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**TESTING OF DOUBLE-LAYER CAPACITORS
FOR HIGH RELIABILITY APPLICATIONS**

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Introduction

Double-Layer Capacitors (DLCs) have been used mainly for computer memory backup in consumer applications during the last ten years. Their high capacitance density, along with maintenance-free operation, makes them suited for these applications. In recent years users, mostly in military applications, have expressed interest in using DLCs in high reliability applications both for backup power and pulse power applications. To meet this need, developers have pursued technologies that use carbon and mixed metal oxides as the electrode material to produce high reliability double-layer capacitors.

In this paper, a carbon-based DLC was manufactured by Evans Company, and a mixed metal oxide (MMO) DLC by Pinnacle Research Inc. were evaluated. There is little published data on their reliability and ageing characteristics. In addition, questions have arisen as to their environmental stability as a function of temperature, shock, vibration, and linear acceleration.

The purpose of this paper is to review the available test data for both types of DLCs under these stress conditions. The data for this paper was generated by Sandia National Laboratories, General Electric Neutron Devices Department, Motorola Company, and Evans Company.

Environmental Tests

Environmental tests were done on individual carbon-based, MMO-based double-layer capacitors, and on carbon-based double-layer capacitors connected in series; and were overpotted with urethane foam in an aluminum case. (This assembly is known as an MC4169.)

Performance of parts before and after environmental tests was measured in three ways:

- 1) Equivalent Series Resistance;
- 2) Capacitance; and
- 3) Activated Life -- time assembly was above 17.5 volts after being charged for 60 seconds to 34 volts and discharged through a 7-watt load.

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Combined Environmental Test

The combined environmental test series was designed to envelope all the usual ground and air transportation environments. The test series consisted of vibration, shock, and linear acceleration. The two vibration spectra used are shown in Figures 1 and 2; shock spectra in Figure 3; and linear acceleration spectra in Figure 4. Tests were run at 75°C and -30°C. Twenty MC4169 assemblies were subjected to the combined environments. Although there is some variability in the measured parameters of equivalent series resistance, capacitance, and activated life, no significant degradation in any property was seen. An example of the before and after activated life data can be seen in Figure 5.

To further test the limits of the assemblies, these combined environments were run five times on five assemblies. Again no significant degradation was observed (Figure 6).

Vibration Only

Vibration spectra as in Figures 1 and 2 were run on a series of parts and assemblies. It was found during these tests that the way the MC4169 assembly was fixtured resulted in 6 to 100 times more the energy input into the part than expected at frequencies above 2000 hz. Figure 7 shows a typical vibration spectra with this enhancement. This result simply means that assemblies were subjected to and survived a significantly harsher environment than expected. (All parts in the combined environmental test were subjected to this effect.) All parts using Evans Company's double-layer capacitors showed no significant degradation in this environment.

High G Shock Only

High G shock tests were run to assess the design limits and the feasibility of using both MMOs and carbon DLCs in penetrator environments. A summary of the tests that have been run thus far are shown in Figure 8 as a function of peak g's and duration. All times greater than 1.5 milliseconds are from penetrator testing through concrete. The data is only for one direction, and usually in these tests there are also high g stress in other directions. Thus the stress on the part was even higher than reported. Failure for a part is defined as a significant voltage drop for any period of time during the test.

Thus far, 16 MMO parts tested by Motorola have passed shock tests similar to that shown in Figure 9. A typical voltage plot is shown in Figure 10. SNL has tested four (4) carbon parts. Figure 11 shows a typical spectra. Two standard carbon parts may have failed at 4500 g/2 millisecond, but further tests need to be done to verify that this is the limit of these parts. After the

suspected failure of those parts, two other parts having special features for shock environments were tested and passed at significantly higher g's.

Temperature

The performance of assemblies and parts were measured at -30°C , $+25^{\circ}\text{C}$, and $+74^{\circ}\text{C}$. The change in equivalent series resistance and capacitance with temperature for one lot of carbon-based DLCs are shown in Figures 12 and 13 (one of three sizes of MMO data are included for comparison). Figure 14 shows a typical discharge plot for an assembly from which activated life was calculated. The MMO parts were also tested in the same way. Figure 15 shows a typical discharge plot for them.

Ageing Data

The goal of the ageing study was to determine the effects of temperature and voltage on the performance of the carbon-based DLCs over a long period of time and to use that data to predict long-term performance.

Experimental Design

Previous studies on similar parts such as capacitors and batteries have shown that temperature, voltage, and time are the most common causes of performance degradation. Thus, a study was designed using these stress factors. The performance measurements used were capacitance, equivalent series resistance, and activated life.

In order to maximize the information obtained in this study, the central composite experimental design was chosen. The central composite design allows for analysis of data with interactions using polynomial, exponential, and/or linear models. The sample space investigated in the study is shown in Figure 16. A maximum temperature of 95°C was chosen since a preliminary study done by Evans Company had shown no abnormal behavior in parts at that temperature. The maximum voltage was chosen as a value below the voltage per cell that would cause irreversible electrochemical degradation of the electrolyte. The duration of the study would be determined by the time to failure of the parts.

Three DLCs and one assembly consisting of three DLCs in series were aged at each selected point in the design. Measurements of capacitance, equivalent series resistance, and activated life time were made at room temperature on the individual DLCs and the MC4169s. In addition, those same measurements were made at -30°C on the MC4169s.

Results and Analysis

Figures 17, 18, and 19 show the average change in capacitance, equivalent series resistance, and activated life versus ageing time for both the MC4169 and the DLCs. Figure 20 compares the changes for measurements made at +25°C and -30°C.

These plots show that the largest changes are in capacitance and in activated life. It should also be noted that the changes are always greater for the individual DLCs than for the MC4169s. Because activated life is the response of most interest, all analysis has been done at variable. Figure 20 also shows that changes in the activated life measured at -30°C are nearly within the measurement error and much less than those at 25°C. This indicates at a minimum that the degradation rate is slower; thus performance at lower temperatures is determined by a different mechanism than at room temperature. Several methods of analysis were used. Polynomial fits were tried first. Unfortunately, they resulted in bowl-shaped predictions as shown in Figure 21. From a physical point of view, we do not expect these parts to get better with time. E. V. Thomas (reliability consultant) used the data generated in the DLC experiments and derived an exponential model to predict change in the capacitance. Since some data from a preliminary ageing study done at 11 volts and 85°C was available, it was used to test. The data fit very well, as can be seen in Figure 21. The only way that the activated life could be modeled was as a function of capacitance. These models were then tested on the MC4169 data. As expected from the data above they predicted more degradation than what occurred.

Results and Conclusions

This study suggests the following:

- Ageing performance of DLCs can be modeled using exponential models to predict long-term performance at room temperature tests;
- predictions made using DLCs for MC4169 will be worst-case predictions;
- a different mechanism determines performance at 25°C and at -30°C;
- additional work needs to be done to understand the mechanisms;
- mixed metal oxides and carbon-based DLCs can survive robust environments if packaged properly; and
- temperature decreases performance of DLCs.

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Figure 1
Input Vibration Spectra
20 minutes each axis

Figure 2
Input Vibration Spectra
30 Seconds each axis

Figure 3
Input Shock Spectra

Figure 4
Input Linear Acceleration Spectra
30 Seconds each Axis

Figure 5
Activated Life Measured Before and
after Environments at -30C, +23C and +73C
(Open-Before, Solid After)

Figure 6
Activated Life Measured at -30C, +23C
and +73C Before and After Environments 4 Times-
(Open-Before, Solid After)

Figure 7
Enhanced Vibration Spectra

Figure 8
Summary of Shock Testing

Figure 9
High G Shock Spectra

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Figure 10
High G Shock
Electrical Response

EGLIN SLED TEST - FUZE 28 - 28 MAR 91

Figure 11
High G Shock SNL Test

Figure 12
ESR as Function of Temperature
(Open-Carbon, Solid-MMO)

Figure 13
Capacitance as Function of Temperature
(Open-Carbon, Solid-MM0)

Figure 14
Activated Life as Function of Temperature
(Carbon Based DLCs)

Figure 15
Activated Life as Function of Temperature
(MMO DLCs)

Figure 16
Sample Space Investigated in this Study

Figure 17
Fraction of Original Capacitance
(Solid points-single DLCs;open points MC4169)

Figure 18
Fraction of Original ESR
(Solid points-single DLCs;open points MC4169)

Figure 21
Predicted Capacitance vs Ageing Time
at Various Temperatures and 5.5 Volts

Figure 22
Model Predictions
(Capacitance vs Ageing Time)

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