DIELECTRIC MODIFICATION OF REPETITION RATE TESTED POLYCARBONATE PERFLUOROCARBON CAPACITORS THE G. H. MAULDIN MEMORIAL REPORT

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Abstract

On December 2, 1986, G. Howard Mauldin, better known to many of us as Howie, passed away. Howie was the programmatic and spiritual leader of the perfluorocarbon impregnated capacitor technology. His work at Sandia National Laboratories in the capacitor area spanned some 38 years. This paper is a status report of the technology and a memorial to a gentle man who quietly carried a flag.

It appears the operational life of a perfluorocarbon impregnated capacitor is a strong function of the crystalline-amorphous character of the polycarbonate (PC) dielectric material. X-ray diffraction studies and thermomechanical analysis (TMA) of the material at the Jet Propulsion Laboratory, Pasadena, California, have shown new information. Gas studies of the impregnate solution have yielded new answers also.

We will also discuss the dynamics of both the equivalent series resistance (ESR) and the equivalent dynamic capacitance of an in situ device as observed during testing at the test facility of the Los Alamos National Laboratory.

George Howard 'Howie' Mauldin

Howie Mauldin came to New Mexico during World War II when efforts at the lab on the hill were in their early stages. He was sent to the famous P.O. Box 1663, Santa Fe New Mexico by the U. S. Army in 1943. Howie graduated from Mississippi State University that year and was selected for the Manhattan Project right out of school. With his degree in electrical engineering he was put to work immediately on the project that would end World War II and begin a new world era. One of the first engineering problems facing his group was the trigger system;i.e. the firing set. In 1949 Howie and about six of his associates moved to the Albuquerque area to staff what was at first a branch of the Los Alamos effort. This new facility ultimately became Sandia National Laboratories.

Engineering improvements and design specifications that could not be attained via the usual industrial sources kept his team busy at the task of firing set component development. A major component of the firing set design was, of course, the capacitor. Development and refinement of this particular component became an obsession and a source of great pride for him in the following years. His requirements were foreign to the industry that already had nearly 40 years to its credit. No one, in a then well established industry ever had to design to such stringent specifications. These same requirements were the fuel for his next 38 years of personal and professional endeavor.

Howie's southern humanism projected into his professional as well as personal surroundings. In the early 60s the first perfluorocarbon impregnated capacitor design that his group produced he dubbed the "Big Mac" in honor of Carol McCampbell, his department manager, who actually brought the fluid to Howie's attention. I believe this era predates the existence of the McDonalds restaurant chain by a significant amount in Albuquerque. He was a division supervisor in those years and was responsible for the hiring and/or early development of many who are in the upper management ranks at Sandia today. By the 1970s he returned to the bench letting others have the task of management; his interest was the hands-on future of this component he so dearly loved. It was this dedication to the effort of capacitor development and the breakthroughs that followed that brought Howie the "Distinguished Member of Technical Staff" award in 1983 from Sandia's management. I remember the pride and honor he felt when the award was made. He called me on the phone the day he received word of his award, as excited as a 10-year-old who just received his first bike for Christmas. I had to keep reminding myself this was a senior citizen I was talking to. Those of us who saw Howie on a regular basis, or not so regular basis will recall the little turquoise lapel pin he wore so proudly. He told me very shortly after receiving it that this made all those years worthwhile. I knew better; I knew all those years were worth it to him all along the way.

Down through the years Howie was responsible, whether by decree or result for several things significant to us who knew him. I believe the single most impressive accomplishment to his name was the successful collection of a team made up of people from three different National Laboratories, (as proud and prejudice as they all are) who have worked together for over 5 years now on the same project.

Repetition Rate Operation

The first series of tests that were begun at Los Alamos (LANL) were done at 100 Hz. Howie's plan was to try to simulate the service life of a capacitor in a few short hours. This led the LANL part of the team to develop the test facility for even faster test rates. The 1 KHz rate was attained in late 1982. The new testing methods introduced his capacitor to the high-repetitive rate power conditioning field and Howie found himself in new territory. Now the entire field of switching devices could be addressed to the perfluorocarbon capacitor technology.

The JPL Connection

Once the repetitive rate test program was producing accelerated test results, Howie began to see the need for sophisticated post-mortem capabilities. It was then that the Jet Propulsion Laboratory, (JPL) was included as a team member. By 1985, JPL

* Honorary author, deceased December 2, 1986.

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14. ABSTRACT
On Decembe~ 2, 1986, G. Howa~d Mauldin, bette~ known to many of us as Howie, passed away. Howie was the p~og~anÂ®atic and spi~itual leade~ of the pe~fluo~ oca~bon imp~egnated capacito~ technology. His wo~k at Sandia National Labo~ato~ies in the capacito~ a~ea spanned some 38 yea~s. This pape~ is a status ~epo~t of the technology and a memo~ial to a gentle man who quietly ca~~ied a flag.

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was utilizing its extensive capabilities in materials science and previous experience with capacitor materials failure analysis to address the chemical post-mortem issues. New characterization techniques were developed that provided valuable insight into the SNL perfluorocarbon-capacitor technology. These activities were continued and extended in 1986 with a stronger emphasis on solid state, chemical, and structural questions of dielectric films associated with electrode deposition processes and pulse charge/discharge repetitive cycle effects.

JPL's approach involved the use of thermal (DSC and TMA) and structural (SEM/EDS and X-ray diffraction) techniques to identify bulk and surface changes in the PC film resulting from the pulse test part of the program. High performance liquid chromatography (HPLC), gel permeation chromatography (GPC) and in situ gas chromatograph/mass spectometry (GC/MS) were used to determine impurity gas content with emphasis on quantifying SF6 levels. X-ray Photoelectron Spectroscopy (XPS) was then used to identify film/fluid/SF6 surface chemical reactions. However, most of the effort involved the adaptation of X-ray diffraction to the analysis of the PC film.

Results of Chemical Analysis

The JPL team carried out gel permeation chromatography and in-situ GC/MS gas analysis of a series of pulse tested capacitors. A comparison of pulsed units with the fluid-only sample reveals that the SF6 concentration decreases with pulse life and is likely consumed during operation. Figure 1 shows the results of our XPS study of the surfaces of:(a) virgin PC and (b) PC film from sample capacitor 005 (a 100 million shot-life specimen).

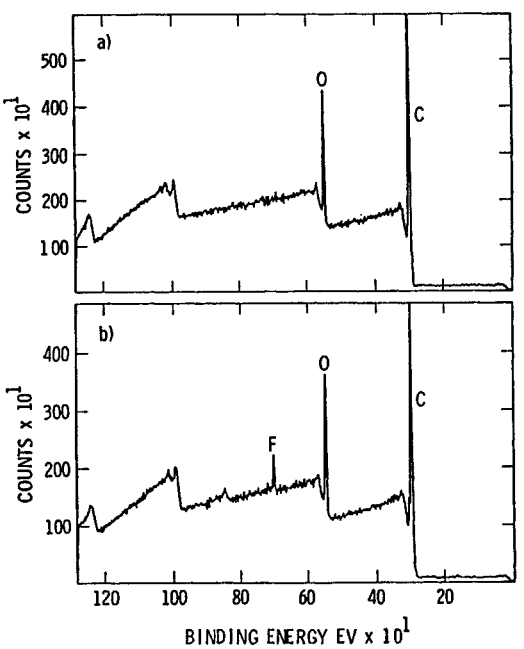

Fig. 1. The fluorine peak in pulsed film (bottom) vs virgin PC film (top) from XPS surface scan.

These studies clearly reveal that a surface reaction between SF6 and polycarbonate is taking place during repetitive high field pulsing. The points to notice are: (1) the emergence of the fluorine (F) peak and (2) the carbon (C) and oxygen (O) peaks are, in reality, multiple peaks as higher resolution scans clearly show. Detailed analysis of the XPS data suggests that the SF6 disassociates in the high electric field environment of the capacitor to yield SF5 and SF4 ions that then attack the ketone group of the polycarbonate. The result is the replacement of the carbonyl oxygen with fluorine. This degradation mechanism is exacerbated by heat. In summary the SF6 concentration was lowest in the device with the longest pulse life, suggesting that SF6 may be consumed during operation. XPS studies clearly reveal a surface reaction between PC and SF6 in which fluorine displacement on the polymer chain occurs.

X-Ray Analysis of Polycarbonate

Much of the latter half of the 1986 effort was devoted to the development and use of X-ray diffraction as a useful diagnostic tool to correlate film structure and response with capacitor performance. In Fig. 2 we show typical X-ray diffraction patterns for a 20 Ga control film of PC.

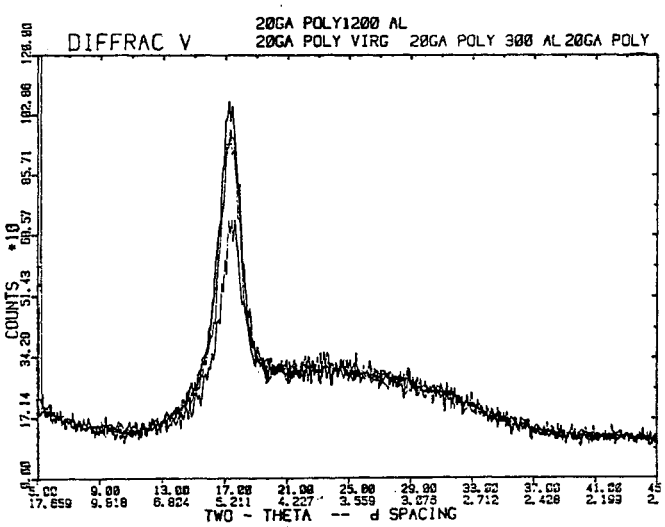

Fig. 2. X-ray diffraction study of virgin polycarbonate film.

The pattern is characterized by a single dominant peak at 18° due to the crystalline phase and a broad peak at 25° due to the amorphous phase. The same sample was then slightly stretched to remove wrinkles, folded three times, and held under light tension in the X-ray sample mount (see Fig. 3). Note the dramatic emergence of a peak at 14° yielding a "double peak" X-ray diffraction pattern. The sample was then relaxed but kept in a folded configuration during X-ray exposure. The 14° peak then disappears. Clearly the 14° peak is related to orientation and/or stress and is quite reversible. We believe that the 14° peak is indicative of an oriented amorphous phase in the PC. That is, upon stretching, (as may occur during winding) the random arrangement of the PC polymer chains (e.g. similar to a bowl of spaghetti) of the amorphous 25° phase rearranges and partially orients, using the crystalline 18° structure as a template reminiscent of epitaxial processes.

The XPS and SEM/EDS measurements displayed in Fig. 1 were all done on the same film that had successfully sustained 100 million shots in capacitor 005. The X-ray diffraction pattern of this film,

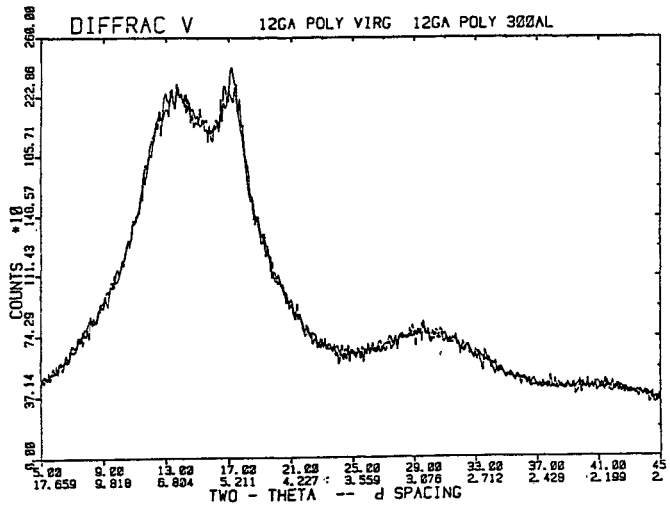

Fig. 3. Mechanically produced 14° peak in polycarbonate film.

(see Fig. 4) also reveals an extremely interesting effect: the "double peak" pattern with the emergence of the same oriented amorphous phase described above. A 12% increase in the growth of this amorphous phase, at the expense of a similar decrease in the crystalline phase when compared to virgin film, is observed after pulsing for better than 100 million shots. This effect is likely associated with thermal as well as with electro-mechanical effects.

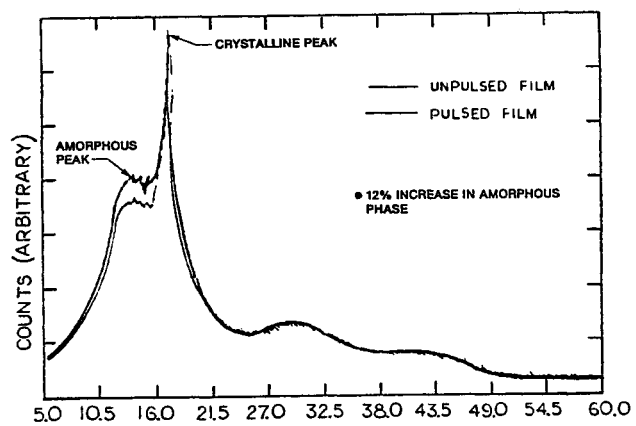

Fig. 4. Long life effect of pulsed operation on population of 14° oriented amorphous phase.

To gain insight about this new effect, X-ray studies were carried out on a new series of samples: (a) four pulsed capacitors(three with relatively long pulse lives and a fourth with a much shorter pulse life) (b) two "control" windings and (c) two control films. Several X-ray measurements were taken on the capacitor film and control winding samples. In general these included (1) one measurement of the film at a point near the start of the winding (2) a second measurement about six inches from the end of the winding and (3) a third measurement about four to ten feet from the end of the winding, or some combination of the above.

The conclusions are as follows: (1) The X-ray diffraction patterns of the 24 Ga and 48 Ga control films are dominated by a single peak at 18° due to the crystalline phase. (2) In the control windings, the double peak structure indicative of the presence of the oriented amorphous phase is found only at the start of the winding and nowhere else. (3) In the good capacitors, the double peak structure has propagated almost throughout the winding. (4) In the short-lived capacitor, there is no evidence of the double peak structure. These data suggest that the existence of the double peak structure is beneficial to capacitor performance. Perhaps some of the amorphous phase at 25° is undergoing subtle orientation during pulsing to yield a film material with more dimensional stability. If this is true, it may be beneficial to pretreat (prewind) the films in advance in order to induce this unusual structure prior to capacitor winding.

We have followed these measurements by determining the thermal response of 48 Ga film wound at sufficient tension to induce the double peak structure and a similar 48 Ga control, or virgin film sample using thermomechanical analysis (TMA). In this technique the sample is heated while suspended with a constant load of 2 g tension. The data are shown in Fig. 5. Note that a negative dimensional change refers to an expansion in the length of the film, while positive changes indicate shrinkage or contraction.

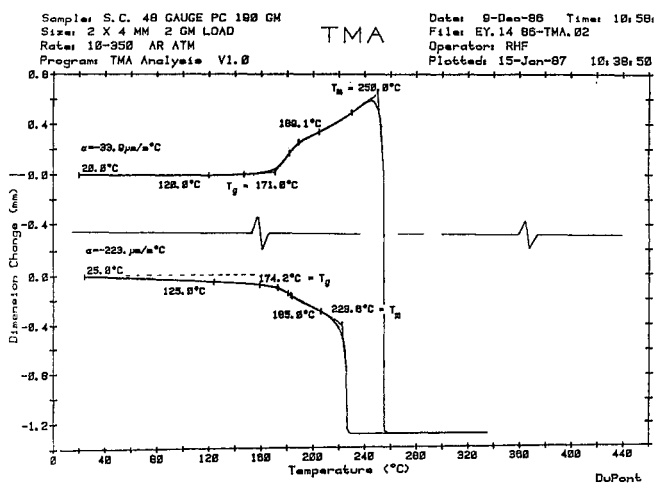

Fig. 5. Thermomechanical Analysis of virgin (top) and double peak (bottom) structures in PC film.

There are several points of interest in Fig. 5: (a) in the control film, expansion occurs almost immediately upon heating, in contrast to the very stable dimensionality (up to 150°C) of the double peak sample; (b) the glass transition temperature (Tg) is observed at 170°C in both samples; (c) most importantly, upon reaching Tg the control film (single peak sample) expands with further heating while the double peak sample contracts. This supports the hypothesis that the low-angle X-ray diffraction peak at 14° is indeed due to an oriented amorphous structure, because upon heating to near Tg, the orientation relaxes and the film contracts. Thus we are confident that the presence of the oriented amorphous phase imparts valuable dimensional stability to the film and enhances capacitor performance and life.

The evidence presented here is based on a small number of test samples. We are in the process of

verifying these data and hypotheses, the bulk of which verifications will not be finished by publication time. However, thus far all subsequent tests have reinforced the foundation of our hypotheses and a following publication from this group will disclose the results by late 1987, or early 1988.

Whole Component Evaluation

In the process of evaluating the performance of various production changes the capacitors are subjected to repetitive pulse service. This test period can run for up to 100 million charge/discharge cycles at the rate of 1000 cycles per second. The real time thermal character of each capacitor is monitored throughout its lifetime. A carefully controlled thermal environment is provided for the capacitors in these tests. By virtue of this thermally stable chamber the case temperature of the device under test can be equated to a power dissipation. When this equivalent power is compared to the RMS system power one can extract an accurate equivalent series resistance (ESR) of the capacitor during full power, real time operation. This method is termed the steady-state calorimetric ESR measurement technique. This is not the same calorimetric method as described by Rust & McDuff [1] at another facility in the Los Alamos complex. Using the steady-state method we have been able to observe the ESR of a capacitor during operation at varying power and stress levels. This has shed light on the "linearity" of the dielectric structure during use. In Fig. 6 we show the ESR of a capacitor wherein the average power has been held constant (thus the core temperature is roughly constant over the test range).

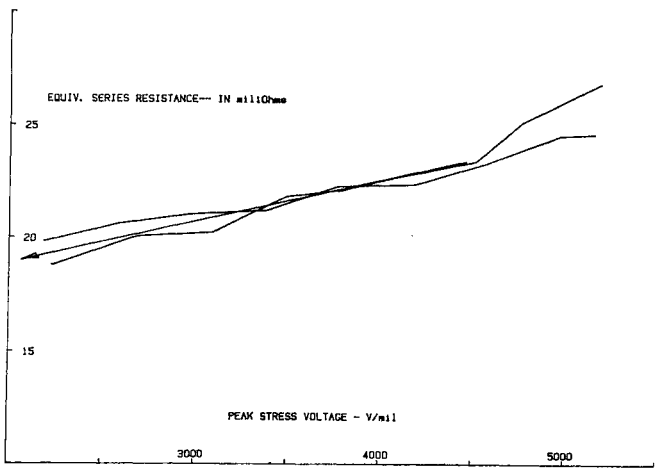

Fig. 6. Equivalent series resistance vs peak electric stress. Arrow shows projection toward zero stress.

There is a near 30% shift in the ESR over the range of 2 KV per mil to slightly over 5 KV per mil stress. The slope of this function is a destructive one, i.e. with increasing stress the ESR rises, increasing the bulk power dissipation as the dielectric stress becomes more tenuous. This has the signature of a runaway situation and in fact is a significant part of the multidimensional, high order function of life vs stress for repetition rate service. The Perfluorocarbon technology has been responsible for totally removing from the data bank the effect of margin punch-through and pin-hole breakdown. The first-order failure mechanism for these capacitors even at these high stress levels has been and continues to be thermal in nature. Therefore, the ESR question is of major importance and implication. We have made repeated measurements by this method and also by the low-level rf resonant technique [2]. Though the ac, Fourier-equivalant-component driving functions differ somewhat between these two techniques the zero intercept of a projected curve (toward zero stress) of the power ESR agrees repeatedly within 5% of the low level rf technique value. This steady state thermal technique has become a standard test procedure in the program.

We are currently using a technique to observe the equivalent capacitance of each device. This technique uses the differential of the discharge current waveform (taken from a Tektronix 7612D transient digitizer). The zero crossing point of this differential can be equated to the equivalent circuit capacitance, 99% of which is the device under test. In Fig. 7 we show the differential functions of several, varied stress discharges with attendant

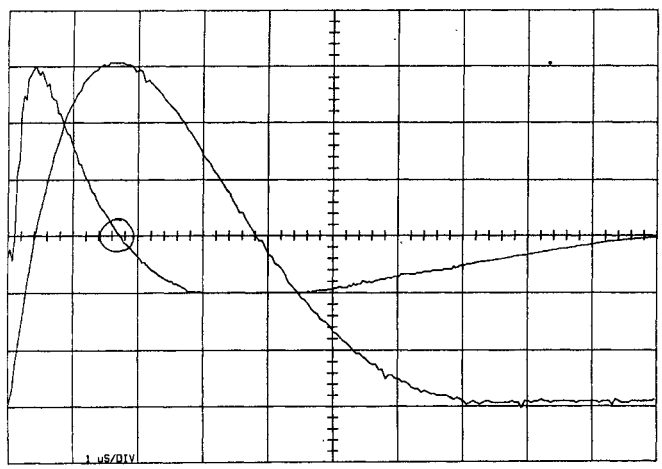

Fig. 7a. Overlay of discharge current and dI/dt waveforms.

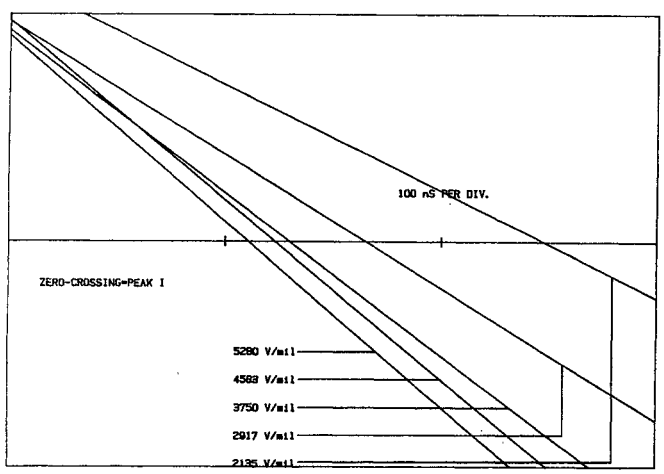

Fig. 7b. Change in zero crossing vs peak electric stress of the dI/dt waveform.

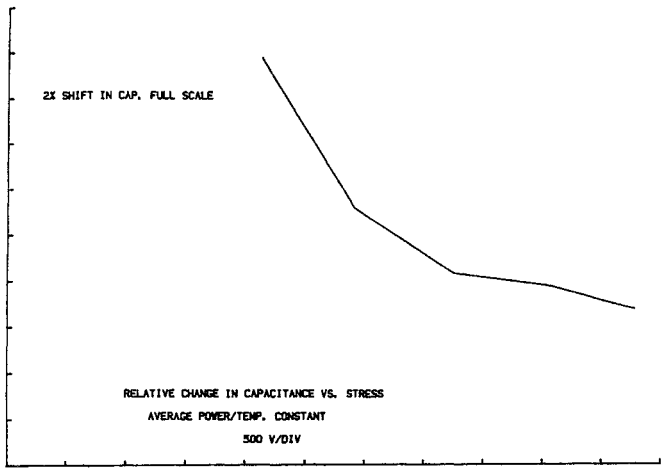

Fig. 7c. Relative shift in capacitance vs peak electric stress.

shift in the zero crossing point and also the function of equivalent capacitance vs stress (device bulk maintained at constant average power and temperature for each stress data set). The resultant function shows a tendency, though not large, for reduced energy storage as the stress is increased.

Conclusion

There is now strong evidence to support the assumed wearing effects of repetitive service in energy storage capacitor usage. One could easily conjecture about the possibilities of chemical modification and ultimate electrical and mechanical changes in the dielectric structure of a capacitor subjected to 2 MV/cm repetitive stress. The tools have been developed at JPL to verify just such activities in the make up of the SNL perfluorocarbon-polycarbonate capacitor. The sensitivity and resolution of these tools will be honed in the next season to detect with exactness the subtleties of these sophisticated chemical alterations. The X-ray diffraction techniques discussed here are receiving much of the attention due to the very exciting double-peak response of certain of the tested and untested samples.

Similar honing of the tools at Los Alamos will proceed in an effort to observe the immediate response to production and material changes. These responses will lead to methods of matching component design to application in a more refined and understood manner. The effects of parasitics and their possible nonlinearities can impact the ultimate application limits of the capacitor. It is our intent to define the character of these nonlinearities.

Howie Mauldin has had an indelible effect on the field of advanced component development and has left a profound and lasting memory for those with whom he worked. We, who knew and worked with him through the years, are deeply appreciative of the IEEE Pulsed Power Conference for permitting this report and memorial, and giving it an "Invited" status at this meeting. He had no plans to quit the race and retire. His most exciting days were his last, as demonstrated by the late developments we present here. The bulk of the chemical developments and findings and hypotheses that have been discussed herein are vintage 1985 to the present. We press on Howard!

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