

[54] COMPOSITION OF ELECTROPLATING
BATH FOR THE ELECTRODEPOSITION OF
BRIGHT NICKEL

[75] Inventors: William E. Rosenberg, Strongsville;
William J. Saas, Fairview Park, both
of Ohio

[73] Assignee: R. O. Hull & Company, Inc.,
Cleveland, Ohio

[22] Filed: Apr. 26, 1974

[21] Appl. No.: 464,558

[52] U.S. Cl. 204/49

[51] Int. Cl. C23b 5/08, C23b 5/46

[58] Field of Search 204/49, 43 T, 43 N, 43 P,
204/44; 106/1; 117/130 E

[56] References Cited

UNITED STATES PATENTS

2,876,177	3/1959	Gundel et al.	204/49
3,314,868	4/1967	Willmund et al.	204/49
3,366,557	1/1968	Foulke et al.	204/49
3,711,384	1/1973	Lyde	204/49

Primary Examiner—G. L. Kaplan

Attorney, Agent, or Firm—Oldham & Oldham Co.

[57] ABSTRACT

An aqueous, acid electroplating bath which contains as brightening agents the synergistic combination of N-(3-sulfopropyl) pyridinium inner salt and an acetylenic alcohol-ethylene oxide adduct.

8 Claims, No Drawings

COMPOSITION OF ELECTROPLATING BATH FOR THE ELECTRODEPOSITION OF BRIGHT NICKEL

BACKGROUND OF THE INVENTION

This invention relates to an aqueous acid electroplating bath for producing extremely bright, level electrodeposits of nickel. The use of N-(3-sulfopropyl) pyridinium inner salts as a bath additive is disclosed in U.S. Pat. No. 2,876,177. It is used alone or in combination with diarylsulfimides. The deposits obtained using a bath containing this combination or the pyridinium inner salt alone are level but only semibright. However, the deposit is somewhat brittle and if more brightener is added to achieve a higher degree of brightness and leveling, the brittleness increases and there is a definite darkening of the plate in low current density areas. Such brittleness and plate discoloration is totally unacceptable for suitable plating.

The use of acetylenic alcohol-ethylene oxide adducts is also known in the electroplating industry and is disclosed in U.S. Pat. No. 3,140,988. They are used alone and in combination with allyl sulfonic acid, and aryl sulfonic amides and acids. U.S. Pat. No. 3,366,557 discloses similar combinations and U.S. Pat. No. 3,111,466 discloses the combination of coumarin and ethylene oxide adducts of acetylenic alcohols.

However, in all three of these disclosures utilizing the acetylenic alcohol adducts at best only semibright and moderately level electrodeposits are obtained. Moreover, it has been found that by excessively increasing the concentration of the brighteners in the electroplating baths, electrodeposits exhibiting extremely high brightness and leveling cannot be obtained.

These brightening systems, therefore are limited in at least the following aspects:

1. The system using the pyridinium inner salt is limited in that increasing the concentration to achieve extremely high luster and leveling produces unacceptable, brittle and dark electrodeposits; and
2. The systems using the acetylenic alcohol adducts cannot produce electrodeposits of extremely high brightness and leveling even at very high concentrations in the electroplating bath.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the invention to provide brightening agents which produce extremely bright, level and ductile electrodeposits of nickel.

It is another object of the present invention to produce an extremely bright electrodeposit of nickel, as above, through the synergistic combination of two groups of compounds, even in low current density areas.

These and other objects of the present invention, together with the advantages thereof over existing prior art compounds and methods which will become apparent from the following specification are accomplished by the compounds and methods herein described and claimed.

In general, a plating bath for the electrodeposition of nickel, comprises, an aqueous acidic solution of at least one nickel salt and, as brightening agents, from 0.02 to about 0.5 grams/liter of N-(3-sulfopropyl) pyridinium inner salt and from 0.005 to about 0.2 grams/liter of an acetylenic alcohol-ethylene oxide adduct having the general formula

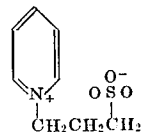


where R_1 is hydrogen, hydroxymethyl, and 2-hydroxyethoxymethyl and R_2 is 2-hydroxyethoxymethyl.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the concepts of the present invention, it has been found that the synergistic combination of an N-(3-sulfopropyl) pyridinium inner salt and an acetylenic alcohol-ethylene oxide adduct produces both extremely bright and level electrodeposits of nickel at very low concentrations in an aqueous acidic nickel plating bath. Additionally, the electrodeposit is extremely ductile. The effect is truly synergistic in that the results obtained with this combination far exceed those of using the two types of compounds separately and at brightener concentrations of only a small fraction of previously required amounts.

The pyridinium inner salt of the present invention has the following formula:



This specific salt is generally not commercially available but may be readily synthesized by the condensation of pyridine and propane sultone.

The acetylenic alcohol-ethylene oxide adducts of the present invention are available in commerce and have the following general formula:



where R_1 is hydrogen, hydroxymethyl, and 2-hydroxyethoxymethyl, and R_2 is 2-hydroxyethoxymethyl. The chemical structures of these compounds are set forth in Table I.

TABLE I

1. $HOCH_2CH_2OCH_2C \equiv CCH_2OH$
2. $HOCH_2CH_2OCH_2C \equiv CH$
3. $HOCH_2CH_2OCH_2C \equiv CCH_2OCH_2CH_2OH$

The brighteners of this invention can readily be used in conjunction with other known conventional brighteners in generally small or conventional amounts such as allyl sulfonic acid, aromatic sulfonic acids, and aromatic sulfonamides and sulfonimides; specific examples include saccharin, dibenzenesulfonimide and naphthalene trisulfonic acid.

The pyridinium inner salt and acetylenic alcohol-ethylene oxide adducts of this invention are generally added as aqueous solutions, but they can be added in concentrated form or dissolved in another suitable solvent such as methanol or ethanol. A general range extends from 0.02 to about 0.5 grams/liter of plating bath for the pyridinium inner salt and from 0.005 to about 0.20 grams/liter of the plating bath for the acetylenic alcohol-ethylene oxide adduct. More specifically, the preferred concentrations are about 0.05 to about 0.3 gms with roughly 0.18 gms being an optimum amount of the pyridinium inner salt and about 0.01 to about 0.10 gms with roughly 0.03 gms being an optimum amount of the acetylenic alcohol-ethylene oxide adduct per liter of bath.

The brighteners of the present invention can be added to any contentional aqueous acidic plating bath for the electrodeposition of nickel well known to those skilled in the art. Of course, the bath contains at least one nickel salt such as any conventional nickel salt. Specific typical examples include nickel sulfate and nickel chloride. The bath solution temperature for electrodeposition may be any conventional temperature such as from about 120°F to about 1160°F. The amount of time will, of course, vary depending upon

—Continued

pH = 4.2
Temperature = 140°F.

Table I shows the tests that were run in this bath under the above mentioned conditions to demonstrate the unique synergism between the N-(3-sulfopropyl) pyridinium inner salt and the ethylene oxide adducts of the acetylenic alcohols.

TABLE II

Test	Brighteners Used*	Concentration in g/l	Results
1	HC ≡ CCH ₂ OCH ₂ CH ₂ OH	0.03	Very dull deposit
2	HC ≡ CCH ₂ OCH ₂ CH ₂ OH	0.15	Very dull deposit
3	HOCH ₂ CH ₂ OCH ₂ C ≡ CCH ₂ OCH ₂ C-H ₂ OH	0.03	Very dull deposit
4	HOCH ₂ CH ₂ OCH ₂ C ≡ CCH ₂ OCH ₂ C-H ₂ OH	0.15	Very dull deposit
5	N-(3-sulfopropyl) pyridinium inner salt	0.06	Very dull deposit
6	N-(3-sulfopropyl) pyridinium inner salt	0.18	Semibright and cloudy deposit
7	N-(3-sulfopropyl) pyridinium inner salt	0.48	Semibright but brittle deposit and dark in low current density
8	HC ≡ CCH ₂ OCH ₂ CH ₂ OH	0.03	Semibright, very little leveling
9	Soluble saccharin	3	Semibright, very little leveling
10	HOCH ₂ CH ₂ OCH ₂ C ≡ C-H ₂ OCH ₂ CH ₂ OH	0.03	little leveling
11	Soluble saccharin	3	Semibright, very little leveling
12	HC ≡ CCH ₂ OCH ₂ CH ₂ OH	0.03	Extremely bright, excellent leveling, and bright in low and bright in low current density
13	N-(3-sulfopropyl) pyridinium inner salt	0.18	Extremely bright, excellent leveling, and bright in low current density
14	HOCH ₂ CH ₂ OCH ₂ C ≡ CCH ₂ OCH ₂ C-H ₂ OH	0.03	Extremely bright, excellent leveling, and bright in low current density
	N-(3-sulfopropyl) pyridinium inner salt	0.18	Extremely bright, excellent leveling, and bright in low current density
	Soluble saccharin	3	Extremely bright, excellent leveling, and bright in low current density

* Note: All test baths contained 0.3 g Sodium Lauryl Sulfate/liter to prevent gas streaking and pitting. Generally, any suitable surfactant may be used. A suitable surfactant is one that prevents gas streaking and pitting but does not interfere with brightness of the electrodeposit.

various factors such as the current density and desired depth or amount of nickel deposit or plating.

All testing was done in a liter cell using mechanical agitation, nickel anodes, and uniformly etched brass panels as cathodes. The average current density applied to the cathode was 20 amperes per square foot and the plating time was 20 minutes in all tests.

The panels were compared and evaluated with regard to brightness and amount of leveling achieved.

The plating bath used was a standard Watts bath as described in the following examples.

EXAMPLE I PLATING BATH USED

INGREDIENT	CONCENTRATION
Nickel Sulfate	36 oz./gal
Nickel Chloride	10 oz./gal
Boric Acid	6.5 oz./gal

As can be seen from the results of Table II, the ethylene oxide adducts of acetylenic alcohols and N-(3-sulfopropyl) pyridinium inner salt act synergistically when both are added to an aqueous acid nickel electroplating bath to produce extremely bright, level electrodeposits of nickel. When these compounds are added separately, even in large amounts, only semi-bright, cloudy, and in some cases brittle deposits result.

Having thus described this invention in such full, clear, concise and exact terms as to enable any person skilled in the art to which it pertains to make and use the same, and having set forth the best mode contemplated of carrying out this invention in accordance with the Patent Statutes, the subject matter which is regarded as being our invention is particularly pointed out and distinctly claimed in what is claimed, it being understood that equivalents or substitutions for, parts of the above specifically described embodiment of the

invention may be made without departing from the scope and concepts of the invention as set forth in what is claimed.

What is claimed is:

1. A plating bath for the electrodeposition of nickel comprising, an aqueous acidic solution of at least one nickel salt and, as brightening agents, from 0.02 to about 0.5g/l of N-(3-sulfopropyl) inner salt and from 0.005 to about 0.02g/l of an acetylenic alcohol-ethylene oxide adduct of the general formula



where R_1 is hydrogen, hydroxymethyl, or 2-hydroxyethoxymethyl, and R_2 is 2-hydroxyethoxymethyl.

2. A plating bath according to claim 1 including a suitable surfactant in an amount sufficient to prevent gas streaking and pitting.

3. A plating bath according to claim 2, including at least one compound selected from the group consisting of allyl sulfonic acids, aromatic sulfonic acids, aromatic sulfonamides and aromatic sulfonimides in an amount sufficient to further enhance the nickel deposit bright-

ness.

4. A plating bath according to claim 2, wherein there is also present saccharin in an amount sufficient to prevent gas streaking and pitting.

5. A plating bath according to claim 2, wherein there is also present dibenzenesulfonimide in an amount sufficient to prevent gas streaking and pitting.

6. A plating bath according to claim 2, wherein there is present naphthalene trisulfonic acid in an amount sufficient to prevent gas streaking and pitting.

7. A plating bath according to claim 1, wherein the amount of said N-(3-sulfopropyl) pyridinium inner salt ranges from about 0.05 to about 0.3g/l and the amount of said acetylenic alcohol-ethylene oxide adduct ranges from about 0.01 to about 0.1g/l.

8. A plating bath according to claim 1, wherein the amount of said N-(3-sulfopropyl) pyridinium inner salt is approximately 0.18g/l and the amount of said acetylenic alcohol-ethylene oxide adduct is approximately 0.03g/l.

* * * * *

25

30

35

40

45

50

55

60

65

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,862,019 Dated January 21, 1975

Inventor(s) William E. Rosenberg and William J. Saas

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 9 delete "0.02" and, in its place, insert --0.2--.

Signed and Sealed this

Tenth Day of September 1985

[SEAL]

Attest:

DONALD J. QUIGG

Attesting Officer Acting Commissioner of Patents and Trademarks - Designate

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,862,019
DATED : January 21, 1975
INVENTOR(S) : William E. Rosenberg and William J. Saas

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 8, after "N-(3-sulfopropyl)" insert
-- pyridinium --.

Signed and Sealed this

second Day of December 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks