TECHNICAL PAPER

Lead-Free Soldering Effect on Tantalum Capacitors

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Abstract

Legislation is being developed worldwide to reduce the lead content in many consumer electronic products. This is being taken as an action to reduce environmental impact when such products are discarded.

Despite the fact that lead containing solders in electronic assemblies account for only 0.49% of world lead consumption, the trend in legislation will likely be to require not only reduced lead content, but also its complete elimination in such products.

There are three principal sources of lead in electronic circuit assemblies; the solderable traces on the circuit card, the solderable finish on the components themselves and the solder alloy used to connect the two (either solder paste for reflow, or liquid solder for wave).

A typical component has negligible lead content in its termination finish in comparison to the amount of solder alloy used in the pcb (print circuit board) process. Nevertheless, changing to a lead-free solder alloy for the soldering process will require the component to have a compatible termination finish to achieve the correct soldering/wetting characteristics with the reduced lead or lead-free soldering system being used. Depending upon the component type, this in itself can be either a straightforward or a complex change. But, regardless of the technology requirements to provide a part with the correct termination characteristics, the major concern will be the compatibility of the component with the higher temperature profiles associated with many reduced lead or lead-free soldering systems. In many cases, this will require modification of current technology relating to internal design or new material development in order to 'survive' the more aggressive reflow or wave soldering conditions as a result of most lead-free solder systems' higher liquidus temperatures.

Many papers have been written that discuss alternate lead-free solder systems, and the emerging consensus is that, in terms of solder joint characteristics, Sn (Cu, Ag, Bi, etc.) and other solders are at least comparable to traditional lead containing alloys. Of these, Sn / Cu has seen most usage to date. Is this option becoming the de facto standard? Some of the main reasons for not pursuing the other alternatives are cost, limited compatibility with the current lead containing systems and metallic property issues (intermetallic alloy formation). More important, from a component perspective, are the higher peak temperatures required for soldering. In an ideal world, all pcb manufacturers would change their lead process to the same lead-free system and all components would be supplied with compatible terminations and the ability to survive the higher thermal stress reflow. But who will make the first move...? This question has been answered recently – some Japanese companies have announced their "green" product plan of reduced lead by the replacement of tin-lead with a lead-free solder 96Sn-2.5Ag-1Bi-0.5Cu as the soldering medium. Many large companies throughout the world have already converted to lead-free assembly based on SnAgCu semieutectic solder paste. These alloys will require an increase of peak reflow temperature to 240 - 260°C. Component suppliers will be required to meet this specification by March 2001 for the first, mainly Japanese, companies to introduce complete lead-free products on the market.

This paper focuses on these issues in relation to one component technology – surface mount tantalum capacitors with MnO_2 and conductive polymer electrodes - and outlines a program that will verify whether these devices are ready to meet this specification.

Current Lead-Free Status

Why lead?

Lead is one of the most widely used toxic elements and is found in many everyday products from glass/ceramic vessels to electronic devices and automobiles. Lead bioaccumulates in the body. That is, it is retained over time and can have adverse health impacts when a sufficient accumulation has occurred. Once in the body, the lead binds strongly to proteins and inhibits normal synthesis and function. Effects include nervous and reproductive system disorders, delays in neurological and physical development, cognitive and behavioral changes, reduced production of hemoglobin with resulting anemia, and hypertension. [Putman, 1986]

Because lead is very soluble in nature it can be dangerous for our environment. Table 1 gives a general toxicity comparison for some common solder paste elements together with price trends and world production/ availability.

Element	Cost 11/98	Cost 11/97	World Prod.	PEL
	[US$ / t]	(US$ 5)	x10^3 tons	mg/m^
Bi - Bismuth	7055	7385	4	none
Sn - Tin	5590	5570	210	2
Cu - Copper	1598	1964	9100	1
Sb - Antimony	1325	1730	60	0.5
Ag - Silver	159,646	156,732	14	0.1
Pb - Lead	488	577	3370	**0.03**

Relative Toxicity PEL = U.S. OSHA Permissible Exposure Limit

Table 1. Toxicity, price and production comparison [4].

Product - worldwide consump.: 2830.10^6	%k/g weight
Storage Batteries	80.81
Oxides (paint, glass, ceramic, chem.)	4.78
Ammunition	4.69
Sheet Lead	1.79
Cable Covering	1.4
Casting Material	1.13
Brass and Bronze	0.72
Pipes, Traps, Other Extrusions	0.72
Solder (non-electronic)	0.7
Solder (electronics)	**0.49**
Miscellaneous	2.77

The storage battery for automotive applications is the single largest lead-consuming product, accounting for 80% of world lead consumption. By comparison, solders containing lead account for only 0.49% of the total. However, the wide range of consumer electronic products now being produced, in conjunction with their relatively short time to obsolescence, is giving rise to concerns regarding their disposal. This has elevated the importance of reduced-lead programs within the electronics industry.

Table 2. Worldwide lead consumption [4].

Legislation

EUROPE

Lead restrictive legislation in the European Community is under discussion and a 4th draft emerged from the European Parliament in June 2000. The 4th draft Directive seeks to postpone the ban of lead in new equipment from 1/1/2004 (3rd draft) to 2008 after some lobbying actions.

JAPAN

In Japan, the complete replacement of current tin-lead processes is recommended by year 2001. Many Japanese manufacturers that supply products to worldwide markets are adopting this date as a target for full implementation. Two Japanese industry organizations JEIDA (Japanese Electronic Industry Development Association) and JIEP (Japanese Institute of Electronic Packaging) have developed their own roadmaps to eliminate lead.

NORTH AMERICA

There is no federal legislation pending on this issue. The organizations presently active include the IPC (Interconnect and Packaging of electronic Circuits), EIA (Electronic Industries Association), and NEMI (National Electronics Manufacturers Initiative).

Lead-free solder paste alternatives

There are a lot of companies that have approved lead-free solder pastes for replacement of standard tin-lead solder. Some are already scaling production this year. Table 3 gives an overview of the various lead-free solder systems currently under evaluation by leading manufacturers:

* - eutectic solder alloy

Table 3. Overview of lead-free solder pastes under evaluation by [1], [3].

	Manufacturer	Solder Alloy	Melting T	Implementation due Part Prod	100% prod
Japan	SONY	Sn2.5Ag1 Bi0 5 Cu	206-213ºC	March 00	March 01
	Panasonic	Sn AgBi-X / SnAgCu	200-230ºC	2000	2001
	Matsushita	Sn3.5Ag0.75 Cu	216-220ºC		2001
	Toshiba	SnAgCu / SnZn			2000
	Hitachi	SnBiAg	206-213ºC	50% 1999	2001
	NEC	SnAg / SnAgCu / SnZn	200-230ºC	50% 2002	
USA	Nortel	Sn0.7Cu eut.*	227ºC	in prod	
	Motorola	?			2004
	Ford	Sn3.5Ag eut.*	221ºC		
	TI	SnAgCuSb	216-222ºC		
BJ	Ericsson	Sn3.8Ag0.7Cu eut.*	217ºC		
	Nokia	Sn3.8Ag0.7Cu eut.*	217ºC		

Conventional Sn60 / Pb40 eutectic tin-lead solder (liquidus temperature: 183°C) can be successfully reflowed at temperatures of 220°C. By comparison, most (not all) lead-free solder alloys have higher liquidus temperatures and will require reflow profiles that include peak temperatures (20-30)°C higher than today's profiles, requiring peak temperatures in the region of (240-260)°C.

What Does This Mean For Component Manufacturers?

Component manufacturers face two key development tasks in order to meet the lead-free requirements. The first need is to select the right lead-free termination finish compatible to the both lead-free solders and also suitable for current tin-lead solder processes. The second is how to make product ready for higher reflow temperatures due to the higher melting points of most of the lead-free solder pastes.

Component termination finish

All molded tantalum chip capacitors have a common construction – a molded body with external wrap-around termination leads. The standard tantalum capacitor termination finish for the termination is currently Sn90 / Pb10 alloy. This alloy is deposited electrochemically as a thin layer over the base termination material to provide a solderable surface. The lead content of this thin (~ 3-6μ) layer is typically about $1x10^{-5}$ g per capacitor. This is considerably less than the lead content of current pcb tracks or the solder medium used (reflow or wave) for pcb assembly. But despite this "low impurity lead level" the amount of lead is still considered to be an issue for manufacturers using Bismuth containing lead-free solder pastes. A small quantity of lead can significantly decrease solderability if Bi solder paste is used. Hence, the development of a lead-free termination finish is necessary for compatibility with Bi lead-free solder pastes.

There are a number of suitable termination finishes compatible with Bi solder pastes and current tin-lead soldering processes. Sn (pure tin), Sn / Ag and Sn / Cu are the leading candidates to replace tin-lead alloys if price/availability and process factors are considered. It has been shown under laboratory conditions that these alloys have proved to be at least adequate alternatives to current lead containing finishes. The latest findings on tantalum capacitor termination show a problematic compatibility of Sn / Ag and Sn / Cu plating with the manufacturing process. In addition there are, at present, no commercial plating operations that can apply these finishes to a leadframe in mass production. Based on this, pure tin remains the only readily available solution for a termination finish compatible with both conventional tin-lead soldering processes and newly emerging lead-free processes.

Pure Tin

Some components with an external termination finish of pure tin, such as ceramic capacitors or resistors, are already available and so there is wide practical experience with this kind of termination finish. The disadvantages of pure tin coatings are the internal stresses and risk of "whisker" growth. "Whiskers" are thin hair like crystals that can grow from the pure tin surface under certain conditions. Concerns remain that if allowed to grow, these may cause short circuits between metallized pcb tracks. Typically, users will assess the risk based on their own pcb processing and end application conditions.

At a component level, under reflow conditions, the solder paste into which the component is placed will wet most of the termination surface. This area will not be susceptible to whisker growth, as the additional elements alloyed in the solder paste will also alloy with the tin from the termination plating. Only a minor portion of the termination area will remain pure tin coated as shown in Figure 3:

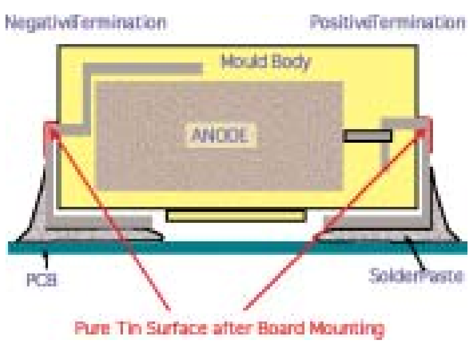


Figure 3. Tantalum Capacitor after Board Mounting.

Hence the whisker growth risk is related mainly to pure tin present on board such as pad plating rather than component termination finish. However both MIL and NASA specifications for tantalum capacitors require a minimum 3% lead content in the termination finish to guarantee a whisker free surface.

Higher Reflow Peak Temperatures

Most lead-free solder systems will require a peak reflow temperature from 240°C to 260°C. Component manufacturers will need to review all design parameters necessary to enable product to cope with the higher thermal stress resulting from these soldering processes. Replacement of some materials and development of low stress alternatives will be necessary to reduce the thermal stress inside the component.

The reflow profile below is recommended and tested by AVX for eutectic SnAgCu and SnAgBiCu based lead-free pastes in combination with pure tin finish tantalum capacitors.

- Initial heating up:	2.5ºC/s max temp gradient
- Pre-heating:	150 ± 15ºC / 60-90 s
- Max peak gradient:	2.5ºC/s
- Peak temperature:	240 ± 5ºC
- Time at >230ºC:	40s max
- Max cooling gradient:	-5ºC/s
- Time to peak:	160 - 200s

Figure 4. Recommended reflow profile specification.

Wetting balance test was used as an objective test method for solderability assessment. Wetting Balance Test results on Sn60Pb40; Sn3.5Ag0.7Cu; Sn2.5Ag1Bi0.5Cu and Sn0.7Cu solders made by independent certified laboratory – see Figure 5 and 6.

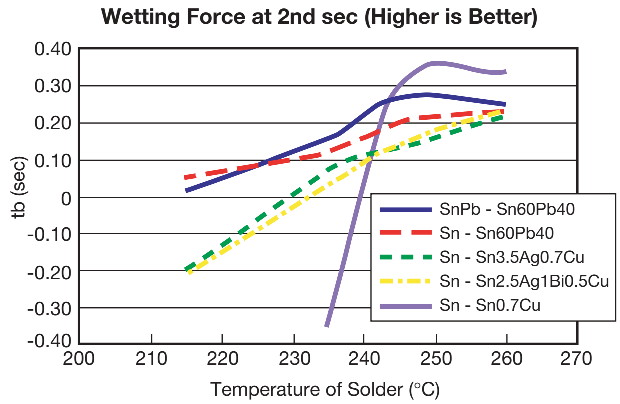


Figure 5. Wetting Force comparison for lead and lead-free solders in combination with conventional (SnPb) and pure tin (Sn) termination finishes.

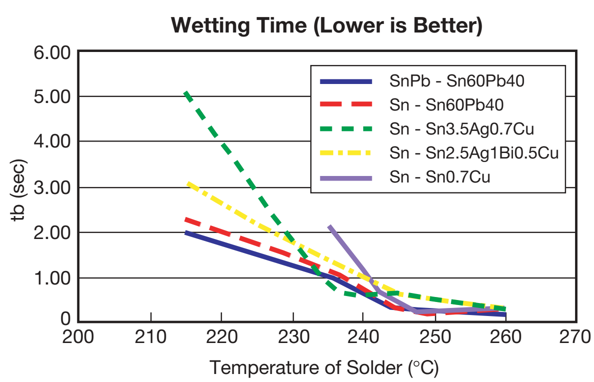


Figure 6. Wetting Time comparison for lead and lead-free solders in combination to conventional (SnPb) and pure tin (Sn) termination finishes.

Experimental tests

TEST 1

An experimental test was prepared to compare the general differences between the current capacitor technologies and manufacturers under high temperature reflow mounting process. 20 units of different capacitor technology were stored in humidity conditions 40°C/90% r.h. for 72 hours followed by two 260°C reflow profiles. Leakage current (DCL), Capacitance, DF and ESR parameters were measured and compared to the initial measurement after each step. This test simulates a typical storage condition under tropical conditions as may exist in Brazil or Singapore. The test then simulates a customers assembly process with the parts being subjected to two IR reflow profiles. Leakage current was found to be the most sensitive parameter in the test – see comparison results Figure 7.

TEST 2

Another 50 units of tantalum capacitors with MnO_2 and Conductive polymer were tested in the same humidity conditions and recommended reflow (245°C peak) to compare these two tantalum technologies in more details. – see Figure 8 to Figure 11.

Conventional tantalum capacitors DCL Limited = 0.01 CV

Failure Criteria: Parametric = > 10xlimit

D case 150mF/10V DCL failures Catastrophic = > 100xlimit

	M0 initial		M1 40/90 72 Hours		M2 reflow 260		M3 reflow 260	
	parametric	catastrophic	parametric	catastrophic	parametric	catastrophic	parametric	catastrophic
Supplier 1	0	0	0	0	0	0	0	0
Supplier 2	**1**	0	**1**	0	0	0	0	0
Supplier 3	0	0	0	0	0	0	0	0
Supplier 4	0	0	0	0	**1**	0	0	0
Supplier 5	0	0	0	0	0	0	0	0
Supplier 6	0	0	0	0	0	0	0	0

Tantalum capacitors with conductive poly DCL Limited = 0.1 CV

D case 100mF/10V DCL failures

	M0 initial		M1 40/90 72 Hours		M2 reflow 260		M3 reflow 260	
	parametric	catastrophic	parametric	catastrophic	parametric	catastrophic	parametric	catastrophic
Supplier 1	0	0	0	0	0	0	0	0
Supplier 2	0	0	**1**	0	**1**	0	**1**	0
Supplier 3	0	0	0	0	**1**	0	**2**	0

Aluminum capacitors with conductive polymer

DCL failures

	M0 initial		M1 40/90 72 Hours		M2 reflow 260		M3 reflow 260	
	parametric	catastrophic	parametric	catastrophic	parametric	catastrophic	parametric	catastrophic
SMD 1	**1**	0	**1**	0	**3**	0	**20**	0
SMD 2	0	0	0	0	**16**	**4**	**8**	**12**
Foil	0	0	0	0	**6**	**14***	**-**	**6* (20)**

* exploded during reflow

Ceramic capacitors

DCL failures

	M0 initial		M1 40/90 72 Hours		M2 reflow 260		M3 reflow 260	
	parametric	catastrophic	parametric	catastrophic	parametric	catastrophic	parametric	catastrophic
Y5V 1	0	0	0	0	0	0	0	0
Y5V 2	0	0	0	0	0	0	0	0

Figure 7. Humidity/260°C reflow 20 units sample size DCL failures of diverse capacitor technologies.

u

TEST 1 RESULTS (Figure 7)

The tantalum samples passed the humidity and double 260°C reflow test (Figure 7) without any significant issues. The good results of tantalum capacitors are stable across the diverse tantalum capacitors types and suppliers showing just minor parametrical failures in some cases. Only one parametric failure occurred during the high temperature reflow. Relatively higher sensitivity to 260°C reflows was found on tantalum capacitors with conductive polymer in parametric fall-out.

The tested Y5V dielectric ceramic samples passed the test without any parametric or catastrophic failures.

Aluminum capacitor samples did not survive the aggressive board mounting process as simulated by the test. High percentages of catastrophic failures were found after the test. Foil Aluminum capacitors exploded during the reflow process.

The small sample size used cannot guarantee conclusive results, but it emphasizes the importance of further focus on higher peak temperature reflow and the development of low stress materials. Additional reliability testing on these parts will be performed to identify whether there will any long term issues resulting from the high temperature reflow, but previous experience suggests that parts with such stable parametric readings post-test would not exhibit any long-term reliability concerns.

TEST 2 RESULTS (Figures 8 – 11)

ESR and DCL parameter histograms of tantalum capacitors with MnO_2 and conductive polymer from different suppliers were compared in order to evaluate the stability of these technologies for lead-free processing. The test consists of humidity load 40°C/90% as a bad or long-term open air storage simulation followed by two reflow profiles with recommended peak 245°C.

Conductive polymer capacitors show a significant level of parametric failure and in some cases also catastrophic failures of DCL and ESR after the reflow – board mounting. Noticeable differences were found in performance of diverse conductive polymer suppliers. Supplier 1 capacitors show smaller DCL parametric shift but catastrophic shift of ESR. Capacitors from supplier 2 have an excellent ESR stability record, however catastrophic DCL (short circuits) and big parametric shift of whole DCL histogram occurred during the reflow process.

All DCL, ESR, CAPACITANCE and IMPEDANCE parameters of these diverse capacitor manufacturers using the conventional MnO_2 second electrode were found to be very stable or exhibit minor parametric shift during the test.

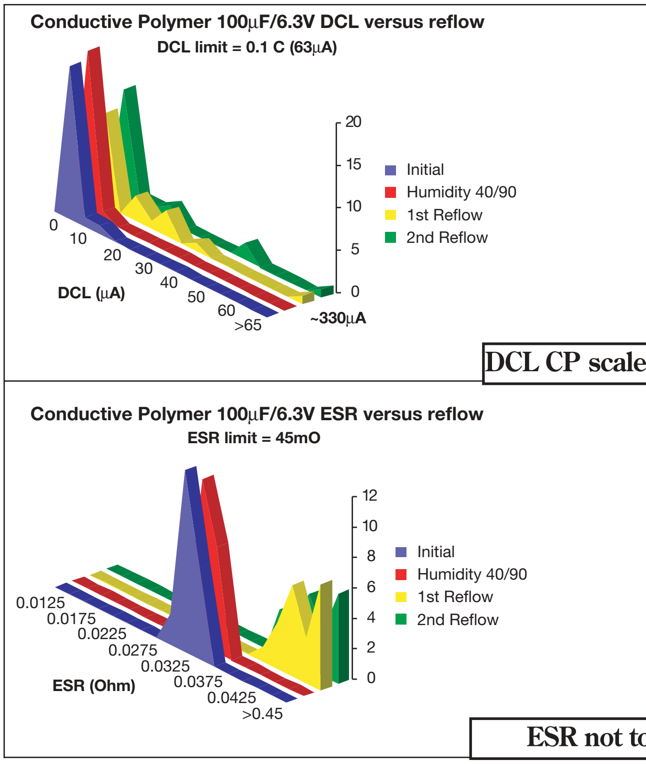


Figure 8. CP supplier 1 DCL and ESR stability.

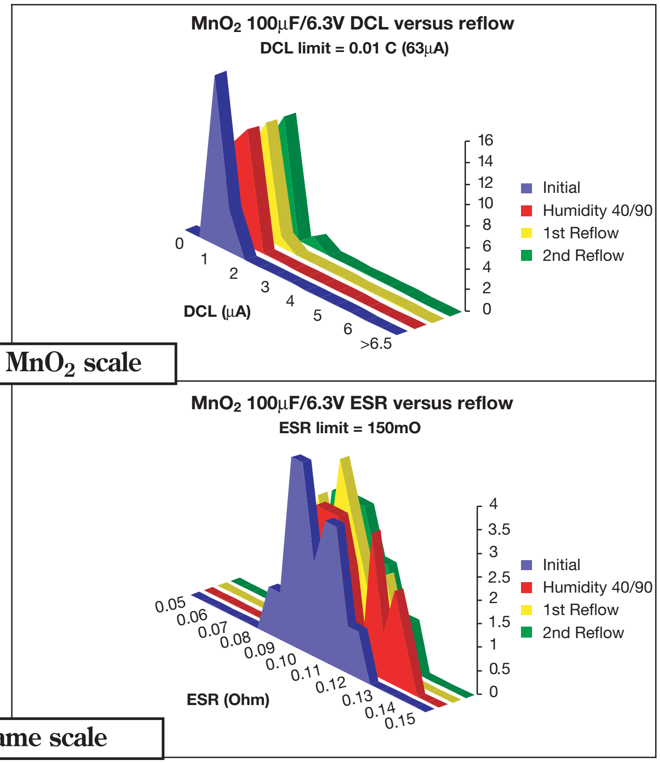


Figure 11. MnO_2 supplier 2 DCL and ESR stability.

DCL CP scale = 10x MnO_2 scale

ESR not to the same scale

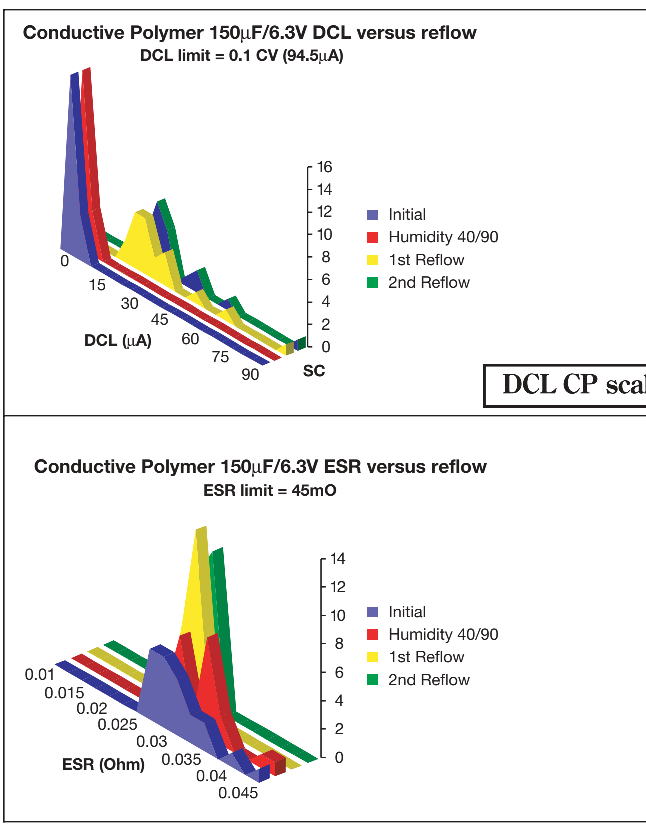
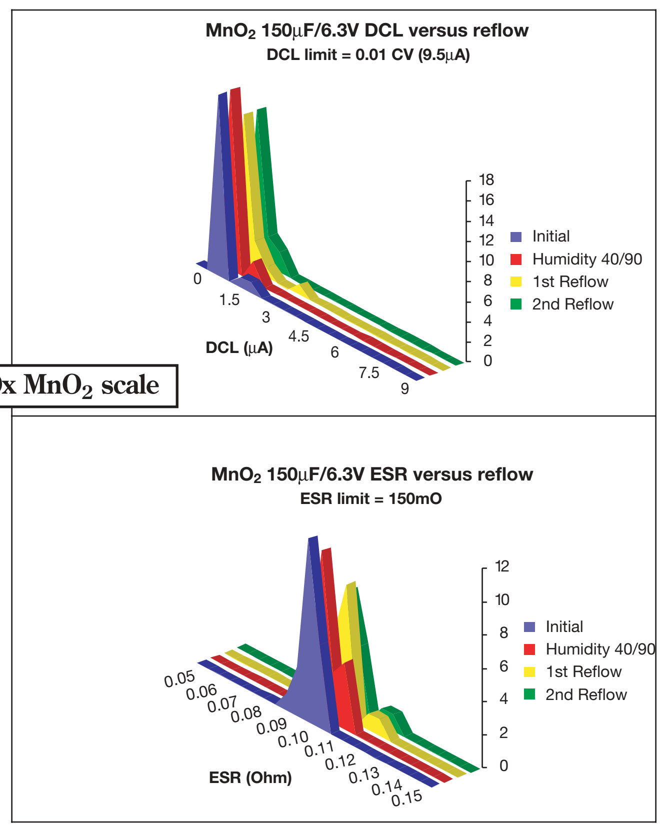


Figure 10. CP supplier 2 DCL and ESR stability.



DCL CP scale = 10x MnO_2 scale

Figure 9. MnO_2 supplier 1 DCL and ESR stability.

Conclusions

This paper summarizes the current status of lead-free technology and AVX's research to date and discusses the necessary development actions for component manufacturer. Sn (pure tin), SnAg and SnCu alloys were previously found to be the most serious candidates for replacement of the conventional tin-lead termination finish. However, pure tin was found to be the only one available termination finish at the moment compatible with conventional tin-lead and new lead-free board mounting systems suitable for massive production of tantalum capacitors.

Wetting Balance test together with some experimental tests on tantalum capacitors proved that 240±5°C would be the sufficient reflow peak temperature for lead-free SnAgCu / SnAgCuBi eutectic solder pastes. Industry peak temperature standard during 1999 – 2000 for the conventional tin-lead pastes is 220°C *(Source: AVX customer reflow database)*. Reflow peak temperature should be increased to approximately 240°C to reach the same Wetting Force and Wetting time of the lead-free pastes according to Figures 5 and 6. Higher reflow temperature further improve wetting characteristic, however higher component fall out may result by this process.

Experimental test of humidity/260°C peak reflow resistance was performed to compare the current status of individual capacitor technology.

The small tested quantity cannot guarantee the conclusive results, but it emphasizes importance of further focus to higher peak temperature reflow and new development of low stress materials. Tantalum and ceramic capacitors' results indicate a better preparedness to higher peak temperature reflow then Aluminum capacitor samples. The results are shown in Figure 7.

Further development on conductive polymer technology would be necessary in order to improve stability of its electrical parameters such as DCL and ESR. Lead-free board mounting simulation results with MnO_2 technology – see Figures 8 – 11.

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