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Materials and Performance Evaluation of Accelerated Aged XTX8003*

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Abstract

Explosively driven ferroelectric firesets from a dismantled nuclear weapon system have been subjected to "accelerated aging" by thermal. The fireset is based on XTX8003, a Pentaerythritol Tetranitrate (PETN) based extrudable explosive. The chemical condition and performance of the accelerated aged explosive was determined and compared to the condition of the "baseline", i.e. naturally stockpile aged, materials to determine:

1. Is there evidence of detrimental reactions in naturally aged materials?
2. If so, can those reactions be enhanced in order to facilitate kinetic and mechanistic determinations?
3. What are the products of those reactions and which of those products should we look for in stockpile surveillance?

The data show that the explosive has been largely unaffected by age and that the design is robust to meet design requirements.

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1.0. Introduction

In FY96 Sandia National Laboratories (SNL) began, at the direction of the DOE, its Enhanced Surveillance Program (ESP) to evaluate nuclear weapon components with the object to develop predictive life models for those components and, ultimately, for the weapon system. SNL then proceeded to select and prioritize components for that program based on: 1) criticality to its weapon system, 2) prevalence in the stockpile and 3) best engineering and scientific judgement as to which components presented the highest probability of being system life limiting.

Based on the above criteria the MC3028 Slim Loop Ferroelectric (SFE) fireset was selected as the highest priority explosive component for this program. The MC3028 is a part of the explosive initiation train for both the Trident and Minuteman missile systems, two of the major components of the US nuclear stockpile. This SFE fireset is designed to produce a fast rising, high current output for the next assembly exploding bridgewire (EBW) detonator. The MC3028 is composed of two major subassemblies, the MC2368 Driver and the MC3027 Transducer. The MC2368 is based on XTX8003 extrudable explosive, a pentaerythritoltetranitrate (PETN) based formulation (80% PETN/20% Sylgard, a polydimethylsiloxane). PETN is the high explosive (HE) used in SNL components with the lowest melting point and the lowest thermal stability; it has noticeable decomposition in advance of melting and rapid decomposition on melting. Based on its relatively low thermal stability, PETN based components were judged likely to be the most susceptible to low (ambient) temperature, age induced degradation. The MC2368 provides an explosive shock input into the MC3027 which is then transduced into electrical energy. Thus the function of the explosive subassembly is critical to reliable function of the overall device.

Fortunately, due to the retirement of the Poseidon system, the MC2370 SFE fireset, which provided the same critical function in the Poseidon missile, was available for surrogate testing and evaluation. The MC2370 is a nearly identical design, in both function and materials, to the MC3028. This report describes an accelerated aging program that was carried out to evaluate the retired MC2370s and to determine their susceptibility to age induced degradation in both materials and performance.

2.0 Accelerated Aging

Accelerated aging, as used by the Explosives Technology Group (ETG) at SNL, is normally done on new, production parts and materials in order to quickly assess a new component design for indication of material incompatibilities which may limit or preclude the component's long term safety and/or reliability. In this case the starting materials, i.e. the MC2370s, were already naturally, stockpile aged for approximately 25-30 years. The compatibility and reliability of the design was already demonstrated for a nearly 30 year stockpile life. The purpose of this accelerated aging study was to evaluate the component for a continued, extended stockpile life. Thus, for the purpose of this report, we have assumed and adopted the following points:

A. A 10° C rise in temperature above ambient, 25° C, will effectively double the time dependent effects of aging.

B. All MC2370s which have not been subjected to elevated temperature accelerated aging would be assigned an age of 25 years.

These points were adopted simply for the purpose of reporting the data in a manner which would represent the worst case time and temperature conditions as increased age. No real equivalent age for the accelerated aged units is implied or should be inferred from the data presented herein. Based on those assumptions units were aged at 60, 80 and 100 °C for 293, 393 and 537 days and were assigned ages of 30.6 years (293 days/60°), 32.5 years (393 days/60°), 33.8 years (293 days/80°), 35.3 years (537 days/60°), 36.8 years (393 days/80°), 37 years (293 days/100°), 41.2 years (537 days/80°), 41.2 years (393 days/100°) and 47.1 years (537 days/100°).

Chemical analysis data for units aged at 100° are included in this report for completeness and for comparison to data obtained at lower temperature conditions. However, performance test data is not presented for those units, because they failed to ignite from the detonator output. This result is believed to be a result of the extreme temperature and not a reflection of the effects of real aging. The chemical data will show that, when compared to the lower temperature data, the condition of the explosive aged at 100° is not greatly different from the rest. It may be that the greater difference in the materials aged at the highest temperature is physical.

3.0 Physical Condition

Scanning electron microscopy (SEM) was used to examine the physical condition of the explosive lens sub-assembly. This was done to determine if any separation of the extruded explosive from the polycarbonate substrate had occurred in the retired units and, if so, to see if it was induced by the accelerated aging conditions. Figure 1 shows the geometry of the explosive tracks which are formed in the lens during the extrusion process.

Figure 2 is a series of SEM photomicrographs which show the formation of pure PETN crystals on the surface of the extruded explosive. The formation of the crystals is almost certainly due to the sublimation of the PETN at the elevated temperatures. Those photographs are from a unit aged for 537 days at 80° C, but are typical of units aged at both 80° and 100° C. Some crystal formation was seen in units aged at 60° C for 537 days, but unaged units and units aged at 60° C for 293 days did not show crystal growth. The photographs also show that some slight separation of the explosive may have occurred at the elevated temperatures; no evidence of separation of the explosive from the substrate was found in the baseline units.

Figure 3 is a comparison of infrared (IR) spectra obtained from crystals removed from an 80° C, 293 day unit and a IR library PETN spectrum. The crystal spectrum is more defined than the library spectrum, probably due to being from a near perfect crystal, while the library data is from a dispersion in KBr. The match between the crystal spectrum and the library data was better than 80%. It is not known at this time if the PETN is subliming off the surface of the extrusion only or if it is being lost homogeneously from the bulk of the XTX8003. Diffusivity studies at SNL will establish a "most likely" mechanism for this observation.

4.0 Chemical Condition

Chemical analysis of both naturally aged and accelerated aged XTX8003 was used to determine the condition of the explosives prior to test firing both explosive lens subassemblies and full up firesets. The chemical analysis consisted of high performance liquid (HPLC) and ion (IC) chromatography. The data from our chemical analyses are summarized in Tables 1 and 2.

The data in Table 1 includes analysis of PETN meeting MIL-P-387 specifications and PETN that was crash precipitated from an acetone solution of the same MIL-P-387 material. The crash precipitated PETN was prepared for use in XTX8003. The PETN used in the production of the MC2368s used in this study was prepared in the same manner, but was done ~ 30 years earlier. No baseline data for this PETN exists. The data show that, with the exception of Tetrapentaerythritoldecanitrate (TetraPEDN), the PETN homologs, Figure 4, are all present in the freshly prepared starting PETN at levels that are comparable to the aged material. The TetraPEDN is not found in the freshly precipitated explosive, but neither is it found in some of the aged materials; suggesting that it is a product of neither aging nor thermally induced reactions. The TetraPEDN may have been present in the aged explosives since the day the PETN was crash precipitated. The same arguments can be made for the presence of the other homologs, especially since some of them are known side products of the synthesis of PETN. It appears then, that without accurate data regarding the initial levels of these homologs, the presence of those homologs in the XTX8003 is not a good indicator of age or extent of degradation of the XTX8003.

The data in Table 2 is plotted in Figure 5. This data shows that there does appear to be an increase in the levels of organic acids as a function of time and temperature; with the most pronounced being the oxalate ion. It is also clear that the higher levels of organic acids are associated with the higher temperatures used to enhance the reaction rates; however, the important point is that oxalic acid is an observed contaminant in aged and degraded PETN and, therefore, may be a better indicator of PETN age and extent of degradation than the homologs. The precise mechanism(s) and kinetics of the responsible reaction(s) are unknown.

5.0 Performance

The performance of the aged firesets is summarized in Table 3. This table contains both the explosive performance data from the MC2368 explosive lens evaluation as well as the peak current output data from the MC2370 fireset.

The explosive performance was evaluated by use of Velocity Interferometry Spectroscopy for Any Reflector (VISAR) technology. VISAR is a laser based technique that uses the doppler shift in reflected light to measure particle velocities and, therefore, the shock produced into a window material by a traveling shock. In this case the window material was polymethylmethacrylate (PMMA) and the shock levels were calculated using the published Hugoniot data for PMMA[1]. This measured shock will differ somewhat from the shock produced at the interface of the explosive and the reflector, Figure 6, due to the attenuation of the shock by the reflector material. For the purpose of comparison of aged and unaged materials the correction for attenuation was not necessary and was, therefore, not done.

The electrical performance was evaluated by use of a test load to replace the next assembly EBW, which were used during all previous lot acceptance and flight testing. Figure 7 shows a typical output of the fireset into that load.

The data in Table 3 suggest only a slight decrease in shock level for those units that were aged at 80° and above, but a more significant change in the scatter of the data for those same units. Comparison of the shock data to the peak current data shows that the slight trend and larger scatter in the MC2368 explosive performance data did not carry over to the data for the MC2370.

6.0 Conclusions

Methods have been developed for evaluating the MC3028 SFE fireset at both the major assembly and explosive subassembly levels. Although no real, aging performance degradation has been found; this effort will allow a surveillance program to better evaluate which sub-assembly, the MC2368 or MC3027, is responsible in the event that future changes are seen.

Evaluation of retired SFE firesets has shown several things. First, it has shown that accelerated aging can be used to induce chemical changes in explosives in order to determine what reaction products might be expected, and used for stockpile surveillance, from naturally aged components. However, the second thing it has shown is that much of the change induced in the components may have been simply a result of elevated temperature and is not likely to be seen in real aging environments. The data suggest that somewhere between 80 and 100 °C there is a change in rate of degradation such that the higher temperature results a more rapid degradation to failure. This rapid degradation in performance may be more a result of thermally induced physical changes than of chemical degradation. Thirdly, and most important for the firesets studied, this study has shown that the firesets are robust to aging. Naturally aged components, which were known to be reliable at retirement, were aged thermally to the point where degradation was induced and then tested. With the exception of units aged at 100°, these components were tested and shown to perform within the same envelopes as the retired units. Although this work did not result in a model for the aging process in firesets, it does suggest that aging effects are not dramatic and that these components are not likely to be the system, life limiting component.

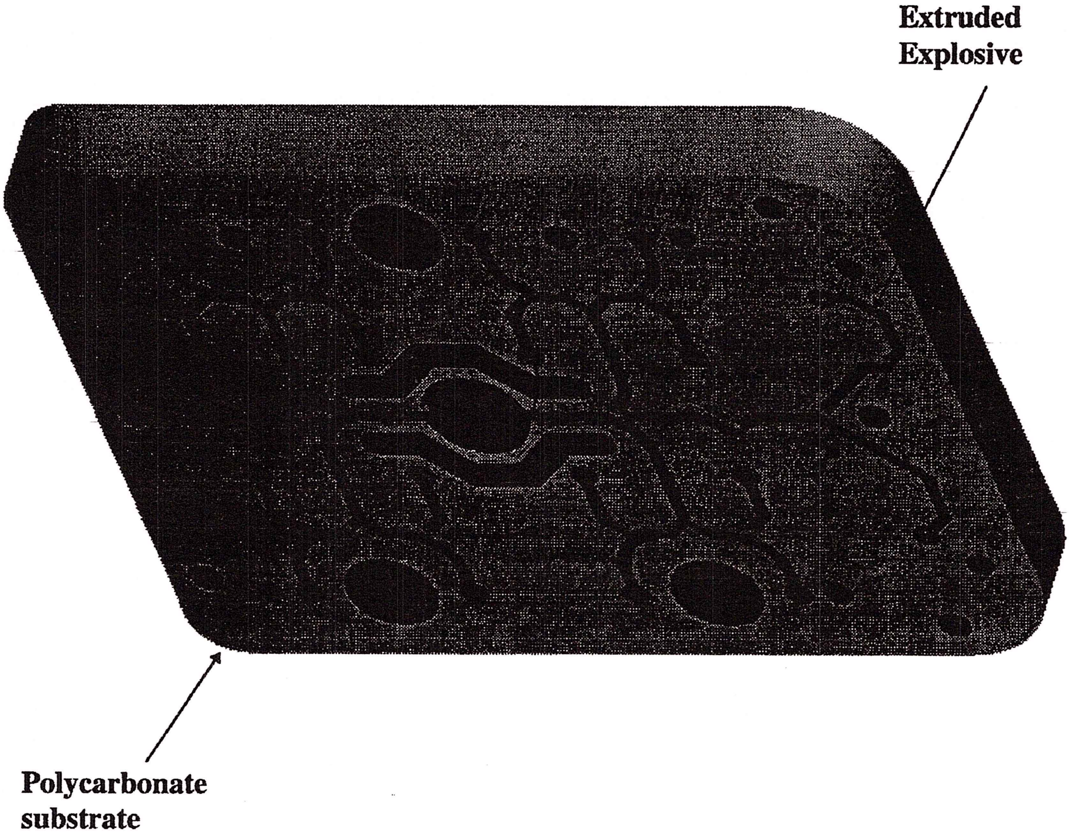

Figure 1. The track plate from the MC2368 explosive lens sub-assembly.

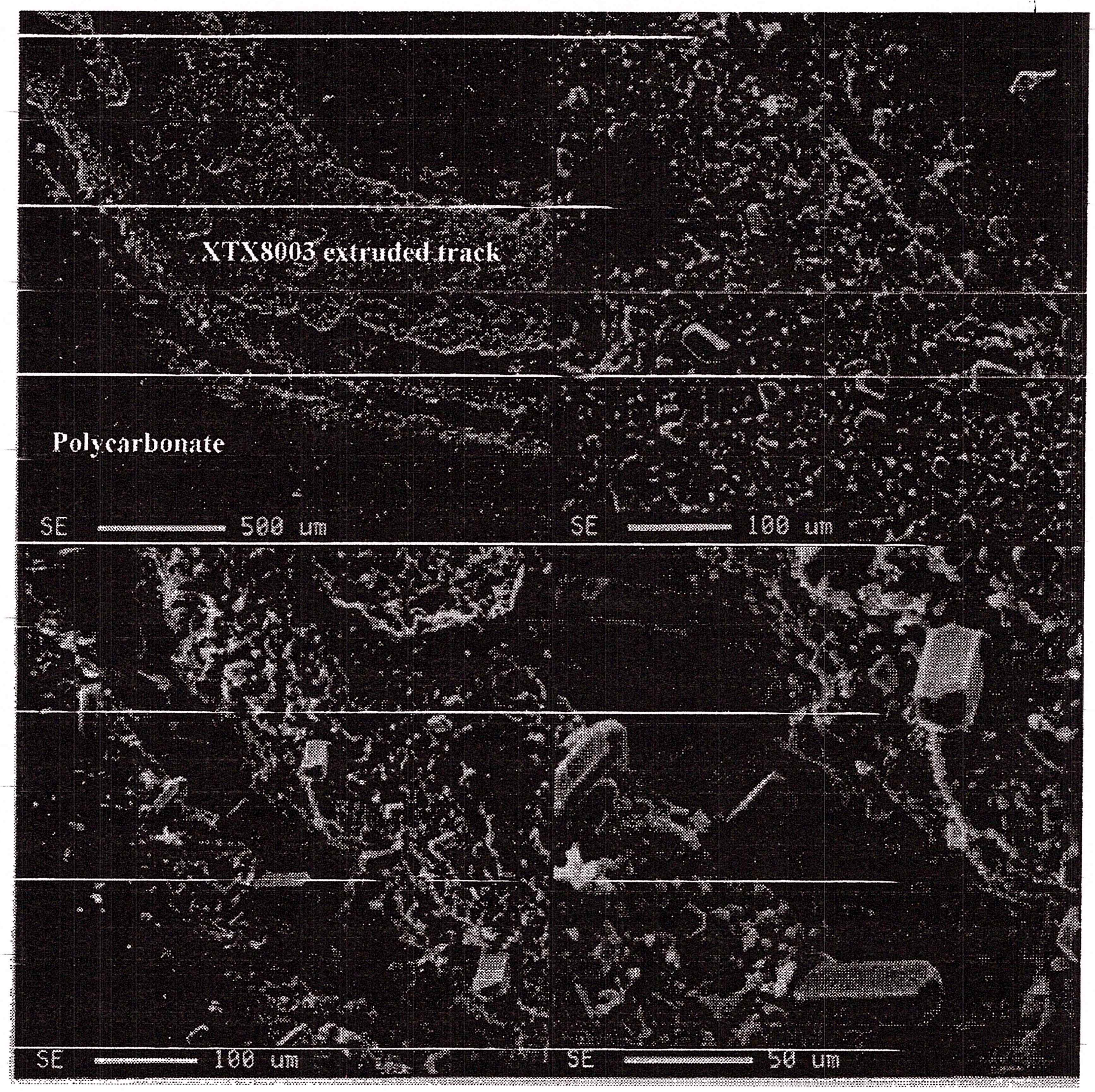

Figure 2. Crystals of PETN formed by sublimation of PETN out of XTX8003.

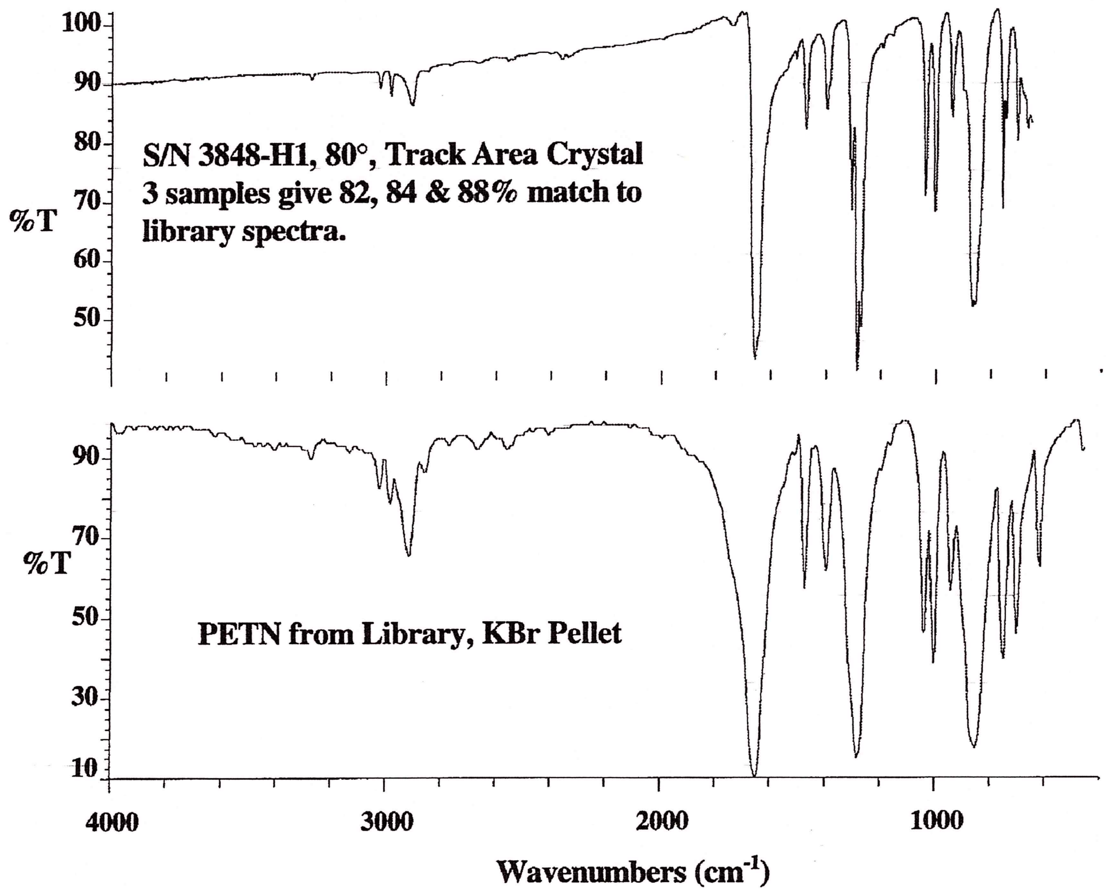

Figure 3. Comparison of FTIR spectra from crystal on XTX8003 and library PETN.

Table 1. Summary of HPLC Data for Aged XTX8003.

Age, Yrs	Wt. % PETRIN	Wt. % DiPEHN	Wt. % TriPEON	Wt. % TetraPEDN
25	.033[3]	0.030 ± .007	.024 ± .003	0
30.6	.020	.061 ± .046	.021	0
32.5	.088	.076	0	.017
33.8	.032	.053	.021	0
35.3	.079	0.135	.005	.025
36.8	.040	0.12	0	0
37	0	0.111	0	.053
41.2[1]	0.136	.059	.002	.031
41.2[1]	0.139	0	0	0
47.1	.063	0	0	0
Mil[2]	.019	0.28	0.012	0
Re-Xtal[2]	.018	0.28	0.013	0

Table 2. Summary of IC Data for Aged XTX8003[4].

Age, Yrs	ppm Nitrate Bulk	ppm Nitrate Surface	ppm Oxalate Bulk	ppm Oxalate Surface	ppm Acetate Bulk	ppm Acetate Surface	ppm Formate Bulk	ppm Formate Surface
25	9	15	0	0	0	0	5	15
30.6	12	21	34	69	9	16	9	16
32.5	20	21	86	90	10	15	16	15
33.8	33	46	32	40	10	19	9	19
35.3	12	15	426	312	26	15	20	15
36.8	32	40	28	40	38	41	9	15
37	29	40	29	47	50	72	9	14
41.2[1]	35	46	34	43	19	34	9	16
41.2[1]	47	564	77	453	69	254	23	166
47.1	108	292	271	403	83	124	29	36

Notes:

1. This value arises from a two separate time at temperature conditions which give the equivalent accelerated age.
2. These materials are included for comparison. The Mil indicates a PETN meeting MIL-387 requirements, the Re-Xtal indicates the same Mil-387 material that was crash precipitated for use in XTX8003. The actual age of the MIL-387 material is unknown.
3. Data presented without a standard deviation is typically from duplicate analysis, data with presented with standard deviations were triplicates or higher.
4. Surface samples were taken from surfaces exposed to the environment, bulk samples were from below the surface.

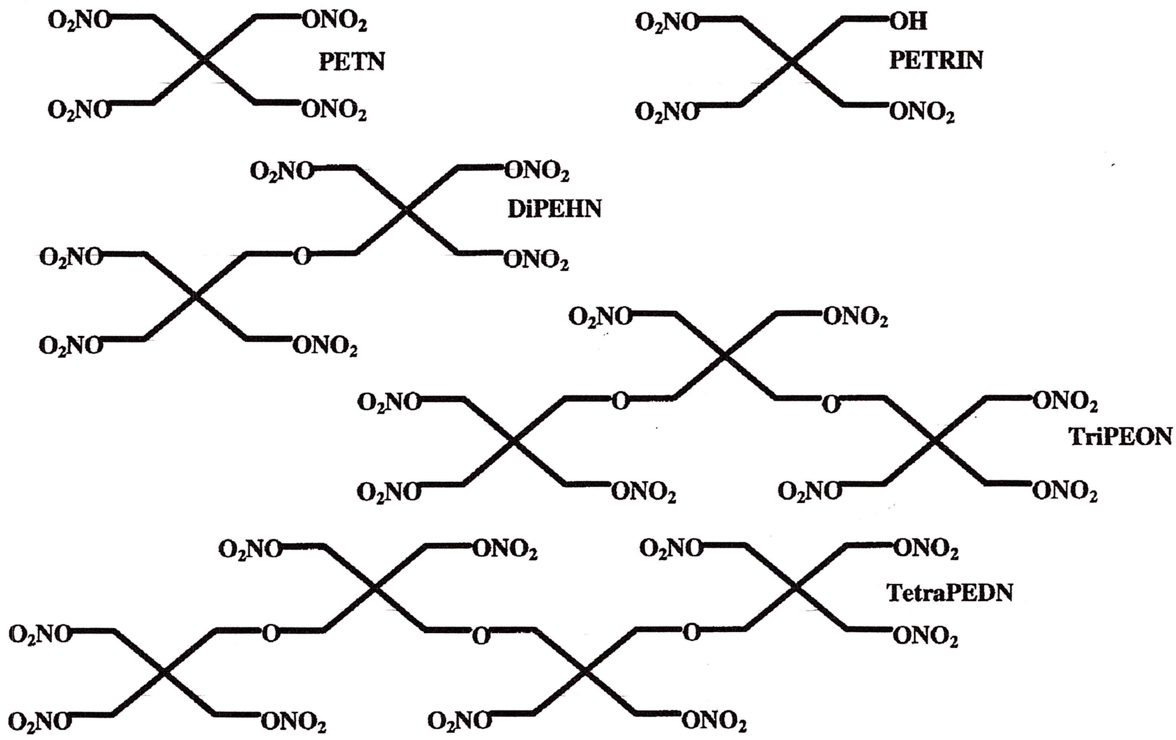

Figure 4. PETN and its homologs.

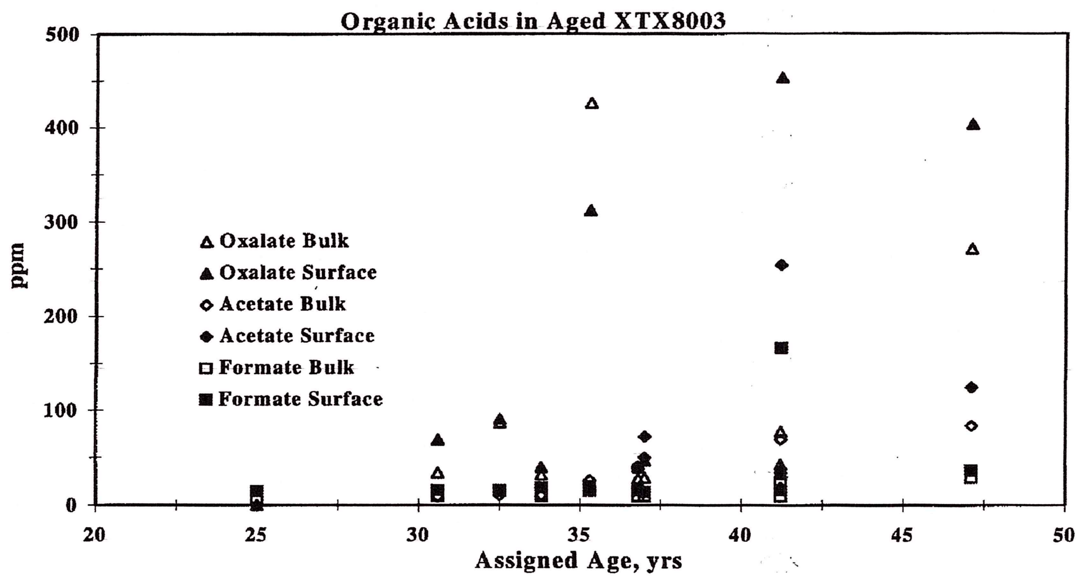

Figure 5. Organic acids in XTX8003.

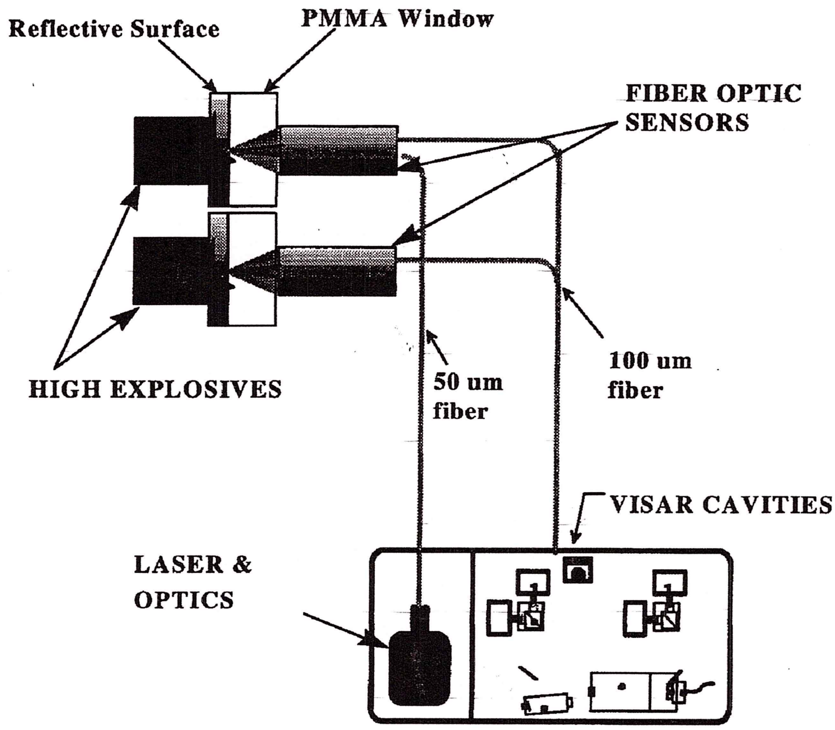

Figure 6. VISAR test schematic.

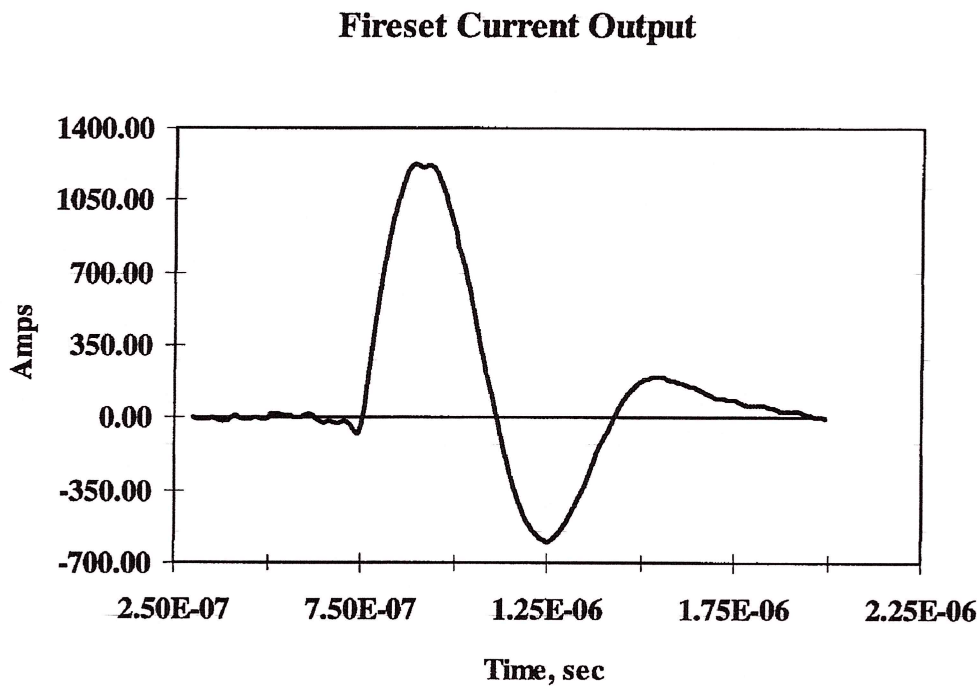

Figure 7. Current output waveform from MC2370.

Table 3. Summary of Performance of Aged MC2370 Firesets.

Age, Yrs	Peak Output Amps[1]	VISAR Shock Data kbar[2]
25	1026.8 ± 38.1	128.4 ± 7.6
30.6	1000.3 ± 53.8	131.0 ± 5.6
32.5	979.7 ± 27.0	129.6 ± 6.2
33.8	1038.8 ± 40.7	118.1 ± 13.4
35.3	1033.6 ± 16.0	122.5 ± 12.1
36.8	1028.5 ± 11.8	125.2 ± 11.8
41.2	990.0 ± 24.8	120.6 ± 12.8

Notes:

1. These values were measured into test loads, lot acceptance test (LAT) data was collected into exploding bridgewire detonators (EBW) and is not directly comparable to this data.
2. This data was calculated from the particle velocity measured with VISAR via the Hugoniot equation for polymethylmethacrylate (PMMA).

References

1. Stanley P. Marsh, Ed.; LASL Shock Hugoniot Data; University of California Press, Los Angeles.

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