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(71) Applicant: **Caoduro Italo**
36010 Monticello Conte Otto (VI) (IT)

(72) Inventor: **Caoduro Italo**
36010 Monticello Conte Otto (VI) (IT)

(74) Representative: **Ziliotto, Tiziano**
Studio Ziliotto
Contrada Porta S. Lucia, 48
36100 Vicenza (IT)

(54) Object with surface covering layer obtained through electrolytic deposition, electrolytic solution used for said deposition and method for making said object.

(57) The invention is an object (1; 51) of the type comprising a main body (2; 52) and a surface covering layer (3) suited to cover said main body (2; 52) at least partially. Said surface covering layer (3) is constituted by an alloy comprising copper in a percentage varying in weight from 70 to 99 %, tin in a percentage varying in weight from 30 to 1% and impurities in a percentage varying in weight from 0 to 1%, and its thickness exceeds 5 micrometres. The invention includes also an aqueous electrolytic solution used in an electrolytic deposition process for the production of an object (1; 51) and a method for making an object (1; 51) of the type comprising a main body (2; 52) and a surface covering layer (3) suited to cover the main body (2; 52) at least partially, wherein this method comprises a stage for making the surface covering layer (3) through electrolytic deposition in an aqueous electrolytic solution.

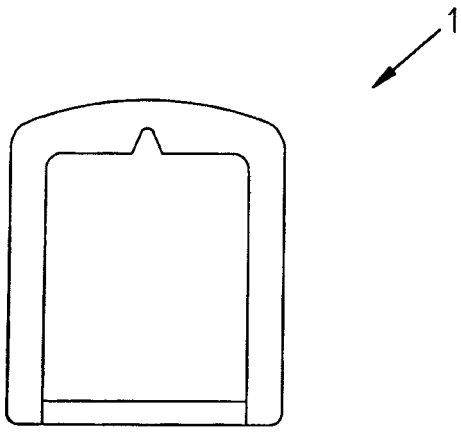

FIG. 1

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Description

FIELD OF APPLICATION OF THE INVENTION

[0001] The present invention concerns the technical field of production of objects with a surface covering.

[0002] In particular, the present invention concerns the production of objects with a surface covering obtained through electrolytic deposition.

[0003] The present invention concerns also the method for making said objects and the electrolytic solution used in said method.

DESCRIPTION OF THE STATE OF THE ART

[0004] Techniques for covering objects, in particular metal objects, are widely used in the most varied sectors.

[0005] We make reference, in particular, to metal objects comprising, for example, accessories for bags, shoes, belts (such as buckles, rings, spring catches, chains, fasteners etc.), parts of glasses (such as sides, bridges, inserts etc.), zip fasteners, buttons, components of watches (such as casings, buckles, bracelet meshes etc.), trinkets (such as bracelets, rings, earrings, pendants etc.), handles (for pieces of furniture, doors, refrigerators etc.), valves, gift items (such as trays, vases and pots, cups, tea pots, milk pots etc.), technical items (such as bushings).

[0006] The objects indicated above are typically produced using brass as base material. The brass that is commonly used and ensures good workability contains a certain percentage of lead. The presence of lead may cause problems related to its toxicity and its release into the environment.

[0007] In order to overcome said drawback, brass alloys without lead have been created that, however, are more expensive and also involve higher processing costs, as they need to be worked with more expensive equipment that wears out more quickly.

[0008] According to the known technique, in order to resolve said problem it has been devised to replace brass with a zama alloy, a material of poorer quality, and to cover said zama alloy with a surface layer in order to improve its aesthetic characteristics and thus make it as similar to a brass object as possible. According to a known technique, the surface layer is obtained by means of a galvanic finishing treatment by means of which a layer of an appropriate alloy suited to cover the underlying part in zama alloy is deposited thereon.

[0009] The deposited layer is typically made with alloys containing copper, tin and zinc or copper and zinc, a few microns thick.

[0010] The same covering technique with a galvanic treatment is used also in sectors where base materials of a different type are used, like for example plastic, resins, low-melting alloys etc.

[0011] Also in this case, the surface layer is typically made with alloys containing copper, tin and zinc or copper and zinc, a few microns thick.

[0012] The covering techniques of the known type, however, pose some drawbacks.

[0013] A first drawback of the objects obtained through the above mentioned covering techniques is represented by the appearance of defects as a result of corrosion phenomena, in particular between the surface covering layer and the underlying material, due to transpiration through the surface layer, which can give rise to dangerous electrochemical processes.

[0014] Another drawback arises if the objects obtained by means of the above mentioned covering techniques have to be subjected to welding operations. The covering layers obtained with the known technique do not guarantee the resistance of the weld, and sometimes may even make it impossible to perform the welding operation.

[0015] Another drawback posed by the objects obtained using the techniques of the known type is due to the wearing action to which the external surface of the object is subjected, which causes a deterioration of the aesthetic characteristics of the object and/or the need to restore the ideal conditions with a new covering treatment.

[0016] Thus, the main object of the present invention is to at least partially overcome the drawbacks described above.

[0017] It is a first object of the present invention to provide an object whose surface covering layer has reduced defects compared to the objects belonging to the known art.

[0018] It is another object of the present invention to provide an object having a surface covering layer that can be subjected to welding operations without affecting the mechanical resistance characteristics and/or the aesthetic aspect of the object itself.

[0019] It is another object of the present invention to provide an object having a surface covering layer that maintains its mechanical resistance and/or ornamental characteristics for a longer time compared to the objects of the known type.

SUMMARY OF THE PRESENT INVENTION

[0020] The present invention is based on the general consideration that it is desirable to make an object having a surface covering layer constituted by an alloy comprising copper and tin whose thickness exceeds 5 micrometres.

[0021] According to a first aspect of the present invention, the subject of the same is, therefore, an object of the type comprising a main body and a surface covering layer suited to at least partially cover said main body, wherein said surface covering layer is constituted by an alloy comprising copper in a percentage varying in weight from 70 to 99 %, tin in a percentage varying in weight from 30 to 1% and impurities in a percentage varying in weight from 0 to 1%, and wherein the thickness of said

surface covering layer exceeds 5 micrometres. Said alloy preferably comprises copper in a percentage varying in weight from 85 to 99 %, tin in a percentage varying in weight from 15 to 1% and impurities in a percentage varying in weight from 0 to 1%.

[0022] Even more preferably, said alloy comprises copper in a percentage varying in weight from 90 to 95 %, tin in a percentage varying in weight from 10 to 5% and impurities in a percentage varying in weight from 0 to 1%.

[0023] The thickness of the surface covering layer preferably exceeds 30 micrometres. In a preferred embodiment of the invention, the main body comprises a conductive material.

[0024] Said main body properly comprises a zama alloy.

[0025] According to another preferred embodiment of the invention, the main body comprises a non-conductive material and an external layer comprising a conductive material.

[0026] Advantageously, the surface covering layer is obtained through electrolytic deposition.

[0027] Preferably, the alloy does not comprise zinc.

[0028] In preferred embodiments, the subject of the invention is an object belonging to the group comprising: accessories for bags, for shoes, for belts, for example buckles, rings, spring catches, chains, fasteners; parts of glasses, for example sides, bridges, inserts; zip fasteners; buttons; components of watches, for example casings, buckles, bracelet meshes; trinkets, for example bracelets, rings, earrings, pendants; handles, for example handles for pieces of furniture, doors, refrigerators; valves; gift items, for example trays, vases and pots, cups, tea pots, milk pots; technical items, for example bushings.

[0029] More preferably, the subject of the invention is a fashion accessory, like for example said accessories for bags, shoes, belts, for example buckles, rings, spring catches, chains, fasteners etc., or it is a trinket like for example said bracelets, rings, earrings, pendants, etc..

[0030] According to a second aspect of the present invention, the subject of the same is an aqueous electrolytic solution used in an electrolytic deposition process for making an object, wherein the solution comprises:

- copper cyanide (CuCN), with values preferably included between 15 and 30 g/l, more preferably included between 24 and 28 g/l, even more preferably equal to 26 g/l;
- potassium stannate (K2SnO3.3H2O), with values preferably included between 10 and 25 g/l, more preferably included between 18 and 22 g/l, even more preferably equal to 20 g/l;
- potassium cyanide (KCN), with values preferably included between 40 and 50 g/l, more preferably included between 43 and 47 g/l, even more preferably equal to 45 g/l;
- free potassium hydroxide (KOH), with values preferably included between 5 and 20 g/l, more preferably included between 8 and 14 g/l, even more preferably equal to 11 g/l.

[0031] Advantageously, the electrolytic solution does not comprise zinc.

[0032] Said electrolytic solution is preferably used to make an object belonging to the group comprising: accessories for bags, for shoes, for belts, for example buckles, rings, spring catches, chains, fasteners; parts of glasses, for example sides, bridges, inserts; zip fasteners; buttons; components of watches, for example casings, buckles, bracelet meshes; trinkets, for example bracelets, rings, earrings, pendants; handles, for example handles for pieces of furniture, doors, refrigerators; valves; gift items, for example trays, vases and pots, cups, tea pots, milk pots; technical items, for example bushings.

[0033] More preferably, said electrolytic solution is used for making a fashion accessory, like for example said accessories for bags, shoes, belts, for example buckles, rings, spring catches, chains, fasteners etc., or a trinket, like for example said bracelets, rings, earrings, pendants, etc..

[0034] According to a third aspect of the present invention, the subject of the same is a method for making an object of the type comprising a main body and a surface covering layer suited to cover said main body at least partially, said method comprising a stage during which said surface covering layer is obtained through electrolytic deposition in an aqueous electrolytic solution, wherein said electrolytic solution is of the type described above.

[0035] Preferably, during the chemical deposition the pH value of the electrolytic solution is maintained between 12 and 12.5.

[0036] Preferably, during the chemical deposition the temperature of the electrolytic solution is maintained between 58 and 62 °C.

[0037] Preferably, during the chemical deposition the process current is maintained between 0.3 and 2.5 A/dm2.

[0038] Said method is preferably used to make an object belonging to the group comprising: accessories for bags, for shoes, for belts, for example buckles, rings, spring catches, chains, fasteners; parts of glasses, for example sides, bridges, inserts; zip fasteners; buttons; components of watches, for example casings, buckles, bracelet meshes; trinkets, for example bracelets, rings, earrings, pendants; handles, for example handles for pieces of furniture, doors, refrigerators; valves; gift items, for example trays, vases and pots, cups, tea pots, milk pots; technical items, for example bushings.

[0039] More preferably, said method is used for making a fashion accessory, like for example said accessories for bags, for shoes, for belts, for example buckles, rings, spring catches, chains, fasteners etc., or a trinket, like for example said bracelets, rings, earrings, pendants,

etc..

BRIEF DESCRIPTION OF THE DRAWINGS

[0040] Further objects, advantages and characteristics, as well as embodiments of the present invention, are defined in the claims and will be illustrated below by means of the following description with reference to the attached drawings. In particular:

- Figure 1 shows a plan view of an object according to a preferred embodiment of the invention;
- Figure 2 shows a sectional view of a detail of the object of Figure 1 at the level of its external surface;
- Figure 3 shows an apparatus for making the object shown in Figure 1;
- Figure 4 shows an exemplification diagram of some stages of the production process of the object of Figure 1 obtained in the apparatus shown in Figure 3;
- Figure 5 shows a sectional view of a detail of a variant embodiment of the object according to the invention, at the level of its external surface;
- Figure 6 schematically shows one stage of the production process of a variant embodiment of the object according to the invention.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0041] Although the present invention is described below with reference to its embodiments illustrated in the drawings, the present invention is not limited to the embodiments described below and illustrated in the drawings. On the contrary, the embodiments described and illustrated herein clarify some aspects of the present invention, the scope of which is defined in the claims.

[0042] The present invention has proved particularly useful when applied to objects comprising a base material constituted by a metallic material, in particular a zama alloy, as is explained in greater detail below. It should however be noted that the present invention is not limited to the production of said objects. On the contrary, the present invention can be conveniently applied in all those cases requiring the production of objects comprising a base material having an external layer made of a non-precious metal, for example objects comprising a base material such as plastic or resin. The base material, furthermore, can be solid or hollow, without distinction.

[0043] A method for making an object according to a preferred embodiment of the invention is described here below with reference to Figures 3 and 4.

[0044] Reference is made, in particular, to the production of a buckle 1 for belts, shown in Figure 1.

[0045] It is evident, however, that the invention can be applied to the production of other objects, in particular metal objects like, for example, accessories for bags, for shoes, for belts (such as buckles, rings, spring catches, chains, fasteners etc.), parts of glasses (such as sides, bridges, inserts etc.), zip fasteners, buttons, components of watches (such as casings, buckles, bracelet meshes etc.), trinkets (such as bracelets, rings, earrings, pendants etc.), handles (for pieces of furniture, doors, refrigerators etc.), valves, gift items (such as trays, vases and pots, cups, tea pots, milk pots etc.), technical items (such as bushings).

[0046] More particularly, the invention can be applied to the production of a fashion accessory, like for example said accessories for bags, for shoes, for belts, for example buckles, rings, spring catches, chains, fasteners etc., or of a trinket, like for example said bracelets, rings, earrings, pendants etc..

[0047] The object of the invention 1, meaning the buckle 1, comprises a base material or core 2 and a surface covering layer 3, as shown in the sectioned detail illustrated in Figure 2.

[0048] In the preferred embodiment of the invention, the base material 2 comprises a metallic material, preferably a zama alloy.

[0049] A known process for the production of said objects uses electrolytic deposition technology.

[0050] An apparatus 101 suited to allow the production of an object 1 according to a preferred embodiment of the invention is described with reference to Figure 3. The apparatus 101 is substantially constituted by an apparatus for electrolytic deposition.

[0051] The apparatus 101 substantially comprises a tank 102 suited to contain an electrolytic solution, or electrolytic bath, in which the elements to be deposited and intended to make up the surface covering layer 3 of the object 1 of the invention are dissolved, as will be described in greater detail below.

[0052] The tank 102 containing the electrolytic solution is preferably arranged inside a suitable external tank 121.

[0053] The apparatus 101 furthermore comprises a supporting system 103 for the objects 1 to be made. Typically, a plurality of said objects 1 are made at the same time in the apparatus 101.

[0054] In the embodiment illustrated herein, and only by way of example, there are six buckles 1. It is evident that in variant embodiments of the invention a different number of objects having any shape can be made, for example rings, earrings, etc., as already explained.

[0055] The supporting system 103 preferably comprises a centre rotary shaft 104 provided with arms 105 on which the objects 1 to be made are properly arranged. The rotary shaft 4 is properly piloted by power means that are not represented herein. A centre control unit of the apparatus 101 is advantageously connected to said power means.

[0056] The centre control unit can be constituted, for example, by a PLC unit installed on a control cabinet.

[0057] The apparatus 101 is also provided with a suitable power supply system suited to create an electric electrodeposition circuit through which a given current I flows. In the embodiment shown in the figure, the power supply system comprises a power supply unit electrically

connected with a first one of its poles, for example the negative one (cathode), to the supporting system 103 and connected with its second pole, for example the positive one (anode), to annular electrodes 112 arranged inside the tank 121.

[0058] The power supply unit is preferably piloted by the control unit, in such a way as to define the voltage and/or current values that are appropriate for the electric electrodeposition circuit.

[0059] The apparatus 101 will also be provided with further elements, not illustrated herein, suited to allow and guarantee the correct operation of the apparatus 101 itself.

[0060] For example, the apparatus 101 will be preferably provided with an electrolytic solution feeding system and a top-up system suited to compensate for the variations in the components of the electrolytic solution during operation. The apparatus 101 will be preferably provided also with a stirring system suited to mix the electrolytic solution in order to maintain its conditions of homogeneity inside the tank 102 during operation. The apparatus 101 will be preferably provided also with a heating system suited to bring the electrolytic solution to a desired operating temperature T and to maintain it at that temperature. The apparatus 101 will be provided with suitable sensors for measuring operating parameters like, for example, sensors for detecting the level and the temperature of the electrolytic solution.

[0061] The apparatus 101 is preferably provided with a filtering system suited to filter any impurities present in the electrolytic solution.

[0062] A method for making the object 1 using the apparatus 101 of Figure 3 illustrated above is described with reference to Figure 4.

[0063] In an initial stage (block 200), a core made of a conductive material in a suitable shape is prepared, for example, in the case illustrated herein, in the shape of a buckle.

[0064] The core 2 is positioned on the supporting system 103 and immersed in the electrolytic solution previously prepared.

[0065] According to the present invention, the electrolytic solution is constituted by an aqueous solution comprising:

- copper cyanide (CuCN), with values preferably included between 15 and 30 g/l, more preferably included between 24 and 28 g/l, even more preferably equal to 26 g/l;
- potassium stannate (K2SnO3.3H2O), with values preferably included between 10 and 25 g/l, more preferably included between 18 and 22 g/l, even more preferably equal to 20 g/l;
- potassium cyanide (KCN), with values preferably included between 40 and 50 g/l, more preferably included between 43 and 47 g/l, even more preferably equal to 45 g/l;
- free potassium hydroxide (KOH), with values preferably included between 5 and 20 g/l, more preferably included between 8 and 14 g/l, even more preferably equal to 11 g/l.

[0066] According to the present invention, therefore, the electrolytic solution comprises the four elements indicated above, in the corresponding quantities, properly dissolved in water.

[0067] In the successive stage of the method (block 210), the values of the parameters that will determine the successive deposition stage (block 220) are then defined. In particular, the values are defined within which a series of process parameters should be maintained, including:

- the pH value of the electrolytic solution;
- the operating temperature T of the electrolytic solution;
- the process current I;
- the expected duration t1 of the deposition stage.

[0068] The pH value is preferably maintained within the range 12÷12.5.

[0069] The temperature T of the electrolytic solution is preferably maintained within the range 58÷62 °C.

[0070] The process current I is preferably maintained within the range 0.3÷2.5 A/dm2. The expected duration t1 of the deposition stage will depend on the desired thickness of the surface covering layer 3, taking into account the deposition speed that derives from the previously set parameter values.

[0071] For example, the process will make it possible to deposit a layer with a thickness of 1 micrometre in a time t1 equal to 100 seconds, with a process current I equal to 2.0 A/dm2, or it will allow the deposit of a layer with a thickness of 1 micrometre in 400 seconds, with a process current I equal to 0.5 A/dm2.

[0072] Once the process parameters (I, pH, T, t1, etc) have been defined,
the deposition stage (block 220) will follow.

[0073] During this stage, thanks to the current I and to the elements that make up the electrolytic solution, a surface covering layer 3 is deposited on the core 2.

[0074] During this stage, inside the tank 102 the electrolytic solution is advantageously kept moving by means of the specific stirrers, not represented herein, while, advantageously, the objects 1 and the supporting element 103 are set rotating through the power means.

[0075] Furthermore, always during said stage, the appropriate checks and corrections will be advantageously made in order to maintain the correct process parameters, like for example the quantity of the various elements of the solution, the pH value, the temperature T, etc.

[0076] At the end of the stage of deposition (block 220) according to the present invention, a surface covering layer 3 will be obtained on the core 2, said layer being constituted by an alloy comprising copper in a percentage varying in weight from 70 to 99 %, tin in a percentage

varying in weight from 30 to 1% and impurities in a percentage varying in weight from 0 to 1 %, wherein the thickness of said alloy layer will exceed 5 micrometres.

[0077] More preferably, the surface covering layer 3 is constituted by an alloy comprising copper in a percentage varying in weight from 85 to 99 %, tin in a percentage varying in weight from 15 to 1% and impurities in a percentage varying in weight from 0 to 1%.

[0078] Even more preferably, the surface covering layer 3 is constituted by an alloy comprising copper in a percentage varying in weight from 90 to 95 %, tin in a percentage varying in weight from 10 to 5% and impurities in a percentage varying in weight from 0 to 1%.

[0079] In a preferred embodiment of the invention, the object 1 obtained as described above is ready for its final use. In variant embodiments of the invention, however, further external finishing operations can be carried out.

[0080] Usable finishing operations may preferably include mechanical polishing treatments, like for example a vibratory finishing treatment, a tumbling treatment, a rumbling treatment, a lapping treatment, or further galvanic finishing treatments intended to deposit layers a few micrometres thick, using, for example, white bronze, silver, palladium, ruthenium, gold, alloys of these elements, etc.

[0081] Advantageously, the possibility to obtain a thickness of 5 micrometres or more for the surface covering layer 3 makes it possible to obtain a substantially tight covering for the underlying layer 2, actually eliminating the phenomenon of transpiration through the surface layer itself, which instead is present in the known art. Consequently, there is a tendency to avoid creating situations that trigger electrochemical processes that would deteriorate the object 1.

[0082] Always according to the present invention, the possibility to obtain thicknesses of 5 micrometres or more derives from the fact that there is no zinc, in any form, in the electrolytic solution.

[0083] Therefore, the possibility to obtain a thickness of 5 micrometres or more makes it possible to obtain a tight surface covering layer that allows the transpiration phenomenon to be avoided, while on the other hand this phenomenon appears in the known art.

[0084] It is to be understood that the surface covering layer may comprise, in addition to copper or tin, low percentages of other elements, or impurities, with values below 1%.

[0085] In a preferred embodiment of the object 1 according to the present invention, the deposition stage (block 220) is performed in such a way as to obtain a surface covering layer 3 whose thickness exceeds 30 micrometres.

[0086] In this case a thicker layer, in addition to further guaranteeing the tightness provided by the surface covering layer 3, makes it possible to carry out welding operations at the level of the surface covering layer 3. Such a thickness value, considerably higher than the values of a few microns obtainable with the known technique, allows the welded object to maintain the desired mechanical resistance characteristics.

[0087] The object 1, therefore, can be welded to other metallic elements, or other elements of the same type obtained according to the process of the present invention.

[0088] Again, the possibility to obtain thicknesses of 30 microns and more derives from the fact that there is no zinc in the electrolytic solution, as already explained above. The presence of zinc, in this case, would cause the generation of cracks and would damage the surface layer 3 itself.

[0089] Again, the possibility to make a thicker surface layer increases the useful life of the object in terms of surface wear.

[0090] A variant embodiment of an object 51 produced according to the present invention is described with reference to Figures 5 and 6.

[0091] The object 51 described differs from the previously described object 1 due to the fact that the core 52 comprises a layer of non-metallic material 54, for example plastic or resin, and a layer of conductive material 55 interposed between the surface covering layer 3 and the layer of non-metallic material 54.

[0092] In this case, according to the method for making the object 51, the layer of non-metallic material 54 is subjected to a metallization stage, schematically represented in Figure 6. It is known, in fact, that in order to deposit a material on an object through electrolysis, said object must have electric conductivity properties.

[0093] The metallization stage makes it possible to create the layer of conductive material 55 on top of the layer of non-metallic material 54 so as to obtain the core 52 to be immersed in the electrolytic solution. The metallization process is preferably carried out by depositing a conductive layer through spraying, as schematically shown exactly in Figure 6, preferably a layer of a material containing microparticles in silver or copper or brass.

[0094] The core 52 obtained in this way, that is, the core 52 provided with the conductive layer 55, is then subjected to the successive deposition stages, according to the description provided above, through the use of the apparatus 101.

[0095] The object 51 obtained in this way will therefore have the same characteristics and offer the same advantages described above with reference to the first embodiment.

[0096] In further embodiments of the invention, not illustrated herein, further intermediate layers can be present between the underlying core and the surface covering layer. For example, according to the invention, it is possible to make a layer of alkaline copper or acid copper, in particular when the core is constituted by a zinc alloy.

[0097] Said intermediate layers make it possible to improve the mechanical and/or ornamental characteristics of the object as a whole.

[0098] It has thus been shown that the present invention allows the set objects to be achieved. In particular,

it makes it possible to produce an object provided with a surface covering layer having reduced defects compared to the objects belonging to the known art.

[0099] While the present invention has been described with reference to the particular embodiments described and shown in the figures, it should be noted that the present invention is not limited to the specific embodiments illustrated and described herein; on the contrary, further variants of the embodiments described herein fall within the scope of the present invention, which is defined in the claims.

Claims

1. Object (1; 51) of the type comprising a main body (2; 52) and a surface covering layer (3) suited to at least partially cover said main body (2; 52), **characterized in that** said surface covering layer (3) is constituted by an alloy comprising copper in a percentage varying in weight from 70 to 99 %, tin in a percentage varying in weight from 30 to 1% and impurities in a percentage varying in weight from 0 to 1%, **and in that** the thickness of said surface covering layer (3) exceeds 5 micrometres.

2. Object (1; 51) according to claim 1, **characterized in that** said alloy comprises copper in a percentage varying in weight from 85 to 99%, tin in a percentage varying in weight from 15 to 1% and impurities in a percentage varying in weight from 0 to 1 %.

3. Object (1; 51) according to claim 1 or 2, **characterized in that** said alloy comprises copper in a percentage varying in weight from 90 to 95%, tin in a percentage varying in weight from 10 to 5% and impurities in a percentage varying in weight from 0 to 1%.

4. Object (1; 51) according to any of the preceding claims, **characterized in that** the thickness of said surface covering layer (3) exceeds 30 micrometres.

5. Object (1; 51) according to any of the preceding claims, **characterized in that** said main body (2; 52) comprises a conductive material.

6. Object (51) according to any of the claims from 1 to 4, **characterized in that** said main body (52) comprises a non-conductive material (54) and an external layer comprising a conductive material (55).

7. Object (1; 51) according to any of the preceding claims, **characterized in that** said surface covering layer (3) is obtained through electrolytic deposition.

8. Object (1; 51) according to any of the preceding claims, **characterized in that** said alloy does not comprise zinc.

9. Object (1; 51) according to any of the preceding claims, **characterized in that** it is an object (1; 51) belonging to the group comprising: accessories for bags, for shoes, for belts, for example buckles, rings, spring catches, chains, fasteners; parts of glasses, for example sides, bridges, inserts; zip fasteners; buttons; components of watches, for example casings, buckles, bracelet meshes; trinkets, for example bracelets, rings, earrings, pendants; handles, for example handles for pieces of furniture, doors, refrigerators; valves; gift items, for example trays, vases and pots, cups, tea pots, milk pots; technical items, for example bushings.

10. Object (1; 51) according to any of the preceding claims, **characterized in that** it is a fashion accessory or a trinket.

11. Aqueous electrolyte solution used in an electrolytic deposition process for making an object (1; 51), **characterized in that** it comprises:

    - copper cyanide (CuCN), with values preferably included between 15 and 30 g/l, more preferably included between 24 and 28 g/l, even more preferably equal to 26 g/l;
    - potassium stannate (K2SnO3.3H2O), with values preferably included between 10 and 25 g/l, more preferably included between 18 and 22 g/l, even more preferably equal to 20 g/l;
    - potassium cyanide (KCN), with values preferably included between 40 and 50 g/l, more preferably included between 43 and 47 g/l, even more preferably equal to 45 g/l;
    - free potassium hydroxide (KOH), with values preferably included between 5 and 20 g/l, more preferably included between 8 and 14 g/l, even more preferably equal to 11 g/l.

12. Solution according to claim 11), **characterized in that** it does not comprise zinc.

13. Solution according to any of the claims from 10 to 12, **characterized in that** said object (1; 51) is an object belonging to the group comprising: accessories for bags, for shoes, for belts, for example buckles, rings, spring catches, chains, fasteners; parts of glasses, for example sides, bridges, inserts; zip fasteners; buttons; components of watches, for example casings, buckles, bracelet meshes; trinkets, for example bracelets, rings, earrings, pendants; handles, for example handles for pieces of furniture, doors, refrigerators; valves; gift items, for example trays, vases and pots, cups, tea pots, milk pots; technical items, for example bushings.

14. Solution according to any of the claims from 10 to 13, **characterized in that** said object is a fashion accessory or a trinket.

15. Method for making an object (1; 51) of the type comprising a main body (2; 52) and a surface covering layer (3) suited to at least partially cover said main body (2; 52), said method comprising a stage for making said surface covering layer (3) through electrolytic deposition in an aqueous electrolytic solution, **characterized in that** said electrolytic solution is obtained according to any of the claims from 11 to 14.

16. Method according to claim 15, **characterized in that** during said chemical deposition the pH value of said electrolytic solution is maintained between 12 and 12.5.

17. Method according to claim 15 or 16, **characterized in that** during said chemical deposition the temperature of said electrolytic solution is maintained between 58° and 62°C.

18. Method according to any of the claims from 15 to 17, **characterized in that** during said chemical deposition the process current is maintained between 0.3 and 2.5 A/dm2.

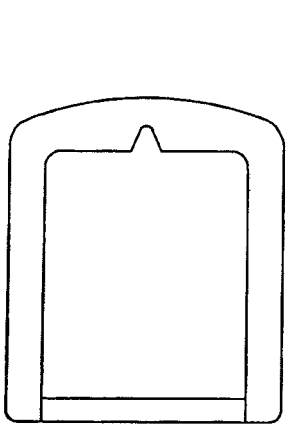

FIG. 1

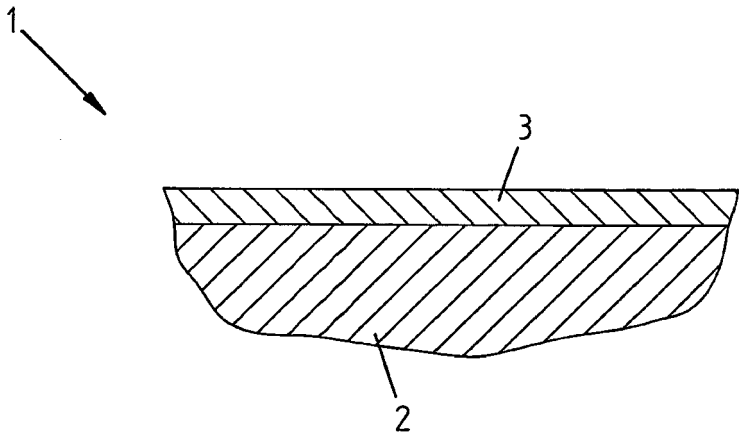

FIG. 2

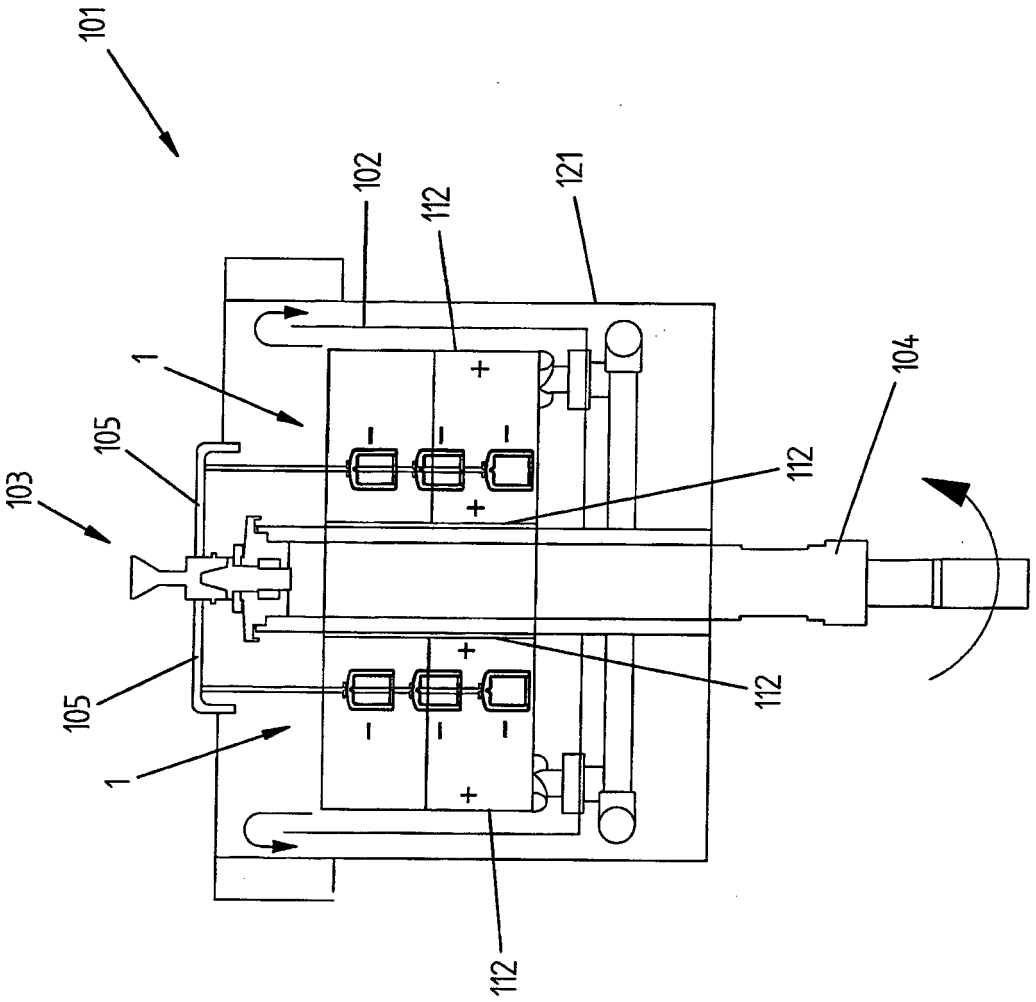

FIG. 3

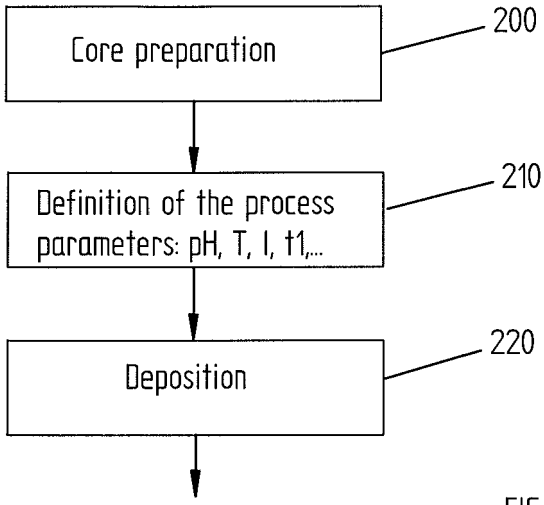

FIG. 4

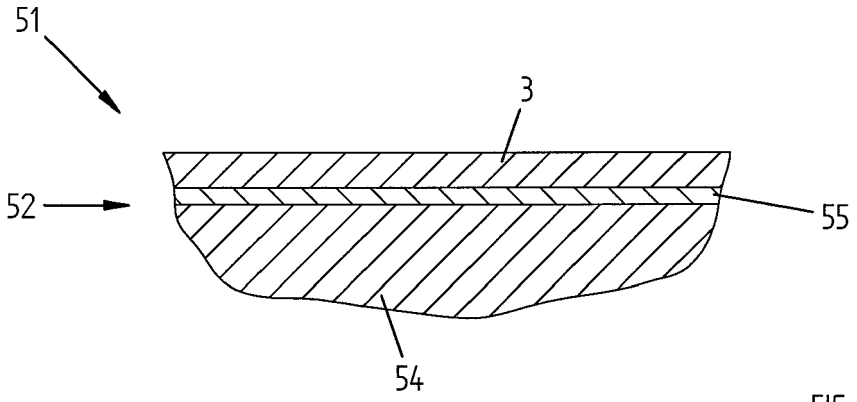

FIG. 5

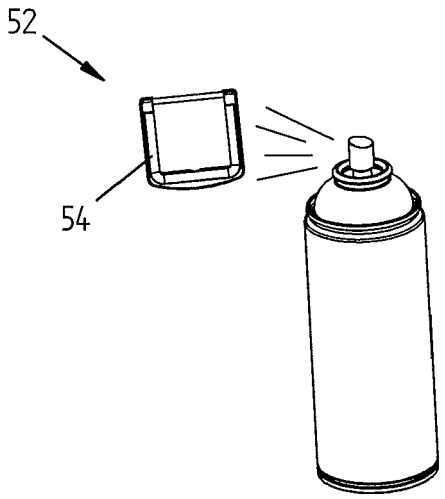

FIG. 6

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EUROPEAN SEARCH REPORT

Application Number
EP 13 00 5253

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 1 970 548 A (BATTEN HARRISON M ET AL) 21 August 1934 (1934-08-21) * page 1, lines 35-99 *	1,2,5-8, 11-15, 17,18	INV. C25D3/58
X	US 1 970 549 A (BATTEN HARRISON M ET AL) 21 August 1934 (1934-08-21) * page 1, lines 18-21 * * page 1, line 74 - page 2, line 7 * * page 2, lines 94-104 *	1,5-7, 11-18	
X	EP 2 071 057 A2 (ROHM & HAAS ELECT MATERIALS [US]) 17 June 2009 (2009-06-17) * paragraphs [0027], [0030], [0031], [0032], [0034], [0036] *	1-3,5-10	
X	EP 0 163 419 A2 (SHERRITT GORDON MINES LTD [CA]) 4 December 1985 (1985-12-04) * abstract * * page 1, lines 4-7 * * page 4, lines 10-23 *	1-7	
X	US 2006/068219 A1 (MCDANIEL PAUL [US] ET AL) 30 March 2006 (2006-03-30) * paragraphs [0028] - [0031] * * claims 1-12 *	1,6-8, 11,12, 15,17,18	TECHNICAL FIELDS SEARCHED (IPC) C25D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	13 January 2014	Haering, Christian

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13-01-2014

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 1970548 A	21-08-1934	FR 743797 A	06-04-1933
		GB 409001 A	18-04-1934
		US 1970548 A	21-08-1934
US 1970549 A	21-08-1934	GB 425846 A	22-03-1935
		US 1970549 A	21-08-1934
EP 2071057 A2	17-06-2009	CN 101514465 A	26-08-2009
		EP 2071057 A2	17-06-2009
		JP 2009185381 A	20-08-2009
		KR 20090063146 A	17-06-2009
		TW 200940751 A	01-10-2009
		US 2009188807 A1	30-07-2009
EP 0163419 A2	04-12-1985	CA 1219708 A1	31-03-1987
		DE 3565411 D1	10-11-1988
		EP 0163419 A2	04-12-1985
		IN 163911 A1	10-12-1988
		JP S6111895 A	20-01-1986
		US 4579761 A	01-04-1986
US 2006068219 A1	30-03-2006	BR PI0515910 A	12-08-2008
		CN 101056760 A	17-10-2007
		ES 2389444 T3	26-10-2012
		JP 4927742 B2	09-05-2012
		JP 2008515050 A	08-05-2008
		US 2006068219 A1	30-03-2006
		US 2006068234 A1	30-03-2006

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82