TECHNICAL PAPER

TA Capacitors With Conductive Polymer Robust to Lead Free Process

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Abstract:
Tantalum capacitors with conductive polymer cathodes have found a place in the market as a low ESR component with reduced ignition. Conductive polymer cathodes however, suffer from instability during multiple high temperature thermal treatments such as lead free soldering due to its limited self healing ability and lower thermal and mechanical strength compared with manganese dioxide. This makes capacitors with conductive polymer cathode more sensitive to thermo-mechanical stresses, which appear during soldering and to negative influences of storage condition after removal from the protective packaging prior to soldering. This paper describes methods of improving the robustness of such capacitors with lead free processes without a negative impact on ESR. Presented procedures enhance the stability and reliability of Tantalum capacitors with conductive polymer cathodes making them comparable to capacitors containing a manganese dioxide counter electrode system.

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Introduction

Lead-free technologies are being increasingly adopted across all of the industry. Both legislation and customer demands are pushing the producers to replace lead in their products and to provide compatibility of parts to lead-free soldering processes. The robustness of components to these new conditions is one of the key focuses for AVX. All new product developments are considered for both their environmental impact and their stability under lead-free reflow conditions. Specifically conductive polymer product, where AVX has engaged in over 8 year's development activity, is taken with special care. The goal of this development was to introduce onto the market a reliable product which meets the lead-free requirements and maintains the high reliability level of AVX components.

Lead Free Process

The reflow profile used in lead-free technology is driven first by the solder melting point, which is typically 20°C higher than for conventional SnPb solder. In more complicated assembly systems, where dimensionally large components are soldered next to small ones, the temperature of soldering is designed so that the solder at the larger component is properly heated. In such cases the temperature of the small components can easily reach or even exceed 260°C and it leads many customers to excessive lead-free profile specifications. A typical current customer lead-free profile specification is described in Table 1 and Figure 1.

- peak temp. max	255±5°C
- time at 260°C	10 sec.
- time at >230°C:	60s
- max heat up gradient:	2.5°C /s

Table 1: Specification of lead-free reflow profile

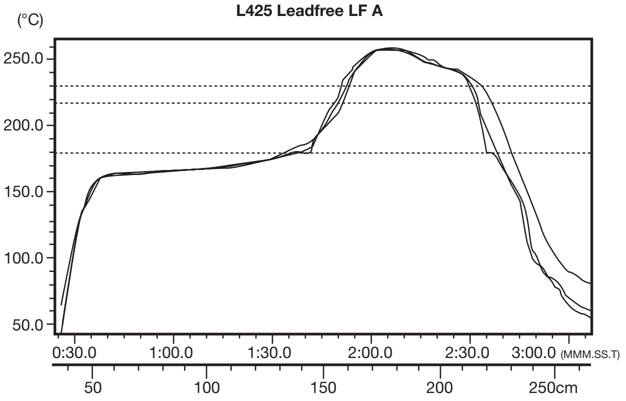


Figure 1: Lead-free profile

Lead-free processes are a threat for many component technologies. Lead-free solder systems will require a peak reflow temperature up to 260°C. Component manufacturers have to review all design parameters necessary to enable the 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 required. Components have problems with cracking, material decomposition, pop-corning, delaminating and other mechanisms caused by high temperature or temperature gradients during heating and cooling. Teams of experts around the world are intensively working on new materials with high temperature stability, high glass transition temperatures, systems with minimal temperature mismatches and adhesives with improved bonding.

Capacitor technologies are fighting with the lead-free process requirements with varying results. Whereas polymeric film capacitors, wet aluminum capacitors or large high CV ceramic capacitors suffer from high temperature stress and often do not meet the industry needs, Tantalum and niobium oxide technology with manganese dioxide cathodes has been successfully developed to survive the lead-free process [1]. The new technology with a conductive polymer electrode is more sensitive, however, and suppliers of Tantalum capacitors with conductive polymer cope with this task with varying degrees of success.

Tantalum capacitors with conductive polymer are required to withstand up to three exposures to the reflow profile, which is a more stringent specification than is often required of manganese dioxide capacitors. A quick search in specifications of maximum reflow temperature among five suppliers (Table 2) from end of year 2004 shows that the recommended profiles are lagging the industry need.

Supplier	Peak Temp	Time at peak
	°C	sec
A	240	10
B	240	5
C	240	10
D	245	10
E	260	0

Table 2:
Maximum peak temperature recommended by suppliers

Reflow Stability of Commercial Products

To prove the specifications and to search the real situation on the market, Tantalum capacitors with conductive polymer electrodes from five suppliers were subjected to reflow stability testing.

It is well known within the industry that conductive polymer capacitors are sensitive to humidity, which strongly affects their stability on reflow. Producers of parts with conductive electrodes mitigate this problem by putting the capacitors in a vacuum sealed bag with labels strongly restricting the usage time after removal from the bag or necessity of drying if the minimum time is exceeded. Therefore not only have multiple reflow tests been chosen, but also accelerated humidity followed by reflow to emphasize differences in technologies.

a) Multiple reflow test

The capacitors were removed from their closed sealed bags and within 30 min. subjected to 3x245°C reflow. Second group was treated to a single 255°C reflow. Electrical parameters were then measured after 24 hrs. recovery. Results are summarized in Table 3.

Supplier	Case	C (μF)	U (V)	Reflow	1Ref	Last Ref
B	D	100	10.0	3x245	0	0
B	Y	100	6.3	3x245	0	0
B	Y	100	6.3	1x255	0	0
C	D	100	10.0	3x245	0	0
C	D	100	10.0	1x255	1xSC	1xSC

Table 3: Stability on multiple reflow

All parts survived the 3x245°C reflow, but parts from supplier C did not pass the 255°C reflow test.

b) Humidity followed by multiple reflow test

This test was designed to show the sensitivity of capacitors to humidity prior to reflow. Typically capacitors with conductive polymer are classified in JEDEC level 3, i.e. the floor life at factory ambient below 30°C/60%RH is 168 hrs. The parts were removed from the sealed bag, and within 30 min. measured, then stored at accelerated conditions 90% humidity at 40°C for 72 hours and then subjected to 3x reflow as in the previous case. Electrical results were measured between each step and are summarized in Table 4.

Supplier	Case	C (μF)	U (V)	Reflow	Hum	1Ref	2Ref	3Ref
B	D	100	10	245°C	0	1%SC	1%SC	2%SC
B	D	100	10	255°C	0	5%SC	5%SC	5%SC
B	Y	100	6.3	245°C	0	4%SC	8%SC	10%SC
C	D	100	10	245°C	0	0	1%SC	10%SC
C	D	100	10	255°C	0	5%SC	5%SC	5%SC
C	D	150	6.3	245°C	0	5%SC	5%SC	10%SC
D	Y	150	6.3	245°C	0	0	0	2%LI
D	Y	150	6.3	255°C	0	0	0	4%SC

Table 4: Stability in humidity 72 hrs. 90%40°C
and multiple reflow

Short circuits appeared mostly after the first reflow. Higher reflow temperatures had greater impact.

c) Accelerated pressure cooker and reflow test

Accelerated humidity testing has been developed internally in AVX to emphasize the effect of humidity before reflow. The parts were subjected to lead-free reflow according to Table 1. After reflow, the parts were allowed to relax for 1 hour and subjected to pressure cooker at 121°C for 4 hrs. Then, after 1 hour relaxation, they were reflowed with the same profile again. Results are summarized in Table 5.

Supplier	Case	C (μF)	U (V)	Reflow	PC+RFL
A	D	220	6.3	6%SC	13%SC
A	D	100	10	2%SC	2%SC
B	Y	100	6.3	8%SC	4%SC
D	B	47	6.3	18%LI	60%LI
E	D	100	10	12%SC	28%SC
E	Y	100	6.3	100%SC	100%SC

Table 5: Stability in
lead-free reflow – pressure cooker – reflow test

From all three tests it followed that Tantalum capacitors with conductive polymer electrodes are very sensitive to storage condition and lead-free processing. As a consequence it was undertaken as a key challenge in the development of AVX's conductive polymer series to produce a more robust polymer product.

Development of Lead Free Reflow Stable Product

A poly[3,4-ethylenedioxy)thiophene] (PEDT) [2] conductive polymer has been chosen as the most suitable material for development of lead free reflow resistant Tantalum capacitors.

PEDT has many advantages over other conductive polymers, because of its simple processability, relatively good mechanical strength and atmospheric stability. PEDT is not a film creating polymer, however. Its structure is brittle and depending on the way of preparation is also often porous and non uniform. External thermo-mechanical stresses during lead free reflow, caused by temperature coefficient expansion mismatches within the capacitor, can easily damage the polymer layer, and result in short circuits or increasing ESR up to open circuits. Key factors which have to be managed, are:

- Anode design
- Quality of dielectric
- Adhesion of polymer to dielectric
- Polymer uniformity
- Stress barrier
- Low stress encapsulation
- In line 100% verification

a) Anode design

Conductive polymer layers can be created in-situ directly in the anode by various methods. It can be deposited by chemical oxidative polymerization from a monomer, an oxidizing agent and a dopant, deposited in one solution or sequentially, or by electro-deposition.

In all cases the polymer process must be tailored to the anode design to obtain a highly conductive and mechanically strong polymer layer. Polymer impregnation and waste removal must be managed.

Anode design depends on the selection of tantalum powders with the proper distribution of pores, which is driven by particle size and agglomerate distribution, pore size distribution within and between agglomerates, and the presence of sinter retarding doping elements. Sinter activity of powder and press density must be taken into account when a sintering profile is set up. Lubricating and adhesive binders together with modern uniform pressing technique will also help to transfer the desirable properties of the powder to a suitably designed anode pellet.

To illustrate this point the stability of capacitors with two different anode structure designs after the pressure cooker/reflow test is shown in Figure 2.

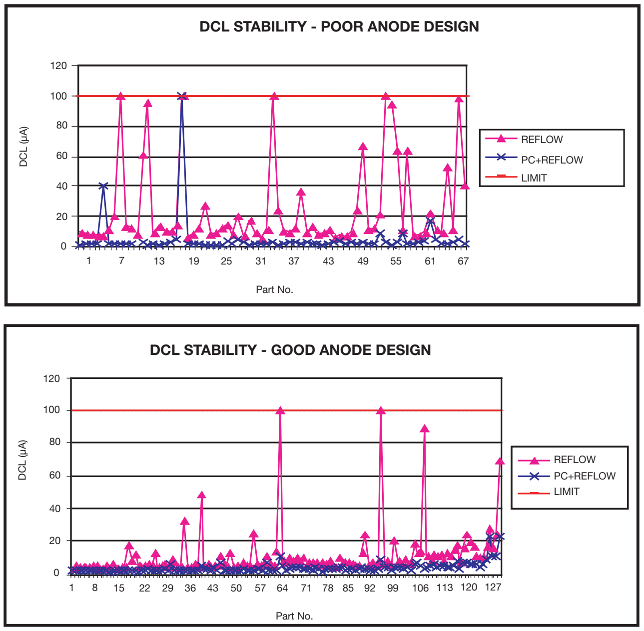


Figure 2: Effect of anode design (DCL Stability of Y case) Lead Free Reflow – Pressure cooker and LF reflow test

b) Strong dielectrics

The solid electrolytic capacitor is designed to utilize a self healing process. If a defect appears in the dielectric, the resistivity is locally reduced and increased current flows through the lower resistivity site. The solid electrolyte must have the property that when overheated, it changes its structure irreversibly to a non-conductive structure to effectively block defects in the conductive site.

PEDT conductive polymer does not have as positive an effect on Tantalum pentoxide dielectrics, as manganese dioxide. Therefore the dielectrics must be more robust to external thermo-mechanical stresses and impurity migration. It is well known that shell formation, which creates a thick external dielectric, will increase the dielectrics robustness. It was found that the thickness of both internal dielectric, and external shell, are crucial factors. Parameters of shell formation have been studied from the point of view of the effect on dielectric robustness. Figure 3 shows the improvement of reflow/PC and reflow DCL stability with optimized shell form conditions.

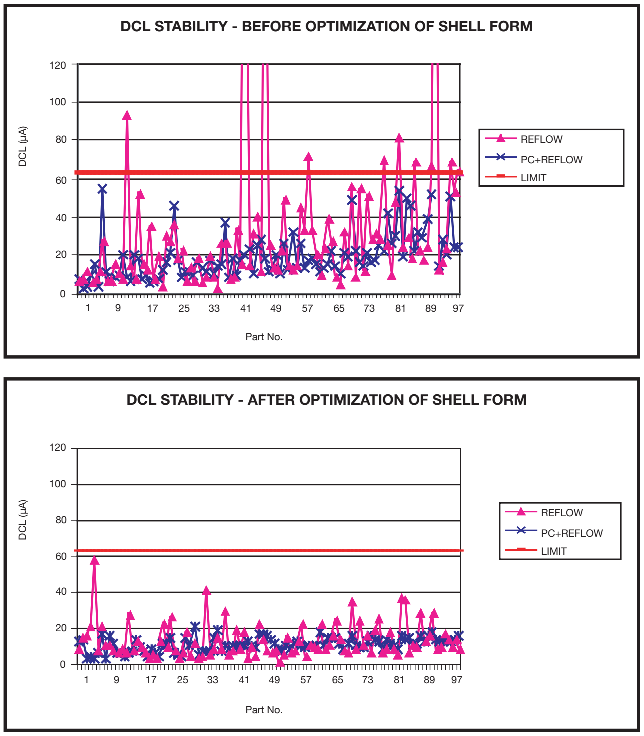


Figure 3: Optimization of shell form
Reflow – Pressure cooker and lead-free reflow test
DCL stability of B case

c) Adhesion of polymer to dielectrics

Conductive polymer itself has a poor adhesion to the dielectric. Peeling off and delaminating, caused by the outgassing of humidity, leads to instability of capacitance, dissipation factor or ESR. It is believed that the adhesion of polymer can be improved by the protective coating between dielectrics and polymer.

Adhesives based on electron donor organic layers, preferably epoxysilane, deposited on the dielectric [3], or added to the polymer solution [4], have been proposed.

A new family of a protective coating containing an insulative, resinous material selected from the group consisting combinations of polyurethanes, polystyrenes, or esters of unsaturated or saturated fatty acids has been chosen [5]. It has been discovered that such a protective coating can inhibit the short-circuiting of the resulting capacitor and also reduce the ESR of the capacitor and improve the ESR stability.

The stability of the interface has been improved, as shown in following graphs. It results in a highly continuous and dense conductive polymer with good stability of ESR, DF and C and good yields.

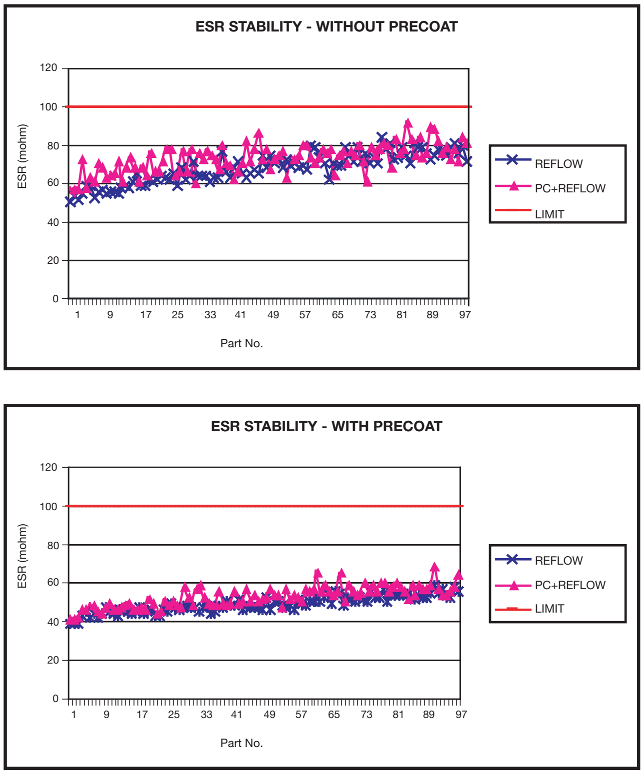
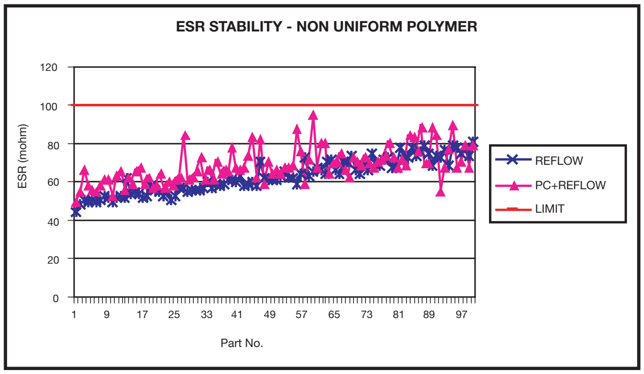


Figure 4: Effect of precoat on dielectrics
Reflow – Pressure cooker and lead-free reflow test
ESR stability of B case

d) Polymer uniformity

The mechanical properties of the polymer depend largely on the structure of the polymer network and the interaction of the network and solvents. The polymer network's toughness is determined by the crosslink structure. PEDT forms a linear or simply branched network, which has low mechanical strength. It is furthermore impacted by the entrapped solvent.

The technology of polymer deposition had to be optimized to allow a high level of crosslinking and to effectively remove salts and solvents from the polymerized material. The improved process gave uniform and homogenous layers which improved reflow stability of ESR (Figure 5).



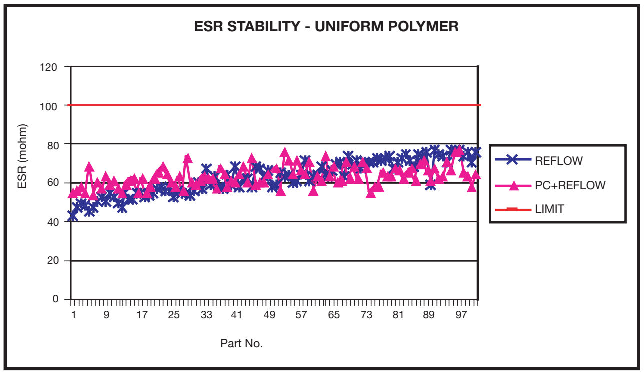


Figure 5: Effect of PEDT uniformity
Reflow – Pressure cooker and lead-free reflow test
ESR stability of B case

e) Stress barrier

Carbon and graphite form the mechanical barrier between the brittle polymer and the encapsulant. Both materials consist of conductive filler, which are carbon, graphite or silver flakes or particles, resin binder and solvent.

The reduction of stress in the polymer requires soft and stress absorbing external layers. This can be achieved by flexible binders contained in both materials, and by thick layers. There are physical barriers, however. Too thick a layer causes delaminating on interfaces due to thermal coefficient mismatch of included materials (see Figure 6). Flexible coatings with good adhesion, high internal strength allowing maximum thickness had to be developed.

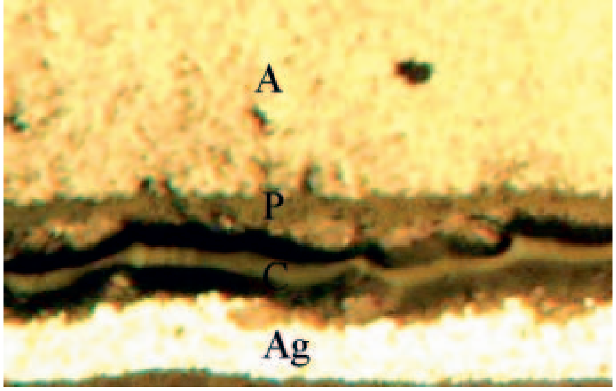


Figure 6: Thick outer coatings causing delaminating
(A – anode, P – polymer, C – carbon, Ag – silver)

f) Low stress encapsulation

Encapsulation material were designed to reduce the stresses coming from thermal shocks, and to create an effective barrier to humidity penetration.

The resistance against thermal shocks was reduced by low thermal expansion and high glass transition temperature of the moulding compound. Reduction of TCE decreased internal mechanical stresses caused by the thermal expansion mismatch by 33% - see Table 6.

Encapsulant	Old	New
Expansion 25-260°C (%)	0.84	0.55

Table 6. Comparison of relative expansion of old and new type molding compound during lead-free reflow

High strength at high temperature and good adhesion to lead frame reduces the chances of cracking the encapsulant and opening the gate for humidity penetration. Low water absorption of encapsulant can further improve the humidity resistance.

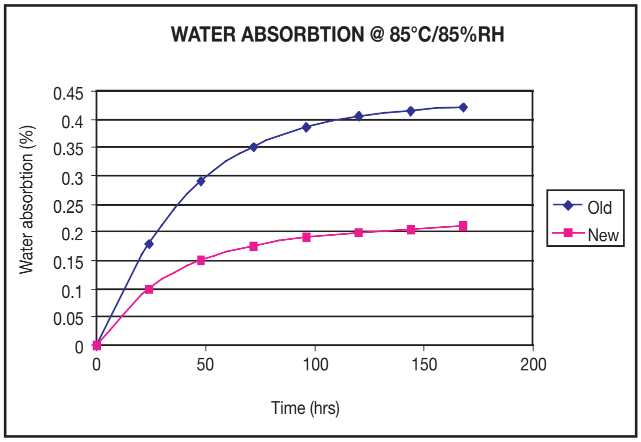


Figure 7: Moisture absorption of old and new encapsulant at 85°C/85%RH

g) In Line 100% Verification

Tantalum capacitors are 100% preconditioned during their production at accelerated conditions to eliminate potential failures. Robust polymer electrodes allowed modification of the screening operations towards temperatures as high as 260°C without losing reliability. All capacitors see the high temperature already at accelerated tests during its production, which guarantees the reliability at end users when used under recommended conditions.

Stability

An improved family of capacitors that are robust to lead-free reflow has been achieved as a result of the above mentioned technical developments. The new series will survive lead-free reflow with peak temperatures as high as 260°C for 10 sec. Humidity stability was improved to such an extent that capacitors survive the lead-free reflow post soaking in humidity, simulated by 4 hrs. pressure cooker.

Figure 8 and Table 7 show typical stability of capacitors during lead-free reflow/pressure cooker/reflow test.

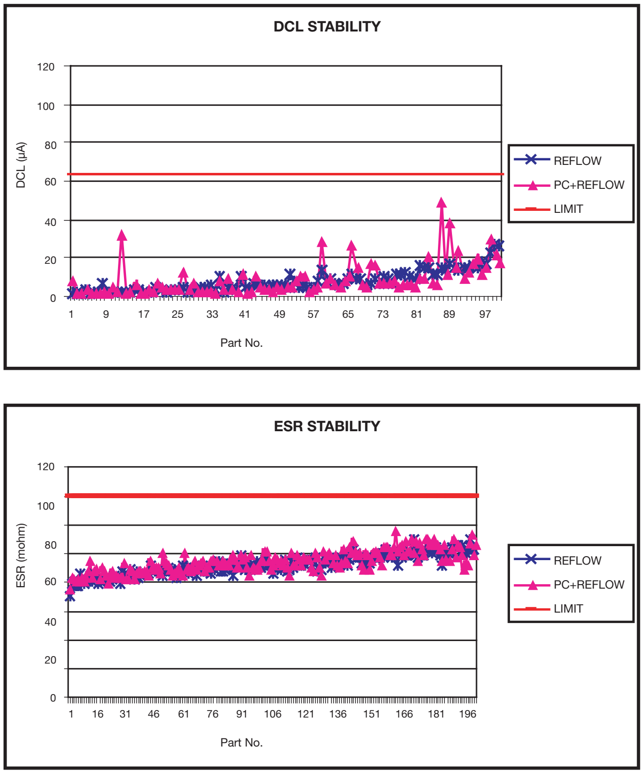


Figure 8: Reflow – Pressure cooker and lead-free reflow test – stability of B case after all improvements

Case	C (µF)	U (V)	M0	Reflow	PC+RFL
A	10	10	0	0	0
B	100	6.3	0	0	0
C	47	10	0	0	0
W	150	6.3	0	0	0

Table 7: Stability in lead-free reflow – pressure cooker – reflow test

Conclusions

The results demonstrated the ability of polymer technology to fulfill lead-free process requirements.

Key factors influencing the stability at lead-free reflow were identified and improvements adopted:

a) *Anode quality* - anode design has to be managed and polymer tailored respectively.

b) *Robust dielectric* – Selective application of thicker dielectric can reduce the possibility of damage.

c) *Polymer adhesion and uniformity* – addition of special adhesive polymer improves the interface between polymer and the dielectric. Uniform polymer layers have greater toughness to lead-free process stresses.

d) *External materials* – carbon, silver and encapsulant have to create a low stress environment and have to be designed has stress absorbing as possible.

e) *In-line verification* – parts have to be overstressed in line to screen potential failures.

Literature

[1] F. Priban et al, Green Environmentally Friendly Technology for Tantalum and Niobium Oxide Capacitors, CARTS Europe 2004

[2] M. Biler et al, Poly(ethylenedioxy)-thiophene Conductor Films, IUPAC 2004-MACRO, July 2004

[3] Sakata et al, U.S. Patent No. 5,729,428

[4] R. Hahn et al, U.S. Patent No. 6,072,694, June 6, 2000

[5] J.A. Fife et al, U.S. Patent No. 6,674,635, January 6, 2004

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