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2,737,484

BRIGHT NICKEL PLATING

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No Drawing. Application October 31, 1952,
Serial No. 318,069

13 Claims. (Cl. 204—49)

This invention relates to the electroplating of bright nickel and provides a bath for electroplating bright nickel having new and advantageous organic addition agents, functioning as brighteners, and also provides a process making use of such a bath.

Conventional baths and processes for electroplating bright nickel are described in "Principles of Electroplating and Electroforming," Blum and Hogaboom, pages 362 to 381, revised third edition, 1949, McGraw-Hill Book Co., Inc., New York; and in "Modern Electroplating," The Electrochemical Society, 1942, pages 235 to 274. The character, control, and operating conditions, including the concentration of the bath ingredients, pH, temperature, cathode current density, etc., of these conventional baths are generally applicable to the present invention. It may be stated, in this connection, that practically all baths for electroplating bright nickel contain nickel sulphate, a chloride, usually nickel chloride, and a buffering agent, usually boric acid. Such types of baths include the well-known Watts type of bath and the high chloride type of bath. Other baths may contain, 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.

Addition agents as brighteners in bright nickel plating baths may be generally divided into two separate classes on the basis of their function in making possible the obtaining of truly bright deposits. One class, which is herein designated "secondary" brighteners, increases the brightness of an ordinarily dull or matte deposit but not to a full or mirror bright stage, and it imparts a ductilizing effect when used in conjunction with the other class of addition agents, which is herein designated "primary" brighteners. The primary brighteners permit the obtaining of mirror bright deposits when used in conjunction with secondary brighteners.

According to the present invention, novel and improved primary brighteners are provided and comprise 2-mercapto-benzimidazole (hereinafter referred to as 2-mbi) and substituted derivatives of the same. Specific examples of such derivatives are 5-amino-2-mbi and 4-amino-2-mbi, wherein the amino group is substituted in the six-membered carbon or benzenoid ring of the 2-mbi; 1,3-(dihydroxymethyl)-2-mbi, wherein a hydroxymethyl group is attached to each nitrogen atom of the five-membered heterocyclic ring of the 2-mbi; 2-carboxymethylmercapto-benzimidazole, wherein the carboxymethyl group is substituted in the heterocyclic ring of the 2-mbi through the sulfur atom. Other derivatives comprise 2-mbi substituted in the 6-membered ring by a radical linked to the 2-mbi through a nitrogen atom, that is, amino and substituted amino radicals. The latter radicals include sulfanilamido, p-toluene sulfanilamido, and acylamido radicals; in the acylamido group the acyl moiety preferably has a small number of carbon atoms, say up to six to ten, for example acetamido, propionamido, butyramido, benzamido, etc. Specific examples of the last-

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mentioned group of derivatives are 6-sulfanilamido-2-mbi, 4-para-toluene sulfanilamido-2-mbi, 5-acetamido-2-mbi, 5-propionamido-2-mbi, 6-butyramido-2-mbi, 6-benzamido-2-mbi, and 4-amino-7-acetamido-2-mbi. Other substituting radicals for producing derivatives of 2-mbi are aliphatic groups connected to the 5-membered ring of 2-mbi through a carbon atom and containing oxygen and hydrogen atoms, for example: hydroxyalkyl or alkylol radicals like methylol (mentioned above), ethylol, and higher carbon atom radicals of this series, preferably having not more than six carbon atoms; and carboxyalkyl radicals like carboxymethyl (mentioned above), carboxyethyl, and radicals of this series having up to six carbon atoms. The position of the foregoing substituent radicals in the 2-mbi is variable, and more than one radical may be present. It may be noted that both the nitrogen and carbon atoms of these radicals, which atoms are connected directly to the 2-mbi, are non-metallic and have at least one hydrogen atom connected to them.

The secondary brighteners which can be used in conjunction with the above primary brighteners are substituted aromatic compounds in which the substituent comprises an $-SO_2$ containing moiety with the S atom linked to the aromatic moiety. These compounds have been designated aromatic sulfon-compounds, and they include naphthalene mono-, di-, or tri-sulfonates, a preferred class, either alone or in various mixtures. Sodium or other alkali metal salts of the foregoing compounds are also preferred, although the compounds are useful in their acid form. Derivatives of the foregoing compounds, for example the chlor- and alkoxy-substituted types, are suitable. Benzene sulfonic acids and toluene sulfonic acids, their salts and their halogenated derivatives, and benzene sulfonamides and toluene sulfonamides are other secondary brighteners. Still others are benzene sulfohydroxamic acid, o-benzoyl sulfimide (saccharin), and 6-chlorosaccharin. Concentrations of the secondary brighteners are usually in the range of 0.5–25 g./l. For example, naphthalene-1,5-disulfonate of sodium is useful at 5–10 g./l.; naphthalene-1,3,6-trisulfonate of sodium, a preferred brightener, is used at 10–25 g./l.; saccharin at about 1–2 g./l.; p-toluene sulfonamide at 1–2 g./l.; benzene sulfohydroxamic acid at 0.2–5 g./l.; sodium salt of o-sulfobenzaldehyde at 6 g./l. In general, mixtures of the foregoing compounds may be used, as well as the individual compounds.

Typical examples of baths and process conditions are:

Example 1

Nickel sulfate	-----g./l.	300
Nickel chloride	-----do	52
Boric acid	-----do	40
Naphthalene-1,3,6-trisulfonate of sodium	-----do	20
2-mercapto-benzimidazole	-----do	0.01
pH (electrometric)	-----	3.5
Temperature	-----° F.	130
Cathode current density	-----amps. per sq. ft.	30

Example 2

Nickel sulfate	-----g./l.	300
Nickel chloride	-----do	52
Boric acid	-----do	40
Naphthalene-1,3,6-trisulfonate of sodium	-----do	20
5-amino-2-mercapto-benzimidazole	-----do	0.01
pH (electrometric)	-----	3.5
Temperature	-----° F.	130
Cathode current density	-----amps. per sq. ft.	30

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Example 3

Nickel sulfate	g./l.	300
Nickel chloride	do	52
Boric acid	do	40
Naphthalene-1,5-disulfonate of sodium	do	7.5
1,3 - (dihydroxymethyl) - 2 - mercapto - benzimidazole	do	0.01
pH (electrometric)		3.5
Temperature	° F.	130
Cathode current density	amps. per sq. ft.	30

Example 4

Nickel sulfate	g./l.	240
Nickel chloride	do	90
Boric acid	do	40
Naphthalene-1,3,6-trisulfonate of sodium	do	20
2-carboxymethylmercapto-benzimidazole	do	0.01
pH (electrometric)		3.5
Temperature	° F.	130
Cathode current density	amps. per sq. ft.	30

Example 5

Nickel fluoborate	g./l.	210
Nickel chloride	do	45
Boric acid	do	40
Naphthalene-1,3,6-trisulfonate of sodium	do	10
5-amino-2-mbi	do	0.01
pH (electrometric)		3.5
Temperature	° F.	130
Cathode current density	amps. per sq. ft.	30

Cathode agitation may be practised, the degree thereof to be determined by the type of work being nickel plated and the operating current density range desired. Excellent results have been obtained without any solution or cathode agitation by suitably regulating the current density range and temperature as per usual practice.

The primary brighteners of this invention can be added directly to the nickel plating bath or, preferably, added in the form of a stock solution prepared by dissolving the solid compound in an alkaline or acid medium like dilute sodium hydroxide solution or dilute sulfuric acid.

The preferred concentration range of the primary brighteners in the nickel plating electrolyte is about 0.005 to 0.05 gram per liter, although useful results are obtainable in the range of 0.001 to 0.05 gram per liter. A particularly useful concentration is about 0.01 to 0.02 gram per liter, at which concentration excellent brightness and ductility of deposits are obtained over a variety of basis metal surfaces including steel, iron, copper, copper alloys such as brass and bronze, and other suitable metals. The concentration of the other constituents of the bath may be varied to meet special requirements, as is conventional.

It is to be understood in this connection that the conventional baths and operating conditions disclosed in the publications cited above are incorporated here by reference, so that additional descriptions of these baths and operating conditions are unnecessary. However, the composition and concentration of one widely used bath is one containing nickel sulfate, 200 to 300 g./l.; nickel chloride, 45 to 90 g./l.; and boric acid, 37 to 45 g./l.

The primary brighteners are resistant to chemical change and breakdown, such as may occur by virtue of oxidation or reduction reactions under bright nickel plating conditions. After prolonged tests, no evidence was found of the accumulation of harmful brightener decomposition products, and no dark film formation on the anodes was observed after either prolonged or intermittent plating runs. Rate of consumption of the brighteners was low and was generally better than in common proprietary processes. The brighteners are compatible with other classes of addition agents of the kind usually employed in bright nickel plating baths. Further, they have been found to render the bath electrolyte less sensitive in certain respects, that is to say, these brighteners have the effect of rendering the bath solution resistant to many or-

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ganic and metallic contaminants that are apt to be encountered.

In regard to the operation of plating baths containing the present primary brighteners, good levelling and smoothening action is possible, the degree of which is favorably influenced by the use of these brighteners. The cathode current density and the temperature may be varied widely while yet obtaining highly lustrous, mirror bright, deposits of nickel plate. Coverage at low current densities is exceptionally good; and sensitivity to current interruption is low. An unusually high rate of brightening, or increase of luster of the deposits with increase of thickness, is obtainable.

Advantages in the plated product following the use of the brighteners include the production of substantially pure, well adherent, coatings that are ductile and have low internal stress and that are not appreciably embrittled by being subjected to the usual plating conditions. The deposits do not require activation before chromium plating, and because of their outstanding brilliance they enable chromium plated articles of more than usual luster to be produced.

Although the invention has been illustrated by certain selected embodiments, it will be appreciated that these are illustrative and that the invention is capable of obvious variations.

In the light of the foregoing description, the following is claimed:

1. In an aqueous acidic bath solution for bright nickel plating containing at least one nickel salt as the source of the nickel and a substituted aromatic compound as a secondary brightener in which said substituent comprises an $-SO_2$ containing moiety with the S atom linked to the aromatic moiety, the combination therewith as a primary brightener of about 0.001 to about 0.05 g./l. of a compound selected from the class consisting of 2-mercapto-benzimidazole and 2-mercapto-benzimidazole substituted by a radical having a non-metallic atom which is directly connected to the mercapto compound and which is selected from the class consisting of nitrogen and carbon.

2. An aqueous bath solution according to claim 1 in which said primary brightener compound is 2-mercapto-benzimidazole.

3. An aqueous bath solution according to claim 1 in which said primary brightener compound is 2-mercapto-benzimidazole substituted by a radical having a non-metallic atom which is directly connected to the mercapto compound and which is selected from the class consisting of nitrogen and carbon.

4. An aqueous bath solution according to claim 1 in which said primary brightener compound is 2-mercapto-benzimidazole substituted by a radical which contains a nitrogen atom linked to said 2-mercapto-benzimidazole.

5. An aqueous bath solution according to claim 4 in which said radical is selected from the group consisting of amino and substituted amino radicals.

6. An aqueous bath solution according to claim 5 in which said radical is an amino radical.

7. An aqueous bath solution according to claim 5 in which said radical is a substituted amino radical.

8. An aqueous bath solution according to claim 1 in which said primary brightener compound is 2-mercapto-benzimidazole substituted by a radical which contains a carbon atom linked to said 2-mercapto-benzimidazole.

9. An aqueous bath solution according to claim 8 in which said radical is an aliphatic radical containing oxygen and hydrogen atoms.

10. An aqueous bath solution according to claim 9 in which said radical is a hydroxyalkyl radical.

11. An aqueous bath solution according to claim 9 in which said radical is a carboxyalkyl radical.

12. In an aqueous acidic bath solution for bright nickel plating containing at least one nickel salt as the source of the nickel and about 0.2 to 25 g./l. of a sulfonated aryl

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compound as a secondary brightener, the combination therewith as a primary brightener of about 0.001 to 0.05 g./l. of a compound selected from the class consisting of 2-mercapto-benzimidazole and 2-mercapto-benzimidazole substituted by a radical having a non-metallic atom which is directly connected to the mercapto compound and which is selected from the class consisting of nitrogen and carbon.

13. A process for electrodepositing bright nickel which comprises electrodepositing said nickel from an aqueous acidic solution containing at least one nickel salt as the source of the nickel, as a secondary brightener an aromatic compound substituted by an SO₂-containing moiety in which the S atom is linked to the aromatic moiety, and about 0.001 to about 0.05 g./l. of a compound selected

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from the class consisting of 2-mercapto-benzimidazole and 2-mercaptobenzimidazole substituted by a radical having a non-metallic atom which is directly connected to the mercapto compound and which is selected from the class consisting of nitrogen and carbon.

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