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

(57) The present invention is related to a nickel electroplating bath for depositing a decorative nickel coating on a substrate to be treated characterized in that 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.

The present invention is also related to a method for depositing a nickel coating on a substrate to be treated; and the use of such an inventive nickel electroplating bath for depositing a bright, semi-bright, satin, matte or non-conductive particle containing nickel coating by conducting such a method.

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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, semi-bright, satin, matte or non-conductive particle containing 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] 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

[0008] 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.

[0009] Additionally, it was especially an object of the present invention to provide a nickel electroplating bath, which shall be suitable as a basis for depositing various kinds of different nickel coatings regarding their optical appearance and their chemical properties, such as bright nickel coating, semi-bright nickel coating, satin nickel coating, matte nickel coating or non-conductive particle containing nickel coating.

[0010] Furthermore, it was an object of the present invention to provide a method for depositing various kinds of different nickel coatings regarding their optical appearance and their chemical properties, such as bright nickel coating, semi-bright nickel coating, satin nickel coating, matte nickel coating or non-conductive particle containing nickel coating.

Summary of the Invention

[0011] 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 14 focus on appropriate modifications of this method. Claim 15 relates to a use of such a nickel electroplating bath for depositing a bright, semi-bright, satin, matte or non-conductive particle containing nickel coating by conducting such a method.

[0012] The present invention accordingly provides a nickel electroplating bath for depositing a decorative nickel coating on a substrate to be treated characterized in that 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.

[0013] 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.

[0014] 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.

[0015] Additionally, it has been successfully achieved to provide a nickel electroplating bath, which is suitable as a basis for depositing various kinds of different nickel coatings regarding their optical appearance and their chemical properties, such as bright nickel coating, semi-bright nickel coating, satin nickel coating, matte nickel coating or non-conductive particle containing nickel coating. The nickel electroplating bath also shows good levelling performance and leads to well-levelled coatings.

Brief Description of the Tables

[0016] 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

[0017] In a preferred embodiment of the present invention, the nickel electroplating bath has a chloride content ranging from 10 to 30 g/l.

[0018] The expression "chloride content" means in the context of the present invention a chloride ion source.

[0019] Nickel chloride may be replaced partly by sodium chloride.

[0020] Further, chloride in the electrolyte may be replaced partly by equivalent amounts of bromide.

[0021] 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.

[0022] 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).

[0023] 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.

[0024] 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.

[0025] 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.

[0026] 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.

[0027] 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.

[0028] 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.

[0029] 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.

[0030] 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.

[0031] 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.

[0032] 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.

[0033] Furthermore, the nickel electroplating bath may comprise in certain embodiments of the present invention at least a wetting agent, such as 2-ethylhex-ylsulfate, 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.

[0034] 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.

[0035] 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.

[0036] 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.

[0037] 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.

[0038] 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.

[0039] Further, such a primary brightener can comprise propargyl alcohol and/or derivatives (ethoxylated or propoxylated) thereof.

[0040] 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.

[0041] 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.

[0042] 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.

[0043] 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.

[0044] 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.

[0045] 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 to 10 g/l, preferably from 1.5 to 7 g/l, more 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 0.1 to 5 g/l, preferably from 0.25 to 3.5 g/l, more preferably from 0.5 to 2.0 g/l.

[0046] 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.

[0047] In another alternative embodiment to the preceding one, 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.

[0048] Hereby, a semi-bright nickel coating is deposited. The selective choice of the above-mentioned additives shows again as in the aforementioned alternate embodiment the unique application of the inventive nickel electroplating bath for the purpose of depositing decorative nickel coatings of different optical appearance and chemical properties.

[0049] Additionally, the object of the present invention is also solved by making use of such a nickel electroplating bath for depositing a bright, semi-bright, satin, matte or non-conductive particle containing nickel coating by conducting such a method.

[0050] The present invention thus addresses the problem of providing a boric acid free nickel electroplating bath for depositing decorative nickel coatings of different optical appearance and chemical properties, such as bright nickel coating, semi-bright nickel coating, satin nickel coating, matte nickel coating or non-conductive particle containing nickel coating.

[0051] 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:

[0052] 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

[0053] 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).

[0054] 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.

[0055] The experiments given in Tables 1, 2 and 3 are numbered in consequent order.

[0056] Turning now to the Tables, Table 1 shows conducted experiments for bright nickel coatings in accordance with embodiments of the present invention.

[0057] 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.

[0058] The nickel concentration was 67 g/l for all experiments listed in Table 1.

[0059] 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 acids have been scrutinized as complexing agent for the nickel ions, there have 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.

[0060] 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

[0061] Table 2 exhibits comparative experiments for bright nickel coatings in accordance with comparative embodiments outside of the present invention.

[0062] 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	Conc	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

[0063] 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.

[0064] 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.

[0065] 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.

[0066] Comparative experiments 30 to 38 are also boric acid free.

[0067] 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.

[0068] Table 3 exhibits inventive experiments for bright nickel coatings in accordance with further embodiments of the present invention.

[0069] 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	Conc	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
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

[0070] 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 **characterized in that** 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.

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, lactic 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/dm^2 (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 to 10 g/l, preferably from 1.5 to 7 g/l, more 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 0.1 to 5 g/l, preferably from 0.25 to 3.5 g/l, more preferably from 0.5 to 2.0 g/l.

14. 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 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.

15. Use of a nickel electroplating bath according to one of the preceding claims 1 to 8 for depositing a bright, semi-bright, satin, matte or non-conductive particle containing nickel coating by conducting a method according to one of claims 9 to 14.

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EUROPEAN SEARCH REPORT

Application Number
EP 21 18 6683

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	DD 154 615 A1 (GALGON HANS U; PETZOLD INGEBORG) 7 April 1982 (1982-04-07) * abstract * * * examples 1, 2 *	1-4,6, 9-11,15	INV. C25D3/12 C25D3/16
X	US 4 159 926 A (BARNES CLIVE ET AL) 3 July 1979 (1979-07-03) * abstract * * examples 8, 10-12 * * claims 1, 6 * * column 2, line 22 - column 3, line 66 * * column 4, lines 36-44 *	1-4,7-15	
X	KR 101 693 514 B1 (POSCO [KR]) 6 January 2017 (2017-01-06) * claims 5, 11, 12, 14, 15 *	1,2, 9-11,15	
X	US 2006/096868 A1 (BUNCE SIONA [GB] ET AL) 11 May 2006 (2006-05-11) * abstract * * examples 2, 3 * * claims 1, 4, 6 * * paragraphs [0019], [0023], [0026] *	1,3-5, 7-12,15	TECHNICAL FIELDS SEARCHED (IPC) C25D
X	DE 10 2014 118614 A1 (HARTING KGAA [DE]) 16 June 2016 (2016-06-16) * abstract * * claims 1-3, 5, 8, 12, 14-18 * * paragraph [0024] *	1,3-5, 7-15	
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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	3 November 2021	Lange, Ronny

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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EUROPEAN SEARCH REPORT

Application Number
EP 21 18 6683

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 0 785 296 A1 (AT & T CORP [US]) 23 July 1997 (1997-07-23) * abstract * * examples 1-8 * * claim 1 * * page 2, line 55 * -----	1,3,4, 7-12,15	
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TECHNICAL FIELDS SEARCHED (IPC)

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

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The Hague	3 November 2021	Lange, Ronny

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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

- [ ] Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

- [ ] No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- [ ] All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

- [X] As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

- [ ] Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

- [ ] None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

- [ ] The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).

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LACK OF UNITY OF INVENTION SHEET B

Application Number
EP 21 18 6683

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 1-15

A nickel electroplating bath

1.1. claims: 2(completely); 1, 6-15(partially)

Inventive concept I regards a nickel electroplating bath for depositing a decorative nickel coating on a substrate to be treated, wherein the electroplating bath comprises at least a nickel ion source, at least one amino acid wherein the total concentration of the amino acid(s) is ranging from 1 to 10 g/l; and wherein the electroplating bath is free of boric acid.
Inventive concept I also regards the use of said electroplating bath and the method using said electroplating bath.

1.2. claims: 3-5(completely); 1, 6-15(partially)

Inventive concept II regards a nickel electroplating bath for depositing a decorative nickel coating on a substrate to be treated, wherein the electroplating bath comprises at least a nickel ion source, at least one one carboxylic acid, which is not an amino acid; wherein the total concentration of the carboxylic acid(s), which is/are not an amino acid, is ranging from 10 to 40 g/l; and wherein the electroplating bath is free of boric acid.
Inventive concept II also regards the use of said electroplating bath and the method using said electroplating bath.

Please note that all inventions mentioned under item 1, although not necessarily linked by a common inventive concept, could be searched without effort justifying an additional fee.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 21 18 6683

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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03-11-2021

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