IMPACT OF HIGHER MELTING LEAD-FREE SOLDERS ON THE RELIABILITY OF PRINTED WIRING ASSEMBLIES

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ABSTRACT

The move toward lead-free electronics has become a rapidly emerging issue for concern and evaluation. The movement has been triggered by the European Union's (EU) proposal for a Directive on Waste from Electrical and Electronic Equipment (WEEE) and by the Japanese focus on environmental marketing. The candidate solder alloys that have been identified as substitutes require high soldering temperatures since these alloys have typical melting temperatures between 198°C and 227°C. Concern has been raised that the higher processing temperatures required for wave and reflow soldering with these alloys will create increased drop out due to printed wiring board (PWB) warpage and component failures, since most components are not qualified in terms of reliability for these higher processing temperatures.

In this paper, we present evidence for an additional reliability concern for lead-free soldered electronic product. Conductive anodic filament (CAF) formation is a failure mode associated with boards, which either operate or are stored in a humid environment. This paper compares the number of CAF formed on boards reflowed at 201°C vs. 241°C after aging under 100V bias at 85°C/85% RH for 28 days. The incidence of CAF under the higher reflow conditions was typically 1-2 orders of magnitude greater than at the lower reflow conditions. The data provide additional reliability concerns for lead-free soldering.

BACKGROUND

The movement toward lead-free electronics has emerged into concrete legislation in Europe. On June 13, 2000 the European Commission adopted two proposals: A Directive on Waste of Electrical and Electronic Equipment (WEEE) and a Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment. The former directive requires Member States to set up take-back centers for end-of-life recovery at no cost to the consumer. The latter directive requires lead-free electronics by 2008, but exempts lead in cathode ray tubes (CRTs), light bulbs and fluorescent tubes, and lead as an alloying agent in steel (< 0.3 wt%), aluminum (< 0.4 wt%), and copper (<4.0 wt%).

Japan also has a "Law for Recycling of Specified Kinds of Consumer Electric Goods" which was approved in February 1998 and which goes into effect in April 2001[3]. This applies to televisions, air conditioners, refrigerators, and washing machines. Japan has also focused on environmental marketing. Panasonic, for example, introduced a lead-free mini-disc, applied the green leaf symbol for environmentally friendly products, and increased its market share from 4.7% to 15%[4].

The Japan Electronic Industry Development Association (JEIDA) has developed a Roadmap 2000 (Table 1) for Commercialization of Lead-free Solder[5]. In January 1999 they launched a program for "Research and Development for Standardizing Lead-free Solder". Alloys identified for wave soldering include Sn-3.5Ag, Sn-(2-4)Ag-(0,5-1)Cu, or Sn-0.7Cu with small amounts of other elements (Ag, Au, Ni, Ge, In). For reflow soldering they identified one low temperature alloy (Sn-57Bi-1Ag), which they noted is incompatible with Sn-Pb plated components. Medium and high temperature alloys included Sn-3.5Ag, Sn-(2-4)Ag-(0,5-1)Cu, Sn-(2-4)Ag-(1-6)Bi including some with 1-2% In, and n-8Zn-(0-3)Bi. No high temperature alloy for chip attach has been identified.

In the US the IPC has developed "Roadmap: A Guideline for Assembly of Lead-Free Electronics"[6] which details the drivers and activities in the US and abroad. It is designed to keep the industry abreast of the status of activities so that companies can be prepared to respond. They have established a web site at http://www.leadfree.org. A second web site in the UK, http://www.lead-free.org, provides additional detailed information on this important issue.

Most lead-free alloys under investigation melt at temperatures that are 30-40°C higher than that of eutectic Sn/Pb solder (Table 2). For the higher melting solders, an increased scrap rate on FR-4 boards is expected due to board warpage. In many cases new substrate materials may be required. In addition, electrolytic capacitors and other components are not rated to experience the higher soldering temperatures, and as a result early field failures are anticipated.

Year	Activity
1999	First mass production using lead-free solders
2000	Adoption of lead-free components
2000	Adoption of lead-free in wave soldering
2001	Expansion of lead-free components
2001	Expansion of lead-free products
2002	General use of lead-free solders in new products.
2003	Full use of lead-free solders in all new products.
2005	Lead-containing solders used only exceptionally.

Table 1: Japan's roadmap for introduction of lead-free solders.

Conductive anodic filament formation (CAF) is a failure mode for printed wiring boards (PWBs) in which a conductive filament forms along the epoxy/glass interface growing from anode to cathode[7,8,9]. It requires humidity in either the storage or use environment and is enhanced by certain processing chemicals[10], increased thermal cycling and high voltage gradient. It has caused catastrophic field failures[11]. Figure 1 shows a cross section of a board with CAF where the white region indicates a copper-containing filament growing along the epoxy/glass interface.

The purpose of this study is to evaluate the effect of certain water-soluble flux vehicles, both with and without halide activators, in enhancing CAF formation. Two processing temperatures, 201°C and 241°C, were used to reflect the expected peak temperature in wave soldering for (1) traditional Sn-37Pb solder and (2) a typical lead-free solder.

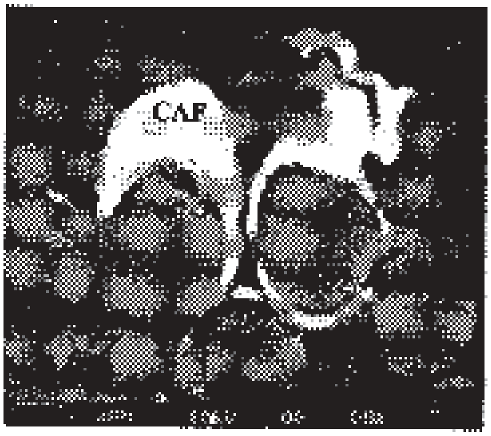

Figure 1: Cross section of a PWB showing CAF growing along the epoxy/glass interface.

EXPERIMENTAL PROCEDURE

The objectives of this study were to evaluate a series of water-soluble fluxes for their propensity to enhance CAF and to determine the effect of reflow temperature on the number of CAF observed. The fluxes in this study contained 20w% of one of the following vehicles: polyethylene glycol [PEG], polypropylene glycol [PPG], polyethylene propylene glycol MW1800 [PEPG 18] and polyethylene propylene glycol MW2600 [PEPG26], glycerine [GLY], octyl phenol ethoxylate [OPE] and a modified linear aliphatic polyether [LAP] dissolved in isopropyl alcohol (IPA). Flux formulations containing 20w% of the different flux vehicles were also tested with 2w% HBr or HCl activators, to see what effects the presence of the halide had on CAF formation.

Standard IPC-B-24 test coupons (Figure 2) were labeled and pre-cleaned using the Zero Ion System. Comb patterns on each board were processed with equimolar solutions of the flux formulation, using a pipette to deposit 400(l on each. One set of boards was reflowed to a maximum board temperature of 201°C in an OK Industries JEM 310 batch convection reflow oven. A second set of boards was processed with a maximum board temperature of 241°C. After reflow the boards were placed on racks and allowed to cool to room temperature. Upon cooling, the boards were cleaned for five minutes at a temperature of 61°C in de-ionized water using a Branson 5210 cleaning system in ultrasonic mode.

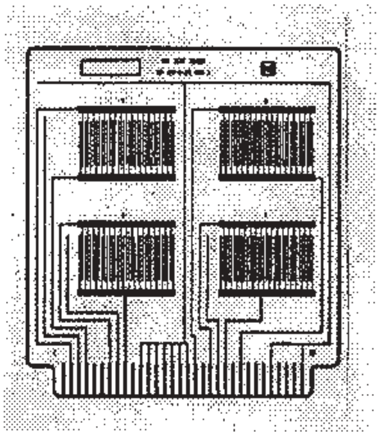

Figure 2: IPC-B-24 test coupon

The boards were then placed in a Thermotron environmental chamber and electrically connected to the test system. Over a period of hours the temperature and humidity were ramped up to the test conditions of 85°C/85% RH in order to prevent localized condensation of moisture on the surface of the test boards. The oven was allowed to stabilize at these conditions overnight, and then a computer program was executed to take the SIR measurements on all the boards at 24-hour intervals over a 28-day period. The SIR testing was done using a bias voltage and a test voltage of 100 V and the same polarity. At the end of 28 days, the temperature and humidity in the chamber were ramped down, the chamber opened, the boards removed and placed into contamination free bags for storage.

Alloy	Melting Point (°C)	Application
Sn-37Pb	183	All
Sn-58Bi	138	Consumer Electronics
Sn-9.0Zn	198.5	Toshiba, NEC
Sn-0.7Cu	227	Nortel
Sn-3.5Ag	221	Automotive
Sn-3.8Ag-0.7Cu	217	Nortel
Sn-2.5Ag-0.8Cu0.5Sb	213-218	Motorola
Sn-3.5Ag-4.8Bi	205-210	Sandia
Sn-2.0Ag--7.5Bi 0.5Cu	217-218	IBM
Sn-2.0Ag-4.0Bi-0.5Cu-0.1Ge	210-217	Sony
Sn-3.5Ag-1.5In	218	Indium Corporation
Sn-2.8Ag-20In	175-187	Indium Corporation

Table 2. Comparison of melting points of lead-free solder alloys with presently used Sn-37Pb solder[6, 12, 13].

Flux	SIR (Ω) 201°C reflow	SIR (Ω) 241°C reflow	#CAF at 201°C reflow	#CAF at 241°C reflow
Polyethylene glycol-600(PEG)	$<10^6$	$<10^6$	90	55
PEG/HCl	$<10^6$	High 10^8	None	None
PEG/HBr	$<10^6$	High 10^8	None	None
Polypropylene glycol 1200 (PPG)	$>10^{10}$	$>10^{10}$	None	455
PPG/HCl	$>10^{10}$	$>10^{10}$	None	379
PPG/HBr	$>10^{10}$	$>10^{10}$	1	423
Polyethylene propylene glycol 1800 (PEPG 18)	High 10^9	High 10^9	1	406
PEPG 18/HCl	High 10^9	High 10^9	10	135
PEPG 18/HBr	10^{10}	High 10^9	9	279
Polyethylene propylene glycol 2600 (PEPG 26)	High 10^9	High 10^9	None	91
PEPG 26/HCl	High 10^9	High 10^9	6	218
PEPG 26/HBr	10^{10}	High 10^9	None	51
Glycerine (GLY)	$>10^{10}$	High 10^9	None	56
GLY/HCl	$>10^{10}$	High 10^9	None	583
GLY/HBr	$>10^{10}$	High 10^9	3	104
Ocyl phenol ethoxylate (OPE)	Low 10^9	Low 10^9	None	83
OPE/HCl	Low 10^9	Low 10^9	14	62
OPE/HBr	$>10^{10}$	High 10^9	2	599
Linear Aliphatic Polyether (LAP)	Low 10^9	Not Tested	None	Not Tested
LAP/HCl	Low 10^9	Low 10^9	15	203
LAP/HBr	Low 10^9	Low 10^9	None	272

Table 3: Comparison of SIR levels and number of CAF associated with two different reflow temperatures.

ANALYSIS

SIR data were measured for each comb pattern on each test coupon and a geometric mean value was determined for each flux at each time period.

An optical microscope (Olympus SZ-40) was used to examine the comb patterns on the boards. Both the transmitted and reflected illumination capabilities of the microscope were used in making observations. Transmission illumination (back-lighting) makes the detection of CAF and dendrites easier (Figure 4).

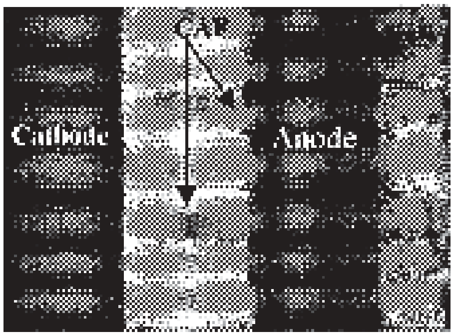

Figure 3: Using back lighting CAF appears as dark shadows coming from the copper anode to the cathode.

RESULTS

Table 2 shows the average SIR levels at the end of the 28-day test for boards reflowed at 201°C and at 241°C. Most of the electrical readings were the same at both reflow temperatures. Exceptions to that include PEG/HCl and PEG/HBr which had acceptably high SIR readings (high 10^8) for the 241°C reflow conditions but failed electrically (< 10^6) at the 201°C reflow temperature. Additionally, glycerine (GLY) gave slightly lower SIR readings (high 10^9 vs. (>10^{10}) under the higher temperature reflow conditions. Table 2 also shows the total number of CAF observed on two boards of each flux chemistry under each of the reflow conditions.

PEG: CAF only forms when no halide activator was present. Also, the numbers of CAF at the lower reflow temperature were almost twice as many as at the higher reflow temperature. For all PEG fluxes the SIR levels were below the value of the limiting resistor in the circuit, i.e. 10^6 indicating that they have failed the SIR electrical test, except halide formulations at higher reflow.

PPG: CAF was almost non-existent at the lower reflow temperature, but many hundreds were observed for all three flux formulations at the higher reflow temperature.

PEPG 18: There were 13x to 400x as many CAF caused by the higher reflow temperature. At the higher reflow temperature the halide-free formulation had the largest number of CAF. At the lower temperature the pattern was: Cl^- activated > Br^- activated. None were observed for the halide free flux.

PEPG 26: At the higher temperature the number of CAF followed the pattern: Cl^- activated > halide-free > Br^- activated flux. At the lower temperature the number of CAF followed a different pattern: Cl^- activated >Br^- activated. None were observed for the halide-free flux. Also, the total number of CAF observed at both temperatures were significantly less than those noted for the lower molecular weight PEPG 18 flux formulations.

GLY: CAF is predominantly associated at the higher reflow temperature with Cl^- activated > Br^- activated > halide-free. At the lower reflow temperature, only the Br^- activated gave a few CAF.

OPE: At the higher reflow temperature, Br^- activated flux >> halide-free > Cl^- activated. At the higher reflow temperature the number of CAF was 4 - 300x as many as at the lower reflow temperature, and at the lower reflow temperature the Cl^- activated flux performed the worst.

LAP: At the higher reflow temperature Br^- activated > Cl^- activated, whereas at the lower reflow temperature only the Cl^- activated flux showed CAF; and this was less than 10x as many as for the higher temperature.

In general the halide effects show:

1. Cl^- activators were most harmful for:
   PEPG 18 - at the low temperature
   PEPG 26 - at both temperatures
   GLY - at the high temperature
   OPE - at the low temperature
   LAP - at the low temperature
2. Br^- activators were most harmful for:
   OPE - at the high temperature
   LAP - at the high temperature
3. Halide-free flux vehicle most harmful:
   PEG - at both temperatures
   PPG - at the high temperature
   PEPG 18 - at the high temperature
4. The most harmful halide activators differ depending upon the flux vehicle.
5. PEG was an anomaly in which only halide-free formulations gave CAF and more CAF formed at the lower reflow temperature.

Diffusion of polyglycols into the PWB substrate occurs during soldering. Since the diffusion process follows Arrhenius behavior, the length of time the board is above the glass transition temperature will have an effect on the amount of polyglycol absorbed into the epoxy; and that will, in turn, affect its electrical properties. It will also depend upon the specific chemistry of the flux vehicle and its interaction with the epoxy. Brous[14] linked the level of polyglycol in a board to surface insulation resistance (SIR) measurements. Jachim[8] reported on water-soluble flux-treated test coupons that were prepared using two different thermal profiles. Those which experienced the higher thermal profile exhibited a SIR level that was an order of magnitude lower than those processed under less aggressive thermal conditions. It is clear that the higher the soldering temperature, the greater the polyglycol absorption. Similarly, for each thermal excursion that occurs, the bonding between the epoxy and glass fibers is weakened due to different coefficient of thermal expansion characteristics of these two materials.

One way of quantifying the effect of the reflow temperature on CAF is to examine the thermal strain (() associated with the difference in coefficient of thermal expansion ((CTE) between the adjacent materials. Table 4 details that comparison for copper vs. FR-4 substrate and e-glass vs. epoxy where:

$$£ = \Delta CTE \ \Delta T$$

It is clear from this table that the higher reflow temperature creates a severe strain on the epoxy/glass interface, weakening the bond and in general, enhancing the rate of CAF formation. This explains the much higher level of CAF observed for the higher reflow temperature.

Material	∆CTE	£ at 201°C	£ at 241°C
	(x10^{-6}/K)	reflow	reflow
Cu/FR-4	2	352	432
e-glass/eopxy	32	5632	6912

Table 4: Thermal strain (x10-6) assuming an initial temperature of 25°.

CONCLUSION

Higher board processing temperatures have been shown to result in increased numbers of CAF for most of the fluxes tested. The 241° C peak temperature represents the wave soldering peak temperature for a typical lead-free solder alloy. Reflow temperatures for solder pastes will be even higher. The flux vehicle used in the water-soluble formulation and the halide activator had different interacting effects.

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BIOGRAPHY

Dr. Laura Turbini is an executive director at the University of Toronto Center for Microelectronic Assembly and Packaging in the Metallurgy & Material Science Department. She has been involved in electronic assembly issues since 1977, specializing in soldering fluxes, cleaning, and reliability testing. She has worked in industry and academia and has been involved in manufacturing management as well as fundamental research. She has presented numerous papers and has written extensively on these issues. Dr. Turbini has served as the chair of the Solder Flux Task Group for the IPC since 1986, and she has been a member of the Surface Mount Council since 1989. She holds a Ph.D. in inorganic chemistry from Cornell University. In 1992 she received the EPA Stratospheric Ozone Protection Award.