Effect of Moisture on Characteristics of Surface Mount Solid Tantalum Capacitors

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Abstract

Several types of molded chip, CRW09-style tantalum capacitors were subjected to environmental stresses, including various humidity testing (20 °C/100% RH, 85 °C/85% RH, 121 °C/100% RH, and 135 °C/85% RH) and high temperature air and vacuum bakes. Variations of the AC (frequency dependencies of C and ESR) and DC (polarization currents) characteristics during these tests, as well as the kinetics of the parametric changes, have been analyzed. To estimate times of moisture ingression into the parts, coefficients of moisture diffusion and sorption have been measured for two types of epoxy molding compounds in temperature range from 30 °C to 170 °C. A sleeping cell model has been suggested to explain parametric changes in tantalum capacitors caused by environmental conditions. Moisture-related degradation of materials used in tantalum capacitors, failure mechanisms, and the effectiveness of the existing moisture resistance qualification testing are discussed.

1. Introduction.

Surface mount solid tantalum capacitors used in military and aerospace applications are typically manufactured in non-hermetic plastic cases. Moisture can penetrate through polymer encapsulating materials degrading characteristics of the solid electrolyte, cathode attachment materials, and tantalum pentoxide dielectric, and causing failures of the capacitors.

Several failures of DC-DC converters caused by short circuits in solid tantalum chip capacitors used in the output circuits of the converters were observed at the Goddard Space Flight Center Parts Analysis Laboratory. In some cases failures occur in parts, that had never been used before but failed during initial bench testing. There were not any indications that these failures are related to moisture effects; however, the root cause for the failures was not clear.

Numerous failures in solid tantalum capacitors caused by humid environments have been reported by Robert Dobson, Raytheon, St. Petersburg [1]. The rate of failures for the parts in the "as received" condition was as high as 1% after storing for a few months at "Florida"-type environments. Note, that these parts were manufactured without silicone barrier layers. The observed failures were not related to a particular lot or vendor of the parts, but rather appeared as a problem specific to all plastic encapsulated tantalum capacitors in humid environments. It was speculated that the failure mechanism is related to the moisture-induced silver dendrite growing from cathode contacts [2]. After shorting, these dendrites are "arcing", igniting the manganese oxide and creating a powerful chemical reaction, thus causing catastrophic failure of the part. However, no evidence supporting the dendrite growth hypothesis was given and the physical mechanism of failures of tantalum capacitors in humid environments remained unclear.

Analysis of the available technical literature failed to reveal any publications related to degradation of the characteristics of solid chip tantalum capacitors in humid environments. Also, we could not find any data on moisture characteristics of molding compounds (MC) used for encapsulation of solid chip capacitors.

In this work, we explore variation of AC and DC characteristics of four types of CRW09-style capacitors caused by different environmental conditions. Moisture sorption and diffusion coefficients were measured for two types of MC in a wide temperature range. Analysis of these experiments gave some insight to the physical processes going on in tantalum capacitors in humid environments.

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2. Experiment

Four groups of surface mount CWR09 type tantalum capacitors manufactured by one supplier were chosen for the experiments performed herein. The parts were manufactured in transfer-molded packages and are described in Table 1.

Table 1. Characteristics of parts.

Part Type	Capacitance	Voltage Rating	Lot Date Code
CWR09JC226KC	22 uF	20 V	9804
CWR09MC685KC	6.8 uF	35 V	9821
CWR09NC475KC	4.7 uF	50 V	9822
CWR09KC106KC	10 uF	25 V	9723

All capacitors had previously passed Weibull grade testing at the "C" failure rate level (0.01%

failures/1000 hours) as part of their screening to the military specification. This screening provides high confidence in the quality of the parts used in our experiments.

Measurements of the AC characteristics (C, ESR, and their frequency dependencies) were carried out using a hp4192A impedance analyzer and the DC characteristics (leakage current and polarization curves) using a Keithley 237 high voltage source measurement unit. Both instruments were incorporated into a PC-based system, which allowed automatic measurements and recording of the C(f), ESR(f), and I(t) characteristics. All environmental experiments were performed on groups of 10 capacitors of each part type.

3. Results.

3.1. Effect of baking and storing in humid conditions.

The first set of environmental experiments was performed to evaluate variation and reproducibility of parameters of the capacitors caused by a sequence of various baking, room temperature storing, vacuum, and humidity chamber conditions. In these experiments, following the initial measurements, the parts were tested after 72 hrs./125 ^{o}C bake; after 168 hrs./85 ^{o}C/85% RH humidity chamber; after baking at 150 ^{o}C for 24, 48, and 72 hrs.; after 2-month storing in laboratory (RH ~50%) at room temperature; after 1 week of baking in vacuum at 150 ^{o}C; and finally after repeat 6-month storing in laboratory conditions. Results of these experiments for the 4.7 uF capacitors are shown in Figure 1.

It is seen that the environmental conditions had no significant effect on the ESR and leakage currents. However, capacitance variations were notable, reproducible, and consistent with the variations of environmental humidity. Similar results were obtained for all tested part types. Average variations in capacitance after some environmental conditions for all tested part types are shown in Figure 2.

Test results show that the capacitance in dry conditions for different part types is 2% to 12% less than in humid conditions (85% RH). After long-term storage in laboratory conditions (T ~22 ^{o}C and RH ~ 50%), the values of capacitance are only 5% to 15% less than the values after 85 ^{o}C/85% RH humidity chamber. Long-term vacuum baking at 150 ^{o}C (168 hours) and air baking at 125 ^{o}C for 72 hrs. or at 150 ^{o}C for 24 to 72 hrs. result in virtually the same values of the capacitance.
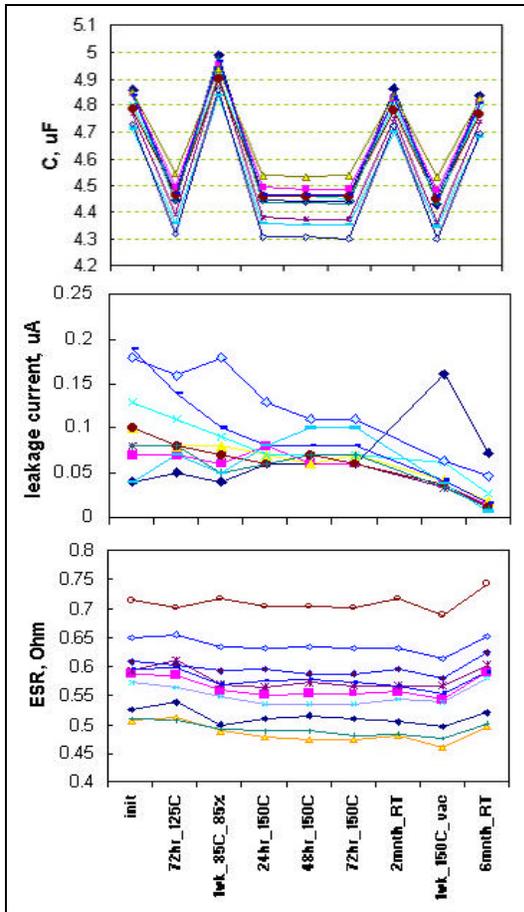
Figure 1. Variation of capacitance, DCL, and ESR for the 4.7 µF capacitors measured after different environmental conditions, sequentially: 72 hrs./125 °C bake; moisturizing at 85 °C/85% RH for 168 hrs.; bake at 150 °C for 24, 48, and 72 hrs.; 2 months at RH ~50% and T ~22 °C; 1 week baking in vacuum at 150 °C; and 6 months at RH ~50% and T ~22 °C (laboratory conditions).

As shown in Figure 3, the frequency dependencies of ESR for the parts tested after humidity chamber and after baking are similar. The C(f) characteristics are also similar except for the values of capacitance at frequencies below a few kHz being larger for the moisturized parts.

Figures 4 a-d show polarization currents for the 10 µF capacitors after different baking and moisturizing conditions. Similar curves were obtained for other types of capacitors. A linear decay in double logarithmic coordinates of the I(t) curves and a trend of saturation with time suggests that the forward currents are a sum of the absorption currents, which decay with time according to the power law (electron hopping transport), and the conduction currents, which do not depend on time and can be described by the Pool-Frenkel mechanism [3]. It is seen that neither

absorption currents nor conduction currents change any significantly due to 1-week moisturizing at $T \leq 85$ °C.
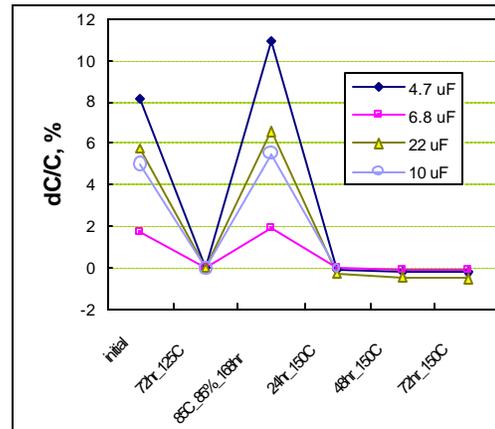
Figure 2. Average capacitance variations for different part types. The variations are normalized to the values of capacitance measured after baking at 125 °C for 72 hours.
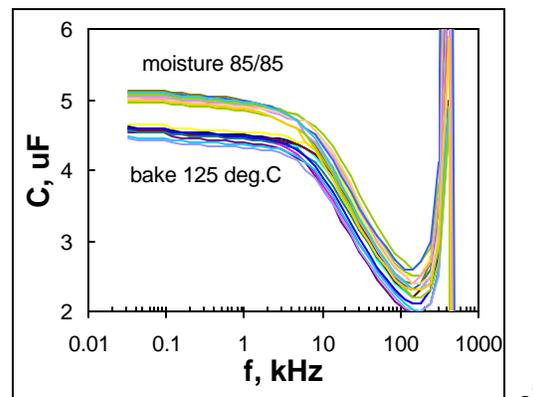
a)
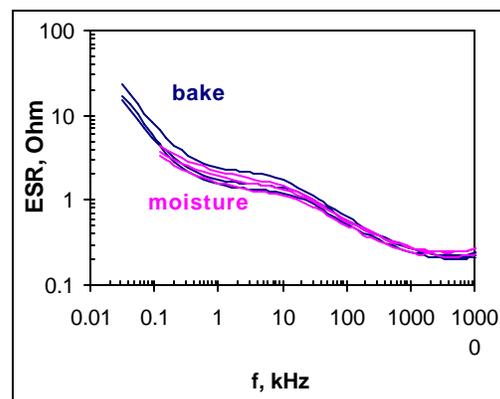
b)

Figure 3. Effect of humidity chamber (168 hrs. 85 °C/85% RH) and bake (72 hrs. at 125 °C) on frequency dependence of capacitance (a) and ESR (b) of the 4.7 µF capacitors. No significant variation in the roll-off effect was observed.
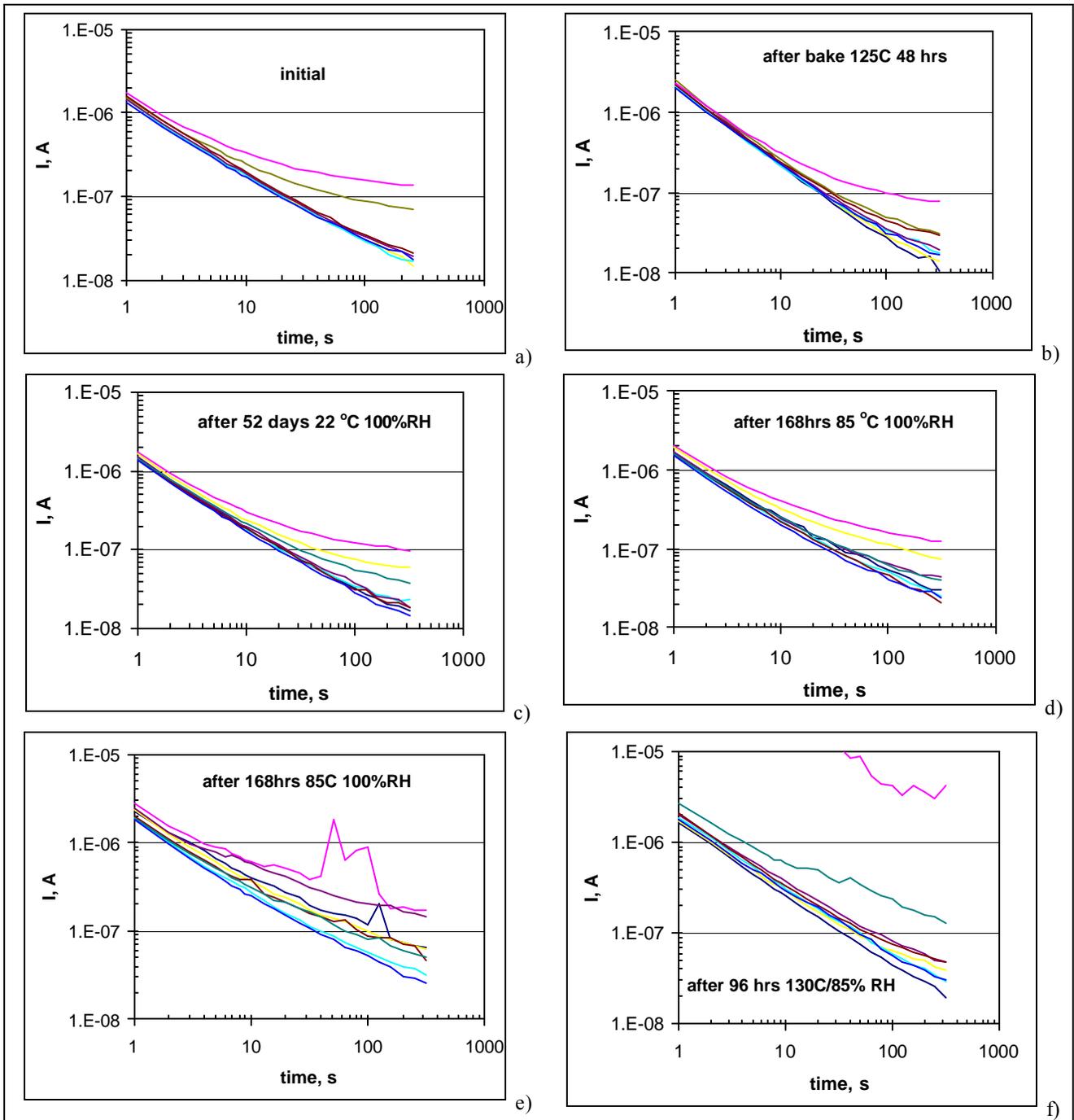
Figure 4. Forward current decay in the 10 µF capacitors at 50 V. Note that no changes in the I(t) curves occurred after storing at 100% RH for 52 days at room temperature and after 1 week at 85 ^{o}C. Accelerated testing at T = 121 ^{o}C (Figure e) and 130 ^{o}C (Figure f) resulted in increase in the conduction leakage currents; however, absorption currents did not change. Note also that the same part, which had maximum leakage current initially, failed eventually after accelerated humidity testing.
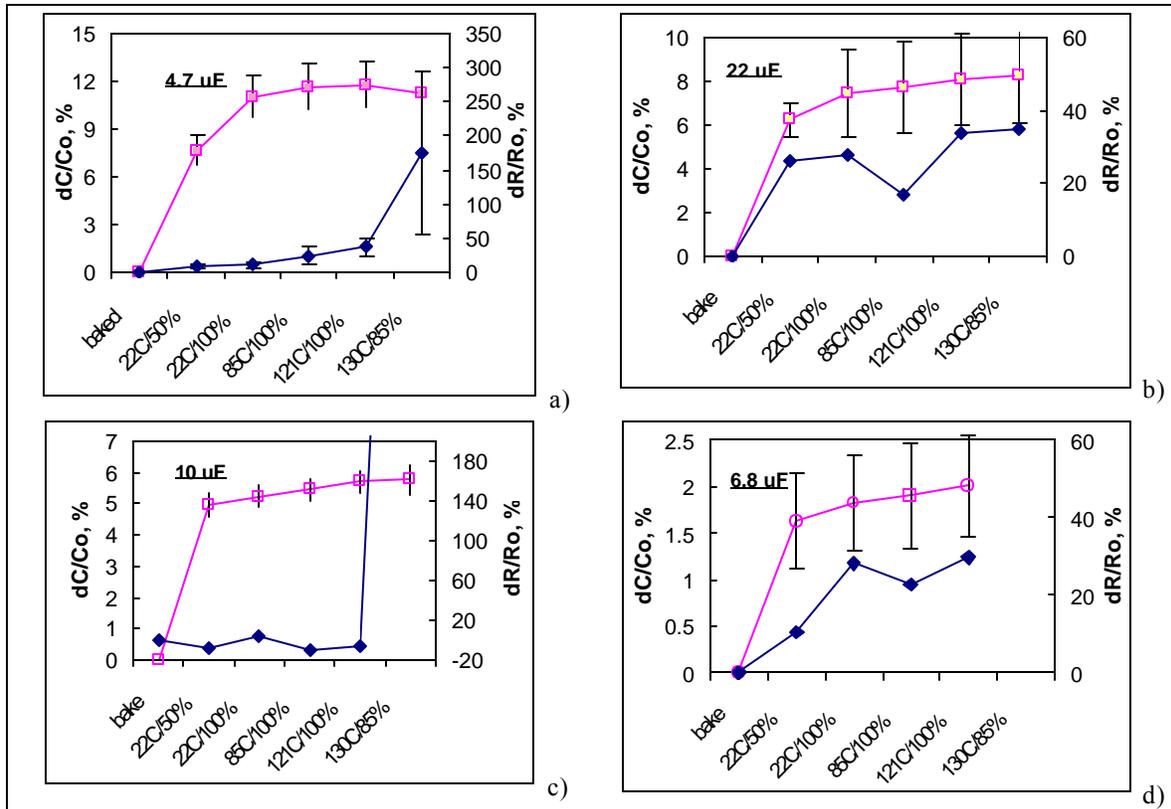
Figure 5. Average variations in capacitance (square marks) and ESR (dimond marks) for four types of capacitors with increasing temperature of humidity stress testing. Note that an increase in temperature did not affect considerably capacitance variations; however, ESR for the 4.7 mF and 10 mF capacitors significantly increased after 130 °C.

3.2. Effect of highly accelerated humidity testing.

Due to a low failure rate at temperatures ≤ 85 °C, moisture resistance of contemporary plastic encapsulated microcircuits (PEMs) is evaluated at higher temperatures using accelerated humidity testing. Typically, two types of testing are used: a saturated humidity test or pressure cooker testing (PCT), which according to JESD22-A102-C standard is performed at 121 °C and 100% RH, and a highly accelerated stress testing (HAST), which per JESD22-A118 standard is performed at non-saturated moisture conditions of 85% RH at 130 °C. Both of these tests were used to evaluate parametric changes in tantalum capacitors. The PCT testing was performed during 72 hours and the HAST testing during 96 hrs.

Variations of the C and ESR, caused by accelerated stress testing, together with the results of measurements at 22 °C/100% RH and 85 °C/100% RH are displayed in Figure 5. The increase in capacitance

that occurred after humidity testing at high temperatures of 121 °C and 130 °C is similar to that observed after the low temperature humidity tests. The ESR values significantly increased for the 4.7 uF and 10 uF capacitors only after 130 °C testing.

Accelerated humidity testing has caused significant changes in the C(f) and ESR(f) characteristics (see Figure 6). These tests resulted not only in increased capacitance at low frequencies, but also caused notable reduction of the roll-off effect, suggesting a decrease in the effective resistance of the manganese layer. For the 22 uF capacitors no variations of ESR were observed at 100 kHz (the rated frequency for the ESR measurements); however, the resistance in the range from 1 to 3 MHz increased two to three times. These variations are most likely due to increased resistance of the cathode attachment materials and might be a result of oxidation of solder or silver particles in the silver epoxy adhesive.
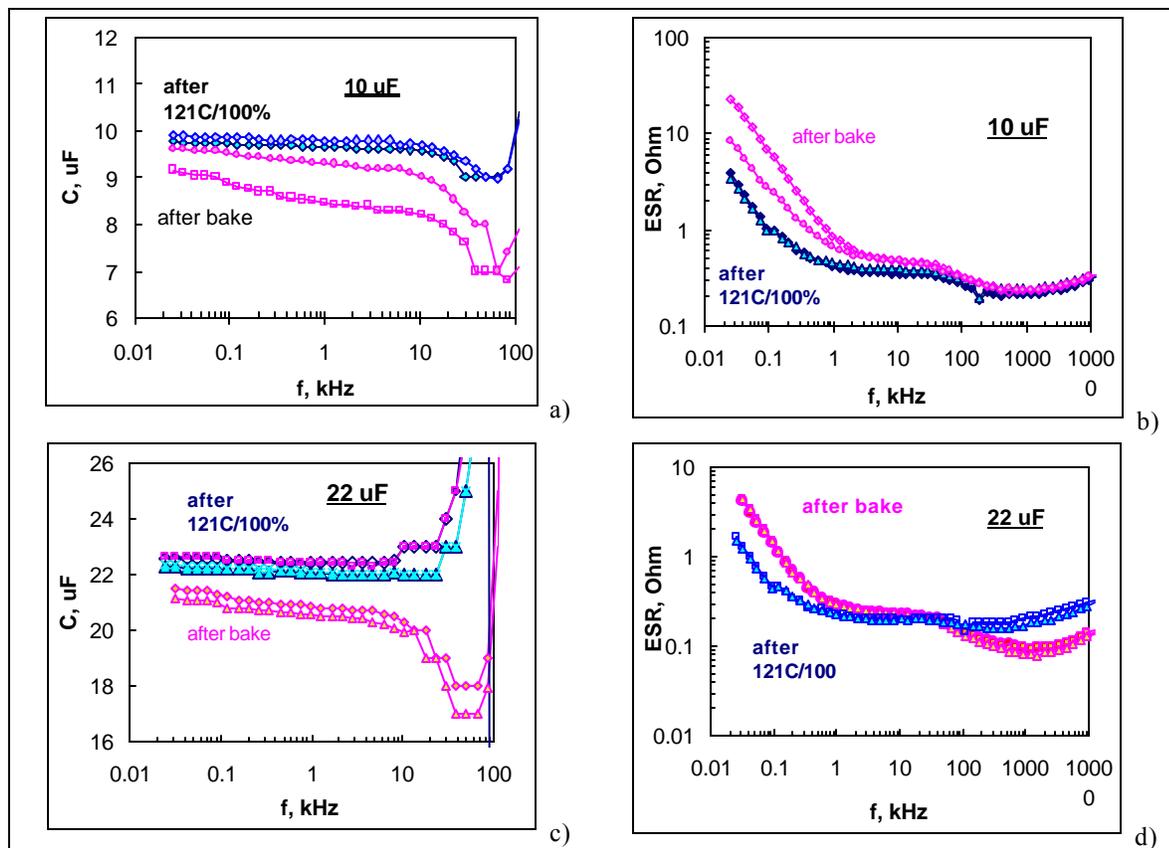
Figure 6. Effect of accelerated humidity testing (PCT) at 121 °C/100% RH on frequency characteristics of capacitance (a, c) and ESR (b, d) for the 10 μF (a, b) and 22 μF (c, d) capacitors. Note a significant reduction in the capacitance roll-off effect for both parts and an increase in ESR in the MHz range for the 22 μF capacitors.

Typical results of measurements of the polarization currents after accelerated testing are shown in Figures 4 (e, f) and 7. For the 22 μF capacitors, exposure to high humidity at 121 °C and 130 °C resulted in the upward shift of the current decay curves without any significant changes in the slope. This indicates an increase in the density of traps responsible for the electron hopping transport mechanism. However, the 22 μF parts had no failures even after 130 °C/ 85% RH testing. For the 10 μF capacitors the absorption currents did not change significantly, but the conduction currents in several samples increased notably, causing a failure in one of the parts. The behavior of leakage currents in the 4.7 uF and 6.8 uF capacitors was similar to the 10 μF parts; however, the proportion of failures after 130 °C/85% RH test was larger: 40% and 60% for the 6.8 μF and 4.7 μF parts,

respectively. Note also that one of the 6.8 μF parts failed after testing at 85 °C/100% RH for 168 hours.

3.3. Moisture diffusion characteristics of molding compounds.

Moisture characteristics were measured on two types of epoxy molding compounds (MC1 and MC2) designed for use in high volume production of tantalum capacitors. Type MC1 is a widely used product featuring low moisture absorption, low ionic level, and temperature cycling stability. MC2 is a new, specially formulated composition featuring ultralow-stress performace in combination with high glass transition temperature and flextural strength properties.
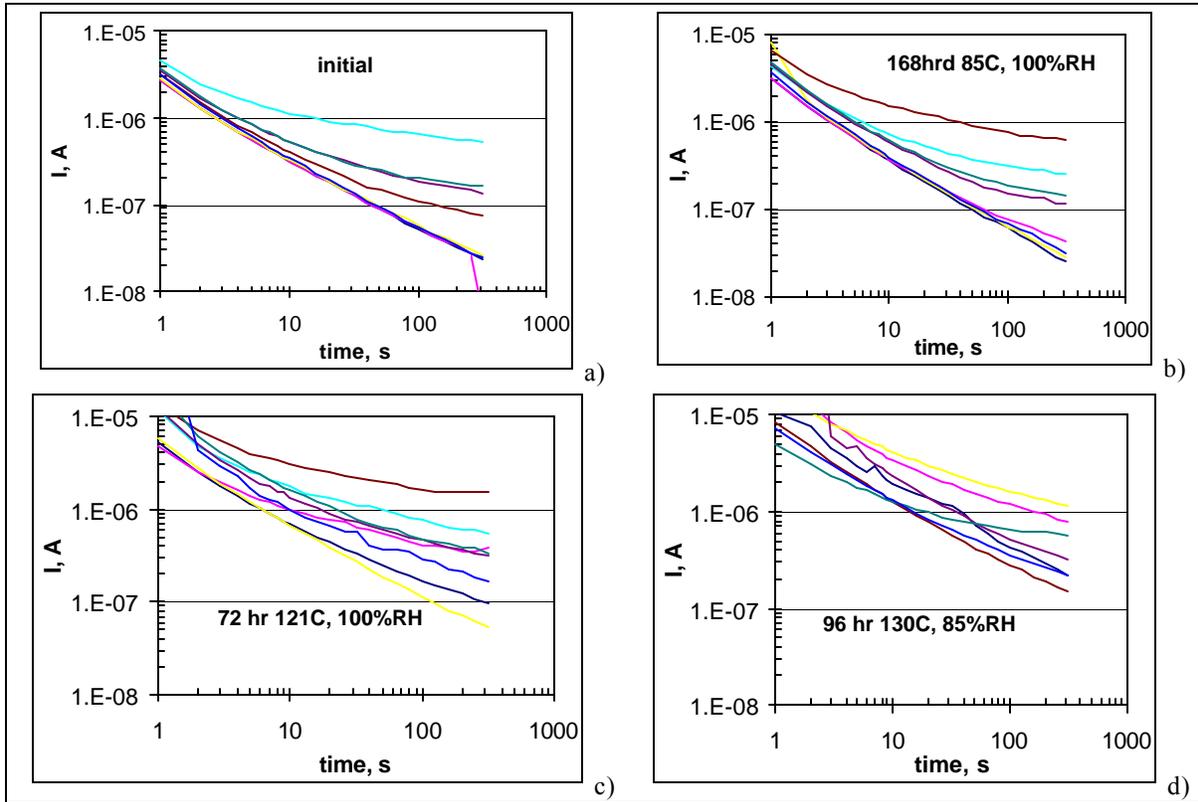
Figure 7. Forward current decay in the 22 μF capacitors at 20 V. Note a three to five times increase in the currents without any significant changes in the slope of the curves, suggesting an increase in the density of electron traps.
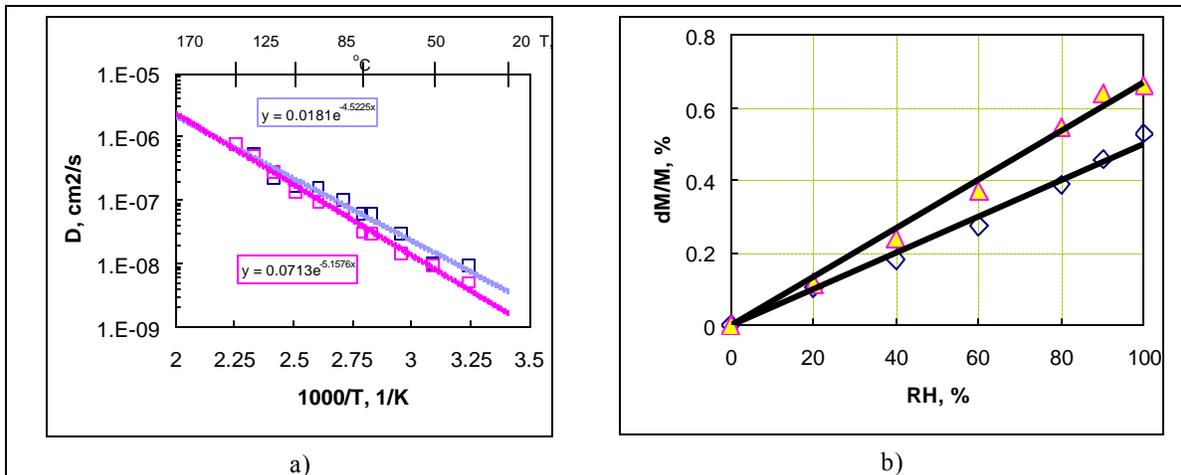
Figure 8. Temperature dependence of the moisture diffusion coefficients (a) and sorption isotherm at 85 ^{o}C for two types of molding compounds.

Experiments were carried out on three samples of each type of MC formed as discs of ~ 2 mm of thickness and 20 mm of diameter. Temperature dependence of the diffusion coefficient, D(T), was measured using a non-isothermal gravimetric technique described in [4]. The samples were saturated with moisture in a humidity chamber at 85 ºC/85% RH for 168 hours and weighted on a scale with accuracy of 0.1 mg. Then the samples were placed in a thermal chamber, which was programmed to perform cycles consisting of a fast heat up to the preset temperature, linear temperature increase during 15 minutes, and then fast cooling down to room temperature. After weighting at room temperature, the heating cycle was repeated starting with the maximum temperature at which the previous cycle had been completed. Typically from 10 to 12 measurements were taken in the range from 30 ºC to 170 ºC in 15 ºC increments.

Averaged results of these measurements are plotted in Arrhenius coordinates in Figure 8a. The D(T) characteristics are in reasonable agreement with Arrhenius law:

$$D(T) = D_o \exp(-U/kT)$$

where D_o is the constant, U is the activation energy, T is the absolute temperature, and $k = 1.38 \times 10^{-23}$ J/K is the Boltzmann's constant.

Using the best fit approximation technique, the constant D_o and activation energy U were calculated to be 7.13 10^{-2} sm^2/s and 0.43 eV for MC1 and 1.81 10^{-2} sm^2/s and 0.38 eV for MC2. These values are fairly close to typical characteristics of epoxy MC used for PEMs [5].

Moisture diffusion characteristics allow for calculation of the characteristic time of moisture diffusion in the package [5]:

$$\tau_D(T) = h^2/D(T)$$

where h is the thickness of molding compound. The τ_D corresponds to the time after which the concentration of moisture at the surface of the chip is stabilizing. The thickness of the MC for the tested CRW09 capacitors is typically 0.5 mm; however, variations from 0.3 to 1 mm were also observed. Calculations for capacitors with h = 0.5 mm encapsulated in two types of molding compounds yield the characteristic times of moisture diffusion at room temperature of 385 hours and 200 hours for MC1 and MC2, respectively.

Another important moisture characteristic of molding compounds is the sorption coefficient η, which reflects the capability of material to absorb moisture.

In equilibrium conditions the concentration of moisture in polymers is described by Henry's law, according to which the equilibrium moisture uptake increases linearly with the pressure of moisture vapor, P:

$$dM_\infty = \boldsymbol{h} \times P = \boldsymbol{h} \times P_s \times (RH)$$

where P_s is the pressure of saturated water vapor; RH is the relative humidity.

The moisture sorption coefficient was calculated based on measurements of sorption isotherm at 85 ºC (see Figure 8b). The samples were weighted after moisture uptake saturation had been reached (after approximately ~168 hrs.) at each of the humidity conditions in the range from 20% to 90% RH. The calculations yield η = 5.3 10^{-3} s^2/m^2 for MC1 and 3.9 10^{-3} s^2/m^2 for MC2. Note, that η exponentially decreases with temperature resulting in a weak dependence of the moisture uptake on temperature.

a)

b)
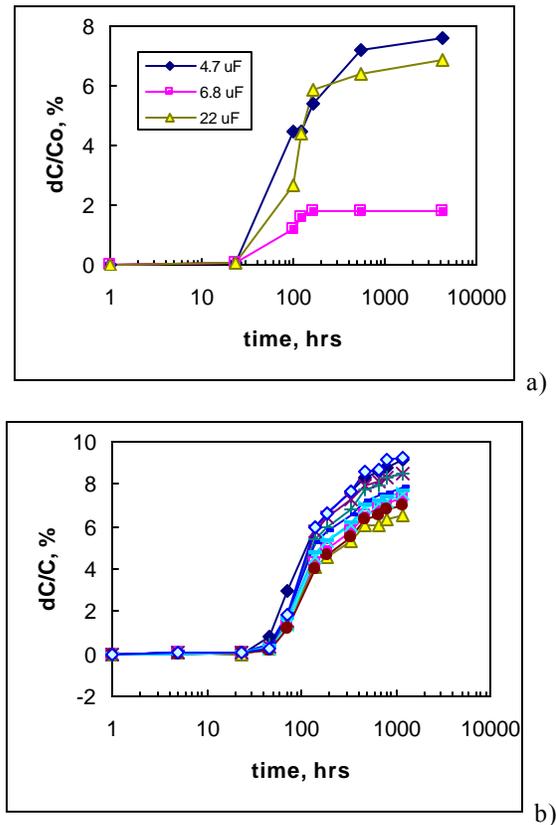
Figure 9. Kinetics of capacitance variations after bake at 125 ºC for 72 hours. Figure 9a shows averaged variations for three part types and Figure 9b shows reproducibility of these variations for all tested 4.7 μF capacitors. Note the kinetics features and induction period and saturation, which are specific to diffusion processes.

3.4. Kinetics of parametric variations.

Kinetics of the capacitance relaxation in laboratory conditions (T ~22 ^{o}C, RH ~50%) after bake at 125 ^{o}C for 72 hours during up to 5000 hours is shown in Figure 9. The presented C(t) characteristics feature an induction period, during which the characteristics remain stable, and saturation, which occurs after a long enough time. Both features are specific for diffusion-related processes. In our case the induction period was approximately 30 to 50 hours, and the saturation occurred after approximately 200 to 500 hours. These data are in reasonable agreement with the calculated characteristic time of moisture diffusion.

Similar kinetics were observed also during relaxation of capacitance after humidity chamber testing (Figure 10a) and during vacuum testing of the parts at room temperature (Figure 10b).

a)

b)
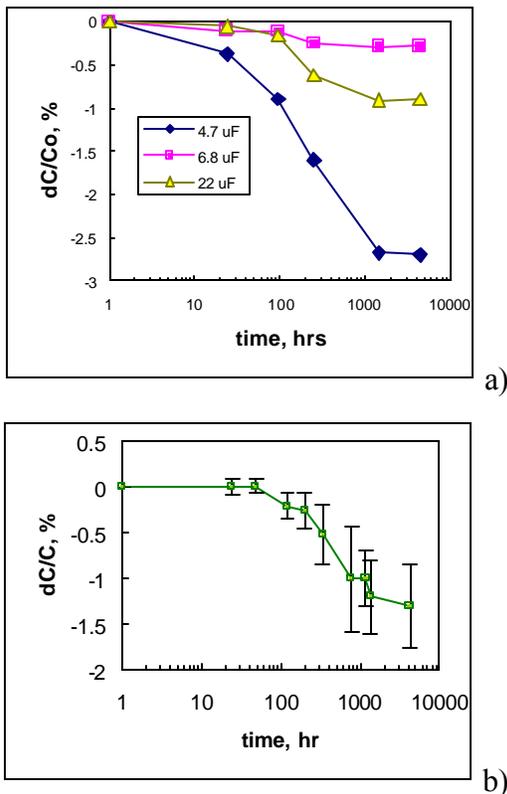
Figure 10. Kinetics of the capacitance relaxation at laboratory conditions (T ~22 ^{o}C, RH ~50%) after humidity chamber testing at 85 ^{o}C/ 85% RH for 168 hours (a) and during vacuum testing at room temperature (b).

4. Discussion.

Tantalum capacitors are manufactured by sintering of a highly dispersed, micrometer-size tantalum powder, which forms a sponge-like porous structure of a pellet with a high surface-to-volume ratio. After anodization of the tantalum pellet and formation of the tantalum pentoxide dielectric, a cathode electrode is applied by dipping the pellet into a manganese nitrate solution. The following pyrolysis at T ~250 ^{o}C to 270 ^{o}C transforms manganese nitrate into a conductive (specific resistance of 5 to 10 Ohm*cm) manganese dioxide layer [Mn $(NO_3)_2$ → Mn O_2 + $2NO_2$↑]. The highly porous structure of the pellet makes it difficult a complete coverage of the whole area of the dielectric, so that some areas might remain uncovered by the manganese oxide.

Besides, during the pyrolyses of the manganese nitride the substance shrinks, creating microscopic voids and gaps between the manganese dioxide and the adjacent surface of Ta_2O_5 [6]. Due to high dielectric permittivity of tantalum pentoxide (ε =27), a gap of only a few nanometers can significantly reduce the capacitance of a surface element compared to a gap free one. This indicates the presence in the structure of tantalum capacitors of capillary-like passive cells without an intimate cathode contact. These cells reduce the capacitance of the parts in proportion to the ratio of the actual cathode contact surface to the whole surface of the Ta_2O_5 dielectric. The size of the passive cells is most likely in the range from tens of nanometers to micrometers.

4.1. Sleeping cells model.

The observed experimental data of capacitance variations in dry and humid environments can be explained assuming that these passive cells remain in a dormant state until they are activated by absorbed moisture. In humid environments moisture diffuses into the passive or sleeping cells, creating a conductive layer on the surface of the dielectric. This water layer plays a role of a cathode electrode, which connects the passive area to the surrounding manganese dioxide, thus increasing the capacitance of the part as it is shown schematically in Figure 11.

To activate a sleeping cell, the resistance of the moisture layer should be low enough to provide necessary electrical conductivity over the passive area and to allow "sensing" of the capacitance at high enough frequencies. This resistance can be estimated considering an equivalent circuit of the cell as a distributed R-C ladder. Figure 12 shows a schematic of such a circuit and kinetics of the distribution of potentials at the surface of the Ta_2O_5 dielectric. The characteristic time of the potential variations depends on the size of the passive area, l, and can be estimated as $\tau_p = \rho \times C_o \times l^2$, where ρ is the specific surface resistance and C_o is the specific capacitance of the

tantalum pentoxide dielectric ($C_o = \varepsilon \times \varepsilon_o / d$, where $\varepsilon_o = 5.58 \ 10^{-12}$ F/m is the permittivity of vacuum and d is the thickness of the oxide).
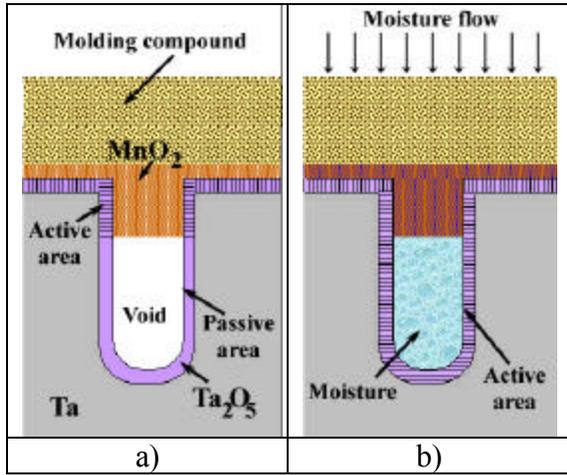
Figure 11. Sleeping cells model. Right picture (a) illustrates dry conditions and left (b) after activation by moisture sorption.
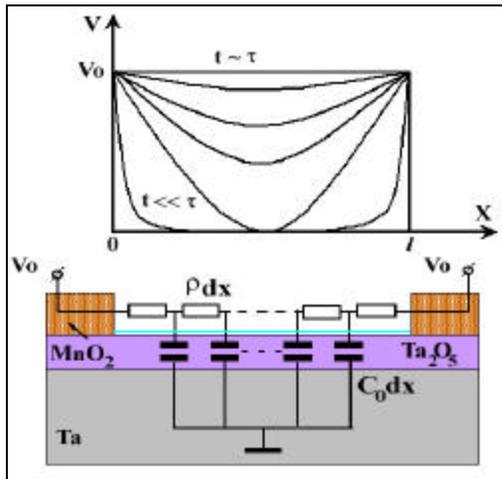
Figure 12 . Equivalent circuit of the passive area of a sleeping cell and distribution of the potential along the surface of tantalum pentoxide layer after applying a step-like voltage to the capacitor.

To "sense" the capacitance in the passive area, the value of τ_p should be much less than the period of the AC signal, $1/f$. This allows for estimation of the maximum permissible surface resistance of the moisture film, which would provide necessary conductivity of the cathode:

$$\rho_{max} = d/(f \times \varepsilon \times \varepsilon_o \times l^2)$$

The results of calculations for a capacitor with a thickness of the Ta_2O_5 dielectric of 100 nm and the size of sleeping cells varying from 1 nm to 10 μm are shown in Figure 13. In the frequency range of interest (below approximately 10 kHz, which is typically an onset point of the roll-off effect) and for a micrometer-size of the passive area, the surface resistance in the active cell should be below ~10^9 Ohm.
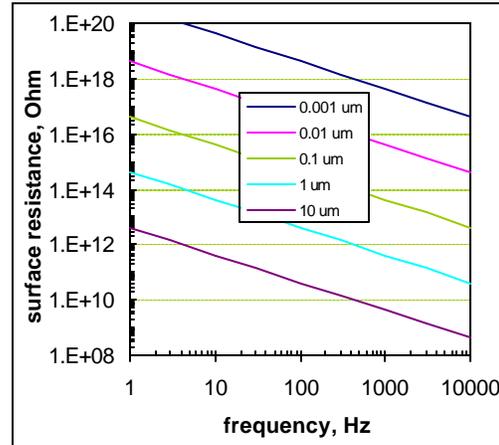
Figure 13. Frequency dependence of the maximum specific surface resistance of the cathode electrode, which allows for "sensing" of the passive areas of different size (from 1 nm to 10 μm).

There are several possible processes of activation of the sleeping cells in moisture environments, which might differ by their kinetics and the effectiveness in formation of the conductive cathode electrode. These processes include formation of a moisture-adsorbed layer, capillary condensation, and moisturizing of the hygroscopic remnants in the cell. Details of these processes are considered below.

4.1.1. Formation of moisture absorption films.

Even at high humidity approaching 100%, moisture forms extremely thin films of only a few monolayers on the surface of oxide dielectrics. The specific surface conductivity of these films for different silicon oxide substrates varies from 10^{-10} to 10^{-13} Ohm^{-1} at RH ~100% and exponentially decreases on two to three orders of magnitude when the relative humidity decreases to ~50% [7]. The formation of these films follows humidity variations virtually without any delays.

Unfortunately a literature search revealed no data on surface conductivity of Ta_2O_5 films. However, even assuming that this conductivity is more than ~10^{-10} Ohm^{-1} at RH ~100%, the necessary level of resistivity can be achieved for very small passive areas of below

~1 µm only. Besides, our experiments show that the decrease of humidity from 100% to 85% and even to 50% causes relatively minor changes in the capacitance, which is difficult to explain by the moisture adsorption film mechanism.

4.1.2. Capillary condensation.

Let us consider a case in which moisture is condensing into a capillary cell with a radius r and length L under the surface of molding compound of a thickness h. For simplicity, we assume that this process starts after a steady moisture concentration distribution over the thickness of molding compound has been established. Also, layers of manganese, graphite, and silver epoxy are considered much thinner and more porous than molding compound, so they do not delay moisture penetration to microvoids in the tantalum pellet.

In this case moisture diffusion flow into the cell is:

$$\frac{dm}{dt} = \frac{D \times h \times (P_o - P_r) \times pr^2}{h}$$

where r is the radius of the cell, and Po and Pr are partial moisture pressures outside the package and inside the cell.

In the cell the vapor of mass Δm is condensing, thus increasing the thickness of the water layer on Δx:

$$\Delta m = pr^2 \times r \times \Delta x$$

where ρ is the specific density of water.

These equations allow for calculation of the time θ, which is necessary to fill up a capillary cell of the length L:

$$J = \frac{L \times h \times r}{D \times h \times (P_o - P_r)} + \frac{h^2}{5 \times D}$$

Note that the second term in this equation reflects the diffusion delay.

Due to the capillary phenomena, the moisture pressure in the cell P_r is less than the environmental moisture pressure P_o. Their ratio will depend on the cell radius and can be estimated using the Thomson equation:

$$RT \times \ln(P_o / P_r) = gn / r$$

where γ is the surface tension of water (7.3×10^{-2} N/m), ν is the molar water volume (1.8×10^{-5} m^3), R is the gas constant (8.3 Nm/mole K).

Results of these calculations at room temperature for a molding compound having diffusion coefficient D = 1.8×10^{-13} m^2/s, solution coefficient η = 5.3×10^{-3} s^2/m^2 and the thickness of h = 0.5 mm for different cell sizes are presented in Table 2.

Table 2. Capillary pressure and characteristic times of moisture condensation for cells of different sizes.

r, mm	Pr/Po	L=0.3 mm	L=1 mm
0.001	0.896243	2.38E+02	6.57E+02
0.01	0.989105	1.77E+03	5.77E+03
0.1	0.998905	1.71E+04	5.69E+04
1	0.99989	1.70E+05	5.68E+05
10	0.999989	1.70E+06	5.68E+06

It is seen that condensation, even into small cells with a radius of only a few nanometers and a length of less than one micrometer, will take hundreds of hours. An increase of the radius above 0.1 µm will require more than a year, which is significantly greater that the observed times of capacitance variations. This is mostly due to a low "driving force" of the condensation process (the difference between the moisture pressures outside the package and inside the cell).

Besides, the resistivity of pure water might be not low enough to provide a proper conduction over the tantalum pentoxide layer in cells of more than 1 µm. Assuming the specific resistivity of water, ρ_w, of more than 0.1 Mohm*cm and the thickness of the water layer, δ, of approximately 1 µm, the effective surface resistivity (ρ_w/δ) will be more than 10^9 Ohm.

4.1.3. Moisturizing of hygroscopic remnants.

The sleeping cells are most likely not empty and clean tantalum pentoxide cylinders as was assumed above, but rather have some contamination remaining after manufacturing processes. The Ta$_2$O$_5$ dielectric is formed by the electrochemical process of anodization, during which the tantalum pellet is dipped into electrolyte containing a weak solution of phosphoric acid. It was shown [8] that in spite of rinsing after anodization, this process results in formation of phosphate deposits in the micropores of the pellets.

These deposits do not allow full coverage of the tantalum pentoxide layer with manganese oxide and are responsible for the "wet-to-solid" capacitance losses observed during manufacturing of tantalum capacitors [8]. The decrease of capacitance was

revealed when measurements of pellets performed prior to manganese dioxide application (by using a liquid electrolyte as a cathode) were compared with the measurements carried out after application of manganese oxide and careful drying of the capacitors. For some parts the capacitance variations during these measurements exceed 30%. Additional experiments showed also that after a high temperature drying, the phosphate deposits form hygroscopic glassy or crystalline solids, which are readily absorbing moisture from atmosphere. Similar behavior is typical for phosphates, which are known as moisture absorbents and are widely used in dessicators.

The presence of the phosphate deposits in a sleeping cell significantly reduces relative humidity inside the cell, thus increasing the driving force of moisture diffusion and decreasing the time for moisture condensation. Assuming relative humidity inside a cell is maintained at ~10% and outside at 100%, the calculations for cells of 1 to 5 μm in length give condensation time in the range from 130 hours to 530 hours. This range of times agrees with the experimental results shown in Figures 9 and 10. Note that in this case the condensation time does not depend on the radius of the cell.

It is also important to note that the phosphates drastically reduce their resistance under humid conditions due to dissociation of the absorbed water molecule into hydrogen and oxygen ions. This process is used in the design of the most sensitive electrolytic hygrometers, which employ a thin film of phosphorus pentoxide deposited on the top of metal interdigitated wafer electrodes.

Relatively short times for moisture condensation and low resistivity of the formed cathode electrode make moisturizing of phosphate remnants the most probable mechanism of activation of the sleeping cells.

4.2. Effect of exposure to humid environments on reliability of the capacitors.

4.2.1. Activation of defects in sleeping cells.

Newly manufactured solid tantalum capacitors are dry, and this state will remain for up to several weeks of storing at normal laboratory conditions. If a part is tested within this period of time, sleeping cells remain in the passive state and the voltage is not applied to a certain portion of the tantalum pentoxide surface area (for our parts this portion varied on average from 3% to 13 % depending on the part type). Besides, all screening and reliability qualification testing of tantalum capacitors per MIL-PRF-55365 are performed at high temperatures (voltage aging, surge voltage, and Weibull grading are performed at 85 ^{o}C; life testing is carried out at 85 ^{o}C or 125 ^{o}C). At T ~85 ^{o}C, even a part containing some moisture initially, will be dried out in less than 18 hours (with a thickness of MC ~0.5 mm), and most of the testing will be performed on parts with non-activated sleeping cells. This means that a certain proportion (in our parts 3% to 13 %) of the surface of Ta_2O_5 dielectric might never have been accessed and probed during manufacturing and/or incoming screening of tantalum capacitors.

It is reasonable to assume that some of the sleeping cells might contain defects, weakening electrical strength of the tantalum pentoxide dielectric. These defects could not be screened out during testing in dry conditions, but they might result in failures provided an electrical contact over the defective area is formed. Activation of these cells as a result of moisture sorption during storage of the parts in high humidity environments or even at normal laboratory conditions might cause breakdown and failures.

Although this scenario seems quite realistic, our data show that failures of the parts occur mostly after highly accelerated stress testing, whereas capacitance measurements showed that most of the sleeping cells have been activated already by moisture during storage in humidity conditions at relatively low temperatures. This suggests that activation of the sleeping cells might not be a prime reason for moisture-induced failures.

4.2.2. Degradation of tantalum pentoxide dielectric.

Another degradation mechanism in Ta capacitors is related to an increase of the concentration of electron traps in Ta_2O_5 dielectric. This degradation was observed only in the 22 uF capacitors after 72 hours of PCT at 121 ^{o}C. Estimations showed that these capacitors had minimal thickness of the dielectric layer of approximately 140 nm. Based on these data, we can assess the diffusion coefficient in the tantalum pentoxide dielectric D $\approx$ d^2/t = 3.8$\times$1^{-16} cm^2/s at 121 ^{o}C, which is consistent by the order of magnitude with the reported values of diffusion coefficients in silicon oxides [9].

Using this value of the diffusion coefficient, similar degradation on other types of capacitors can be expected after approximately 250 to 600 hours of PCT. However, further analysis is necessary to evaluate the significance of this type of degradation, to estimate the activation energy of the process, and to predict its occurrence at low temperature conditions.

4.2.3. Degradation of manganese oxide

It is known that some manganese oxides, Mn_3O_4 in particular, can be oxidized by moisture and manifest humidity sensitivity of electrical characteristics high enough to develop humidity sensors [10]. The effect of increasing conductivity of the manganese layer caused by moisture sorption also explains significant decrease of the capacitance roll-off effect after accelerated humidity testing (see Figure 6). This effect might also play a negative role, causing failures in tantalum capacitors due to reactivation of the self-healed sites and to enhancement of the breakdown conditions.

Reactivation of the self-healed sites. The low-level manganese oxides MnO_x, $x<2$, are electrically much less conductive compared to manganese dioxide, MnO_2. A drastic increase in the resistivity of the manganese oxide at the defective sites in the Ta_2O_5 caused by local overheating during electrical breakdown plays an important role in providing reliability of Ta capacitors by the so-called self-healing mechanism [11]. At T > 380 °C the manganese dioxide at the breakdown site reduces to a lesser oxidized form (e.g., Mn_2O_3 or Mn_3O_4), which has much higher resistivity thus limiting current and preventing catastrophic failure of the part. A reverse process might be expected in humid environments when the manganese oxides at the self-healed sites will oxidize and reduce resistance of the layer. This would restore electrical contact to the defective site in the tantalum pentoxide dielectric and might cause failures after the part has been stored for sufficient time in humid environments.

Enhancement of the breakdown at weak sites. Processing of the parts during reflow soldering or operation under stressful conditions might generate new defects in the tantalum pentoxide dielectric. The probability of failure in this case would depend on the conductivity of the manganese oxide layer. High conductivity of the layer will facilitate delivery of energy from the surrounding areas of the capacitor to the defective site, thus increasing the probability of breakdown and catastrophic failure. This mechanism is specific to tantalum and niobium capacitors which manifest relatively leaky and soft breakdown of their dielectric films.

Details of the kinetics of oxidation of MnOx in humid environments are not known. Based on our data we can assume that it will take more than 52 days of storing at room temperature and 100 % RH or more than one week of storing at 85 °C and 100 %. However, at T > 120 °C this process can be observed already after 72 hours.
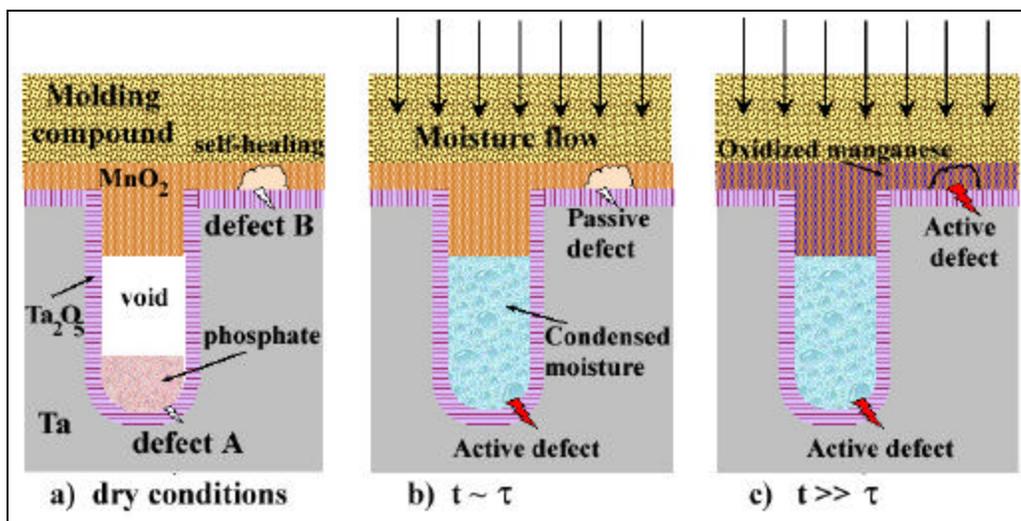
Figure 14. Illustration of the moisture-induced failure mechanisms in solid tantalum capacitors. In dry conditions (a) defects of type A and B are isolated from the cathode and do not affect characteristics of the part. After storing in humid environments during the time τ, which can be estimated based on the thickness and moisture characteristics of the molding compound, sleeping cells are moisturized and defects of type A are activated (b). Further storing in humid environments results in oxidation of the reduced manganese oxide at the self-healed areas thus reactivating defects of type B (c).

4.2.4 Moisture-induced failure mechanism.

Moisture-induced transformations in the manganese oxide layer suggest a two-stage model of degradation of tantalum capacitors in humid environments. A schematic of this process is shown in Figure 14.

It is assumed that initially, in dry conditions, a certain fraction of the surface area of the oxide in tantalum capacitors is not covered with manganese oxide, thus forming sleeping cells containing solid phosphate remnants. In the absence of moisture these remnants are not conductive, so that a possible defect in a sleeping cell (defect A in Figure 14 a) does not affect characteristics of the part. Also, all defects in the Ta_2O_5 dielectric under manganese oxide layer (defect B in Figure 14 a) are considered to be isolated from the cathode by local high resistive MnO_x areas formed as a result of manganese dioxide reduction during the self-healing process.

In humid environments after a time, which can be estimated as the characteristic time of moisture diffusion and which depends on moisture characteristics and the thickness of the molding compound, the sleeping cells are filled up with condensed water. This water reacts with phosphate remnants, forming a conductive electrolyte over the previously passive area of the Ta_2O_5 surface. This increases the capacitance and activates the defect in the sleeping cell (defect A). Depending on the type of this defect and the conductivity of the formed electrode, this activation might not only increase the leakage currents in the capacitor, but also result in its failure.

Further storing of the capacitors in humid environments results in oxidation of the low oxide forms of the manganese oxide layer, thus increasing its conductivity. Oxidation of the reduced manganese oxide at the self-healed defects would reactivate these defects, causing breakdown in the part. Due to the overall increase in the conductivity of the manganese layer and thus enhanced delivery of energy to the defective site, this breakdown might result in more detrimental consequences than the initial breakdown, which caused only scintillation of the current and eventually self-healed the part.

It should be noted that moisture intrusion in tantalum capacitors is mostly limited by molding compound and, in the case of Ta_2O_5 degradation, by the dielectric itself. Silicone barrier layers are used before molding in some tantalum capacitors to reduce the probability of pop-corning effect during reflow soldering. However, these barrier layers most likely will not improve reliability of the product during storing in humid environments because moisture diffusion coefficients of silicones are two to three orders of magnitude larger than of epoxy molding compounds. The protective action of silicones in microcircuits is due to the passivation effect, which is a result of chemical reaction with the hydroxyl groups on the surface of the die. It is possible that the passivation effect on tantalum capacitors might be achieved by a hydrophobization treatment of the assembly before molding with a low molecular weight silicone liquid. Small silicone molecules might penetrate to the micropores of the pellet, modifying the surface of the tantalum pentoxide in sleeping cells and thus reducing the probability of activation of defects in the dielectric.

Application of conformal coatings after soldering parts onto a board will also not prevent moisture from penetrating inside the capacitors, but rather would slightly delay this process (the major purpose of conformal coating is prevention of direct water condensation on the part).

4.3. Moisture resistance qualification testing.

Military specification MIL-PRF-55365D requires periodic moisture resistance testing of tantalum capacitors in accordance with test method 106 of MIL-STD-202. According to this method the parts are subjected to twenty 24-hour cycles in humidity chamber without applying voltage to the parts. During each of the cycles the relative humidity and temperature varies several times from 80% to 100% RH at 25 ^{o}C to 90% to 100% RH at 65 ^{o}C. Total duration of the high temperature/high humidity conditions during each of the cycles is 6 hours. After the testing C, DC leakage, dissipation factor, and ESR are measured. Measurements of the dielectric withstand voltage are not required. Changes of the capacitance after the test shall not exceed $\pm$15% of the initially measured values and of the DCL 200% of the rated values.

The purpose of this test is the evaluation of resistance of the parts to deteriorative effects of high-humidity and heat conditions typical in tropical environments where direct surface wetting of metals and insulation might happen. It is assumed that this test is especially effective due to employment of temperature cycling, which provides alternate periods of condensation and

drying essential to the development of the corrosion processes.

Interestingly enough, in spite of this purpose, the user is advised to avoid condensation of water on the parts. However, it is not clear how this recommendation can be accomplished in a chamber with 100% RH.

Total duration of the exposure of the parts in a humidity chamber to high temperature conditions is 120 hours. Temperature exponentially accelerates moisture diffusion through molding compounds, so to estimate whether 120 hours is sufficient for moisture penetration to the pellet (or into the sleeping cells), we need to compare this time with the characteristic time of moisture diffusion at $65\ ^{o}C$, $\tau_D(65)$. Calculations showed that $\tau_D(65) \approx 45$ hrs. at h = 0.5 mm and ~170 hrs at h = 1 mm. This means that the duration of the test might not be sufficient for parts with the thickness of molding compound of more than 0.7 mm, and failures related to the presence of defects in the sleeping cells might not be activated during this testing.

The purpose of qualification testing is to ensure that no wear-out mechanisms will cause premature failures in the part. Failures related to the degradation of the dielectric and manganese oxide layers, and to increase in the resistance of cathode attachment materials, can be considered as wear-out mechanisms in solid chip tantalum capacitors. Obviously, the existing moisture resistance testing is not stressful enough to sense these mechanisms, and therefore positive results of this test will not guarantee moisture robustness of the parts in harsh environments.

The absence of adequate test methods makes field failures of the parts after long-term storing in humid environments quite possible. Additional testing of tantalum capacitors, research of moisture-induced degradation processes in used materials, and analysis of accelerated factors of the degradation processes are necessary to develop qualification techniques, which would assure reliability of the parts in moisture environments.

5. Conclusion.

1. Characteristics of four types of CRW09-style tantalum capacitors have been measured after different baking and high humidity conditions. The results of these measurements can be summarized as follows:
   1.1. Capacitance of the parts varied reproducibly and consistently with environmental humidity increasing 3% to 13% in humid environments compared to dry conditions.
   1.2. Kinetics of capacitance variations at room temperature feature an induction period of 30 to 50 hours and saturation after approximately 200 to 500 hours and are consistent with the diffusion model.
   1.3. Humidity testing at relatively low temperatures (52 days at ~22 ^{o}C or 168 hours at 85 ^{o}C) did not cause any significant changes in the capacitance roll-off effect, ESR, or leakage currents.
   1.4. Accelerated humidity testing, PCT at 121 ^{o}C during 72 hours or HAST at 130 ^{o}C/85% RH during 96 hours, drastically reduced the capacitance roll-off effect. Leakage currents in some parts remained unchanged, however for 10% to 60% of the 10 μF, 4.7 μF, and 6.8 μF capacitors the currents increased above the specified limits. Absorption currents in the 22 μF capacitors increased three to five times; however, no failures occurred.
   1.5. One part type manifested a two to three times increase in the ESR measured in the megahertz range after the accelerated humidity testing (PCT).

2. Moisture characteristics (diffusion and sorption coefficients) of two types of molding compounds used to encapsulate tantalum capacitors were measured and found to be similar to the characteristics of the compositions used for plastic encapsulated microcircuits (PEMs).

3. A sleeping cells model has been suggested to explain increase in capacitance of the parts in humid environments. Different mechanisms of activation of the sleeping cells by moisture diffusion have been considered and their probability has been estimated.

4. A possible mechanism of failures of tantalum capacitors in humid environments based on the sleeping cells model and oxidation of the manganese oxide at the self-healed sites has been suggested.

5. Analysis of the existing moisture resistance testing showed that the level of the stress is not sufficient for most military and aerospace applications and is far below the requirements for plastic encapsulated microcircuits. Additional investigation of moisture induced degradation in manganese oxide, tantalum pentoxide, and silver epoxy is necessary to estimate acceleration factors of the degradation processes and develop an

adequate accelerated humidity stress testing for solid tantalum capacitors.

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7. Acknowledgment.