditions of use.

The nickel sulphate can also be partly or entirely replaced by one or other different nickel salts and can be employed in all concentrations hitherto used in nickel plating baths.

The simultaneous presence of chlorine in the bath of the invention permits the avoidance after a certain period of use of the bath of passivation of the anodes which would necessitate either a depassifying treatment or their replacement; the upper limit of concentration of chlorine ions which can be used without producing discontinuity of the cathodic deposit is around 15 g./liter of solution; the lower concentration limit is theoretically nil and a lower limit is only reached in practice due to the rapid passivation of the electrodes and the low current density obtainable when the quantity of chlorine ions present in the solution tends towards zero.

In order that the invention and the manner of performing it may be fully understood, there are described below various non-limitative examples of the nickel plating bath of the invention.

Example 1

A first experimental bath, without chloride, was employed; its composition and conditions of use are as follows.

Constituents:

Nickel sulphate, $NiSO_4 \cdot 7H_2O$ ——g./l——	280
Potassium alum, $K_2Al_2(SO_4)_4 \cdot 24H_2O$ ——g./l——	70
Temperature ——° C——	40–60
pH	3–3.5
Current density ——a./dm.²——	1

The deposits obtained in this bath are excellent; they do not include discontinuities and it is clearly apparent that they do not have an abnormal internal tension, their physical and mechanical characteristics being similar to those of known nickel deposits.

They are thus excellently utilizable for various applications and in particular for the covering of uranium bars. This nickel plating bath, which does not contain chlorine in order to reduce the risk of discontinuities in the cathode, only operates at a relatively low current density and after a certain time of use can cause, in the absence of special known precautions, a passivation of the nickel anodes.

Example 2

Another bath containing a small amount of chloride has the following composition and characteristics.

Constituents:

Nickel sulphate, $NiSO_4 \cdot 7H_2O$	280 g./l.
Potassium alum, $Al_2K_2(SO_4)_4 \cdot 24H_2O$	70 g./l.
Nickel chloride, $NiCl_2 \cdot 6H_2O$	3–6 g./l. or 0.9–1.8 g./l. (Cl^-).
Temperature	40°–60° C.
pH	3–3.5.
Current density	1.5–2 a./dm.².

This bath can be operated more easily than one not containing chloride and it can be utilized at a higher current density and for a longer time without passivation of the anodes, whilst the nickel deposits obtained have the same qualities as in the preceding example; it is also clearly apparent that the presence of chloride does not cause any discontinuity in the deposits obtained.

Example 3

By increasing the concentration of the chloride, a third bath was obtained ensuring perfect anodic corrosion without passivation of the anodes, without changing its composition during the course of its use, and giving deposits of normal quality and constant appearance without discontinuities. This bath had the following composition and characteristics.

Constituents:

Nickel sulphate	280 g./l.
Potassium alum	70–90 g./l.
Nickel chloride	35 g./l. or 10.5 g./l. (Cl^-).
Temperature	40°–60° C.
pH	3–3.5.
Current density	1.5–2 a./dm.².

Example 4

A fourth bath utilized contained a low concentration of alum, near the minimum indicated above (15 g./l.) and was as follows.

Constituents:

Nickel sulphate ——g./l——	280
Potassium alum ——g./l——	35
Nickel chloride ——g./l——	18
Temperature ——° C——	50
pH	3.25
Current density ——a./dm.²——	1–2

Example 5

A fifth bath according to the invention contained a high concentration of alum; furthermore, the alum utilized in this case was sodium alum; this bath had the following composition and characteristics.

Constituents:

Nickel sulphate ——g./l——	280
Sodium alum, $Na_2Al_2(SO_4)_4 \cdot 24H_2O$ ——g./l——	460
Nickel chloride ——g./l——	35
Temperature ——°C——	50
pH	3.25
Current density ——a./dm.²——	5–10

These bath formulae, which are given merely by way of example, allow the production of nickel deposits which are of excellent quality, without pittings, and not containing boron or carbon or porosities or discontinuities and are produced with an optimum yield. These baths are easy to produce and utilize, being in this respect very similar to standard baths. They are perfectly adapted to the production of electrolytic deposits on uranium bars which have previously been subjected to the pickling and other treatments necessary for the preparation of the surface; also, they give excellent deposits on all other metals which are currently nickel-plated by means of traditional baths.

Although the pH of the baths indicated in the examples ranged from 3 to 3.5, the pH can be substantially higher or lower than these values, and the temperature indicated as being between 40° and 60° C. can also be higher or lower than these values; however, if the temperature is increased, care must be taken, especially at high pH values, that temperatures are not attained at which hydrolysis of of the alums occurs under the conditions of use.

What we claim is:

1. A boron and carbon free electrolytic nickel plating bath for pit free nickel plating of uranium bars for use in nuclear reactors consisting of an aqueous solution of approximately 280 grams per liter of water soluble nickel salt and an aluminum alum at a concentration from 15 grams per liter to 460 grams per liter, said nickel plating bath having a pH of from 3 to 3.5, a temperature between 40° C. and 60° C. and a current density from 1–10 a./dm.².

2. A boron and carbon free electrolytic nickel plating bath for pit free nickel plating of uranium bars for use in nuclear reactors consisting of an aqueous solution of approximately 280 grams per liter of water soluble nickel salt, and aluminum alum at a concentration from 15 grams per liter to 460 grams per liter and chloride ions in quantity not more than 15 grams per liter of the bath, said nickel plating bath having a pH of from 3 to 3.5, a temperature between 40° C. and 60° C. and a current density from 1–10 a./dm.².

3. A bath as described in claim 1 in which the aluminum alum is potassium alum.

4. A bath as described in claim 1 in which the alum is sodium alum.

5. A bath as described in claim 1 in which the nickel salt is nickel sulphate.

6. A bath as described in claim 2 in which the chloride is nickel chloride.

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