"Tantalum Capacitors - Challenges and Developments" by John Moore, and John Prymak KEMET Electronics Corp. Greenville, SC, 29650 USA

### Brief Abstract:

The past five years have seen an erosion of tantalum capacitor market shares, beyond overall market decline. Challenges facing this device as the market recovers include perceptions of limited supplies or future restrictions impacting cost and availability, as well as concerns over failure modes. Additionally, the growth of niobium based capacitors is adding to these concerns as this alternative emphasizes that it holds solutions to all of these concerns, at reduced pricing.

Developments for the tantalum capacitors must emphasize better performance, reliability, and a more benign failure mode to address the niobium challenge. The manufacturers and ore suppliers must show where the supply issues of the past have been addressed, and can be flexible to the market demands in the future.

### Tantalum shortage leads downturn

From a simple statement of fact, there is derived an unjust understanding that the tantalum capacitor was the primary cause of the business collapse. In many cases it was the shortage of the tantalum capacitors that first slowed the burgeoning electronics growth of the early 2000s. This device was seen as a restricted commodity that would soon be scarce, and in every attempt to eliminate shortages, over stocking became an accepted practice. This practice soon was mirrored in other commodi-



ties such as other capacitor types, memory chips, and other semiconductor devices. In an attempt to stave off shortages, stocks were over built, and in the consequence, the shortage came into fruition.

The tantalum industry was projecting a normal growth along the lines of 18 to 20 percent per year, but this purge soon encompassed this growth and more. Manufacturing lines were expanded, pricing grew with increased demands, and the future appeared to have no ceiling. In the chain of development from ore to capacitors, the one week link initially appeared to be the ore itself, but later revealed itself to be refining. The capacity to dig more ore, or process the refined ore into capacitors had some limitations, but the major squeeze was created by the refining.

This process involved a major capital investment and a time delay of up to two years to achieve the demanded expansion of the market in crisis. At the peak of demand, allocation was devised to protect those customers deemed "important", and preferential responses were given to these chosen few. For those not so lucky, third party brokers set to take every advantage of this situation by demanding prices that were multiples of the already skyrocketing values for these products.

This enveloping flood kept rising until it reached the edge of a cliff in which the market collapsed. Each manufacturer in each sector, especially telecommunications and computers, were building at rates that envisioned each of them to capture the majority of the market. A glut of products above the demand soon brought productions to a halt. The inventories created by this overzealous projection of sales soon became apparent not only in the products sitting dormant, but in the components and hardware stockpiled for years of undisturbed sales. The crash was inevitable.

### Getting even - getting tantalum out

Many manufacturers felt that they could have ridden this wave of unfettered sales for a longer period of time if it was not for the untimely restrictions first felt by the tantalum capacitor shortage. If it were not for their being put on allocation, or being put on an allocation with them as priority, they may have truly met their expectations of growth in this brief tidal wave of sales. The problem is that each would believe that they were the one cheated by the shortages, and tantalum was the first and leading commodity that created this shortfall.

Now the bubble has burst, and lessons are demanded to be learned from this experience. In unison, the finger of guilt pointed to the tantalum capacitors. If this is accepted, then how can the future be protected from any villainous effects from this commodity device? Easy, eliminate them from the future.

#### Claims against tantalum

First, the profits of these tantalum capacitors in these furious days rose enormously. There were claims that the market was being strangled to drive up the pricing; but this ignores that the manufacturers made every attempt to expand their capabilities to meet the increasing demands. It would have been more profitable for any manufacturer to expand his capability tenfold to cash in on the margins that were created in these times. Such and expansion by any one of the manufacturers could have immediately shifted positions they would hold in the market in comparison to their competitors.

If it wasn't the manufacturers, then the mob mentality soon picked out the ore suppliers as the culprit in this malaise. After all, there is just so much tantalum ore on this earth, and surely we must be running out of reserves.

Tantalum ranks as 53<sup>rd</sup> of the elements in abundance on this earth. True, there is a limited amount of ore, but with present day usage, and projecting a growth rate of usage of 18%, there is enough ore being mined today to satisfy the world demands for the next 50 years.

What about these refiners living off the poor victims of the Congo wars, where people are killing each other for this mineral? As with any war, the properties accumulated through death should not be a measure of the brutality of the act, but the act of killing in itself should be held as primary point of disgust. As users of this material, we require that our suppliers assure us of the point of origin for these materials, and do not accept the war created supplies as acceptable in any manner.

Niobium is an alternative that offers a more abundant supply, less density, and higher dielectric constant, that when combined create a cheaper less restrictive solution. The problem with this alternative is that it requires a higher thicker dielectric to match the base reliability of tantalum, and the dielectric advantage disappears. It is also required to be refined form the ore, and the same refiners dealing with tantalum, are required to refine the niobium. At this point the price advantages disappear.

Aluminum offers another alternative, but the wet electrolytes used in many of these are not applicable for surface mount solder processes. With the solid electrolyte, the disadvantage is in its volumetric efficiency – it cannot achieve the capacitance per unit volume that tantalum can.

### Tantalum capacitor changes – MnO<sub>2</sub>

The offerings from this industry have targeted their improvements to improve their efficiencies in power filtering and decoupling applications. The inherent problems in using  $MnO_2$  as a cathode contact are relegated to two major categories: first, the high resistance of this semiconductive material creates high ESR (effective series resistance) and an accompanying capacitance roll-off; and secondly, the material is classified as an oxidizing element and contributes to the catastrophic ignition failures.

The high ESR multiplied by the discharge current creates a step voltage that robs the allowable voltage change allowed in a decoupling application, demanding higher capacitance to compensate for this theft. The structure of the pellet in this solid device also defines an RC-Ladder that prevents the device from acting as its capacitance value, and instead acts as a much lower capacitance value initially. Both of these faults require higher capacitance to be used than theoretically required.



Improvements in the methods of process and materials showed dramatic improvements with a 'Low-ESR' family of products released (T495). Manipulation of the anode pellet's geometry created multiple anode devices (T510) which lowered the ESRs further still.

The ignition failure mode for these devices is an exothermic reaction of pure tantalum combining with free oxygen that is driven out of the  $MnO_2$  as the device goes into a failure mode. The failure is triggered by voltage (always voltage) stress that col-



lapses the dielectric at a weak point. Current into this flaw generates heat to convert the dielectric from an insulative, amorphous structure, into a crystalline, conductive structure. Heat generated in this reaction creates a release of oxygen in the MnO<sub>2</sub> adjacent to the site, as well as heating the pure tantalum on the other side of the dielectric. Free oxygen in the presence of heated tantalum combines to form crystalline  $Ta_2O_5$ , and releases large amounts of energy as heat – the ignition.

Replacing this highly resistive material has always been a goal to impact its dominating effect on ESR; but, the material to replace it must allow some type of healing mechanism to occur.

# Tantalum – Polymer

The first commercial application of the conductive polymers was in 'anti-static' sprays for clothing. In this dispersed particulate, the polymer created a conductive film that prevented the isolation of charge into small areas.

As a substitute for  $MnO_2$ , it had to have a selfhealing characteristic because we cannot make this angstrom thick film of  $Ta_2O_5$  without imperfection. There are two theories as to how these materials



create the healing effect.

One theory details that this material has almost no oxygen in its most conductive state. The absorption of oxygen in its chain structure creates an increase in resistivity – in much the same manner as oxygen depletion from  $MnO_2$  creates an increase in resistivity for that material. The healing is activated when the polymer, in contact with the isolated fault site, is heated by the current through it and absorbs oxygen from the free space within the pellet structure. As this absorption increases in time, the resistivity increases and the fault current is "pinched" off.

The other theory relies on the low boilingvaporization temperature as the mechanism of healing. As the heat from the current increases in this material, it evaporates in time, leaving an open connection to the fault site. This mechanism creates a fusing effect whereby the fault site is disconnected form the circuit.



Besides the higher conductivity of this material it is almost entirely void of oxygen, we are replacing an oxidizing agent in the capacitive structure. As such, the ignition or exothermic reaction of the heated tantalum in a shorted capacitor must rely on the free, random oxygen in the package to become active. The results are that these device fail short, but their propensity for the "spectacular" failure is dramatically reduced.

The improvement in ESR is not the same ratio of material resistivities, because we cannot load the system with a very thick application of polymer, like we can with the  $MnO_2$ . Yet the ESRs of the tanta-lum-polymer are in the range of 50% to 30% of those using the  $MnO_2$  system.

# Aluminum Polymer

Using the same conductive polymers as in the tantalum system, we now have the ability to create an anode structure using aluminum plates as the anode element and aluminum oxide as the dielectric. Unlike the previous capacitors with this structure, we

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can substitute the conductive polymers in place of the wet electrolyte for the first cathode contact.

It is built using etched aluminum foils, and the



dielectric is electrochemically created on the surface of the foil in contact with the electrolyte. The polymer is applied (polymerization) to the dielectric surface, followed by a thin film of carbon, then silver paint. The sliver pain is the outermost cathode contact and when the capacitor is built using multiple plates, a conductive adhesive is used to bind these contacts together with the leadframe. The anode contact is made by welding the other end of these plates to the leadframe allowing electrical connec-



tion to the aluminum base metal.

The change in structure basic from pellet to plate has an enormous impact on ESR for these devices. With a 47  $\mu$ F capacitor (A700 series), we were able to achieve ESRs below 20 milliohms, a level we could not achieve until we were in the 680  $\mu$ F tantalum capacitors, at that time. These devices are approaching ESR levels more like ceramic capacitors, with capacitance capability much higher than the ceramic. In addition, these devices have immeasurable loss of capacitance with applied voltage, whereas ceramics can loose a considerable amount of their capacitance.

Projections of ESR for the future are to be equal to comparative ceramic chip capacitors.

# Niobium substitute for Tantalum

Niobium is close to tantalum in the periodic chart and is a viable valve metal. There is no impetus to push niobium from a reliability and performance standpoint. The clear advantage that makes niobium a valid substitute for tantalum is pricing; just remember that pricing in many cases will rule the world. As the disparity in refined material costs become greater (niobium being lower), its penetration into the tantalum markets will rise.

Arguments discounting this material as poorer quality will be overcome by increasing the piece counts and still be cost advantageous. Present offerings of the niobium include nitrogen and oxygen doped materials – both offering higher stability over pure niobium. The key for this product's growth (as with all others) will be cost.

# Ceramic substitute for Tantalum

Most of the previous designs with tantalum that are being changed are being changed over to ceramics. Consider a filter circuit at 100 kHz, with a desired capacitance impedance of 100 milliohms. A perfect capacitor with no ESR and frequency independent capacitance would require a unit of 16 µF using 22 µF as a standard EIA value. A standard tantalum chip (T491B226M006) would have an impedance of 582 milliohms at 100 kHz, because at this point the impedance is dominated by the ESR of the device. Looking at a ceramic chip offering of 22 µF in a 1206 chip size (X5R) would offer an impedance of 76 milliohms at this frequency - a viable solution for the filter. If the tantalum was designed in previously, it would have required a larger chip with lower ESR and higher capacitance to offer a viable solution - T495D157M010 has an impedance of 92 milliohms at 100 kHz. Now with the mandate to design out where possible, this 150 µF capacitor can now be substituted with a 1206 ceramic that is 1/8<sup>th</sup> the capacitance, and near that in volume.

# **Customer Response**

As we are in the early stages of recovery, it is hard to separate what the customers are telling us their plans, from a point where demand increases and availability factors both pricing and delivery. Early indications from many manufacturers are that they are designing tantalum out. Substitutions available include aluminum (both polymer and new "wet" electrolytics) and ceramics. As the capacitance available in ceramic chips increases, the substation will increase further still. The difference in ESRs between tantalum and ceramics is still so vast that the substations are one for five or one for eight (capacitance ratios).

	In Manufacturing Use Today	In Development	Needed
Volt	CV/g	CV/g	CV/g
2 to 10V	100,000	150,000	180,000
16 to 20V	55,000	70,000	100,000
25V	23,000	28,000	40,000
35V	20,000	NA	28,000
50V	10,000	N/A	20,000

### **Tantalum Capacitor Future**

The most volumetric of the electrostatic capacitors is the tantalum capacitor. Used under proper conditions, the useful life of this product will far ex-



ceed any circuit's life expectancy. Defining these 'proper conditions' to our customers will gain them the capability of using these capacitors with no failures. Powder developments are necessary to maintain or extend the volumetric efficiency of the tantalum capacitors. Extending the polymer technology into more products will also be necessary to both improve performance and reduce risk.

The immediate future will reveal how much market share we will loose to alternative types of designs; but it is important to recognize that there is a definite goal of elimination where possible. The driving factor in any design change will not be revenge, or mistrust; but it will be cost balanced by performance. We could cut the design margins to gain volumetric efficiencies, but the results would be poor performance. We need to maintain and improve the reliability of these products as we achieve the volumetric and performance improvements; but mostly, improvements in cost.