The present invention relates to a cyanide-free electrolyte which contains a phosphate and aliphatic or aromatic thio compounds and also to a process for the electrolytic deposition of an alloy of the elements copper and tin and optionally zinc. The electrolyte and the process are characterized in that stannate ions and copper ions and optionally zinc(II) ions and also aliphatic and/or aromatic thio compounds are present in the electrolyte used. The electrolyte can optionally additionally contain carboxylic acids, wetting agents and/or brighteners. The present invention further provides a process for the electrolytic deposition of alloys of copper, tin and optionally zinc on consumer goods and decorative goods using the electrolyte of the invention.
The present invention relates to a cyanide-free electrolyte which contains a phosphate and aliphatic or aromatic thioc compounds and also to a process for the electrolytic deposition of an alloy of the elements copper and tin and optionally zinc. The electrolyte and the process are characterized in that stannate ions and copper ions and optionally zinc(II) ions and also aliphatic or aromatic thioc compounds are present in the electrolyte used.

The electrolytic deposition of brass (Cu—Zn alloy) and bronzes (Cu—Sn alloy) on consumer goods or decorative goods is adequately known. These alloys serve, inter alia, as substitute for nickel-containing finishing layers and are applied, for example, to appropriate substrates in electrochemical drum coating or rack coating processes.

In the production of brass and bronze layers for the electronics industry, the solderability of the resulting layer and possibly its mechanical adhesive strength are the critical properties. The appearance of the layers is generally less important than their functionality for use in this field. In contrast, in the production of bronze or brass layers on consumer goods, the decorative effect and also durability of the layer with an appearance which is as unchanged as possible are the important target parameters.

For the production of brass and bronze layers, not only the conventional process using cyanide-containing and thus highly toxic, alkaline baths but also various electrochemical processes which can usually be assigned to one of two main groups known in the prior art as a function of the composition of their electrolytes are known: processes using organosulfonic acid-based electrolytes and processes using phosphoric acid-based baths. Diphosphoric acid is also referred to as pyrophosphoric acid. Both processes have specific disadvantages which significantly restrict their practical usability. Thus, tin in divalent form is added in both electrolyte systems and oxidizes to ineffective tin(IV) during operation of the bath, which considerably limits the life of the electrolytes. A further restriction arises in the case of the group of organosulfonic acid-based electrolytes. These operate in the strongly acidic pH range and are thus not suitable for particular fields of use, for example coating of pressure-cast zinc.

EP 2 032 743 B1 describes an electrolyte for producing Cu—Sn—Zn alloy layers for photovoltaic cells. This electrolyte is phosphate-pyrophosphate-based and uses tin in tetravalent form as stannate, in contrast to all known cyanide-free systems. Matt Cu—Sn—Zn layers can be deposited from this electrolyte in a very narrow current density window. This type of electrolyte in the form described is not suitable for production of decorative bronze layers in drum or rack plating.

EP 1 961 840 A1 discloses a non-toxic electrolyte for the deposition of decorative bronze alloy layers, which contains the metals to be deposited in the form of water-soluble salts, with the electrolyte containing one or more phosphoric acid derivatives as complexing agents and being free of cyanides, thiourea derivatives and thio derivatives. The electrolyte contains copper and tin or copper, tin and zinc as metals to be deposited. Tin can be used as divalent or tetravalent tin salt in this case. Stannates are not disclosed.

EP 1 961 840 A1 teaches that bronze layers which have been deposited electrochemically from baths with addition of thioc compounds have a spotty or matt-veiled appearance and are therefore not suitable for decorative coating of consumer goods.

WO 2013/092312 A1 discloses a cyanide-free, pyrophosphate-containing electrolyte and a process for the electrolytic deposition of a ternary alloy of copper, tin and zinc. In this case, stannate ions are present in addition to zinc(II) ions and copper(II) ions in the electrolyte. It is not possible to produce uniformly white coatings over a wide current density range when using this electrolyte, so that it is unsuitable for coating decorative articles.

WO 2013/092314 A1 discloses a cyanide-free, pyrophosphate-free and phosphoric acid-free electrolyte and a process for the electrolytic deposition of a ternary alloy of copper, tin and zinc. In this case, stannate ions are present in addition to zinc(II) ions and copper(II) ions in the electrolyte. As in the case of the electrolyte disclosed in WO 2013/092312 A1, it is also not possible to produce uniformly white coatings over a wide current density range when using this electrolyte, so that it is unsuitable for coating decorative articles.

EP 2 071 057 A2 describes a composition for the electrolytic deposition of white bronzes, which contains tin, copper and zinc ions and at least one mercaptan selected from the group consisting of mercaptotriazoles and mercaptotetrazoles. Copper can be present in the form of Cu(I) and Cu(II) salts in the composition according to that invention. The tin compounds disclosed are Sn(II) salts. The composition does not contain any phosphates, pyrophosphates or phosphonates. In all examples, bronzes are deposited at pH values of ±3.

EP 1 001 054 A2 discloses electrochemical baths for the deposition of tin-copper alloys. The baths comprise a water-soluble tin(II) or tin(IV) salt, a water-soluble copper(I) or copper(II) salt, an organic or inorganic acid or a water-soluble salt thereof and also at least one compound selected from the group consisting of thiourea and thio compounds. When sodium stannate(IV) is used, Cu(I) cyanide is also used at the same time—the electrolytes are thus not cyanide-free. The tin compounds serve as bath stabilizers or complexing agents. The inorganic acid or the salt thereof can be phosphoric acid, condensed phosphoric acid, viz. pyrophosphoric acid, and phosphonic acid. The electrochemical baths according to EP 1 001 054 A2 do not contain any zinc compounds. The electrochemical baths according to EP 1 001 054 A2 allow the deposition of tin-copper alloys whose appearance can vary as a function of the copper content, the presence or absence of brighteners and the selected water-soluble metal salts from white to greyish white and from bright to matt.

WO 2010/003621 A1 discloses electrolyte baths for the deposition of decorative bronzes, which baths contain copper, tin and optionally zinc and also one or more phosphonic acid derivatives, a disulfide and a carbonate or hydrogen carbonate. The tin is present as tin(II) salt in this case.

It is an object of the present invention to provide cyanide-free electrolytes and corresponding processes for the deposition of white copper-tin alloys and white copper-tin-zinc alloys, which are able to deposit coatings of uniform color on decorative articles over a wide current density range. Said deposition should be able to be brought about very optimally with a preferred stoichiometry. The electrolyte should have a very simple make-up. Furthermore, the
process and the electrolytes of the invention should be superior to the processes and electrolytes known from the
prior art from ecological and economic points of view.

[0013] These objects and further objects which will be
obvious to a person skilled in the art from the prior art are
achieved by electrolytes having the features of the present
claim 1 and by a corresponding process as claimed in claim
10. Preferred embodiments of the respective invention may
be found in the dependent claims dependent on these claims.

[0014] The object of providing electrolytes for the depo-
sition of white copper-tin alloys and white copper-tin-zinc
alloys is achieved according to the invention by an aqueous,
cyanide-free electrolyte for the electrolytic deposition of an
alloy of copper, tin and optionally zinc, which comprises
at least one salt from the group consisting of phosphates,
phosphonates, polyphosphates, diphosphates and mixtures
thereof
and
at least one compound selected from the group consisting of
aliphatic and aromatic thio compounds, wherein the metals
copper and optionally zinc to be depos-
ited are present in dissolved form and tin is present as
dissolved Sn(IV) salt
and wherein the pH of the aqueous, cyanide-free electrolyte
is greater than or equal to 9.

[0015] It has been found that advantageous copper-tin and
copper-tin-zinc alloy compositions can be obtained from the
electrolyte described here when at least one salt from the
group consisting of phosphates, phosphonates, polyphos-
phates, diphosphates and mixtures thereof is present in the
electrolyte in an excess over the copper and tin ions, when
a particular ratio of copper to tin ions is set at the same time
and when tin is present at the same time as dissolved Sn(IV)
salt. If the electrolyte additionally contains zinc in order to
be able to deposit a ternary alloy, both zinc and copper are
present in dissolved form. The electrolyte additionally con-
tains an aliphatic or aromatic thio compound which com-
plexes dissolved Cu salts. The pH of the aqueous electrolyte
of the invention is greater than or equal to 9 and thus
alkaline. The use of aliphatic and aromatic thio compounds
in phosphate- and Sn(IV)-based Cu—Sn alloy electrolytes,
which optionally additionally contain Zn, makes it possible
to complex copper and at the same time promote the
codeposition of tin and optionally zinc in current density
ranges from 0.1 to 100 A/dm², advantageously from 0.3 to
1.0 A/dm². The usable current density window is thereby
considerably widened compared to known electrolytes.
When the electrolytes of the invention are used, uniformly
white coatings of copper-tin and copper-tin-zinc bronzes
are deposited over a wide working range.

[0016] “Uniformly” here means that the coatings have a
homogeneous appearance, i.e. same color and same layer
properties in respect of gloss, hardness and corrosion resis-
tance.

[0017] Uniformly white coatings of copper-tin bronzes
and copper-tin-zinc bronzes can be deposited with the aid of
the electrolyte composition of the invention. The color white
can be defined more precisely by means of an L*a*b* color
measurement.

[0018] Electrolytes which use stannate as tin source are
known for the deposition of copper-tin and copper-tin-zinc
alloys in the prior art, for example EP 1 001 054 A2 as men-
tioned at the outset. However, stannates are always used
in combination with copper cyanides there. In cyanide
complexes, Cu is essentially present as Cu(I) cyanide, i.e. as
[Cu(CN)₂]⁻. The deposition of Cu—Sn layers from electro-
ytes containing stannate and Cu(I) cyanide was carried out
in EP 1 001 054 A2 at pH values in the range from 12 to 13
and led to bronze layers whose structure and color was
nonuniform. In addition, the bronze layers displayed burnt
deposits. The alkaline baths comprising stannate and Cu(I)
cyanide also had a poor bath stability.

[0019] The use of Sn(II) salts in combination with Cu(I)
cyanide instead of stannate and Cu(I) cyanide likewise does
not lead to uniform Cu—Sn layers since Sn(II) is at least
partly oxidized to Sn(IV) in the presence of Cu(I) cyanide,
as a result of which the abovementioned disadvantages of
baths containing stannate and Cu(I) cyanide also occur here.

[0020] Phosphates and pyrophosphates are used in the
prior art for stabilizing Cu—Sn and Cu—Sn—Zn electro-
ytes, for example in the documents WO 2013/092312 A1
and WO 2013/092314 A1 cited at the outset. However, it is
not possible to produce uniformly white coatings over a
wide current density range when using these cyanide-free
electrolytes based on pyrophosphates or phosphates and
stannate. In the case of the electrolytes disclosed there, the
alloy composition is very dependent on the current density
employed. In the relatively low current density range, red
coatings having a high proportion of Cu and a low propor-
tion of Zn are obtained, while in the high current density
range, the proportion of Zn is significantly higher but the
coatings are matt gray. These electrolytes are therefore not
suitable for decorative coatings. In high pH ranges, i.e. in
particular at pH values greater than or equal to 9, there have
hitherto been no known cyanide-free electrolytes in which
Sn(IV) salts are stable and Cu and Sn can be deposited
jointly in the form of uniformly white coatings.

[0021] The aqueous electrolytes of the invention and the
process for the deposition of Cu—Sn and Cu—Sn—Zn
alloys are explained below, with the invention encompassing
all the embodiments indicated below, both individually and
in combination with one another.

[0022] Copper can be added to the electrolyte in the form of
monovalent or divalent copper salts or mixtures thereof.
Any zinc optionally used is present in the form of divalent
ions in the electrolyte. Under the reaction conditions ac-
cording to the invention, copper and optionally zinc are de-
posited from their water-soluble layerphases. Suitable water-
soluble compounds of copper and zinc are selected from the
group consisting of pyrophosphates, carbonates, hydrogen-
carbonates, sulfites, sulfates, phosphates, nitrates, nitrates,
halides, hydroxides, oxo-hydroxides, oxides and combi-
nations thereof. Halides can be fluorides, chlorides, bro-
nides or iodides. Preference is given to using carbonates,
hydrogencarbonates, sulfates or pyrophosphates of copper
and zinc. For the present purposes, the term “water-soluble”
refers to salts of copper and zinc whose solubility in water is
at least 0.1 g/l at 25°C.

[0023] In an advantageous embodiment, copper is added
to the electrolyte in the form of a Cu(I) salt.

[0024] In an advantageous embodiment, copper is added
to the electrolyte in the form of a Cu(II) salt.

[0025] Tin is added to the electrolyte of the invention as
Sn(IV) salt, i.e. in tetraenolic form. Suitable Sn(IV) salts are
SnO₂, Sn(OH)₄, SnCl₂, SnBr₂, SnI₂, Sn(SO₄)₂, SnSO₃, SnS₂, Na₂SnO₃, K₂SnO₃, K₂SnO₂Cl₂. In an advantageous
embodiment, the Sn(IV) salt is a stannate. The stannate is
advantageously sodium stannate Na₂SnO₃ or potassium stannate K₂SnO₃. In a particularly advantageous embodiment, the Sn(IV) salt is sodium stannate. In a further particularly advantageous embodiment, the Sn(IV) salt is potassium stannate.

[0026] The salts of copper, tin and optionally zinc present in the electrolyte of the invention will hereinafter be summarized under the term “brass-forming salts”.

[0027] The electrolyte of the invention further comprises at least one salt from the group consisting of phosphates, phosphonates, polyphosphates, diphosphates and mixtures of these salts.

[0028] Suitable phosphates are, for example, disodium hydrogenphosphate and dipotassium hydrogenphosphate. A person skilled in the art will know that the tribasic phosphoric acid dissociates over three stages and that both dihydrogenphosphates and hydrogenphosphates are ampholytes. The ratio of phosphate (PO₄³⁻), hydrogenphosphate (HPO₄²⁻) and dihydrogenphosphate (H₂PO₄⁻) ions in a solution is known to depend on the pH of the solution. For the purposes of the present invention, phosphate, hydrogenphosphate and dihydrogenphosphate ions will therefore be referred to summarily as “phosphate ions”. In an analogous way, the tribasic phosphonic acid also dissociates over three stages, and both dihydrogenphosphonates and hydrogenphosphonates are ampholytes. The salts of phosphoric acid are referred to summarily as “phosphonates”. A person skilled in the art will know that diphosphoric acid and polyphosphoric acids are also polybasic and the ratio of the corresponding anions of these acids which are present depends, as in the case of phosphoric and phosphonic acids, on the pH of the solution. For the purposes of the present invention, it is possible to use their ammonium, lithium, sodium and potassium salts, independently of the number of hydrogen atoms of phosphoric acid or polyphosphoric acids that have been replaced by ammonium, lithium, sodium or potassium cations. The compounds from the group consisting of phosphates, phosphonates, polyphosphates and diphosphates which are used in the electrolyte of the invention are salts of phosphoric acid, phosphoric acid, polyphosphoric acid and diphosphoric acid. The salts here are advantageously ammonium, lithium, sodium or potassium salts of these acids. In the case of polybasic acids in which more than one hydrogen has been replaced by ammonium, lithium, sodium or potassium cations, these cations can be identical or different.

[0029] “Mixtures” of phosphates, phosphonates, polyphosphates and diphosphates can be mixtures of at least two phosphates, at least two phosphonates, at least two polyphosphates or at least two diphosphates. As an alternative, these mixtures can be mixtures of at least two compounds from different groups of salts containing phosphorus and oxygen, i.e., for example, a phosphate and a phosphonate or two phosphates and one diphosphate. Phosphates, phosphonates, polyphosphates and diphosphates are the four groups of salts containing phosphorus and oxygen which are used for the purposes of the present invention.

[0030] As indicated above, the phosphates, phosphonates, polyphosphates and diphosphates are present in excess over the copper and tin ions in the electrolyte. Here, “excess” means that the sum of the molar amounts of the phosphates, phosphonates, polyphosphates and diphosphates is greater than the sum of the molar amounts of the copper and tin ions.

[0031] In an advantageous embodiment the total concentration of the at least one salt from the group consisting of phosphates, phosphonates, polyphosphates, diphosphates and mixtures thereof in the electrolyte is from 0.05 mol/l to 5.0 mol/l.

[0032] In a particularly advantageous embodiment of the present invention, the at least one salt from the group consisting of phosphates, phosphonates, polyphosphates and diphosphates in the aqueous, cyanide-free electrolyte of the invention is a hydrogenphosphate. Particularly suitable hydrogenphosphates are sodium hydrogenphosphosphate and dipotassium hydrogenphosphate. In an advantageous embodiment, the electrolyte contains from 20 to 150 g/l of dipotassium hydrogenphosphate.

[0033] In a further advantageous embodiment, the electrolyte contains from 20 to 150 g/l of disodium hydrogenphosphate.

[0034] Suitable pyrophosphates are, for example, sodium pyrophosphate and potassium pyrophosphate or mixtures thereof. In an advantageous embodiment, the electrolyte contains from 5 to 40 g/l of potassium pyrophosphate. In a further advantageous embodiment, the electrolyte contains from 5 to 40 g/l of sodium pyrophosphate.

[0035] In a further advantageous embodiment, the electrolyte contains from 20 to 150 g/l of hydrogenphosphate, preferably 90 g/l of hydrogenphosphate, in the form of disodium and/or dipotassium hydrogenphosphate and from 5 to 40 g/l of pyrophosphate, in the form of sodium and/or potassium pyrophosphate.

[0036] The electrolyte of the invention additionally contains at least one compound selected from the group consisting of aliphatic and aromatic thio compounds. In an advantageous embodiment, at least one compound from the group consisting of aliphatic and aromatic thio compounds is present in a concentration of from 0.02 to 10 g/l in the electrolyte.

[0037] Here, “at least one compound from the group consisting of aliphatic and aromatic thio compounds” means that the electrolyte of the invention comprises

[0038] precisely one aliphatic thio compound or

[0039] precisely one aromatic thio compound or

[0040] at least two thio compounds which are all aliphatic or

[0041] at least two thio compounds which are all aromatic or

[0042] at least one aliphatic thio compound and at least one aromatic thio compound.

[0043] Suitable aliphatic thio compounds are, by way of example but not exhaustively, aliphatic carboxylic and sulfonic acids which contain a thio group. Suitable aromatic thio compounds are, by way of example but not exhaustively, pyridine, pyrimidine, pyrazine and hydantoin derivatives which contain a thio group. In an advantageous embodiment, the thio compound is selected from among 2-mercaptopropanoic acid, mercaptosuccinic acid, 2-thiocroproanedicarboxylic acid, Na 3-mercapto-1-propanesulfonate, 2-mercaptoanionic acid, 2-thiouracil, 4,6-dihydroxy-2-mercaptothymidin, 2-mercaptothimidine, 2-thiocytoise, 6-mercaptothimidine-4-carboxylic acid, 2-mercaptothimidine-4-ol, 2-thiohydantoin, 5-sulfosaliclyc acid. It is particularly advantageous to use mercaptosuccinic acid and 4,6-dihydroxy-2-mercaptothimidine.

[0044] In a further advantageous embodiment, the thio compound is selected from among from 1 to 10 ml of
2-mercaptopropionic acid, from 0.5 to 10 g of thiopropanedicarboxylic acid, from 0.05 to 5 g of Na 3-mercaptopropanesulfonate, from 0.05 to 5 g of 2-mercaptopnicotinic acid, from 0.02 to 5 g of 2-thiourea and from 0.5 to 10 g of 4,6-dihydroxy-2-mercaptopirimidine, in each case per liter of electrolyte.

[0045] The pH of the aqueous electrolyte of the invention is greater than or equal to 9. In a particularly advantageous embodiment, the electrolyte has a pH of greater than or equal to 11.

[0046] In a particularly advantageous embodiment, the electrolyte of the invention additionally contains at least one aliphatic saturated or unsaturated dicarboxylic or tricarboxylic acid, an aromatic carboxylic acid, salts and mixtures thereof. "At least one carboxylic acid, salts and mixtures thereof" means that carboxylic acids and salts thereof mentioned below can be used either individually or in any combination. The aliphatic saturated dicarboxylic acid is advantageously selected from among oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, tartaric acid, malic acid. The aliphatic unsaturated dicarboxylic acid is advantageously selected from among maleic acid and fumaric acid. A suitable tricarboxylic acid is citric acid. Suitable aromatic carboxylic acids are, for example, benzoic acid, benzen-1,3,5-tricarboxylic acid and salicylic acid.

The salts of the carboxylic acids mentioned are advantageously the ammonium, lithium, sodium or potassium salts. In the case of salts of polybasic carboxylic acids, the hydrogen atoms of one or more or all carboxyl groups can be replaced by ammonium, lithium, sodium or potassium ions.

[0047] If in the case of polybasic carboxylic acids at least two carboxyl hydrogen atoms have been replaced by ammonium, lithium, sodium or potassium ions, these ions can be identical or different. The total concentration of the carboxylic acids or salts thereof is advantageously from 5 to 100 g/l of electrolyte.

[0048] In an advantageous embodiment, the carboxylic acid is selected from among oxalic acid, tartaric acid and citric acid or the carboxylic acid salt is selected from among oxalates, tartrates and citrates.

[0049] In a particularly advantageous embodiment, the carboxylic acid or salt thereof is oxalic acid or an oxalate. The use of dipotassium oxalate \( K_2C_2O_4 \) is very particularly advantageous.

[0050] In a further particularly advantageous embodiment, tartaric acid or a salt thereof, for example potassium sodium tartrate, is used.

[0051] In a further particularly advantageous embodiment, citric acid or a citrate, for example potassium citrate, is used.

[0052] In a further advantageous embodiment, the electrolyte of the invention contains at least one further salt. The anions of these salts are selected from the group consisting of sulfates, fluorides, chlorides, bromides, iodides, carbonates, formates, acetates, propionates, butyrates, valerates, nitrates, nitrites, sulfonates, alkylsulfonates, in particular methanesulfonates, amidox sulfonates, sulfamates, anions of aminoancarbonylic acids and N-heterocyclic carboxylic acids. The cations of these salts are selected from among ammonium, lithium, sodium and potassium ions. In the case of polybasic acids, one or all hydrogen atoms can have been replaced by the cations mentioned. If more than one hydrogen atom has been replaced by one of the abovementioned cations, these cations can be identical or different. The at least one further salt will hereinafter also be referred to as “conducting salt”.

[0053] In a further advantageous embodiment, the electrolyte of the invention additionally comprises at least one brightener. Additions of brighteners to electrolytes for the deposition of bronzes are known to those skilled in the art and can be employed without going outside the scope of protection of the claims. The brightener is advantageously selected from among bis(3-sulfopropyl) disulfide disodium salt, 3-sulfopropyl O-ethylthiocarbonate potassium salt, 1-(3-sulfopropyl)pyridinium betaine, 1-(2-hydroxy-3-sulfopropyl)pyridinium betaine, 3-(2-benzothiazole-2-mercapto)propanesulfonic acid sodium salt, S-isothiouronium 3-propanesulfonate, N,N-dimethylthiocarbamate sodium salt, benzyl-3-sodicarboxypyrindinium chloride, 3-formyl-1-(3-sulfopropyl)pyridinium betaine, N-(3-sulfopropyl)saccharin sodium salt, saccharin sodium salt, carbethoxyisothiouronium betaine, cocoadamidopropyldimethylammonium 2-hydroxypropanesulfato betaine, N-(3-cocoadamideprop-N,N-dimethyl)-(3-sulfopropyl)ammonium betaine, 6-carboxy-2, 4-dihydroxypropyrimidine, 2-butenoic acid.

[0054] In a further advantageous embodiment, the electrolyte of the invention additionally comprises at least one wetting agent. Wetting agent additions to the electrolytes for the deposition of bronzes are known to those skilled in the art and can be employed without going outside the scope of protection of the claims. The wetting agent is advantageously selected from among

[0055] a cationic, amine polymer having urea groups,

[0056] a cationic polymer which is made up of the monomers morpholine, epichlorohydrin and imidazole and has the general formula \( (C_2H_4NO)_x(C_2H_4C(O))_y(C_2H_4N_2)_z \),

[0057] a cationic polymer which is made up of the monomers epichlorohydrin and imidazole and has the general formula \( (C_2H_4C(O))_x(C_2H_4N_2)_y \),

[0058] N-alkyl-N-(1-oxoalkyl)amino acids and derivatives and salts thereof

[0059] and mixtures of these wetting agents.

[0060] When salts of N-alkyl-N-(1-oxoalkyl)amino acids are used, they are advantageously the ammonium, lithium, sodium or potassium salts.

[0061] The use of brighteners and wetting agents enables the gloss of the layer to be set in all gradations between silk-matt and high-gloss.

[0062] Particularly advantageous embodiments of the present invention are electrolytes having the following compositions:

General Composition 1:

[0063] bronze-forming salts,

[0064] at least one salt from the group consisting of phosphates, phosphonates, polyphosphates, diphosphates and mixtures of these salts,

[0065] at least one compound from the group consisting of aliphatic and aromatic thi compounds.
General Composition 2:

- [0066] bronze-forming salts,
- [0067] at least one salt from the group consisting of phosphates, phosphonates, polyphosphates, diphosphates and mixtures of these salts,
- [0068] at least one compound from the group consisting of aliphatic and aromatic thio compounds,
- [0069] at least one aliphatic saturated or unsaturated dicarboxylic or tricarboxylic acid, an aromatic carboxylic acid, salts and mixtures thereof.

General Composition 3:

- [0070] bronze-forming salts,
- [0071] at least one salt from the group consisting of phosphates, phosphonates, polyphosphates, diphosphates and mixtures of these salts,
- [0072] at least one compound from the group consisting of aliphatic and aromatic thio compounds,
- [0073] at least one conducting salt.

General Composition 4:

- [0074] bronze-forming salts,
- [0075] at least one salt from the group consisting of phosphates, phosphonates, polyphosphates, diphosphates and mixtures of these salts,
- [0076] at least one compound from the group consisting of aliphatic and aromatic thio compounds,
- [0077] at least one aliphatic saturated or unsaturated dicarboxylic or tricarboxylic acid, an aromatic carboxylic acid, salts and mixtures thereof,
- [0078] at least one conducting salt.

Furthermore, embodiments of the present invention in which the electrolytes having the abovementioned general compositions 1 to 4 additionally contain at least one brightener, at least one wetting agent or at least one brightener and at least one wetting agent are particularly advantageous. All particularly advantageous embodiments of the electrolyte of the present invention are aqueous, cyanide-free and have a pH of greater than or equal to 9.

According to the invention, the metals copper and optionally zinc are present in ionically dissolved form in the electrolyte and tin is present as stannate or another Sn(IV) salt. The ion concentration of copper is advantageously from 0.05 to 10 g/l, the ion concentration of tin as stannate is advantageously from 0.5 to 40 g/l and the ion concentration of zinc is advantageously from 0.1 to 10 g/l. It is particularly advantageous for the ion concentration of copper to be from 0.5 to 2 g/l of electrolyte, that of tin as stannate to be from 10 to 20 g/l of electrolyte and that of zinc to be from 2.0 to 4.0 g/l. The indicated advantageous ion concentrations of copper, tin and optionally zinc apply to all abovementioned advantageous embodiments.

The present invention likewise provides a process for the electrolytic deposition of Cu—Sn and Cu—Sn—Zn alloy layers, in which the substrate to be coated is dipped as cathode into an electrolyte according to the invention and current flow is established between the anode and the cathode. It goes without saying that the embodiments named as preferred for the electrolyte are likewise preferred for the process.

It is advantageous for the proportion of copper in the ternary alloy deposited to be in the range from 20 to 80% by weight, the proportion of tin to be in the range from 10 to 60% by weight and the proportion of zinc to be in the range from 1 to 30% by weight. Here, the sum of the proportions of all participating metals in the alloy is in each case 100% by weight.

In the case of the binary alloy, the proportion of copper is in the range from 30 to 90% by weight and the proportion of tin is in the range from 10 to 70% by weight. The sum of the proportions of all participating metals in the alloy is in each case 100% by weight.

In an advantageous embodiment, the ternary alloy deposited is a white layer having a proportion of copper of from 50 to 60% by weight, a proportion of tin of 35-45% by weight and a proportion of zinc of 5-15% by weight, where the sum of the proportions of all participating metals in the alloy is in each case 100% by weight.

The deposited alloy can in all embodiments described here have a thickness of 0.4-5 μm, preferably 0.5-3 μm and very particularly preferably 1-2 μm.

It may be remarked that the alloy composition can likewise change with the temperature prevailing in the electrolysis. The electrolysis is therefore carried out in the range from 20 to 90° C., preferably from 30 to 60° C. and very preferably at about 45° C.

Likewise, the composition of the binary alloy of copper and tin or the ternary alloy of copper, tin and zinc can change with the current density set in the electrolysis. It is advantageous to set a current density in the range from 0.1 to 100 ampere per square decimeter. The current density is preferably from 0.2 to 5.0 ampere per square decimeter, very preferably from 0.3 to 1 ampere per square decimeter.

As anode, it is possible to use all electrodes which a person skilled in the art would consider for this purpose. Preference is given to using insoluble anodes (e.g. platinated titanium anodes or mixed metal oxide anodes). In this context, soluble anodes composed of a material selected from the group consisting of electrolytic copper, phosphorus-containing copper, tin, tin-copper alloy, zinc-copper alloy and zinc-tin-copper alloy or combinations of these anodes can likewise be used.

The electrolyte of the invention and the process of the invention can be used for the electrolytic deposition of alloys of copper, tin and optionally zinc on consumer goods and decorative goods.

EXAMPLES

Example 1

Electrolyte without Addition of a Thio Compound

<table>
<thead>
<tr>
<th>Basic composition</th>
<th>90 g/l of dipotassium hydrogenphosphate</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>15 g/l of dipotassium oxalate</td>
</tr>
<tr>
<td></td>
<td>10 g/l of potassium pyrophosphate</td>
</tr>
<tr>
<td></td>
<td>10 g/l of Sn as sodium stannate</td>
</tr>
<tr>
<td></td>
<td>2.0 g/l of Zn as zinc sulfate</td>
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<tr>
<td></td>
<td>0.5 g/l of Cu as copper sulfate</td>
</tr>
<tr>
<td>pH</td>
<td>pH 11.5</td>
</tr>
<tr>
<td>Temperature</td>
<td>45° C.</td>
</tr>
<tr>
<td>Current density</td>
<td>0.3 A/dm²</td>
</tr>
</tbody>
</table>

Appearance: grey, matt, nonuniform
Example 2

Electrolyte with 2-mercaptopropionic acid

<table>
<thead>
<tr>
<th>Basic composition</th>
<th>50 g/l of dipotassium hydrogen phosphate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50 g/l of dipotassium oxalate</td>
</tr>
<tr>
<td></td>
<td>10 g/l of potassium pyrophosphate</td>
</tr>
<tr>
<td></td>
<td>10 g/l of Sn as potassium stannate</td>
</tr>
<tr>
<td></td>
<td>2.0 g/l of Zn as zinc sulfate</td>
</tr>
<tr>
<td></td>
<td>0.5 g/l of Cu as copper (I) chloride</td>
</tr>
<tr>
<td></td>
<td>2 ml/l of 2-mercaptopropionic acid</td>
</tr>
<tr>
<td>pH</td>
<td>pH 10.5</td>
</tr>
<tr>
<td>Temperature</td>
<td>50° C.</td>
</tr>
<tr>
<td>Current density</td>
<td>0.5 A/dm²</td>
</tr>
</tbody>
</table>

Appearance: white, matt

Example 3

Electrolyte with Na 3-mercapto-1-propanesulfonate

<table>
<thead>
<tr>
<th>Basic composition</th>
<th>70 g/l of potassium dihydrogen phosphate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 g/l of potassium citrate</td>
</tr>
<tr>
<td></td>
<td>20 g/l of potassium pyrophosphate</td>
</tr>
<tr>
<td></td>
<td>10 g/l of Sn as sodium stannate</td>
</tr>
<tr>
<td></td>
<td>10 ml/l of methanesulfonic acid</td>
</tr>
<tr>
<td></td>
<td>2.0 g/l of Zn as zinc sulfate</td>
</tr>
<tr>
<td></td>
<td>0.5 g/l of Cu as copper (I) iodide</td>
</tr>
<tr>
<td></td>
<td>2 g/l of Na 3-mercapto-1-propanesulfonate</td>
</tr>
<tr>
<td>pH</td>
<td>pH 10.0</td>
</tr>
<tr>
<td>Temperature</td>
<td>45° C.</td>
</tr>
<tr>
<td>Current density</td>
<td>0.4 A/dm²</td>
</tr>
</tbody>
</table>

Appearance: white, shiny

Example 4

Electrolyte with Thiopropanedicarboxylic Acid

<table>
<thead>
<tr>
<th>Basic composition</th>
<th>80 g/l of dipotassium hydrogen phosphate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 g/l of dipotassium oxalate</td>
</tr>
<tr>
<td></td>
<td>10 g/l of Sn as potassium stannate</td>
</tr>
<tr>
<td></td>
<td>2.0 g/l of Zn as zinc sulfate</td>
</tr>
<tr>
<td></td>
<td>0.5 g/l of Cu as copper (I) chloride</td>
</tr>
<tr>
<td></td>
<td>2 g/l of thiopropanedicarboxylic acid</td>
</tr>
<tr>
<td></td>
<td>50 mg/l of 3-formyl-1-(3-sulfopropyl)pyridinium betaine</td>
</tr>
<tr>
<td>pH</td>
<td>pH 10.5</td>
</tr>
<tr>
<td>Temperature</td>
<td>40° C.</td>
</tr>
<tr>
<td>Current density</td>
<td>0.5 A/dm²</td>
</tr>
</tbody>
</table>

Appearance: white, shiny

Example 5

6-mercaptopuridine-4-carboxylic acid

<table>
<thead>
<tr>
<th>Basic composition</th>
<th>30 g/l of dipotassium hydrogen phosphate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>70 g/l of dipotassium oxalate</td>
</tr>
<tr>
<td></td>
<td>10 g/l of Sn as sodium stannate</td>
</tr>
</tbody>
</table>

Appearance: white, matt

Example 6

Thiouracil

<table>
<thead>
<tr>
<th>Basic composition</th>
<th>80 g/l of dipotassium hydrogen phosphate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 g/l of dipotassium oxalate</td>
</tr>
<tr>
<td></td>
<td>15 g/l of Sn as potassium stannate</td>
</tr>
<tr>
<td></td>
<td>3.0 g/l of Zn as zinc sulfate</td>
</tr>
<tr>
<td></td>
<td>1.0 g/l of Cu as copper sulfate</td>
</tr>
<tr>
<td>pH</td>
<td>pH 11.0</td>
</tr>
<tr>
<td>Temperature</td>
<td>45° C.</td>
</tr>
<tr>
<td>Current density</td>
<td>0.3 A/dm²</td>
</tr>
</tbody>
</table>

Appearance: white, shiny, inhomogeneous

Example 7

4,6-Dihydroxy-2-mercaptopuridine

<table>
<thead>
<tr>
<th>Basic composition</th>
<th>50 g/l of dipotassium hydrogen phosphate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 g/l of dipotassium oxalate</td>
</tr>
<tr>
<td></td>
<td>10 g/l of Sn as sodium stannate</td>
</tr>
<tr>
<td></td>
<td>3.0 g/l of Zn as zinc sulfate</td>
</tr>
<tr>
<td></td>
<td>1.0 g/l of Cu as copper sulfate</td>
</tr>
<tr>
<td></td>
<td>5 g/l of 4,6-dihydroxy-2-mercaptopuridine</td>
</tr>
<tr>
<td>pH</td>
<td>pH 11.0</td>
</tr>
<tr>
<td>Temperature</td>
<td>45° C.</td>
</tr>
<tr>
<td>Current density</td>
<td>0.4 A/dm²</td>
</tr>
</tbody>
</table>

Appearance: white, semigloss

Example 8

4,6-Dihydroxy-2-mercaptopuridine

<table>
<thead>
<tr>
<th>Basic composition</th>
<th>30 g/l of dipotassium hydrogen phosphate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>70 g/l of potassium sodium tartrate</td>
</tr>
<tr>
<td></td>
<td>15 g/l of Sn as sodium stannate</td>
</tr>
<tr>
<td></td>
<td>1.0 g/l of Cu as copper sulfate</td>
</tr>
<tr>
<td></td>
<td>5 g/l of 4,6-dihydroxy-2-mercaptopuridine</td>
</tr>
<tr>
<td>pH</td>
<td>pH 11.0</td>
</tr>
<tr>
<td>Temperature</td>
<td>45° C.</td>
</tr>
<tr>
<td>Current density</td>
<td>0.8 A/dm²</td>
</tr>
</tbody>
</table>

1. An aqueous, cyanide-free electrolyte for the electrolytic deposition of an alloy of copper, tin and optionally zinc, which comprises
at least one salt from the group consisting of phosphates, phosphonates, polyphosphates, diphosphates and mixtures thereof.

and at least one compound selected from the group consisting of aliphatic and aromatic thio compounds, wherein the metals copper and optionally zinc to be deposited are present in dissolved form and tin is present as dissolved Sn(IV) salt and wherein the pH of the aqueous, cyanide-free electrolyte is greater than or equal to 9.

2. The electrolyte as claimed in claim 1, characterized in that it further comprises at least one aliphatic saturated or unsaturated dicarboxylic or tricarboxylic acid, an aromatic carboxylic acid, salts and mixtures thereof.

3. The electrolyte as claimed in claim 1, characterized in that it additionally contains at least one further salt, wherein the anion is selected from the group consisting of sulfates, fluorides, chlorides, bromides, iodides, carbonates, acetates, formates, propionates, butyrates, valerates, benzoates, nitrates, nitrites, sulfonates, alkylsulfonates, amidosulfonates, sulfamates, anions of amino carboxylic acids and N-heterocyclic carboxylic acids, wherein the cation is selected from among ammonium, lithium, sodium and potassium ions.

4. The electrolyte as claimed in claim 1, characterized in that it additionally contains at least one brighter selected from the group consisting of bis(3-sulfopropyl) disulfide disodium salt, 3-sulfopropyl O-ethylthiodiacetate potassium salt, 1-(3-sulfopropyl)pyridinium betaine, 1-(2-hydroxy-3-sulfopropyl)pyridinium betaine, 3-(2-benzothiazole-2-mercaptocapro)propanesulfonic acid sodium salt, 5-isothiouronium 3-propanesulfonate, 5-(sulfopropyl) N,N-dimethylthiodiacetamidinium chloride, 3-formyl-1-(3-sulfopropyl)pyridinium betaine, N-(3-sulfopropyl) saccharin sodium salt, saccharin sodium salt, carbomethoxysalicyluronium betaine, cocoamidopropyl dimethylammonium 2-hydroxypropanesulfonate betaine, N-(3-cocoamidopropyl-N,N-dimethyl)-N-(3-sulfopropyl)ammonium betaine, 6-carboxy-2,4-dihydroxypropyrimidine, 2-butenoic acid.

5. The electrolyte as claimed in claim 1, characterized in that it additionally contains at least one wetting agent selected from among a cationic, amine polymer having 11 groups, a cationic polymer which is made up of the monomers morpholine, epichlorohydrin and imidazole and has the general formula (C_5H_11NO)•(C_6H_5ClO)•(C_4H_9N_2) 彝 (C_4H_9N_2) 彝 (C_4H_9N_2)

cationic polymer which is made up of the monomers epichlorohydrin and imidazole and has the general formula (C_5H_11NO)•(C_6H_5ClO)•(C_4H_9N_2) 彅 (C_4H_9N_2) 彅 (C_4H_9N_2).

N-alkyl-N-(1-oxoalkyl) amino acids and derivatives and salts thereof and mixtures of these wetting agents.

6. The electrolyte as claimed in claim 1, characterized in that the metals copper and optionally zinc to be deposited are present in ionically dissolved form and the tin is present as Sn(IV) salt, wherein the ion concentration of copper is in the range from 0.05 to 10 g/l of electrolyte, the ion concentration of tin is in the range from 0.5 to 40 g/l of electrolyte and the ion concentration of zinc is in the range from 0.1 to 10 g/l of electrolyte.

7. The electrolyte as claimed in any of claim 1, characterized in that the compounds of the metals copper and optionally zinc to be deposited which are water-soluble under the given conditions are selected from the group consisting of pyrophosphates, carbonates, hydrogencarbonates, sulfites, sulfates, phosphates, nitrates, nitrites, halides, hydroxides, oxide-hydroxides, oxides and combinations thereof.

8. The electrolyte as claimed in claim 1, characterized in that the dissolved Sn(IV) salt is a stannate.

9. The electrolyte as claimed in claim 1, characterized in that the thio compound is selected from among 2-mercapto-pyridine carboxylic acid, mercaptosuccinic acid, 2-thiopropanedicarboxylic acid, Na3-mercapto-1-propanesulfonate, 2-mercaptoisonicotinic acid, 2-thiouracil, 4,6-dihydroxy-2-mercaptopyrimidine, 2-mercaptopyrimidine, 2-thiocytosine, 6-mercaptopirimidine-4-carboxylic acid, 2-mercaptopirimidine-4-ol, 2-thiohydantoin, 5-sulfosalicilic acid.

10. A process for the electrolytic deposition of an alloy of the elements copper and tin and optionally zinc, wherein the substrate to be coated is dipped into an electrolyte as claimed in claim 1 and current flow is established between the anode and the cathode.

11. The process as claimed in claim 10, characterized in that the proportion of copper in the alloy is in the range from 20 to 80% by weight, the proportion of tin is in the range from 10 to 60% by weight and the proportion of zinc is in the range from 1 to 30% by weight, where the sum of the proportions of all participating metals in the alloy is in each case 100% by weight.

12. The process as claimed in claim 10, characterized in that the proportion of copper in the alloy is from 50 to 60% by weight, the proportion of tin is from 35 to 45% by weight and the proportion of zinc is from 5 to 15% by weight, where the sum of the proportions of all participating metals in the alloy is in each case 100% by weight.

13. The process as claimed in claim 10, characterized in that the proportion of copper in the alloy is in the range from 30 to 90% by weight and the proportion of tin is in the range from 10 to 70% by weight, where the sum of the proportions of all participating metals in the alloy is in each case 100% by weight.

14. The process as claimed in claim 10, characterized in that the electrolyte is kept in the range from 20 to 90°C.

15. The process as claimed in claim 10, characterized in that a current density in the range from 0.1 to 100 ampere per square decimeter is set.

16. The process as claimed in claim 10, characterized in that insoluble anodes (e.g. platined titanium anodes or mixed metal oxide anodes) or soluble anodes composed of a material selected from the group consisting of electrolytic copper, phospho-
rus-containing copper, tin, tin-copper alloy, zinc-copper alloy and zinc-tin-copper alloy or combinations of these anodes are used.

* * * * *