The invention relates to a modified copper-tin electrolyte which is free of toxic constituents such as cyanides or thio compounds. The invention further relates to a process for the deposition of decorative bronze layers on consumer goods and industrial articles using the electrolyte of the invention. The electrolyte comprises an additive formed from epichlorohydrin and hexamethylenetetramine and contains carbonate or hydrogencarbonate ions.
MODIFIED COPPER-TIN ELECTROLYTE AND PROCESS FOR THE DEPOSITION OF BRONZE LAYERS

[0001] The invention relates to a modified pyrophosphate-containing copper-tin electrolyte which is free of toxic constituents such as cyanides or thiourea compounds. The invention further relates to a process for the deposition of decorative bronze layers on consumer goods and industrial articles using the electrolyte of the invention.

[0002] Consumer goods or consumer articles as are defined in the consumer article regulations are upgraded by means of thin, oxidation-stable metal layers for decorative purposes and to prevent corrosion. These layers have to be mechanically stable and should not display any discoloration due to tarnishing or wear phenomena even on prolonged use. The sale of consumer goods coated with nickel-containing upgrading alloys has no longer been permitted in Europe since 2001 in accordance with EU Directive 94/27/EC or is possible only under strict rules since nickel and nickel-containing metal layers are contact allergens. Bronze alloys, in particular, have become established as a replacement for nickel-containing upgrading layers and these enable such mass-produced consumer goods to be upgraded inexpensively in electrolytic barrel or rack plating processes to give allergen-free, tracked products.

[0003] In the production of bronze layers for the electronics industry, the stability of the resulting layer and possibly 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 the production of bronze layers on consumer goods, the decorative effect of the resulting layer together with long-term durability of the layer with an essentially unchanged appearance are the important target parameters.

[0004] Known processes for producing bronze layers include not only conventional processes which use cyanide-containing and thus highly toxic alkali baths, but also various electrolytically processes which can, according to the composition of their electrolytes, usually be assigned to one of two main groups found in the prior art: processes using electrolytes based on organosulfonic acids or processes using baths based on phosphoric acid. For the purposes of the present text, "nontoxic" means that the electrolyte according to the invention designated in this way does not contain any materials which are classified as "toxic" (I) or "very toxic" (II) under the regulations for handling dangerous goods and hazardous materials which apply in Europe.

[0005] For example, EP111097A2 describes an electrolyte which contains not only an organosulfonic acid and ions of tin and of copper and also dispersants and brighteners but also, if appropriate, antioxidants. EP 1 408 141 A1 describes a process for the electrochemical deposition of brasses, in which an acidic electrolyte containing tin and copper ions and also an alkylsulfonic acid and an aromatic, nonionic wetting agent is used. DE 100 46 600 A1 describes a bath containing alkylsulfonic or alkanosulfonic acid together with soluble tin and copper salts and organic sulfur compounds and also a process using this bath.

[0006] EP1146148A2 describes a cyanide-free copper-tin electrolyte which is based on phosphoric acid and contains the reaction product of an amine and an epichlorohydrin in a molar ratio of 1:1 and also a cationic surfactant. The amine can be hexamethylenetetramine. Current densities of 0.5, 1.5, 2.5 and 3.0 A/dm² are used in the electrolytic deposition.

[0007] 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 text to achieve a further widening of the current density range in which uniform deposition of the metals in a bright layer can be achieved. It is explicitly stated that such deposition can only be achieved when the additive added is made up of all three of the abovementioned components.

[0008] Different coating processes are usually used in the electroplating industry as a function of the type and nature of the parts to be coated. The processes differ, inter alia, in respect of the current densities which can be employed. Mention may be made of essentially three different plating processes:

[0009] 1. Barrel plating for loose material and mass-produced parts:
   In this coating process, relatively low working current densities are employed (order of magnitude: 0.05-0.5 A/dm²).

[0010] 2. Rack plating for individual parts:
   In this coating process, medium working current densities are employed (order of magnitude: 0.2-5 A/dm²).

[0011] 3. High-speed plating for strips and wires in continuous plants:
   In this plating field, very high working current densities are employed (order of magnitude: 5-100 A/dm²).

[0012] For plating with copper-tin, the first two plating processes (barrel and rack) are of greatest importance. Depending on different types of electrolyte, either barrel plating (relatively low current densities) or rack plating (medium current densities) is possible.

[0013] In view of the abovementioned prior art, it can be determined that, especially for rack applications, deposition processes which ensure uniform deposition of metals beyond the current density range normally considered and also employ electrolytes which appear less complicated in terms of the composition are particularly advantageous.

[0014] It was therefore an object of the present invention to provide an electrolyte and a deposition process which meets these requirements. In particular, the electrolyte should be able to be used even at current densities which are advantageous for rack applications and deposit bright, shiny layers in a uniform way. Its composition should be simplified compared to the prior art, since this appears to be particularly advantageous from economic and ecological points of view.

[0015] These objects and further objects which have not been mentioned here but can be derived in an obvious form from the prior art are achieved by provision of an electrolyte having the features of the present claim 1 and its use in a deposition process according to the invention as claimed in claim 11. Preferred embodiments which refer back to these claims may be found in claims 2 to 10 and 12-16.

[0016] The provision of a nontoxic pyrophosphate-containing electrolyte for the deposition of decorative bronze alloy layers on consumer goods and industrial articles, which contains the metals to be deposited in the form of water-soluble salts and comprises a brightener system composed of the reaction product of epichlorohydrin with hexamethylenetetramine and also carbonate ions or hydrogencarbonate ions,
completely surprisingly but nonetheless advantageously achieves the stated objects. The electrolytes according to the invention which have a different composition compared to the prior art make it possible to obtain excellent electrolytic deposits of bronze alloys even in a medium current density range. The alloy composition remains approximately constant over the wide current density range, which is particularly advantageous for the rack application in particular and is not rendered obvious by the prior art.

The electrolyte of the invention comprises a reaction product of epichlorhydrin with hexamethylenetetramine as brightener constituent. According to the invention, this additive consists exclusively of a mixture or reaction product of hexamethylenetetramine and epichlorhydrin. The molar ratio of hexamethylenetetramine to epichlorhydrin in the reaction product is preferably 1:1.5-5 and very particular preference is given to a ratio of 1:2-3. A ratio of 1: about 2.7 is especially preferred. Such a product can be procured commercially under the name J146 from URSA Chemie GmbH (Cat. No. 33786).

The reaction product can be added to the electrolyte in an amount of from 0.01 ml/l to 5.0 ml/l, more preferably from 0.1 ml/l to 3.0 ml/l, particularly preferably from 0.5 to 2.0 ml/l and especially preferably from 1.0 ml/l to 1.5 ml/l, based on the total solution.

The electrolyte of the invention has a certain concentration of carbonate or hydrogen-carbonate ions. These can be added in the form of soluble salts of the alkaline and alkaline earth metals, in particular sodium or potassium carbonate or hydrogen carbonate, to the electrolyte. However, the embodiment in which the metals used and to be deposited are also added entirely or partly in the form of the carbonates or hydrogen carbonates to the electrolyte is preferred. Addition of the abovementioned salts advantageously enables a concentration of carbonate or hydrogen carbonate ions in the electrolyte which is from 1 to 50 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 25 g/l.

In the embodiment of the invention, the metals copper and tin or copper, tin and zinc to be deposited are present in the form of their ions. They are preferably introduced in the form of water-soluble salts which are preferably selected from the group consisting of pyrophosphates, carbonates, hydroxycarbonates, hydrogencarbonates, sulfites, sulfates, phosphates, nitrates, chlorides, sulfites, oxalates, oxalides, oxides and 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, hydroxycarbonate, oxalate, oxalide, hydroxide and hydrogen carbonate. The type and amount of salts introduced into the electrolyte can be decisive for the color of the resulting decorative bronze layers and can be set according to customer requirements. The metals to be deposited are, as indicated, present in ionically dissolved form in the electrolyte for the application of decorative bronze layers on consumer goods and industrial articles. The ion concentration of copper can be in the range from 0.2 to 10 g/l of electrolyte, preferably from 0.3 to 4 g/l of electrolyte, the ion concentration of tin can be in the range from 1.0 to 20 g/l of electrolyte, preferably 2-10 g/l of electrolyte, and, if present, the ion concentration of zinc can be in the range from 1.0 to 20 g/l of electrolyte, preferably from 0 to 3 g/l of electrolyte. In the upgrading of consumer goods, preference is given to introducing the metals to be deposited as pyrophosphate, carbonate or hydroxycarbonate so that the resulting ion concentration is in the range from 0.5 to 4 g/l of copper, 2 to 10 g/l of tin and from 0 to 5 g/l of zinc, in each case per liter of electrolyte.

The application of the decorative bronze layers on consumer goods and industrial articles by means of using the electrolytes of the invention is carried out, as indicated, in an electrochemical process. It is important here that the metals to be deposited are kept permanently in solution during the process, regardless of whether electrochemical coating is carried out in a continuous process or in a batch process. To ensure this, the electrolyte of the invention contains pyrophosphate as complexing agent.

The amount of pyrophosphate ions can be set in a targeted 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 bring about the intended effect to a satisfactory 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 EP1461448 and the information given there. The amount of pyrophosphate to be used in the electrolyte is preferably 50-400 g/l. Particular preference is given to using an amount of 250-350 g/l electrolyte, very particularly preferably about 300 g/l of electrolyte. The pyrophosphate can, if it is not introduced as a salt constituent of the metals to be deposited, be used as alkaline metal or alkaline earth metal diphosphate or as H2P2O7 in combination with an alkaline metal or alkaline earth metal carbonate/hydrogen carbonate. Preference is given to using K2P2O7 for this purpose.

The pH of the electrolyte is in the range from 6 to 13 required for electroplating use.

Preference is given to a range of 6-12 and very particularly preferably 6-10. The process is especially preferably carried out at a pH of from about 7.9 to 8.1.

The electrolyte can contain, apart from the metals to be deposited, the pyrophosphate used as complexing agent and the brightener system used, further organic additives which act as 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 when the appearance of the decorative bronze layers to be deposited have to meet special requirements. These make it possible to adjust, in addition to the color of the bronze layers which depends mainly on the ratio of the metals to be deposited, the brightness of the layer in all gradations between matt silk and high gloss. Preference is given to adding one or more compounds selected from the group consisting of monocarboxylic and dicarboxylic acids, alkanesulfonic acids, 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 nitrobenzenetrazoles or mixtures thereof. Suitable alkanesulfonic acids may be found in EP1001054. A possible carboxylic acid is, for example, citric acid (Jordan, Manfred, Die galvanische Abscheidung von Zinn und Zinnlegierungen, Sautgnau 1993, page 156). Betaines to be used are preferably those which may be found in WO2004/005528 or in Jordan, Manfred (Die galvanische Abscheidung von Zinn und Zinnlegierungen, Sautgnau 1993, page 156). Particular preference is given to those described in EP636713. In this context, very particular preference is given to using 1-(3-sulfopropyl)pyridinium betaine.
or 1-(3-sulfopropyl)-2-vinylpyridinium betaine. Further additives may be found in the literature (Jordan, Manfred, Die galvanische Abscheidung von Zinn und Zinnlegierungen, Sahlau 1993).

[0026] The electrolyte of the invention is free of hazardous materials classified as toxic (T) or very toxic (T*). No cyanides, no thiourea derivatives and no thiol derivatives are present. The nontoxic electrolyte according to the invention is particularly suitable for electrochemical application of decorative bronze layers on consumer goods and industrial articles. It can be used in barrel, rack, belt or continuous transport plating plants. However, it is preferably employed in rack processes (see introductory explanation and "Praktische Galvanotechnik", Eugen G. Leutze Verlag 1997 page 74 ff.).

[0027] Furthermore, the present invention proposes an electrolytic deposition process for the electrochemical application of decorative bronze alloy layers on consumer goods and industrial articles, in which the substrates to be coated are immersed in an electrolyte according to the invention. The preferred embodiments of the electrolyte which have been discussed above apply analogously to the process presented here.

[0028] The process of the invention can be operated at a temperature which a person skilled in the art will choose on the basis of his general technical knowledge. Preference is given to a range from 20 to 60° C. In which the electrolytic bath is maintained during the electrolysis. Greater preference is given to selecting a range of 30-50° C. The process is especially preferably carried out at a temperature of about 40°.

[0029] An important advantage of the present invention is that the alloy composition does not alter significantly over a wide current density range. This also results in a surface quality which appears to be sufficiently homogeneous even at high current densities which are relatively high for rack applications. It is possible to obtain the alloy composition of a specific and desirable intermetallic Cu/Sn phase (114 phase; Ref.: E. Raub, F. Snitter; Der Aufbau galvanischer Legierungsniederschläge XII, Metalloberfläche 11, 1957 number 8) when the deposition is carried out in the range 0.2 A/dm² to 5 A/dm². The current density in the deposition is preferably 0.5 A/dm² to 2 A/dm², particularly preferably 0.75 A/dm².

[0030] When the nontoxic electrolyte of the invention is used, it is possible to use various anodes. Soluble or insoluble anodes are both suitable, as is the combination of soluble and insoluble anodes.

[0031] As soluble anodes, preference is given to using anodes composed of a material selected from the group consisting of electrolytic copper, phosphorus-containing copper, tin, tin-copper alloy, zinc-copper alloy and zinc-tin-copper alloy. Preference is given to combinations of various soluble anodes composed of these materials, and also combinations of soluble tin anodes with insoluble anodes.

[0032] As insoluble anodes, preference is given to using anodes composed of a material selected from the group consisting of platinum, graphite, iridium-transition metal mixed oxide and a specific carbon material ("diamond-like carbon", DLC) or combinations of these anodes. Preference is given to combinations of various soluble anodes composed of iron-ruthenium mixed oxide, iron-ruthenium-titanium mixed oxide or iridium-tantalum mixed oxide. Further materials may be found in Cobley, A.J. et al. (The use of insoluble


[0033] When insoluble anodes are used, a particularly preferred embodiment of the process is obtained when the substrates which are to be provided with decorative bronze layers and represent the cathode are separated by an ion exchange membrane from the insoluble anode so that a cathode space and an anode space are formed. In such a case, only the cathode space is filled with the nontoxic electrolyte of the invention. The anode space preferably contains a spent solution containing only an electrolyte salt such as potassium pyrophosphate, potassium carbonate, potassium hydroxide, potassium hydrogen carbonate or a mixture thereof. Such an arrangement prevents anodic oxidation of tin(II) ions to tin (IV) ions which would have an adverse effect on the coating process. 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.

[0034] The current densities typical of rack applications can likewise be achieved by means of conventional pyrophosphate-containing electrolytes. However, metals are not deposited in a visually defect-free quality. Such electrolytes tend to form (in the range customary for rack operation) dark, streaky deposits.

[0035] Only when the electrolyte of the invention is used is the deposition of bright and shiny layers made possible over the entire current density range customary for rack applications. The formation of dark streaks is substantially suppressed.

[0036] The electrolyte of the invention and the present process are therefore distinguished by the use of an additive formed from hexamethylenetetramine and epichlorohydrin in combination with the presence of carbonate or hydrogen carbonate ions in the electrolyte. The alloy composition and the brightness of the deposited layers are in this way controlled in a manner which is ideal for rack applications. In rack applications, a medium current density range is important. The additive combination enables, firstly, the alloy composition to be kept approximately constant (brass alloys containing 40-70% by weight, preferably 50-60% by weight, of copper and 60-30% by weight, preferably 50-40% by weight, of tin are advantageous) at relatively high current densities over a wide current density range and, secondly, satisfactorily bright and shiny layers to be obtained. Without this additive combination, the desired alloy composition is obtained only in a very narrow current density window which is unsuitable in industrial practice. Gloss and brightness of the layers are unsatisfactory without the additive combination in the majority of practical applications. The achievement of these advantages by means of the electrolyte according to the invention was not rendered obvious by the prior art.

EXAMPLES

[0037] Plating of Test Plates:

[0038] Substrates: 0.5 and 0.75 dm² brass plates

[0039] Coating:

[0040] 0.5-2 μm copper-tin at various current densities (0.5, 1.0, 1.5 and 2.0 A/dm²)

[0041] Experimental Setup:

[0042] The components indicated for the example electrolytes are dissolved in 41 of distilled water in a 51 glass beaker
provided with magnetic stirrer and movement of the goods. The article to be coated is subsequently treated under the conditions indicated.

**Example Electrolytes**

Electrolytes for rack deposition of white bronze can have the following composition:

<table>
<thead>
<tr>
<th>Example Electrolyte</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1st Example Electrolyte</strong></td>
<td>300 g/l of potassium pyrophosphate, 20 ml/l of methanesulfonic acid, 20 g/l of potassium carbonate, 5.21 g/l of copper(II) carbonate, 8.66 g/l of tin pyrophosphate, 5.35 g/l of zinc pyrophosphate, 1.25 ml/l of reaction product of hexamethylenetetramine and epichlorohydrin. Temperature: 40°C. pH: 7.4.</td>
</tr>
<tr>
<td><strong>2nd Example Electrolyte</strong></td>
<td>300 g/l of potassium pyrophosphate, 20 ml/l of methanesulfonic acid, 20 g/l of potassium carbonate, 5.21 g/l of copper(II) carbonate, 8.66 g/l of tin pyrophosphate, 5.35 g/l of zinc pyrophosphate, 0.125 ml/l of reaction product (J146). Temperature: 40°C. pH: 8.0.</td>
</tr>
<tr>
<td><strong>3rd Example Electrolyte</strong></td>
<td>100 g/l of potassium pyrophosphate, 50 ml/l of methanesulfonic acid, 50 g/l of potassium carbonate, 2.0 g/l of copper sulfate, 20 g/l of tin sulfate, 5.0 ml/l of reaction product (J146). pH: 9.0. Temperature: 30°C.</td>
</tr>
<tr>
<td><strong>4th Example Electrolyte</strong></td>
<td>160 g/l of potassium pyrophosphate, 20 ml/l of methanesulfonic acid, 5 g/l of sodium carbonate, 4 g/l of copper hydroxidecarbonate, 5 g/l of tin pyrophosphate, 0.5 ml/l of reaction product of hexamethylenetetramine and epichlorohydrin. pH: 7.5. Temperature: 45°C.</td>
</tr>
</tbody>
</table>

The assessment of the layers is carried out:

- **a)** by visual appearance
- **b)** by measurement of gloss and brightness
- **c)** by measurement of the alloy composition (the higher the copper content, the darker the layers)
- **d)** by tarnishing tests, corrosion tests

**Comparison of “Example Electrolyte 2” with “Prior Art”**

<table>
<thead>
<tr>
<th>Current densities (A/dm²)</th>
<th>Example electrolyte 2</th>
<th>Prior art</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>84.08</td>
<td>81.0</td>
</tr>
<tr>
<td>0.75</td>
<td>85.9</td>
<td>82.9</td>
</tr>
<tr>
<td>1.0</td>
<td>85.74</td>
<td>83.1</td>
</tr>
<tr>
<td>1.5</td>
<td>86.86</td>
<td>83.2</td>
</tr>
<tr>
<td>2.0</td>
<td>86.1</td>
<td>82.8</td>
</tr>
</tbody>
</table>

**Comparison of “Example Electrolyte 2” with “Prior Art”**

<table>
<thead>
<tr>
<th>Current densities (A/dm²)</th>
<th>Example electrolyte 2</th>
<th>Prior art</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>60% Cu 50% Sn</td>
<td>60% Cu 50% Sn</td>
</tr>
<tr>
<td>1.0</td>
<td>50% Cu 50% Sn</td>
<td>47% Cu 53% Sn</td>
</tr>
<tr>
<td>1.5</td>
<td>47% Cu 53% Sn</td>
<td>48% Cu 52% Sn</td>
</tr>
<tr>
<td>2.0</td>
<td>52% Sn</td>
<td>48% Cu 52% Sn</td>
</tr>
</tbody>
</table>
A higher copper content of the layer results in a darker color of the coating and tends to produce poorer tarnishing behavior.

1. A nontoxic pyrophosphate-containing electrolyte for the deposition of decorative bronze alloy layers on consumer goods and industrial articles, which contains the metals to be deposited in the form of water-soluble salts, wherein it comprises a brightener system composed of the reaction product of epichlorohydrin with hexamethylenetetramine and also carbonate ions or hydrogen carbonate ions.

2. The electrolyte as claimed in claim 1, wherein the reaction product has a molar ratio of hexamethylenetetramine to epichlorohydrin of 1:1-10.

3. The electrolyte as claimed in claim 1, wherein the reaction product is used in an amount of 0.01-5 ml/l of electrolyte.

4. The electrolyte as claimed in claim 1, wherein the carbonate or hydrogen carbonate ions are present in an amount of 1-50 g/l of electrolyte.

5. The electrolyte as claimed in claim 1, wherein the electrolyte comprises copper and tin or copper, tin and zinc as metals to be deposited.

6. The electrolyte as claimed in claim 1, wherein the water-soluble salts of the metals to be deposited are selected from the group consisting of pyrophosphates, carbonates, hydroxide carbonates, hydrogen carbonates, sulfites, sulfates, phosphates, nitrates, nitrites, halides, hydroxides, oxides and combinations thereof.

7. The electrolyte as claimed in claim 1, wherein the metals to be deposited are present in ionically dissolved form, with the ion concentration of copper being in the range from 0.2 to 10 g/l of electrolyte, the ion concentration of tin being in the range from 1.0 to 20 g/l of electrolyte and, if present, the ion concentration of zinc being in the range from 1.0 to 20 g/l of electrolyte.

8. The electrolyte as claimed in claim 1, wherein the amount of pyrophosphate in the electrolyte is 50-400 g/l.

9. The electrolyte as claimed in claim 1, wherein the pH of the electrolyte is in the range from 6 to 13.

10. The electrolyte as claimed in claim 1, wherein one or more compounds having a stabilizing action selected from the group consisting of monocarboxylic and dicarboxylic acids, alkanesulfonic acids, betaines and aromatic nitro compounds are present.

11. An electrolytic deposition process for the electrochemical application of decorative bronze alloy layers on consumer goods and industrial articles, wherein the substrates to be coated are immersed in an electrolyte as claimed in claim 1.

12. The process as claimed in claim 11, wherein the electrolyte is maintained in the temperature range from 20 to 60°C.

13. The process as claimed in claim 11, wherein a current density in the range from 0.2 to 5 ampere per square decimeter is set.

14. The process as claimed in claim 11, wherein a soluble anode composed of a material selected from the group consisting of electrolytic copper, phosphorus-containing copper, tin, tin-copper alloy, zinc-copper alloy and zinc-tin-copper alloy or a combination of these anodes is used.

15. The process as claimed in claim 11, wherein an insoluble anode composed of a material selected from the group consisting of platinized titanium, graphite, iridium-transition metal mixed oxide and a specific carbon material ("diamond-like carbon", DLC) or a combination of these anodes is used.

16. The process as claimed in claim 11, wherein the cathode and the insoluble anode are separated from one another by an ion-exchange membrane to form a cathode space and an anode space and only the cathode space contains the nontoxic electrolyte so that anodic oxidation of Sn⁺⁺ to Sn⁴⁺ is suppressed.

* * * *