PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :
C25D 3/32, 3/36, B23K 35/36
C25D 3/60

A1

(11) International Publication Number: WO 93/09276

(43) International Publication Date: 13 May 1993 (13.05.93)

(21) International Application Number: PCT/US92/09134

(22) International Filing Date: 28 October 1992 (28.10.92)

(30) Priority data:
786,594 1 November 1991 (01.11.91) US

(71) Applicant: NATIONAL-STANDARD COMPANY [US/US]; 1618 Terminal Road, Niles, MI 49120 (US).

(72) Inventors: RIFE, Ronald, J. ; 405 Dublin, Niles, MI 49120 (US). BISHOP, Ronald, L. ; 2006 Ontario Drive, Niles, MI 49120 (US). EDGINGTON, Robert, J. ; 15582 Huntington Ridge Triangle, Granger, IN 46530 (US).

(74) Agent: BROWN, Paul, L.; Emrich & Dithmar, 150 North Wacker Drive, Suite 3000, Chicago, IL 60606 (US).

(81) Designated States: AU, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE).

Published
With international search report.

(54) Title: AGE RESISTANT SOLDER COATINGS

(57) Abstract

The present invention is directed to a lead-in metal substrate possessing superior resistance to corrosion and oxidation and to the loss of solderability due to aging. The resultant lead metal substrate is coated with a fusible solder coating containing between about 0.5-20 x 10^{-4} weight per cent of an aromatic aldehyde.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

Code	Country	Code	Country	Code	Country
AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TG	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

AGE RESISTANT SOLDER COATINGS

Background of the Invention

The present invention relates to an electronic lead-in metallic substrate coated with a fusible solder coating possessing enhanced resistance to loss of solderability due to aging.

In the electronic manufacturing industry of printed circuit boards, active and passive devices and other components, it is necessary that the electronic lead-in wires or metal substrates utilized in such manufacture be resistant to deterioration of solderability from external environmental agents. The loss in device solderability of the metal substrates and the consequent deterioration in printed circuit board manufacturing yields due to oxidation and corrosion under storage conditions is a primary concern to the electronics industry. Although storage conditions vary considerably, it will be appreciated that under ideal conditions, superb and excellent solderability must be maintained for long periods of time. It is generally considered commercially acceptable to require the electronic lead-in components to provide excellent solderability even after the components have been stored for a minimum of three years.

Several prior treatments and processes to prevent oxidation and corrosion of electronic lead-in components during storage have been disclosed. For example, benzotriazole and other aminotriazoles have been used extensively in the industry to provide a corrosion free and oxygen free metal surface that is amenable to subsequent soldering and usage as electronic lead-in metallic substrates. These chemicals act as corrosion and oxidation inhibitors when coated directly onto the copper, silver or other metal conductor in the metal substrate. However, such chemical coatings tend to have a limited-shelf life and interfere with the subsequent solderability of the electronic lead-in metallic substrate.

A further attempt to improve the aging and produce a corrosion oxygen free surface on a electronic lead-in metal

substrate is reported in the U.S. Patent 4,395,294, which relates to a deposit on copper and other metals of 5-methyl benzotriazole material, which material reportedly does not interfere with subsequent soldering of the treated copper substrate. Although, it is reported that this material provides superior aging over benzotriazole, such chemicals provide only limited corrosion resistance for periods of several days. Also, such materials are somewhat difficult to apply to the metal substrate which results in interference with the subsequent soldering of the treated metal surfaces. Additionally, the use of organic compounds for corrosion and oxygen inhibition of the metal substrate requires additional processing steps beyond the conventional steps of removing contamination from the metal substrate and applying the organic coating to the metal substrate to prevent corrosion and oxidation of the metal substrate. Such additional coating steps necessarily results in increase costs of processing such treated metal substrates.

Summary of the Invention

It is one object of the present invention to provide an electronic lead-in metallic substrate possessing resistance to the loss of solderability due to aging wherein the lead-in metallic substrate is coated with a fusible solder coating containing between about $0.5-20 \times 10^{-4}$ weight per cent of an aromatic aldehyde selected from a group including aminobenzaldehyde, benzaldehyde, chlorobenzaldehyde, dichlorobenzaldehyde, methylbenzaldehyde, nitrobenzaldehyde and trichlorobenzaldehyde.

It is a further object of the present invention to provide a novel electronic lead-in metal substrate possessing superior resistance to the loss of solderability due to accelerated steam aging wherein the solder coating on the substrate includes an aromatic aldehyde included therein, with the resultant solder coated metal substrate exhibiting long term resistance to normal storage conditions and natural aging.

A further object of the present invention is to provide a novel method of depositing and controlling a Sn/Pb solder coating onto the electronic lead-in metal substrate to provide lead-in metal substrates which resist corrosion and oxidation, thus rendering the metal substrate resistant to the loss of solderability due to natural aging.

A further object of the present invention is the novel method of depositing and controlling an alloy solder coating onto a electronic lead-in metal substrate which consist of plating the Sn/Pb solder alloys from a fluoborate or methylsulfonic acid solution containing aromatic aldehydes, to provide a tin-lead solder coating containing molecules of the organic material included or entrapped therein.

As used within the present specification, the phrase electronic lead-in wire or metallic substrate is used to designate the current carrying conductor containing the solder coating. Also, as used herein, the solder coating will be referred to as including the elements Sn/Pb.

The electronic lead-in metal substrate useful as a electronic lead-in component, which possesses increased resistance to the loss solderability due to natural or accelerated steam aging, is first cleaned utilizing conventional methods and then a Sn/Pb solder coating is applied to the lead-in metal substrate with the solder coating containing between about 0.5-20 x 10^{-4} weight per cent of an aromatic aldehyde. The aromatic aldehyde may be selected from a group which includes aminobenzaldehyde, chlorobenzaldehyde, benzaldehyde, dichlorobenzaldehyde, methylbenzaldhyde, nitrobenzaldehyde, and trichlorobenzaldehyde.

The method of applying the fusible Sn/Pb solder coating to the electronic lead-in metal substrate consists of plating the solder coating from either a fluoborate or methylsulfonate plating solution containing the selected aromatic aldehyde. The plating solution may include a long chain alcohol and wetting agents, as is known in the art. A typical fluoborate solder plating bath, preferably includes,

between about 100-400 grams per liter of stannous (Sn) fluoborate, between about 20-100 grams per liter of lead (Pb) fluoborate, between about 100-300 grams per liter fluoboric acid and between about 0.1-0.5 grams per liter of the age resistant additive or aromatic aldehyde. As set forth above, the bath may further include a long chain alcohol and wetting agent.

It has been found that the resultant coating may be applied to the lead-in metal substrate at a thickness of between 5-800 micro inches. For example, if the plating is done upon a lead-in wire substrate, the wire may be coated with a solder coating at a thickness of about 350 micro inches and then the wire may be drawn through a die such that the wire drawn fusible soldered coating has a reduced thickness relative to the applied thickness. The solder acts as a lubricant and the entrapped or included organic aromatic aldehyde molecules that are randomly and uniformly distributed throughout the deposited solder coating do not detract from the ability of the coated lead-in substrate to be drawn to a reduced size nor does drawing the wire detract from the solder coatings effectiveness in reducing the loss of solderability due to natural aging or steam aging.

It has been found that the fusible Sn/Pb solder coating must contain between about $0.5\text{-}20 \times 10^{-4}$ weight per cent aromatic aldehyde in the solder coating deposit or the enhanced and superior corrosion and oxidation resistance of the lead metal substrate is not achieved. If the concentration of the aromatic aldehyde in the coating is below the given range, the resultant coated lead-in metal substrate does not exhibit satisfactory long term resistance to normal aging conditions, and if the concentration of the aromatic aldehyde is above a given range, the resultant lead-in metal substrate severely out gasses upon soldering thereby adversely effecting the solderability of the lead-in metal substrate.

The present invention consist of certain novel features and details hereinafter fully described and particularly pointed out in the appended claims, it being

understood that various changes in the details may be made without departing from the spirit and scope thereof or sacrificing any advantages of the present invention.

Description of the Preferred Embodiment

For the purpose of facilitating and understanding the scope of the present invention, the present invention is directed to a novel lead-in metallic substrate possessing superior resistance to corrosion and oxidation and to the loss of solderability due to aging. The resultant lead-in metallic substrate is coated with a fusible solder coating containing between about 0.5-20 x 10^{-4} weight per cent of an aromatic aldehyde.

The aromatic aldehyde, preferably, is selected from a group comprising nitro, amino, alkyl, halogenated substituted and normal benzaldehydes. Specifically, the aromatic aldehydes that are particularly applicable in steam aged solder coatings include aminobenzaldehyde, benzaldehyde, chlorobenzaldehyde, dichlorobenzaldehyde, trichlorobenzaldehyde, methyl benzaldehyde, nitrobenzaldehyde. It is within the scope of the present invention that the age resistant material may be a mixture of single ring aromatic aldehydes.

The method of applying the fusible Sn/Pb solder coating to the lead-in metal substrate consists of first cleaning the metal substrate and then plating the solder coating from a fluoborate or methylsulfonic acid plating solution containing the selected age resistant additive or aromatic aldehyde. The fluoborate plating solution may include a long chain alcohol and a wetting agent, as is known in the art. A typical fluoborate solder plating bath includes between about 100-400 grams per liter of stannous(Sn) fluoborate, between about 20-100 grams per liter of lead(Pb) fluoborate, between about 100-300 grams per liter fluoboric acid and between about 0.1.5 gram per liter of the age resistant additive or aromatic aldehyde. As set forth above, the bath may further include a long chain alcohol and a wetting agent.

A typical methylsulfonic acid solder plating bath, preferably includes, between about 150-400 grams per liter of stannous(Sn) methylsulfonic acid, between about 80-150 grams per liter of lead(Pb) methylsulfonic acid, between about 100-400 grams per liter of methonesulfonic acid and between about 0.2-1.0 grams per liter of the age resistant additive or aromatic aldehyde. The plating solution may include a long chain alcohol and a wetting agent, as is known in the prior art.

It has been found that either the fluoborate or methylsulfonic coating may be applied to the lead-in metal substrate at a thickness of between 5-800 micro inches. For example, if the plating is done upon a lead-in wire substrate, the wire may be coated with a solder coating at a thickness of about 350 micro inches. Then, the wire may be drawn through a die such that the wire drawn fusible soldered coating has a reduced thickness relative to the applied thickness. The solder acts as a lubricant and it is believed that the entrapped or included organic aromatic aldehyde molecules that are randomly and uniformly distributed or occluded throughout the deposited solder coating layer and on the surface thereof do not detract from the ability of the coated lead-in substrate to be drawn to a size thickness nor does drawing the wire detract from the solder coating's effectiveness in reducing the loss of solderability due to natural aging or steam aging.

An additional example of a solder coating to a lead-in metal substrate is the working of plated lead-in metal substrate by cold forging to change the shape and, as a consequence, thereby thinning the solder coating to approximately 5 micro inches.

Much work has been conducted and published within the past few years to establish an accelerated aging test capable of predicting long term resistance to normal storage conditions. An 8 or 16 hour exposure of the fusible coated metal substrate to steam at 85-100°C and at atmospheric pressure followed by solderability testing has resulted in a test which predicts resistance to aging in storage. An

acceptable solderability test result is indicative of a satisfactory fusible coated metal substrate storage for a minimum of three years. The published literature shows a relationship between accelerated aging in steam and natural aging in storage under various conditions. See for example Printed Circuit Assembly, Vol. 2, No. 6, June 1988. It is believed that approximately 16 hours under steam aging equals to approximately 3 years of natural storage under conditions considered normal for electronic devices.

TABLE I

Solderability After Steam Aging 16 hrs for Various Age Resistant Additive Occlusion Levels (Additive: dichlorbenzaldhyde) in Nominal 90/10 Sn/Pb Alloy Plated Connector Pins

SOLDER PLATING		SOLDER PLATING COMPOSITION		SOLDERING CHARACTERISTICS	
THICKNESS, μ INCHES	AMT. ON PIN WT.%	Wt% Sn	WT.% Additive	SOLDERABILITY	OUTGASSING
327	3.66	87	None	Very Poor	None (Excellent)
451	4.78	89	None	Very Poor	None (Excellent)
454	4.67	90	1.41×10^{-4}	Excellent	None (Excellent)
327	3.40	92	3.95×10^{-4}	Excellent	None (Excellent)
296	3.04	87	$12.12 - \times 10^{-4}$	Excellent	Trace (Good)
327	3.40	91	12.7×10^{-4}	Excellent	Trace (Good)
223	2.91	95	18.80×10^{-4}	Excellent	Moderate (Acceptable)
970	13.47	88	21.40×10^{-4}	Excellent	Moderate (Acceptable)
341	3.71	89	37.40×10^{-4}	Dewetting due to out-gassing	Unacceptable
284	3.21	93	38.21×10^{-4}	Dewetting due to out-gassing	Unacceptable

It has been found in Table I that the fusible Sn/Pb solder coating must contain between about $0.5-20 \times 10^{-4}$ weight per cent aromatic aldehyde in the solder coating deposit layer or the enhanced and superior corrosion and oxidation resistance of the lead-in metal substrate is not achieved. If the concentration of the aromatic aldehyde in the coating is below this predetermined range, the resultant coated lead-in metal substrate does not exhibit satisfactory long term resistance to normal aging conditions and possesses very poor solderability, and if the concentration of the aromatic aldehyde is above this given range, the resultant lead-in metal substrate results in severe out gassing thereby adversely effecting the solderability of the lead metal substrate. Thus, the preferred range of weight per cent aromatic aldehyde in the solder coating deposit layer is about $1.0-10.0 \times 10^{-4}$ to provide superior corrosion and oxidation resistance.

Claims

1. A lead-in metal substrate possessing resistance to the loss of solderability due to aging wherein the substrate is coated with a fusible solder coating containing between about 0.5-20 x 10^{-4} weight per cent of an age resistant additive.

2. The lead-in metal substrate in accordance with claim 1 wherein said age resistant additive is an aromatic aldehyde.

3. The lead-in metal substrate in accordance with claim 2 wherein said aromatic aldehyde is benzaldehyde.

4. The lead-in metal substrate in accordance with claim 2 wherein said aromatic aldehyde is selected from a group comprising nitro, amino, alkyl, and halogenated substituted benzaldehydes.

5. The lead-in metal substrate in accordance with claim 1 wherein said solder coating is obtained from a fluoborate plating bath containing said age resistant additive.

6. The lead-in metal substrate in accordance with claim 1 wherein said solder coating is obtained from a methylsulfonic acid plating bath containing said age resistant additive.

7. The lead-in metal substrate in accordance with claim 1 wherein said solder coating has a coating thickness of between about 5-800 micro inches.

8. The lead-in metal substrate in accordance with claim 4 wherein said aromatic aldehyde is a mixture of age resistant additives selected from said group comprising nitro, amino, alkyl and halogenated substituted benzaldehydes.2

9. The lead-in metal substrate in accordance with claim 1 wherein said solder coating is a nominal 90/10 weight per cent Sn/Pb.

10. The lead-in metal substrate in accordance with claim 9 with said solder coating containing between about 1.0-10 x 10^{-4} weight per cent of an age resistant aromatic aldehyde.

11. The lead-in metal substrate in accordance with claim 10 wherein said aromatic aldehyde is benzaldehyde.

12. The lead-in metal substrate in accordance with claim 10 wherein said aromatic aldehyde is selected from a group comprising nitro, amino, alkyl, and halogenated substituted benzaldehydes.

13. The lead-in metal substrate in accordance with claim 9 wherein said solder coating has a coating thickness of between about 50-500 micro inches.

14. A method of depositing a fusible Sn/Pb solder coating onto a cleaned lead-in metal substrate, including the step of

plating the lead-in metal substrate from a Sn/Pb solder plating bath containing between about 0.5-20 x 10^{-4} weight per cent of an age resistant additive to provide the solder plated substrate with resistance to the loss of solderability due to aging.

15. The method according to claim 14 wherein said age resistant additive in an aromatic aldehyde.

16. The method according to claim 15 wherein said aromatic aldehyde is benzaldehyde.2

17. The method according to claim 15 wherein said aromatic aldehyde is selected from a group comprising nitro, amino, alkyl and halogenated substituted benzaldehydes.

18. The method in accordance with claim 17 wherein said aromatic aldehyde is a mixture of age resistant additives selected from said group comprising nitro, amino, alkyl and halogenated substituted benzaldehydes.

19. The method in accordance with claim 14 wherein said solder plating bath is a fluoborate plating bath containing said age resistant additive.

20. The method in accordance with claim 14, wherein said solder plating bath is a methylsulfonic acid plating bath containing said age resistant additive.

21. A fusible Sn/Pb solder alloy containing between about 0.5-20 x 10^{-4} weight per cent of an age resistant additive for use as a coating on a lead-in metal substrate

to provide resistance to the loss of solderability due to aging.

22. The solder alloy in accordance with claim 21 wherein said age resistant additive is an aromatic aldehyde.

23. The solder alloy in accordance with claim 22 wherein said aromatic aldehyde is benzaldehyde.

24. The solder alloy in accordance with claim 22 wherein said aromatic aldehyde is selected from a group comprising nitro, amino, alkyl and halogenated substituted benzaldehydes.

25. The solder alloy in accordance with claim 1 wherein said solder coating is obtained from a fluoborate plating bath containing said age resistant additive.

26. The solder alloy in accordance with claim 21 wherein said solder coating is obtained from a methylsulfonic acid plating bath containing said age resistant additive.

27. The solder alloy in accordance with claim 21 wherein said Sn/Pb solder is a nominal 90/10 weight per cent.

28. The solder alloy in accordance with claim 24 wherein said aromatic aldehyde is a mixture of age resistant additives selected from said group comprising nitro, amino alkyl and halogenated substituted benzaldehydes.

INTERNATIONAL SEARCH REPORT

PCT/US92/09134

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C25D 3/32, 3/36, ; B23K 35/36 ; C25D 3/60
US CL :428/643, 935; 228/214; 205/253
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)

U.S. : 428/643, 935; 228/214; 205/253, 644, 645, 646, 647, 648; 420/557, 558, 563, 570; 205/252, 254, 304

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 3,755,096 (PASSAL) 28 APRIL 1973 See claim 1.	1-28
X	US, A, 3,769,182 (BECKWITH ET AL) 30 OCTOBER 1973; See column 2, lines 4-23	1-28
X	US, A, 3,785,939 (HSV) 15 JANUARY 1974 See column 2, lines 8-29	1-28
X	US, A, 3,954,573 (DAHLGREN ET AL) 04 MAY 1976	1-28
A	US, A, 4,395,294 (HOBBINS ET AL) 26 JULY 1983; See abstract	1-28
X	US, A, 4,582,576 (OPASKAR ET AL) 15 APRIL 1986; See column 8, lines 40-68	1-28

[X] 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 part of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 DECEMBER 1992	14 JAN 1993

Name and mailing address of the ISA/ US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	fn JOHN J. ZIMMERMAN NGUYEN NGOC-HO INTERNATIONAL DIVISION
Facsimile No. NOT APPLICABLE	Telephone No. (703) 308-2512

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/09134

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,849,059 (DERESH ET AL) 18 JULY 1989; See column 4, lines 8-66.	1-28