## (19) World Intellectual Property Organization International Bureau





#### (43) International Publication Date 17 October 2002 (17.10.2002)

#### **PCT**

## (10) International Publication Number WO 02/081143 A1

- (51) International Patent Classification<sup>7</sup>: B23K 35/02
- (21) International Application Number: PCT/US02/05721
- (22) International Filing Date: 27 February 2002 (27.02.2002)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 09/825,706

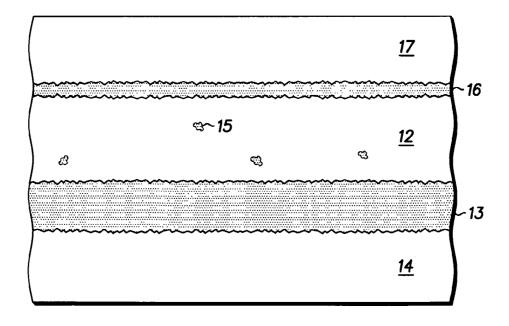
4 April 2001 (04.04.2001) U

- (71) Applicant: MOTOROLA, INC. [US/US]; 1303 East Algonquin Road, Schaumburg, IL 60196 (US).
- (72) Inventors: HUANG, Rong-Fong,; 1969 East Palomino Drive, Tempe, AZ 85284 (US). SHANG, Jian-Ku,; 2307 Aspen Drive, Champaign, IL 61821 (US). MIESEM, Ross, A.; 12513 Crestline Avenue, NE, Albuquerque, NM 87122 (US).

- (74) Agents: KOCH, William, E.; Corporate Law Department, Intellectual Property Section, 3102 North 56th Street, MD: AZ11/56-238, Phoenix, AZ 85018 et al. (US).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, 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, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

#### (54) Title: ANTI-SCAVENGING SOLDERS FOR SILVER METALLIZATION



10

WO 02/081143 A1

(57) Abstract: Solder and a method of manufacturing the solder are disclosed wherein powdered free silver (15) is added to a solder alloy (12) with a particle size sufficient to preserve silver metallization during use and with a concentration sufficient to maximize the effectiveness and avoid adverse effects on solder reflow characteristics. Preferably, the particle size is in a range of approximately  $5 \mu m$  to  $20 \mu m$  and the powdered free silver is added in a concentration of approximately 5 % to 10 %.

### WO 02/081143 A1



#### Published:

with international search report

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.

1

# ANTI-SCAVENGING SOLDERS FOR SILVER METALLIZATION

#### Field of the Invention

5

10

15

20

25

This invention relates to apparatus and methods for improved silver metallization of electronic components and, more particularly, to apparatus and methods including anti-scavenging solders.

#### Background of the Invention

Silver metallization is widely used as the electrical conductor material in soldering or forming metal contacts for electronic components. During the initial soldering or formation and subsequent service (e.g. rework or reflow), tin in the solder alloy leaches or scavenges silver to cause loss of silver into the solder alloy, which degrades electrical performance and mechanical reliability of electronic components or devices. The dissolution of silver in the solder also makes it very difficult to rework or reflow the solder.

Current solutions to the silver scavenging problem generally include two methods or apparatus. The first is to use silver-alloyed metallization, the primary one being

2

to replace pure silver with silver-palladium alloy. second method or apparatus used to solve the problem is to increase the silver thickness in the metallization. Silver-palladium alloy has about one-tenth of the electrical conductivity of silver and, therefore, is not 5 an ideal replacement for silver. In various electronic components and particularly ceramic substrates, the desired or ideal metallization thickness is approximately 10 micrometers. At this desired thickness, silver and silver-palladium metallizations were found to be nearly 10 all consumed by a common silver-alloyed eutectic solder (62Sn - 36Pb - 2Ag). However, increasing the metallization thickness is not desirable because of the cost of the metal and the difficulty to maintain good adhesion with the component (e.g. with ceramic 15 substrates).

Accordingly it is highly desirable to provide apparatus and a method for improving silver metallization, i.e. preventing silver scavenging, in electronic components which is inexpensive and easy to use.

#### Brief Description of the Drawings

25 Referring to the drawings:

20

FIG. 1 is an X-ray map of silver distribution in a cross-section of a solder joint made between two

3

metallizations in accordance with the present invention, after one reflow; and

FIG. 2 is a sectional view, similar to FIG. 1 illustrating the silver metallization after three reflows.

5

#### Description of the Preferred Embodiment

Turning now to the figures wherein like characters indicate like parts throughout the drawings, FIG. 1 is an 10 X-ray map of silver distribution in a cross-section of a solder joint 10 made between two metallizations in accordance with the present invention. Solder joint 10 was formed by reflowing a solder alloy including powdered 15 free silver. Illustrated in the X-ray map is a perferred embodiment comprising reflowed solder alloy 12 with copper metallization 13 positioned on a printed circuit board 14. Also included in the solder alloy 12 are remaining particles of free silver 15. A silver metallization layer 20 16 and a ceramic layer 17 are formed on the solder alloy 12. Additionally, FIG. 2 is a sectional view, similar to FIG. 1, illustrating solder joint 10 and copper metallization 13 after three reflows. It should be understood that other materials could be used, e.g., the 25 metallization layer 13 could comprise silver.

Here it can be seen that the thickness of the original silver metallization, 8 -  $10~\mu m$ , remains

4

unchanged following the reflow, indicating that the silver leaching is stopped. Also, a few free silver particles 15 appear in solder joint 10 proving their effectiveness during subsequent reworks or reflows. Here it should be noted that free silver particles 15 in solder joint 10 also serve as a positive identification of the novel solder alloy including powdered free silver. Referring specifically to FIG. 2, it can be seen that after three reflows of solder joint 10 some free silver particles 15 still remain in solder alloy 12.

5

10

15

20

25

The novel anti-scavenging solder is manufactured by adding powdered free silver to a solder alloy. The free silver is added in a powder form to provide a high surface reactivity. Typical examples of common solder alloys that can be used include: 62Sn - 36Pb - 2AG; 95.5Sn - 4.5Ag; and 96.5Sn - 3.5AG. All of these common solders are supplied in a solid or pliable (e.g. paste) state for ease in application. The powdered free silver added to the solder alloy should have a particle size sufficient to preserve silver metallization during use. Too small a particle dissolves in the solder too quickly and too large a particle reacts with the solder alloy too slowly to preserve the silver metallization. Extensive tests show that the optimum size of the silver particles lies in a range of approximately 5 μm to 20 μm. It will of course be understood that a variation of a micron or two in particle size may be acceptable in some specific

5

applications requiring less rigid standards.

5

10

15

20

25

Further, the powdered free silver added to the solder alloy should have a concentration sufficient to maximize the effectiveness and avoid adverse effects on solder reflow characteristics. Thus, the concentration of the free silver added to the solder alloy should be kept in a range which is sufficient to maximize the effectiveness of the free silver during reflow but which avoids adverse effects on solder reflow characteristics that occur with too high a free silver concentration. Extensive tests show that the optimum concentration of the silver particles lies in a range of approximately 5% to 10%. It will of course be understood that a variation of one or two per cent in particle concentration may be acceptable in some specific applications requiring less rigid standards.

Thus, in a preferred embodiment, silver scavenging in solder is substantially prevented, or silver metallization is improved, by providing a solder alloy and adding powdered free silver to the solder alloy with a particle size in a range of approximately 5 µm to 20 µm and a concentration of approximately 5% to 10%. Pull strength tests were performed on solder joints made with various combinations of particle size and concentration and the results indicate that in some instances the pull strengths increased while maintaining the desired or ideal metallization thickness at approximately 10 micrometers.

6

The novel solder contains sufficient free silver particles to allow a good initial reflow and one or more subsequent reflows while maintaining the desired silver metallization and the required strength of the solder joint.

5

10

15

20

Thus, a new and improved anti-scavenging solder and method of manufacture is disclosed which maintains good adhesion with electronic substrates and especially ceramic substrates. Also, the new and improved anti-scavenging solder contains sufficient free silver particles to allow subsequent solder rework, and making it possible for the new solder to be reworked on silver metallization.

Further, the new and improved anti-scavenging solder maintains electrical performance and mechanical reliability of electronic components or devices and the free silver particles in the solder makes one or more reworks or reflows of the solder possible.

While we have shown and described specific embodiments of the present invention, further modifications and improvements will occur to those skilled in the art. We desire it to be understood, therefore, that this invention is not limited to the particular forms shown and we intend in the appended claims to cover all modifications that do not depart from the spirit and scope of this invention.

7

What is claimed is:

1. Anti-scavenging solder comprising a solder alloy including powdered free silver.

- 5 2. Anti-scavenging solder as claimed in claim 1 wherein the solder alloy is in a paste state.
  - 3. Anti-scavenging solder as claimed in claim 1 wherein the solder alloy includes powdered free silver with a particle size sufficient to preserve silver metallization during use.
- 4. Anti-scavenging solder as claimed in claim 1 wherein the solder alloy includes powdered free silver with a particle size in a range of approximately 5  $\mu m$  to 20  $\mu m$ .
- 5. Anti-scavenging solder as claimed in claim 1
  wherein the solder alloy includes powdered free silver
  with a concentration sufficient to maximize the
  effectiveness and avoid adverse effects on solder reflow
  characteristics.
- 6. Anti-scavenging solder as claimed in claim 1
  wherein the solder alloy includes powdered free silver in a concentration of approximately 5% to 10%.

8

7. A method of preventing silver scavenging in solder comprising the steps of:

providing a solder alloy; and adding powdered free silver to the solder alloy.

5

15

20

- 8. A method of preventing silver scavenging in solder as claimed in claim 7 wherein the step of adding powdered free silver includes adding powdered free silver with a particle size sufficient to preserve silver metallization during use.
- 9. A method of preventing silver scavenging in solder as claimed in claim 7 wherein the step of adding powdered free silver includes adding powdered free silver with a particle size in a range of approximately 5  $\mu m$  to 20  $\mu m$ .
  - 10. A method of preventing silver scavenging in solder as claimed in claim 7 wherein the step of adding powdered free silver includes adding powdered free silver with a concentration sufficient to maximize the effectiveness and avoid adverse effects on solder reflow characteristics.
- 25 11. A method of preventing silver scavenging in solder as claimed in claim 7 wherein the step of adding

9

powdered free silver includes adding powdered free silver in a concentration of approximately 5% to 10%.

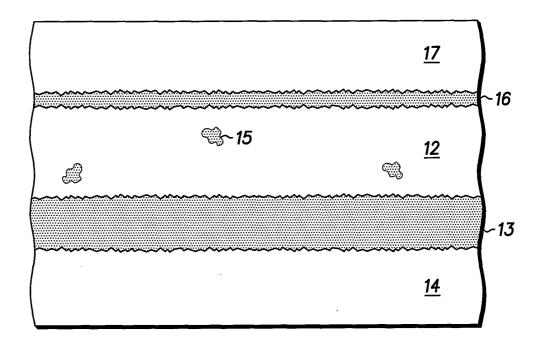
12. A method of preventing silver scavenging in solder comprising the steps of:

providing a solder alloy; and

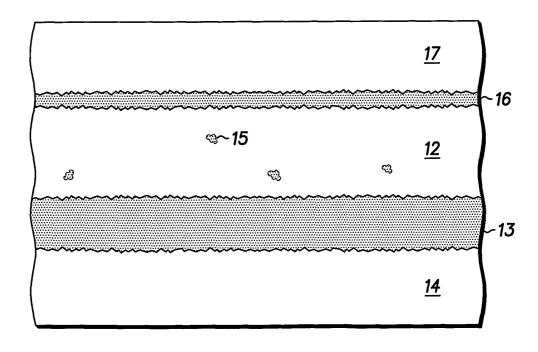
adding powdered free silver to the solder alloy with a particle size in a range of approximately 5  $\mu m$  to 20  $\mu m$  and a concentration of approximately 5% to 10%.

10

1/1



<sup>10</sup> FIG. 1



<sup>10</sup> FIG. 2

#### INTERNATIONAL SEARCH REPORT

Intermedial Application No PCT/US 02/05721

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 B23K35/02

According to International Patent Classification (IPC) or to both national classification and IPC

#### B. FIELDS SEARCHED

 $\label{localization} \begin{array}{ll} \mbox{Minimum documentation searched (classification system followed by classification symbols)} \\ \mbox{IPC 7} & \mbox{B23K} \end{array}$ 

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 practical, search terms used)

EPO-Internal, PAJ, WPI Data

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 01 72466 A (MOTOROLA INC) 4 October 2001 (2001-10-04) the whole document	1-12
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 502 (E-0997), 2 November 1990 (1990-11-02) -& JP 02 207539 A (SANKEN ELECTRIC CO LTD), 17 August 1990 (1990-08-17) abstract	1-12
X	US 5 429 292 A (BECKENBAUGH WILLIAM ET AL) 4 July 1995 (1995-07-04) column 2, line 54 - line 56; claims 1,2	1,7
X	US 4 487 638 A (HOGE CARL E) 11 December 1984 (1984-12-11) claims 1,2	1,7

	-/
X Further documents are listed in the continuation of box C.	χ Patent family members are listed in annex.
<ul> <li>Special categories of cited documents:</li> <li>"A" document defining the general state of the art which is not considered to be of particular relevance</li> <li>"E" earlier document but published on or after the international filing date</li> <li>"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)</li> <li>"O" document referring to an oral disclosure, use, exhibition or other means</li> <li>"P" document published prior to the international filing date but later than the priority date claimed</li> </ul>	"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  24 June 2002	Date of mailing of the international search report  15/07/2002
Name and mailing address of the ISA  European Patent Office, P.B. 5818 Patentlaan 2  NL – 2280 HV Rijswijk  Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  Fax: (+31-70) 340-3016	Authorized officer  Alvazzi Delfrate, M

#### INTERNATIONAL SEARCH REPORT

Intermonal Application No
PCT/US 02/05721

he relevant passages  ET AL)  BERT ET AL)	1,7
ET AL) BERT ET AL)	1,7
BERT ET AL)	
	1,7
)	
	1,7
	1,7

#### INTERNATIONAL SEARCH REPORT

information on patent family members

Inter nal Application No
PCT/US 02/05721

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
WO 0172466	A	04-10-2001	AU WO US	4937801 A 0172466 A2 2001048888 A1	08-10-2001 04-10-2001 06-12-2001
JP 02207539	A	17-08-1990	NONE		
US 5429292	A	04-07-1995	US AT CA DE DE EP JP KR WO	5389160 A 194533 T 2140253 A1 69425224 D1 69425224 T2 0655961 A1 7509662 T 213695 B1 9427777 A1	14-02-1995 15-07-2000 08-12-1994 17-08-2000 08-03-2001 07-06-1995 26-10-1995 02-08-1999
US 4487638	A	11-12-1984	CA CA DE EP HK SG WO	1200625 A1 1218764 C 3380430 D1 0110307 A2 81492 A 70892 G 8402097 A1	11-02-1986 03-03-1987 21-09-1989 13-06-1984 30-10-1992 04-09-1992 07-06-1984
US 4740252	<b>A</b>	26-04-1988	JP	62179889 A	07-08-1987
US 3900153	Α	19-08-1975	DE BE FR GB IT JP	2228703 A1 800673 A1 2188307 A1 1440196 A 989087 B 49051872 A	10-01-1974 01-10-1973 18-01-1974 23-06-1976 20-05-1975 20-05-1974
WO 9004490	Α	03-05-1990	AU WO	4517589 A 9004490 A1	14-05-1990 03-05-1990
US 2431611	- <b>-</b>	25-11-1947	NONE		