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3,726,768
**NICKEL PLATING BATHS CONTAINING
 AROMATIC SULFONIC ACIDS**

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16 Claims

ABSTRACT OF THE DISCLOSURE

The stress of nickel deposits from plating solutions can be altered from tensile to near zero, and also to compressive stress by adding to nickel plating baths, such as those containing nickel sulfate and nickel bromide, amino naphthalene di- and tri-sulfonic acids, and naphthol disulfonic acids and their salts, such as, for example, 3-amino-2,7-naphthalenedisulfonic acid, and 2-naphthol-6,8-disulfonic acid, and their sodium and nickel salts. When the nickel salts of the above sulfonic acids are used as plating solutions rather than in the small amounts require as additive, bright or semibright, adherent and nonporous nickel deposits are formed and the stress of such nickel deposits range from approximately zero p.s.i. to -26,000 p.s.i. (compressive). Similar results were also obtained with the nickel salts of benzenesulfonic acid, benzenedisulfonic acids, naphthalenesulfonic acids, and naphthalenedisulfonic acids. Preferably all plating solutions contain nickel bromide. These plating solutions can be used for electroplating nickel on any substrate, including uranium.

CONTRACTUAL ORIGIN OF THE INVENTION

The invention described herein was made in the course of, or under, a contract with the United States Atomic Energy Commission.

This invention relates to the electrodeposition of nickel from aqueous baths onto uranium or other substrates, using nickel organo-sulfonates as plating solutions or using the organo-sulfonic acids or their soluble salts as additives to known nickel plating solutions.

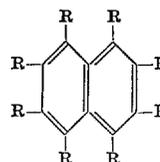
It is necessary that uranium fuel elements used in water cooled nuclear reactors be protected from corrosion. One method is to clad a nickel plated fuel element with aluminum. The nickel plate acts as a diffusion and secondary corrosion barrier, prevents the formation of undesirable aluminum-uranium compounds, and the uranium-nickel-aluminum bond formed in the cladding operation provides good heat transfer. The reliability of the fuel elements is a very important factor in the operation of a nuclear reactor. Any technique which will increase the integrity of the fuel elements will lower the cost of operation. One problem associated with the use of nickel electrodeposited from conventional plating solutions used in nuclear processes is that the nickel has high residual stresses which can contribute to poor adherence of the deposit, thus providing poor heat transfer in the fuel element.

The novel plating solutions disclosed herein were developed to improve the heat transfer properties of the uranium-nickel-aluminum bond by controlling the stress of the nickel deposit. Another application of these plating solutions is in electro-forming articles, where control of stress is necessary if the product must meet close tolerances. Still another use of these plating solutions is in the deposition of low stress nickel coat under chromium, which can lower the stress of the chromium deposit. In general these plating solutions can be useful in any situation where nickel needs to be deposited under controlled stress. In ad-

dition these plating solutions can be used to produce semi-bright and mirror bright nickel deposits for decorative purposes. Some of these nickel organo-sulfonates used to make up the plating solutions can be used as additions to conventional plating solutions. From these solutions bright and semibright nickel plates with reduced stress can be deposited.

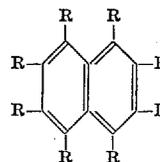
In accordance with one embodiment of this invention, reduced stress of nickel deposits are obtained by adding to known aqueous acidic nickel plating baths an organic sulfonic acid or its soluble salt, particularly a sodium or nickel salt selected from one of the groups of organo-sulfonic acids given below:

GROUP I



wherein two or three of the R groups are $-\text{SO}_3\text{H}$ and one of the R groups is $-\text{NH}_2$ and the remaining R groups are $-\text{H}$. An example of one of these acids is 3-amino-2,7-naphthalenedisulfonic acid.

GROUP II



wherein two of the R groups are $-\text{SO}_3\text{H}$ and one R group is $-\text{OH}$ the remaining R groups being $-\text{H}$. An example of one of these acids is 2-naphthol-6,8-disulfonic acid.

In accordance with another embodiment of this invention nickel plating baths which have substantially zero stress of nickel deposits or which can even be under compression, comprise one or more of the nickel salts of a sulfonic acid of Group I and Group II, above, or a nickel salt of one of the group of organic sulfonic acids given below:

GROUP III

- m-benzenedisulfonic acid
- p-benzenedisulfonic acid
- o-benzenedisulfonic acid

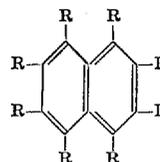
GROUP IV

- benzenesulfonic acid

GROUP V

- 1-naphthalenesulfonic acid
- 2-naphthalenesulfonic acid

GROUP VI



wherein two groups are SO_3H and the remaining groups are H. An example of these acids is 2,7-naphthalenedisulfonic acid.

When the above mentioned sulfonates were used as plating solutions, we found that bright or semibright, adherent and nonporous nickel deposits were formed. The stress of these nickel deposits ranged from approximately 0 p.s.i. to -26,000 p.s.i. (compressive), and the carbon contents were as high as 3700 p.p.m.

An example of a plating solution from each one of the groups is shown below. Some properties of the nickel deposit are also shown.

3 GROUP I

Typical plating solution:
 Nickel (II) salt of 3-amino-2,7-naphthalenedisulfonic acid: 0.6 M
 Nickel bromide: 0.1 M
 Ph: 3.5
 Temperature: 50° C.
 Current density: 30 ma./cm.²
 Properties of the nickel deposit: Surface of the deposit—
 mirror-bright
 (GROUP I):
 Adherence: Excellent
 Porosity: Low
 Stress: —13,000 p.s.i.
 Carbon content: 3700 p.p.m.

GROUP II

Typical plating solutions:
 Nickel (II) salt of 2-naphthol-6,8-disulfonic acid: 0.3 M
 Nickel bromide: 0.1 M
 pH: 2.1
 Temperature: 50° C.
 Current density: 30 ma./cm.²
 Properties of the nickel deposit:
 Surface of the deposit: Semibright
 Adherence: Excellent
 Porosity: Low
 Stress: —6,400 p.s.i.
 Carbon content: 300 p.p.m.

GROUP III

Typical plating solution:
 Nickel (II) salt of m-benzenedisulfonic acid: 0.7 M
 Nickel bromide: 0.1 M
 pH: 3.5
 Temperature: 50° C.
 Current density: 30 ma./cm.²
 Properties of the deposit:
 Surface of the deposit: Semibright
 Adherent: Excellent
 Porosity: Low
 Stress: —6,900 p.s.i.
 Carbon content: 700 p.p.m.

GROUP IV

Typical plating solution:
 Nickel (II) salt of benzenesulfonic acid: 0.4 M
 Nickel bromide: 0.1 M
 pH: 2.5
 Temperature: 50° C.
 Current density: 30 ma./cm.²
 Properties of the deposit:
 Surface of the deposit: Semibright
 Adherence: Excellent
 Porosity: Low
 Stress: 600 p.s.i.
 Carbon content: 250 p.p.m.

GROUP V

Typical plating solution:
 Nickel (II) salt of 1-naphthalenesulfonic acid: 0.2 M
 Nickel bromide: 0.1 M
 pH: 2.5
 Temperature: 50° C.
 Current density: 30 ma./cm.²
 Properties of the deposit:
 Surface of the deposit: Semibright
 Adherence: Excellent
 Porosity: Low
 Stress: —500 p.s.i.
 Carbon content: 750 p.p.m.

4 GROUP VI

Typical plating solution:
 Nickel (II) salt of 2,7-naphthalenedisulfonic acid: 0.6 M
 Nickel bromide: 0.1 M
 pH: 2.8
 Temperature: 50° C.
 Current density: 30 ma./cm.²
 Properties of the deposit:
 Surface of the deposit: Semibright
 Adherence: Excellent
 Porosity: Low
 Stress: 20,000 p.s.i.
 The sulfonates from Groups I and II were found to be novel additives to existing plating solutions. By using these compounds as additives we found that the stress of the nickel deposits from the plating solutions could be altered from tensile to near zero, and also to compressive stress. An example of a stress reducer from the two groups is shown below, and stress of the deposits are compared to deposits from the reference Watts-bromide plating solution

Reference plating solution (Watts-bromide)

Nickel sulfate: 1.2 M
 Nickel bromide: 0.20 M
 Boric acid: 0.62 M
 Temperature: 52° C.
 pH: 4.0
 Current density: 60 ma./cm.²
 Stress: 18,000 p.s.i.
 Group I.—Additive to reference plating solution:
 Nickel (II) salt of 3-amino-2,7-naphthalenedisulfonic acid: .05 M
 Stress: —12,000 p.s.i.
 Change in stress: 30,000 p.s.i. more compressive
 Group II.—Additive to reference plating solution:
 Nickel (II) salt of 2-naphthol-6,8-disulfonic acid, .05 M
 Stress: —6,900 p.s.i.
 Change in stress: 25,000 p.s.i. more compressive
 In addition the organo sulfonates from Group I and Group II can be used as brighteners for existing plating solutions. An example from each group is shown below.

GROUP I

Typical plating solution:
 Nickel sulfate: 1.2 M
 Nickel bromide: 0.20 M
 Nickel (II) salt of 3-amino-2,7-naphthalenedisulfonic acid: 0.05 M
 Boric acid: 0.62 M
 Temperature: 52° C.
 pH: 4.0
 Current density: 60 ma./cm.²
 Properties of the deposit:
 Surface of the deposit: Mirror-bright
 Adherence: Excellent
 Porosity: Low
 Stress: —12,000 p.s.i.
 Carbon content: 1250 p.p.m.

GROUP II

Typical plating solution:
 Nickel sulfate: 1.2 M
 Nickel bromide: 0.20 M
 Nickel (II) salt of 2-naphthol-6,8-disulfonic acid: 0.05 M
 Boric acid: 0.62 M
 Temperature: 52° C.
 pH: 4.0
 Current density: 60 ma./cm.²

5

Properties of the deposit:

Surface of the deposit: Semibright

Adherence: Excellence

Porosity: Low

Stress: -6,900 p.s.i.

Carbon content: 170 p.p.m.

In the examples the amounts given as M are mols per liter. The term ma./cm.² means milliamperes per square centimeter.

In place of the nickel salts of the examples of Group I and Group II compounds used as additives, the organo-sulfonic acid itself or other soluble salts thereof may be used, the sodium salts and nickel salts being preferable.

Likewise, when the organo-sulfonic acids or salts are used as additives, they may be added to any of the common plating solutions such as those comprising nickel sulfate, nickel sulfamate, nickel bromide, nickel fluoborate and nickel chloride or other nickel salts or mixtures of such salts, preferably with buffer materials as, for example, boric acid. The amounts of such nickel salts which may be employed are quantities which are now conventional in this art for such baths. Preferably the plating solution to which the Group I or Group II compounds or salts are added comprises nickel sulfate and nickel bromide.

For additives, the concentrate of organo-sulfonic acid for sulfonate may suitably range about 0.01 mol per liter to about 0.1 mol per liter, but there is no critical upper limit and they can be used up to saturation concentration value.

For nickel plating solutions the nickel salt of the organo-sulfonic acid of Group I and Group II is preferably used with nickel bromide. The concentration of the nickel sulfamate may suitably range from about .1 mol per liter to 1.0 mol per liter and up to saturation, and the nickel bromide from preferably .05 mol per liter to 0.2 mol per liter.

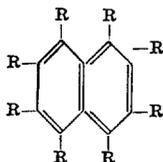
The baths are aqueous solutions on the acid side, such as those of a pH of 2.0-5.0.

The baths of this invention can be used for electroplating nickel or any substrate, including uranium, by means well known to the art for electroplating nickel from nickel plating baths. Current densities of 30 milliamperes per square centimeter-60 milliamperes per square centimeter (30 ma./cm.²-60 ma./cm.²) are suitable as shown in the examples. Higher current densities can be used, such as 50-100 amperes (sq. dm.) particularly with agitation of the bath.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A bath for depositing nickel plate consisting essentially of an aqueous acidic solution of at least one nickel salt selected from the group consisting of nickel sulfate, nickel sulfamate, nickel bromide, nickel fluoborate, and nickel chloride, and contained dissolved in said nickel plating solution in a concentration of about .01 mol per liter to saturation, a compound selected from the group of organic sulfonic acids and their salts in which the organic sulfonic acid is selected from the group of compounds having the formula

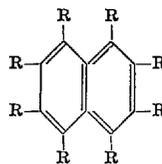
(I)



wherein two or three of the R groups are -SO₃H and one of the R groups is -NH₂ and the remaining R groups are -H,

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(II)

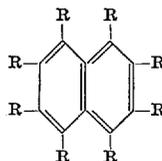


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wherein two of the R groups are -SO₃H and one R group is -OH, the remaining R groups being -H.

2. A bath for depositing nickel plate consisting essentially of an aqueous acidic solution of at least one nickel salt of an organic sulfonic acid selected from the group of compounds having the formula

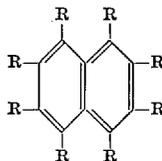
15 (I)



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wherein two or three of the R groups are -SO₃H and one of the R groups is -NH₂ and the remaining R groups are -H,

(II)



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wherein two of the R groups are -SO₃H and one of R group is -OH, the remaining R groups being -H,

(III)

m-benzenedisulfonic acid
p-benzenedisulfonic acid
o-benzenedisulfonic acid,

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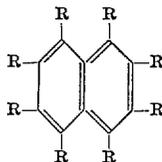
(IV)

benzenesulfonic acid,

(V)

1-naphthalenesulfonic acid
2-naphthalenesulfonic acid,

45 (VI)



50

wherein two groups are SO₃H and the remaining groups are H, said compounds being present in from 0.1 mol per liter to saturation.

3. The bath of claim 1 in which the solution consisting essentially of nickel sulfate, nickel bromide and 3-amino-2,7-naphthalenedisulfonic acid or its nickel or sodium salt.

4. The bath of claim 1 in which the solution consisting essentially of nickel sulfate, nickel bromide and 2-naphthol-6,8-disulfonic acid or its nickel or sodium salt.

5. The bath of claim 2 in which the solution consisting essentially of nickel bromide and nickel (II) salt of 3-amino-2,7-naphthalene-disulfonic acid.

6. The bath of claim 2 in which the solution consisting essentially of nickel bromide and nickel (II) salt of 2-naphthol-6,8-disulfonic acid.

7. The bath of claim 2 in which the solution consisting essentially of nickel bromide and nickel (II) salt of m-benzene-disulfonic acid.

8. The bath of claim 2 in which the solution consisting essentially of nickel (II) salt of benzenesulfonic acid.

9. The bath of claim 2 in which the solution consisting essentially of nickel bromide and nickel (II) salt of 1-naphthalenesulfonic acid.

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7

10. The bath of claim 2 in which the solution consisting essentially of nickel bromide and nickel (II) salt of 2,7-naphthalenedisulfonic acid.

11. A method of electrodepositing nickel comprising the step of electrodepositing nickel from the solution defined in claim 1.

12. A method of electrodepositing nickel comprising the step of electrodepositing nickel from the solution defined in claim 2.

13. The method of claim 12 wherein the nickel is deposited on a substrate of uranium.

14. In the method of electroplating a substrate with nickel by contacting said substrate with a solution containing nickel ion and passing an electric current there-through, the improvement comprising adding a nickel salt of 3-amino-2,7-naphthalenedisulfonic acid to said solution.

15. The method of claim 14 wherein the substrate is uranium.

8

16. A bath for depositing nickel plate consisting essentially of an acidic aqueous solution of nickel sulfate 1.2 mols per liter, nickel bromide 0.2 mol per liter, nickel (II) salt of 3-amino-2,7-naphthalenedisulfonic acid .05 mol per liter, boric acid .62 mol per liter, said aqueous solution having a pH of 4.0.

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