(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 445 352 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
11.08.2004 Bulletin 2004/33

(51) Int Cl.^{7}: **C25D 11/34**

(21) Application number: **04001036.5**

(22) Date of filing: **20.01.2004**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PT RO SE SI SK TR
Designated Extension States:
AL LT LV MK

(30) Priority: **21.01.2003 IT TO20030027**

(71) Applicant: **Europa Metalli S.p.A.**
50127 Firenze (IT)

(72) Inventor: **Billi, Alberto**
55027 Gallicano (IT)

(74) Representative: **Pietrzykowski, Anja**
Klosterstrasse 29
49074 Osnabrück (DE)

(54) A method for forming a passivation layer on an article having at least one tin-plated surface

(57) Described herein is a method for forming a passivation layer on an article having at least one tin-plated surface, comprising the step of subjecting the tin-plated surface to electrochemical oxidation for forming thereon a layer of tin dioxide in crystalline form of the type of natural cassiterite. Oxidation takes place in an electrolytic solution preferably comprising at least one compound chosen in the group constituted by salts of the gluconic acids, salts of citric acid, and salts of boric acid. Preferably, the article is made of copper and coated with a layer of tin obtained via hot tin-plating or electrolytic deposition.

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to a method for forming a passivation layer on an article having at least one tin-plated surface.

[0002] There are known methods of treatment for "passivating" a metal surface, i.e., reducing or eliminating dissolution of the metal itself in an environment. Said methods comprise a step in which the metal surfaces are treated so as to form, for instance in an aqueous solution, a passivated layer, for example a layer of oxide, which is not very reactive and will have a smaller degree of dissolution.

[0003] It is known practice, for example, to passivate articles coated with a layer of metal tin, obtained, for example, by electrodeposition or hot deposition, such as wires made of copper for superconductors or internal surfaces of cans made of aluminium.

[0004] In particular, it is known to oxidize electrochemically tin-plated surfaces so as to form a layer of oxide of bivalent tin SnO as passivation layer.

[0005] Current research is, however, directed towards methods that will enable improved passivation layers to be obtained and, in particular, that will make possible passivation layers which are continuous, thin, and are very adherent to the substrate of tin or tin alloys, present excellent mechanical characteristics, and possibly also have different colours so as to enable application on as many materials as possible.

[0006] A purpose of the present invention is, hence, to provide a method for obtaining a passivation layer on an article having at least one tin-plated surface which will enable electrochemical oxidation to be carried out in bland conditions of pH, and current density and in short times and thus obtain articles that will have improved characteristics as compared to the known art and, in particular that will be provided with a passivation layer, which is continuous, thin, and highly adherent to the substrate, presents excellent mechanical characteristics, and will also possibly have different colours so as to enable application on as many materials as possible.

[0007] A further purpose of the present invention is to provide a method for forming a passivation layer that will be universally usable for different articles on which it is necessary to form a passivation layer and which may even be very different from one another.

[0008] According to the present invention, there is consequently provided a method for forming a passivation layer on an article having at least one tin-plated surface characterized in that it comprises the step of subjecting said tin-plated surface to electrochemical oxidation for forming on said tin-plated surface a layer of tin dioxide having a crystalline structure of the type of natural cassiterite.

[0009] According to the present invention, there is moreover provided a tin-plated article, characterized in that it is coated with a layer of tin dioxide having a crystalline structure of the type of natural cassiterite.

[0010] The invention will now be described also with reference to the annexed figures, which illustrate a non-limiting example of embodiment thereof, and in which:

- Figure 1 is the x-ray diffraction spectrum of an article made of tin-plated copper, plated via electrochemical tin-plating and subsequently oxidized electrochemically;

- Figure 2 is the x-ray diffraction spectrum of an article made of tin-plated copper obtained via hot tin-plating and oxidized electrochemically;

- Figure 3 shows a XPS - Auger panoramic spectrum of surface made of tin oxidized anodically; and

- Figure 4 is a graph of the specular reflectivity (Gloss %) of strips of copper tin-plated electrolytically according to the present invention and re-melted thermally (PEM) and hot tin-plated (STT2) before (Virgin) and after anodization treatment, said measurements being carried out at 20°C and 60°C.

[0011] A method is proposed for forming a passivation layer on an article having at least one tin-plated surface, said method comprising the step of subjecting the tin-plated surface to electrochemical oxidation in order to form, on the tin-plated surface itself, a layer of tin dioxide SnO_2 having a crystalline structure of the type of natural cassiterite.

[0012] For the purpose of the present invention the solutions preferred are electrolytic solutions comprising at least one compound chosen in the group constituted by salts of gluconic acid, salts of citric acid, and salts of boric acid.

[0013] Electrochemical oxidation takes place preferably at a pH of between 6 and 9, hence in almost neutral conditions or just slightly alkaline conditions.

[0014] The current density is preferably between 0.1 A/dm^2 and 10 A/dm^2, and the potential difference of between 2.5 V and 31 V.

[0015] The temperature is preferably between 30°C and 80°C, and the oxidation time is between 0.5 min and 4 min.

[0016] As a material for the cathode, stainless steel or titanium coated with platinum may preferably be used.

[0017] Particularly preferred are electrolytic solutions comprising as complexing agents a mixture of sodium tetraborate, boric acid and sodium gluconate.

[0018] In this case a temperature of between 20°C and 80°C is to be preferred, and a pH of between 7 and 8.

[0019] For the electrolytic bath a current density of between 2 A/dm^2 and 10 A/dm^2 is preferred, with a potential difference of between 8 V and 31 V.

[0020] In particular, in the case where an electrolytic solution comprising sodium tetraborate, boric acid and sodium gluconate is used, the preferred concentrations are the following:

sodium tetraborate: 0.05 - 0.5 M;
boric acid: 0.25 - 1.0 M; and
sodium gluconate: 0.01 - 0.05 M.

[0021] Alternatively, an electrolytic solution comprising as complexing agents a mixture of sodium carbonate and sodium gluconate may preferably be used.

[0022] In this case a temperature of between 30°C and 50°C is to be preferred and a pH of between 11 and 11.5. The time for anodization is preferably between 1 min and 4 min.

[0023] For the electrolytic bath a current density of between 0.31 A/dm^2 and 10 A/dm^2 is preferred, with a potential difference of between 3.6 V and 25 V.

[0024] In particular, in the case where an electrolytic solution comprising sodium carbonate and sodium gluconate is used the preferred concentrations are the following:

sodium gluconate: 0.01 - 0.05 M; and
sodium carbonate: 0.075 - 0.125 M.

[0025] Alternatively, an electrolytic solution comprising, as complexing agents, a mixture of sodium bicarbonate and sodium gluconate may preferably be used.

[0026] In this case a temperature of between 30°C and 50°C is preferred and a pH of between 7.0 and 11.5. The time for anodization is preferably between 1 and 4 min.

[0027] For the electrolytic bath a current density of between 0.30 A/dm^2 and 10 A/dm^2 is preferred, with a potential difference of between 3.6 V and 25 V.

[0028] In particular, in the case where an electrolytic solution comprising sodium carbonate and sodium gluconate is used, the preferred concentrations are the following:

sodium gluconate: 0.01 - 0.30 M; and
sodium bicarbonate: 1.80 - 2.20 M.

[0029] Alternatively, an electrolytic solution comprising, as complexing agents, a mixture of sodium bicarbonate, sodium carbonate and sodium gluconate may preferably be used.

[0030] In this case, a temperature of between 30°C and 80°C is preferred, and a pH of between 9.0 and 9.5. The time for anodization is preferably between 1 min and 4 min.

[0031] For the electrolytic bath a current density of between 3 A/dm^2 and 10 A/dm^2 is preferred, with a potential difference of between 8 V and 15 V.

[0032] In particular, in the case where an electrolytic solution comprising sodium bicarbonate, sodium carbonate and sodium gluconate is used, the preferred concentrations are the following:

sodium gluconate: 0.01 - 0.05 M;
sodium bicarbonate: 0.25 - 1 M; and
sodium carbonate: 0.05 - 0.2 M.

[0033] Alternatively, an electrolytic solution comprising, as complexing agents, a mixture of disodium hydrogen phosphate (Na_2HPO_4) and sodium gluconate may preferably be used.

[0034] In this case, a temperature of between 36°C and 60°C is preferred, and a pH of between 9.10 and 10. The time for anodization is preferably between 1 min and 4 min.

[0035] For the electrolytic bath a current density of between 6 A/dm^2 and 10 A/dm^2 is preferred, with a potential difference of between 10 V and 17 V.

[0036] In particular, in the case where an electrolytic solution comprising disodium hydrogen phosphate Na_2HPO_4 and sodium gluconate is used, the preferred concentrations are the following:

sodium gluconate: 0.01 - 0.05 M; and
disodium hydrogen phosphate: 0.20 - 0.30 M.

[0037] Alternatively, an electrolytic solution comprising, as complexing agents, a mixture of sodium gluconate and potassium gluconate may preferably be used.

[0038] In this case, a temperature of between 30°C and 80°C is preferred, and a pH of between 7 and 8. The time for anodization is preferably between 0.5 min and 2 min.

[0039] For the electrolytic bath a current density of between 2 A/dm^2 and 10 A/dm^2 is preferred, with a potential difference of between 8 V and 15 V.

[0040] In particular, in the case where an electrolytic solution comprising a mixture of sodium gluconate and potassium gluconate is used, the preferred concentration of complexing agent is between 0.085 M and 0.120 M.

[0041] Alternatively, an electrolytic solution comprising, as complexing agents, a mixture of sodium citrate and sodium gluconate may preferably be used.

[0042] In this case a temperature of between 32°C and 50°C is preferred, and a pH of between 9 and 9.5. The time for anodization is preferably between 1 min and 4 min.

[0043] For the electrolytic bath a current density of between 5 A/dm^2 and 10 A/dm^2 is preferred, with a potential difference of between 10.3 V and 16.8 V.

[0044] In particular, in the case where, as an electrolytic solution, a mixture of sodium gluconate and sodium citrate is used, the preferred concentrations are the following:

sodium gluconate: 0.01 - 0.05 M; and
sodium citrate: 0.08 - 0.12 M.

[0045] Using the electrolytic solutions described previously, a passivation layer is obtained by electrolytic oxidation or anodization, said layer consisting of tin dioxide SnO_2 having a crystallization state of a tetragonal type, hence similar to that of the natural mineral of tin, i.e., cassiterite.

[0046] The tin dioxide formed using the electrolytic solutions described above can be characterized via diffractometric studies capable of detecting the presence of tin dioxide itself and the absence of tin monoxide or tin oxide SnO (where tin presents the oxidation state +2), as illustrated in Figures 1 and 2.

[0047] In particular, x-ray diffractometry studies were conducted using a Siemens D500 diffractometer and GENERAL STRUCTURES ANALYSIS SYSTEM (GSAS) software [A.C. LARSON AND R.B. VON DREELE, LOS ALAMOS NATIONAL LABORATORIES, LOS ALAMOS, CA, USA]. Figure 1 refers to an article made of tin-plated copper produced via electrochemical tin-plating, whilst Figure 2 refers to an article made of tin-plated copper obtained via hot tin-plating. Both of said articles underwent electrochemical oxidation or anodization.

[0048] In both cases, perfectly identifiable in the graphs are the reflections corresponding to copper (base material), elementary tin, and tin dioxide SnO_2, whilst the reflection corresponding to tin monoxide SnO is absent.

[0049] A further confirmation of the exact chemical nature of the deposit formed by controlled anodization using the baths and applying the operating conditions described for each bath, is provided by XPS (X-Ray Photoemission Spectroscopy) studies, which were conducted on surfaces made of anodically oxidized tin using an XPS-Auger spectrometer. Figure 3 shows a typical XPS - Auger panoramic spectrum of the anodically oxidized tin surface. Said spectrum shows clearly that the tin ion is only and exclusively tetravalent (Sn^{+4}) whilst the bivalent form (Sn^{+2}) of the oxide SnO is totally absent. The analyses of the surfaces were carried out using, as exciting radiation, the Ka of magnesium (1253.6 eV) with a power of 180 W (12 kV x 15 mA) with energy steps of 90 eV, whilst in regions corresponding to the XPS and Auger transitions the step was 44 eV in order to improve resolution of the peak. Traces of sodium (see XPS peak Na 1 s) were detected. The comparison of the binding energies obtained for the XPS peak Sn $3d_{5/2}$ of tin with the data provided in the literature, for both of the oxidized forms SnO and SnO_2, in some cases does not enable perfect differentiation of the two oxidized forms. From a comparison of the values of the Auger parameter, differentiation between SnO and SnO_2 is possible. The experimental data obtained for all the specimens show that, on the surfaces oxidized electrochemically, only tetravalent tin (SnO_2) is present and not bivalent tin (SnO).

[0050] Further characterization tests conducted on a laminated article made of tin-plated copper are listed in the table below.

Test conducted	Measuring method	Result
Thickness of film of tin dioxide SnO_2	Parasitic-current method DIN50984	Approximately 2 µm
	Constant-current coulombometric reduction (chronopotentiometry)	Coulombmetric reduction was performed with a current density of 100 mA/cm^2 in a 0.1-M solution of hydrochloric acid, at 25°C
Adhesion	ASTM B 545/X4, B 571	No loss of material after bending at 90° and 180° and subsequent peeling test with adhesive tape Tesa 600
Flexibility - bending	ASTM B 545/X4.4	No failure of the film of tin dioxide after bending of the strip on its thickness (0.5 mm)
Erichsen Test (Ball Punching)	ASTM E 643, UNI 4693	No failure of the film of tin dioxide SnO_2
Deep drawing	UNI 6124	No failure or exfoliation of the film of tin dioxide SnO_2
Welding		In certain cases, the surface tin dioxide may not require removal
GLOSS, i.e., measurement of specular reflectivity	ASTM	In all cases, a very marked reduction of the specular reflectivity was observed See Figure 4

[0051] The articles obtained using the method described previously can be applied to a wide range of technical fields, amongst which preferred applications are for roofing layers in order to obtain layers of tin dioxide which are adherent, opaque, slightly coloured, and do not present problems of adhesion during formation of the reels and storage in the form of plates or laminas. The tin-dioxide layer constitutes an insoluble barrier to corrosion due to atmospheric agents thanks to its extremely low solubility even in the presence of acid rain (log $\mathbf{Ks}_0$ SnO_2 = -58 to -64.5; log $\mathbf{Ks}_0$ SnO = -0.9 to -26.2 - values drawn from the International Union of Pure and Applied Chemistry - "Solubility Constants of Metal Oxides, Metal Hydroxides and Metal Hydroxide Salts in Aqueous Solution", W. Feitknecht and P. Schindler, Butterworths, London 1963) and reduces dissolution of the tin-plated layer, maintaining the natural colour of the tin-plated surface unaltered for a longer period of time.

[0052] A further preferred application is to facades, windows and in the production of implements having tin-plated surfaces.

[0053] A further preferred application is in the steel industry for passivation of the internal surfaces made of tin-plated steel in the foodstuff-canning industry in order to prevent direct contact with the food, in so far as cassiterite or tin dioxide is considerably less soluble than tin monoxide also in these conditions.

[0054] A further particularly preferred application is in the field of superconductors, in particular in superconductor wires or cables made of niobium-titanium alloys or other alloys or ceramic compounds, englobed in a sheath made of copper or other metals, such as silver or aluminium, coated with tin or tin alloys, for example tin-silver (SnAg5) alloy. Cassiterite or tin dioxide, which is an electrically insulating material, when it is electrochemically deposited in controlled conditions, enables a uniform, very adherent and continuous layer to be obtained, with a drastic reduction in energy losses due to mutual coupling of single and/or assembled superconductor wires.

[0055] Finally, a further preferred application is in water-distribution systems, for example for pipe connectors, valves, and a wide variety of tin-plated components, which can be treated for limiting dissolution of the underlying tin and of copper in drinking water or in other liquids. Cassiterite or tin-dioxide coatings are able to reduce dissolution of lead considerably in the components used for distribution of drinking water, when they have previously been tin-plated.

[0056] The invention will now be described in what follows also by means of examples, without, however, the invention being limited to said examples.

[0057] Seven different electrolytic baths were prepared, each containing a different electrolytic solution. Then, each bath was tested as regards the coating obtained. Each of the seven baths given in the following examples provides coating layers made of tin dioxide in the tetragonal crystalline form, of the cassiterite type, according to the present invention.

EXAMPLE 1

[0058] A solution was prepared with sodium tetraborate, boric acid and sodium gluconate, according to what is specified in Table 1.

Table 1

Electrolytic aqueous solution	Sodium tetraborate ($Na_4B_4O_7 \times 10H_2O$): 0.10 M + Boric acid (H_3BO_3): 0.50 M + Sodium gluconate $C_6H_{11}NaO_7$: 0.05 M
Temperature	50°C ± 5°C
pH	7.60; buffered solution
Current density	7.50 A/dm^2
Potential difference	15 - 18 V
Cathode	Stainless steel AISI 316
Anode-cathode distance	30 - 60 mm
Anodization time	1-4 min
Stirring	Not necessary
Pre-treatment	Not necessary

EXAMPLE 2

[0059] A solution was prepared with sodium carbonate and sodium gluconate, according to what is specified in Table 2.

Table 2

Electrolytic aqueous solution	Sodium carbonate (Na_2CO_3): 0.1 M + Sodium gluconate: 0.025 M
Temperature	35°C ± 2 °C
pH	11.0
Current density	7.5 A/dm^2
Potential difference	15 V
Cathode	Stainless steel AISI 316
Anode-cathode distance	30 - 60 mm
Anodization time	2 min
Stirring	Not necessary
Pre-treatment	Not necessary

EXAMPLE 3

[0060] A solution was prepared with sodium bicarbonate and sodium gluconate, according to what is specified in Table 3.

Table 3

Electrolytic aqueous solution	Sodium bicarbonate ($NaHCO_3$): 2,0 M + Sodium gluconate: 0.05 M
Temperature	50°C ± 2°C
pH	7.87

Table 3 (continued)

Current density	10 A/dm^2
Potential difference	8.5 V
Cathode	Stainless steel AISI 316
Anode-cathode distance	30 - 60 mm
Anodization time	1 - 4 min
Stirring	Not necessary
Pre-treatment	Not necessary

EXAMPLE 4

[0061] A solution was prepared with sodium carbonate, sodium bicarbonate and sodium gluconate, according to what is specified in Table 4.

Table 4

Electrolytic aqueous solution	Sodium carbonate: 0.1 M + Sodium bicarbonate: 0.25 M + Sodium gluconate: 0.025 M
Temperature	50°C ± 5°C
pH	9.09 - 9.10 buffered solution
Density of current	7.5 A/dm^2
Potential difference	8.9 -10.9 V
Cathode	Stainless steel AISI 316
Distance Anode - Cathode	30 - 60 mm
Anodization time	1 - 4 min
Stirring	Not necessary
Pre-treatment	Not necessary

EXAMPLE 5

[0062] A solution was prepared with disodium hydrogen phosphate and sodium gluconate according to what is specified in Table 5.

Table 5

Electrolytic aqueous solution	Disodium hydrogen phosphate ($Na_2HPO_4 \times 12\ H_2O$) 0.25 M + Sodium gluconate 0.025 M.
Temperature	45°C ± 5°C
pH	9.20
Current density	8.5 A/dm^2
Potential difference	10 - 11 V
Cathode	Stainless steel AISI 316
Anode-cathode distance	30 - 60 mm
Anodization time	2 min
Stirring	Not necessary
Pre-treatment	Not necessary

EXAMPLE 6

[0063] A solution was prepared with sodium gluconate and potassium gluconate according to what is specified in Table 6.

Table 6

Electrolytic solution	Sodium gluconate and potassium gluconate 0.1 M ($C_6H_{11}NaO_7$; formula weight = 218,14 + $C_6H_{11}KO_7$, formula weight = 234.24)
Temperature	50°C ± 2 °C
pH	7.44
Current density	7.5 A/dm^2
Potential difference	8.9 - 10.9 V
Cathode	Stainless steel AISI 316
Anode-cathode distance	30 - 60 mm
Anodization time	1.5 min
Stirring	Not necessary
Pre-treatment	Not necessary

EXAMPLE 7

[0064] A solution was prepared with sodium gluconate and sodium citrate according to what is specified in Table 7.

Table 7

Electrolytic solution	Dehydrated sodium citrate ($Na_3C_6H_{11}O_7 \times 2H_2O$):0.10M+ Sodium gluconate: 0.025 M
Temperature	37°C ± 2°C
pH	9.10
Current density	8.5 A/dm^2
Potential difference	12 V
Cathode	Stainless steel AISI 316
Anode-cathode distance	30 - 60 mm
Anodization time	1.5 min
Stirring	Not necessary
Pre-treatment	Not necessary

[0065] From the foregiong description the advantages that the method according to the present invention makes possible are evident.

[0066] The present method enables improved passivation layers to be obtained and, in particular, layers which are continuous, thin, and very adherent to the substrate, have optimal mechanical characteristics and have different colours so as to enable their application on different base materials, according to the various requirements.

[0067] In particular, it enables electrochemical oxidation of tin-plated articles obtained by hot tin-plating, electrochemical tin-plating, or by chemical or physical deposition, affording a considerable improvement in resistance to atmospheric agents, and making available an opaque surface more similar to aged zinc or else to natural grey stone, both of which are used for roofings.

[0068] The adherent crystalline coating moreover prevents problems of sticking between one coil and another in reels of large dimensions, which in certain cases reach the weight of 10 000 kg or else between plates or laminas set on top of one another, rendering interposition of sheets of paper between one surface and another unnecessary, with benefits from both the economic and environmental standpoints.

[0069] Finally, from the foregoing description it clearly emerges that modifications and variations may be made to the method described, without thereby departing from the sphere of protection of the present invention.

[0070] In particular, the compounds and ratios between compounds used as complexing agents in the electrolytic solution may vary, as likewise may vary the conditions of execution of the electrochemical oxidation, such as pH, temperature, applied current density, potential difference, and anodization time.

Claims

1. A method for forming a passivation layer on an article having at least one tin-plated surface, **characterized in that** it comprises the step of subjecting said tin-plated surface to electrochemical oxidation for forming on said tin-plated surface a layer of tin dioxide SnO_2 having a crystalline structure similar to that of natural cassiterite.

2. The method according to Claim 1, **characterized in that** said electrochemical oxidation takes place in an electrolytic solution comprising at least one compound chosen in the group consisting of salts of gluconic acid, salts of citric acid, and salts of boric acid.

3. The method according to Claim 2, **characterized in that** said electrochemical oxidation takes place at a pH of between 6 and 9.

4. The method according to any one of Claims 1 to 3, **characterized in that** for said electrochemical oxidation a current density of between 0.1 A/dm^2 and 10 A/dm^2 is used.

5. The method according to any one of Claims 1 to 4, **characterized in that** for said electrochemical oxidation there is set a potential difference of between 2.5 V and 31 V.

6. The method according to any one of Claims 1 to 5, **characterized in that** said electrochemical oxidation takes place at a temperature of between 30°C and 80°C.

7. The method according to any one of Claims 1 to 6, **characterized in that** for said electrochemical oxidation the oxidation time is between 0.5 and 4 min.

8. The method according to any one of the preceding claims, **characterized in that** said electrolytic solution is an aqueous solution comprising sodium tetraborate, boric acid and sodium gluconate.

9. The method according to Claim 8, **characterized in that** said electrolytic solution comprises sodium tetraborate in a concentration of between 0.05 M and 0.5 M, boric acid in a concentration of between 0.25 M and 1 M, and sodium gluconate in a concentration of between 0.01 M and 0.05 M.

10. The method according to Claim 2, **characterized in that** said electrolytic solution is an aqueous solution comprising sodium carbonate and sodium gluconate.

11. The method according to Claim 10, **characterized in that** said electrolytic solution comprises sodium carbonate in a concentration of between 0.075 M and 0.125 M and sodium gluconate in a concentration of between 0.01 M and 0.05 M.

12. The method according to Claim 2, **characterized in that** said electrolytic solution is an aqueous solution comprising sodium bicarbonate and sodium gluconate.

13. The method according to Claim 12, **characterized in that** said electrolytic solution comprises sodium gluconate in a concentration of between 0.01 M and 0.30 M and sodium bicarbonate in a concentration of between 1.80 M and 2.20 M.

14. The method according to Claim 2, **characterized in that** said electrolytic solution is an aqueous solution comprising sodium gluconate, sodium bicarbonate and sodium carbonate.

15. The method according to Claim 14, **characterized in that** said electrolytic solution comprises sodium gluconate in a concentration of between 0.01 M and 0.05 M, sodium bicarbonate in a concentration of between 0.25 M and 1 M, and sodium carbonate in a concentration of between 0.05 M and 0.2 M.

16. The method according to Claim 2, **characterized in that** said electrolytic solution is an aqueous solution comprising disodium hydrogen phosphate and sodium gluconate.

17. The method according to Claim 16, **characterized in that** said electrolytic solution comprises sodium gluconate in a concentration of between 0.01 M and 0.05 M and disodium hydrogen phosphate in a concentration of between 0.20 M and 0.30 M.

18. The method according to Claim 2, **characterized in that** said electrolytic solution is an aqueous solution comprising a mixture of sodium gluconate and potassium gluconate.

19. The method according to Claim 18, **characterized in that** said electrolytic solution comprises a mixture of sodium gluconate and potassium gluconate in a concentration of between 0.085 M and 0.120 M.

20. The method according to Claim 2, **characterized in that** said electrolytic solution is an aqueous solution comprising sodium citrate and sodium gluconate.

21. The method according to Claim 18, **characterized in that** said solution comprises sodium gluconate in a concentration of between 0.01 M and 0.05 M and sodium citrate in a concentration of between 0.08 M and 0.12 M.

22. The method according to any one of Claims 1 to 21, **characterized in that** said tin-plated surface is obtained via hot tin-plating or electrolytic deposition or chemical or physical deposition.

23. The method according to any one of the preceding claims, **characterized in that** the thickness of said layer of tin dioxide is between 0.001 mm and 0.004 mm (1 - 4 μm)

24. The method according to any one of the preceding claims, **characterized in that** said article has a base of copper or copper alloys.

25. The method according to any one of the preceding claims, **characterized in that** said articles are in the form of wires or rods or bars of different geometry.

26. A tin-plated article, **characterized in that** it is coated with a layer of tin dioxide having a crystalline structure of the type of natural cassiterite.

27. The article according to Claim 26, **characterized in that** it is in the form of wire.

28. The article according to Claim 27, **characterized in that** it has superconductive properties.

29. The article according to Claim 28, **characterized in that** it is in the form of cord, or flat, either englobed or not in a metal or ceramic matrix.

30. The article obtained according to the method of any one of Claims 1 to 25.

31. Use of an article according to any one of Claims 25 to 30 as coating in building applications.

32. The use of an article according to any one of Claims 25 to 30 in metal or ceramic superconductors.

33. The use of an article according to any one of Claims 25 to 30 for passivation of the internal surface of containers for foodstuffs.

34. The use of an article according to any one of Claims 25 to 30, for limiting the release of metal ions in water-distribution systems.

35. The use of an article according to Claim 34, in which the article is made of CuZnSn or CuZnPbSn alloy containing high values of tin, for limiting the release of tin, copper, zinc and lead, in water-distribution systems.

36. The use of an article according to any one of Claims 25 to 30 for superconductor materials.

37. The use of an article according to Claim 35 for the reduction of losses of energy due to mutual coupling in multi-filament superconductor systems.

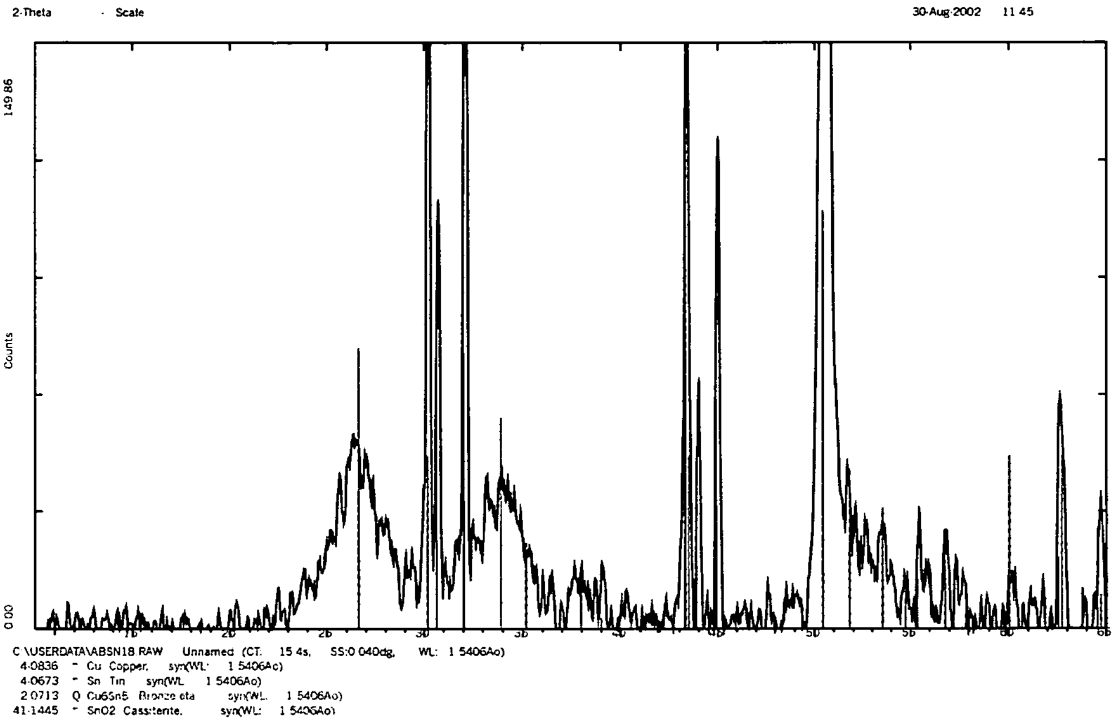
2-Theta - Scale
30-Aug-2002 11 45
149 86
Counts
0 00
15
20
25
30
35
40
45
50
55
60
65
C:\USERDATA\ABSN18.RAW Unnamed (CT: 15 4s, SS:0 040dg, WL: 1 5406Ao)
4-0836 - Cu Copper, syn(WL: 1 5406Ao)
4-0673 - Sn Tin syn(WL 1 5406Ao)
2 0713 Q Cu6Sn5 Bronze eta syn(WL 1 5406Ao)
41-1445 - SnO2 Cassiterite, syn(WL: 1 5406Ao)

Figure 1

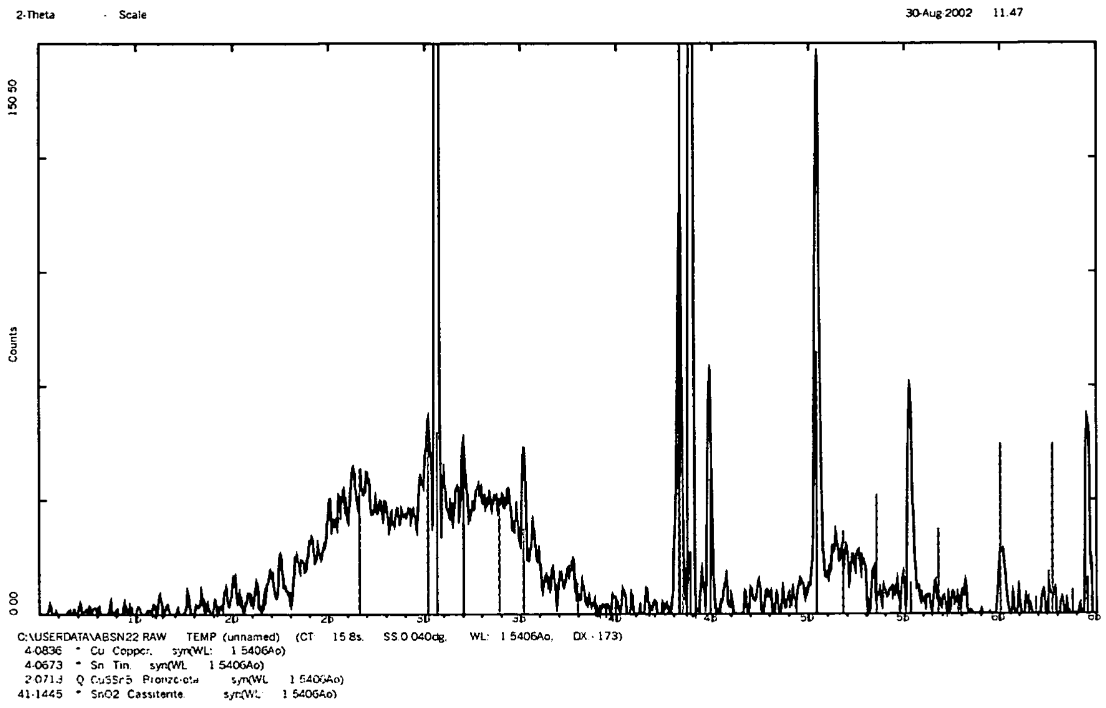
2-Theta - Scale
30-Aug-2002 11.47
150.50
Counts
0.00
10
20
25
30
35
40
45
50
55
60
65
C:\USERDATA\ABSN22.RAW TEMP (unnamed) (CT: 15.8s, SS:0.040dg, WL: 1.5406Ao, DX: -173)
4-0836 * Cu Copper, syn(WL: 1.5406Ao)
4-0673 * Sn Tin, syn(WL: 1.5406Ao)
2-0713 Q Cu5Sn5 Bronze-eta syn(WL: 1.5406Ao)
41-1445 * SnO2 Cassiterite, syn(WL: 1.5406Ao)

Figure 2

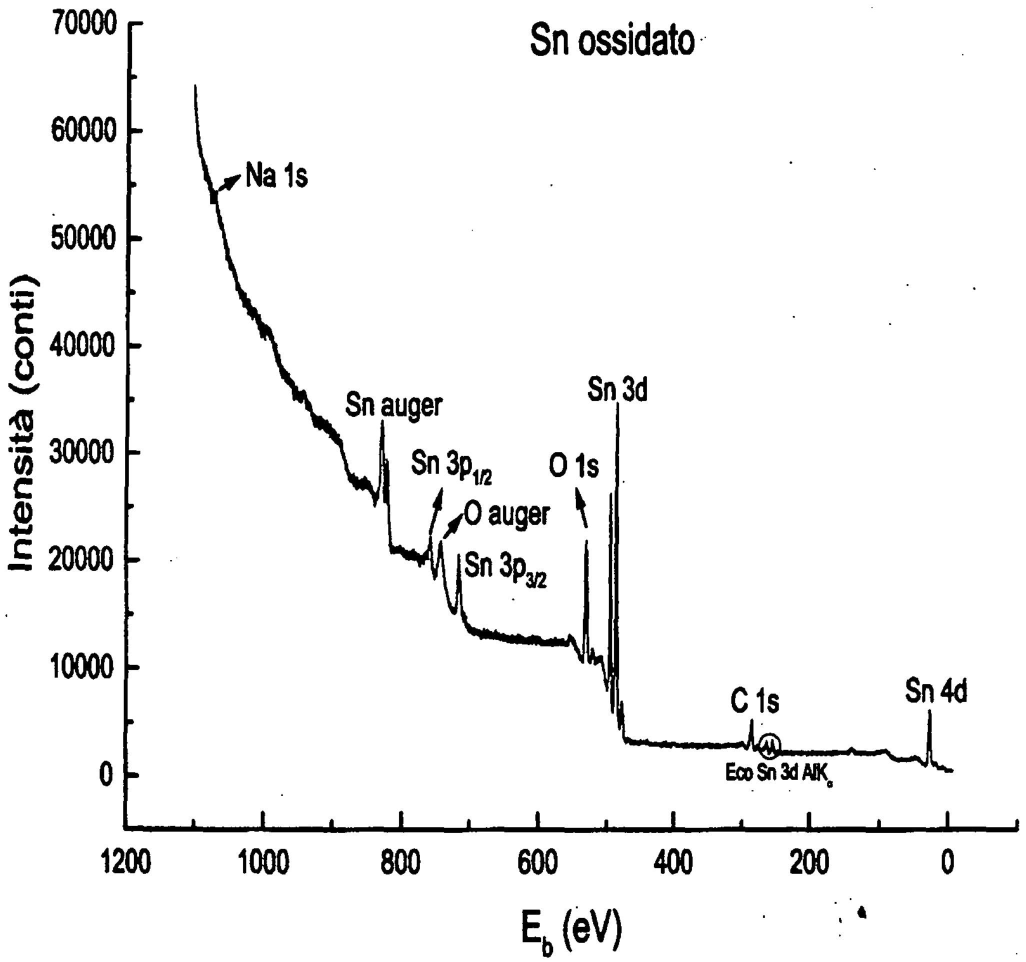

Figura 1. Spettro panoramico.

Figure 3

Panoramic spectrum

Sn oxidized;

Intensity (counts)

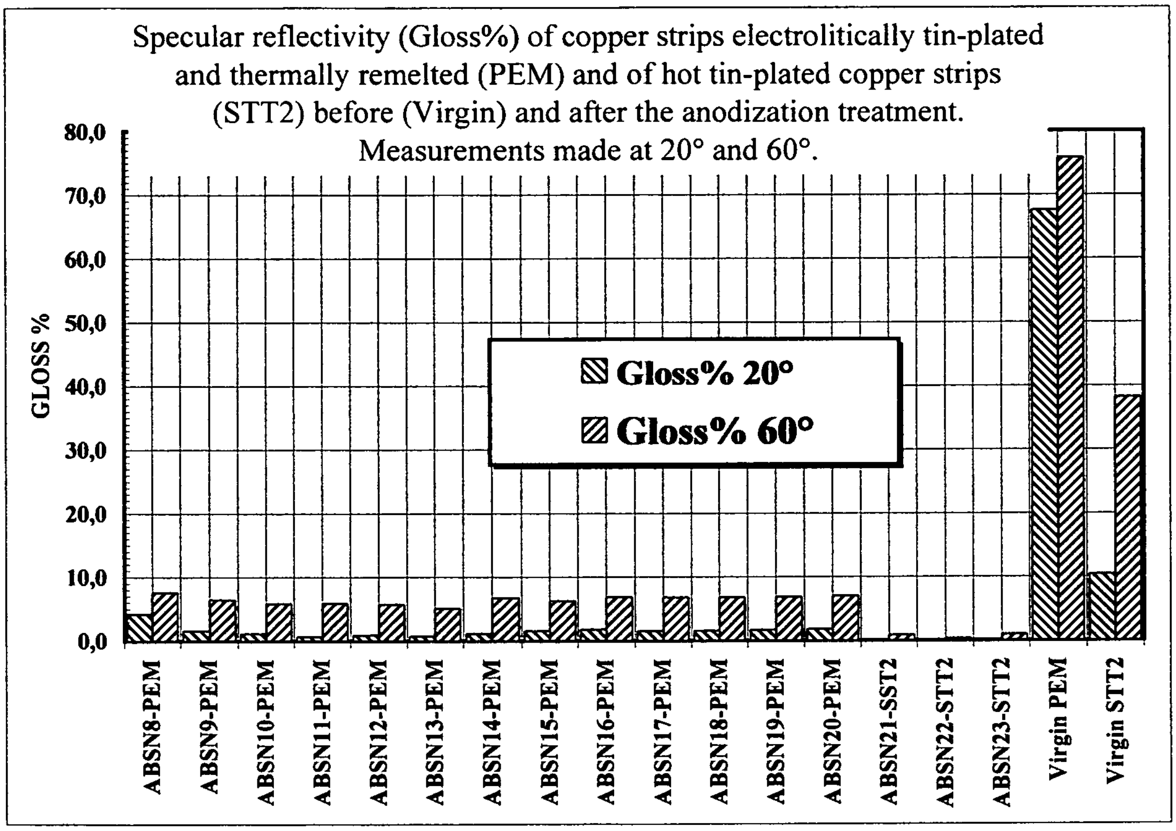
Specular reflectivity (Gloss%) of copper strips electrolitically tin-plated and thermally remelted (PEM) and of hot tin-plated copper strips (STT2) before (Virgin) and after the anodization treatment. Measurements made at 20° and 60°.
GLOSS %
80,0
70,0
60,0
50,0
40,0
30,0
20,0
10,0
0,0
▧ Gloss% 20°
▨ Gloss% 60°
ABSN8-PEM
ABSN9-PEM
ABSN10-PEM
ABSN11-PEM
ABSN12-PEM
ABSN13-PEM
ABSN14-PEM
ABSN15-PEM
ABSN16-PEM
ABSN17-PEM
ABSN18-PEM
ABSN19-PEM
ABSN20-PEM
ABSN21-SST2
ABSN22-STT2
ABSN23-STT2
Virgin PEM
Virgin STT2

Figure 4

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 04 00 1036

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X A	GB 486 752 A (JOHN CAMPBELL; KERR ROBERT; DUNCAN JAMES MACNAUGHTAN) 9 June 1938 (1938-06-09) * page 1, lines 17-21,44-46,70-79 * * page 2, lines 53-63 * * claims 1,3,4 * -----	1-4,26,30,33 6	C25D11/34
X	GB 819 305 A (EKCO PRODUCTS COMPANY) 2 September 1959 (1959-09-02) * page 1, lines 11,12,57,58,80-84 * * page 2, lines 17,18 * * page 3, lines 8,9,21-52 * treatment B treatment H * page 5, lines 5-7 * * page 6, lines 1-4,17,27-35 * -----	1-4,6,7,23,30,33	
X	US 2 312 076 A (ROMINE HUGH E ET AL) 23 February 1943 (1943-02-23) * page 1, column 1, lines 6-16 * * page 1, column 2, lines 36-44 * * page 3, column 1, lines 13-24 * -----	1,2,4,6,30,33	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C25D
X	DATABASE WPI Section Ch, Week 198627 Derwent Publications Ltd., London, GB; Class M14, AN 1986-172372 XP002284379 & JP 61 104099 A (KAWASAKI STEEL CORP) 22 May 1986 (1986-05-22) * abstract * -----	1,26,30	
A	GB 2 020 695 A (NIPPON KOKAN KK) 21 November 1979 (1979-11-21) -----		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	15 June 2004	Zech, N

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 04 00 1036

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15-06-2004

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 486752 A	09-06-1938	NONE	
GB 819305 A	02-09-1959	NONE	
US 2312076 A	23-02-1943	NONE	
JP 61104099 A	22-05-1986	NONE	
GB 2020695 A	21-11-1979	JP 1139879 C	24-03-1983
		JP 54142135 A	06-11-1979
		JP 57032720 B	13-07-1982
		AU 519734 B2	17-12-1981
		AU 4588479 A	01-11-1979
		CA 1138373 A1	28-12-1982
		DE 2916411 A1	31-10-1979
		FR 2424336 A1	23-11-1979

EPO FORM P0459

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