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— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ,*

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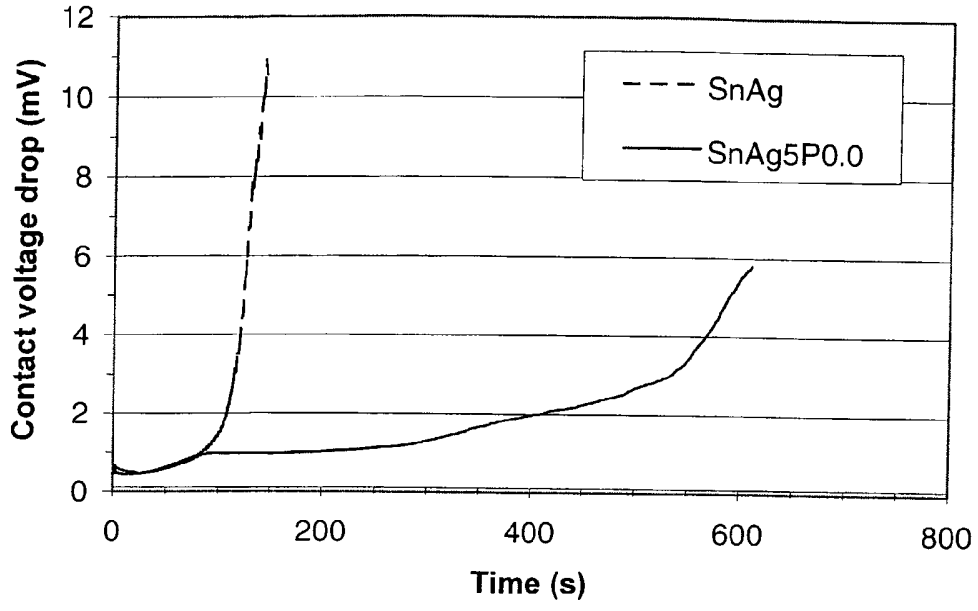
(54) Title: TIN ALLOY COATING FOR CONTACT PURPOSES



(57) Abstract: The invention relates to a tin alloy coating in a connector for electric contact purposes, such as in contact terminals. The tin alloy coating of the invention is alloyed with at least one reducing agent to achieve an essentially oxide free metal-to-metal contact.

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CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

TIN ALLOY COATING FOR CONTACT PURPOSES

The invention relates to a tin alloy coating with at least one reducing agent to achieve an essentially oxide free metal-to-metal contact in electric contact purposes, such as in contact terminals.

The ultimate connection between two conductors is a welded joint. A cold welded spot will restrict detrimental microsliding and wear during vibration. Moreover, a cold welded contact spot will prevent the ingress of air or moisture, which could cause corrosion. Provided that a cold-welded contact spot can be maintained the contact resistance will be low and stable during a long-term operation.

With a soft coating such as tin, tin alloys or silver coatings, it is possible to achieve a cold welded contact spot during insertion. In order to achieve a cold welded contact spot it is of decisive importance to achieve an oxide-free metal-to-metal contact at the interface during insertion. A high contact force and a thick and soft coating will in general promote a cold welded contact spot, since any free space at the interface is restricted, and subsequently a gas-tight joint contact spot is achieved during insertion.

The trend with increasing number of contact terminals in a connector requires a reduced insertion force for each contact terminal. A reduced insertion force is achieved by using a low contact force in combination with a soft thin coating. It is desirable to increase the hardness of the coating by adding for instance silver in order to further reduce the insertion force and to extend the number of insertion and withdrawal before the coating is wear off.

The US patent application 2002096662 describes an electrically conducting metal strip comprising a base material made from copper or a copper alloy with a coating made from a tin-silver alloy containing 1 – 3,8 weight % silver. When manufacturing this strip an intermetallic phase is formed between the base

material and the coating. Also the US patent application 2001055697 relates to a similar tin-silver alloy for coating of a base material from copper or a copper alloy. In this case the tin-silver alloy contains in addition to silver also 0,1 – 5 weight % indium. The addition of silver and indium achieves a higher hardness in a thinner coating.

With the higher hardness of the thin coating in combination with a low contact force will result in infinitesimal small spaces at the contact interface containing oxygen. This results oxides in a thin surface at parts of the contact interface, with a subsequently mechanical weak cold welded contact spot. This cold welded contact spot will easily be ruptured when subjected to cyclic mechanical stress, such as vibration.

The object of the present invention is to eliminate some drawbacks of the prior art and to achieve an improved tin alloy coating to achieve an essentially oxide free metal-to-metal contact in electric contact purposes by adding at least one reducing agent to the tin alloy coating. The essential features of the invention are enlisted in the appended claims.

According to the invention at least one reducing agent is added to a tin alloy coating of a connector to be used in electric contact purposes in order to achieve an essentially oxide free metal-to-metal contact in electric contact purposes. This addition of the reducing agent improves the life-length of the connector because an oxide free metal-to-metal contact during the insertion is achieved. The reducing agent will react with the possible residual oxygen, which is left at the contact interface. The reducing agent also reduces an eventually formed surface oxide on the surface of the connector. Thus a thin oxide film is prevented to form at the interface during the insertion.

The reducing agent in accordance with the invention is preferably phosphorus and the amount of the added phosphorus is between 50 to 1000 ppm, preferably 100 to 250 ppm. Also other elements having a reducing effect as

phosphorus for the tin alloy coating of the connector is used. Other possible elements as a reducing agent in the tin alloy coating of the invention are for instance lithium and boron. These reducing agents are added as such in the tin coating, but these reducing agents can be used as reducing agents with phosphorus.

The tin alloys, which are suitable for the coating of the invention, are for instance tin-copper alloys, tin-bismuth alloys and tin-silver alloys. One or two more metallic components can be advantageously added to the tin-silver alloys in addition with the reducing agent in order to achieve the reducing effect during the insertion of the contact between conductors.

The tin-silver alloys having one or two more metallic components are suitable for the coating of the invention. The tin-silver alloys with one more component have a component from the group of bismuth, copper, indium and lead. The desired alloys are thus tin-silver-bismuth, tin-silver-copper, tin-silver-indium and tin-silver-lead, which are also added by the reducing agent.

The tin-silver-bismuth alloy can further be advantageously alloyed by indium. In case of the tin-silver-copper alloy the alloy can further be advantageously alloyed by one of the elements from the group of bismuth, cobalt, indium and antimony.

The amount of silver in the tin-silver alloys for the invention is between 2 to 10 weight % silver, while the amount of copper in the tin-copper alloys for the invention is between 0,5 to 5 % by weight copper.

The advantageous compositions of the tin silver alloys for the coating in accordance with the invention are for instance tin with 3,5 % by weight silver, tin with 3,2 % by weight silver and 0,8 % by weight copper as well as tin with 2,5 % by weight silver, 0,8 % by weight copper and 0,5 % by weight antimony.

When using the reducing agent, as phosphorus, in the tin alloy coating for contact purposes a thin oxide film is prevented in a contact where a thin and harder coating can be used in combination with a low contact force. This can be done without affecting the possibility to achieve a good cold-welded contact spot.

The present invention will be illustrated in more details referring to the attached drawing, where

Fig. 1 shows the contact voltage drop in fretting tests as a function of time.

The present invention to use phosphorus as a reducing doped additive in the tin – silver coating was tested in the fretting tests in a test bench, which consists of an electronic controlled shaker and a measurement system. Before the fretting tests all contacts were subjected to one long sliding stroke to wipe off the initial surface layer. During the fretting tests, the contacts were subjected to a vibration displacement stroke of 20 micrometer at a frequency of 100 Hz, and also a current loads of 2 A DC. The contact geometry was crossed cylinders with a diameter of 10 mm.

In the test the samples constituted of solid rods of the present tin alloys, in order to avoid uncontrolled influence of the substrate material during fretting. Tin with 5% by weight silver with and without phosphorus were tested. The amount of phosphorus added to the tin-silver-phosphorus alloy was 0.025 % by weight.

According to Fig. 1 the contact voltage drop was tested in fretting tests as a function of time. A normal load 13.9 N was applied. As shown the phosphorus added to the tin-silver restricts significant the increase in contact voltage drop. The observed enhanced performance of the phosphorus doped tin-silver sample was caused by the formation of a cold-welded contact spot.

CLAIMS

1. Tin alloy coating in a connector for electric contact purposes, such as in contact terminals, **characterized** in that the tin alloy coating is alloyed with at least one reducing agent to achieve an essentially oxide free metal-to-metal contact.

2. Tin alloy coating according to the claim 1, **characterized** in that the reducing agent is phosphorus.

3. Tin alloy coating according to the claim 2, **characterized** in that the amount of phosphorus in the tin alloy is between 50 to 1000 ppm, preferably between 100 and 250 ppm.

4. Tin alloy coating according to the claim 1, **characterized** in that the reducing agent is lithium.

5. Tin alloy coating according to the claim 1, **characterized** in that the reducing agent is boron.

6. Tin alloy coating according to any of the preceding claims, **characterized** in that the tin alloy is a tin-silver alloy.

7. Tin alloy coating according to the claim 6, **characterized** in that the tin-silver alloy contains 2 to 10 % by weight silver.

8. Tin alloy coating according to the claim 6 or 7, **characterized** in that the tin alloy is a tin-silver-bismuth alloy.

9. Tin alloy coating according to the claim 6 or 7, **characterized** in that the tin alloy is a tin-silver-copper alloy.

10. Tin alloy coating according to the claim 6 or 7, **characterized** in that the tin alloy is a tin-silver-indium alloy.

11. Tin alloy coating according to the claim 6 or 7, **characterized** in that the tin alloy is a tin-silver-lead alloy.

12. Tin alloy coating according to any of the preceding claims 1 - 5, **characterized** in that the tin alloy is a tin-copper alloy.

13. Tin alloy coating according to the claims 12, **characterized** in that the tin-copper alloy contains 0,5 to 5 % by weight copper.

14. Tin alloy coating according to any of the preceding claims 1 - 5, **characterized** in that the tin alloy is a tin-bismuth alloy.

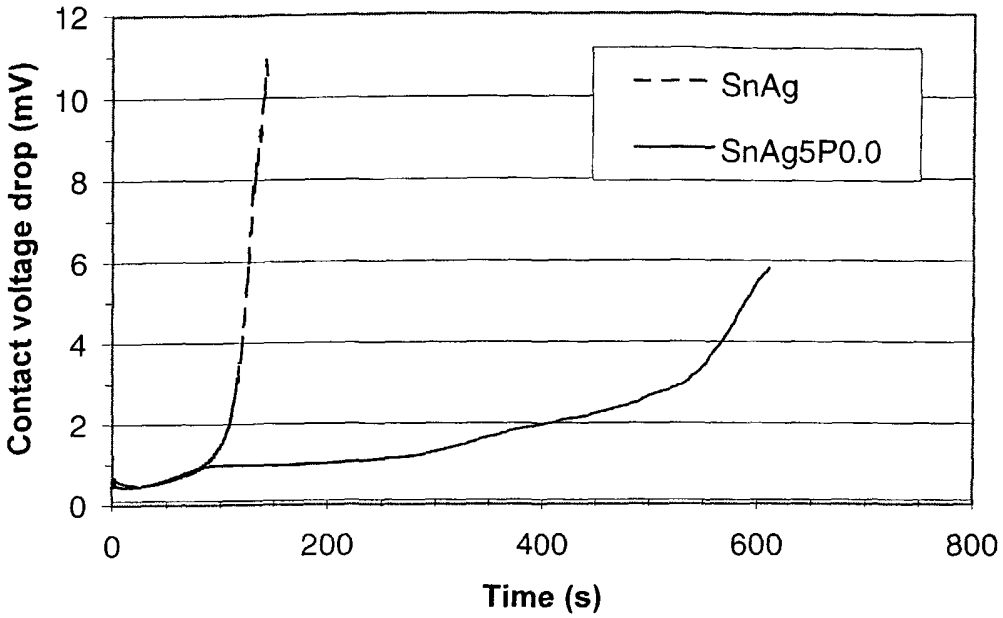
12
10
8
6
4
2
0
Contact voltage drop (mV)
0
200
400
600
800
Time (s)
SnAg
SnAg5P0.0

Fig. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 2004/000745

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: H01R 13/03
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: H01R

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL,WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03050920 A1 (OUT OKUMPU OYJ), 19 June 2003 (19.06.2003), page 2, line 10 - line 11, claims 1-3 --	1,2
A	US 5075176 A (HANS W.BRINKMANN), 24 December 1991 (24.12.1991), abstract -- --------	1

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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29 March 2005	31-03-2005
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				EP	0443291	A,B	28/08/1991
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