



Degradation and ESR Failures in MnO₂ Chip Tantalum Capacitors

Alexander Teverovsky

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NASA Electronic Parts and Packaging (NEPP) Program

alexander.a.teverovsky@nasa.gov

List of Acronyms

AC	alternative current	MC	molding compound
CME	coefficient of moisture expansion	PCT	pressure cooker testing
CTE	coefficient of thermal expansion	RH	relative humidity
DCL	direct current leakage	S&Q	screening and qualification
ESR	equivalent series resistance	T	temperature
HAST	highly accelerated stress testing	TC	temperature cycling
HTS	high temperature storage	TSD	terminal solder dip

Outline

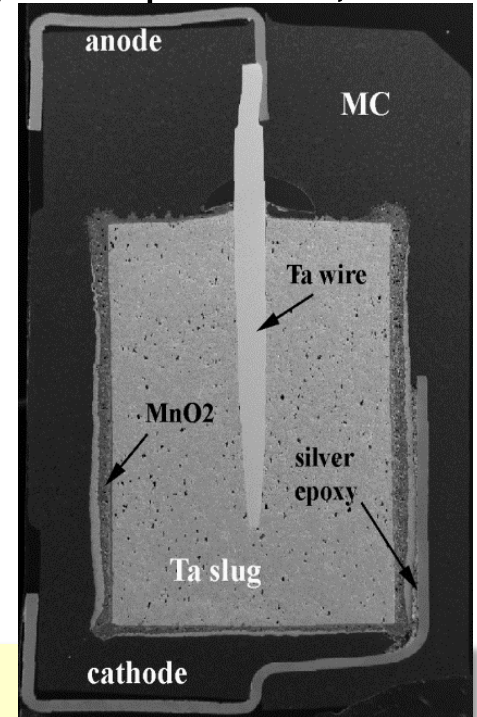
- ❑ Introduction.
 - Catastrophic and parametric failures.
 - Specified and experimental ESR values.
- ❑ Degradation in different environments.
 - Effect of vacuum.
 - Effect of high temperature storage.
 - Effect of temperature cycling.
 - Effect of moisture.
 - Effect of soldering.
- ❑ Conclusion.

Notes:

- Failures of Ta caps during environmental tests are often due to DCL.
- Damage to dielectric typically does not affect ESR.
- Only ESR failures and degradation are considered in this presentation.

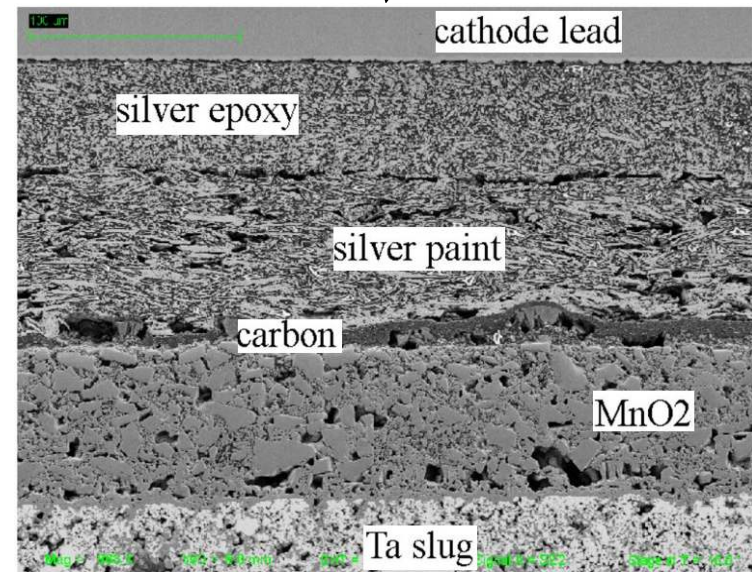
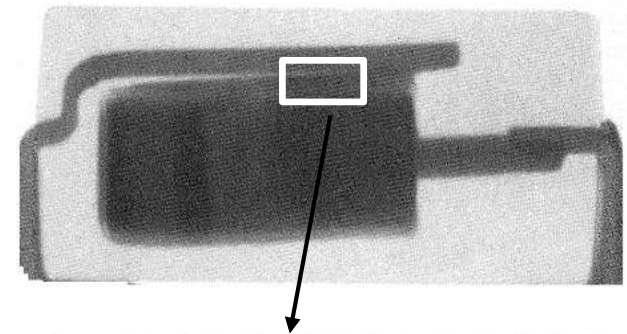
Catastrophic and Parametric Failures

- ❑ ESR determines:
 - dissipated power and thus temperature and reliability of capacitors;
 - the level of V_{ripple} in filtering applications;
 - the rate of the energy delivery in pulse power applications.
 - ❑ ESR can change the phase of signals and cause oscillations if becomes too low.
 - ❑ Catastrophic ESR failures might be due to:
 - cracking in welding of anode riser wires;
 - significant delamination between cathode layers;
 - solder reflow if cathode pad is solder plated.
- ✓ Catastrophic ESR failures are rare.
- ✓ Parametric failures are observed more often now because of increased use of low-ESR capacitors and more stringent requirements for performance.
- ✓ If a parametric failure is observed, can ESR degrade further?



Mechanisms of Degradation

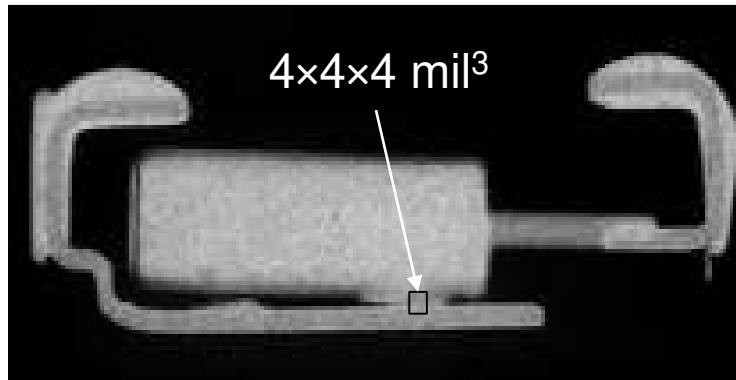
- ❑ ESR depends on conductivity of cathode materials: MnO_2 , graphite, silver paint, silver-epoxy attachment, and lead frame.
- ❑ At 100 kHz only a surface area of the pellet is effective, so degradation depends on conditions at the surface.
- ❑ Treatment in silicone solutions after graphite coating can cause delaminations and increase ESR.
- ❑ Stresses that might affect ESR: T, RH, TC, surge currents, soldering.



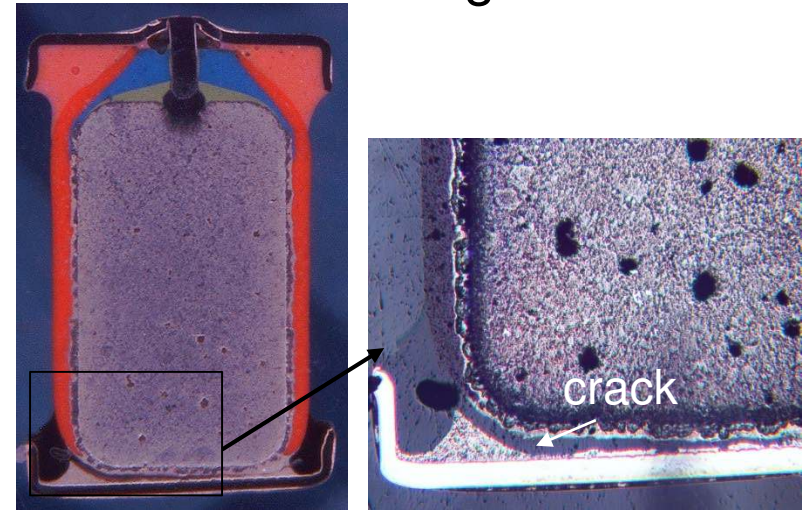
✓ Degradation of ESR is typically attributed to delaminations and increased resistances at interfaces in cathode layers.

Mechanisms of Degradation, Cont'd

At ρ from 2×10^{-4} to 4×10^{-4} ohm-cm and thickness of silver epoxy of ~ 3 mil, a spot, 4×4 mil² would have $R \sim 20$ to 40 mohm.



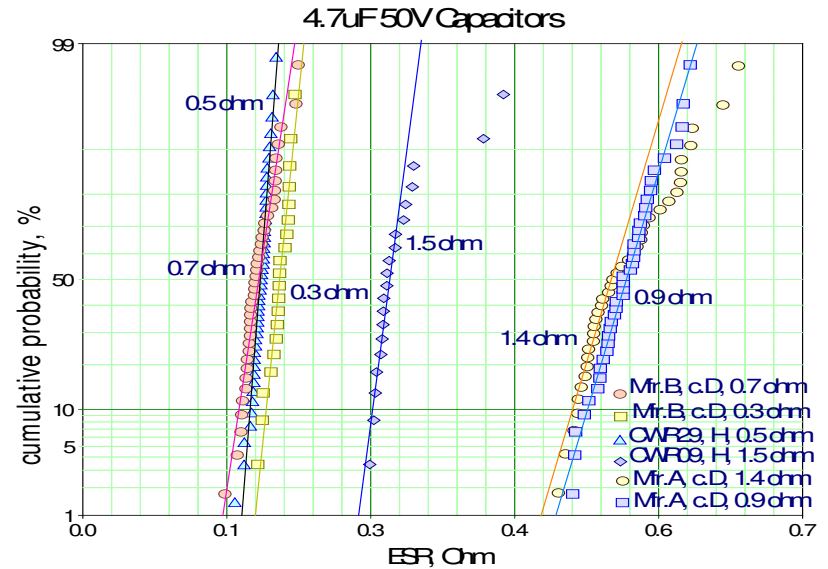
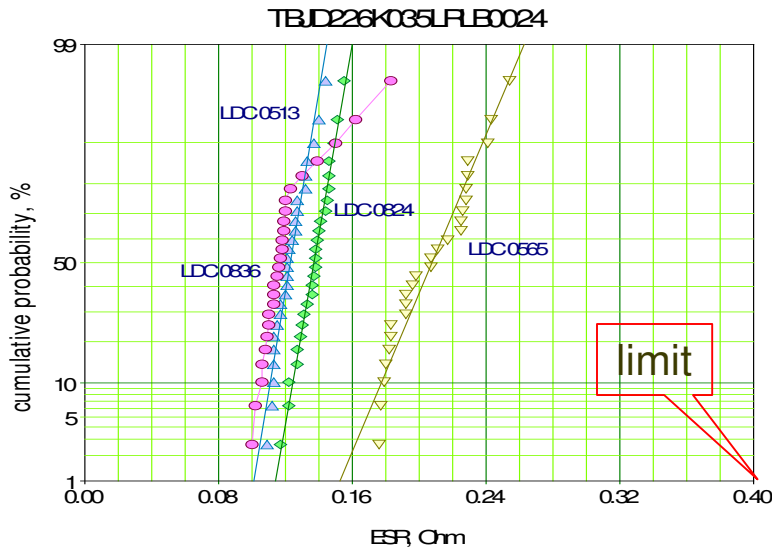
A part with significant crack at cathode attachment had ESR close to the average values.



- ✓ Even a relatively small spot of silver epoxy might be sufficient to assure low ESR values.
- ✓ Delaminations and cracks might not result in high ESR initially, but increase the risk of further degradation under environmental stresses.

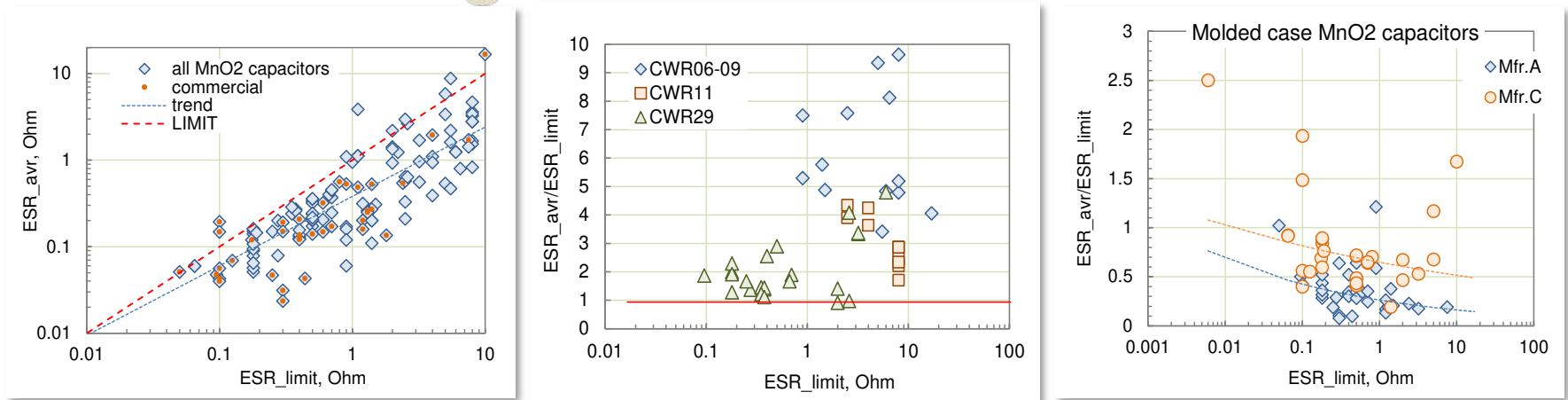
ESR Distributions

Examples of distributions



- ✓ Distributions can be approximated with normal functions.
- ✓ The spread is relatively small and outliers can be detected by the 3-sigma criterion.
- ✓ There might be significant lot-to-lot variations of ESR.
- ✓ Lots specified to larger ESR_{max} might have lower actual ESR values.

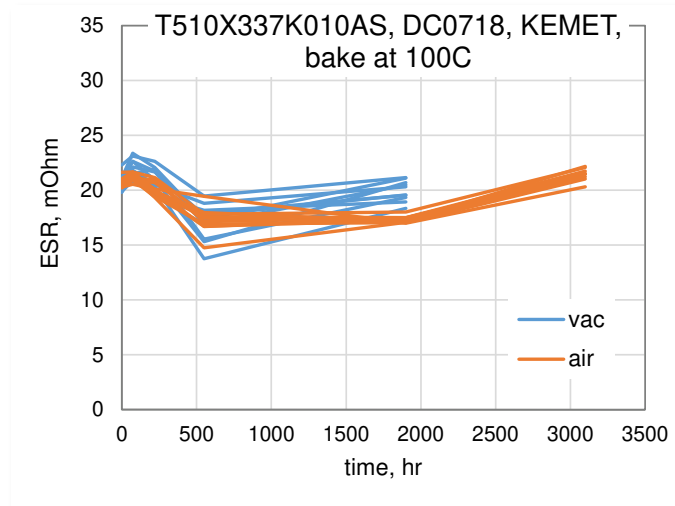
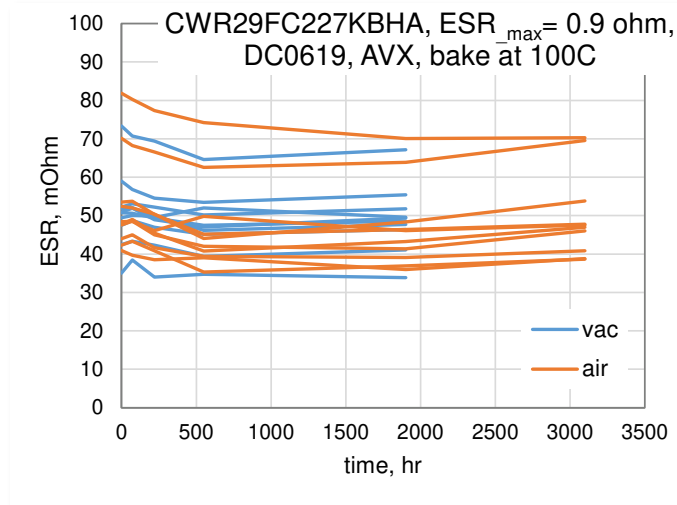
Average ESR Values vs. Limits



- ✓ The spread of data for military and commercial parts is similar.
- ✓ The margin for low ESR parts is smaller.
 - On average, CWR06 capacitors are ~ 5 to 10 times below the spec. limit, CWR11 – 2 to 4 times, and CWR29 – 30% to 60%.
 - According to J.Brusse, ASRC/GSFC 2016, 4 out of 26 lots of CWR29 capacitors had from 7% to 92% of ESR failures.
- ✓ Manufacturers might have different rules for setting ESR limits.
- ✓ Insufficient margin might be one of the major reasons of parametric failures.

Effect of Vacuum

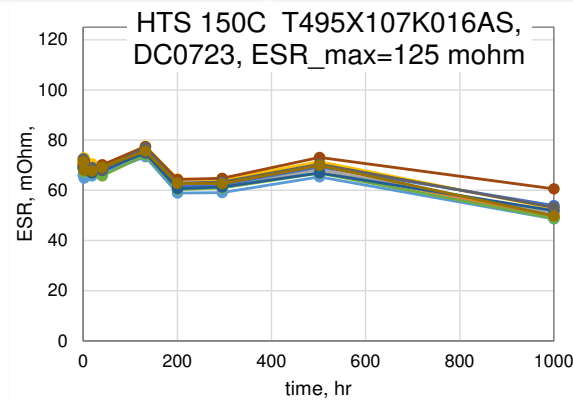
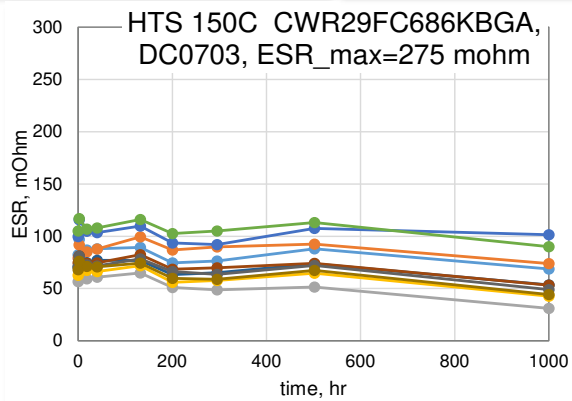
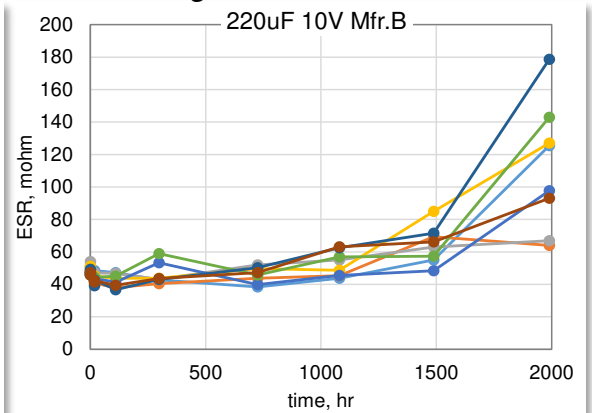
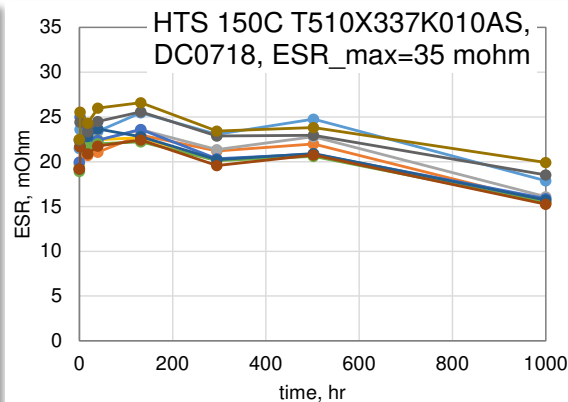
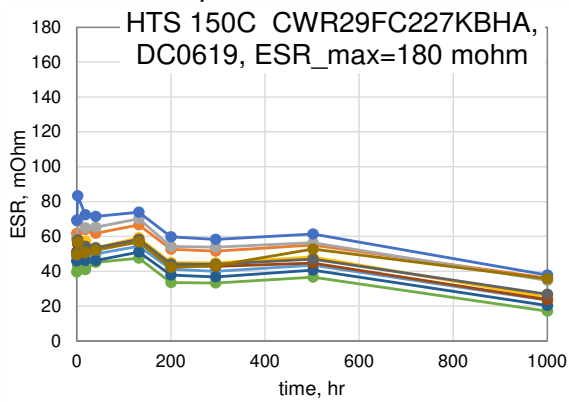
- ❑ **Concern:** Possible reduction of MnO_2 in vacuum might result in increasing resistivity of cathode layers and ESR.
- ❑ **Experiment:** Two groups of T510, $\text{ESR}_{\text{max}} = 35$ mohm, and two groups of CWR29, $\text{ESR}_{\text{max}} = 0.9$ ohm, were baked at 100°C in air and vacuum ($<10^{-6}$ torr).



- ✓ Long-term ageing in vacuum did not cause degradation of ESR.
- ✓ No substantial difference in behavior of capacitors during storage in vacuum and air conditions at 100°C .

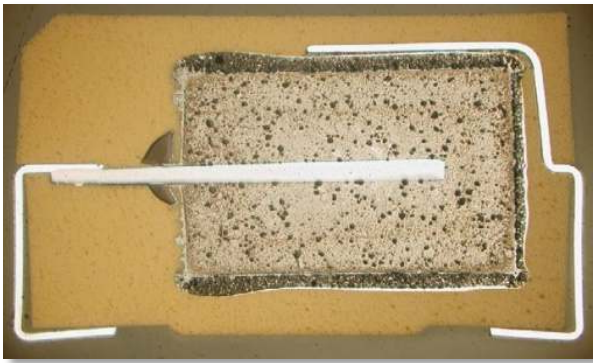
High Temperature Storage at 150 °C

At $T_{oper. max} = 125\text{ }^{\circ}\text{C}$ it is reasonable to expect that the $T_{storage max} = 150\text{ }^{\circ}\text{C}$.



- ✓ Normal quality parts can sustain 1000 hour storage at 150 °C.
- ✓ Additional testing showed that ESR in MnO_2 chip Ta capacitors does not degrade after more than 300 hours at 175 °C.

Temperature Cycling



❑ Ta caps contain materials with substantially different CTE.

❑ M55365 screening:

5 cycles from -55 °C to +125 °C.

At the option of manufacturer (?): -65 °C and/or +150 °C.

❑ M55365 qualification: mounted parts, 10 cycles from -65 °C to +125 °C. 12 samples and 1 can fail (with gr.III, IV, and V).

❑ AEC-Q200: 1000 cycles from -55 °C to +125 °C.

Material	Tg. °C	CTE1, ppm/°C	CTE2, ppm/°C
MC	145	17.3	59.2
Silver epoxy	50 - 90	30 - 50	160 - 170
Ta		6.6	
Ta ₂ O ₅		~5	
MnO ₂		~10?	
LF (phosphor bronze)		17	
LF (alloy 194, FeNi42)		5.3	

✓ TC might result in cracking and delaminations in cathode layers due to CTE mismatch.

✓ M55365 requirements are much less severe compared to other electronic components and to automotive industry.

Effect of Temperature Cycling

ESR was measured during TC testing for different lots (10 to 20 pcs).

Gr	Parts	Test conditions	Result
1	3 lots CWR09	1000c -65 to +125 °C	2 lots – no degr. or failures; 1 lot –several failures.
2	5 lots CWR11	300c -65 to +125 °C	No degradation.
3	9 lots of COM and MIL parts	500c -65 to +150 °C	8 lots – no degr. or failures; 1 lot – several failures.
4	5 lots of COM parts	3c +50 to +240 °C 100c -65 to +125 °C	No degradation.
5	4 lots, COM and MIL	500c +25 to -196 °C	No degradation.
6	3 lots COM part	30c +30 to +240 °C	Degradation after 3 cycles

- ✓ Degradation and failures were observed in 2 out of 26 lots.
- ✓ Normal quality parts can withstand 3 cycles simulating solder reflow and 100 cycles between -65 and +125 °C.
- ✓ Some lots can sustain 1000 cycles between -65 °C and +125 °C.
- ✓ Capacitors can survive multiple cryo-cycles and cycling to 150 °C.

Requirements for Moisture Resistance

- ❑ M55365 scope: “... used in moisture protected environments” (?!)

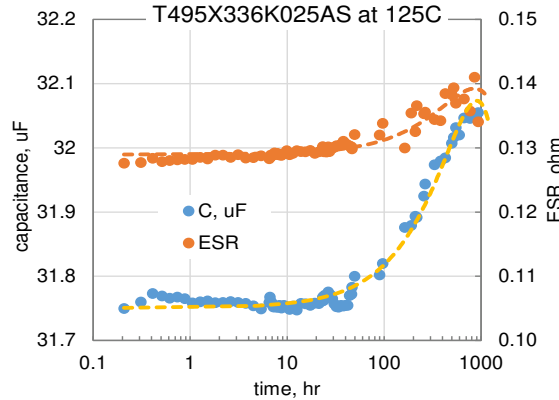
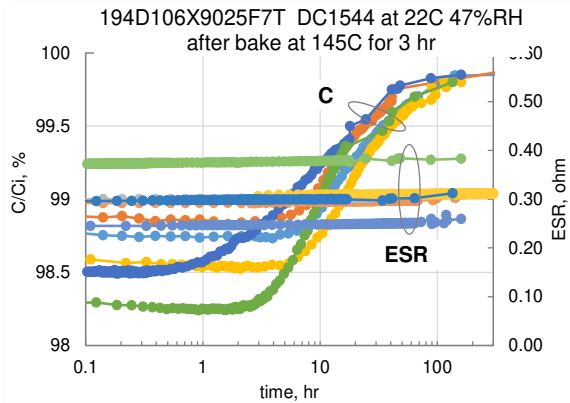
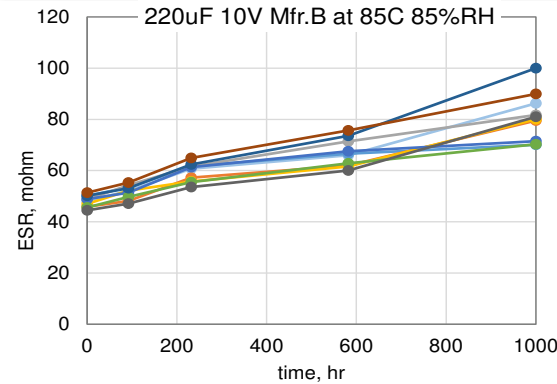
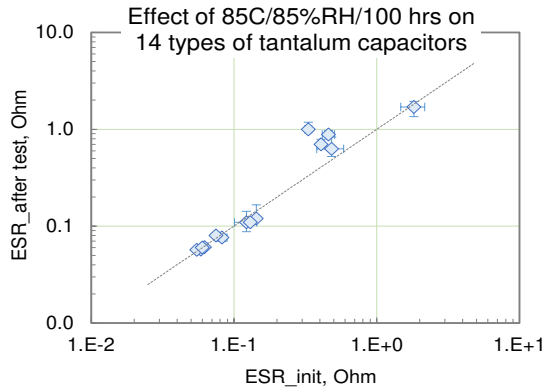
1.1 Scope. This specification covers the general requirements for non-established reliability (non-ER), established reliability (ER), and high reliability tantalum dielectric, fixed chip capacitors, primarily intended for use in thick and thin film hybrid circuits or surface mount applications for filter, bypass, coupling, and other applications where the alternating current (ac) component is small compared to the direct current (dc) rated voltage and where supplemental moisture protection is available (see 6.1). The established reliability capacitors have reliability ratings established on the basis of life tests performed at specified voltage at +85°C for failure rate levels (FRL) ranging from:

Long term exposure to high humidity conditions may affect the equivalent series resistance of these capacitors and possibly result in damage during solder reflow.

- ❑ M55365 qualification test: “Moisture resistance” per MIL-STD-202, TM 106 (includes periods of RH ~ 100%)
- ❑ AEC-Q200: biased testing at 85°C/85% RH for 1000 hrs.

- ✓ M55365 testing is not suitable for space components, and moisture resistance requirements are much weaker compared to commercial parts.
- ✓ Unbiased testing in humidity chamber at 85 °C and 85% RH for 10 days would be a more appropriate test.
- ✓ The testing should be carried out on parts preconditioned to simulate soldering stresses.

Effect of Moisture



- ❑ 14 lots were tested before and after exposure to 85°C/85%RH for 240 hrs.
- ❑ ESR was monitored during 1000 hours testing for 4 lots.

✓ Severe degradation and failures occur after highly accelerated humidity testing PCT, 121 °C/100%RH/72hr, or HAST, 130 °C/85%RH/96hr.

- ✓ No ESR failures were observed.
- ✓ Most of lots did not have any substantial variations of ESR distributions.
- ✓ Some lots increased ESR 1.5 to 2.5 times.

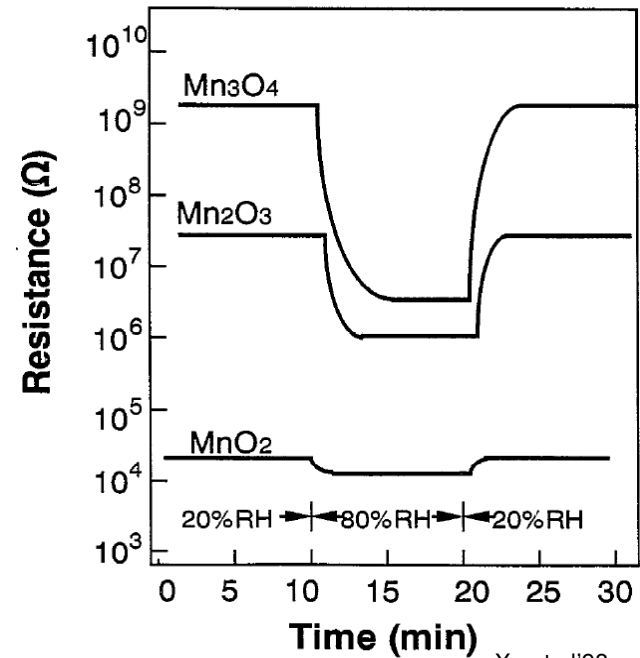
Mechanisms of Moisture-Induced Degradation

Processes decreasing ESR:

- decreased resistance of MnO_2 due to proton conduction in presence of moisture; (The effect is especially significant for reduced oxides and might partially explain DCL degradation and failures in moisture)

Processes increasing ESR:

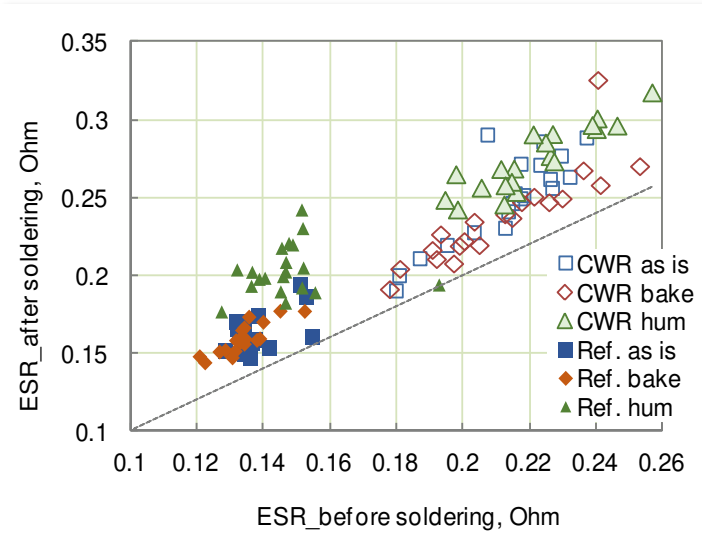
- decreased conductivity of silver epoxy due to galvanic corrosion;
- Increased delaminations due to swelling of molding compound.
 - Moisture sorption at room conditions or desorption in vacuum might cause significant (up to 0.35%) variations in the volume of MCs.
 - At CME $\sim 0.27\%$ and CTE = 17 ppm/°C, swelling at 85 °C/85% RH would be equivalent to temperature increase to ~ 160 °C.



Xu et al.'98

- ✓ Compressive stresses reduce delaminations and squeeze microcracks in cathode layers resulting in reduction of ESR.
- ✓ Swelling of MC and stress relaxation in moisture have an opposite effect.

Effect of Moisture Content on Results of Reflow Soldering



Two types of CWR29 capacitors (CWR and ref.) were reflow soldered after different preconditioning: (1) “as is” after long-term storage at room conditions, (2) after bake at 125 ° C for 15 hr, and (3) after 85 °C, 85% RH for 100 hr.

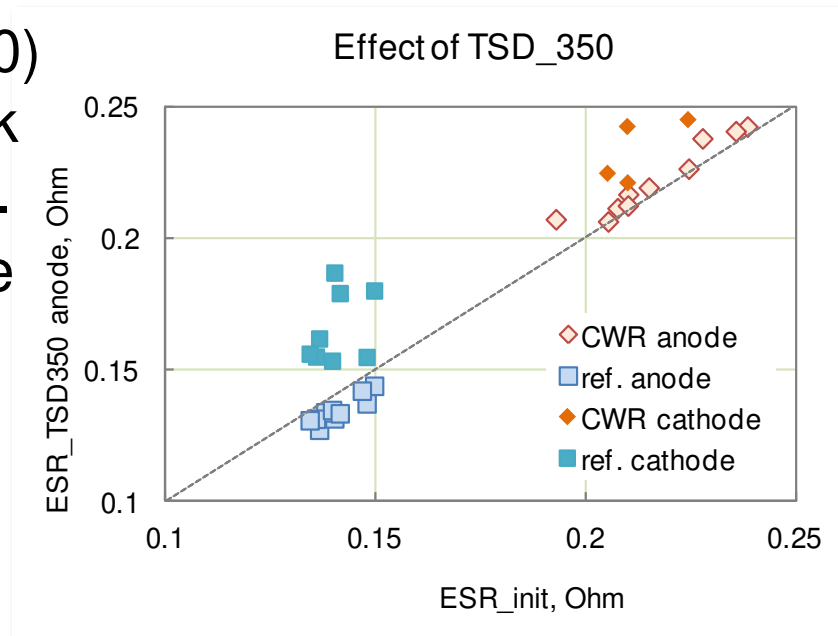
characteristic	as is	hum	bake
Δ ESR_CWR, %	16.8 (7.68)	28.7 (6.03)	10.8 (7.17)
Δ ESR_ref, %	18.3 (7.5)	46.3 (8.2)	15.7 (4.5)

- ✓ ESR increases as a result of soldering for all types of preconditioning; however, degradation was greater for capacitors after moisture soak.
- ✓ Parts after baking increase ESR by 10% to 16%, but in the presence of moisture the increase was 29% to 46%.
- ✓ Internal pop-corning in Ta capacitors might cause delaminations and increase ESR.

Effect of TSD350

- ❑ Terminal solder dip testing (TSD350) was used to simulate thermal shock conditions during manual soldering.
- ❑ 11 lots, 3 anode and 3 cathode side cycles at $T_{\text{solder}} = 350\text{ }^{\circ}\text{C}$.
- ❑ Two out of 11 lots had failures.

TSD350 for two lots of CWR29 capacitors after long-term storage at room conditions



- ✓ Anode-side TSD does not change ESR substantially; whereas 10% to 20% increase occurs after cathode side testing.
- ✓ Robustness towards TSD testing is lot related and is sensitive to presence of moisture
- ✓ Some lots are more susceptible to failures caused by thermal shock during manual soldering.

Conclusion

- ❑ Different types of capacitors and same type capacitors from different vendors have different ESR margins.
- ❑ Lots with insufficient margin have high probability of failures due to relatively minor variations of ESR with time under environmental stress.
- ❑ To reduce the probability of failures, manufacturers should assure adequate margins and M55365 requirements for S&Q should be revised.
- ❑ Environmental testing requirements for automotive industry capacitors are much more severe compared to M55365 requirements.
- ❑ Long-term ageing in vacuum does not cause degradation of ESR.
- ❑ Normal quality lots can pass without substantial ESR degradation:
 - unbiased testing at 85 °C 85% RH for 1 wk;
 - 1000 hour storage at 150 °C;
 - 1000 cycles -55 °C to +125 °C;
 - 3 cycles between room and soldering temperatures.
- ❑ Due to internal pop-corning, the presence of moisture can cause substantial increase in ESR after soldering.
- ❑ TSD350 might be useful to assess robustness of capacitors to manual soldering stresses.