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**(54) METHOD FOR ELECTRODEPOSITION OF BRONZES**

VERFAHREN ZUR GALVANISCHEN ABSCHIEDUNG VON BRONZEN

METHODE D'ELECTRODEPOSITION DE BRONZES

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**Description**

## FIELD OF THE INVENTION

5 **[0001]** This invention concerns a method for electrodeposition of bronzes, with which the substrate to be coated is plated in an acid electrolyte that contains at least tin and copper ions, an alkylsulfonic acid and a wetting agent, and the preparation of such an electrolyte.

## BACKGROUND OF THE INVENTION

10 **[0002]** Methods for deposition of tin and tin alloys on the basis of various types of electrolytes are known from the prior art and are already widely used in practice. Methods for deposition of tin and/or tin alloys from cyanide electrolytes are very common. Such electrolytes, however, are highly toxic, which makes their use problematic from the environmental standpoint, so that for some years there has been a push to develop cyanide-free electrolytes, for example electrolytes  
15 based on pyrophosphates or oxalates, which operate in a pH region of 5-9. However, such methods have both economic and technical disadvantages, of which the relatively slow deposition rates may be mentioned here.

**[0003]** For these reasons development is currently going mostly in the direction of making available methods for deposition of tin and/or tin alloys from acid electrolytes, since, for one thing, divalent tin can be very easily reduced to metallic tin in acid electrolytes, which leads to better deposition rates while having qualitatively equivalent coatings, and  
20 for another the disadvantageous effect of alkaline electrolytes on substrates, for example ceramic structural elements, is prevented by this.

**[0004]** Thus, acid electrolytes and methods for deposition of qualitatively high grade tin or tin alloys with a higher deposition rate are known from EP 1 111 097 A2 and US 6,176,996 B1. These are electrolytes that contain at least two divalent metal salts of an organic sulfonic acid and from which are deposited solderable and corrosion resistant coatings  
25 that can be used, for example, as substitutes for lead-containing solderable coatings in electronics for manufacture of circuit boards, etc.

**[0005]** However, such methods have their limits in the deposition of tin-copper alloys with high copper contents, such as the so-called "true" bronzes, which have a copper content of at least 10%. For example, due to the high difference of potential between tin and copper higher rates of oxidation of the divalent tin can occur, due to which it very easily  
30 becomes oxidized to tetravalent tin in acid electrolytes. However, in this form tin can no longer be electrolytically deposited in an acid and thus is withdrawn from the process, which leads to uneven deposition of the two metals and to a decrease of the deposition rate. In addition, oxidation to tetravalent tin leads to increased sludge formation, which can prevent stable operation and long lifetime of the acid electrolyte. Moreover, because of such contaminated of a firmly bonding and pore-free coating is no longer guaranteed.

35 Because of such technical process disadvantages, there is currently no large area of use for electrolytically deposited bronze coatings. Occasionally bronze coatings are used in the jewelry industry as a substitute for expensive silver or allergy-triggering nickel. In the same way methods for electrodeposition of bronzes are also gaining importance in some technical fields, for example in electronics for coating electronic components or in mechanical engineering and/or in process technology for coating bearing overlays and friction layers. However, in this case mainly white bronzes or the  
40 so-called "false bronzes," whose copper content can be kept quite low due to process conditions, are deposited as nickel substitutes.

## SUMMARY OF THE INVENTION

45 **[0006]** Therefore, the invention is based on the task of providing a method for deposition of bronzes that, in contrast to the methods known from the prior art, enables uniform deposition of at least tin and copper side by side from an acid electrolyte at considerably higher deposition rates. Moreover, with this method firmly bonding and pore-free bronze coatings with high copper contents as well as various decorative and mechanical properties are said to be deposited.

50 **[0007]** In addition, an acid electrolyte that can have a high content of divalent copper ions, is stable with respect to oxidation-caused sludge formation, and is both economical and environmentally friendly when used over a long period of time, is to be made available.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

55 **[0008]** The task is solved in accordance with the invention by a method of the kind mentioned at the start, which is characterized by the fact that an aromatic, nonionic wetting agent is added to the electrolyte.

**[0009]** With this invention a method for electrodeposition of bronzes according to claim 1 is made available.

**[0010]** Through the method in accordance with the invention the disadvantages known in the prior art are remedied

with the offering of a new electrolyte composition and in this way considerably better deposition results are achieved. Moreover, the conduct of the method is made to be simpler and more economical. This, too, is mainly based on the advantageous composition of the electrolyte. For example, the method is carried out at room temperature, or between 17 and 25°C, and the substrate to be coated is plated in a highly acid environment at a pH <1. The electrolyte is particularly stable in this temperature range. In addition, there are no longer any costs for heating the electrolyte and the plated substrates also do not have to be cooled very much, with large expenditures of time and money. Moreover, deposition rates of 0.25 microns/min at a current density of 1 A/dm<sup>2</sup> are achieved due to, among other things, the pH value and the advantageous addition of at least one aromatic non-ionic wetting agent. By increasing the metal content this rate can be raised up to 7 A/dm<sup>2</sup> in rack operation and even up to 120 A/dm<sup>2</sup> for continuous plants. Thus, usable current densities in a range from 0.1-120 A/dm<sup>2</sup> are reached in each case according to plant type.

**[0011]** Surprisingly, the wetting of the surfaces to be plated, above all those of more complex substrates, is considerably improved in particular through the addition of at least one nonionic wetting agent to the electrolyte. This advantageously has the result that not only are the considerably higher deposition rates achieved through the use of the method in accordance with the invention, but moreover the coatings produced by the method are uniform and qualitatively high grade, have very good adhesion and are generally pore-free.

**[0012]** Another advantage of the nonionic wetting agent that is used is that because of the advantageous wetting properties the electrolyte and/or the substrate in the electrolyte need to be agitated only a little or even not at all, in order to achieve the desired deposition results, so that additional devices for agitation of the electrolyte can be omitted. In addition, because of the advantageous use of the aromatic nonionic wetting agent, electrolyte residues drain from the plated substrate better when it is removed from the electrolyte, which leads to reduced entrainment losses and thus to lower process costs.

**[0013]** The addition of 2-40 g/L of one or more aromatic nonionic wetting agents is especially advantageous, with beta-naphthol ethoxylate and/or nonylphenol ethoxylate are especially preferred. Also preferred is sulfopropylated polyalkoxylated naphthol, potassium salt.

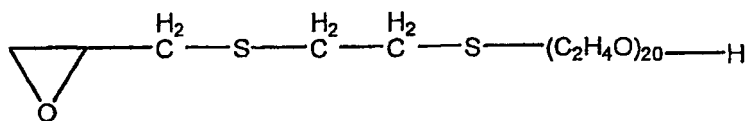
**[0014]** The proposed method is therefore advantageously economical and environmentally friendly compared to the cyanide processes.

**[0015]** The additional or alternative use of one or more anionic and/or aliphatic nonionic wetting agent that is known from the prior art is also optionally possible, provided these wetting agents support or even enhance the advantageous effects of the aromatic nonionic wetting agent. In this regard polyethylene glycols and/or anionic surfactants are preferably added to the electrolyte as anionic and/or aliphatic nonionic wetting agents. Additional exemplary aliphatic nonionic wetting agents include aliphatic fatty alcohol ethoxylates, with compounds having from 13 to 15 carbon atoms (C-13 to C-15) being especially preferred. In one embodiment, the fatty alcohol ethoxylate is incorporated in a concentration of, for example, about 0.1 to 10 g/L; preferably about 0.5 to about 5 g/L. These compounds work as emulsifiers for the degradation products of the nonionic wetting agent, and improve uniformity and brightness in combination with the wetting agent and brightener system.

**[0016]** It has also been discovered that substituted dithioglycols act advantageously as wetting agents and brighteners. These compounds provide a source of sulphur which has a positive effect on copper plating. Therefore, the invention include substituted dithioglycols, such as, for example, those selected from the group consisting of:

- (1) Thiobis(diethyleneglycol) represented by H- (OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-S-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>-H,
- (2) Thiobis(hexaethylene glycol),
- (3) Thiobis(pentadecaglycelol) represented by H-(OCH<sub>2</sub>CH(OH)CH<sub>2</sub>)<sub>15</sub>-S-(CH<sub>2</sub>CH(OH)CH<sub>2</sub>O)<sub>15</sub>-H,
- (4) Thiobis(icosaehtyleneglycol) represented by H- (OCH<sub>2</sub>CH<sub>2</sub>)<sub>20</sub>-S-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>20</sub>-H,
- (5) Thiobis(pentacontaethyleneglycol),
- (6) 4,10-dioxa-7-thiatridecane-2,12-diol represented by HO-CH(CH<sub>3</sub>)CH<sub>2</sub>-OCH<sub>2</sub>CH<sub>2</sub>-SCH<sub>2</sub>CH<sub>2</sub>-OCH<sub>2</sub>CH(CH<sub>3</sub>)-OH,
- (7) Thiodiglycerin represented by HOCH<sub>2</sub>CH (OH) CH<sub>2</sub>-S-CH<sub>2</sub>CH (OH) CH<sub>2</sub>OH,
- (8) Thiobis(triglycerin) represented by H- (OCH<sub>2</sub>CH (OH)CH<sub>2</sub>)<sub>3</sub>-S- (CH<sub>2</sub>CH (OH) CH<sub>2</sub>O)-H,
- (9) 2,2'-thiodibutanolbis(octaethyleneglycolpentaglycerol) ether represented by H-(OCH<sub>2</sub>CH(OH)CH<sub>2</sub>)<sub>5</sub>-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>8</sub>-OC<sub>4</sub>H<sub>8</sub>-SC<sub>4</sub>H<sub>8</sub>-O-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>8</sub>- (CH<sub>2</sub>CH (OH) CH<sub>2</sub>O) -H,
- (10) Thiobis(octaethyleneglycol)bis(2-chloroethyl)ether represented by Cl-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>- (OCH<sub>2</sub>CH<sub>2</sub>)<sub>8</sub>-S-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>8</sub>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-Cl,
- (11) Thiobis(decaethyleneglycol)bis(carboxymethyl)ether,
- (12) Thiobis(dodecaethyleneglycol)bis(2-nitroethyl)ether,
- (13) Thiodiglycolbis(carboxymethyl)ether represented by HOOCCH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-S-CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>COOH,
- (14) Dithiodiglycolbis(carboxymethyl)ether represented by HOOCCH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>- S - S - CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>COOH,
- (15) Thiobis(dodecaethyleneglycol) represented by H- (OCH<sub>2</sub>CH<sub>2</sub>)<sub>12</sub>-S-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>12</sub>-H,
- (16) Dithiobis(hentetracontaethyleneglycol) represented by H-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>41</sub>-S-S-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>41</sub>-H,

- (17) Dithiobis(icosaeethyleneglycolpentapropyleneglycol) represented by  $\text{H}-(\text{OC}_3\text{H}_6)_5-(\text{OC}_2\text{H}_4)_{20}-\text{S}-\text{S}-(\text{OC}_2\text{H}_4)_{20}-(\text{OC}_3\text{H}_6)_5-\text{H}$ ,  
 (18) Dithiobis(triglycerol) represented by  $\text{H}-(\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2)_3-\text{S}-\text{S}-(\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O})_3-\text{H}$ ,  
 (19) Dithiobis(decaglycelol),  
 (20) 3,6-Dithiaoctane-1,8-diol represented by  $\text{HOCH}_2\text{CH}_2\text{S}-\text{CH}_2\text{CH}_2-\text{SCH}_2\text{CH}_2\text{OH}$  (also 2,2'-(Ethylenedithio)diethanol),  
 (21) 1,3-Propanedithiolbis(decaethyleneglycol)thioether represented by  $\text{H}-(\text{OC}_2\text{H}_4)_{10}-\text{S}-\text{C}_3\text{H}_6-\text{S}-(\text{OC}_2\text{H}_4)_{10}-\text{H}$ ,  
 (22) 1,4-Buthanedithiolbis(pentadecaglycerol)thioether represented by  $\text{H}-(\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2)_{15}-\text{S}-\text{C}_4\text{H}_8-\text{S}-(\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O})_{15}-\text{H}$ ,  
 (23) 1,3-Dithioglycerolbis(pentaethyleneglycol)thioether represented by  $\text{H}-(\text{OCH}_2\text{CH}_2)_5-\text{SCH}_2\text{CH}(\text{OH})\text{CH}_2\text{S}-(\text{CH}_2\text{CH}_2\text{O})_5-\text{H}$ ,  
 (24) 1,2-Ethanedithiolbis(penta(1-ethyl)ethyleneglycol)thioether represented by  $\text{H}-(\text{OCH}(\text{C}_2\text{H}_5)\text{CH}_2)_5-\text{SC}_2\text{H}_4-\text{S}-(\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{O})_5-\text{H}$ ,  
 (25) 1,3-Dithioglycerolbis(di(1-ethyl)ethyleneglycol)thioether represented by  $\text{H}-(\text{OCH}(\text{CH}_3)\text{CH}_2)_2-\text{SCH}_2\text{CH}(\text{OH})\text{CH}_2\text{S}-(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_2-\text{H}$ ,  
 (26) 2-Mercaptoethylsulfide bis(hexatriacontaethylene-glycol) represented by  $\text{H}-(\text{OC}_2\text{H}_4)_{18}-\text{SC}_2\text{H}_4-\text{SC}_2\text{H}_4-\text{S}-(\text{C}_2\text{H}_4\text{O})_{18}-\text{H}$ ,  
 (27) 2-Mercaptoethylsulfidebis(icosaeethyleneglycol)dimethylether represented by  $\text{CH}_3-(\text{OC}_2\text{H}_4)_{10}-\text{SC}_2\text{H}_4-\text{SC}_2\text{H}_4-\text{S}-(\text{C}_2\text{H}_4\text{O})_{10}-\text{CH}_3$ ,  
 (28) 2-Mercaptoethyletherbis(diethyleneglycol) represented by  $\text{H}-(\text{OC}_2\text{H}_4)_2-\text{S}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-\text{S}-(\text{C}_2\text{H}_4\text{O})_2-\text{H}$ ,  
 (29) Thiodiglyceroltetra(decaethyleneglycol)ether represented by the above formula (6),  
 (30) Diethyleneglycolmonomethylthioether represented by  $\text{CH}_3-\text{S}-(\text{CH}_2\text{CH}_2\text{O})_2-\text{H}$ ,  
 (31) Decaglycerolmono(6-methylthiohexyl)thioether represented by  $\text{CH}_3-\text{S}-\text{C}_6\text{H}_{12}-\text{S}-(\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O})_{10}-\text{H}$ ,  
 (32) 2-Mercaptoethylsulfide- $\omega$ -{(2-bromoethyl)icosaeethyleneglycol}thioether- $\omega'$ -{(2-bromoethyl)heptaethyleneglycol}thioether represented by  $\text{BrCH}_2\text{CH}_2-(\text{OCH}_2\text{CH}_2)_{20}-(\text{S}-\text{CH}_2\text{CH}_2)_3-(\text{OCH}_2\text{CH}_2)_{10}-\text{OCH}_2\text{CH}_2\text{Br}$ ,  
 (33) 1,4-Butanediol- $\omega$ -{(2-benzyloxy-1-methyl)ethyl}thioether- $\omega'$ -(decapropyleneglycoloctacontaethyleneglycol)thioether represented by  $\text{PhCH}_2\text{OCH}_2\text{CH}(\text{CH}_3)-\text{S}-\text{C}_4\text{H}_8-\text{S}-(\text{CH}_2\text{CH}_2\text{O})_{80}-(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{10}-\text{H}$ ,  
 (34) Dithiobis(icosaeethyleneglycol)bis(2-methyl-thioethyl)ether represented by  $\text{CH}_3-\text{S}-\text{CH}_2\text{CH}_2-(\text{OCH}_2\text{CH}_2)_{20}-\text{S}-\text{S}-(\text{CH}_2\text{CH}_2\text{O})_{20}-\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_3$ ,  
 (35) 1,2-Ethanediol- $\omega$ -(4-methoxybenzyl)thioether- $\omega'$ -(pentacontaethyleneglycol)thioether represented by  $\text{CH}_3\text{O}-\text{Ph}-\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_2-(\text{CH}_2\text{CH}_2\text{O})_{50}-\text{H}$ ,  
 (36) Triacontaethyleneglycolmono(4-cyanobenzyl)thioether represented by  $\text{NC}-\text{Ph}-\text{CH}_2-\text{S}-(\text{CH}_2\text{CH}_2)_{30}-\text{H}$ ,  
 (37) Thiobis(pentadecaethyleneglycol)bisallylether represented by  $\text{CH}_2=\text{CHCH}_2-(\text{OCH}_2\text{CH}_2)_{15}-\text{S}-(\text{CH}_2\text{CH}_2\text{O})_{15}-\text{CH}_2\text{CH}=\text{CH}_2$ ,  
 (38) Tricoethyleneglycolmono(4-formylphenetyl)thioether represented by  $\text{OHC}-\text{Ph}-\text{CH}_2\text{CH}_2-\text{S}-(\text{CH}_2\text{CH}_2\text{O})_{23}-\text{H}$ ,  
 (39) Pentadecaethyleneglycolmono{(acetylmethyl)thioethyl}thioether represented by  $\text{CH}_3\text{COCH}_2-\text{S}-\text{CH}_2\text{CH}_2-\text{S}-(\text{CH}_2\text{CH}_2)_{15}-\text{H}$ ,  
 (40) 1,2-Ethanediol- $\omega$ -(glycidyl)thioether- $\omega'$ -icosaeethyleneglycolthioether represented by



- (41) Octadecaethyleneglycolbis(2-methylthioethyl)ether represented by  $\text{CH}_3-\text{S}-\text{CH}_2\text{CH}_2\text{CO}-(\text{CH}_2\text{CH}_2\text{O})_{18}-\text{CH}_2\text{CH}_2\text{S}-\text{CH}_3$ ,  
 (42) Hexadecaethyleneglycolmono(2-methylthioethyl)thioether represented by  $\text{CH}_3-\text{S}-\text{CH}_2\text{CH}_2-\text{S}-(\text{CH}_2\text{CH}_2\text{O})_{16}-\text{H}$ ,  
 (43) Icosaeethyleneglycolmonomethylthioether represented by  $\text{CH}_3-\text{S}-(\text{CH}_2\text{CH}_2\text{O})_{20}-\text{H}$ ,  
 (44) Undecaethyleneglycoldi(n-propyl)thioether represented by  $\text{C}_3\text{H}_7-\text{S}-(\text{CH}_2\text{CH}_2\text{O})_{10}-\text{CH}_2\text{CH}_2\text{S}-\text{C}_3\text{H}_7$ ,  
 (45) Dodecaethyleneglycolbis(2-hydroxyethyl)thioether represented by  $\text{HOCH}_2\text{CH}_2-\text{S}-(\text{CH}_2\text{CH}_2\text{O})_{11}-\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_2\text{OH}$ ,  
 (46) Undecaethyleneglycoldimethylthioether,  
 (47) Pentatriacontaethyleneglycolmono(2-n-butylidithioethyl)dithioether represented by  $\text{C}_4\text{H}_9-\text{S}-\text{S}-\text{CH}_2\text{CH}_2-\text{S}-\text{S}-(\text{CH}_2\text{CH}_2\text{O})_{35}-\text{H}$ ,  
 (48) 4,8,12-trithiapentadecane-1,2,6,10,14,15-hexaol represented by  $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2-\text{S}-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-\text{S}-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-\text{S}-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ ,  
 (49) Icosaglycerolmono(2-ethylthioethyl)thioether represented by  $\text{C}_2\text{H}_5-\text{S}-\text{CH}_2\text{CH}_2-\text{S}-(\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O})_{20}-\text{H}$ ,

- (50) Triacontaethyleneglycolmono(2-methylthioethyl)thioether represented by  $\text{CH}_3\text{-S-CH}_2\text{CH}_2\text{-S-(C}_2\text{H}_4\text{O)}_{30}\text{-H}$ ,  
 (51) Dithiobis(icaosaethyleneglycol)dibenzylether represented by  $\text{Ph-CH}_2\text{-(OC}_2\text{H}_4\text{)}_{20}\text{-S-S-(C}_2\text{H}_4\text{O)}_{20}\text{-CH}_2\text{-Ph}$ ,  
 (52) Tridecaethyleneglycolmonomethylthioether represented by  $\text{CH}_3\text{-S-(CH}_2\text{CH}_2\text{O)}_{10}\text{-H}$ ,  
 (53) Hexadecaethyleneglycol dimethylthioether represented by  $\text{CH}_3\text{-S-(CH}_2\text{CH}_2\text{O)}_{15}\text{-CH}_2\text{CH}_2\text{-S-CH}_3$ ,  
 (54) 1,2-Ethanedithiolbis(icaosaethyleneglycol)thioether represented by  $\text{H-(OCH}_2\text{CH}_2\text{)}_{20}\text{-S-CH}_2\text{CH}_2\text{-S-(CH}_2\text{CH}_2\text{O)}_{20}\text{-H}$ ,  
 (55) Dithiobis(pentadecaethyleneglycol) represented by  $\text{H-(OCH}_2\text{CH}_2\text{)}_{15}\text{-S-S-(CH}_2\text{CH}_2\text{O)}_{15}\text{-H}$ , and  
 (56) 3,3'-thiodipropanol represented by  $\text{HO-CH}_2\text{CH}_2\text{CH}_2\text{-S-CH}_2\text{CH}_2\text{CH}_2\text{-OH}$ . In the above-listed structural formulae, Ph represents a phenyl group.

**[0017]** In one embodiment, the substituted dithioglycol is incorporated in a concentration of about 5 to about 100 mg/L; preferably about 10 to about 50 mg/L.

**[0018]** As already mentioned above, the method in accordance with the invention is characterized in particular by the special composition of the electrolyte. It contains essentially tin and copper ions, an alkylsulfonic acid and an aromatic nonionic wetting agent substituted dithioglycol brightener, and oxidation inhibitor. In addition, stabilizers and/or complexing agents, anionic and/or nonionic, brighteners, and other metal salts can optionally be contained in the electrolyte.

**[0019]** The metals that are primarily added to the electrolyte for deposition of bronzes in accordance with the invention - tin and copper - can first and foremost be in the form of salts of alkylsulfonic acids, preferably as methanesulfonates, or as salts of mineral acids, preferably as sulfates. Tin methanesulfonate is especially preferably used as tin salt in the electrolyte preferably in an amount of 5-195 g/L of electrolyte, preferably 11-175 g/L of electrolyte. This corresponds to a use of 2-75 g/L, preferably 4-57 g/L divalent tin ions. Copper methanesulfonate is especially preferably used in the electrolyte as the copper salt, which is advantageously added to the electrolyte in an amount of 8-280 g/L of electrolyte, preferably 16-260 g/L of electrolyte. This corresponds to the use of 2-70 g/L, preferably 4-65 g/L divalent copper ions.

**[0020]** Since the deposition is clearly higher in an acid environment, an acid, preferably a mineral and/or an alkylsulfonic acid, is added to the electrolyte in amounts of 140-382 g/L of electrolyte, preferably 175-245 g/L of electrolyte. The use of methanesulfonic acid turned out to be especially advantageous, since for one thing this produces advantageous solubility of metal salts and for another, because of its acid strength, it produces or facilitates the adjustment of the pH needed for the process. In addition, methanesulfonic acid has the advantageous property of contributing considerably to the stability of the bath.

**[0021]** In accordance with an additional characteristic of the invention at least one additional metal and/or chloride is added to the electrolyte. Advantageously, the metals are in the form of their soluble salts. In particular, the addition of zinc and/or bismuth has a considerable effect on the properties of the deposited coatings. The metals zinc and/or bismuth added to the electrolyte can namely be in the form of salts of alkylsulfonic acids, preferably as methanesulfonates or as salts of mineral acids, preferably as sulfates. Zinc sulfate is especially preferably used in the electrolytes as zinc salt, and is advantageously added in an amount of 0-25 g/L of electrolyte, preferably 15-20 g/L of electrolyte. Bismuth methane sulfate is especially preferably used in the electrolyte as bismuth salt and is advantageously added to the electrolyte in an amount of 0-5 g/L of electrolyte, preferably 0.05-0.2 g/L of electrolyte.

**[0022]** In addition, various additives; for example stabilizers and/or complexing agents, that are usually used in acid electrolytes for deposition of tin alloys can be added to the electrolyte.

**[0023]** In particular, the use of suitable compounds for stabilizing the electrolyte is an important condition for rapid as well as qualitative high grade deposition of bronzes. Gluconates are advantageously added to the electrolyte and stabilizers and/or complexing agents. Here in the method in accordance with the invention the preferred use of sodium gluconate turned out to be especially advantageous. The concentration of the stabilizers and/or complexing agents is 0-50 g/L of electrolyte, preferably 20-30 g/L of electrolyte. Compounds from the class of the dihydroxybenzenes, for example mono- or polyhydroxyphenyl compounds like pyrocatechol or phenolsulfonic acid are preferably used as oxidation inhibitors. The concentration of oxidation inhibitors is 0-5 g/L of electrolyte. Sodium hypophosphite is optionally used as an additional oxidation inhibitor. In one embodiment, the electrolyte contains hydroquinone as oxidation inhibitor.

**[0024]** The conduct of the method in accordance with the invention enables the deposition of bronzes onto various substrates. For example, all of the usual methods for making electronic components can be used. In the same way especially hard and wear-resistant bronze coatings can be deposited on materials like bearings, etc., to the method in accordance with the invention. The method in accordance with the invention is advantageously also used in the fields of decorative coating of, for example, fixtures and jewelry, etc., where the deposition of multi-component alloys that contain tin, copper, zinc and bismuth is particularly advantageous in these areas.

**[0025]** A really special advantage is that the so-called "true" bronzes that have a copper content >60% can be deposited with the method in accordance with the invention, where the copper content can be up to 95 wt% in each according to the desired properties. In addition, the ratio of the amount of copper to the amount of tin in the electrolyte has a considerable effect of properties like hardness and color of the bronze coatings. For instance, at a tin/copper ratio of 40/60 silver-colored coatings, the so-called white bronzes, which are relatively soft, are deposited. At a tin/copper ratio of 20/80

yellow gold colored coatings result, the so-called yellow bronzes, and at a tin/copper ratio of 10/90 red gold colored coatings are formed, the so-called red bronzes. As illustrated in the examples below, the invention is effective for forming white bronze deposits having a tin/copper weight ratio of about 40/60 or less, yellow bronze deposits having a tin/copper weight ratio of about 20/80 or less, and even red bronze deposits having a tin/copper weight ratio of about 10/90 or less.

[0026] Moreover, the deposition of high-tin white bronzes with a copper content = 10% is also possible.

[0027] In each case according to the desired appearance of the bronze coatings additives such as brighteners are added to the electrolyte, in addition to it having a varying copper content. Advantageously, the electrolyte contains brighteners from the class of the aromatic carbonyl compounds and/or  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds. The concentration of brighteners is 0-5 g/L of electrolyte.

[0028] Some preferred embodiments are presented below for illustration of the invention in more detail, but the invention is not limited to these embodiments.

Electrolyte composition:

[0029] The base electrolyte of the highly acid electrolyte in accordance with the invention contains essentially (per liter of electrolyte)

- 2-75 g divalent tin,
- 2-70 g divalent copper,
- 2-40 g of an aromatic nonionic wetting agent, and
- 140-382 g of a mineral and/or alkylsulfonic acid.

[0030] Optionally, other components can be added to the electrolyte (per liter of electrolyte):

- 0-10 g of an anionic and/or aliphatic nonionic wetting agent,
- 0-50 g of a stabilizer and/or complexing agent,
- 0-5 g of an oxidation inhibitor,
- 0-5 g of a brightener
- 0-5 trivalent bismuth
- 0-25 g divalent zinc.

[0031] In order to achieve a specific color of the deposited bronze coatings the electrolyte is prepared by varying the individual components, as given below as a matter of example. Additional information about the corresponding process conditions as well as other properties of the individual coatings can be seen in Table 1. Examples 1 to 8 are comparative examples only and are not a subject of the claimed invention.

Example 1 (red bronze; comparative only)

[0032]

- 4 g/L  $\text{Sn}^{2+}$
- 18 g/L  $\text{Cu}^{2+}$
- 286 g/L methanesulfonic acid
- 3 g/L aromatic nonionic wetting agent
- 0.4 g/l aliphatic nonionic wetting agent
- 2 g/L oxidation inhibitor
- 20 mg/L complexing agent

Example 2a (yellow bronze; comparative only)

[0033]

- 4 g/L  $\text{Sn}^{2+}$
- 18 g/L  $\text{Cu}^{2+}$
- 240 g/L methanesulfonic acid
- 32.2 g/L aromatic nonionic wetting agent
- 2 g/L oxidation inhibitor
- 25 mg/L stabilizer/complexing agent

Example 2b (yellow bronze; comparative only)

**[0034]**

5        4 g/L  $\text{Sn}^{2+}$   
        18 g/L  $\text{Cu}^{2+}$   
        286 g/L methanesulfonic acid  
        32.2 g/L aromatic nonionic wetting agent  
        6 mg/L brightener  
 10       2 g/L oxidation inhibitor  
        50 mg/L stabilizer/complexing agent

Example 3 (white bronze; comparative only)

15       **[0035]**

       5 g/L  $\text{Sn}^{2+}$   
        10 g/L  $\text{Cu}^{2+}$   
        240 g/L methanesulfonic acid  
 20       32.2 g/L aromatic nonionic wetting agent  
        6 mg/L brightener  
        2 g/L oxidation inhibitor  
        25 mg/L stabilizer/complexing agent

25       Example 4 (matte white bronze; comparative only)

**[0036]**

       18 g/L  $\text{Sn}^{2+}$   
 30       2 g/L  $\text{Cu}^{2+}$   
        258 g/L methanesulfonic acid  
        9 g/L aromatic nonionic wetting agent

35       **[0037]** To improve the hardness and/or ductility of the deposited bronze coatings the contents of zinc and/or bismuth indicated below as examples are added to the electrolyte. Additional data on the corresponding process conditions and other properties of the individual coatings can be seen in Table 1.

Example 5 (high ductility; comparative only)

40       **[0038]**

       4 g/L  $\text{Sn}^{2+}$   
        18 g/L  $\text{Cu}^{2+}$   
        238 g/L methanesulfonic acid  
 45       32.2 g/L aromatic nonionic wetting agent  
        3 mg/L brightener  
        2 g/L oxidation inhibitor  
        25 mg/L stabilizer/complexing agent  
        20 g/L  $\text{ZnSO}_4$   
 50

Example 6 (hardness; comparative only)

**[0039]**

55       4 g/L  $\text{Sn}^{2+}$   
        18 g/L  $\text{Cu}^{2+}$   
        238 g/L methanesulfonic acid  
        32.2 g/L aromatic nonionic wetting agent

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2 g/L oxidation inhibitor  
25 mg/L stabilizer/complexing agent  
0.1 g/L Bi<sup>3+</sup>

5 Example 7 (yellow bronze; comparative only)

### [0040]

10 14.5 g/L Sn<sup>2+</sup>  
65.5 g/L Cu<sup>2+</sup>  
382 g/L methanesulfonic acid  
32.2 g/L aromatic nonionic wetting agent  
4 g/L oxidation inhibitor  
25 mg/L stabilizer/complexing agent  
15 20 g/L ZnSO<sub>4</sub>

Example 8 (yellow bronze; comparative only)

### [0041]

20 2 g/L Sn<sup>2+</sup>  
8 g/L Cu<sup>2+</sup>  
400 g/L methanesulfonic acid  
2.5 g/L aromatic nonionic wetting agent  
25 1 g/L aliphatic fatty alcohol ethoxylate  
4 g/L oxidation inhibitor

Example 9 (white bronze)

### [0042]

4 g/L Sn<sup>2+</sup>  
8 g/L Cu<sup>2+</sup>  
400 g/L methanesulfonic acid  
35 1 g/L aromatic nonionic wetting agent  
40 mg/L substituted dithioglycol  
4 g/L oxidation inhibitor

40 **[0043]** With these exemplary electrolyte compositions coatings with specific properties were deposited under the process conditions listed in the following table.

| Example No. | Coating/Amounts in wt% |    |    |    | Properties of coating |           |       |        |
|-------------|------------------------|----|----|----|-----------------------|-----------|-------|--------|
|             | Sn                     | Cu | Zn | Bi | Hardness              | Ductility | Gloss | Color  |
| 1           | 10                     | 90 | -  | -  | 180 HV <sub>50</sub>  | ++        | Yes   | Red    |
| 2a          | 20                     | 80 | -  | -  | 283 Hv <sub>50</sub>  | ±         | Yes   | Yellow |
| 2b          | 20                     | 80 | -  | -  | 317 HV <sub>50</sub>  | ±         | Yes   | Yellow |
| 3           | 40                     | 60 | -  | -  | 360 HV <sub>50</sub>  | ±         | Yes   | White  |
| 4           | 90                     | 10 | -  | -  | -                     | -         | No    | White  |
| 5           | 20                     | 80 | <1 | -  | -                     | +++       | Yes   | Yellow |
| 6           | 20                     | 80 | -  | <1 | 345 HV <sub>50</sub>  | -         | Yes   | Yellow |
| 7           | 20                     | 80 | <1 | -  | -                     | ++        | Yes   | Yellow |

Example 10 (white bronze)**[0044]**

- 5        3 g/L Sn<sup>2+</sup>  
        6 g/L Cu<sup>2+</sup>  
        300 - 400 g/L methanesulfonic acid  
        2 g/L aromatic nonionic wetting agent  
        15-30 mg/L substituted dithioglycol  
 10       4 g/L oxidation inhibitor

**[0045]** Electrolytic coating was performed on a copper plated brass substrate at 25 C and a current density of 1.2 A/dm<sup>2</sup> with soluble bronze (60Cu/40Sn) anodes for 8 minutes to a thickness of 3 microns. Ductility was acceptable; uniformity was good; hardness was 350 HV25; gloss was very good. The specimens passed a thio acetamide tarnish resistance test (storage 4 hours at 180 C).

**[0046]** When introducing elements of the present invention or the preferred embodiment(s) thereof, the articles "a," "an," "the," and "said" are intended to mean that there are one or more of the elements. The terms "comprising," "including," and "having" are intended to be inclusive and mean that there may be additional elements other than the listed elements.

20

**Claims**

1. A method for electrolytic deposition of bronze onto a substrate, the method comprising:

25        immersing a substrate in an aqueous acidic electrolyte having a pH of less than 1 and containing:

- a) tin ions;  
        b) copper ions;  
        c) methanesulfonic acid;  
 30       d) an aromatic non-ionic wetting agent;  
        e) a substituted dithioglycol brightener; and  
        f) an oxidation inhibitor;

       wherein a ratio of tin ion concentration to copper ion concentration is sufficient to electrolytically deposit a bronze comprising at least 60% by weight Cu; and  
 35       electrodepositing onto said substrate bronze comprising at least 60% by weight Cu, wherein said electrodepositing occurs by passing current through a copper-tin anode and the substrate

2. The method of claim 1 wherein the copper ions are present in a concentration of 4-65 g/L, and wherein the substituted dithioglycol brightener is present in the composition in a concentration of 10-50 mg/L.

3. The method of claim 1 wherein the electrolyte further contains a dihydroxybenzene compound as an oxidation inhibitor.

45    4. The method of claim 1 wherein the non-ionic wetting agent is present in the electrolyte at a concentration of from 2 to 40 g/L.

5. The method of any one of claims 1 through 4 wherein tin methanesulfonate is present in the electrolyte in an amount of from 5 to 195 g/L of electrolyte, thereby providing the tin ions at a concentration of from 2 to 75 g/L of electrolyte.

50    6. The method of any one of claims 1 through 5 wherein copper methanesulfonate is present in the electrolyte in an amount of from 16 to 260 g/L of electrolyte, thereby providing the copper ions at a concentration of from 4 to 65 g/L of electrolyte.

55    7. The method of any one of claims 1 through 6 wherein the substituted dithioglycol is selected from the group consisting of Thiobis(diethyleneglycol), Thiobis(hexaethylene glycol), Thiobis(pentadecaglycelol), Thiobis(icosaethyleneglycol), Thiobis(pentacontaethyleneglycol), 4,10-dioxo-7-thiatridecane-2,12-diol, Thiodiglycerin, Thiobis(triglycerin), 2,2'-thiodibutanolbis(octaethyleneglycolpentaglycerol) ether, Thiobis(octaethyleneglycol)bis(2-chloroethyl)ether,

Thiobis(decaethyleneglycol)bis(carboxymethyl)ether, Thiobis(dodecaethyleneglycol)bis(2-nitroethyl)ether, Thiodiglycolbis(carboxymethyl)ether, Dithiodiglycolbis(carboxymethyl)ether, Thiobis(dodecaethyleneglycol), Dithiobis(hentetracontaethyleneglycol), Dithiobis(icosaeethyleneglycol)pentapropyleneglycol, Dithiobis(triglycerol), Dithiobis(decaglycerol), 3,6-Dithiaoctane-1,8-diol, 1,3-Propanedithiolbis(decaethyleneglycol)thioether, 1,4-Butanedithiolbis(pentadecaglycerol)thioether, 1,3-Dithioglycerolbis(pentaethyleneglycol)thioether, 1,2-Ethanedithiolbis(penta(1-ethyl)ethyleneglycol)thioether, 1,3-Dithioglycerolbis(di(1-ethyl)ethyleneglycol)thioether, 2-Mercaptoethylsulfidebis(hexatriacontaethylene-glycol), 2-Mercaptoethylsulfidebis(icosaeethyleneglycol)di-methylether, 2-Mercaptoethyl-etherbis(diethyleneglycol), Thiodiglyceroltetra(decaethyleneglycol)ether, Diethyleneglycolmonomethylthioether, Decaglycerolmono(6-methylthiohexyl)thioether, 2-Mercaptoethylsulfide- $\omega$ -{(2-bromoethyl) icosaeethyleneglycol}thioether- $\omega$ '-{(2-bromoethyl) heptaethyleneglycol}thioether, 1,4-Butanediol- $\omega$ -{(2-benzyloxy-1-methyl)ethyl}thioether- $\omega$ '-(de capropyleneglycol)octacontaethyleneglycol)thioether, Dithiobis(icosaeethyleneglycol)bis(2-methylthioethyl)ether, 1,2-Ethandiol- $\omega$ -(4-methoxybenzyl)thioether- $\omega$ '-(pentacontaethyleneglycol)thioether, Triacontaethyleneglycolmono(4-cyanobenzyl)thioether, Thiobis(pentadecaethyleneglycol)bisallyether, Tricosaethyleneglycolmono(4-formylphenetyl)thioether, Pentadecaethyleneglycolmono{(acetylmethyl)thioethyl}thioether, 1,2-Ethandiol- $\omega$ -(glycidyl)thioether- $\omega$ '-icosaeethyleneglycolthioether, Octadecaethyleneglycolbis(2-methylthioethyl)ether, Hexadecaethyleneglycolmono(2-methylthioethyl)thioether, Icosaethyleneglycolmonomethylthioether, Undecaethyleneglycoldi(n-propyl)thioether, Dodecaethyleneglycolbis(2-hydroxyethyl)thioether, Undecaethyleneglycoldimethylthioether, Pentatriacontaethyleneglycolmono(2-nbutyldithioethyl) dithioether, 4,8,12-trithiapentadecane-1,2,6,10,14,15-hexaol, Icosaglycerolmono(2-ethylthioethyl)thioether, Triacontaethyleneglycolmono(2-methylthioethyl)thioether, Dithiobis(icosaeethyleneglycol)dibenzylether, Tridecaethyleneglycolmonomethylthioether, Hexadecaethyleneglycol dimethylthioether, 1,2-Ethanedithiolbis(icosaeethyleneglycol)thioether, Dithiobis(pentadecaethyleneglycol), 3,3'-thiodipropanol, and combinations thereof.

8. The method of any one of claims 1 through 7 wherein said aqueous acidic electrolyte further contains a gluconate.

9. The electrolyte method of any one of claims 1 through 8 wherein said aqueous acidic electrolyte further contains hydroquinone.

10. A method according to claim 1 for electrolytic deposition of bronze onto a substrate, the method comprising:

immersing a substrate in an aqueous acidic electrolyte having a pH of less than 1 and containing:

- a) tin ions;
- b) copper ions in a concentration of 4 - 65 g/L;
- c) methanesulfonic acid in a concentration between 140 g/L and 382 g/L;
- d) a nonionic wetting agent in a concentration from 2 g/L to 40 g/L which is an aromatic, non-ionic wetting agent;
- e) a substituted dithioglycol brightener; and
- f) an oxidation inhibitor;

wherein a ratio of tin ion concentration to copper ion concentration is sufficient to electrolytically deposit a bronze comprising at least 60% by weight Cu; and electrodepositing onto said substrate bronze comprising at least 60% by weight Cu.

11. The method of any one of claims 1 through 10 wherein the ratio of tin ion concentration to copper ion concentration is sufficient to electrolytically deposit a bronze comprising at least 80% by weight Cu.

12. The method of any one of claims 1 through 10 wherein the ratio of tin ion concentration to copper ion concentration is sufficient to electrolytically deposit a bronze comprising at least 90% by weight Cu.

13. The method of any one of claims 1 through 10 wherein the substrate is a decorative article.

14. The method of any one of claims 1 through 10 wherein the ratio of tin ion concentration to copper ion concentration is 40/60.

15. The method of any one of claims 1 through 10 wherein the ratio of tin ion concentration to copper ion concentration is 20/80.

16. The method of any one of claims 1 through 10 wherein the ratio of tin ion concentration to copper ion concentration is 10/90.
17. The method of any one of claims 1 through 10 the aromatic, non-ionic wetting agent is a  $\beta$ -naphthol ethoxylate.
18. The method of anyone of claims 1 through 10 wherein the substituted dithioglycol brightener is present in the composition at a concentration of 40 mg/L.
19. The method of claim 11 wherein said aqueous acidic electrolyte consisting essentially only of the stated components.

## Patentansprüche

1. Verfahren zum elektrolytischen Abscheiden von Bronze auf einem Substrat, wobei das Verfahren die Schritte aufweist:

Eintauchen eines Substrats in einen wässrigen, sauren Elektrolyt, der einen pH-Wert von weniger als 1 hat und enthält:

- a) Zinnionen;
- b) Kupferionen;
- c) Methansulfonsäure;
- d) ein aromatisches nichtionisches Benetzungsmittel;
- e) ein substituiertes Dithioglycol-Glanzmittel; und
- f) einen Oxidationsinhibitor;

wobei das Verhältnis zwischen der Zinnionenkonzentration und der Kupferionenkonzentration ausreichend ist, um Bronze, die mindestens 60 Gew.-% Cu enthält, elektrolytisch abzuscheiden; und  
Elektroabscheiden von Bronze, die mindestens 60 Gew.-% Cu enthält, auf dem Substrat, wobei die Elektroabscheidung ausgeführt wird, indem ein Strom durch eine Kupfer-Zinn-Anode und das Substrat geleitet wird.

2. Verfahren nach Anspruch 1, wobei die Kupferionen in einer Konzentration von 4-65 g/l vorhanden sind, und wobei das substituierte Dithioglycol-Glanzmittel in der Zusammensetzung in einer Konzentration von 10-50 mg/l enthalten ist.
3. Verfahren nach Anspruch 1, wobei der Elektrolyt ferner eine Dihydroxybenzolverbindung als Oxidationsinhibitor aufweist.
4. Verfahren nach Anspruch 1, wobei das nichtionische Netzungsmittel in dem Elektrolyten in einer Konzentration von 2 bis 40 g/l vorhanden ist.
5. Verfahren nach einem der Ansprüche 1 bis 4, wobei Zinn-Methansulfonat im Elektrolyt in einer Menge von 5 bis 195 g/l Elektrolyt vorhanden ist, wodurch die Zinnionen in einer Konzentration von 2 bis 75 g/l Elektrolyt bereitgestellt werden.
6. Verfahren nach einem der Ansprüche 1 bis 5, wobei Kupfer-Methansulfonat im Elektrolyt in einer Menge von 16 bis 260 g/l Elektrolyt vorhanden ist, wodurch die Kupferionen in einer Konzentration von 4 bis 65 g/l Elektrolyt bereitgestellt werden.
7. Verfahren nach einem der Ansprüche 1 bis 6, wobei das substituierte Dithioglycol ausgewählt wird aus Thiobis(diethylenglykol), Thiobis(hexa-ethylenglykol), Thiobis-(pentadecaglycelol), Thiobis(icosaeethylenglykol), Thiobis-(pentacontaethylenglykol), 4,10-Dioxa-7-thiatridecan-2,2-diol, Thiodiglycerin, Thiobis(triglycerin), 2,2'-thiodibutanol-bis(octaethylen-glycolpentaglycerol)ether, Thiobis(octaethylenglykol)bis(2-chlorethyl)ether, Thiobis(decaethylen-glykol)bis(carboxymethyl)ether, Thiobis(dodecaethylenglykol)bis(2-nitroethyl)ether, Thiodiglycolbis(carboxymethyl)ether, Dithiodiglycolbis(carboxymethyl)ether, Thiobis(dodecaethylenglykol), Dithiobis(hentetracontaethylenglykol), Dithiobis(icosaeethylenglycolpentapropylenglykol), Dithiobis(triglycerol), Dithiobis(decaglycerol), 3,6-Dithio-octan-1,8-diol, 1,3-Propandithiolbis(deca-ethylenglykol)thioether, 1,4-Butandithiolbis(pentadecaglycerol)thioether, 1,3-Dithioglycerolbis(pentaethylenglykol)thioether, 1,2-Ethandithiolbis(penta-(1-ethyl)ethylenglykol)thioether, 1,3-

Dithioglycerolbis(di(1-ethyl)ethylenglycol)thioether, 2-Mercaptoethylsulfid-bis(hexatriacontaethylenglycol), 2-Mercaptoethylsulfidbis(icosaeethylenglycol)di-methylether, 2-Mercaptoethylether-bis(diethylenglycol), Thiodiglycerolterra(decaethylenglycol)ether, Diethylenglycolmonomethylthioether, Decaglycerolmono(6-methylthiohexyl)thioether, 2-Mercaptoethylsulfid- $\omega$ -{(2-bromomethyl)icosaeethylenglycol}thioether- $\omega'$ -{(2-bromomethyl)hectaethylenglycol}thioether, 1,4-Butandiol- $\omega$ -{(2-benzyloxy-1-methyl)ethyl}thioether- $\omega'$ -(decapropylenglycoloctacontaethylenglycol)thioether, Dithiobis(icosaeethylenglycol)bis(2-methyl-thioethyl)ether, 1,2-Ethandiol- $\omega$ -(4-methoxybenzyl)thioether- $\omega'$ -(pentacontaethylenglycol)thioether, Triacontaethylenglycolmono(4-cyanobenzyl)thioether, Tiobis(pentadecaethylenglycol)bisallylether, Tricosaethylenglycolmono(4-formylphenetyl)thioether, Pentadecaethylenglycolmono(acetylmethyl)thioethyl}thioether, 1,2-Ethandiol- $\omega$ -(glycidyl)thioether- $\omega'$ -icosaeethylenglycolthioether, Octadecaethylenglycolbis(2-methylthioethyl)ether, Hexadecaethylenglycolmono(2-methylthioethyl)thioether, Icosaethylenglycolmonomethylthioether, Undecaethylenglycoldi(n-propyl)thioether, Dodecaethylenglycolbis(2-hydroxyethyl)thioether, Undecaethylenglycoldimethylthioether, Pentatriacontaethylenglycolmono(2-n-butylthioethyl)dithioether, 4,8,12-trithiapentadecan-1,2,6,10,14,15-hexaol, Icosaglycerolmono(2-ethylthioethyl)thioether, Triacontaethylenglycolmono(2-methylthioethyl)thioether, Dithiobis(icosaeethylenglycol)dibenzylether, Tridecaethylenglycolmonomethylthioether, Hexadecaethylenglycoldimethylthioether, 1,2-Ethandithiolbis(icosae-ethylenglycol)thioether, Dithiobis(pentadecaethylenglycol), 3,3'-Thiodipropanol und Kombinationen davon.

8. Verfahren nach einem der Ansprüche 1 bis 7, wobei der wässrige, saure Elektrolyt ferner ein Gluconat enthält.

9. Verfahren nach einem der Ansprüche 1 bis 8, wobei der wässrige, saure Elektrolyt ferner Hydrochinon enthält.

10. Verfahren nach Anspruch 1, wobei das Verfahren aufweist:

Eintauchen eines Substrats in einen wässrigen, sauren Elektrolyt, der einen pH-Wert von weniger als 1 hat und enthält:

- a) Zinnionen;
- b) Kupferionen in einer Konzentration von 4-65 g/l;
- c) Methansulfonsäure in einer Konzentration zwischen 140 g/l und 382 g/l;
- d) ein nichtionisches Netzungsmittel in einer Konzentration von 2 g/l bis 40 g/l, das ein aromatisches, nichtionisches Netzungsmittel ist;
- e) ein substituiertes Dithioglycol-Glanzmittel; und
- f) einen Oxidationsinhibitor;

wobei das Verhältnis zwischen der Zinnionenkonzentration und der Kupferionenkonzentration ausreichend ist, um Bronze, die mindestens 60 Gew.-% Cu enthält, elektrolytisch auf dem Substrat abzuscheiden; und Abscheiden von Bronze, die mindestens 60 Gew.-% Cu enthält, auf dem Substrat durch eine Elektroabscheidung.

11. Verfahren nach einem der Ansprüche 1 bis 10, wobei das Verhältnis zwischen der Zinnionenkonzentration und der Kupferionenkonzentration ausreichend ist, um Bronze, die mindestens 80 Gew.-% Cu enthält, elektrolytisch abzuscheiden.

12. Verfahren nach einem der Ansprüche 1 bis 10, wobei das Verhältnis zwischen der Zinnionenkonzentration und der Kupferionenkonzentration ausreichend ist, um Bronze, die mindestens 90 Gew.-% Cu enthält, elektrolytisch abzuscheiden.

13. Verfahren nach einem der Ansprüche 1 bis 10, wobei das Substrat ein Dekorartikel ist.

14. Verfahren nach einem der Ansprüche 1 bis 10, wobei das Verhältnis zwischen der Zinnionenkonzentration und der Kupferionenkonzentration 40/60 beträgt.

15. Verfahren nach einem der Ansprüche 1 bis 10, wobei das Verhältnis zwischen der Zinnionenkonzentration und der Kupferionenkonzentration 20/80 beträgt.

16. Verfahren nach einem der Ansprüche 1 bis 10, wobei das Verhältnis zwischen der Zinnionenkonzentration und der Kupferionenkonzentration 10/90 beträgt.

17. Verfahren nach einem der Ansprüche 1 bis 10, wobei das aromatische, nichtionische Netzungsmittel ein  $\beta$ -Naphthothoethoxylat ist.

18. Verfahren nach einem der Ansprüche 1 bis 10, wobei das substituierte Dithioglycol-Glanzmittel in der Zusammensetzung in einer Konzentration von 40 mg/l vorhanden ist.

19. Verfahren nach Anspruch 11, wobei der wässrige, saure Elektrolyt im Wesentlichen nur aus den genannten Komponenten besteht.

## Revendications

1. Procédé de dépôt électrolytique de bronze sur un substrat, le procédé comprenant :

l'immersion d'un substrat dans un électrolyte acide aqueux dont le pH est inférieur à 1 et contenant :

- a) des ions étain ;
- b) des ions cuivre ;
- c) de l'acide méthanesulfonique ;
- d) un agent mouillant non ionique aromatique ;
- e) un azurant de type dithioglycol substitué ; et
- f) un inhibiteur d'oxydation ;

le rapport de la concentration en ions étain sur la concentration en ions cuivre étant suffisant pour déposer par voie électrolytique un bronze comprenant au moins 60 % en masse de Cu ; et l'électrodéposition sur ledit substrat de bronze comprenant au moins 60 % en masse de Cu, ladite électrodéposition étant mise en oeuvre par passage d'un courant à travers une anode de cuivre-étain et le substrat.

2. Procédé conforme à la revendication 1, où les ions cuivre sont présents à une concentration comprise entre 4 et 65 g/L, et où l'azurant de type dithioglycol substitué est présent dans la composition à une concentration comprise entre 10 et 50 mg/L.

3. Procédé conforme à la revendication 1, où l'électrolyte contient en outre un dihydroxybenzène au titre d'inhibiteur d'oxydation.

4. Procédé conforme à la revendication 1, où l'agent mouillant non ionique est présent dans l'électrolyte à une concentration comprise entre 2 et 40 g/L.

5. Procédé conforme à l'une quelconque des revendications 1 à 4, où du méthanesulfonate d'étain est présent dans l'électrolyte à une teneur comprise entre 5 et 195 g/L d'électrolyte, ce qui fournit une concentration en ions étain comprise entre 2 et 75 g/L d'électrolyte.

6. Procédé conforme à l'une quelconque des revendications 1 à 5, où du méthanesulfonate de cuivre est présent dans l'électrolyte à une teneur comprise entre 16 et 260 g/L d'électrolyte, ce qui fournit une concentration en ions cuivre comprise entre 4 et 65 g/L d'électrolyte.

7. Procédé conforme à l'une quelconque des revendications 1 à 6, où le dithioglycol substitué est choisi dans le groupe constitué par les suivants : Thiobis(diéthylèneglycol), Thiobis(hexaéthylène glycol), Thiobis(pentadécaglycérol), Thiobis(icoséthylèneglycol), Thiobis(pentacontaéthylèneglycol), 4,10-dioxa-7-thiatridécane-2,12-diol, Thiodiglycérine, Thiobis(triglycérine), 2,2'-thiodibutanolbis(octaéthylèneglycolpentaglycérol)éther, Thiobis(octaéthylèneglycol)bis(2-chloroéthyl)éther, Thiobis(décaéthylèneglycol)bis(carboxyméthyl)éther, Thiobis(dodécaéthylèneglycol)bis(2-nitroéthyl)éther, Thiodiglycolbis(carboxyméthyl)éther, Dithiodiglycolbis(carboxyméthyl)éther, Thiobis(dodécaéthylèneglycol), Dithiobis(hentetracontaéthylèneglycol), Dithiobis(icoséthylèneglycolpentapropylèneglycol), Dithiobis(triglycérol), Dithiobis(décaglycérol), 3,6-Dithiaoctane-1,8-diol, 1,3-propanedithiolbis(décaéthylèneglycol)thioéther, 1,4-Butanedithiolbis(pentadécaglycérol)thioéther, 1,3-Dithioglycérolbis(pentaéthylèneglycol)thioéther, 1,2-Éthanedithiolbis(penta(1-éthyl)éthylèneglycol)thioéther, 1,3-Dithioglycérolbis(di(1-éthyl)éthylèneglycol)thioéther, 2-Mercaptoéthylsulfure bis(hexatriacontaéthylène-glycol), 2-Mercaptoéthylsulfure bis(icoséthylèneglycol)di-méthyléther, 2-Mercaptoéthylétherbis(diéthylèneglycol), Thiodiglycéroltétra(décaéthylèneglycol)éther,

Diéthylèneglycolmonométhylthioéther, Décaglycérolmono(6-méthylthiohexyl)thioéther, 2-Mercaptoéthylsulfure- $\omega$ -{(2-bromoéthyl)icosaéthylèneglycol}thioéther- $\omega'$ -[(2-bromoéthyl)heptaéthylèneglycol]thioéther, 1,4-Butanediol- $\omega$ -{(2-benzyloxy-1-méthyl)éthyl}thioéther- $\omega'$ -(décapropylèneglycoloctacontaéthylèneglycol)thioéther, Dithiobis(ico-  
 5 saéthylèneglycol)bis(2-méthyl-thioéthyl)éther, 1,2-Éthanediol- $\omega$ -(4-méthoxybenzyl)thioéther- $\omega'$ -(pentacontaéthylè-  
 neglycol)thioéther, Triacontaéthylèneglycolmono(4-cyanobenzyl)thioéther, Thiobis(pentadécaéthylèneglycol)bisal-  
 lyléther, Tricosaéthylèneglycolmono(4-formylphénéthyl)thioéther, Pentadécaéthylèneglycolmono {(acetylmé-  
 10 thyl)thioéthyl}thioéther, 1,2-Éthanediol- $\omega$ -(glycidyl)thioéther- $\omega'$ -icosaéthylèneglycolthioéther, Octadécaéthylènegly-  
 colbis(2-méthylthioéthyl)éther, Hexadécaéthylèneglycolmono(2-méthylthioéthyl)thioéther, Icosaéthylèneglycolmo-  
 nométhylthioéther, Undécaéthylèneglycoldi(n-propyl)thioéther, Dodécaéthylèneglycolbis(2-hydroxyéthyl)thioéther,  
 10 Undécaéthylèneglycoldiméthylthioéther, Pentatriacontaéthylèneglycolmono(2-nbutyldithioéthyl)dithioéther, 4,8,12-  
 trithiapentadécane-1,2,6,10,14,15-hexaol, Icosaglycérolmono(2-éthylthioéthyl)thioéther, Triacontaéthylèneglycol-  
 mono(2-méthylthioéthyl)thioéther, Dithiobis(icosaéthylèneglycol)dibenzyléther, Tridécaéthylèneglycolmonométhyl-  
 thioéther, Hexadécaéthylèneglycoldiméthylthioéther, 1,2-Éthanedithiolbis(icosaéthylèneglycol)thioéther, Dithio-  
 bis(pentadécaéthylèneglycol), 3,3'-thiodipropanol, ainsi que leurs combinaisons.

8. Procédé conforme à l'une quelconque des revendications 1 à 7, où ledit électrolyte acide aqueux contient en outre un gluconate.

9. Procédé électrolytique conforme à l'une quelconque des revendications 1 à 8, où ledit électrolyte acide aqueux contient en outre de l'hydroquinone.

10. Procédé de dépôt électrolytique de bronze sur un substrat conforme à la revendication 1, le procédé comprenant :

l'immersion d'un substrat dans un électrolyte acide aqueux dont le pH est inférieur à 1 et contenant :

- a) des ions étain ;
- b) des ions cuivre à une concentration comprise entre 4 et 65 g/L ;
- c) de l'acide méthanesulfonique à une concentration comprise entre 140 g/L et 382 g/L ;
- d) un agent mouillant non ionique à une concentration comprise entre 2 g/L et 40 g/L, qui est un agent mouillant non ionique aromatique ;
- e) un azurant de type dithioglycol substitué ; et
- f) un inhibiteur d'oxydation ;

le rapport de la concentration en ions étain sur la concentration en ions cuivre étant suffisant pour déposer par voie électrolytique un bronze comprenant au moins 60 % en masse de Cu ; et l'électrodéposition sur ledit substrat de bronze comprenant au moins 60 % en masse de Cu.

11. Procédé conforme à l'une quelconque des revendications 1 à 10, où le rapport de la concentration en ions étain sur la concentration en ions cuivre est suffisant pour déposer par voie électrolytique un bronze comprenant au moins 80 % en masse de Cu.

12. Procédé conforme à l'une quelconque des revendications 1 à 10, où le rapport de la concentration en ions étain sur la concentration en ions cuivre est suffisant pour déposer par voie électrolytique un bronze comprenant au moins 90 % en masse de Cu.

13. Procédé conforme à l'une quelconque des revendications 1 à 10, où le substrat est un article décoratif.

14. Procédé conforme à l'une quelconque des revendications 1 à 10, où le rapport de la concentration en ions étain sur la concentration en ions cuivre est de 40/60.

15. Procédé conforme à l'une quelconque des revendications 1 à 10, où le rapport de la concentration en ions étain sur la concentration en ions cuivre est de 20/80.

16. Procédé conforme à l'une quelconque des revendications 1 à 10, où le rapport de la concentration en ions étain sur la concentration en ions cuivre est de 10/90.

17. Procédé conforme à l'une quelconque des revendications 1 à 10, où l'agent mouillant non ionique aromatique est l'éthoxylate de  $\beta$ -naphtyle.

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18. Procédé conforme à l'une quelconque des revendications 1 à 10, où l'azurant de type dithioglycol substitué est présent dans la composition à une concentration de 40 mg/L.
- 5 19. Procédé conforme à la revendication 11, où ledit électrolyte acide aqueux est essentiellement uniquement constitué des composants indiqués.

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**REFERENCES CITED IN THE DESCRIPTION**

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