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ELECTRODEPOSITION OF STRESS-FREE METAL DEPOSITS

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ABSTRACT OF THE DISCLOSURE

Electroplating baths and processes for electrodeposition of stress-free nickel, cobalt, zinc or copper wherein the stress-reducing additive present in the bath is an alpha-keto carboxylic acid having 3 to 10 carbon atoms or the water soluble salts, esters or amides of said acid and said stress reducing additive is present in a concentration between about 0.25 g./l. and 15 g./l.

This invention relates to metal electroplating baths and to a process for the production of stress-free metal electrodeposits. More particularly it relates to additives that serve as stress-reducing agents in such baths.

Electroplating is widely used for the purpose of altering the surface characteristics of metals and nonmetals so as to provide improved appearance, ability to withstand chemical attack, and improved resistance to tarnish and corrosion or to alter dimensions. In addition it is also used for the direct electro-forming of articles which because of their intricate shapes or requirements for surface finish would be difficult or costly to produce by conventional metal working procedures.

A number of metals are deposited from electroplating baths in a condition of internal stress which may be either tensile (positive) stress or compressive (negative) stress. This condition may be evidenced, for example, by lack of adhesion or by the cracking or peeling of the metal electroplate. It is particularly disadvantageous in electroforming applications where the products formed may be warped or may have poor dimensional stability as the result of internal stress.

It is known that the amount of internal stress in an electroplate is dependent to a large degree upon such factors as the composition of the bath and its current density, acidity, and temperature and that the stress can be reduced to some extent by the choice of conditions under which the plating is carried out. In addition the presence in the bath of certain materials, for example, primary brighteners such as saccharin, is known to reduce stress in the electrodeposits. In some cases these additives reduce the stress from a high tensile stress to a low tensile stress; in others they reduce a tensile stress to a compressive stress. No agent has been previously reported that will reduce either tensile stress or compressive stress to zero and maintain it at zero over a wide range of acidity, current density, temperature, and concentration.

In accordance with the present invention, it has been found that metal electrodeposits having zero internal stress can be prepared by electrolyzing an aqueous solution of at least one water-soluble salt of the metal which contains a small amount of an α-keto acid having from 3 to 10 carbon atoms or a water-soluble salt, ester, or amide of said acid. These stress-reducing additives can be used in both electroplating baths that ordinarily produce positively-stressed metal deposits, such as Watts baths, and electroplating baths that ordinarily produce negatively-stressed metal deposits, such as zinc sulfate baths, to produce metal deposits that are stress-free over a wide range of acidity, current density, temperature, and concentration.

In addition to being free from internal stress, the metal

electrodeposits prepared in accordance with this invention are characterized by excellent hardness, ductility, adhesion, and corrosion resistance.

A wide variety of α-keto acids may be used as stress-reducing additives in the electroplating baths of this invention. These include both aliphatic and aromatic monocarboxylic and dicarboxylic acids having from 3 to 10 carbon atoms. Illustrative of these acids are pyruvic acid, α-ketobutyric acid, α-ketocaproic acid, α-ketocaprylic acid, α-ketopelargonic acid, α-ketocapric acid, ketomalonic acid, ketosuccinic acid, α-ketoglutaric acid, α-ketoadipic acid, and benzoylformic acid. Water-soluble salts, such as the alkali metal, ammonium, alkylamine, alkanolamine, and magnesium salts of these are fully equivalent to the acids as stress-reducing agents and may be used in their place in the various embodiments of the invention. Salts of the α-keto acids that have limited solubility in water, such as the cobalt and nickel salts, may be used in those baths that require only a small amount of the additive or in combination with the more soluble salts. Water-soluble esters and amides as well as those derivatives of the acids that are hydrolyzed during electrolysis to the α-keto acids or their water-soluble salts may also be used. These include the lower alkyl esters, the lower alkanol esters, lower glycol esters, the unsubstituted amides, and lower alkyl substituted amides, for example, the methyl, ethyl, propyl, butyl, hydroxyethyl, hydroxypropyl, ethylene glycol, and propylene glycol esters and the unsubstituted amide, N-methylamide, N,N-dimethylamide, and N,N-dipropylamide.

The stress-reducing additives disclosed herein may be used advantageously in conjunction with many types of acidic and alkaline electroplating baths and especially with electroplating baths for the production of electrodeposits of nickel, cobalt, iron, zinc, copper, cadmium, tin, chromium, and alloys or other mixtures of these metals. These include, for example, Watts baths, nickel sulfamate baths, nickel chloride baths, nickel fluoborate baths, nickel sulfate baths, copper sulfate baths, copper pyrophosphate baths, copper fluoborate baths, cobalt sulfate baths, cobalt sulfamate baths, zinc sulfate baths, chromic acid baths, and the like. They are of particular value in acidic baths since their use in these baths results in the formation of deposits having an excellent combination of mechanical properties that heretofore could be obtained only when alkaline baths were used.

Only relatively small amounts of the α-keto acids or their water-soluble salts, esters, or amides need be used in the electroplating bath since concentrations as low as 0.25 g. per liter have been found to reduce the internal stress of the metal electrodeposits to zero. In most cases approximately 0.5 g. to 10 g. per liter of the additive is used, with especially advantageous results being obtained from the use of 0.75 g. to 6 g. per liter. As much as 15 g. per liter or more of the α-keto compound can be used, but the use of these larger amounts brings about no particular advantage. The amount of the α-keto compound used in any case is largely dependent upon such factors as the type of electroplating bath being used and the molecular weight and water solubility of the additive.

While these additives will produce stress-free metal electrodeposits when used as the sole additives in electroplating baths, they may also be used in conjunction with brighteners, leveling agents, sequestering agents, inhibitors, wetting agents, conductivity-promoting salts, porosity-preventing agents, and other additives customarily used to improve metal electrodeposits.

The surface of the objects to be electroplated in accordance with the processes of this invention may be formed of any material upon which electroplates are ordinarily deposited. For example, it may be a metal, such as iron, steel, zinc, copper, aluminum, lead, or a metal

alloy or a non-metal, such as a synthetic resin, wax paper, cloth, wood, plaster, or glass.

The stress-reducing additives may be added to the electroplating bath in any convenient way. For example, the additive or an aqueous solution of the additive may be added directly to the electroplating bath all at once or continuously throughout the process. Alternatively, the additive may be combined with or incorporated in the metal that acts as the anode and gradually dissolved in the bath during the course of the electroplating process.

A preferred process according to this invention for producing stress-free electrodeposits of a metal selected from the group consisting of nickel, cobalt, iron, zinc, copper, cadmium, tin, chromium, and mixtures thereof comprises electrodepositing said metal from an electroplating bath comprising an aqueous solution of at least one water-soluble salt of the metal to be deposited and approximately 0.25 g. to 15 g. per liter of said bath of a stress-reducing additive which is an α-keto acid having from 3 to 10 carbon atoms or a water-soluble salt, ester, or amide of said acid.

Example 1

The use of the electroplating baths of this invention for the production of stress-free electrodeposits of various metals is shown in Table I. In each case a well-known type of electroplating bath was used with and without the stress-reducing additives in order to demonstrate the effect on the internal stress of the electrodeposit of the addition of a small amount of the additive.

In these tests as well as in those described in the other examples, internal stress was measured by means of the Brenner-Senderoff spiral contractometer. This instrument indicates stress by a change in the radius of curvature of a helix as the helix is electroplated. The stress in the deposit causes the helix to wind more tightly or to unwind depending on whether the deposit stress is compressive or tensile. The change in radius of curvature as indicated by the angular displacement of one end of the helix while the other end is held rigid is a measure of the internal stress of the deposit and can be converted into conventional stress units, such as pounds per square inch.

TABLE I

Ex. No.	Metal Deposited	Ingredients of Bath	Concentration, g./l.	pH	Temperature, ° F.	Cathode Current Density, amp/ft.²	Additive	Concentration, g./l.	Internal Stress, p.s.i.
1A-1	Nickel	$NiSO_4 \cdot 6H_2O$ $NiCl_2 \cdot 6H_2O$ Boric Acid	300 60 37.5	4.0	140	40	None	----------	21,300
1A-2				4.0	140	40	Pyruvic Acid	2.25	0
1B-1	Cobalt	$CoSO_4 \cdot 7H_2O$ $CoCl_2 \cdot 6H_2O$ Boric Acid	450 45 38	2.4	100	40	None	----------	92,200
1B-2				2.4	100	40	Pyruvic Acid	4.5	0
1-C	Copper	$CuSO_4 \cdot 5H_2O$ H_2SO_4	188 74	<0.5	100	100	None	----------	12,600
1C-2				<0.5	100	100	Pyruvic Acid	1.87	0
1D-1	Copper	$Cu_2P_2O_7 \cdot 3H_2O$ $K_4P_2O_7$ NH_4OH	94 337.5 4.7	8.7	138	40	None	----------	−4,000
1D-2				8.7	138	40	Sodium Pyruvate	1.25	0
1E-1	Zinc	$ZnSO_4 \cdot 7H_2O$ $(NH_4)_2SO_4$	350 30	3.9	120	100	None	----------	−2,300
1E-2				3.5	120	100	Pyruvic Acid	2.1	0
1E-3				3.9	120	100	Benzoylformic Acid	1.0	0

The following examples demonstrate the way in which this invention may be practiced. It is to be understood, however, that these examples are not to be construed as being limitative, but are furnished merely for the purpose of illustration.

Example 2

The effect of the use of the stress-reducing additives on various types of nickel electroplating baths is shown in Table II.

TABLE II

Ex. No.	Type of Bath	Ingredients of Bath	Concentration, g./l.	pH	Temperature, ° F.	Cathode Current Density	Additive	Concentration, g./l.	Internal Stress, p.s.i.
2A-1	Watts Bath	$NiSO_4 \cdot 6H_2O$ $NiCl_2 \cdot 6H_2O$ Boric Acid	300 60 37.5	4.0	140	40	None	----------	21,300
2A-2				4.0	140	40	Sodium Pyruvate	2.8	0
2A-3				4.0	140	40	Ammonium Pyruvate	2.0	0
2A-4				4.0	140	40	Magnesium Pyruvate	2.1	0
2A-5				4.0	140	40	Triethanolamine Pyruvate	6.0	0
2B-1	Sulfamate	$Ni(SO_3NH_2)_2$ Boric Acid	330 30	4.0	120	100	None	----------	7,200
2B-2				4.0	120	100	Sodium Pyruvate	1.9	0
2B-3				4.0	120	40	None	----------	3,000
2B-4				4.0	120	40	Sodium Pyruvate	0.94	0
2B-5				4.0	120	40	Sodium Pyruvate	1.9	0
2C-1	Chloride	$NiCl_2 \cdot 6H_2O$ Boric Acid	300 38	2.0	140	40	None	----------	64,200
2C-2				2.0	140	40	Pyruvic Acid	2.1	0
2D-1	Fluoborate	$Ni(BF_4)_2$ Boric Acid	300 30	1.8	120	40	None	----------	30,800
2D-2				1.8	120	40	Sodium Pyruvate	3.0	0

Example 3

Stress-reducing additives were used in Watts baths that contained sulfo-oxygen compounds as primary brighteners alone or in combination with a secondary luster-producing brightener. The composition of the baths and the operating conditions employed are given in Table III. From the data in this table it will be seen that the baths containing a stress-reducing additive produced bright or semi-bright stress-free nickel electrodeposits, whereas those that did not contain one of these additives produced deposits having high compressive stress.

TABLE IV

Ex. No.	pH	Temperature, ° F.	Cathode Current Density, amp/ft.²	Internal Stress, p.s.i.
4A	4.0	140	20	0
4B	4.0	140	80	0
4C	4.5	140	20	0
4D	4.5	140	40	0
4E	4.5	140	80	0
4F	3.0	140	40	0
4G	4.0	115	20	0
4H	4.0	115	40	0
4I	4.0	115	80	0
4J	4.5	115	20	0
4K	4.5	115	40	0
4L	4.5	115	80	0
4M	3.0	115	40	0
4N	3.0	115	80	0

TABLE III

Ex. No.	Type of Bath	Brightener	Concentration, g./l.	pH	Temperature, ° F.	Cathode Current Density	Additive	Concentration, g./l.	Internal Stress, p.s.i.
3A-1	Watts Bath [1] (Semi-bright)	Sodium salt of saccharin	1.9	4.0	140	40	None	----------	−14,000
3A-2				4.0	140	40	Sodium Pyruvate	4.7	0
3B-1	Watts Bath [1] (semi-bright)	Sodium salt of benzaldehyde-o-sulfonic acid	1.12	4.0	145	40	None	----------	−5,000
3B-2				4.0	145	40	Sodium Pyruvate	1.4	0
3C-1	Watts Bath [1] (semi-bright)	Sodium salt of benzaldehyde-o-sulfonic acid	2.25	4.0	145	40	None	----------	−9,800
3C-2				4.0	145	40	Sodium Pyruvate	1.4	0
3D-1	Watts Bath [1] (semi-bright)	Sodium salt of benzaldehyde-o-sulfonic acid	3.37	4.0	145	40	None	----------	−13,000
3D-2				4.0	145	40	Sodium Pyruvate	2.8	0
3E-1	Watts Bath [1] (semi-bright)	Sodium salt of naphthalene-1,3,6-trisulfonic acid	1.12	4.0	140	40	None	----------	−10,600
3E-2				4.0	140	40	Sodium Pyruvate	0.9	0
3F-1	Watts Bath [1] (Bright)	Sodium salt of saccharin Methyl butynol-ethylene oxide adduct	5.0 0.05	4.0	140	40	None	----------	−18,900
3F-2				4.0	140	40	Pyruvic Acid	0.97	0

[1] Ingredients of Watts bath are given in Table II.

Example 4

The effect of variations in the acidity, temperature, and cathode current density of a bright nickel Watts bath containing a stress-reducing additive on the internal stress of nickel deposits is shown in Table IV. The bath used in each case contained 300 g. of $NiSO_4 \cdot 6H_2O$, 60 g. of $NiCl_2 \cdot 6H_2O$, 37.5 g. of boric acid, 2.4 g. of the sodium salt of saccharin, 0.065 g. of methyl butynol-ethylene oxide adduct, and 0.75 g. of pyruvic acid per liter. From the data in this table it will be seen that bright stress-free nickel deposits were obtained over a wide range of operating conditions.

Example 5

The effect of the addition of various α-keto acids to a nickel sulfamate bath or to a bright nickel Watts bath on the internal stress of the nickel deposit is shown in Table V.

TABLE V

Ex. No.	Type of Bath	Ingredients of Bath	Concentration, g./l.	pH	Temperature, ° F.	Cathode Current Density	Additive	Concentration, g./l.	Internal Stress, p.s.i.
5A-1	Nickel Sulfamate	$Ni(SO_3NH_2)_2$ Boric Acid	330 30	4.0	120	40	None	--------	3,000
5A-2				4.0	120	40	α-Ketobutyric acid	1.0	0
5A-3				4.0	120	40	Sodium Ketomalonate	1.5	0
5A-4				3.1	120	40	2-Ketoglutaric acid	1.0	0
5A-5				3.1	120	40	α-Ketosuccinic acid	1.0	0
5A-6				3.1	120	40	α-Ketoadipic acid	1.0	0
5B-1	Bright nickel Watts Bath	$NiSO_4 \cdot 6H_2O$ $NiCl_2 \cdot 6H_2O$ Boric Acid Sodium salt of saccharin Methyl butynol-ethylene oxide adduct	300 60 37.5 2.4 0.065	4.0	140	40	None	--------	−12,000
5B-2				4.0	140	40	α-Ketobutyric acid	2.0	0
5B-3				4.0	140	40	Sodium Ketomalonate	4.0	0

What is claimed is:

1. An electroplating bath for producing stress-free metal electrodeposits of a metal selected from the group consisting of nickel, cobalt, zinc and copper, comprising an aqueous solution of at least one water-soluble salt of the metal to be electrodeposited and an effective amount of a stress-reducing additive selected from the group con-

sisting of α-keto carboxylic acids having from 3 to 10 carbon atoms and the water-soluble salts, esters, and amides of said acids.

2. An electroplating bath for producing stress-free electrodeposits of a metal selected from the group consisting of nickel, cobalt, zinc, and copper, comprising an aqueous solution of at least one water-soluble salt of the metal to be electrodeposited and approximately 0.25 g. to 15 g. per liter of said bath of a stress-reducing additive selected from the group consisting of α-keto carboxylic acids having from 3 to 10 carbon atoms and the water-soluble salts, esters, and amides of said acids.

3. An electroplating bath according to claim 2 wherein the quantity of the stress-reducing additive is 0.5 g. to 10 g. per liter.

4. An electroplating bath for producing stress-free nickel electrodeposits comprising an aqueous solution of at least one water-soluble salt of nickel and approximately 0.25 g. to 15 g. per liter of said bath of a stress-reducing additive selected from the group consisting of α-keto carboxylic acids having from 3 to 10 carbon atoms and the water-soluble salts, esters, and amides of said acids.

5. An electroplating bath for producing stress-free nickel electrodeposits comprising an aqueous solution of at least one inorganic salt of nickel and 0.5 g. to 10 g. per liter of said bath of a stress-reducing additive selected from the group consisting of α-keto carboxylic acids having from 3 to 10 carbon atoms and the water-soluble salts, esters, and amides of said acids.

6. An electroplating bath according to claim 5 wherein the stress-reducing additive is pyruvic acid.

7. An electroplating bath according to claim 5 wherein the stress-reducing additive is sodium pyruvate.

8. An electroplating bath according to claim 5 wherein the stress-reducing additive is ammonium pyruvate.

9. An electroplating plate according to claim 5 wherein the stress-reducing additive is 2-ketoglutaric acid.

10. An electroplating bath according to claim 5 wherein the stress-reducing additive is α-ketobutyric acid.

11. An electroplating bath according to claim 5 wherein the stress-reducing additive is sodium ketomalonate.

12. A method of producing a stress-free electrodeposit of a metal selected from the group consisting of nickel, cobalt, zinc, and copper, which comprises electrodepositing said metal from an electroplating bath comprising an aqueous solution of at least one water-soluble salt of the metal to be deposited and approximately 0.25 g. to 15 g. per liter of said bath of a stress-reducing additive selected from the group consisting of α-keto carboxylic acids having from 3 to 10 carbon atoms and the water-soluble salts, esters, and amides of said acids.

13. A method of producing a stress-free nickel electrodeposit which comprises electrodepositing nickel from an electroplating bath comprising an aqueous solution of at least one water-soluble salt of nickel and 0.5 g. to 10 g. per liter of said bath of a stress-reducing agent selected from the group consisting of α-keto carboxylic acids having from 3 to 10 carbon atoms and the water-soluble salts, esters, and amides of said acids.

14. The method of claim 13 wherein the stress-reducing additive is pyruvic acid.

15. The method of claim 13 wherein the stress-reducing additive is sodium pyruvate.

16. The method of claim 13 wherein the stress-reducing additive is 2-ketoglutaric acid.

17. The method of claim 13 wherein the stress-reducing additive is α-ketobutyric acid.

18. The method of claim 13 wherein the stress-reducing additive is sodium ketomalonate.

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