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(54) NICKEL ELECTROPLATING BATH FOR DEPOSITING A DECORATIVE NICKEL COATING ON A SUBSTRATE

NICKELELEKTROPLATTIERUNGSBAD ZUR ABSCHEIDUNG EINER DEKORATIVEN NICKELBESCHICHTUNG AUF EINEM SUBSTRAT

BAIN GALVANOPLASTIQUE DE NICKEL CONÇU POUR DÉPOSER UN REVÊTEMENT DE NICKEL DÉCORATIF SUR UN SUBSTRAT

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Description

Field of the Invention

[0001] The present invention relates to a nickel electroplating bath for depositing a decorative nickel coating on a substrate to be treated. The present invention is also directed to a method for depositing a decorative nickel coating on a substrate to be treated. Furthermore, the invention is related to the use of such an inventive nickel electroplating bath for depositing a bright nickel coating by conducting such a method.

Background of the Invention

[0002] In nickel electroplating baths, it is generally very important to keep the pH value in a defined range.

[0003] Thus, in the past there have been buffer systems applied to the nickel bath in order to fulfill this object.

[0004] The most conventional system is based on the so-called "Watts electrolytic bath", which has the following general composition:

240- 550 g/l	nickel sulfate ($NiSO_4 \cdot 7\ H_2O$ or $NiSO_4 \cdot 6\ H_2O$),
30-150 g/l	nickel chloride ($NiCl_2 \cdot 6\ H_2O$), and
30-55 g/l	boric acid (H_3BO_3).

[0005] The large amount of nickel sulfate provides the necessary concentration of nickel ions, while nickel chloride improves anode corrosion and increases conductivity. Boric acid is used as a weak buffer to maintain the pH value.

[0006] In addition, in order to achieve bright and lustrous appearance of the nickel plating coating, organic and inorganic agents (brighteners) are often added to the electrolyte. The types of added brighteners and their concentrations determine the appearance of the nickel coating, i.e., brilliant, bright, semi-bright, satin, matte etc.

[0007] US 4,159,926 refers to a nickel electroplating bath comprising in aqueous solution at a pH of from 4 to 7, nickel ions at a Molar concentration of at least 0.25, chloride ions at a Molar concentration of at least 0.25, and a weak complexant for the nickel selected from formate, acetate, citrate, glutamate, anions and lactones of sugar acids and anions and lactones of acids having the formula $X(C_nH_{2n})COOH$ where X is OH or NH_2 and n is 1 to 5, preferably 1 to 2, present at a Molar concentration of from 0.5 to 4.0 times that of the nickel.

[0008] US 2006/0096868 A1 refers to a nickel electroplating bath comprising an additive package comprising (i) sulphonic acid or sulphonic acid salts, (ii) sulfonated alkoxylate and (iii) organic acid selected from the group consisting of tolylacetic acid, salicylic acid, hydroxy-benzoic acid, benzyloxyacetone and mixtures of the foregoing.

[0009] DE 10 2014 118614 A1 refers to a boric acid-free nickel bath.

[0010] EP 2 878 711 A1 refers to a deposition bath for depositing nickel, the bath comprising nickel ions, a conducting salt, and boric acid as buffer in a concentration equal or below 10 g/L.

[0011] DE 10 2014 207778 B3 refers to a deposition bath for depositing a bright nickel layer comprising boric acid.

[0012] However, boric acid has been classified as toxic in the meantime and is considered to be banned for the world market. So, the industry has a strong demand to replace boric acid by other non-toxic substances.

Objective of the present Invention

[0013] In view of the prior art, it was thus an object of the present invention to provide a nickel electroplating bath, which shall be boric acid free.

[0014] Additionally, it was especially an object of the present invention to provide a nickel electroplating bath for depositing nickel coatings, such as bright nickel coating.

[0015] Furthermore, it was an object of the present invention to provide a method for depositing nickel coatings, such as bright nickel coating.

Summary of the Invention

[0016] These objects and also further objects which are not stated explicitly but are immediately derivable or discernible from the connections discussed herein by way of introduction are achieved by a nickel electroplating bath having all features of claim 1. Appropriate modifications to the inventive bath are protected in dependent claims 2 to 8. Further, claim 9 relates to a method for depositing a decorative nickel coating on a substrate to be treated, while claims 10 to 13 focus on appropriate modifications of this method. Claim 14 relates to a use of such a nickel electroplating bath for depositing a bright nickel coating by conducting such a method.

[0017] The present invention accordingly provides a nickel electroplating bath for depositing a decorative nickel coating on a substrate to be treated, the electroplating bath comprises at least a nickel ion source, at least one amino acid and/or at least one carboxylic acid, which is not an amino acid; wherein the total concentration of the amino acid(s) is ranging from 1 to 10 g/l, wherein the total concentration of carboxylic acid(s), which is/are not an amino acid, is ranging from 10 to 40 g/l; wherein the electroplating bath is free of boric acid; wherein the total concentration of the nickel ions is ranging from 55 to 80 g/l; and wherein the nickel electroplating bath has a chloride content ranging from 7.5 to 40 g/l, characterized in that the nickel electroplating bath further comprises

- saccharin and/or a saccharin derivative in form of a saccharin salt at a concentration ranging from 1.5 to 10 g/l, and
- at least a sulfonic acid and/or a derivative of a sulfonic acid in form of a sulfonic acid salt at a total concentration ranging from 0.1 to 5 g/l.

[0018] Herein, the at least one amino acid and/or the at least one carboxylic acid are representing complexing agents for complexing the nickel ions in the respective nickel electroplating bath. Herein, the "classical" complexing agent of the prior art, namely boric acid, shall and has been avoided. Thus, the nickel electroplating bath of the present invention is boric acid free.

[0019] It is thus possible in an unforeseeable manner to provide a nickel electroplating bath, which is boric acid free causing less impact on the environment.

[0020] Additionally, it has been successfully achieved to provide a nickel electroplating bath for depositing nickel coatings, such as bright nickel coating. The nickel electroplating bath also shows good levelling performance and leads to well-levelled coatings.

Brief Description of the Tables

[0021] Objects, features, and advantages of the present invention will also become apparent upon reading the following description in conjunction with the tables, in which:

Table 1 exhibits inventive experiments for bright nickel coatings in accordance with embodiments of the present invention.

Table 2 exhibits comparative experiments for bright nickel coatings in accordance with comparative embodiments outside of the present invention.

Table 3 exhibits inventive experiments for bright nickel coatings in accordance with further embodiments of the present invention.

Detailed Description of the Invention

[0022] In a preferred embodiment of the present invention, the nickel electroplating bath has a chloride content ranging from 10 to 30 g/l.

[0023] The expression "chloride content" means in the context of the present invention a chloride ion source.

[0024] Nickel chloride may be replaced partly by sodium chloride.

[0025] Further, chloride in the electrolyte may be replaced partly by equivalent amounts of bromide.

[0026] A nickel ion source in the context of the present invention can be any kind of nickel salt or nickel complex, which is suitable to provide a free nickel ion in the respective nickel electrodeposition bath, such as nickel chloride and/or nickel sulfate.

[0027] The nickel electroplating bath of the present invention can be used for depositing decorative nickel coatings on a plurality of different kind of substrates to be treated based on a metal and/or metal alloy, in particular steel, copper, brass, aluminum, bronze, magnesium and/or zinc diecasting; or on "POP" substrates. "POP" means in the sense of the invention "plating on plastics". Thus, POP substrates comprise a synthetic substrate, preferably based on at least one polymeric compound, more preferably based on acrylonitrile-butadiene- styrene (ABS), polyamide, polypropylene or ABS/PC (polycarbonate).

[0028] In a preferred embodiment of the present invention, the nickel electroplating bath is substantially free, preferably completely free, of any other metal ion (additionally to the nickel ion source, which is always provided in the inventive electroplating bath), which can be electrolytically deposited together with the nickel ion source as nickel alloy layer.

[0029] In particular, it is preferred that the nickel electroplating bath is substantially free, preferably completely free, of an iron, gold, copper, bismuth, tin, zinc, silver, lead, and aluminum ion source.

[0030] The expression "substantially free" means in the context of the present invention a concentration of less than

1 g/l, preferably less than 0.1 g/l, and more preferably less than 0.01 g/l of the respective metal ion source.

[0031] In one embodiment, the at least one amino acid is selected from the group consisting of β alanine, glycine, glutamic acid, DL- aspartic acid, threonine, valine, glutamine or L-serine.

[0032] In one embodiment, the at least one carboxylic acid, which is not an amino acid, is selected from the group consisting of mono carboxylic acids, di carboxylic acids or tri carboxylic acids.

[0033] In a preferred embodiment thereof, the at least one carboxylic acid, which is not an amino acid, is selected from the group consisting of tartaric acid, glycolic acid, malic acid, acetic acid, lactic acid, citric acid, succinic acid, propanoic acid, formic acid or glutaric acid.

[0034] In one embodiment, the electroplating bath comprises at least two different carboxylic acids, which are both not amino acids; wherein the total concentration of said two different carboxylic acids, is ranging from 10 to 40 g/l.

[0035] In one embodiment, the electroplating bath comprises at least one amino acid and one carboxylic acid, which is not an amino acid; wherein the total concentration of said amino acid is ranging from 1 to 10 g/l, wherein the total concentration of said carboxylic acid, which is not an amino acid, is ranging from 10 to 40 g/l.

[0036] In a preferred embodiment, the total concentration of the nickel ions is ranging from 60 to 75 g/l, and preferably from 62 to 72 g/l.

[0037] In one embodiment, the pH-Value of the electroplating bath ranges from 2 to 6, preferably from 3 to 5, more preferably from 3.5 to 4.7.

[0038] Furthermore, the nickel electroplating bath may comprise in certain embodiments of the present invention at least a wetting agent, such as 2-ethylhexylsulfate, di-alkylsulfusuccinate, polymerized naphtalenesulfonate, lauryl sulfate or lauryl ether sulfate, wherein the concentration of such a wetting agent, is used, is ranging from 5 to 500 mg/l, preferably ranging from 10 to 350 mg/l, and more preferably ranging from 20 to 250 mg/l.

[0039] The electroplating bath may further comprise benzoic acid or an alkali metal, benzoate at a concentration ranging from 0.005 to 5 g/l, preferably from 0.02 to 2 g/l, more preferably from 0.05 to 0.5 g/l. Such additive compounds help to reduce internal stress of the deposited coatings.

[0040] The electroplating bath may also further comprise salicylic acid at a concentration ranging from 0.1 to 10 g/l, preferably from 0.3 to 6 g/l, more preferably from 0.5 to 3.5 g/l. Such an additive affects positively the hardness, durability and the optical properties of the achieved coatings.

[0041] The electroplating bath may further comprises additional compounds selected from brighteners, leveling agents, internal stress reducers, and wetting agents, in particular at a concentration ranging from 0.005 to 5 g/l, preferably from 0.02 to 2 g/l, more preferably from 0.05 to 0.5 g/l.

[0042] Exemplarily, a primary brightener can be comprised in certain embodiments, preferably for bright nickel coatings, unsaturated, in most cases aromatic sulfonic acids, sulfonamides, sulfimides, N-sulfonylcarboxamides, sulfinates, diarylsulfones or the salts thereof, in particular the sodium or potassium salts. The nickel electroplating bath of the present invention comprises at least a sulfonic acid and/or a derivative of a sulfonic acid in form of a sulfonic acid salt at a total concentration ranging from 0.1 to 5 g/l.

[0043] The most familiar compounds are for example m-benzenedisulfonic acid, benzoic acid sulfimide (saccharine), trisodium 1,3,6- naphthalene trisulfonate, sodium benzene monosulfonate, dibenzene sulfonamide, sodium benzene mono-sulfinate, vinyl sulfonic acid, allyl sulfonic acid, sodium salt of allyl sulfonic acid, p-toluene sulfonic acid, p-toluene sulfonamide, sodium propargyl sulfonate, benzoic acid sulfimide, 1,3,6-naphthalenetrisulfonic acid and benzoyl benzene sulfonamide. The nickel electroplating bath of the present invention comprises saccharin and/or a saccharin derivative in form of a saccharin salt at a concentration ranging from 1.5 to 10 g/l.

[0044] Further, such a primary brightener can comprise propargyl alcohol and/or derivatives (ethoxylated or propoxylated) thereof.

[0045] The primary brighteners can be added to the electrolyte bath at a concentration ranging from 0.001 to 8 g/l, preferably from 0.01 to 2 g/l, more preferably from 0.02 to 1 g/l. It is also possible to use several primary brighteners simultaneously.

[0046] Further, the object of the present invention is also solved by a method for depositing a decorative nickel coating on a substrate to be treated comprising the following method steps:

i) Bringing the substrate to be treated into contact with such an inventive nickel electroplating bath;

ii) Bringing at least one anode into contact with the nickel electroplating bath;

iii) Applying a voltage to the substrate to be treated and the at least one anode; and

iv) Electrodepositing a decorative nickel coating on the substrate to be treated.

[0047] In one embodiment, the method for depositing is executed in a working temperature range from 30°C to 70°C, preferably from 40°C to 65°C, and more preferably from 50°C to 60°C.

[0048] In one embodiment, the method for depositing is executed in a working current density range from 1 to 7 Ampere/dm^2 (ASD), preferably from 1.5 to 6 ASD, and more preferably from 2 to 5 ASD.

[0049] In one embodiment, the method for depositing is executed in a working time for applying the voltage and the subsequent electrodeposition of the decorative nickel coating (method steps iii) and iv)) ranging from 5 to 50 minutes, preferably from 6 to 35 minutes, and more preferably from 8 to 25 minutes.

[0050] In one embodiment, the electroplating bath further comprises at least a saccharin and/or a saccharin derivative in form of a saccharin salt, preferably the sodium salt of saccharin, at a concentration ranging from 1.5 to 7 g/l, preferably from 2 to 6 g/l; and at least a sulfonic acid and/or a derivative of a sulfonic acid in form of a sulfonic acid salt, preferably selected from the group consisting of allyl sulfonic acid, vinyl sulfonic acid, sodium salt of allyl sulfonic acid, sodium salt of vinyl sulfonic acid, or mixtures thereof, at a total concentration ranging from 0.25 to 3.5 g/l, preferably from 0.5 to 2.0 g/l. Hereby, a bright nickel coating is deposited. The selective choice of the above-mentioned additives shows the unique application of the inventive nickel electroplating bath for the purpose of depositing decorative nickel coatings of different optical appearance and chemical properties.

[0051] In another alternative embodiment to the preceding one (but not according to the present invention), the electroplating bath further comprises at least a diol, preferably selected from the group consisting of 2,5 hexinediol and 1,4 butinediol, at a concentration ranging from 10 to 300 mg/l, preferably from 50 to 250 mg/l, more preferably from 100 to 220 mg/l; or at least an additive selected from the group of pyridiniumpropylsulfobetaine (PPS) or derivatives thereof (such as PPS-OH), at a total concentration ranging from 5 to 350 mg/l, preferably from 10 to 200 mg/l, more preferably from 50 to 150 mg/l.

[0052] Hereby, a semi-bright nickel coating is deposited.

[0053] Additionally, the object of the present invention is also solved by making use of such a nickel electroplating bath for depositing a bright nickel coating by conducting such a method.

[0054] The present invention thus addresses the problem of providing a boric acid free nickel electroplating bath for depositing decorative nickel coatings, such as bright nickel coating.

[0055] The following non-limiting examples are provided to illustrate an embodiment of the present invention and to facilitate understanding of the invention, but are not intended to limit the scope of the invention, which is defined by the claims appended hereto.

General description:

[0056] The substrates have been always pretreated in the following manner before their use for the nickel deposition:

i) Degreasing by hot soak cleaner

ii) Electrolytic degreasing

iii) Rinsing,

iv) Acid dipping with 10 vol% sulfuric acid

[0057] Sample substrates have been scratched for subjective optical judgment of leveling. The glance of the resulting nickel coatings on the substrates has been also judged optically. The size of the sample substrates have been always 7 cm x 10 cm (width x length) leading to a surface to be treated of 70 cm^2 on one side (Tables 1,2, and 3).

[0058] All concentrations given in Tables 1, 2 and 3 for the complexing agent in form of the acid are listed in g/l, if not stated differently.

[0059] The experiments given in Tables 1, 2 and 3 are numbered in consequent order.

[0060] Turning now to the Tables, Table 1 shows conducted experiments for bright nickel coatings in accordance with embodiments of the present invention.

[0061] The nickel deposition took place for all experiments listed in Table 1 in a Hull cell wherein 2.5 Ampere (A) was applied for 10 minutes at a temperature of 55°C +/- 3°C. Further, 3 liter/min pressure air was introduced during nickel deposition.

[0062] The nickel concentration was 67 g/l for all experiments listed in Table 1.

[0063] It is clearly to see that all inventive experiments listed in Table 1 resulted in uniform bright and levelled nickel coatings. Even when numerous different been always good remarkable results in these boric acid free baths. All acids have been used in the specific respective concentration ranges claimed in claim 1, depending on the chemical nature of the acid being an amino acid or a carboxylic acid, which is not an amino acid.

[0064] The respective columns are showing the number of the experiment, the used acid as complexing agent, the concentration of the acid used as complexing agent, the pH-value of the nickel bath, and the achieved result of the nickel coating in the range from highest current density to lowest current density on the hull cell panel (regarded on the total length of 10 cm) (columns have been described from the left to the right of Table 1).

Table 1: Experiments for bright nickel coatings

Exp.	Acid	Conc	pH	Result
1	Tartaric Acid	20	4.1	Uniform bright and levelled coating
2	Tartaric Acid	40	3.5	Uniform bright and levelled coating
3	Tartaric Acid	40	4.7	Uniform bright and levelled coating
4	Glycolic Acid	10	4.7	Uniform bright and levelled coating
5	Glycolic Acid	20	4.1	Uniform bright and levelled coating
6	Glycolic Acid	40	4.7	Uniform bright and levelled coating
7	Glycolic Acid	40	3.5	Uniform bright and levelled coating
8	Malic Acid	10	4.1	Uniform bright and levelled coating
9	Malic Acid	10	3.5	Uniform bright and levelled coating
10	Acetic Acid	20	4.1	Uniform bright and levelled coating
11	Acetic Acid	40	3.5	Uniform bright and levelled coating
12	Lactic Acid	40	4.1	Uniform bright and levelled coating
13	Citric Acid	20	4.1	Uniform bright and levelled coating
14	Citric Acid	40	4.7	Uniform bright and levelled coating
15	Succinic Acid	20	4.7	Uniform bright and levelled coating
16	Succinic Acid	40	3.5	Uniform bright and levelled coating
17	Succinic Acid	40	4.1	Uniform bright and levelled coating
17a	Succinic Acid	10	3.5	Uniform bright and levelled coating
17b	Succinic Acid	10	4.1	Uniform bright and levelled coating
17c	Succinic Acid	20	3.5	Uniform bright and levelled coating
17d	Succinic Acid	20	4.1	Uniform bright and levelled coating
18	Propanoic Acid	40	4.7	Uniform bright and levelled coating
19	Formic Acid	40	4.7	Bright and levelled coating with little haze
20	Glutaric Acid	10	3.5	Uniform bright and levelled coating
21	Glutaric Acid	20	3.5	Uniform bright and levelled coating
22	Glutaric Acid	40	4.7	Uniform bright and levelled coating
23	β Alanine	10	3.5	Uniform bright and levelled coating
23a	β Alanine	5	3.5	Uniform bright and levelled coating
24	Glycine	10	3.5	Uniform bright and levelled coating
25	Glutamic Acid	10	3.5	Uniform bright and levelled coating
26	DL- Aspartic Acid	10	3.5	Uniform bright and levelled coating
27	Threonine	10	3.5	Uniform bright and levelled coating
28	Valine	10	3.5	Uniform bright and levelled coating
29	L-Serine	10	3.5	Uniform bright and levelled coating

[0065] Table 2 exhibits comparative experiments for bright nickel coatings in accordance with comparative embodiments outside of the present invention.

[0066] The nickel deposition took place for all experiments listed in Table 2 in a Hull cell at a temperature of 55°C +/- 3 °C as in the experiments listed in Table 1. Further, 3 liter/min pressure air was introduced during nickel deposition. The respective columns are showing the number of the experiment, the used acid as complexing agent, the concentration of the acid used as complexing agent, the pH-value of the nickel bath, the applied current in Ampere (A), the nickel ion concentration in g/l, the application time of the current in minutes, and the achieved result of the nickel coating (columns have been described from the left to the right of Table 2).

Table 2: Comparative experiments for bright nickel coatings

Exp.	Acid	Cone	pH	A	Ni	time	Result
30	Glutamic Acid	18	3.5	2.5	67	10	Severe crackings
31	Aspartic Acid	18	4.7	2.5	67	10	Severe crackings
32	Citric Acid	60	4.1	2.5	67	10	Milky and hazy appearance
33	Tartaric Acid	5	3.5	2.5	67	10	Black, powdery coating with bad adherence
34	Tartaric Acid	5	4.1	2.5	67	10	Black, powdery coating with bad adherence
35	Tartaric Acid	5	4.7	2.5	67	10	Black, powdery coating with bad adherence
36	Glycolic Acid	20	4.1	**8**	67	10	Dendrite formation
37	Citric Acid	20	4.1	2.5	67	**1**	Weak levelling, low brightness
38	Tartaric Acid	20	4.1	2.5	**45**	10	Green, powdery coating with bad adherence
39	Boric Acid	42	3.5	2.5	67	10	Uniform bright and levelled coating
40	Boric Acid	42	4.1	2.5	67	10	Uniform bright and levelled coating
41	Boric Acid	42	4.7	2.5	67	10	Uniform bright and levelled coating

[0067] Experiments 30 to 35 show comparative experiments making use of the same respective acids as complexing agent as in certain experiments in Table 1, but with a different concentration. Experiments 30 to 35 all have a too low or too high concentration of the complexing agent for the nickel ions compared to the claimed concentration ranges.

[0068] Experiments 36 to 38 show comparative experiments. Herein, the acids have been used in the concentration range claimed, but with a changed working parameter, namely current (Exp.36), application time (Exp. 37), and nickel ion concentration (Exp. 38). The respective values have been highlighted and underlined in Table 2 for illustration purposes.

[0069] It is clearly to see that all comparative experiments listed in Table 2 resulted in worse results than the experiments of Table 1. Obviously, the selection of the suitable different parameters to deposit a uniform bright nickel coating is not predictable. Therefore, the claimed bath and method is inventive as selection invention based on the inventive selection of the required parameters, wherein it is clearly to see that even the change of just one parameter lead to poor nickel coatings instead of bright and uniform nickel coatings.

[0070] Comparative experiments 30 to 38 are also boric acid free.

[0071] Experiments 39 to 41 show comparative experiments being based on the up to now commonly used boric acid as complexing agent for the nickel ions. Therefore, this represents common prior art.

[0072] Table 3 exhibits inventive experiments for bright nickel coatings in accordance with further embodiments of the present invention.

[0073] The experiments listed in Table 3 have been executed in the same manner as the experiments listed in Table 1. Herein, experiments 42 to 46 show a combination of two carboxylic acids, wherein both are not an amino acid (Exp. 42 and 43), and a combination of one amino acid with one carboxylic acid not being an amino acid (Exp. 44 to 46). All results of these inventive examples of Table 3 have the same good achievements as in Table 1. All have been led to uniform bright nickel coatings. The column (Conc) has the concentration of both acids.

Table 3: Further experiments for bright nickel coatings

Exp.	Acid	Cone	pH	Result
42	Glycolic Acid + Acetic Acid	20 + 10	4.7	Uniform bright and levelled coating
43	Glycolic Acid + Succinic Acid	20 + 10	4.1	Uniform bright and levelled coating

(continued)

Exp.	Acid	Cone	pH	Result
44	Glycolic Acid + DL Aspartic Acid	20 + 5	4.1	Uniform bright and levelled coating
45	Glycolic Acid + DL Aspartic Acid	40 + 5	3.5	Uniform bright and levelled coating
46	Glycolic Acid + Glycine	20 + 5	3.5	Uniform bright and levelled coating

[0074] While the principles of the invention have been explained in relation to certain particular embodiments, and are provided for purposes of illustration, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims. The scope of the invention is limited only by the scope of the appended claims.

Claims

1. Nickel electroplating bath for depositing a decorative nickel coating on a substrate to be treated, the electroplating bath comprises at least a nickel ion source, at least one amino acid and/or at least one carboxylic acid, which is not an amino acid; wherein the total concentration of the amino acid(s) is ranging from 1 to 10 g/l, wherein the total concentration of carboxylic acid(s), which is/are not an amino acid, is ranging from 10 to 40 g/l; wherein the electroplating bath is free of boric acid; wherein the total concentration of the nickel ions is ranging from 55 to 80 g/l; and wherein the nickel electroplating bath has a chloride content ranging from 7.5 to 40 g/l,
characterized in that the nickel electroplating bath further comprises

- saccharin and/or a saccharin derivative in form of a saccharin salt at a concentration ranging from 1.5 to 10 g/l, and
- at least a sulfonic acid and/or a derivative of a sulfonic acid in form of a sulfonic acid salt at a total concentration ranging from 0.1 to 5 g/l.

2. Nickel electroplating bath according to claim 1 **characterized in that** the at least one amino acid is selected from the group consisting of β alanine, glycine, glutamic acid, DL- aspartic acid, threonine, valine, glutamine or L-serine.

3. Nickel electroplating bath according to claim 1 or 2 **characterized in that** the at least one carboxylic acid, which is not an amino acid, is selected from the group consisting of mono carboxylic acids, di carboxylic acids or tri carboxylic acids.

4. Nickel electroplating bath according to claim 3 **characterized in that** the at least one carboxylic acid, which is not an amino acid, is selected from the group consisting of tartaric acid, glycolic acid, malic acid, acetic acid, lac-tic acid, citric acid, succinic acid, propanoic acid, formic acid or glutaric acid.

5. Nickel electroplating bath according to one of the preceding claims **characterized in that** the electroplating bath comprises at least two different carboxylic acids, which are both not amino acids; wherein the total concentration of said two different carboxylic acids, is ranging from 10 to 40 g/l.

6. Nickel electroplating bath according to one of the preceding claims **characterized in that** the electroplating bath comprises at least one amino acid and one carboxylic acid, which is not an amino acid; wherein the total concentration of said amino acid is ranging from 1 to 10 g/l, wherein the total concentration of said carboxylic acid, which is not an amino acid, is ranging from 10 to 40 g/l.

7. Nickel electroplating bath according to one of the preceding claims **characterized in that** total concentration of the nickel ions is ranging from 60 to 75 g/l, preferably from 62 to 72 g/l.

8. Nickel electroplating bath according to one of the preceding claims **characterized in that** the pH-Value of the electroplating bath ranges from 2 to 6, preferably from 3 to 5, more preferably from 3.5 to 4.7.

9. Method for depositing a decorative nickel coating on a substrate to be treated comprising the following method steps:

i) Bringing the substrate to be treated into contact with a nickel electroplating bath according to any of claims 1 to 8;
ii) Bringing at least one anode into contact with the nickel electroplating bath;
iii) Applying a voltage to the substrate to be treated and the at least one anode; and
iv) Electrodepositing a decorative nickel coating on the substrate to be treated.

10. Method for depositing a decorative nickel coating according to claim 9 **characterized in that** the method for depositing is executed in a working temperature range from 30°C to 70°C, preferably from 40°C to 65°C, and more preferably from 50°C to 60°C.

11. Method for depositing a decorative nickel coating according to claim 9 or 10 **characterized in that** the method for depositing is executed in a working current density range from 1 to 7 Ampere/dm2 (ASD), preferably from 1.5 to 6 ASD, and more preferably from 2 to 5 ASD.

12. Method for depositing a decorative nickel coating according to one of claims 9 to 11 **characterized in that** the method for depositing is executed in a working time for applying the voltage and the subsequent electrodeposition of the decorative nickel coating (method steps iii) and iv)) ranging from 5 to 50 minutes, preferably from 6 to 35 minutes, and more preferably from 8 to 25 minutes.

13. Method for depositing a decorative nickel coating according to one of claims 9 to 12 **characterized in that** the electroplating bath further comprises at least a saccharin and/or a saccharin derivative in form of a saccharin salt, preferably the sodium salt of saccharin, at a concentration ranging from 1.5 to 7 g/l, preferably from 2 to 6 g/l; and at least a sulfonic acid and/or a derivative of a sulfonic acid in form of a sulfonic acid salt, preferably selected from the group consisting of allyl sulfonic acid, vinyl sulfonic acid, sodium salt of allyl sulfonic acid, sodium salt of vinyl sulfonic acid, or mixtures thereof, at a total concentration ranging from 0.25 to 3.5 g/l, preferably from 0.5 to 2.0 g/l.

14. Use of a nickel electroplating bath according to one of the preceding claims 1 to 8 for depositing a bright nickel coating by conducting a method according to one of claims 9 to 13.

Patentansprüche

1. Nickelgalvanisierungsbad zur Abscheidung einer dekorativen Nickelbeschichtung auf einem zu behandelnden Substrat, wobei das Galvanisierungsbad mindestens eine Nickelionenquelle, mindestens eine Aminosäure und/oder mindestens eine Carbonsäure, bei der es sich nicht um eine Aminosäure handelt, umfasst; wobei die Gesamtkonzentration der Aminosäure bzw. der Aminosäuren im Bereich von 1 bis 10 g/l liegt, wobei die Gesamtkonzentration der Carbonsäure bzw.
der Carbonsäuren, bei der bzw. denen es sich nicht um eine Aminosäure handelt, im Bereich von 10 bis 40 g/l liegt; wobei das Galvanisierungsbad borsäurefrei ist; wobei die Gesamtkonzentration der Nickelionen im Bereich von 55 bis 80 g/l liegt und wobei das Nickelgalvanisierungsbad einen Chloridgehalt im Bereich von 7,5 bis 40 g/l aufweist, **dadurch gekennzeichnet, dass** das Nickelgalvanisierungsbad ferner

- Saccharin und/oder ein Saccharinderivat in Form eines Saccharinsalzes in einer Konzentration im Bereich von 1,5 bis 10 g/l und
- mindestens eine Sulfonsäure und/oder ein Derivat einer Sulfonsäure in Form eines Sulfonsäuresalzes in einer Gesamtkonzentration im Bereich von 0,1 bis 5 g/l

umfasst.

2. Nickelgalvanisierungsbad nach Anspruch 1, **dadurch gekennzeichnet, dass** die mindestens eine Aminosäure aus der Gruppe bestehend aus β-Alanin, Glycin, Glutaminsäure, DL-Asparaginsäure, Threonin, Valin, Glutamin oder L-Serin ausgewählt ist.

3. Nickelgalvanisierungsbad nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** die mindestens eine Carbonsäure, bei der es sich nicht um eine Aminosäure handelt, aus der Gruppe bestehend aus Monocarbonsäuren, Dicarbonsäuren oder Tricarbonsäuren ausgewählt ist.

4. Nickelgalvanisierungsbad nach Anspruch 3, **dadurch gekennzeichnet, dass** die mindestens eine Carbonsäure, bei der es sich nicht um eine Aminosäure handelt, aus der Gruppe bestehend aus Weinsäure, Glykolsäure, Äpfelsäure, Essigsäure, Milchsäure, Citronensäure, Bernsteinsäure, Propansäure, Ameisensäure oder Glutarsäure ausgewählt ist.

5. Nickelgalvanisierungsbad nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** das Galvanisierungsbad mindestens zwei verschiedene Carbonsäuren, bei denen es sich bei beiden nicht um Aminosäuren handelt, umfasst; wobei die Gesamtkonzentration der zwei verschiedenen Carbonsäuren im Bereich von 10 bis 40 g/l liegt.

6. Nickelgalvanisierungsbad nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** das Galvanisierungsbad mindestens eine Aminosäure und eine Carbonsäure, bei der es sich nicht um eine Aminosäure handelt, umfasst; wobei die Gesamtkonzentration der Aminosäure im Bereich von 1 bis 10 g/l liegt, wobei die Gesamtkonzentration der Carbonsäure, bei der es sich nicht um eine Aminosäure handelt, im Bereich von 10 bis 40 g/l liegt.

7. Nickelgalvanisierungsbad nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die Gesamtkonzentration der Nickelionen im Bereich von 60 bis 75 g/l, vorzugsweise von 62 bis 72 g/l, liegt.

8. Nickelgalvanisierungsbad nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der pH-Wert des Galvanisierungsbads im Bereich von 2 bis 6, vorzugsweise von 3 bis 5, weiter bevorzugt von 3,5 bis 4,7, liegt.

9. Verfahren zur Abscheidung einer dekorativen Nickelbeschichtung auf einem zu behandelnden Substrat, das die folgenden Verfahrensschritte umfasst:

   i) Inkontaktbringen des zu behandelnden Substrats mit einem Nickelgalvanisierungsbad nach einem der Ansprüche 1 bis 8;
   ii) Inkontaktbringen mindestens einer Anode mit dem Nickelgalvanisierungsbad;
   iii) Anlegen einer Spannung an das zu behandelnde Substrat und die mindestens eine Anode und
   iv) galvanisches Abscheiden einer dekorativen Nickelbeschichtung auf dem zu behandelnden Substrat.

10. Verfahren zur Abscheidung einer dekorativen Nickelbeschichtung nach Anspruch 9, **dadurch gekennzeichnet, dass** das Abscheidungsverfahren in einem Arbeitstemperaturbereich von 30 °C bis 70 °C, vorzugsweise von 40 °C bis 65 °C und weiter bevorzugt von 50 °C bis 60 °C durchgeführt wird.

11. Verfahren zur Abscheidung einer dekorativen Nickelbeschichtung nach Anspruch 9 oder 10, **dadurch gekennzeichnet, dass** das Abscheidungsverfahren in einem Arbeitsstromdichtebereich von 1 bis 7 Ampere/dm^2 (ASD), vorzugsweise von 1,5 bis 6 ASD und weiter bevorzugt von 2 bis 5 ASD durchgeführt wird.

12. Verfahren zur Abscheidung einer dekorativen Nickelbeschichtung nach einem der Ansprüche 9 bis 11, **dadurch gekennzeichnet, dass** das Abscheidungsverfahren in einer Arbeitszeit für das Anlegen der Spannung und die anschließende galvanische Abscheidung der dekorativen Nickelbeschichtung (Verfahrensschritte iii) und iv)) im Bereich von 5 bis 50 Minuten, vorzugsweise von 6 bis 35 Minuten und weiter bevorzugt von 8 bis 25 Minuten durchgeführt wird.

13. Verfahren zur Abscheidung einer dekorativen Nickelbeschichtung nach einem der Ansprüche 9 bis 12, **dadurch gekennzeichnet, dass** das Galvanisierungsbad ferner mindestens ein Saccharin und/oder ein Saccharidderivat in Form eines Saccharinsalzes, vorzugsweise das Natriumsalz von Saccharin, in einer Konzentration im Bereich von 1,5 bis 7 g/l, vorzugsweise von 2 bis 6 g/l, und mindestens eine Sulfonsäure und/oder ein Derivat einer Sulfonsäure in Form eines Sulfonsäuresalzes, vorzugsweise ausgewählt aus der Gruppe bestehend aus Allylsulfonsäure, Vinylsulfonsäure, Natriumsalz von Allylsulfonsäure, Natriumsalz von Vinylsulfonsäure oder Mischungen davon, in einer Gesamtkonzentration im Bereich von 0,25 bis 3,5 g/l, vorzugsweise von 0,5 bis 2,0 g/l, umfasst.

14. Verwendung eines Nickelgalvanisierungsbads nach einem der vorhergehenden Ansprüche 1 bis 8 zum Abscheiden einer Glanznickelbeschichtung durch Durchführen eines Verfahrens nach einem der Ansprüche 9 bis 13.

Revendications

1. Bain de placage électrolytique de nickel pour le dépôt d'un revêtement décoratif de nickel sur un substrat devant

être traité, le bain de placage électrolytique comprenant au moins une source d'ions nickel, au moins un acide aminé et/ou au moins un acide carboxylique, qui n'est pas un acide aminé ; la concentration totale de l'acide aminé ou des acides aminés étant dans la plage de 1 à 10 g/l, la concentration totale de l'acide carboxylique ou des acides carboxyliques, qui n'est/ne sont pas un acide aminé, étant dans la plage de 10 à 40 g/l ; le bain de placage électrolytique étant exempt d'acide borique ; la concentration totale des ions nickel étant dans la plage de 55 à 80 g/l ; et le bain de placage électrolytique de nickel possédant une teneur en chlorures dans la plage de 7,5 à 40 g/l, **caractérisé en ce que** le bain de placage électrolytique de nickel comprend en outre

- de la saccharine et/ou un dérivé de saccharine sous forme d'un sel de saccharine à une concentration dans la plage de 1,5 à 10 g/l, et
- au moins un acide sulfonique et/ou un dérivé d'un acide sulfonique sous forme d'un sel d'acide sulfonique à une concentration totale dans la plage de 0,1 à 5 g/l.

2. Bain de placage électrolytique de nickel selon la revendication 1 **caractérisé en ce que** l'au moins un acide aminé est choisi dans le groupe constitué par la β-alanine, la glycine, l'acide glutamique l'acide DL-aspartique, la thréonine, la valine, la glutamine et la L-sérine.

3. Bain de placage électrolytique de nickel selon la revendication 1 ou 2 **caractérisé en ce que** l'au moins un acide carboxylique, qui n'est pas un acide aminé, est choisi dans le groupe constitué par des acides monocarboxyliques, des acides dicarboxyliques et des acides tricarboxyliques.

4. Bain de placage électrolytique de nickel selon la revendication 3 **caractérisé en ce que** l'au moins un acide carboxylique, qui n'est pas un acide aminé, est choisi dans le groupe constitué par l'acide tartrique, l'acide glycolique, l'acide malique, l'acide acétique, l'acide lactique, l'acide citrique, l'acide succinique, l'acide propanoïque, l'acide formique et l'acide glutarique.

5. Bain de placage électrolytique de nickel selon l'une des revendications précédentes **caractérisé en ce que** le bain de placage électrolytique comprend au moins deux différents acides carboxyliques, qui ne sont tous deux pas des acides aminés ; la concentration totale desdits deux différents acides carboxyliques, étant dans la plage de 10 à 40 g/l.

6. Bain de placage électrolytique de nickel selon l'une des revendications précédentes **caractérisé en ce que** le bain de placage électrolytique comprend au moins un acide aminé et un acide carboxylique, qui n'est pas un acide aminé ; la concentration totale dudit acide aminé étant dans la plage de 1 à 10 g/l, la concentration totale dudit acide carboxylique, qui n'est pas un acide aminé, étant dans la plage de 10 à 40 g/l.

7. Bain de placage électrolytique de nickel selon l'une des revendications précédentes **caractérisé en ce que** la concentration totale d'ions nickel est dans la plage de 60 à 75 g/l, préférablement de 62 à 72 g/l.

8. Bain de placage électrolytique de nickel selon l'une des revendications précédentes **caractérisé en ce que** la valeur de pH du bain de placage électrolytique se situe dans la plage de 2 à 6, préférablement de 3 à 5, plus préférablement de 3,5 à 4,7.

9. Procédé pour le dépôt d'un revêtement décoratif de nickel sur un substrat devant être traité comprenant les étapes de procédé suivantes :

i) mise en contact du substrat devant être traité avec un bain de placage électrolytique de nickel selon l'une quelconque des revendications 1 à 8 ;
ii) mise en contact d'au moins une anode avec le bain de placage électrolytique de nickel ;
iii) application d'une tension au substrat devant être traité et à l'au moins une anode ; et
iv) électrodéposition d'un revêtement décoratif de nickel sur le substrat devant être traité.

10. Procédé pour le dépôt d'un revêtement décoratif de nickel selon la revendication 9 **caractérisé en ce que** le procédé pour le dépôt est exécuté dans une plage de température de travail de 30 °C à 70 °C, préférablement de 40 °C à 65 °C, et plus préférablement de 50 °C à 60 °C.

11. Procédé pour le dépôt d'un revêtement décoratif de nickel selon la revendication 9 ou 10 **caractérisé en ce que** le procédé pour le dépôt est exécuté dans une plage de densité de courant de travail de 1 à 7 Ampère/dm^2 (ASD), préférablement de 1,5 à 6 ASD, et plus préférablement de 2 à 5 ASD.

12. Procédé pour le dépôt d'un revêtement décoratif de nickel selon l'une des revendications 9 à 11 **caractérisé en ce que** le procédé pour le dépôt est exécuté dans un temps de travail pour l'application de la tension et pour l'électrodéposition subséquente du revêtement décoratif de nickel (étapes de procédé iii) et iv)) dans la plage de 5 à 50 minutes, préférablement de 6 à 35 minutes, et plus préférablement de 8 à 25 minutes.

13. Procédé pour le dépôt d'un revêtement décoratif de nickel selon l'une des revendications 9 à 12 **caractérisé en ce que** le bain de placage électrolytique comprend en outre au moins une saccharine et/ou un dérivé de saccharine sous forme d'un sel de saccharine, préférablement le sel de sodium de saccharine, à une concentration dans la plage de 1,5 à 7 g/l, préférablement de 2 à 6 g/l ; et au moins un acide sulfonique et/ou un dérivé d'un acide sulfonique sous forme d'un sel d'acide sulfonique, préférablement choisi dans le groupe constitué par un acide allylsulfonique, un acide vinylsulfonique, le sel de sodium d'un acide allylsulfonique, le sel de sodium d'un acide vinylsulfonique, et des mélanges correspondants, à une concentration totale dans la plage de 0,25 à 3,5 g/l, préférablement de 0,5 à 2,0 g/l.

14. Utilisation d'un bain de placage électrolytique de nickel selon l'une des revendications précédentes 1 à 8 pour le dépôt d'un revêtement brillant de nickel par la mise en œuvre d'un procédé selon l'une des revendications 9 à 13.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

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