CONDUCTIVE POLYMER BASED TANTALUM CAPACITOR FOR AUTOMOTIVE APPLICATION

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INTRODUCTION

KEMET has been manufacturing conductive polymer based surface mount tantalum capacitors (KO-CAP1) since 1999. In the last 15 years we have focused on expanding our Ta polymer capacitor portfolio to meet the increasing adoption into circuit designs. Many capabilities have been successfully introduced into the market, such as low equivalent series resistance (ESR) series for decoupling, high voltage series for DC-DC converter and power management, and high energy series for enterprise solid state drives (SSD) applications.1 A recent application trend of conductive polymer based tantalum capacitors requires high performance in harsh environments. One example is the application in the automotive industry which requires AEC-Q200 qualification. 2 Amongst all of the AEC-Q200 requirements, 3 the most challenging one for tantalum polymer capacitors with traditional technology is the highly accelerated 85 °C / 85% relative humidity (RH) with DC bias up to rated voltage for 1000 hours. Other industries such as telecommunication are also starting to request 85 °C / 85% RH qualification. The possible reason is an extrapolation based on data from other components that any device passing the 85°C/85%RH condition for 1000 hours could have a field use life 5 to 10 years under the real life environmental conditions. 4

In August 2015 KEMET launched a new series of our KO-CAP, T598, polymer based Ta capacitor, which meets the full requirement of AEC-Q200 including the 1000 hours endurance test at 85 °C / 85% RH with the load of rated voltage. 5 These new offerings allow Automotive Segment to take full advantages of KO-CAP capacitors, such as high CV/cc, low ESR for higher ripple capability, and lower profile. 1

In this paper the basic construction and manufacturing process of polymer based tantalum capacitors will be described. The challenges for polymer Ta capacitors under unbiased and biased high temperature and high humidity will be discussed. This will be followed by possible technical solutions and the performance of our current T598 series of products.

CONSTRUCTION OF POLYMER TANTALUM ELECTROLYTIC SOLID CAPACITORS

KO-CAP is a polymer based Tantalum capacitor in which conductive polymer serves as the cathode instead of manganese dioxide. The basic construction is shown in Figure 1. Figure 2 shows the scanning electron microscope (SEM) photos of conductive polymer inside an anode.

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1 KO-CAP is a registered trademark of KEMET Electronics Corporation
PROCESS OF POLYMER TANTALUM SOLID ELECTROLYTIC CAPACITORS
Manufacturing of Ta capacitors is a relatively complex process comprising more than 200 steps. An outline of this process is shown in Figure 3.

The manufacturing process of polymer tantalum capacitors begins with the pressing and sintering of micrometer-size tantalum powder to form porous pellets which are electrochemically anodized to produce tantalum pentoxide (Ta₂O₅) dielectric. Conductive polymer as the first layer of cathode is deposit onto the surface of the dielectric via in situ chemical polymerization, electrochemical polymerization, or coating by premade conductive polymer dispersion. Washing and reformation may be used as necessary after each polymerization cycle. Carbon and silver coatings are applied to connect the cathode layer to the leadframe which, after encapsulation, provides the electric connection from the capacitor to the application circuit. The molded case typically consists of epoxy compound containing a filler. It protects the capacitor from moisture, oxygen, chemical or mechanical stress. The molded semi-finished products undergo laser marking, inline burn-in, and 100% electrical testing, before final packaging into reels.

THE STEDY-STATE TEMPERATURE HUMIDITY UNBAISED LIFE

According to MIL-STD-202G, Method 103B,[4] 40 °C ± 2 °C, 95 to 98% RH humidity steady test at specified DC bias is used to detect deterioration of electrical, physical and mechanical properties of components. To be in good compliance to the standard, all tantalum polymer capacitor manufacturers commit to some level of high temperature and humidity test in the qualification plan. However, due to limited acceleration of 40 °C ± 2 °C, 95 to 98% RH this test condition is not harsh enough to simulate failures in the real world.

The most commonly adopted condition for elevated temperature and humidity is 60 °C 90% RH. It was reported that acceleration factor of 60°C 90%RH is approximately 3 times of 40°C 95%RH.[5] Most of KEMET polymer Ta capacitors meet the specification of 500 hours under 60 °C 90% RH. [1] One typical example of a KO-CAP product is shown in Figure 4(a-d).

![Figure 4 (a): KO-CAP EIA7343-28, 33 µF 25V ESR, 0.06Ω. Capacitance change post several intervals under](image-url)
60 °C 90%RH without DC voltage

Figure 4 (b): KO-CAP EIA7343-28, 33 µF 25V, ESR 0.06Ω. DF% post several intervals under 60 °C 90%RH without DC voltage

Figure 4 (c): KO-CAP EIA7343-28, 33 µF 25V, ESR 0.06Ω. ESR post several intervals under 60 °C 90%RH without DC voltage
Although all the parts demonstrated a performance well within the specification beyond the required 500 hours, some slight shift of DC leakage in the small tails of population was observed. When the conditions were further increased to 85 °C / 85% RH, the population began to demonstrate more variations in ESR shift and leakage tails. The ESR and leakage results under unbiased 85 °C / 85% RH of the aforementioned KO-CAP part types are shown in Figure 5 (a-c).

Figure 4 (d): KO-CAP EIA7343-28, 33µF 25V, ESR 0.06Ω. DC leakage tested at 25V by several intervals post 60 °C 90% RH without DC voltage

Figure 5(a): KO-CAP EIA7343-28, 33µF 25V, ESR 0.06Ω. ESR post several intervals under 85°C 85% RH without DC
Figure 5(b): KO-CAP EIA7343-28, 33µF 25V, ESR 0.06Ω. DC leakage tested at 25V post several intervals under 85°C 85% RH without DC voltage. IL= 0.1CV, µA, PL= 0.5CV, 412µA as reference

ESR changes for 85°C 85%RH and 60°C 90%RH both without DC voltage are shown in Figure 5(c). ESR increased rapidly from 250 hours to 500 hours 85 °C 85%RH. The ESR difference between 85 °C 85% RH and 60 °C 90% RH became even bigger at 1000 Hours.

Figure 5(c): KO-CAP EIA7343-28, 33µF 25V, ESR 0.06Ω. ESR shift trend comparison between 85 °C 85% RH and 60 °C 90% RH.

Another observation was that 5% more leakage tailed from 250Hrs and 1 capacitor presented much higher leakage right at the 0.5CV under 85 °C 85%RH condition.

Possible mechanism is related to the stress induced by moisture adsorption. Polymeric materials in the encapsulation and in cathode layers adsorb water under elevated humidity. Increased temperature accelerates the adsorption process. The difference of hydroscopic swelling from the layers of materials results in hydro-mechanical strain and stress similar to the stress from CTE (coefficient of thermal expansion) mismatch. The magnitude of moisture swelling stress is often comparable to or even larger than the thermal stress. This could explain the ESR increase. In addition, the adsorbed water would
facilitate chemical corrosion by the reactive chemical residuals left from the manufacturing process. The ionic conduction may lead to increased DC leakage or shorts.

THE STEADY-STATE TEMPERATURE HUMIDITY BIASED LIFE

The biased temperature and humidity test continues to grow in popularity as it is an effective way to detect failure of non-hermetically packaged solid-state devices in the field with voltage application. The combined stresses in this case are humidity, temperature, and DC voltage up to rated voltage. For moisture adsorption dominated by epoxy type molding compound the maximum adsorption concentration is determined by the relative humidity. There is also some good hope of less failure in contrast to unbiased temperature and humidity test because the conductive polymer could be thermally de-doped to prevent DC leakage failures. However, the experimental results of our T598 development proved a trend that is the opposite.

At one of examples of the development, the test results of KO-CAP EIA 3538-21, 330µF, 6.3V at 6.3V bias under 60 °C 90% RH and 85 °C 85% RH are presented in Figure 6.

![Figure 6: KO-CAP EIA 3538-21, 330µF 6.3V ESR 0.04Ω. Electrical performance during 60 °C 90% RH and 85 °C 85% RH with and without bias](image)

For all conditions capacitance went up nearly by 20%. This is well known in the Ta capacitor industry as wet to dry capacitance loss and is considered as typical for the µF/g of the Ta powder utilized to make these samples. This is attributed to some dielectric surface area that is not covered by the conductive polymer solid electrolyte but is still reachable by liquid electrolyte solution or water. DF, ESR and DC
leakage, for both biased and unbiased, 85 °C 85% RH showed more severe degradation than 60 °C 90% RH.

Due to the limitations of the test duration and sample size, it was not possible to determine the acceleration factor of 85 °C 85% RH over 60 °C 90% RH precisely. There were three noticeable differences between unbiased and biased life tests.

1. ESR increase of biased test was approximately two times of that with no bias;
2. For the life test with bias of rated voltage, instead of expected healing, DC leakage went up. There was 1 short at 60 °C 90% RH and 6 shorts at 85 °C 85% RH, both with 6.3V bias. In contrast no short was observed for the condition without bias.
3. DC leakage started to increase from 500 hours under 60 °C 90%RH biased test. It deteriorated rapidly. This seems to be consistent with the avalanche type of failure mode reported. [10]

Another example of our development was from EIA 7343-28, 33µF, 25V at 25V bias under 85 °C 85% RH (see Table 1). Figure 7 is the graphic summary of results.

<table>
<thead>
<tr>
<th>Voltage</th>
<th>0Hr</th>
<th>250 Hrs</th>
<th>500Hrs</th>
<th>1000 Hrs</th>
<th>Failures</th>
<th>Final % of change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delta Cap %</td>
<td>0V</td>
<td>0.0%</td>
<td>8.9%</td>
<td>9.4%</td>
<td>8.5%</td>
<td>0</td>
</tr>
<tr>
<td>DF</td>
<td>25V</td>
<td>0.0%</td>
<td>9.1%</td>
<td>9.2%</td>
<td>8.1%</td>
<td>0</td>
</tr>
<tr>
<td>0V</td>
<td>0.0%</td>
<td>2.01</td>
<td>2.50</td>
<td>2.77</td>
<td>2.97</td>
<td>0</td>
</tr>
<tr>
<td>26V</td>
<td>1.96</td>
<td>2.78</td>
<td>3.13</td>
<td>3.56</td>
<td>0</td>
<td>81.3%</td>
</tr>
<tr>
<td>ESR Ohm</td>
<td>0V</td>
<td>0.0247</td>
<td>0.0265</td>
<td>0.0389</td>
<td>0.0754</td>
<td>0</td>
</tr>
<tr>
<td>25V</td>
<td>0.0252</td>
<td>0.0316</td>
<td>0.0530</td>
<td>0.1126</td>
<td>16 pcs &gt; 2 x IL</td>
<td>347.1%</td>
</tr>
<tr>
<td>LEAK uA</td>
<td>0V</td>
<td>1.21</td>
<td>0.6240</td>
<td>0.8105</td>
<td>1.2628</td>
<td>0</td>
</tr>
<tr>
<td>26V</td>
<td>1.52</td>
<td>0.0680</td>
<td>0.0829</td>
<td>2.0859</td>
<td>2 &gt; IL</td>
<td>36.9%</td>
</tr>
</tbody>
</table>

Table 1: KO-CAP EIA 7343-28, 33µF 25V, ESR 0.06Ω. Biased and unbiased test results post 85 °C 85% RH with a sample size of 80 pieces. High limit for ESR was 0.12Ω, i.e. twice of initial Limit (IL)

DF, ESR and DC leakage under biased 85 °C 85% RH showed more severe degradation than unbiased. 20% ESR population was over 120 mΩ, 2 capacitors reached 0.2 to 0.3 Ω at 1000 hour interval. The most interesting observation was the leakage trend. With 25V DC voltage on capacitors, the healing effectiveness was much better than no voltage on parts until 500 hour interval, when leakage then started to increase dramatically and 2 capacitors went out of initial limit (0.1CV). This different behavior in contrast to example 1 of EIA 3538-21, 330µF, 6.3V could be explained by capacitor design and the voltage applied. Such as the formation voltage to rated voltage ratio difference: ratio 2.4 of example 1 is much lower than ratio 3.2 for example 2. It is easily to understand the voltage stress received by these 2 group of capacitors is different. Also the noticeable difference is capacitance increase, i.e. wet to solid capacitance loss: example 1 was higher than example 2, caused by different powder application and different polymerization process.
Figure 7: KO-CAP EIA 7343-28, 33µF 25V, ESR 0.06Ω. Performance under 85 °C 85% RH with and without bias

**FAILURE ANALYSIS**

In order to understand the mechanism, failed parts from both unbiased and biased 85 °C and 85% RH life tests were subjected to extensive failure analysis. Reference [11] listed the failure analysis protocols of tantalum capacitors.

**Short circuit capacitors from KO-CAP EIA 3528-20 330µF 6.3V ESR 0.04Ω**

Short parts were fractured and examined under optical microscope and then by SEM-EDS. Copper was detected along the lead wire and on the molding compound side of the fracture as shown in Figure 8 (a). It showed a dendritic morphology matching that of copper migration (see Figure 8 (b)). The suspected source of copper is the leadframe made of copper alloy with high copper content. During the process of assembly, the Ta wire is welded onto the leadframe tab, further exposing the surface of the leadframe that is un-plated.
An experiment was designed to confirm the possibility of copper migration on tantalum polymer capacitors. Some strips of polymer capacitors assembled with a copper alloy based leadframe were taken before encapsulation. A low concentration of ferric tosylate solution was applied to the strips and dried to simulate the chemical residuals from the in situ polymerization of PEDOT. Then pre-treated strips were placed into a chamber of 121 °C 85% RH with a pressure of 1.7 atmosphere. This is a similar setting to pressure cooker test (PCT). A DC voltage of 0.67Vr was applied to the capacitors and for 42 hours. Samples were pulled out and examined for electrical characteristics and visual inspection. Most of capacitors were short circuited. Dendritic copper growth on the anode and wire were observed (see Figure 9).

Krumbein described electrochemical metal migration phenomena and listed some primary factors that promote the process. [12] Four major factors are listed below:
1) Moisture from a high humidity condition at an elevated temperatures;
2) Ionic contamination on the insulator surface, from manufacturing process as mentioned in previous section;
3) Narrow spatial distance between cathode (PEDOT) and anode (wire connected to leadframe);
4) DC voltage difference between cathode and anode ( “bias”)

High ESR from KO-CAP EIA 7343-28, 33µF, 25V ESR 0.06

Parts with high ESR (see Figure 10 (a)) were cross-sectioned and inspected with SEM. ESR increase was attributed to the delamination and crack of conductive polymer layer (see Figure 10 (b)). In some cases of failure analysis, knit line cracks were observed due to inferior molding epoxy property.

![Normal Distribution of ESR 85°C/85%RH at 25V](image)

Figure 10 (a): KO-CAP EIA 7343-28, 33µF, 25V, ESR 0.06Ω. 20% ESR failures during 85 °C 85% RH at 25V. Maximum ESR reading was 0.26Ω.

![SEM pictures](image)

Figure 10 (b): KO-CAP EIA 7343-28, 33µF, 25V, ESR 0.06Ω. Typical SEM picture of higher ESR 0.12 Ω to 0.26Ω at Figure 10 (a). Crack and delamination was found.

The crack of polymer typically happened at corner of capacitors where the stress from moisture induced swell is highest due to the curvature. Another hypothesis was conductive polymer de-doping. With a delamination generated and high DC voltage at the presence of ionic species, conductive polymer could
be chemically de-doped result in a reduction of conductivity. The four major factors list for high leakage and shorts could also contribute to the ESR fliers.

**IMPROVEMENT TO ACHIEVE 85 °C 85% RH AT RATED VOLTAGE ENDURANCE**

With consideration of the construction and process of Ta polymer capacitors, following 8 recommended design actions were list to mitigate the copper migration, conductive polymer delamination and de-dope.

1) Moisture from a high humidity condition at an elevated temperatures;
   - I. Use lower moisture permeability mold compound
   - II. Use an improved mold compound that exhibits better self-joint or knit performance
   - III. Optimize the application of moisture barrier to polymer capacitors

2) Ionic contamination on the insulator surface, from manufacturing process as mentioned in previous section;
   - IV. Further optimize polymerization and wash processes
   - V. Reduce ionic species in mold compound, in combination with action I

3) Narrow spatial distance between cathode (PEDOT) and anode (Ta wire connected to leadframe);
   - VI. Improve the wire laser clean technology

4) Leadframe substrate and plating
   - VII. Noble plating on the positive welding area, restrain of cost and effect
   - VIII. Use different alloy with more resistance to corrosion

Among many factors that contribute to the performance of Ta polymer capacitors under high humidity and temperature moisture adsorption may be arguably the most important. JESD22-A120 \([13]\) described the Test Method for the Measurement of Moisture Diffusivity and Water Solubility in Organic Materials Used in Integrated Circuits. Although it has clear definition of the sample preparation and measurement method, it does not address the moisture adsorption by the finished product. For example, the poor adhesion between epoxy molding compound and the leadframe may leave some gap at the egress. The construction may have metal pieces blocking the path of the moisture diffusion (see Figure 11). In some cases, the cathode layers may be more hydrophilic and hence promote moisture adsorption.

![Possible path of moisture adsorption into Ta polymer capacitor](image)

**Figure 11:** Possible path of moisture adsorption into Ta polymer capacitor
During the development, the moisture adsorption of finished parts made with different mold compounds was studied. KO-CAP EIA 7343-28 33μF 25V was used in the study. The procedure described in JESD22-A120 \(^{(12)}\) was closely followed. Enough parts were selected to allow the detection of weight change due to moisture adsorption by using an analytical balance. Parts were dried at 125 °C for 72 hours before being placed in a humidity chamber set at 75 °C and 97% RH. They were taken out and weighed at different time intervals. The weight gain versus exposure time (soaking time) was shown in Figure 12. Epoxy molding compound C showed lowest moisture adsorption by the finished parts and was selected for our design in conjunction with the material properties listed in Table 2.

Table 2 Mold compound physical and chemical properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>EMC-A</th>
<th>EMC-B</th>
<th>EMC-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>In mass production</td>
<td>New</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture solubility</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Tab pull (on Cu)</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>CTE</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
</tr>
</tbody>
</table>

![Figure 12: KO-CAP EIA 7343-28, 33μF, 25V, ESR 0.06Ω. Moisture absorption of capacitors under 75 °C 97% RH by different soak hours.](image)

The group of capacitors using EMC-C did show the least ESR shift post 85 °C 85%RH without DC bias (see Figure 13). Additional benefit was improved ESR performance during 125 °C life for 1000 hours.
Figure 13: KO-CAP EIA 7343-28, 33µF 25V, ESR 0.06Ω. ESR performance 85 °C 85%RH without bias. Comparison between EMC-A, B, C under 85 °C 85%RH without bias. IL= initial limit, PL= post Limit

In order to reduce ionic residuals to prevent copper migration a number of experiments were performed by improving polymerization. The ionic residuals as measured by conductivity of an extraction solution was reduced by more than 50% (see Figure 14). Meanwhile the polymer coverage was also improved (see Figure 14 SEM surface Scan).

Figure 14: Improvement of Ionic content % of KO-CAP. Pictures are SEM surface scan post polymerization

Left is before wash and polymerization improvement, right is after

In addition to the epoxy molding compound and polymerization improvement, a type of leadframe with a good corrosion resistance was implemented in addition to further optimizing the moisture barrier coating that has been used for many years at KEMET. These new material and process improvements have enabled KEMET to qualify the KO-CAP to meet full AEC-Q200 requirements. Initial part number offering includes capacitance up to 330µF and 16V rated voltage. Figure 15(a) was ESR performance of KO-CAP 100µF 16V commercial grade parts tested at 85 °C 85%RH without 16V Bias. ESR shift was a concern. Figure 15
(b) is ESR performance of Auto grade T598. Leakage performance improvement presented in Figure 15 (c-d).

Figure 15(a): ESR performance of KO-CAP EIA7343-20 100μF 16V, ESR 0.05Ω commercial grade parts tested at 60°C 90%RH with 16V bias

Figure 15(b): ESR performance of KO-CAP EIA7343-28 100μF 16V, ESR 0.05Ω. T598 Auto grade parts tested at 85°C 85%RH with 16V bias
Figure 15(c): Leakage performance of KO-CAP EIA7343-20 100µF 16V, ESR 0.05Ω. Commercial grade parts tested at 60 °C 90%RH with 16V bias.

Figure 15(d): Leakage performance of KO-CAP EIA7343-28 100µF 16V, ESR 0.05Ω. Auto grade parts tested at 85 °C 85%RH with 16V DC bias. *DC leakage is well within initial limit*

KEMET plans to expand the T598 product line with additional part numbers for the automotive market and to develop a new series (T599) that has 150 °C 1000 hour life in addition to the specification of T598 in the near future. This would further expand the application of tantalum polymer capacitor in the automotive and other market where harsh operating environment is of concern.
ACKNOWLEDGE

The authors acknowledge the great contribution and cooperation of KEMET R&D and Technical Marketing team members across multiple locations.

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