



(11) **EP 2 310 558 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
14.03.2012 Bulletin 2012/11

(51) Int Cl.:
C25D 3/58 (2006.01) C25D 3/02 (2006.01)

(21) Application number: **09776985.5**

(86) International application number:
PCT/EP2009/004879

(22) Date of filing: **06.07.2009**

(87) International publication number:
WO 2010/003621 (14.01.2010 Gazette 2010/02)

(54) **IMPROVED COPPER-TIN ELECTROLYTE AND PROCESS FOR THE DEPOSITION OF TIN-BRONZE LAYERS**

VERBESSERTER KUPFER-ZINN-ELEKTROLYT UND VERFAHREN ZUR AUFTRAGUNG VON
ZINN-BRONZESCHICHTEN

ELECTROLYTE CUIVRE-ÉTAIN AMÉLIORÉ ET PROCÉDÉ DE DÉPÔT DE COUCHES DE ÉTAIN-
BRONZE

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL
PT RO SE SI SK SM TR**

(30) Priority: **10.07.2008 DE 102008032398**

(43) Date of publication of application:
20.04.2011 Bulletin 2011/16

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Description

[0001] The invention relates to a copper-tin electrolyte which is free of toxic constituents such as cyanides. In particular, the invention relates to a corresponding electrolyte having a novel brightener system. It likewise encompasses a process for the deposition of decorative, white and yellow bronze layers on consumer goods and industrial articles using the electrolyte of the invention.

[0002] Consumer goods or consumer articles as defined in the consumer articles regulations are finished with thin, oxidation-stable metal layers for decorative reasons and in order to prevent corrosion. These layers have to be mechanically stable and should not display any tarnishing or signs of wear even after prolonged use. Since 2001, the sale of consumer goods coated with nickel-containing finishing alloys has no longer been permitted, or is possible only with observance of strict conditions, in Europe pursuant to EU directive 94/27/EC since nickel and nickel-containing metal layers are contact allergens. Bronze alloys in particular have become established as a replacement for nickel-containing finishing layers and these enable such mass-produced consumer goods to be finished inexpensively in barrel or rack electroplating processes to give allergen-free, attractive products.

[0003] In the production of bronze layers for the electronics industry, the solderability of the resulting layer and, if appropriate, its mechanical adhesive strength are the critical properties of the layer to be produced. For use in this field, the appearance of the layers is generally less important than their functionality. On the other hand, for production of bronze layers on consumer goods, the decorative effect (shine and brightness) and also a long service life of the resulting layer with an essentially unchanged appearance are the important target parameters.

[0004] Apart from the conventional processes for producing bronze layers, which use cyanide-containing and thus highly toxic, alkaline baths, various electroplating processes which can, according to the composition of their electrolytes, usually be assigned to one of two main groups found in the prior art are also known: processes using electrolytes based on organosulfonic acids or processes using baths based on diphosphoric acid (pyrophosphoric acid). For the purposes of the present text, "nontoxic" means that the electrolytes according to the invention described in this way do not contain any materials which are classified as "toxic" (T) or "very toxic" (T⁺) according to the regulations applicable in Europe for handling dangerous goods and hazardous materials.

[0005] For example, EP 1 111 097 A2 describes an electrolyte comprising an organosulfonic acid and ions of tin and copper together with dispersants and brightening additives and also, if appropriate, antioxidants. EP 1 408 141 A1 describes a process for the electrochemical deposition of bronzes, in which an acidic electrolyte comprising tin and copper ions together with an alkylsulfonic acid and an aromatic, nonionic wetting agent. DE 100 46 600 A1 describes an alkylsulfonic or alkanolsulfonic acid-containing bath which comprises soluble tin and copper salts together with organic sulfur compounds, and a process using this bath.

[0006] A significant disadvantage of such electrolytes produced on the basis of organosulfonic acids is their high corrosivity. For example, baths based on methanesulfonic acids frequently have pH values below one. The high corrosivity of these baths limits their use range in respect of the substrate materials to be finished and requires the use of particularly corrosion-resistant working materials for carrying out the process.

[0007] EP 1 146 148 A2 describes a cyanide-free copper-tin electrolyte based on diphosphoric acid, which in addition to the reaction product of an amine and an epihalohydrin in a molar ratio of 1:1 contains a cationic surfactant. WO 2004/005528 describes a cyanide-free diphosphoric acid-copper-tin electrolyte which contains an additive composed of amine derivative, an epihalohydrin and a glycidyl ether compound. Electrolytes based on diphosphoric acid generally have very limited long-term stabilities and have to be renewed frequently.

[0008] In addition, processes for producing solderable copper-tin layers which can be used as replacement for tin-lead solders and in which a wide selection of acidic base electrolytes can be used are known from the electronics industry. Thus, EP 1 001 054 A2 describes a tin-copper electrolyte which comprises a water-soluble tin salt, a water-soluble copper salt, an inorganic or organic acid or a water-soluble salt thereof and also one or more compounds from the group consisting of generally toxic thiourea or thiol derivatives. The inventive bath described there can additionally contain one or more compounds selected from the group consisting of carboxylic acids, lactones, phosphoric acid condensates, phosphonic acid derivatives or water-soluble salts of these or combinations thereof.

[0009] WO2004/005528 describes a cyanide-free diphosphoric acid-copper-tin electrolyte which contains an additive composed of an amine derivative, an epichlorohydrin and a glycidyl ether compound in a molar ratio of 1:0.5 - 2:0.1 - 5. It was an object of this document to further widen the current density range in which uniform deposition of the metals in a shiny layer can be achieved. It is explicitly mentioned that such deposition can only be attained when the additive added is made up of all three of the abovementioned components.

[0010] US 2005067297A1 describes a pyrophosphate copper electroplating solution.

[0011] In view of the prior art just cited, it can be noted that those deposition processes which ensure uniform deposition on metals over a wide current density range and also use electrolytes which appear economically and ecologically advantageous in terms of their composition are particularly advantageous. Furthermore, a successful electrolyte should allow uniformly bright and shiny layers to be obtained, regardless of the thickness of the bronze layer deposited.

[0012] It is therefore an object of the present invention to provide an electrolyte which has long-term stability, is suitable for appropriately advantageous deposition of mechanically stable and decoratively advantageous bronze layers on consumer goods and industrial articles and is free of toxic constituents. It is a further object of the present invention to provide a process for the application of decorative bronze layers to consumer goods and industrial articles using such an electrolyte.

[0013] These objects and further objects which are not mentioned at the present juncture but can be derived in an obvious way from the prior art are achieved by specification of an electrolyte having the features of the present claim 1 and its use in a deposition process according to the invention as set forth in claim 13. Preferred embodiments referring back to these claims are defined in claims 2 to 12 and 14 -15.

[0014] The provision of a nontoxic electrolyte for the deposition of decorative bronze alloy layers on consumer goods and industrial articles, which electrolyte contains the metals to be deposited in the form of water-soluble salts and further comprises one or more phosphonic acid derivatives as complexing agents and also a brighter system composed of a disulfide compound and a carbonate or hydrogencarbonate salt, completely surprisingly but nonetheless advantageously achieves the stated objects. The inventive electrolyte having a different composition than in the prior art makes it possible to obtain excellent electrolytic deposits of bronze layers. In particular, the good brightness and shine of the bronze layers can be obtained independently of their thickness. The alloy composition remains approximately constant over a wide current density range, which is in no way suggested by the prior art.

[0015] In the electrolyte of the invention, the metals copper and tin or copper, tin and zinc to be deposited are present in dissolved form as their ions. They are preferably introduced in the form of water-soluble salts which are preferably selected from the group consisting of pyrophosphates, carbonates, hydroxide-carbonates, hydrogencarbonates, sulfites, sulfates, phosphates, nitrites, nitrates, halides, hydroxides, oxide-hydroxides, oxides or combinations thereof. Very particular preference is given to the embodiment in which the metals are used in the form of salts with ions selected from the group consisting of pyrophosphate, carbonate, hydroxide-carbonate, oxide-hydroxide, hydroxide and hydrogencarbonate. Which salts are introduced in which amount into the electrolyte can determine the color of the resulting decorative bronze layers and can be adjusted according to customer requirements. The metals to be deposited are, as indicated, present in ionically dissolved form in the electrolyte for application of decorative bronze layers to consumer goods and industrial articles. The ion concentration of copper can be set in the range from 0.2 to 10 g/l, preferably from 0.3 to 4 g/l, of electrolyte, the ion concentration of tin can be set in the range from 1.0 to 30 g/l, preferably 2 - 20 g/l, of electrolyte and, if present, the ion concentration of zinc can be set in the range from 1.0 to 20 g/l, preferably 0 - 3 g/l, of electrolyte. For the finishing of consumer goods, the metals to be deposited are particularly preferably introduced as salt of a pyrophosphate, carbonate, hydrogencarbonate or hydroxide-carbonate in such a way that the resulting ion concentration is in the range from 0.3 to 4 gram of copper, from 2 to 20 gram of tin and from 0 to 3 gram of zinc, in case per liter of electrolyte.

[0016] The electrolyte of the invention has some concentration of carbonate or hydrogencarbonate ions. These can be present in the electrolyte in the form of preferably soluble salts selected from the group consisting of alkali metal and alkaline earth metal salts, in particular sodium or potassium carbonate or sodium or potassium hydrogencarbonate. However, the embodiment in which the metals which are used and are to be deposited are also added either completely or partly in the form of carbonates or hydrogencarbonates to the electrolyte is preferred. The embodiment in which only copper is present as carbonate in the bath formulation is advantageous. Tin and zinc and also, during operation of the bath, copper are then advantageously added as pyrophosphate. Addition of the abovementioned salts enables a concentration of carbonate or hydrogencarbonate ions in the electrolyte of from 0.5 to 100 g/l of electrolyte to be set. The concentration is particularly preferably in the range from 5 to 40 g/l and very particularly preferably from 15 to 30 g/l.

[0017] As further components of the electrolyte, mention may be made of disulfide compounds. These can advantageously be selected from the group consisting of substituted and unsubstituted bisalkyl or bis(hetero)aryl or alkyl (hetero) aryl disulfides, in particular those of the general formula (I),



wherein

R and R' can each be, independently of one another, substituted or unsubstituted (C₁-C₈)-alkyl, (C₃-C₆)-cycloalkyl, (C₇-C₁₉)-alkylaryl, (C₆-C₁₈)-aryl, (C₇-C₁₉)-aralkyl, (C₃-C₁₈)-heteroaryl, (C₄-C₁₉)-alkylheteroaryl, (C₄-C₁₉)-heteroaralkyl. R and R' can also be joined to form a ring. Possible substituents for R and R' are in principle all groups of substituents which a person skilled in the art would consider for this purpose. These are, in particular, substituents selected from the group consisting of amine radicals, nitro groups, hydroxyl radicals, halide radicals, acid radicals such as carboxylic acids, sulfonic acids and phosphonic acids.

[0018] Particularly advantageous disulfide compounds are compounds selected from the group consisting of 2,2'-dithiodipyridine, 4,4'-dithiodipyridine, 6,6'-dithiodinicotinic acid, bis(4-aminophenyl) disulfide, 2,2'-dithiosalicylic acid, D-cystine, L-cystine, DL-cystine, 2,2'-dithio(bis)benzothiazole, 2,2'-dithiobis(5-nitropyridine). Very particular preference is

given in this context to the compound bis-(3-sodium sulfopropyl) disulfide, referred to as SPS for short. The disulfide compounds are preferably used in an amount of from 0.01 mg per liter to 10.0 g per liter of electrolyte. Particular preference is given to use in a concentration range from 0.5 mg per liter to 7.5 g per liter of electrolyte. The disulfide compound, in particular the abovementioned SPS, is very particularly preferably used in a concentration range from 0.1 mg per liter to 5 g per liter in the electrolyte.

[0019] The application of the decorative bronze layers to consumer goods and industrial articles using the electrolyte of the invention is effected, as indicated, in an electroplating process. It is important here that the metals to be deposited are kept permanently in solution during the process, regardless of whether electroplating is carried out in a continuous process or in a batch process. To ensure this, the electrolyte of the invention contains phosphonic acids as complexing agents.

Preference is given to using compounds selected from the group consisting of hydroxyphosphonic, nitrilophosphonic or aminophosphonic acid, e.g. 1-aminomethylphosphonic acid AMP, aminotris(methylenephosphonic acid) ATMP, 1-aminoethylphosphonic acid AEP, 1-aminopropylphosphonic acid APP, (1-acetyl-amino-2,2,2-trichloroethyl)phosphonic acid, (1-amino-1-phosphonooctyl) phosphonic acid, (1-benzoylamino-2,2,2-trichloroethyl)phosphonic acid, (1-benzoylamino-2,2-dichlorovinyl)phosphonic acid, (4-chlorophenylhydroxymethyl)phosphonic acid, diethylenetriaminepenta(methylenephosphonic acid) DTPMP, ethylenediaminetetra(methylenephosphonic acid) EDTMP, 1-hydroxyethane(1,1-diphosphonic acid) HEDP, hydroxyethylamino-di(methylenephosphonic acid) HEMPA, hexamethylenediaminetetra(methylphosphonic acid) HDTMP, ((hydroxymethylphosphonomethylamino)methyl)phosphonic acid, nitrilotris(methylenephosphonic acid) NTMP, 2,2,2-trichloro-1-(furan-2-carbonyl)amino ethylphosphonic acid, salts derived therefrom and condensates derived therefrom, or combinations thereof.

[0020] Particular preference is given to using one or more compounds selected from the group consisting of aminotris(methylenephosphonic acid) ATMP, diethylenetriamine-penta(methylenephosphonic acid) DTPMP, ethylenediaminetetra(methylenephosphonic acid) EDTMP, 1-hydroxyethane(1,1-diphosphonic acid) HEDP, hydroxyethylamino-di(methylenephosphonic acid) HEMPA, hexamethylenediaminetetra(methylphosphonic acid) HDTMP, salts derived therefrom and condensates derived therefrom, or combinations thereof. Preference is given to using from 10 to 400 gram of phosphonic acid derivatives per liter of electrolyte, particularly preferably from 20 to 200 gram per liter of electrolyte and very particularly preferably from 50 to 150 gram per liter of electrolyte.

[0021] The pH of the electrolyte is in the range from 6 to 14 required for the electroplating application. Preference is given to a range of 8 - 12 and very particular preference to about 10.

[0022] Apart from the metals to be deposited, the phosphonic acid derivatives used as complexing agent and the brightener system composed of hydrogencarbonate salt and disulfide compound which is used, the electrolyte can contain further organic additives which assume functions as complexing ligands, brighteners, wetting agents or stabilizers. The electrolyte of the invention can also dispense with the use of cationic surfactants. The addition of further brighteners and wetting agents is only preferred in the case of the appearance of the decorative bronze layers to be deposited having to meet special requirements. They make it possible to adjust not only the color of the bronze layers, which depends critically on the ratio of the metals to be deposited, but also the shine of the layers in all gradations from matt silk to high gloss.

[0023] Preference is given to adding one or more compounds selected from the group consisting of monocarboxylic and dicarboxylic acids and their salts, sulfonic acids and their salts, betaines and aromatic nitro compounds. These compounds act as electrolyte bath stabilizers. Particular preference is given to using oxalic acid, alkanesulfonic acids, in particular methanesulfonic acid, or nitrobenzotriazoles or mixtures thereof. Suitable alkanesulfonic acids are disclosed, for example, in EP1001054.

[0024] As sulfonic acids, it can also be advantageous to use those of the general formula (II) or salts thereof



where

R is substituted or unsubstituted (C₁-C₈)-alkyl, (C₃-C₆)-cycloalkyl, (C₇-C₁₉)-alkylaryl, (C₆-C₁₈)-aryl, (C₇-C₁₉)-aralkyl, (C₃-C₁₈)-heteroaryl, (C₄-C₁₉)-alkylheteroaryl, (C₄-C₁₉)-heteroaralkyl. Possible substituents for R and R' are in principle all groups of substituents which a person skilled in the art would consider for this purpose. These are, in particular, substituents selected from the group consisting of amine radicals, nitro groups, hydroxyl radicals, halide radicals, acid radicals such as carboxylic acids, sulfonic acids and phosphonic acids. This applies analogously to the corresponding salts, in particular salts with cations of the alkali metals or alkaline earth metals.

[0025] Preferred compounds are those selected from the group consisting of 3-mercapto-1-propanesulfonic acid Na salt, 3-(2-benzothiazolyl-2-mercapto)propanesulfonic acid Na salt, saccharin-N-propylsulfonate Na salt, 3-sulfopropyl N,N-dimethyl dithiocarbamate Na salt, 1-propanesulfonic acid and 3[(ethoxythioxomethyl)thio] K salt.

[0026] In this context, very particular preference is given to the disulfide required for the brightener system and the sulfonic acid being present in one compound, as is the case, for example, for bis-(3-sodium sulfopropyl) disulfide.

[0027] It is also possible to use, for example, citric acid as carboxylic acid (Jordan, Manfred, Die galvanische Abscheidung von Zinn und Zinnlegierungen, Saulgau 1993, page 156). Betaines to be used can preferably be found in WO2004/005528 or in Jordan, Manfred (Die galvanische Abscheidung von Zinn und Zinnlegierungen, Saulgau 1993, page 156). Particular preference is given to those presented in EP636713. Further additives may be found in the literature (Jordan, Manfred, Die galvanische Abscheidung von Zinn und Zinnlegierungen, Saulgau 1993).

[0028] Further complexing ligands which can advantageously be used are pyrophosphate ions. These can be present in the electrolyte and can advantageously be introduced into the electrolyte as anions of the metal salts to be deposited. However, the embodiment in which the pyrophosphate ions are added in the form of salts of other metals, in particular of alkali and alkaline earth metals in the electrolyte, is likewise possible. The amount of pyrophosphate ions can be set in a precise manner by a person skilled in the art. It is limited by the fact that the concentration in the electrolyte should be above a minimum amount in order to be able still to bring about the effect discussed to a sufficient extent. On the other hand, the amount of pyrophosphate to be used is guided by economic aspects. In this context, reference may be made to EP1146148 and the relevant information presented there. The amount of pyrophosphate to be used in the electrolyte is preferably 1 - 400 g/l. Particular preference is given to using an amount of 2 - 200 g/l of electrolyte. The pyrophosphate can, if it is, as indicated, not introduced as salt constituent of the metals to be deposited, be used as sodium or potassium diphosphate or as $H_2P_2O_7$ in combination with a base of the alkali or alkaline earth metals. Preference is given to using $K_2P_2O_7$ for this purpose.

[0029] The electrolyte of the invention is free of hazardous materials classified as toxic (T) or very toxic (T⁺). No cyanides, no thiourea derivatives or similarly toxic materials are present. The nontoxic electrolyte of the invention is particularly suitable for the electrochemical application of decorative bronze layers to consumer goods and industrial articles. It can be used in barrel, rack, belt or reel to reel electroplating plants.

[0030] In a corresponding process for the electrochemical application of decorative bronze alloy layers, the consumer goods and industrial articles to be coated (hereinafter referred to collectively as substrates) dip into the nontoxic electrolyte of the invention and form the cathode. The electrolyte is preferably maintained in the range from 20 to 70°C. It is possible to set a current density which is in the range from 0.01 to 100 ampere per square decimeter [A/dm^2] and depends on the type of plating plant. In barrel plating plants, current densities in the range from 0.05 to 0.75 A/dm^2 are preferred, more preferably from 0.1 to 0.5 A/dm^2 and very particularly preferably about 0.3 A/dm^2 . In rack plating processes, current densities in the range from 0.2 to 10.0 A/dm^2 are preferably chosen, particularly preferably from 0.2 to 5.0 A/dm^2 and very particularly preferably from 0.25 to 1.0 A/dm^2 .

[0031] Various anodes can be employed when using the nontoxic electrolyte of the invention. Soluble or insoluble anodes are suitable, as is the combination of soluble and insoluble anodes.

[0032] As soluble anodes, preference is given to using anodes made 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. Particular preference is given to combinations of different soluble anodes made of these materials, and also combinations of soluble tin anodes with insoluble anodes.

[0033] As insoluble anodes, preference is given to using anodes made of a material selected from the group consisting of platinized titanium, graphite, iridium-transition metal mixed oxide and special carbon material ("Diamond Like Carbon", DLC) or combinations of these anodes. Particular preference is given to mixed oxide anodes composed of iridium-ruthenium mixed oxide, iridium-ruthenium-titanium mixed oxide or iridium-tantalum mixed oxide.

[0034] If insoluble anodes are used, this is a particularly preferred embodiment of the process when the substrates to be provided with decorative bronze layers, which represent the cathode, are separated from the insoluble anode by an ion-exchange membrane so as to form a cathode space and an anode space. In such a case, only the cathode space is filled with the nontoxic electrolyte of the invention. An aqueous solution containing only a conductive salt is preferably present in the anode space. Such an arrangement prevents the anodic oxidation of tin(II) ions Sn^{2+} to tin(IV) ions Sn^{4+} , which would have an adverse effect on the plating process.

[0035] In membrane processes which are operated using insoluble anodes and the nontoxic electrolyte of the invention, current densities in the range from 0.05 to 2 A/dm^2 are preferably set. The electrolyte is preferably maintained in the range from 20 to 70°C. As ion-exchange membranes, it is possible to use cationic or anionic exchange membranes. Preference is given to using membranes composed of Nafion which have a thickness of from 50 to 200 μm .

[0036] The disadvantage of additive-free phosphonate-based copper-tin electrolytes is the restriction to a narrow current density range and the lack of shine and the lower brightness of the layers deposited. The novel brightener system avoids these disadvantages in the phosphonate-based electrolyte system. Only when the electrolyte of the invention is used is the deposition of bright and shiny layers made possible over a wide current density range. None of the known cyanide-free substitute processes (pyrophosphate, phosphonate, alkylsulfonate) achieves the properties of cyanide-containing baths (particularly in the case of shine and brightness, also only to an extent). The use of the brightener combination according to the invention for the first time makes it possible to achieve the shine and brightness which is comparable to the cyanide-containing electrolytes of the prior art and is thus significantly better than in all known cyanide-free substitute processes.

[0037] In addition, management of the bath is simpler in the case of the electrolyte of the invention. The novel brightener system enables the electrolyte to be operated at higher copper contents. The combination of the compounds used, in particular those of the brightener system comprising carbonate ions and disulfide compounds, is critical here. In the presence of carbonate ions, even very small amounts of organic disulfidates influence copper-tin alloy formation. In contrast to additive-free baths, a largely constant alloy composition is obtained over a wider current density range as a result of the addition of the brightener system (fig. 1 - comparison of copper-tin electrolyte based on phosphonic acid with and without brightener system). In the case of additive-free baths, tin is deposited preferentially at higher current densities, which leads to a loss of shine of the layers.

[0038] For the purposes of the invention, (C₁-C₈)-alkyl is an alkyl radical having from 1 to 8 carbon atoms. This can be branched as desired or in the case of (C₃-C₆)-cycloalkyl be cyclic. This is, in particular, radicals such as methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, isobutyl, pentyl, hexyl, cyclopropyl, cyclopentyl, cyclohexyl etc.

[0039] (C₆-C₁₈)-Aryl is an aromatic system which is made up entirely of from 6 to 18 carbon atoms. This is, in particular, selected from the group consisting of phenyl, naphthyl, anthracenyl etc.

[0040] (C₇-C₁₉)-Alkylaryl radicals are radicals which have a (C₁-C₈)-alkyl radical on the (C₆-C₁₈)-aryl radical.

[0041] (C₇-C₁₉)-Aralkyl radicals are radicals which have a (C₆-C₁₈)-aryl radical on a (C₁-C₈)-alkyl radical, via which the radical is bound to the molecule concerned.

[0042] According to the invention, a (C₃-C₁₈)-heteroaryl radical is an aromatic system which has at least three carbon atoms. In addition, further heteroatoms are present in the aromatic system. These are preferably nitrogen and/or sulfur. Such heteroaromatics are described, for example, in the book Bayer-Walter, Lehrbuch der Organischen Chemie, S. Hirzel Verlag, 22nd edition, p. 703 ff.

[0043] For the purposes of the invention, (C₄-C₁₉)-alkylheteroaryl is a (C₃-C₁₈)-heteroaryl radical which is supplemented by a (C₁-C₈)-alkyl substituent. The bonding to the molecule under consideration is via the heteroaromatic here.

[0044] Conversely, (C₄-C₁₉)-heteroaralkyl is a (C₃-C₁₈)-heteroaryl which is bound to the molecule concerned via a (C₁-C₈)-alkyl substituent.

[0045] For the purposes of the invention, halide encompasses chloride, bromide and fluoride.

[0046] The examples described below and the comparative example illustrate the invention.

[0047] Alkyl(hetero)aryl is alkylaryl and alkylheteroaryl.

Examples:

[0048] Comparison of brightness values for phosphonate electrolyte with and without brightener system (in L units according to the Cie-Lab method [<http://www.cielab.de>])

	L*-values		
	Current density 0.05 A/dm ²	Current density 0.1 A/dm ²	current density 0.2 A/dm ²
Phosphonate electrolyte "without brightener system"	79.5	81.5	81.9
Phosphonate electrolyte "with brightener system"	83.5	83.5	83.8

[0049] The formation of dark streaks is significantly suppressed. Furthermore, the quality of the layer is maintained even in the case of thick deposits.

[0050] An insoluble platinum-titanium anode was used in all experiments described.

Example 1 - general procedure:

[0051] Barrel deposition of white bronze layers was carried out using a nontoxic electrolyte according to the invention containing 100 g/l of ethylenediaminetetra(methylenephosphonic acid) EDTMP, 1.5 g/l of copper as copper hydroxide carbonate, 5 g/l of tin as tin pyrophosphate, 2 g/l of zinc as zinc pyrophosphate, 10 ml/l of methanesulfonic acid (70%), 20 g/l of potassium hydrogencarbonate and 10 mg/l of bis(3-sodium sulfopropyl) disulfide.

[0052] During the entire deposition procedure, the electrolyte was maintained at 50°C. At a set current density of from 0.05 to 0.5 A/dm², optically uniform, high-shine bronze layers having the color typical of white bronze were obtained in a drum plating apparatus.

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Example 2:

[0053]

5	80 g/l	of HEDP
	50 ml/l	of methanesulfonic acid (70%)
	10 g/l	of potassium carbonate
	30 mg/l	of 2,2'-dithiodipyridine
10	1.47 g/l	of copper pyrophosphate
	10.2 g/l	of tin pyrophosphate
	2.5 g/l	of zinc pyrophosphate
	Parameters:	pH 8.0 / 40°C / current densities: 0.05 - 0.5 A/dm ²

15 Example 3:

[0054]

20	200 g/l	of HEMPA
	5 ml/l	of propanesulfonic acid
	2 g/l	of potassium hydrogencarboonate
	25 mg/l	2,2'-dithiodipyridine
	1.47 g/l	of copper pyrophosphate
25	10.2 g/l	of tin pyrophosphate
	1.5 g/l	of zinc pyrophosphate
	10 g/l	citric acid
	Parameters:	pH 11.0 / 25°C / current densities: 0.05 - 0.5 A/dm ²

30 Example 4:

[0055]

35	50 g/l	of ATMP
	100 g/l	of potassium pyrophosphate
	20 g/l	of citric acid
	4.2 g/l	of copper hydroxide carbonate
	8.66 g/l	of tin pyrophosphate
40	4.5 g/l	of zinc pyrophosphate
	10 g/l	of potassium hydrogencarbonate
	0.5 g/l	of 6,6'-dithiodinicotinic acid
	Parameters:	pH 9.0 / 60°C / current densities: 0.05 - 0.5 A/dm ²

45 Example 5: yellow bronze

[0056]

50	150 g/l	of EDTMP
	10 ml/l	of methanesulfonic acid (70%)
	20 g/l	of potassium carbonate
	9 g/l	of copper hydroxide carbonate
	8.66 g/l	of tin pyrophosphate
55	5.5 g/l	of zinc pyrophosphate
	15 mg/l	of bis(3-sodium sulfopropyl) disulfide
	Parameters:	pH 10 / 60°C / current densities 0.05 - 0.5 A/dm ²

Claims

1. An electrolyte for the deposition of decorative tin-bronze alloy layers on consumer goods and industrial articles, which contains the metals to be deposited in the form of water-soluble salts,
 wherein
 the electrolyte comprises one or more phosphonic acid derivatives as complexing agents and a brightener system composed of a disulfide compound and a carbonate or hydrogencarbonate salt.
2. The electrolyte as claimed in claim 1,
 wherein ,
 it contains the metal ions of copper and tin or copper, tin and zinc to be deposited.
3. The electrolyte as claimed in claim 2,
 wherein
 the water-soluble salts of the metals to be deposited are selected from the group consisting of pyrophosphates, carbonates, hydroxide-carbonates, hydrogencarbonates, sulfites, sulfates, phosphates, nitrites, nitrates, halides, hydroxides, oxide-hydroxides, oxides and combinations thereof.
4. The electrolyte as claimed in one or more of the preceding claims,
 wherein
 the metals to be deposited are present in dissolved form, with the ion concentration of copper being in the range from 0.2 to 10 gram per liter of electrolyte, the ion concentration of tin being in the range from 1.0 to 30 gram per liter of electrolyte and the ion concentration of zinc, if present, being in the range from 1.0 to 20 gram per liter of electrolyte.
5. The electrolyte as claimed in claim 1,
 wherein
 it comprises, as carbonate or hydrogencarbonate salt, a salt of this type selected from the group consisting of alkali metal and alkaline earth metal salts.
6. The electrolyte as claimed in claim 5,
 wherein
 the carbonate or hydrogencarbonate ions are present in an amount of 0.5 - 100 g/l of electrolyte.
7. The electrolyte as claimed in claim 1,
 wherein
 it comprises, as disulfide compound, a compound of this type selected from the group consisting of substituted and unsubstituted bisalkyl or bis(hetero)aryl or alkyl (hetero)aryl disulfides.
8. The electrolyte as claimed in claim 7,
 wherein
 the disulfide compound is present in the electrolyte in an amount of 0.01 mg/l - 10.4 g/l.
9. The electrolyte as claimed in claim 1,
 wherein
 it contains, as phosphonic acid derivatives, one or more compounds selected from the group consisting of 1-aminomethylphosphonic acid AMP, aminotris(methylenephosphonic acid) ATMP, 1-aminoethylphosphonic acid AEP, 1-aminopropylphosphonic acid APP, (1-acetylaminomethyl-2,2,2-trichloroethyl)phosphonic acid, (1-amino-1-phosphonooctyl)phosphonic acid, (1-benzoylamino-2,2,2-trichloroethyl)phosphonic acid, (1-benzoylamino-2,2-dichlorovinyl)phosphonic acid, (4-chlorophenylhydroxymethyl)phosphonic acid, diethylenetriamine-penta(methylenephosphonic acid) DTPMP, ethylenediaminetetra(methylenephosphonic acid) EDTMP, 1-hydroxyethane(1,1-diphosphonic acid) HEDP, hydroxyethylaminodi(methylenephosphonic acid) HEMPA, hexamethylenediaminetetra(methylphosphonic acid) HDTMP, ((hydroxymethylphosphonomethylamino)methyl)phosphonic acid, nitrilotris(methylenephosphonic acid) NTMP, 2,2,2-trichloro-1-(furan-2-carbonyl)amino-ethylphosphonic acid, salts derived therefrom and condensates derived therefrom, or combinations thereof.
10. The electrolyte as claimed in one or more of the preceding claims,
 wherein

the pH of the electrolyte is in the range from 6 to 14.

11. The electrolyte as claimed in one or more of the preceding claims,
wherein
pyrophosphate ions are present in the electrolyte.

12. The electrolyte as claimed in one or more of the preceding claims,
wherein
one or more stabilizing compounds selected from the group consisting of monocarboxylic and dicarboxylic acids,
alkanesulfonic acids, betaines and aromatic nitro compounds are present.

13. A process for the electrochemical application of decorative tin-bronze alloy layers to consumer goods and industrial
articles, in which the substrates to be coated are dipped into an electrolyte containing the metals to be deposited
in the form of water-soluble salts,
wherein
an electrolyte as claimed in one or more of claims 1 to 12 is used.

14. The process as claimed in claim 13,
wherein
the electrolyte is maintained in the range from 20 to 70°C during deposition of the metals.

15. The process as claimed in claim 13,
wherein
a current density in the range from 0.01 to 100 ampere per square decimeter is set.

Patentansprüche

1. Elektrolyt zur Abscheidung von dekorativen Zinn-Bronze-Legierungsschichten auf Gebrauchsgütern und techni-
schen Gegenständen, der die abzuscheidenden Metalle in Form von wasserlöslichen Salzen enthält, **dadurch**
gekennzeichnet, dass der Elektrolyt ein oder mehrere Phosphonsäurederivate als Komplexbildner und ein Glanz-
bildnersystem aus einer Disulfidverbindung und einem Carbonat- bzw. Hydrogencarbonatsalz aufweist.

2. Elektrolyt nach Anspruch 1, **dadurch gekennzeichnet, dass** er die abzuscheidenden Metallionen von Kupfer und
Zinn oder Kupfer, Zinn und Zink enthält.

3. Elektrolyt nach Anspruch 2, **dadurch gekennzeichnet, dass** die wasserlöslichen Salze der abzuscheidenden
Metalle aus der Gruppe bestehend aus Pyrophosphaten, Carbonaten, Hydroxidcarbonaten, Hydrogencarbonaten,
Sulfiten, Sulfaten, Phosphaten, Nitriten, Nitraten, Halogeniden, Hydroxiden, Oxidhydroxiden, Oxiden und Kombi-
nationen davon ausgewählt sind.

4. Elektrolyt nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die abzu-
scheidenden Metalle in gelöster Form vorliegen, wobei die Ionenkonzentration des Kupfers im Bereich von 0,2 bis
10 Gramm pro Liter Elektrolyt, die Ionenkonzentration des Zinns im Bereich von 1,0 bis 30 Gramm pro Liter Elektrolyt
und die Ionenkonzentration des Zinks, sofern vorhanden, im Bereich von 1,0 bis 20 Gramm pro Liter Elektrolyt liegt.

5. Elektrolyt nach Anspruch 1, **dadurch gekennzeichnet, dass** er als Carbonat- bzw. Hydrogencarbonatsalz ein Salz
dieses Typs, das aus der Gruppe bestehend aus Alkali- und Erdalkalimetallsalzen ausgewählt ist, aufweist.

6. Elektrolyt nach Anspruch 5, **dadurch gekennzeichnet, dass** die Carbonat- bzw. Hydrogencarbonationen in einer
Menge von 0,5-100 g/l Elektrolyt zugegen sind.

7. Elektrolyt nach Anspruch 1, **dadurch gekennzeichnet, dass** er als Disulfidverbindung eine Verbindung dieses
Typs, die aus der Gruppe bestehend aus substituierten und unsubstituierten Bisalkyl- oder Bis(hetero)aryl- oder
Alkyl(hetero)aryldisulfiden ausgewählt ist, aufweist.

8. Elektrolyt nach Anspruch 7, **dadurch gekennzeichnet, dass** die Disulfidverbindung in einer Menge von 0,01 mg/l-
10,0 g/l im Elektrolyt zugegen ist.

9. Elektrolyt nach Anspruch 1, **dadurch gekennzeichnet, dass** er als Phosphonsäurederivate eine oder mehrere Verbindungen aus der Gruppe bestehend aus 1-Aminomethylphosphonsäure AMP, Aminotris-(methylenphosphonsäure) ATP, 1-Aminoethylphosphonsäure AEP, 1-Aminopropylphosphonsäure APP, (1-Acetylamino-2,2,2-trichlorethyl)phosphonsäure, (1-Amino-1-phosphonooctyl)phosphonsäure, (1-Benzoylamino-2,2,2-trichlorethyl)phosphonsäure, (1-Benzoylamino-2,2-dichlorvinyl)phosphonsäure, (4-Chlorphenylhydroxymethyl)phosphonsäure, Diethylentriaminpenta(methylenphosphonsäure) DTPMP, Ethylendiamintetra(methylenphosphonsäure) EDTMP, 1-Hydroxyethan-(1,1-diphosphonsäure) HEDP, Hydroxyethylamino-di(methylenphosphonsäure) HEMPA, Hexamethylendiamintetra(methylphosphonsäure) HDTMP, ((Hydroxymethylphosphonomethylamino)-methyl)phosphonsäure, Nitrilotris(methylenphosphonsäure) NTMP, 2,2,2-Trichlor-1-(furan-2-carbonyl)aminoethylphosphonsäure, davon abgeleiteten Salzen und davon abgeleiteten Kondensaten oder Kombinationen davon enthält.
10. Elektrolyt nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der pH-Wert des Elektrolyts im Bereich von 6 bis 14 liegt.
11. Elektrolyt nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** in dem Elektrolyt Pyrophosphationen vorhanden sind.
12. Elektrolyt nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** eine oder mehrere stabilisierend wirkende Verbindungen aus der Gruppe bestehend aus Mono- und Dicarbonsäuren, Alkansulfonsäuren, Betainen und aromatischen Nitroverbindungen enthalten sind.
13. Verfahren zur galvanischen Aufbringung von dekorativen Zinn-Bronze-Legierungsschichten auf Gebrauchsgüter und technische Gegenstände, wobei die zu beschichtenden Substrate in einen Elektrolyt getaucht werden, der die abzuscheidenden Metalle in Form von wasserlöslichen Salzen enthält, **dadurch gekennzeichnet, dass** ein Elektrolyt gemäß einem oder mehreren der Ansprüche 1 bis 12 verwendet wird.
14. Verfahren nach Anspruch 13, **dadurch gekennzeichnet, dass** der Elektrolyt während der Abscheidung der Metalle im Bereich von 20 bis 70°C temperiert wird.
15. Verfahren nach Anspruch 13, **dadurch gekennzeichnet, dass** eine Stromdichte eingestellt wird, die im Bereich von 0,01 bis 100 Ampere pro Quadratdezimeter liegt.

Revendications

1. Electrolyte pour le dépôt de couches décoratives d'alliage étain-bronze sur des biens de consommation et des articles industriels, qui contient les métaux à déposer sous la forme de sels hydrosolubles, l'électrolyte comprenant un ou plusieurs dérivés d'acide phosphonique comme agents complexants et un système brillanteur constitué d'un composé de disulfure et d'un sel de carbonate ou d'hydrogénocarbonate.
2. Electrolyte selon la revendication 1, qui contient les ions métalliques de cuivre et d'étain ou de cuivre, d'étain et de zinc à déposer.
3. Electrolyte selon la revendication 2, dans lequel les sels hydrosolubles des métaux à déposer sont choisis dans le groupe constitué par les pyrophosphates, les carbonates, les hydroxycarbonates, les hydrogénocarbonates, les sulfites, les sulfates, les phosphates, les nitrites, les nitrates, les halogénures, les hydroxydes, les oxyhydroxydes, les oxydes, et les combinaisons de ceux-ci.
4. Electrolyte selon l'une quelconque des revendications précédentes, dans lequel les métaux à déposer sont présents sous forme dissoute, la concentration en ions cuivre se situant dans la gamme de 0,2 à 10 grammes par litre d'électrolyte, la concentration en ions étain se situant dans la gamme de 1,0 à 30 grammes par litre d'électrolyte, et la concentration en ions zinc, si présents, se situant dans la gamme de 1,0 à 20 grammes par litre d'électrolyte.
5. Electrolyte selon la revendication 1, qui comprend, comme sel de carbonate ou d'hydrogénocarbonate, un sel de ce type choisi dans le groupe constitué par les sels de métaux alcalins et de métaux alcalino-terreux.
6. Electrolyte selon la revendication 5, dans lequel les ions carbonate ou hydrogénocarbonate sont présents dans une quantité de 0,5-100 g/l d'électrolyte.

7. Electrolyte selon la revendication 1, qui comprend comme composé de disulfure, un composé de ce type choisi dans le groupe constitué par les disulfures de bisalkyle ou de bis(hétéro)aryle ou d'alkyl(hétéro)aryle substitués et non substitués.

8. Electrolyte selon la revendication 7, le composé de disulfure étant présent dans l'électrolyte dans une quantité de 0,01 mg/l 10,0 g/l.

9. Electrolyte selon la revendication 1, qui contient, comme dérivés d'acide phosphonique, un ou plusieurs composés choisis dans le groupe constitué par l'acide 1-aminométhylphosphonique AMP, l'aminotris(acide méthylènegphosphonique) ATMP, l'acide 1-aminoéthylphosphonique AEP, l'acide 1-aminopropylphosphonique APP, l'acide (1-acétylamino-2,2,2-trichloroéthyl)phosphonique, l'acide (1-amino-1-phosphonooctyl)phosphonique, l'acide (1-benzoylamino-2,2,2-trichloroéthyl)phosphonique, l'acide (1-benzoylamino-2,2-dichlorovinyl)phosphonique, l'acide (4-chlorophénylhydroxyméthyl)phosphonique, le diéthylènetriamine-penta(acide méthylènegphosphonique) DTPMP, l'éthylènediamine-tétra(acide méthylènegphosphonique) EDTMP, le 1-hydroxyéthane(1,1-diacide phosphonique) HEDP, l'hydroxyéthylaminodi(acide méthylènegphosphonique) HEMPA, l'hexaméthylènediamine-tétra(acide méthylphosphonique) HDTMP, l'acide ((hydroxyméthylphosphonométhylamino)méthyl)phosphonique, le nitrilotris(acide méthylènegphosphonique) NTMP, l'acide 2,2,2-trichloro-1-(furan-2-carbonyl)amino-éthylphosphonique, les sels dérivés de ceux-ci et les condensats dérivés de ceux-ci, ou leurs combinaisons.

10. Electrolyte selon l'une quelconque des revendications précédentes, le pH de l'électrolyte se situant dans la gamme de 6 à 14.

11. Electrolyte selon l'une quelconque des revendications précédentes, des ions pyrophosphate étant présents dans l'électrolyte.

12. Electrolyte selon l'une quelconque des revendications précédentes, dans lequel un ou plusieurs composés stabilisants choisis dans le groupe constitué par les acides monocarboxyliques et dicarboxyliques, les acides alcanesulfoniques, les bétaines et les composés aromatiques nitrés sont présents.

13. Procédé d'application électrochimique de couches décoratives d'alliage étain-bronze sur des biens de consommation et des articles industriels, dans lequel les substrats à revêtir sont plongés dans un électrolyte contenant les métaux à déposer sous la forme de sels hydrosolubles, un électrolyte selon une ou plusieurs des revendications 1 à 12 étant utilisé.

14. Procédé selon la revendication 13, dans lequel l'électrolyte est maintenu dans la gamme de 20 à 70 °C pendant le dépôt des métaux.

15. Procédé selon la revendication 13, dans lequel une densité de courant dans la gamme de 0,01 à 100 ampères par décimètre carré est imposée.

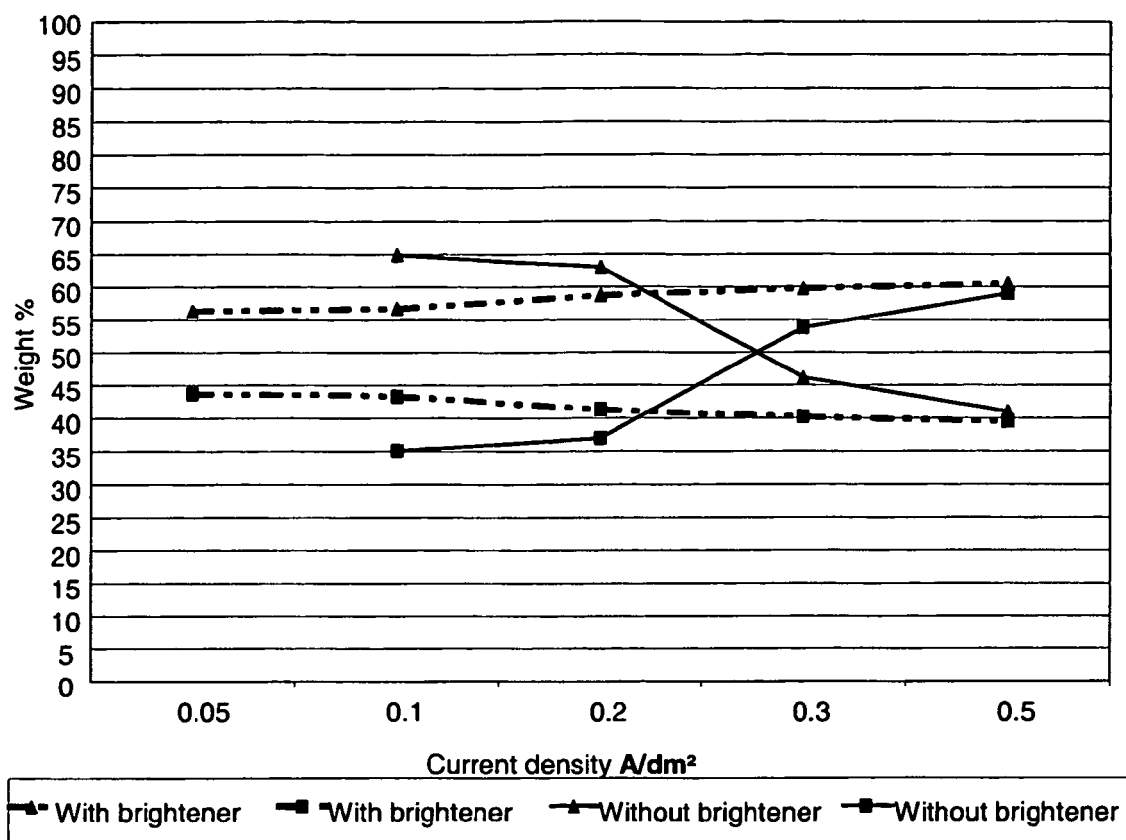


Fig. 1

REFERENCES CITED IN THE DESCRIPTION

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