

A New Polymeric Carbon Undercoat for Improved Leakage Current Performance of Tantalum Capacitors

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Abstract

Equivalent series resistance and leakage current are two critical parameters that help define the performance of tantalum capacitors. Trends in the industry are to seek ever decreasing values of ESR and leakage current whilst maintaining stability of both parameters over time. The composition of the carbon and silver layers are critical to both aspects of performance. An effective moisture barrier would prevent ingress of water vapour carrying silver ions to the MnO₂ layer and thus improve the stability of electrical parameters in humid environments. A polymeric layer may achieve this goal, but the disadvantage of using a polymeric carbon/graphite layer is that its conductivity might be lower, leading to an unacceptable increase in ESR.

In the present study, designed experiments were performed to optimise the composition of a polymer/carbon/resin ink. With this information a new carbon/graphite ink was developed which achieves superior moisture resistance and outstanding leakage current performance while having minimal impact on the ESR. The thermal stability of this polymeric carbon/graphite ink was demonstrated to be comparable to existing systems.

Introduction

There are factors which make tantalum capacitor technology stand out from competing technologies such as aluminium polymer capacitors or high capacitance ceramics. This makes tantalum capacitors the component of choice for applications in decoupling and filtering. The properties which make tantalum chips so useful include the high volumetric efficiency, performance stability as a function of temperature, low equivalent series resistance (ESR), and reliability over time [1].

The need for low ESR

A widespread trend in tantalum capacitor developments has been to pursue technologies with lower ESR. Low ESR is desirable since this reduces the amount of noise generated at high frequencies [2]. Additionally, low ESR equates to lower power losses from within the circuit.

However; in this pursuit sight must not be lost of the other factors which give tantalum its edge over the competing technologies.

Tantalum capacitors have a capacity for self healing, which is a major part of the reason for their superior reliability. Where there is a hole or defect in the Ta₂O₅ dielectric layer a current will flow, resulting in localised heating and thermal decomposition of the semiconducting MnO₂ to insulating Mn₂O₃. This blocks off the site of the defect and the oxygen liberated from the MnO₂ dopes the underlying Ta₂O₅ layer, filling the hole in the dielectric.

There are other factors that can occur over time that cannot be healed and so must be prevented. In a survey of the reliability of tantalum capacitors from an unknown supplier [3] 67% of failures were related to leakage current effects.

The importance of leakage current

Leakage current within a capacitor arises from a number of sources. All capacitors will exhibit a background level of leakage current due to dielectric absorption. The extent of dielectric absorption is thought to be a function of the anodisation step. It is, therefore; a property of the capacitor that cannot be altered during subsequent processing, but this level of leakage current is only a small fraction of the typical tolerance threshold. Dielectric leakage normally accounts for around 0.1nA/μFV compared to a normal specification of 10nA/μFV.

Other causes of leakage current include [4]:

- Impurities
- MnO₂ on anode wire
- Mechanical damage
- Moisture ingress

Minimising dielectric absorption, avoiding impurities and preventing MnO₂ contacting the anode wire are factors which can be avoided by a well-controlled manufacturing route, but sustaining mechanical damage and encountering humid environments are factors over which a chip manufacturer has no control. The

manufacturer must rely on the quality of the components within the capacitor to give a performance level differentiated from the competition.

The mechanism by which moisture ingress is thought to cause an increase in leakage current is through the transport of silver ions from the outer silver layer through holes or thin regions in the MnO₂ layer. Defects in the Ta₂O₅ layer in these regions can lead to a conductive channel between the tantalum metal and the cathode layers. Some manufacturers have attempted to mitigate this mechanism by using an insulating silicone barrier to hinder silver ion migration [5].

One method that would seem to offer improvements in resistance to moisture is the inclusion of a polymeric layer into the system. Increasing the thickness of polymer through which silver ions must be carried would prevent their accumulation at the MnO₂ layer thereby reducing the incidence of dielectric bypass and leakage current faults. A polymeric layer would also reduce the appearance of mechanical damage. The ability of compliant layers to relieve strain in order to avoid fracture of brittle phases is well recognised. Indeed, this is how most structural composites function.

The disadvantage of using a polymeric layer to provide a barrier to moisture and silver ions is that the polymer will also act as a barrier to the current flow, in other words; a thick polymeric coating might increase the ESR. The degradation of ESR would render improvements in leakage current performance moot, thus; it is critical to ensure that improvements made to the leakage current performance do not adversely affect ESR. In the current development program efforts were concentrated on finding the optimum composition of polymeric carbon ink in terms of the best observed ESR and then proving the effectiveness of the coating on leakage current performance.

Background

The structure of a tantalum capacitor is shown in Figure 1. It is a complicated system of materials, structures and interfaces. The inner structure consisting of the tantalum wire and sponge, the Ta₂O₅ dielectric layer and the MnO₂ layer are the components that give the component capacitive behaviour. The function of the outer layers of carbon and silver is to provide an electrical connection to the MnO₂ layer.

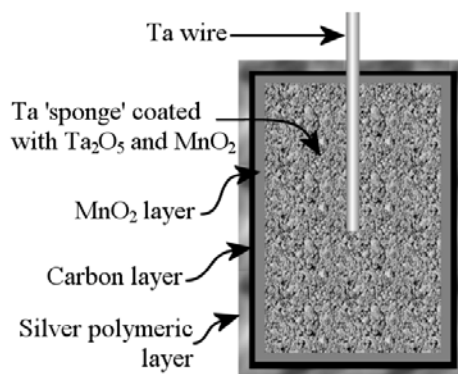


Figure 1 Schematic diagram of a MnO₂-type tantalum capacitor

The silver layer

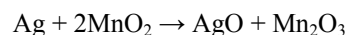
The outermost silver layer is connected to the chip lead frame either by gluing or soldering. It has to have very low resistivity since charge passes along the length and breadth of the chip. The layer may be typically 20µm thick. Inks usually consist of silver powder or flake, resin, solvent, and, because the inks are usually applied as low viscosity suspensions, a surfactant to help to alleviate the problems of settling.

The resin system chosen needs to be capable of withstanding the temperatures encountered during soldering and rework. This might mean several cycles to temperatures up to 260°C. In addition to good bulk conductivity the silver layer must also make good electrical contact with the carbon layer beneath.

The carbon layer

Although DuPont has had product offerings for silver coatings for several years [6] we have not previously looked at the carbon layer for optimisation. Typical carbon compositions have very low binder contents, and a blend of carbon powder and graphite as the conductive filler. The carbon layer is typically less than 10µm thick.

The function of the carbon layer is to isolate the silver layer from the MnO₂ layer. Contact would result in the following redox reaction:



Both AgO and Mn₂O₃ are insulating materials, therefore contact between the silver and the MnO₂ layer must be prevented, adding as little resistivity to the system as possible.

Carbon inks are not as conductive as silver inks, however; current does not need to travel long distances along the layer. The current need only flow perpendicularly from the MnO₂ to the silver layer. This

is different from the many other applications of carbon inks in electronics, where conductivity in-plane with the deposit is more relevant. Since the conductivity of graphite is anisotropic, good conductivity in-plane does not necessarily guarantee good conductivity in the perpendicular direction.

The carbon layer interfaces with the silver layer and the MnO₂ layer, therefore; the ability of the ink to yield low resistivity interfaces is arguably the most important characteristic. The ability to maintain that contact is also important. Low-binder carbon inks are inherently weak and can be the source of delaminations when anode bodies are mechanically tested.

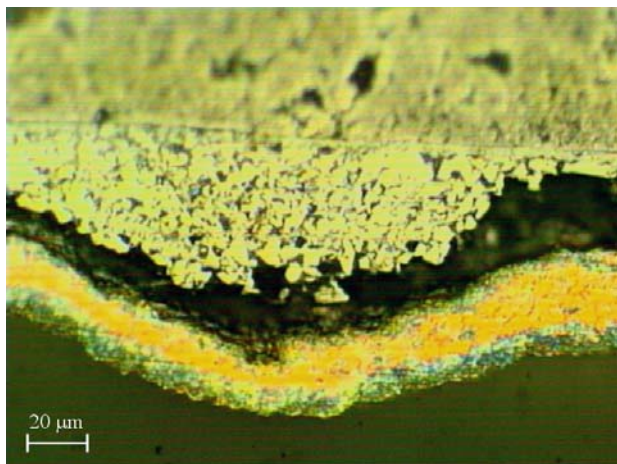


Figure 2 Cross section through a tantalum chip body showing cohesive failure of the carbon layer induced by the sectioning process

Figure 2 shows the damage that was caused by sectioning a chip with a conventional, low binder carbon ink. The possibility of failures of this kind should be avoidable using a system with a higher binder content to elastically absorb the stresses. Additionally, where the possibility of cracks exists, so to does the possibility that moisture could accumulate in these cracks, eventually forming a moisture bridge and thus lead to leakage current faults.

Experimental and results

It was felt that there would be some interaction between the components, meaning that the optimum concentration of the three principal ingredients would have to be determined in parallel. To this end, a designed experimental matrix was created using a multivariate data analysis package.

The resin system chosen for this optimisation was an existing high temperature resin system used in our silver ink. The carbon and graphite were chosen from their proven performance in other electrical applications. Initially a broad matrix was planned, illustrated in Figure 3.

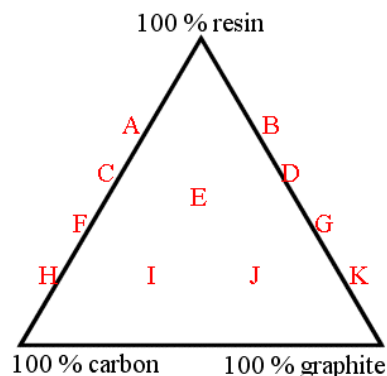


Figure 3 Approximate compositions used for round 1 of the optimisation

Each of the inks from the matrix was milled and diluted down to the same solids level. Tantalum chip anodes prepared as far as manganisation were dipped into the carbon and cured at a fixed temperature of 80°C for 2 hours. Following the application of the carbon the silver layer was applied and cured using the manufacturer's recommended processing conditions.

Following completion of the parts, the ESR was measured at 100kHz on an Agilent LCR meter in 4-wire mode with compensated leads and kelvin clips. Not all of the compositions resulted in usable inks. C, F, I and H (the inks richest in carbon) had such poor adhesion that it was not possible to process the parts. The ESR of parts created with the remaining inks is presented in Table 1.

Table 1 ESR of inks from round 1 of optimisation experiment

Ink	ESR /mΩ
A	137
B	627
D	532
E	134
G	439
J	135
K	466

The numbers by themselves are fairly indigestible. They only point to a few compositions which show more promise than the others, however; when the data is analysed as a contour response plot the trend becomes more apparent, as demonstrated in Figure 4. Figure 4 shows that the best compositions appear to lie in a line at around 30% carbon. The ESR is apparently quite insensitive to the resin : graphite ratio.

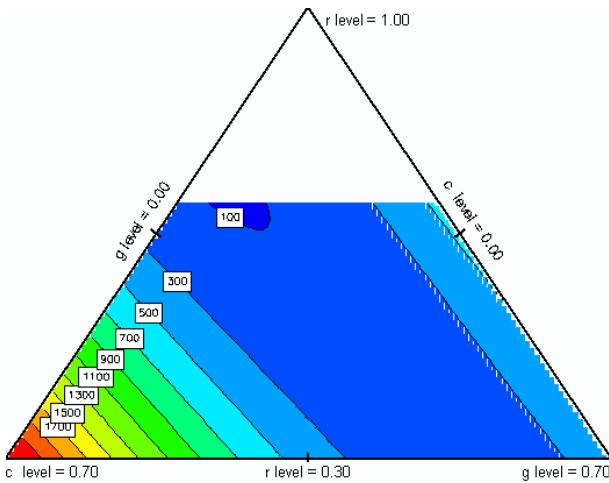


Figure 4 Response contour plot of the inks in round 1 with respect to ESR

Before the next iteration of the optimisation process was started, the behaviour of those inks from the good region of the response contour plot at different frequencies was observed. For this experiment a gain phase complex waveform analyser was used which was capable of recording ESR over a continuous sweep of frequencies from 1kHz up to 1MHz. The responses, shown in Figure 5 indicate that although the ESR at 100kHz was very similar for the three compositions tested, the response at lower frequencies was different, and ink J appeared to show the best behaviour.

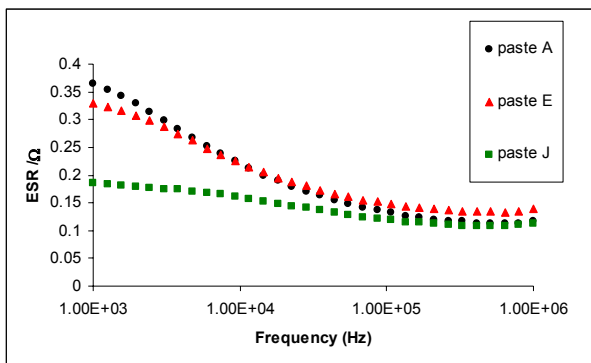


Figure 5 Graph of ESR vs. frequency for tantalum capacitors coated with different carbon coatings

A second round of compositional optimisation was performed around the composition of ink J. The matrix of ink compositions shown in Figure 6 were prepared and tested in the same way as those parts in the first round.

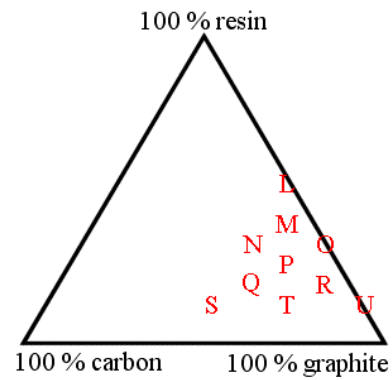


Figure 6 Approximate compositions used for round 2 of the optimisation

Again, some of these compositions were not viable. When the inks were tested and the ESR plotted on a contour plot, the best compositions were clearly indicated to lie towards composition N (see Figure 7)

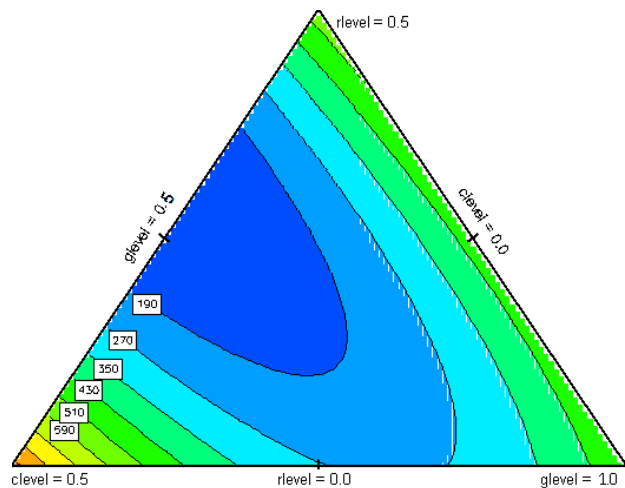


Figure 7 Response contour plot of the inks in round 2 with respect to ESR

Thus, within two rounds of experimentation, a composition was determined which appears to offer optimised ESR.

Samples of chips coated with composition N were then tested for leakage current performance. A 1000 hour ageing test at 85°C and 85 % r.h. was carried out to test the hydrolytic stability of the coatings. The results, including ESR are presented in Figure 8.

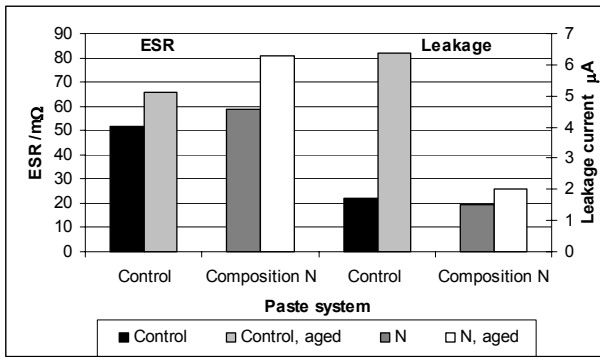


Figure 8 ESR and leakage current of tantalum capacitors with the control and ink N

The improvement of the leakage current was remarkably good. Unfortunately, despite the ESR being optimised, it was still a little worse than the control. The approach that was taken to try to reduce the ESR further was to try different resin systems. Despite initial fears over stability, a new flexible thermoplastic resin system was chosen for further investigation. Rather than repeat the entire designed matrix of experiments again a simple ladder was performed varying the resin : carbon + graphite ratio. As Figure 9 shows, the optimum formulation for ESR was composition X. This composition had the same resin : carbon : graphite ratio as composition N.

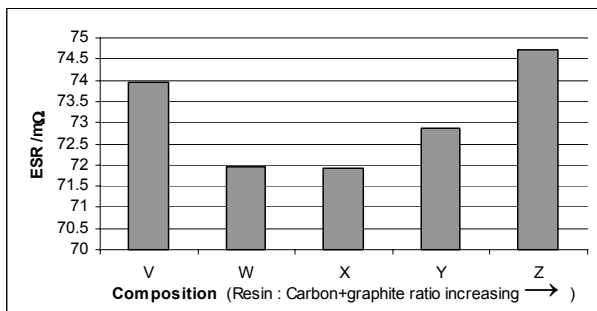


Figure 9 ESR of tantalum capacitors coated with the new thermoplastic resin-based carbon coatings with different resin : carbon + graphite ratios

It was essential to demonstrate that the new resin system chosen was able to withstand the sorts of thermal treatments that tantalum chips might see *i.e.* solder

reflow. Tantalum chips were fabricated as far as the silver coating, including the new composition X. The parts were repeatedly dipped into solder at 260°C for 10 seconds and tested for ESR after each cycle. An increase in ESR would be proof that the product were not stable enough to withstand circuit fabrication processes. The results are shown in Figure 10 and indicate that the resin in the coating composition is not degrading as a result of these repeated cycles to 260°C. A subsequent experiment where parts were immersed in solder at 260°C for 10 minutes showed that the ESR of parts coated with composition X was actually slight lower than those which had not seen the same exposure, again indicating that the grade of resin chosen was of a sufficient thermal stability.

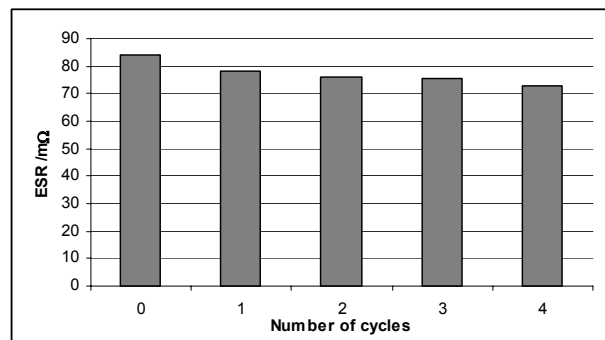


Figure 10 ESR vs. number of thermal cycles for tantalum chips coated with composition X

Following the success of this composition in the thermal tests, parts were tested for leakage current and ESR performance. These results show that the leakage current is still far superior to the control ink and the ESR is approximately the same, thus; with this composition the initial aim of developing a ink with improved leakage current performance whilst minimising the impact on the ESR has been fulfilled.

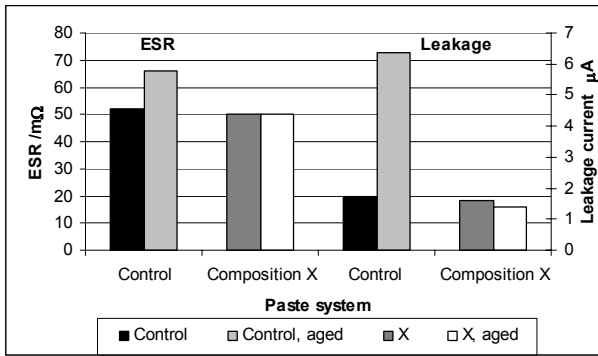


Figure 11 ESR and leakage current of tantalum capacitors with the control and ink X

In Figure 2 it was shown that the control carbon layer was not mechanically robust due to the low quantity of binder in the composition. When parts coated with composition X were sectioned the appearance was quite different. Figure 12 shows that the carbon is conformally and coherently attached to the MnO₂ underneath. The coating thickness is typically around 20μm thick, which is greater than the thickness of a typical carbon. The fact that this thickness has not led to an increase in ESR agrees with previous publications (e.g. [7]) which have shown no correlation between ESR and bulk resistivity.

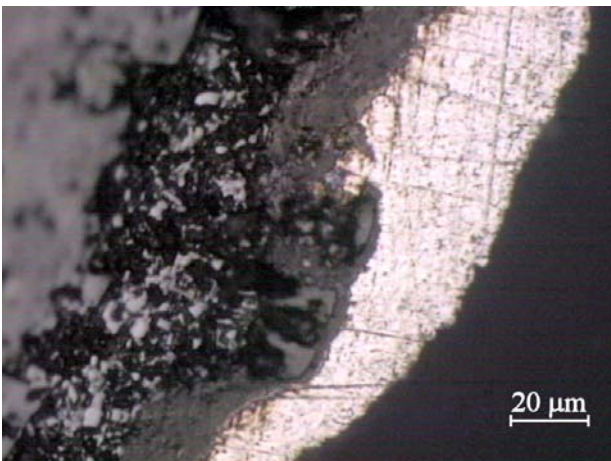


Figure 12 Cross section through a capacitor coated with composition X and standard silver

Conclusions

A composition of carbon/graphite in a polymeric binder has been developed which dramatically reduces the damage caused by high humidity in MnO₂-type tantalum capacitors with respect to leakage current behaviour. The leakage current following 1000 hours of ageing at 85°C and 85% r.h. was unchanged for those samples coated with the new composition.

The coating functions as a moisture and silver ion diffusion barrier and improves the mechanical stability of the carbon layer compared to existing technologies. Ground and polished sections through capacitors with the new composition showed no evidence of cracking

and therefore maintain a coherent barrier to moisture ingress.

The coating works well with existing silver inks so that the ESR of the finished capacitors is not significantly degraded by the addition of a polymeric layer.

References

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