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3,180,808

## NICKEL PLATING BATH

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No Drawing. Filed Nov. 29, 1963, Ser. No. 327,102

Claims priority, application Sweden, May 28, 1963,

5,909/63

14 Claims. (Cl. 204-49)

The present invention relates to the electrodeposition of nickel from an aqueous acidic nickel plating bath and, more particularly, to a method of preparing a composite coating providing greatly improved corrosion protection, and to agents used as corrosion resistance additives in electrolytic nickel baths.

It is known to provide a composite electroplate on a metal base to secure outdoor corrosion protection, such metal base being, for instance, steel, copper and its alloys, zinc and its alloys, aluminum and its alloys, or magnesium and its alloys. Such composites are based on the fact that the uppermost layer or coating of the composite has an electrode potential lower than the lowermost layer or coating, i.e., the coating next adjacent the basis metal to be protected. Further, intermediate layers of differing electrode potential have also been provided but like the known double layer systems the uppermost layer has an electrode potential lower than the layer next adjacent to it.

These systems while offering corrosion protection to basis metals under certain atmospheric conditions, i.e., a marine or saline atmosphere, offer substantially ineffective corrosion protection in an industrial atmosphere, i.e., one which contains sulfur vapors in corrosion promoting amounts. It has been found that such an atmosphere creates an environment whereby with a usual composite coating, the uppermost layer has a higher electrode potential and the desired electrochemical corrosion resistance is not obtained.

It is the principal object of this invention to provide a firmly bonded laminated corrosion protective composite coating on a metal base susceptible to industrial atmospheric corrosion.

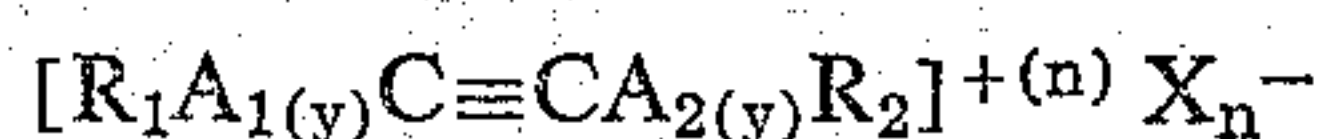
It is another object of this invention to provide a bath composition for a semi-bright nickel plating having an electrode potential substantially greater than conventional semi-bright nickel coatings.

It is still another object of this invention to provide a novel brightener of the second class for use in nickel plating baths and especially in nickel plating baths to produce a composite coating.

It is a further object of the invention to provide a nickel plating bath resulting in a coating possessing good ductility and improved corrosion resistance properties.

With the foregoing objects in view, as well as others which will become apparent as the description proceeds, the invention consists in the novel composite coating, the novel plating process and bath compositions which will be described in certain illustrative examples hereinafter and will then be more particularly pointed out in the appended claims.

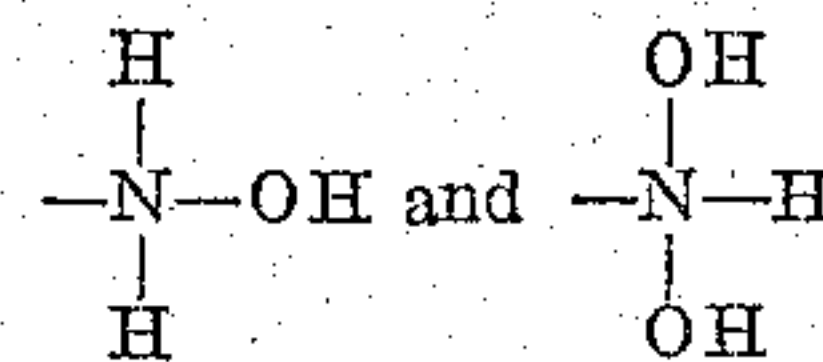
According to the invention a nickel composite coating having a high luster and corrosion resistance is obtained by employing a lowermost layer of electrodeposited nickel having an electrode potential sufficiently great to reduce corrosion effected in industrial atmospheres. The lowermost nickel-containing layer is obtained by using a nickel plating bath provided with a brightener of the second class having the following structural formula:



in which  $A_1$  and  $A_2$  are selected from the group consisting

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of lower alkyl radicals and  $y=0-1$ ,  $R_1$  and  $R_2$  are selected from the group consisting of H, OH,



X is selected from the group consisting of hydrogen and a halogen, and  $n$  is an integer equal to the number of quaternary N atoms in  $R_1$  and  $R_2$  with the proviso that the compound contain at least one quaternary N atom. The novel brightener of this invention is generally used in amounts between 0.1 to 10 millimoles per liter of bath solution and preferably between 0.2 to 2.0 millimoles per liter of solution.

In general, the process of the invention involves operating a bath at conventional nickel plating temperatures ranging from about 30° C. to as high as 80° C. with a range of 40-65° C. being especially desirable. The pH of the plating bath, as determined electrochemically, can range from around 1.5 to 5.0 with 3.0 to 5.0 being found especially suitable in the majority of cases. Practically all baths for electroplating nickel contain nickel sulfate, a chloride, usually nickel chloride; a buffering agent, usually boric acid; and a wetting agent, e.g., sodium lauryl sulfate, sodium lauryl ether sulfate, and 7-ethyl-2-methyl-4 undecanol sulfate. Such types of baths include the well-known Watts-type bath and high chloride type bath. The Watts bath solution to which the brightener of the second class of this invention can be added typically comprises around 300 grams per liter of nickel sulfate, 60 grams per liter of nickel chloride and 40 grams per liter of boric acid. The foregoing bath composition and specified operating conditions are not critical in the basic Watts bath solution and the particular temperature and pH thereof may vary within the indicated ranges without adverse effect. Considerable latitude is also permissible in respect to the types and concentrations of the nickel salts employed, for instance, as the source of the nickel, a combination of nickel fluoborate with nickel sulfate and nickel chloride, or a combination of nickel fluoborate with nickel chloride can be used.

The upper nickel layer of the composite coating may be deposited from a basic bath similar to the ones used for plating the lowermost layer but it should include a brightener of the first class preferably an organic sulfon-compound such as p-toluene sulfonamide, o-benzoyl sulfimide, benzene sulfonamide, naphthalene sulphonic acid, benzene sulphonic acid, 2-butyne, 1,4-disulphonic acid, or allyl sulphonic acid together with 2-butyne 1,4-dioxyethanesulphonic acid. Generally the organic sulphon-compound will be present in amounts ranging from 1 to 10 grams per liter of solution.

Preferably also, the upper nickel layer of the composite coating can contain a second brightener of the second class, i.e., one which is different from the novel secondary brighteners of this invention provided in the lower nickel layer. Representative examples of such other brighteners of the second class are: 1-propargyl amino ethylene imidazol, 2-propenyl imidazol, 2-ethynyl imidazol, 2-vinyl imidazol, 2-propenyl-3-diethylene-diamin-imidazol, 2-( $\beta$ -phenylethenyl)-3-( $\beta$ -hydroxyethyl) imidazol, 3-propynyl imidazol, 2-propenyl-3-( $\beta$ -hydroxyethyl) imidazol, 3-propenyl imidazol, 2-propenyl-3-amino ethyl imidazol, 2-propenyl-3-butyl imidazol, 2-propenyl-4,5-dimethyl-imidazol, 3-propynyl amino ethyl imidazol. Other brighteners of the second class which can be used in the upper plate are disclosed, for instance, in U.S. Patents 2,485,149, 2,712,522, 2,800,440, and 2,876,177. These brighteners can be provided in amounts of 0.01 to 1 gram/liter of solution.

While the novel brightener of the second class of this invention advantageously is used to produce a lowermost



coating on a base metal, the lowermost coating being superimposed by one or more coatings preferably of bright nickel to effect a composite coating, it can also advantageously be employed as a single coating to produce a ductile and corrosion resistant sulphur-free coating for a basis metal having a chemical resistance generally about 2.5 times greater than that exhibited by conventional semi-bright coatings. Further a brightener of the first class can be provided to the plating bath containing the novel brighteners of the second class of this invention and especially effective brighteners of the first class are aromatic sulphonic acid compounds which when so included produce a sulphur-containing nickel coating possessing favorable stress-free properties as well as good ductility and corrosion resistance characteristics. The addition of the sodium salt of naphthalene trisulphonic acid, for example, is quite effective. Other tri- and di-naphthalene sulphonics may likewise be employed. Such other agents include naphthol and sulphonic acids, naphthalamine sulphonic acids, toluidine sulphonic acids and tolidine sulphonic acids or their salts. These aromatic sulphonic acid compounds can be employed in amounts ranging from 0.5 to 25 grams per liter of bath solution.

For the purpose of giving those skilled in the art a better understanding of the invention, illustrative examples are given. In the examples, an aqueous acidic nickel-containing bath was made up with the specified components. Electrodeposition was carried out by passing electric current through an electric circuit comprising an anode and a sheet metal or rod cathode, both immersed in the bath. The baths were agitated, usually by a moving cathode. The examples utilizing the novel brighteners of the second class of this invention resulted in a nickel coating with favorable ductility and corrosion resistance properties. In the examples employing, additionally, a brightener of the first class, i.e., an aromatic sulphonic compound, the resulting sulphur-containing nickel coating also exhibited favorable stress-free properties. In the example including a bath to provide a bright nickel coating over the novel nickel coating resulting from use of the novel brighteners of the second class of this invention, a composite coating was produced which resulted in wholly electrochemical corrosion resistance in severe industrial atmospheres.

In the examples, the following standard Watts-type bath was used as a base solution:

|                       |                          |         |
|-----------------------|--------------------------|---------|
| Nickel sulfate        | g./l.                    | 300     |
| Nickel chloride       | g./l.                    | 60      |
| Boric acid            | g./l.                    | 40      |
| Sodium lauryl sulfate | g./l.                    | 0.2-0.5 |
| pH                    |                          | 3.0-5.0 |
| Temperature           | ° C                      | 40-65   |
| Current density       | amperes/dm. <sup>2</sup> | 1-10    |

#### Example 1

Propargyl-hydroxy-ammonium bromide mmol/l. 0.2

#### Example 2

Propargyl-hydroxy-ammonium bromide mmol/l. 0.5  
Sodium salt of naphthalene trisulphonic acid g./l. 10

#### Example 3

Propargyl-dihydroxy-ammonium bromide mmol/l. 0.5  
Sodium salt of naphthalene trisulphonic acid g./l. 10  
Sodium saccharate g./l. 0.5

#### Example 4

1-hydroxy-2-butyne-N-hydroxy ammonium chloride mmol/l. 0.2  
Sodium salt of naphthalene trisulphonic acid g./l. 10

#### Example 5

1-hydroxy-2-butyne-N-hydroxy ammonium chloride mmol/l. 0.5  
Sodium salt of naphthalene trisulphonic acid g./l. 10

#### Example 6

1-hydroxy-2-butyne-N-dihydroxy ammonium chloride mmol/l. 0.2

#### Example 7

2-butyne, 1,4-N-hydroxy ammonium chloride mmol/l. 0.5  
Sodium salt of naphthalene trisulphonic acid g./l. 10

#### Example 8

4-nonyne, 1,9-N-dihydroxy ammonium chloride mmol/l. 0.5

#### Example 9

Propargyl dihydroxy ammonium chloride mmol/l. 0.5  
Sodium salt of naphthalene trisulphonic acid g./l. 10

#### Example 10

3-heptyne, 1,7-N-hydroxy ammonium chloride mmol/l. 10  
Sodium salt of naphthalene trisulphonic acid g./l. 25

#### Example 11

Propargyl dihydroxy ammonium hydroxide mmol/l. 0.1  
Sodium salt of naphthalene trisulphonic acid g./l. 0.5

#### Example 12

##### [BI-NICKEL PLATE]

Lower plate: Propargyl hydroxy ammonium bromide mmol/l. 0.5  
Upper plate: Same basic bath as for lower plate except that 2 grams per liter of one or more of the following brighteners of the first class: p-toluene sulfonamide, o-benzoyl sulfimide, benzene sulfonamide, naphthalene sulphonic acid, benzene sulphonic acid together with 0.001 g./l of a brightener of the second class such as propargylaminoethylene imidazol are dissolved in the bath.

#### Example 13

##### [BI-NICKEL PLATE]

Lower plate: Propargyl dihydroxy ammonium bromide mmol/l. 10  
Sodium salt of naphthalene trisulphonic acid g./l. 10  
Sodium saccharate g./l. 0.5  
Upper plate: Same basic bath as for lower plate except that 10 grams per liter of one or more of the following brighteners of the first class: p-toluene sulfonamide, o-benzoyl sulfide, benzene sulfonamide, naphthalene sulphonic acid and benzene sulphonic acid together with 0.001 g./l of a brightener of the second class such as 3-propynyl imidazol are dissolved in the bath.

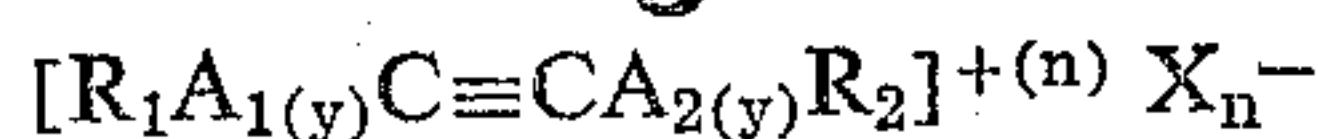
Unless otherwise specified all parts and percentages in the specification and claims are by weight. The foregoing examples illustrate specific baths and processes, several being preferred. It is to be understood that the compositions and conditions can be varied. Therefore as many embodiments of this invention may be made without departing from the spirit and scope thereof and the invention includes all such modifications and variations as come within the scope of the appended claims.

What is claimed is:

1. An aqueous acid bath solution for electroplating nickel containing at least one nickel salt as a source of nickel which plating solution includes a brightener of the second class having the structural formula



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in which  $A_1$  and  $A_2$  are selected from the group consisting of lower alkyl radicals and  $y$  is equal to 0 to 1;  $R_1$  and  $R_2$  are selected from the group consisting of H, OH,  $NH_2OH$ ,  $NH(OH)_2$ ;  $X$  is selected from the group consisting of halogen and OH and  $n$  is an integer equal to the number of quaternary N atoms in  $R_1$  and  $R_2$  with the proviso that at least one of  $R_1$  and  $R_2$  contains a quaternary N atom.

2. A nickel plating solution as defined in claim 1 wherein the amount of brightener of the second class ranges from 0.1 to 10 mmols. per liter of solution.

3. The nickel plating solution of claim 1 wherein the brightener of the second class is propargyl hydroxy ammonium bromide.

4. The nickel plating solution of claim 1 wherein the brightener of the second class is propargyl dihydroxy ammonium bromide.

5. The nickel plating solution of claim 1 wherein the brightener of the second class is 1-hydroxy-2-butyne-N-hydroxy ammonium chloride.

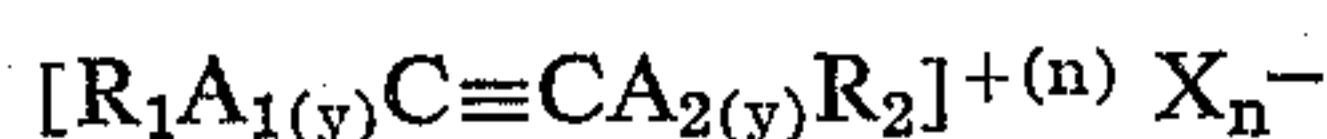
6. The nickel plating solution of claim 1 wherein the brightener of the second class is 1-hydroxy-2-butyne-N-dihydroxy ammonium chloride.

7. The nickel plating solution of claim 1 wherein the brightener of the second class is 2-butyne, 1,4-N-hydroxy ammonium chloride.

8. A nickel plating solution as defined in claim 1 which further includes an aromatic sulfonic acid compound in amounts sufficient to provide stress-free properties to the electroplated nickel.

9. The nickel plating solution of claim 8 wherein the aromatic sulphonic acid compound is the sodium salt of naphthalene trisulphonic acid.

10. An aqueous acid bath solution for electroplating nickel containing at least one nickel salt as a source of nickel, which plating solution includes a brightener of the second class having the structural formula:

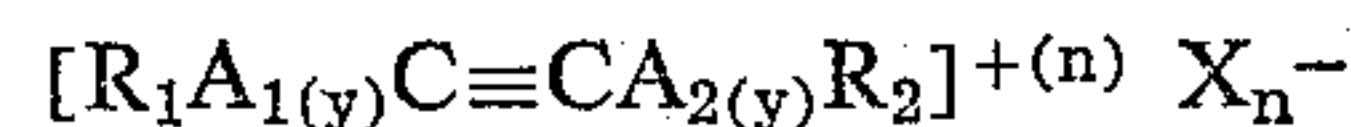


in which  $A_1$  and  $A_2$  are selected from the group consisting of lower alkyl radicals and  $y$  is equal to 0 to 1;  $R_1$  and  $R_2$  are selected from the group consisting of H, OH,  $NH_2OH$ ,  $NH(OH)_2$ ;  $X$  is selected from the group consisting of halogen and OH and  $n$  is an integer equal to the number of quaternary N atoms in  $R_1$  and  $R_2$  with the proviso that at least one of  $R_1$  and  $R_2$  contains a quaternary N atom, said brightener of the second class being present in amounts from 0.1 to 10 mmols. per liter of solution and an aromatic sulfonic acid compound in amounts of 0.5 to 25 grams per liter of said solution.

11. The process of producing nickel deposits of improved ductility and corrosion resistance characteristics

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on a metal base, which comprises electrodepositing nickel from an aqueous acid bath containing nickel mainly in the form of a soluble inorganic salt, in the presence of a brightener of the second class having the structural formula

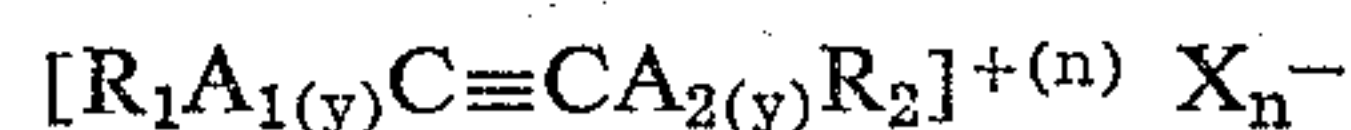


in which  $A_1$  and  $A_2$  are selected from the group consisting of lower alkyl radicals and  $y$  is equal to 0 to 1;  $R_1$  and  $R_2$  are selected from the group consisting of H, OH,  $NH_2OH$ ,  $NH(OH)_2$ ;  $X$  is selected from the group consisting of halogen and OH and  $n$  is an integer equal to the number of quaternary N atoms in  $R_1$  and  $R_2$  with the proviso that at least one of  $R_1$  and  $R_2$  contains a quaternary N atom.

12. The process of producing nickel deposits as defined in claim 11 wherein the brightener of the second class is present in amounts ranging from 0.1 to 10 mmols. per liter of solution.

13. The process of producing nickel deposits as defined in claim 11 wherein said bath further includes an aromatic sulphonic acid compound in amounts sufficient to provide stress-free properties to the nickel deposits.

14. The process of producing nickel deposits of improved ductility and corrosion resistance characteristics on a metal base, which comprises electroplating nickel from an aqueous acid bath containing nickel mainly in the form of a soluble inorganic salt, in the presence of a brightener of the second class having the formula



in which  $A_1$  and  $A_2$  are selected from the group consisting of lower alkyl radicals and  $y$  is equal to 0 to 1;  $R_1$  and  $R_2$  are selected from the group consisting of H, OH,  $NH_2OH$ ,  $NH(OH)_2$ ;  $X$  is selected from the group consisting of halogen and OH and  $n$  is an integer equal to the number of quaternary N atoms in  $R_1$  and  $R_2$  with the proviso that at least one of  $R_1$  and  $R_2$  contains a quaternary N atom, said brightener of the second class being present in amounts from 0.1 to 10 mmols. per liter of solution and an aromatic sulphonic acid compound in amounts of 0.5 to 25 grams per liter of solution.

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