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AGING AND PBX 9502

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ABSTRACT

Components made from PBX 9502, an insensitive high explosive formulated with triaminotrinitrobenzene (TATB) and Kel-F 800 binder, have been in service for nearly two decades. Since that time, samples have been destructively evaluated to determine if potential changes that might affect safety, reliability, or performance have occurred in the high explosive with time. Data from routine, historical testing is reported elsewhere. This paper focuses on specific tests conducted to evaluate the effects of natural aging on handling sensitivity (through the small-scale tests of Human Electrostatic Discharge, friction, and Drop Weight Impact), compressive strength, and thermal ignition. Also reported are the effects of a radiation environment on TATB.

Small-scale sensitvity tests show no differences between aged and unaged material. Observed differences in compressive strength behavior are attributed to conditions of original material rather than aging effects. Thermal ignition by flame and laser methods showed no changes between aged and unaged material. Extreme levels of radiation are shown to have only minimal effects in explosive response tests. PBX 9502 is concluded, once again, to be a very stable material, aging gracefully.

INTRODUCTION

Components made from the high explosive, PBX 9502, have been in the U.S. nuclear stockpile since 1979. PBX 9502 was qualified by the U.S. Department of Energy as an Insensitive High Explosive (IHE)[1] prior to inclusion in the stockpile. Since that time potential aging trends have been closely monitored. This paper describes experiments recently completed with this material to evaluate the effects of aging on small-scale sensitivity, compressive strength, and thermal ignition. Also reported are the results of experiments to evaluate the effects of radiation on TATB. The TATB was not aged, but the radiation doses are comparable to thousands of years of stockpile service life. Service life in this context includes transportation and storage environments but does not include unusual or hostile radiation environments.

PBX 9502 is a simple, two-component formulation consisting of the explosive particulate material TATB, approximately 95 % by weight and volume, in a polymeric binder matrix consisting of a single ingredient, Kel-F 800 (polychlorotriflouroethylene). The PBX 9502 used in these experiments was commercially produced by Holston Defense Corporation.

The process of putting a PBX 9502 component into service involves many steps, each of which could be considered a commencement of the natural aging process. These steps include synthesis of the constituents, formulation into molding powder, consolidation into a pressed charge, and final assembly into a weapon. For the purposes of this paper, service life is considered to begin when the component is introduced into a weapon assembly and to end at disassembly. There is an estimated one to two years from first synthesis to assembly and another one to two years from dissassembly to testing. This may be considered an additional two to fours years of natural age, but because it is oustide the service-life window, and because

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those details are frequently difficult to obtain, they are not included in the reported component ages provided in this paper. The term "nominal" as used in this paper refers to components that were made from typical lots of PBX 9502 that did not see any nuclear weapon service life. The natural age, or shelf age, is generally unknown.

SMALL-SCALE SENSITIVTY

Three types of small-scale sensitivity tests were conducted on material taken from each of six components produced from three different lots of PBX 9502. These three lots are represented as shown in Table 1 along with relevant age data. There were two components chosen for testing from each lot and each pair was the same age. As shown in Table 1, one pair of components represented a lot of typical formulation. Another pair, also of typical formulation, was heated, after removal from stockpile service, to 68°C and held at temperature over a period of 31 hours. The third pair represented a formulation lot composed of 50% PBX 9502 recycled from machining scraps and 50% PBX 9502 from new molding powder. These materials do not have the longest stockpile service life. They were made available by other projects. The three types of sensitivty tests performed were Human Electrostatic Discharge (HESD), friction, and Type 12a Drop Weight Impact (DWI). Each of these is briefly described below followed by a summary of the results. Each type of test was conducted on thirteen specimens per component.

HESD tests were conducted by placing approximately 30 mg of PBX 9502 between an electrically grounded needle and a steel dowel charged to 15.24 kV. The spark gap between the needle and dowel was 2.16 mm. A lead foil (0.076 mm thick) was used as a witness plate to assess reaction. Total energy deposited in the test was 0.36 J. The relative humidity in the test room varied from 31.8% to 37.4% while the temperature varied from 21.1°C to 24.7°C.

The friction test was conducted by placing approximately 30 mg between a ceramic dowel and ceramic plate. A 36 kg load (maximum capacity) was applied as the plate was moved 1 cm relative to the dowel. The relative humidity in the test room varied from 42.8% to 45.8% while the temperature varied from 20.5°C to 20.9°C.

The Los Alamos National Laboratory (LANL) Type 12a DWI test releases a 2.5 kg mass onto a steel striker. The striker is in direct contact with a 40 mg specimen centered on a piece of dimpled sandpaper. All of the PBX 9502 tests were conducted at the maximum drop height for the LANL instrument which is 320 cm. The relative humidity in the test room varied from 47.6% to 51.3% while the temperature varied from 19.0°C to 20.1°C

There was no indication of PBX 9502 reaction in any of the 234 small-scale sensitivity tests. The aged PBX 9502, with over seven years of stockpile life, behaved the same as nominal PBX 9502 in the HESD, friction, and DWI small-scale sensitivity tests. Based on these results, it was decided that it was not necessary to conduct a full test matrix, and it was concluded that there would be no observable differences between the typical formulation, heated components, and recycled material in these tests.

COMPRESSIVE STRENGTH

Compressive strength tests were performed[2] on specimens obtained from the components described in Table 1. Ten specimens were machined from each component. Each specimen was a 1.0-in. right circular cylinder with an aspect ratio of 1.0) for direct correlation with historical data. Average specimen densities ranged from 1.890 to 1.893 g/cm^3.

All specimens were tested at ambient temperature (18°C to 24°C, below Kel-F 800 Tg = 28°C) and relative humidity (8% to 42%) using an Instron 1123 Materials Testing Workstation. Strain was measured with an extensometer at a

Table 1. PBX 9502 Component Data

Lot #	Stockpile Lifetime (yrs)	Description
890-022	7	typical formulation
890-019	7	heated material
891-005	10	formulated from 50% recycled PBX 9502

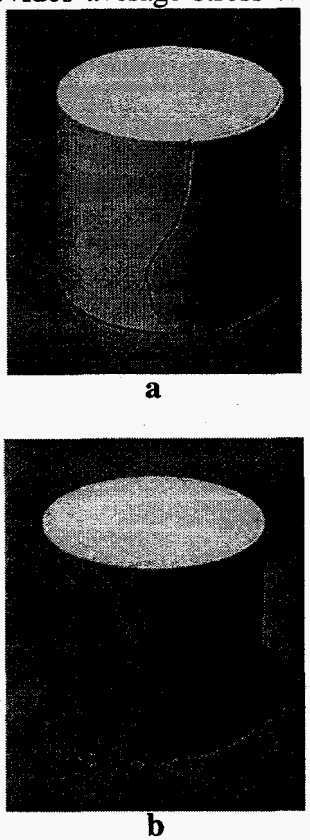
constant crosshead speed of 0.05 in/min. An approximate strain rate of 0.00083 s^{-1} was assumed based on this crosshead speed and specimen dimensions.

Half (5) of the specimens from each component were tested under lubricated conditions and half under unlubricated conditions. Lubrication was achieved by applying Dow Corning 321 Dry Film Lubricant to the compression anvils and allowing to dry for 24 hours prior to testing. Additional lubrication was achieved by application of a thin layer of Molykote 33 grease to each end of a specimen just prior to testing.

The qualitative effects of lubrication within a given lot of material are illustated in Figures 1 and 2. Figure 1a shows an unlubricated specimen with macrocracking along the vertical axis. Figure 1b shows no visible evidence of macrocracking when the sample is lubricated. Figure 2 also shows a qualitative difference in cracking patterns for another lot of material. Figure 3 provides average stress-strain diagrams for all three lots of material. Detailed interpretation of the effects of lubrication on stress-strain behavior are described elsewhere.[2]

Within statistical error (5%), the unlubricated and lubricated specimens produced the same ultimate compressive strength for a given PBX 9502 lot. The average values are 23.8 MPa for the typical formulation (lot 890-022) and 23.9 MPa for the heated material (lot 890-019). These values compare well with the 23.2 MPa reported by Gibbs & Popolato[3] for nominal PBX 9502 (density 1.886 g/cm^3 tested at 24°C).

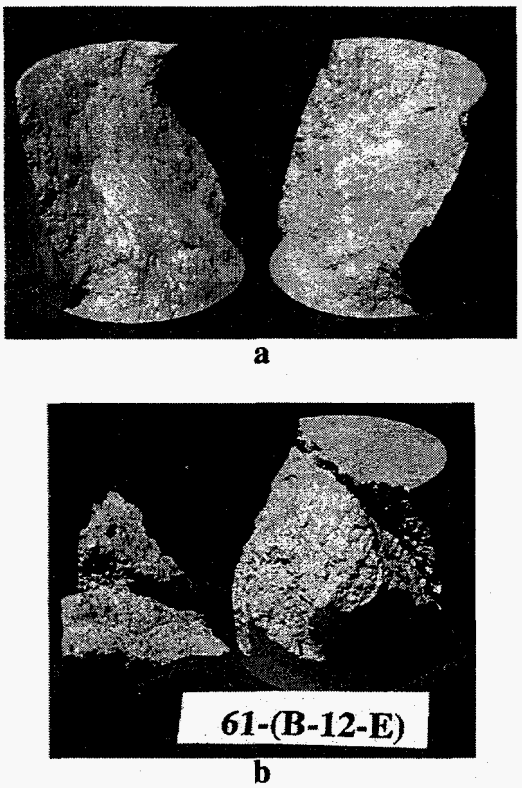
The average ultimate compressive strength for specimens from the recycled PBX 9502 (891-005) lot is 27.6 MPa, approximately 14% higher. Although this material had been in the stockpile three years longer, the higher strength is attributed to the effect of using recycled PBX 9502 for the following reasons. First, the trends in compressive strength behavior are consistent with tensile strength behavior reported for recycled and nominal PBX 9502 lots as tested by Mason & Hanger-Silas Mason Company[4]. Second, age effects were not observed in



a

b

Figure 1. Compression tested specimens obtained from the heated PBX 9502 lot 890019 a) without lubrication. b) with lubrication



a

b

Figure 2. Compression tested specimens obtained from recycled PBX 9502 lot 891-005. a) without lubrication. b) with lubrication

specimens from the other components. Further, Duncan[5] has found that smaller, preformulated particle-size of TATB produces higher compressive strength in PBX 9502. The process of recycling PBX 9502 machining scrap is likely to result in a reduced particle size TATB.

Another effect of the recycled PBX 9502 on mechanical properties was observed. There were two consistent indications that the specimens obtained from the recycled PBX 9502 failed in a brittle mode; 1) a discontinuity in the stress-strain curve at maximum stress, and, 2) evidence of a fragmented specimen during post-test inspection. Specimens from the two other lots exhibited a gradual decline in stress with increasing strain (such as is typical of ductile

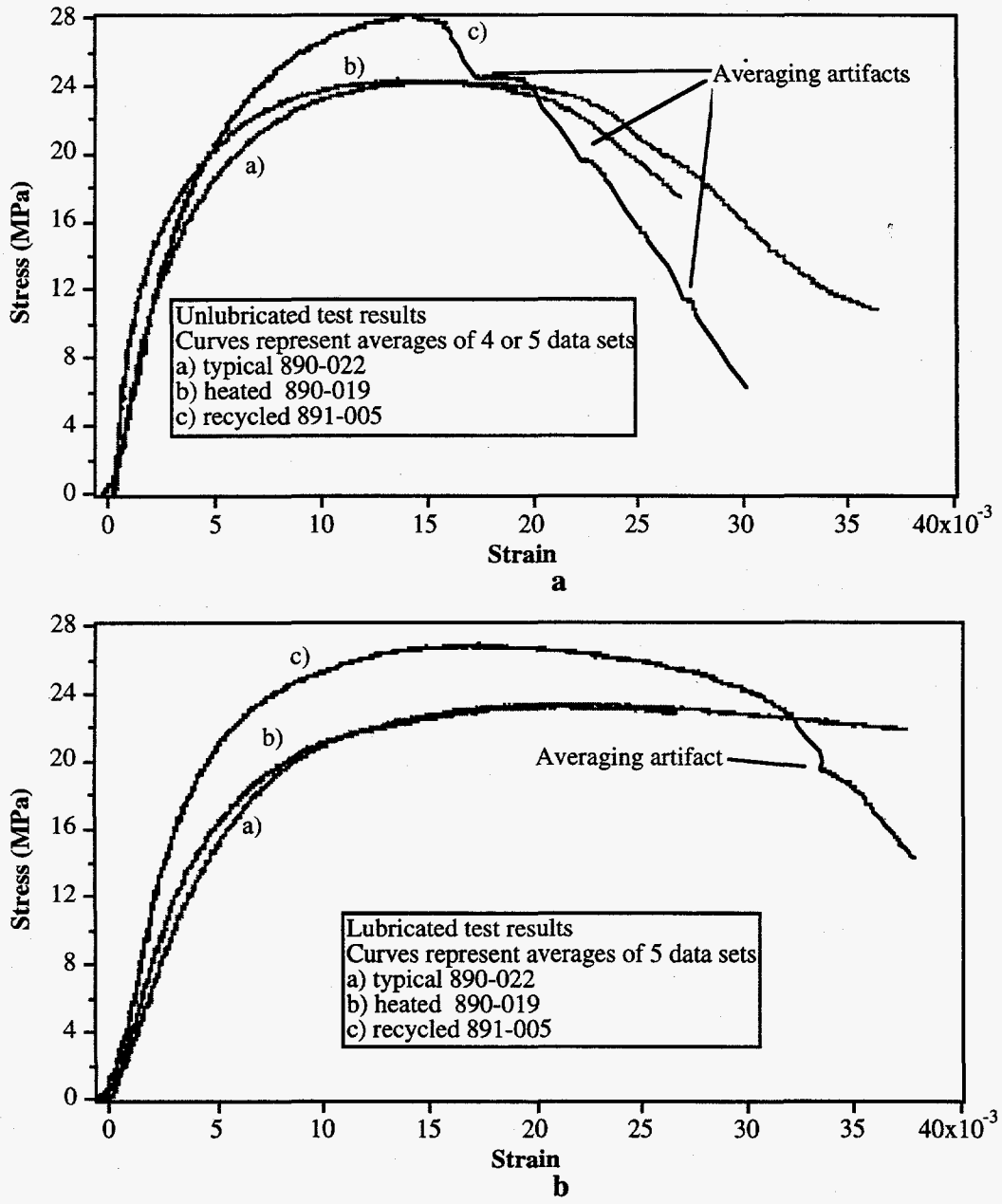


Figure 3. Average values of the stress (MPa) versus strain curves for the three PBX 9502 lots. a) without lubrication b) with lubrication.

failure) and the specimen remained intact as one piece with some cracking evident on the surface. Figures 1 and 2 show this qualitative comparison. As shown in Figure 2a, compression resulted in brittle fracture at 45° to the vertical axis. One of the two pieces shown has been rotated 180° for the image. Figure 2b also shows evidence of brittle fracture.

Figure 3 shows that the PBX 9502 recycled lot, 891-005, exhibits greater compressive strength, a higher elastic modulus, and brittle behavior under comparable strains as compared to the nominal lots.

THERMAL IGNITION

Thermal ignition experiments were conducted on nominal and aged pellets of PBX 9502 (500 - 800 mg each). The nominal pellets were pressed locally. The aged samples (lot 890-018) had experienced over 9 years of stockpile life and an additional 2-3 years of shelf life.

Two modes of ignition were employed to unconfined samples in air: 1) flame ignited (butane flame) and 2) CO_2 laser ignition (see Figures. 5 - 7). After ignition, the samples were permitted to burn through self-heating. A large amount of residue remained after burning, and sometimes the samples would self-extinguish.

Both nominal and aged samples exhibited significant ignition delays (time from first heat flux to self-sustaining reaction) when flame ignited. The butane flame was applied to a sheathed thermocouple to estimate the minimum temperature (850°C) applied to the sample. For comparison, Hatler[6] reported a maximum flame temperature of 1070°C by tungsten/rhenium thermocouple and 1125°C by optical pyrometer for a pressed cylinder of nominal PBX 9502 burning at approximately 2.5 mm/min.

The ignition delay was in excess of one minute with the flame applied to an exposed edge of the pellet. The surface of the pellet blackened within 15 seconds, followed by a glow within about 45 seconds, followed by self-sustained burning after more than 1 minute. In contrast, HMX or PBX 9501 pellets can be flame-ignited within 10 seconds. Figure 4 illustrates a typical flame ignition sequence of aged PBX 9502. No significant differences between aged and nominal PBX 9502 pellets were observed.

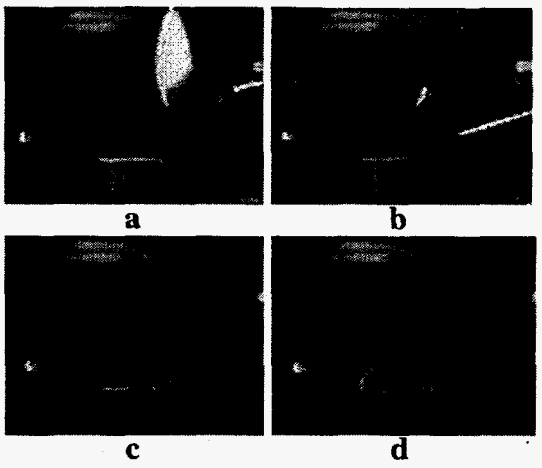


Figure. 4 Sequential pictures of flame-ignited and burning, aged PBX 9502.

While the butane flame may simulate abnormal environments (heating by conduction and convection) more suitably, the laser method provides a well-defined flux with more reproducible and quantitative results. The laser energy spatial distribution is homogonized using a SPAWR beam integrator, yielding a 1.2 cm square beam profile. This yields nearly 1D conditions. Various diagnostics are used to characterize ignition events. A schematic of the laser ignition experiment is shown in Figure 5 and a typical ignition event is shown in Figure 6. Figure 6a shows the initial condition of the aged PBX 9502. Figures 6b-c are during the ignition transient and Figure 6d is self-sustained burning. One indication of ignition is the "first light" as measured using a photodiode.

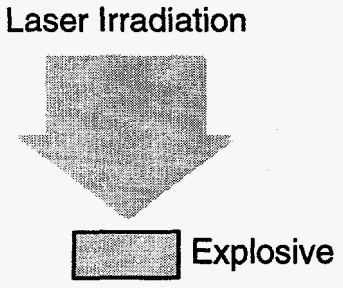


Figure. 5 Schematic of laser ignition experiments.

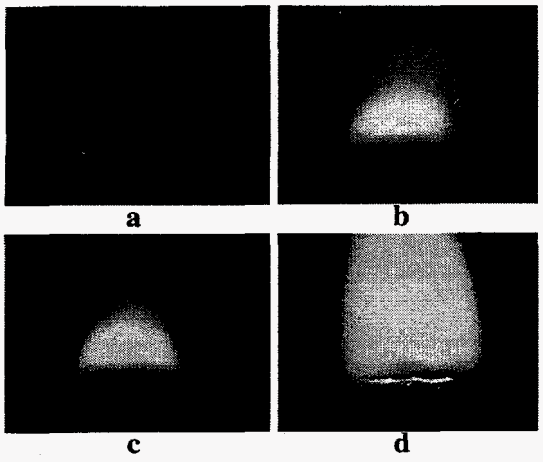


Figure. 6 Sequential pictures of laser ignition experiments of aged PBX 9502.

Figure 7 shows the "first light" as a function of radiation flux. This figure shows that the ignition delay for TATB and PBX 9502 is significantly longer than HMX, PBX 9501, or RDX. Further, the response of aged PBX 9502 is not significantly different from nominal PBX 9502. Further, PBX 9502 and TATB appear to fall on the same ignition line. Pristine PBX 9502 failed to ignite at 27 W/cm^2. Radiant heat fluxes in the range of 30 W/cm^2 to 50 W/cm^2 correspond to black body temperatures of 1244°C to 1450°C. More details of these experiments will be reported elsewhere.

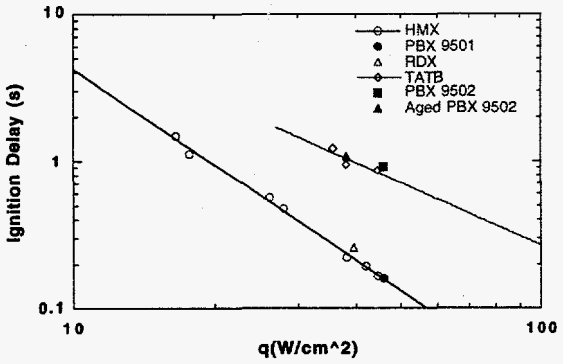


Figure 7. Ignition Delay as a Function of Incident Radiation.

RADIATION EFFECTS

One stimulus, unique to nuclear weapon applications, that may induce aging effects in PBX 9502 is a service life environment that includes penetrating radiation. TATB exposed to ordinary room or sun light turns from yellow to a shade of green proportional to exposure and qualitatively dependent upon the wavelength of incident radiation. It is actually that portion of the electromagnetic spectrum falling below 450 nm responsible for the darkening of TATB.[7] it has been shown by others that TATB exposed to impact, shock, ultra violet (UV) light, heat or electron beams decomposes to other chemical species, which can be isolated.[8,9,10] Some of these species are explosives with sensitivity known to be greater than that of TATB.[8] Electron spin resonance (ESR) measurements on solid (and solutions of) photo-irradiated TATB show large concentrations of free radical species exhibiting unusual stability (no evidence of decay after two years).[11] Since the darkening of TATB from light is a surface phenomenon, the number of radical species formed is probably insufficient to affect bulk properties. Penetrating radiation, however, might cause similar chemical changes affecting bulk properties. Other studies have been performed on explosives using different radiation sources.[12,13,14]

The effect of penetrating radiation on sensitivity of bulk samples of TATB was explored for this study in the following way. Nominal TATB samples (commercially produced Hercules lot 12-11-81-0921-264) were subjected to gamma radiation from enriched uranium fuel rods at the Omega West Reactor of LANL, and proton beam radiation from LINAC at the Radiation Effects Facility of Brookhaven National Laboratory. Samples were pressed, without binder, to nominal densities of 1.840 ±.004 g/cm^3 for the tests that required a consolidated piece. The gamma-irradiated powder was pressed after irradiation while the proton-irradiated powder was pressed prior to irradiation. Samples were analyzed for chemical and thermal stability, impact and shock sensitivity, and performance. All analyses and tests were conducted in parallel with control samples (i.e., not irradiated) of the same material lot.

For the gamma experiments, dose rates were measured as a function of time by placing Lithium fluoride thermoluminscent detectors (TLD-700 dosimeters) in the same radiation environment as the TATB. The dose rate was corrected for density, atomic composition, thickness and gamma energy (average 700 keV) to give an average dose rate of 17 rad/s. At this

dose rate, no sample warming occurred. One hundred gram batches of TATB were given estimated doses of 9 and 70 megarads and accumulated until sufficient material was accumulated for testing. These doses are comparable to thousands of years of stockpile life.

Dosimetry for the proton experiments consisted of thin aluminum activation foils placed on the upstream face of each TATB target. The foil pieces were placed in a germanium crystal scintillation counter as soon as possible following retrieval of the targets. From the dosimetry data provided in protons/cm^2, the energy deposition in the TATB targets was calculated using a Monte Carlo neutron transport code. Proton beam energy for the LINAC was 180 Mev. The estimated dose rate for these experiments was 300 Krad/s. Results are reported only for the samples receiving the highest dose, 17 Mrad. Sample temperature was monitored and remained below 125°C.

Chemical analyses of irradiated and control samples for impurities were performed using a thin layer chromatographic (TLC) scheme reported by Britt, et al.[11] for identifying TATB decomposition products. Spectrometric determinations by the techniques of infrared (IR), mass spectrometer (MS), and electron spin resonance (ESR) were made using standard methods. Scanning electron micrographs were also taken. High temperature vacuum stability tests were performed by heating 200 mg samples at 250°C, 275°C, and 300°C for 120 minutes and measuring the volume of gas evolved. The differential thermal analysis (DTA) test heated a 4 mg sample at 10°C/ minute and determined the onset temperature for a runaway exotherm. The Differential Scanning Calorimeter test is similar to the DTA with the additional quantification of energy evolution (DSC). The accelerated rate calorimeter (ARC) test measured induction time to runaway reaction for a sample (200 mg) held at 240°C.

The Drop Weight Impact (DWI) tests were performed using 40-mg samples on a Type-12a striker/anvil assembly impacted with a 2.5-kg weight. The ballistic impact chamber (BIC) test was performed by Steve Coffey at NSWC and is described elsewhere.[15] This test measures the total energy release and rate of release for a specific impact stimulus. The mushroom test is a sensitive measure of initiability and corner turning ability of pressed explosives and is, therefore, a measure of explosive performance. In this test 1-in. hemispheres of pressed explosive are initiated with a thin cylindrical PBX 9407 booster, which makes up the stem. Streak cameras are used to monitor detonation-wave breakout on the surface of the pressed part.

All irradiated samples showed some degree of color change to green proportional to the received dose (e.g. lime green for the 9 Mrad samples and dark green for the 70 Mrad samples). The color change is not nearly so dramatic as one might expect, however, based upon TATB's reactivity towards room light. Chemical analysis by TLC identified mono and difurazan decomposition products only in the 17 and 70 Mrad samples. IR, MS and SEM analyses showed no changes in any of the irradiated samples. ESR spectra showed the presence of large concentrations of free radicals. The ESR specrum from gamma-irradiated TATB is qualitatively different (broader) than that of room-light-irradiated TATB. This is not surprising due to the higher energy of the gamma spectrum in comparison to ambient light. Photodecomposition reactions with higher energy thresholds are accessible with gamma-irradiation.

Vaccum stability test results are shown in Table 2. and suggest a decrease in thermal stability as a function of radiation dose. The DTA exotherm of irradiated (70 Mrad) TATB shows a decrease in the exotherm onset temperature of about 3.5°C. Multiple runs of control and irradiated material indicate this shift is indeed real. To further explore this subtle, but definite effect, TATB was dissolved and then recrystallized. After one cycle, the exotherm onset was closer to that of the control. After two cycles, the trace from the contol was matched. Presumably, the recrystallization process removed any impurity compounds that may have caused the reduction in onset temperature.

DSC results also showed a decrease in exotherm onset termperature, from 325°C for the control material to 310°C for the 70 Mrad irradiated material. The ARC test indicated a reduced induction time from 54 hours (control sample) to 28 hours (70 Mrad sample).

There were no reactions of any TATB samples during DWI testing. BIC test data are shown in Table 3. These results indicate a very reduced total energy release and rate for the 9 Mrad samples.

Mushroom test data from samples of all three levels of irradiated material matched the control. Particle velocities and Chapman-Jouget pressures were measured for control samples and 16.7 Mrad TATB cylinders using Fabry Perot interferometry and found to be identical.

Irradiation of TATB with penetrating radiation, both gamma and particle beam, had little to no effect on macroscopic behavior. Small concentrations of previously identified chemical impurities[8,9,10] were formed in TATB samples subjected to radiation doses equivalent to thousands of years in the nuclear stockpile. It is presumed these impurities are responsible for the slight changes in thermal sensitivity observed in DTA and DSC tests. A decrease in reactivity to mechanical impact in the BIC test was observed for irradiated samples. One possible explanation is that furazan/furoxan formation results in the release of water. Perhaps these water molecules are adsorbed into the TATB powder and provide some desensitization. Performance of irradiated TATB samples, as measured using the mushroom test and Fabry Perot interferometry, was identical with that of the control material. There is, therefore, no reason to expect any degradation of TATB high explosives in the nuclear stockpile, other than possible changes to the binder of the formulated material. Recent work, however, indicates that even the binder in TATB-based formulations used in the nuclear stockpile (Kel-F 800) is extremely insensitive to radiation-induced changes.[16,17]

CONCLUSION

Several experiments were conducted on PBX 9502 with over 7 years of stockpile life. No changes attributable to aging effects were observed. Test results from the small-scale sensitivity experiments of Human Electrostatic Discharge, friction, and Drop Weight Impact showed no changes in the behavior of the PBX 9502 with age. Compressive strength tests display differences between the recycled and nominal PBX 9502 lots which are attributed to the differences in the particle size distribution of TATB in the original lots, not with age effects.

Thermal ignition tests were conducted on pellets from PBX 9502 with over 9 years of stockpile life and compared with newly pressed pellets. There were no observable differences between the two materials when ignited by flame or laser.

TATB proved largely immune to effects from penetrating radiation. Small concentrations of chemical impurities are formed in TATB when subjected to radiation doses comparable to thousands of years of nuclear stockpile life. These modify, slightly, the onset response of TATB in thermal tests. It is difficult to envision an accident scenario involving TATB with such an extremely high level of radiation damage and one in which a slight reduction in onset temperature would make a difference in the final outcome. Ballistic Impact Chamber test results indicate reduced reaction violence from irradiated material when subjected to low amplitude mechanical insult. Tests more relevant to conditions of intended use indicate that shock sensitivity and performance are unchanged. These results with TATB may be extrapolated to conclude that safety and reliability are not compromised by radiation-induced aging of PBX

Table 2. Vacuum Stability Test Results (cm^3 gas evolved/gram TATB in 120 minutes)

	250°C	275°C	300°C
Control	0.2	1.2	12
9 Mrad	0.4	2.0	22.8
70 Mrad	0.7	4.3	>23.0

Table 3. Ballistic Impact Chamber Results

	Control Sample	9 Mrad sample
Total energy release (J/g TATB)	50	6
Energy release rate (psi/μsec	45	0.12

9502 in a nuclear weapon service life environment.

PBX 9502 continues to age gracefully in the nuclear stockpile, proving itself to be a very stable material.

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