PERFORMANCE OF MIL-TYPE HYBRID TANTALUM CAPACITORS

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ABSTRACT

Mil-style tantalum wet-slug capacitors incorporating Evans hybrid technology have been designed, constructed, and tested. This approach mates an electrochemical capacitor cathode with an electrolytic capacitor anode. It offers a four-fold increase in energy density over state-of-the-art electrolytic capacitors. Qualification testing of 680 μF, 50 V prototype devices per MIL-C-39006 has begun. Electrical characteristics, including frequency response performance, and qualification test data are reported.

BACKGROUND

A new capacitor technology combining elements of electrochemical and electrolytic capacitors was reported by the Evans Company last year. This hybrid capacitor (U S Patent 5,369,547) used a sintered tantalum slug anode, aqueous electrolyte, and a Ru02 ceramic cathode. A four-fold increase in energy density over existing electrolytic capacitors was achieved for a 200 volt, 480 μF prismatic single cell capacitor. [1]

In the Evans hybrid capacitor, an electrochemical capacitor electrode is substituted for the cathode in an electrolytic capacitor. This allows the capacitance of the cathode to be increased by a factor of 100. The anode is unchanged, so high working voltage is maintained. The energy density is increased by this approach.

For capacitors in series

$$l/Ct = 1/Ca + l/Cc \quad (1)$$

where Ct is the total capacitance, Ca is the anode capacitance and Cc is the cathode capacitance. For an electrolytic capacitor where Cc = Ca, Ct=0.5Ca. For the hybrid capacitor Cc=100Ca, so Ct = .99Ca. This represents a doubling of the device capacitance.

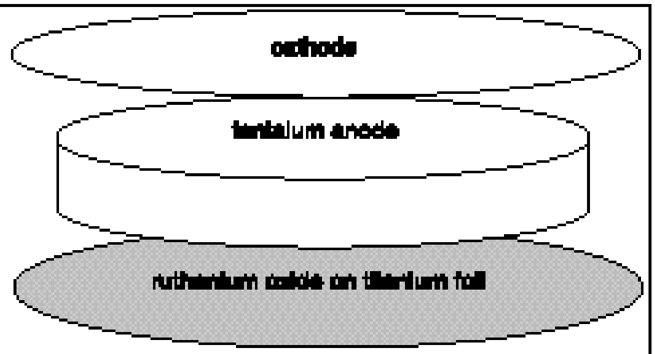

Figure 1. Hybrid prismatic capacitor construction

Since the cathode in a hybrid capacitor occupies only a small fraction of the volume of a typical cathode, additional capacitance density is gained.

The first hybrid capacitor prototypes used the construction shown in Figure 1. They had a tantalum pellet anode, two parallel connected ruthenium oxide coated titanium cathodes, and phosphoric acid electrolyte.

Table 1. data from three of these devices shows that capacitance is dependent on frequency and the Nyquist plot in Figure 2. shows the impedance behavior over the frequency range of 100 Hz to 79 kHz.

Table 1. Hybrid prismatic capacitor measurements.

Part	Capacitance (µF)			ESR (ohms)
	dc	1kHz	120Hz	1kHz
1	606	250	469	0.92
2	541	226	429	0.99
3	575	241	445	0.94

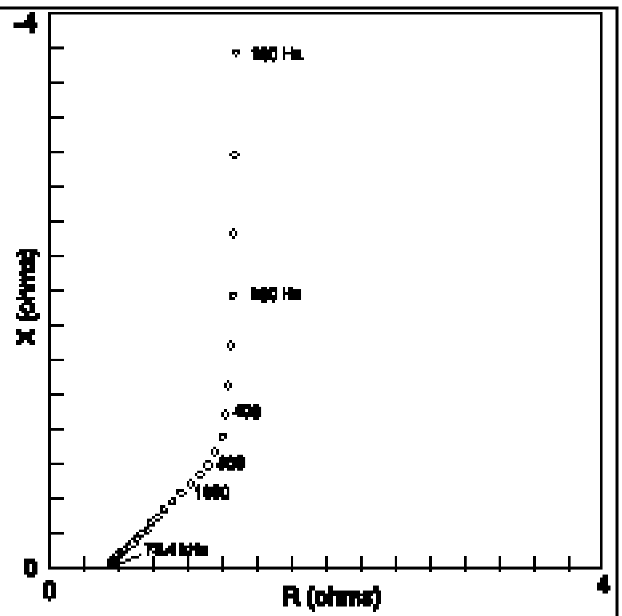

Figure 2. Hybrid prismatic capacitor Nyquist plot.

The performance of this prototype suggested the direction for our next efforts in the development of the Evans hybrid technology. To be applied in ac circuits, the frequency response of the capacitor needed improvement.

A capacitor with porous electrodes can be thought of as a network of connected capacitor-resistor elements. Each element has an associated time constant. At a given rate, only elements with a sufficiently small time constant can contribute to the overall performance. For a RC element, the time constant is

$$T = RC \quad (2)$$

where R and C are resistance and capacitance. Minimizing R allows C to be maximized for a given T. For a porous metal electrode, most of the resistance is due to the electrolyte, and is proportional to the square of the electrolyte path length and to the electrolyte resistivity. Both factors were investigated to improve device frequency response.

The electrolyte resistivity can be changed by changing electrolyte temperature, concentration, or species. The most highly conductive aqueous electrolyte is sulfuric acid.

Although ruthenium oxide coatings are stable in sulfuric acid, the titanium substrates are attacked. Electrodes on tantalum and titanium substrates were tested by soaking them in 38% sulfuric acid at a temperature of 85°C. In less than one week, the titanium substrates were completely dissolved. However, the tantalum substrates were not affected after many months of testing. Processing methods have now been developed to produce ruthenium oxide electrodes with Ta substrates, permitting stable performance in sulfuric acid electrolyte. [2]

MIL-TYPE HYBRID CAPACITOR

Military style hermetic tantalum capacitors (like CLR-81) incorporating the hybrid technology were assembled by North American Capacitor Co. Figure 3 shows the construction in a schematic view. These parts had a nominal rating of 680 µF at 50 V. The rating for the standard part in the same case size (T4) was 680 µF at 25 V. Thus the hybrid had the same capacitance at twice the voltage rating, and thereby increased the stored energy by a factor of four.

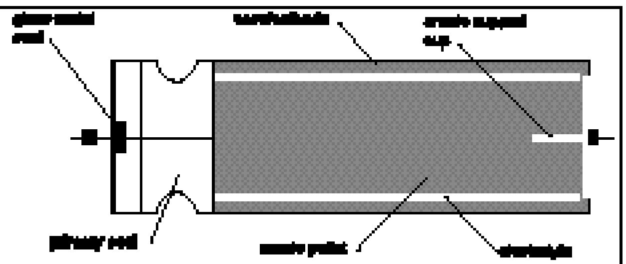

Figure 3. Hermetic tantalum hybrid construction.

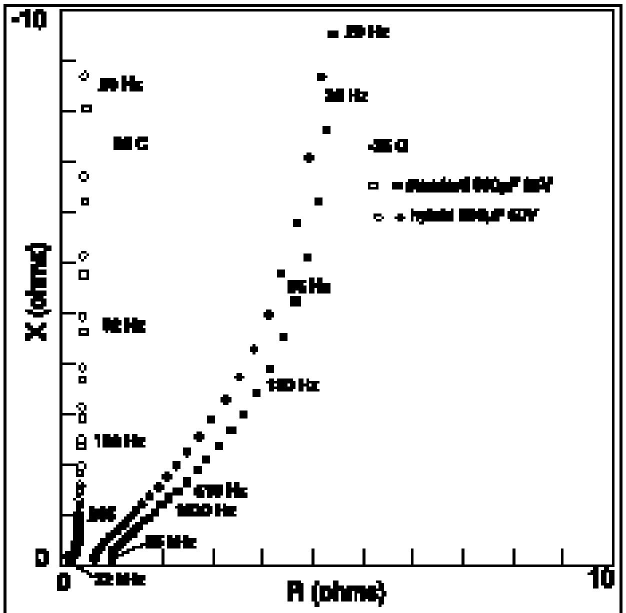

Figure 4. Nyquist plots of the hybrid and standard Mil capacitors.

In addition to regular electrical measurements, frequency response analysis was done using a Solartron 1250. The frequency response of the hybrid is compared to that of a 680 µF, 25 V CLR810216, as shown in the Nyquist plots in Figure 4. The frequency response of the hybrid is significantly improved over previous hybrid prototypes and is very comparable to the standard device. This improvement was due mainly to the use of high conductivity sulfuric acid electrolyte.

Table 2. Electrode and total capacitance for standard and hybrid capacitors.

type	anode capacitance µF	cathode capacitance µF	device capacitance µF
standard	745	7800	680
hybrid	690	50000	680

TEST RESULTS

Qualification testing according to MIL-C-39006 was initiated by North American Capacitor Co. Much of the testing is ongoing, and so far results are promising. A summary of the tests is given in Table 3.

Table 3. Summary of MIL-C-39006 testing.

TEST	# parts
85˚ life	20
125˚ life	20
reverse voltage	10
surge voltage	10
thermal shock	20
shock	12
vibration	14

85˚C life 20 parts

The units have completed 1000 hours on 85˚C, 50 VDC life test and the results given in Figs. 5,6,& 7 are excellent.

125˚C life 20 parts

The units have completed 1000 hours on 125˚C, 30 VDC life test and the results are mixed. All parts met the capacitance and ESR requirement. One half of the lot met the dc leakage requirement. Six units exceeded the allowable 25˚C dc leakage, but met the 125˚C requirement. Four units had no voltage when removed from the test chamber, possibly due to bad connections to the test equipment.

85˚C reverse voltage 10 parts

The units have completed the reverse voltage test on 25˚C, -l VDC. The electrical characteristics were measured after 120 hours at -1 volt and after 120 hours at 50 volts. Three of the units showed an excellent performance with only slight changes in capacitance, ESR, and dc leakage. The other seven units showed a very significant loss of capacitance and an increase in ESR after the reverse voltage portion of the test.

Surge voltage 10 parts

After 1000 applications of 57.5 VDC through 1000 Ω for 30 s then discharge through 1000 Ω for 330 s, all at 85˚C, the performance of these units was excellent. 25˚C data are summarized in Figs. 8, 9,& 10.

Thermal shock 20 parts

All parts passed 300 -55˚ to 125˚C thermal shock cycles. 25˚C data are given in Figs. 11, 12,& 13.

Shock 12 parts

The units were subjected to three 100g shocks in each of three mutually perpendicular axes. The 25˚C properties changed only slightly as a result of the test, but remained within specified parameters.

Vibration 14 parts

The units were subjected to vibration according to MIL-STD-202 method 204D test condition D. Capacitance, ESR, and dc leakage current were measured before and after the test. Although the capacitance and ESR changed less than 2%, several of the parts failed due to high dc leakage.

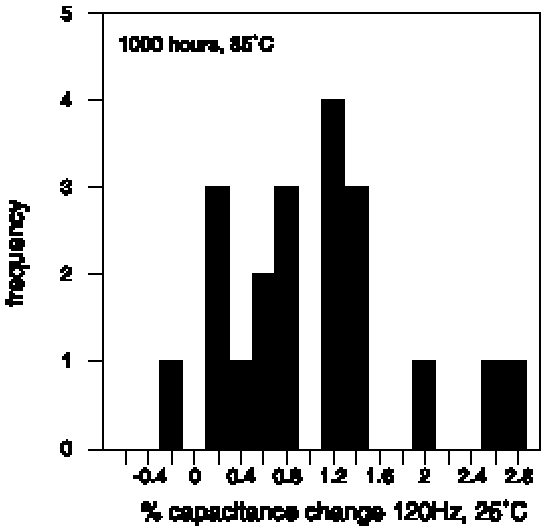

Fig. 5. 85˚C life capacitance change

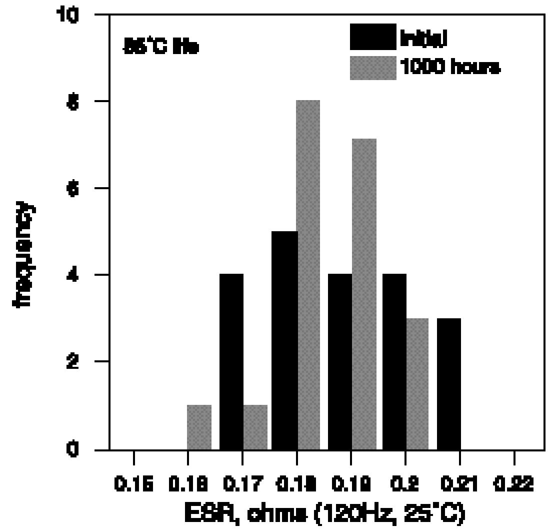

Fig. 6. 85˚C life ESR

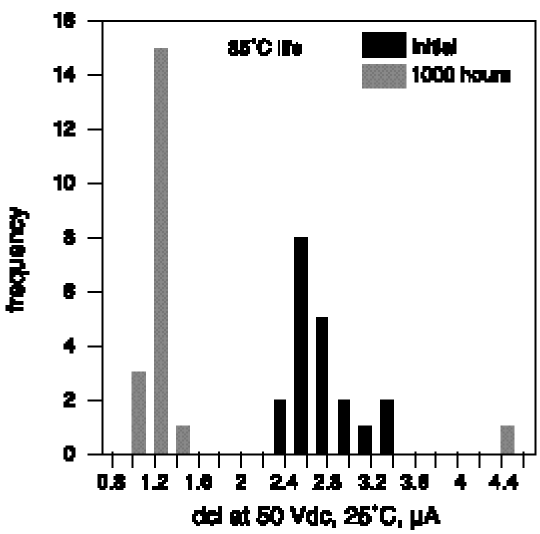

Fig. 7. 85˚C life dc leakage

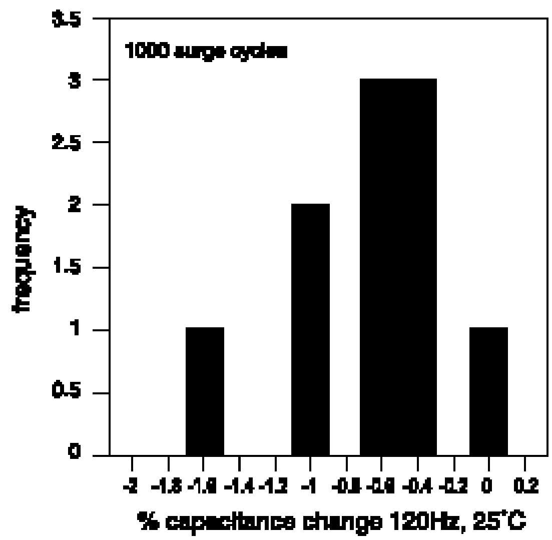

Fig. 8. Surge voltage capacitance change

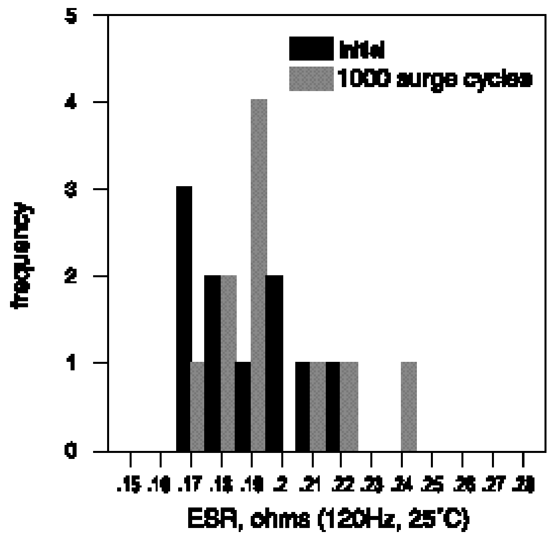

Fig. 9. Surge voltage ESR

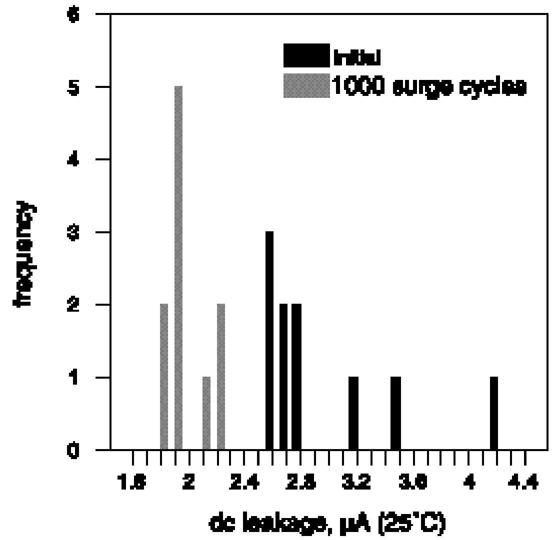

Fig. 10. Surge voltage dc leakage

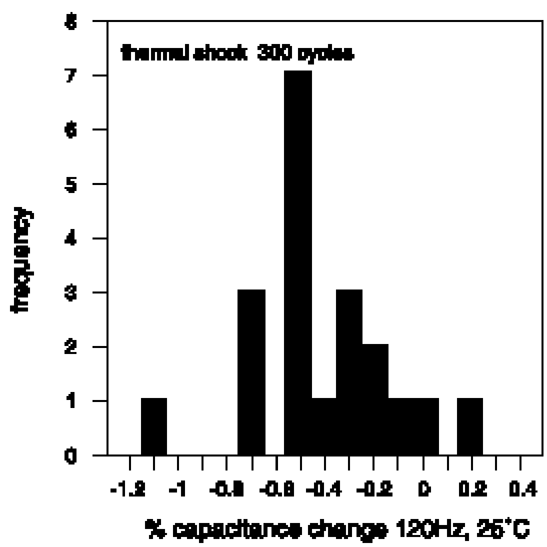

Fig. 11. Thermal shock capacitance change

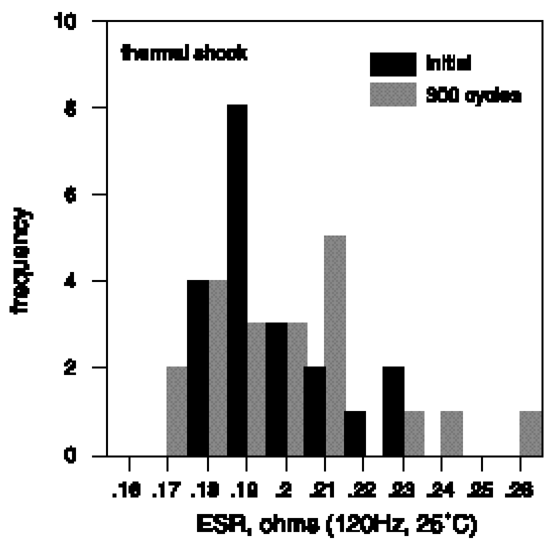

Fig. 12. Thermal shock ESR

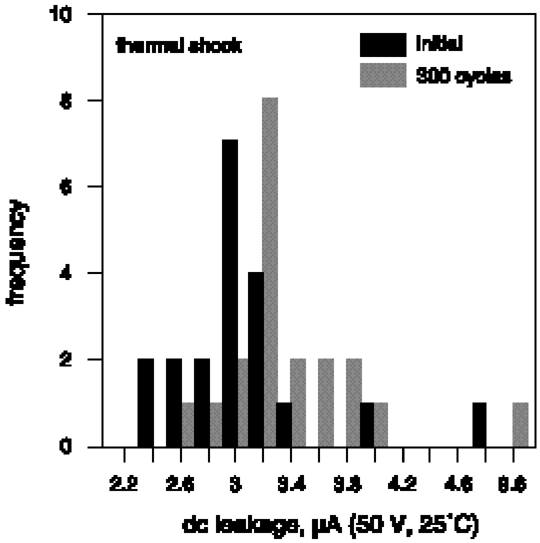

Fig. 13. Thermal shock dc leakage

DISCUSSION

Test requirements for surge voltage, thermal shock, and 100g shock have been met. After 1000 hours of 35˚C life testing, electrical characteristics are in the expected range.

In each of the other tests, at least some of the parts passed. This suggests that remaining problems could be solved by common engineering approaches such as identifying and controlling critical process and design parameters. For example, investigation has shown that the performance loss for the 125˚C life test parts and the failure of some of the reverse voltage parts may be related to a variation in the process affecting the electrical stability of the tantalum ruthenium oxide interface. Another sample of ten parts was subjected to the same reverse voltage test and each capacitor met the requirement.

Experimentation is planned for optimizing the electrical characteristics of the tantalum oxide underlying the ruthenium oxide cathode. This may help provide better life performance, lower ESR, and higher reverse voltage capability.

Because the anode in the hybrid capacitor prototype is more massive than the standard capacitor anode, the mechanical design has been enhanced to provide better support. Although the ruthenium oxide coating is a tough ceramic material, the tenacity of the bond to the tantalum case, and cathode impact on vibration performance will be investigated.

CONCLUSION

The Evans hybrid capacitor provides a four-fold increase in energy density over standard Mil-type hermetic tantalum wet-slug capacitors. Prototype devices have successfully completed part of MIL-C-39006 qualification, with part of the testing ongoing. Continuing activity is directed toward solving remaining difficulties using engineering approaches.

REFERENCES

[1] D. A. Evans, “High Energy Density Electrolytic-Electrochemical Hybrid Capacitor" Proc. 14th CARTS, Jupiter, Florida, 3/94.

[2] D. A. Evans, "Developments in Hybrid Capacitor Technology”, The Fourth Int. Seminar on Double Layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, Florida, 12/94.