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(54) **Bright nickel plating bath and process and composition therefor.**

(57) Plating defects may occur during the electrodeposition of nickel using compositions containing primary and secondary brighteners.

According to the invention such defects are avoided by including 0.01 to 1 g/l of a sulfonated acetylenic compound or a salt of such a compound in an aqueous acidic nickel plating bath containing 0.2 to 10 g/l of saccharin, and 20 to 500 parts per million of Zn ions. The acetylenic bond and the sulfonate radical of the sulfonated acetylenic compound are connected by a carbon chain of at least one carbon atom and not more than 6 carbon atoms.

The invention relates to the composition of such a bath, to the method of bright nickel plating using such a bath and to compositions for forming the bath.

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"BRIGHT NICKEL PLATING BATH AND PROCESS AND COMPOSITION THEREFOR"

This invention relates to improved processes and compositions for the electrodeposition of nickel and alloys thereof.

It has been found that the presence of zinc impurities tends to produce plating defects during the electrodeposition of nickel electroplates using compositions containing primary and secondary brighteners. The problem is especially acute during plating when the secondary brightener is saccharin (o-benzoyl sulfimide). In this case inadequate basis metal coverage may occur in low current density areas; unsightly striated (ribbed) deposits may occur; and dark, thin non-metallic appearing deposits may be produced which not only detract from the final appearance of the article being plated, but may also interfere with the receptivity, appearance, luster, etc. of subsequent deposits such as chromium plate.

In order to overcome the deleterious effects of zinc in the presence of saccharin, the use of sulfinic acids or hydroxy-sulfonates has been used.

While these compounds do reduce the problem, their use also reduces the overall brightness and levelling of the deposit. This results in having to use thicker nickel deposits or higher levels of the primary additives in order to obtain commercially acceptable deposits.

An alternative approach has been to replace saccharin with another Class I additive, i.e., sodium benzene sulfonamide, sodium toluene sulfonate. These Class I additives while not as sensitive to zinc impurities as is saccharin, are inferior to saccharin with respect to stress reduction, luster building (in cooperation with Class II additives), sulfur contribution (especially important in duplex plating).

It is an object of this invention to provide processes and compositions for depositing electrodeposits of nickel in the presence of saccharin and zinc impurities. It is also an object of this invention to accomplish this without affecting the brightness or levelling of the deposit.

In accordance with certain of its aspects, this invention relates to an improved process and composition for the preparation of nickel or nickel alloy electrodeposits which comprises passing current from an anode to a cathode through an aqueous acidic electroplating solution containing:

(1) at least one nickel compound

(2) saccharin

(3) zinc ions

the improvement comprising the presence of a sulfonated acetylenic compound or salts thereof, where the acetylenic bond and the sulfonate radical are connected by a carbon chain of at least one carbon atom and not more than 6 carbon atoms.

The concentrations of said compounds are

(1) saccharin - 0.2-10 g/l
(2) zinc ions - 20-500 ppm
(3) sulfonated acetylenics or salts thereof - 0.01-1.0 g/l

with a preferred range of

(1) saccharin - 0.5-4.0 g/l
(2) zinc - 20-150 ppm
(3) sulfonated acetylenics or salts thereof - .2 g/l

Examples of sulfonated acetylenics of this invention, but not restricted thereto, are

2-butyne-1,4-disulfonic acid
2-butyne sulfonic acid
propyne sulfonic acid
1-butyne sulfonic acid
1-pentyne sulfonic acid

The baths of this invention may also contain an effective amount of at least one member selected from the group consisting of:

(a) other Class I brighteners in addition to saccharin
(b) Class II brighteners
(c) anti-pitting or wetting agents.

The term "Class I brighteners" as used herein, and as described in <u>Modern Electroplating</u>, Third Edition, F. Lowenheim, Editor, is meant to include aromatic sulfonates, sulfonamides, sulfonimides, etc., as well as aliphatic or aromatic-aliphatic olefinically unsaturated sulfonates, sulfonamides, sulfonimides, etc. Specific examples of such plating additives are:

(1) disodium 1,5-naphthalene disulfonate
(2) trisodium 1,3,6-naphthalene trisulfonate
(3) sodium benzene monosulfonate
(4) dibenzene sulfonimide
(5) sodium 3-chloro-2-butene-1-sulfonate
(6) sodium β-styrene sulfonate
(7) sodium allyl sulfonate
(8) monoallyl sulfamide
(9) diallyl sulfamide
(10) allyl sulfonamide

Such plating additive compounds, which may be used singly or in suitable combinations, are desirably employed in amounts ranging from about 0.5 to 10 grams per liter and provide the advantages described in the above reference and which are well known to those skilled in the art of nickel electroplating.

The term "Class II brighteners" as used herein, and as described in Modern Electroplating, Third Edition, F. Lowenheim, Editor, is meant to include plating additive compounds such as reaction products of epoxides with alpha-hydroxy acetylenic alcohols such as diethoxylated 2-butyne-1,4-diol, N-heterocyclics, dye-stuffs, acetylenic amines, etc.

Specific examples of such plating additives are:

(1) 1,4-di-(β-hydroxyethoxy)-2-butyne
(2) 1,4-di-(β-hydroxy-γ-chloropropoxy)-2-butyne
(3) 1,4-di-(β-,γ-epoxypropoxy)-2-butyne

(4) 1,4-di-(β-hydroxy-γ-butenoxy)-2-butyne
(5) 1,4-di(2'-hydroxy-4'-oxa-6'-heptenoxy)-2-butyne
(6) N-(2,3-dichloro-2-propenyl)-pyridinium chloride
(7) 2,4,6-trimethyl N-propargyl pyridinium bromide
(8) N-allylquinaldinium bromide
(9) 2-butyne-1,4-diol
(10) propargyl alcohol
(11) 2-methyl-3-butyn-2-ol
(12) quinaldyl-N-propanesulfonic acid betaine
(13) butynoxy ethane sulfonic acids
(14) propynoxy ethane sulfonic acids
(15) quinaldine dimethyl sulfate
(16) N-allylpyridinium bromide
(17) isoquinaldyl-N-propanesulfonic acid betaine
(18) isoquinaldine dimethyl sulfate
(19) N-allylisoquinaldine bromide
(20) 1,4-di-(β-sulfoethoxy)-2-butyne
(21) 3-(β-hydroxyethoxy)-propyne
(22) 3-(β-hydroxypropoxy)-propyne
(23) 3-(β-sulfoethoxy)-propyne
(24) phenosafranin
(25) fuchsin
(26) propargyl amine
(27) 1-diethylamino-2-propyne
(28) 5-dimethylamino-2-methyl-3-pentyn-2- ol
(29) 1-dimethylamino-2-pentyne
(30) 1-dimethylamino-2-butyne

When used alone or in combination, desirably in amounts ranging from about 5 to 1000 milligrams per liter, a Class II brightener may produce no visual effect on the electrodeposit, or may produce semi-lustrous, fine-grained deposits. However, best results are obtained when Class II brighteners are used with one or more Class I brighteners in order to provide optimum deposit luster, rate of brightening, leveling, bright plate current density range, low current density coverage, etc.

The term "anti-pitting or wetting agents" as used herein is meant to include a material which functions to prevent or minimize gas pitting. An anti-pitting agent, when used alone or in combination, desirably in amounts ranging from about 0.05 to 1 gram per liter, may also function to make the baths more compatible with contaminants, such as oil, grease, etc. by their emulsifying, dispersing, solubilizing, etc. action on such contaminants and thereby promote attaining of sounder deposits. Preferred anti-pitting agents may include sodium lauryl sulfate, sodium lauryl ether-sulfate and sodium dialkylsulfosuccinates.

The nickel compounds employed for electrodepositing nickel are typically added as the sulfate, chloride, sulfamate, or fluoborate salts. The sulfate, chloride, sulfamate and fluoborate salts of nickel are employed in concentrations sufficient to provide nickel in the electroplating solutions of this invention in concentrations ranging from about 10 to 150 grams per liter.

The nickel electroplating baths of this invention additionally may contain from about 30 to 60 grams per liter, preferably about 45 grams per liter of boric acid or other buffering agents to control the pH (e.g.; from about 3.0-5.0, preferably 4.0) and to prevent high current density burning.

In order to prevent "burning" of high current density areas, and provide for more even temperature control of the solution, solution agitation may be employed. Air agitation, mechanical stirring, pumping, cathode rod and other means of solution agitation are all satisfactory. Additionally, the solutions may be operated without agitation.

The operating temperature of the electroplating baths of this invention may range from about 40°C to about 70°C, preferably from about 50°C to 62°C.

The average cathode current density may range from about 0.5 to 12 amperes per square decimeter, with 3 to 6 amperes per square decimeter providing an optimum range.

Typical aqueous nickel-containing electroplating solutions (which may be used in combination with effective amounts of cooperating additives) include the following wherein all concentrations are in grams per liter (g/l) unless otherwise indicated.

TABLE I

Aqueous Nickel-Containing Electroplating Solutions

Component	Minimum	Maximum	Preferred
$NiSO_4 \cdot 6H_2O$	75 g/l	500 g/l	300 g/l
$NiCl_2 \cdot 6H_2O$	20 g/l	135 g/l	60 g/l
H_3BO_3	30 g/l	60 g/l	45 g/l
pH (electrometric)	3.0	5/0	4.0

During bath operation, the pH may normally tend to rise and may be adjusted with acids such as hydrochloric acid, sulfuric acid, etc.

Anodes used in the above baths may be electrolytic or sulfur containing nickel bars, strips or small chunks in titanium baskets. All anodes are usually suitably covered with cloth or plastic bags of desired porosity to minimize introduction into the bath of metal particles, anode slime, etc. which may migrate to the cathode either mechanically or electrophoretically to give roughness in cathode deposits.

The substrates on which the nickel electrodeposits of this invention may be applied may be metal or metal alloys such as are commonly electrodeposited and used in the art of electroplating such as nickel, cobalt, nickel-cobalt, copper, tin, brass, etc. Other typical substrate basis metals from which articles to be plated are manufactured may include ferrous metals such as iron, steel, alloy steels, copper, tin and alloys thereof such as with lead, alloys of copper such as brass, bronze, etc., zinc, particularly in the form of zinc-base die castings; all of which may bear plates of other metals, such as copper, etc. Basis metal substrates may have a variety of surface finishes depending on the final appearance desired, which in turn depends on such factors as luster, brilliance, leveling, thickness, etc. of the nickel electroplate applied on such substrates.

It is in the electroplating of zinc base die castings that the application of this invention is very useful, as die castings fall into the electroplating solution and cause high levels of zinc impurities. These impurities in the presence of saccharin cause the unsightly electrodeposits mentioned previously and can result in high operating costs.

The addition or inclusion of specified amounts of a sulfonated acetylenic compound or salts thereof, where the acetylenic bond and the sulfonate radical are connected by a carbon chain where C=1-6, to an aqueous acidic nickel electroplating containing saccharin and zinc impurities, will result in a bright, well leveled deposit free from the previously mentioned defects.

The following examples are presented as an illustration to provide those skilled in the art of electroplating a better understanding of the various embodiments and aspects of this invention. These examples should not be construed as limiting the scope of the invention in any way.

		Panel #1	Panel #2	Panel #3
1.	$NiSO_4 \cdot 6H_2O$	300 g/l	300 g/l	300 g/l
2.	$NiCl_2 \cdot 6H_2O$	60 g/l	60 g/l	60 g/l
3.	H_3BO_3	45 g/l	45 g/l	45 g/l
4.	pH	4.0	4.0	4.0
5.	Temperature	60°C	60°C	60°C
6.	Saccharin	1.8 g/l	1.8 g/l	1.8 g/l
7.	Zinc Ion	100 ppm	100 ppm	50 ppm
8.	Sodium Salt of Propyne Sulfonic Acid	Nil	0.1 g/l	Nil
9.	Sodium Salt of 1-Butyne Sulfonic Acid	Nil	Nil	0.1 g/l
10.	Propargyl Alcohol	0.0075 g/l	0.0075 g/l	0.0075 g/l
11.	Diethoxylated 2-Butyne-1, 4-Diol	0.015 g/l	0.015 g/l	0.015 g/l
12.	2-Butyne-1,4-Diol	0.02 g/l	0.02 g/l	0.02 g/l

The conditions for plating the panels from the above aqueous nickel electroplating compositions were as follows:

A zinc coated steel test panel was stripped in 50% hydrochloric acid, rinsed and then scribed with a horizontal single pass of 4/0 grit emery polishing paper and another scribe in a similar manner with #2 grit emery polishing paper. The cleaned panel was then plated in a 267 ml Hull Cell using the aforementioned compositions for 10 minutes at 2 amps. cell current, using cathode rod agitation.

Observations

Panel 1 - Shows a bright, well leveled deposit, with low current density skip plate, severe darkness and striations.

Panel 2 - Shows a bright, well leveled deposit, free from defects, over the entire current density range.

Panel 3 - Shows a bright, well leveled deposit with only a very small amount of low current density darkness.

Although this invention has been illustrated by reference to specific embodiments, modifications thereof which are clearly within the scope of the invention will be apparent to those skilled in the art.

CLAIMS :

1. A process for the preparation of an electrodeposit which contains bright nickel which comprises passing current from an anode to a cathode through an aqueous acidic plating solution containing at least one nickel compound, 0.2 gram per liter to 10 grams per liter of saccharin, and 20 parts per million to 500 parts per million of zinc ions, characterised by the presence in the plating solution of 0.01 gram per liter to 1.0 gram per liter of at least one sulfonated acetylenic compound or salt thereof such that the acetylenic bond and the sulfonate radical are connected by a carbon chain of at least one and not more than six carbon atoms.

2. The process of Claim 1 wherein said sulfonated acetylenic compound is 2-butyne-1,4-disulfonic acid.

3. The process of Claim 1 wherein the sulfonated acetylenic compound is 2-butyne sulfonic acid.

4. The process of Claim 1 wherein said sulfonated acetylenic compound is propyne sulfonic acid.

5. The process of Claim 1 wherein said sulfonated acetylenic compound is 1-butyne sulfonic acid

6. The process of Claim 1 wherein said sulfonated acetylenic compound is 1-pentyne sulfonic acid.

7. An aqueous acidic electroplating solution containing at least one nickel compound providing nickel ions for electrodepositing nickel, 0.2 gram per liter to 10 grams per liter of saccharin, and 20 to 500 parts per million of zinc ions, characterised by the presence of 0.01 gram

per liter to 1.0 gram per liter of at least one sulfonated acetylenic compound or salt thereof such that the acetylenic bond and the sulfonate radical are connected by a carbon chain of at least one and not more than six carbon atoms.

8. The electroplating solution of Claim 7 wherein said sulfonated acetylenic compound is 2-butyne-1,4,di-sulfonic acid.

9. The electroplating solution of Claim 7 wherein said sulfonated acetylenic compound is 2-butyne sulfonic acid.

10. The electroplating solution of Claim 7 wherein said sulfonated acetylenic compound is propyne sulfonic acid.

11. The electroplating solution of Claim 7 wherein said sulfonated acetylenic compound is 1-butyne sulfonic acid.

12. The electroplating solution of Claim 7 wherein said sulfonated acetylenic compound is 1-pentyne sulfonic acid.

13. A mixture of compounds adapted to form the electroplating solution of any one of claims 7 to 12.

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EUROPEAN SEARCH REPORT

Application number
EP 80303183.0

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	DE - A1 - 2 654 040 (MC GEAN CHEMICAL CO) + Claims; pages 16-23 + --	1,7
	DE - A1 - 2 460 247 (E.I. DU PONT DE NEMOURS) + Claims + --	1,7
	GB - A - 1 456 583 (OXY METAL IND.) + Claims + --	1,7
	GB - A - 1 441 972 (OXY METAL IND.) + Page 6 + --	1,7
	US - A - 4 016 051 (GELDZAHLER) + Totality + --	1,7
	US - A - 3 884 773 (MERKER) + Totality + ----	1,7

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

C 25 D 3/12
C 25 D 3/16

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

C 25 D

CATEGORY OF CITED DOCUMENTS

- X: particularly relevant
- A: technological background
- O: non-written disclosure
- P: intermediate document
- T: theory or principle underlying the invention
- E: conflicting application
- D: document cited in the application
- L: citation for other reasons
- &: member of the same patent family, corresponding document

X	The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	11-11-1980	SLAMA

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