LA-13389-MS

Sensitivity of Once-Shocked, Weathered High Explosives

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Edited by Noel Fletcher, Weirich and Associates, Inc., for CIC-1

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LA-13389-MS

UC-901,
UC-902, and
UC-741
Issued: July 1998

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* Note: All "F" labeled specimens were fresh cut from the weathered piece, while "W" labeled specimens were weathered.

GLOSSARY

AMR	American Metals Research
CEF	Tris(beta-chloroethyl) phosphate
CNC	Computer numerical control
Composition B	TNT/RDX explosive; also called cyclotol
DTA	Differential thermal analysis
DOP	Dioctyl phthalate [bis(2-ethylhexyl)phthalate]
DX	Dynamic experimentation
Estane	Polyester-polyurethane (B.F. Goodrich)
Gap	As in space between entities
HE	High (energy) explosives
HMX	Cyclotetramethylene tetranitramine
HPLC	High-performance liquid chromatography
IR	Infrared
kV	Kilovolt
Kel-F	Chlorotrifluoroethylene/vinylidene fluoride copolymer (3M)
LANL	Los Alamos National Laboratory
LX-10	Livermore explosive (HMX/Viton A)
MDA	Material disposal areas
NC	Nitrocellulose
NMIMT	New Mexico Institute of Mining and Technology
NMR	Nuclear magnetic resonance
OSW-HE	Once-shocked, weathered high explosives
PBX	Plastic bonded explosive
RDX	Cyclotrimethylenetrinitramine

SEM	Scanning electron microscope
TA	Technical area
T_c	Critical temperature
TNT	2,4,6-trinitrotoluene
UXO	Unexploded ordnance
Viton A	Vinylidine (or vinylidene) fluoride/hexafluoropylene copolymer

SENSITIVITY OF ONCE-SHOCKED, WEATHERED HIGH EXPLOSIVES

Kema L. Williams and Betty W. Harris

ABSTRACT

Effects caused by stimulating once-shocked, weathered high explosives (OSW-HE) are investigated. The sensitivity of OSW-HE to mechanical stimuli was determined using standard industry tests. Some initial results are given. Pieces of OSW-HE were collected from active and inactive firing sites and from an area surrounding a drop tower at Los Alamos where skid and spigot tests were done. Samples evaluated were cast explosives or plastic bonded explosive (PBX) formulations containing cyclotrimethylenetrinitramine (RDX), cyclotetramethylene tetranitramine (HMX), 2,4,6-trinitrotoluene (TNT), mock or inert HE [tris(beta-chloroethyl) phosphate (CEF)], barium nitrate, cyanuric acid, talc, and Kel-F. Once-shocked, weathered LX-10 (Livermore explosive [HMX/Viton A, (95/5 wt %)], PBX 9011 [HMX/Estane, (90/10 wt %)], PBX 9404 [HMX/nitrocellulose, tris(beta-chloroethyl) phosphate, (94/3/3 wt %)], Composition B or cyclotol (TNT/RDX explosives), and PBX 9007 (90% RDX, 9.1% styrene, 0.5% dioctyl phthalate, and 0.45 resin) were subjected to the hammer test, the drop-weight impact sensitivity test, differential thermal analysis (DTA), the spark test, the Henkin's critical temperature test, and the flame test. Samples were subjected to remote, wet cutting and drilling; remote, liquid-nitrogen-cooled grinding and crushing; and scanning electron microscope (SEM) surface analyses for morphological changes.

I. INTRODUCTION

Since 1943, research, development, and testing of explosives have been done at Los Alamos National Laboratory (LANL), Fig. 1.

This work has resulted in extensive contamination of the soil, buildings, equipment, underground storage tanks, material disposal areas (MDAs), and the industrial and sanitary drain systems, including connecting subsurface structures. Environmentalists tasked with the assessment, sampling, and cleanup of contaminated facilities and grounds are concerned for their safety both from injuries due to premature explosions and poisoning from toxic substances.

Initially, the sensitivity of the energetic material will depend upon the material's particle-size distribution, density, and method of preparation. However, in theory, once-shocked, weathered high explosives (OSW-HE) can become sensitized by previous mechanical stimuli, foreign

materials, biodegradation products, and aging. This study re-examines some mechanical properties of samples of OSW-HE using standard sensitivity tests.

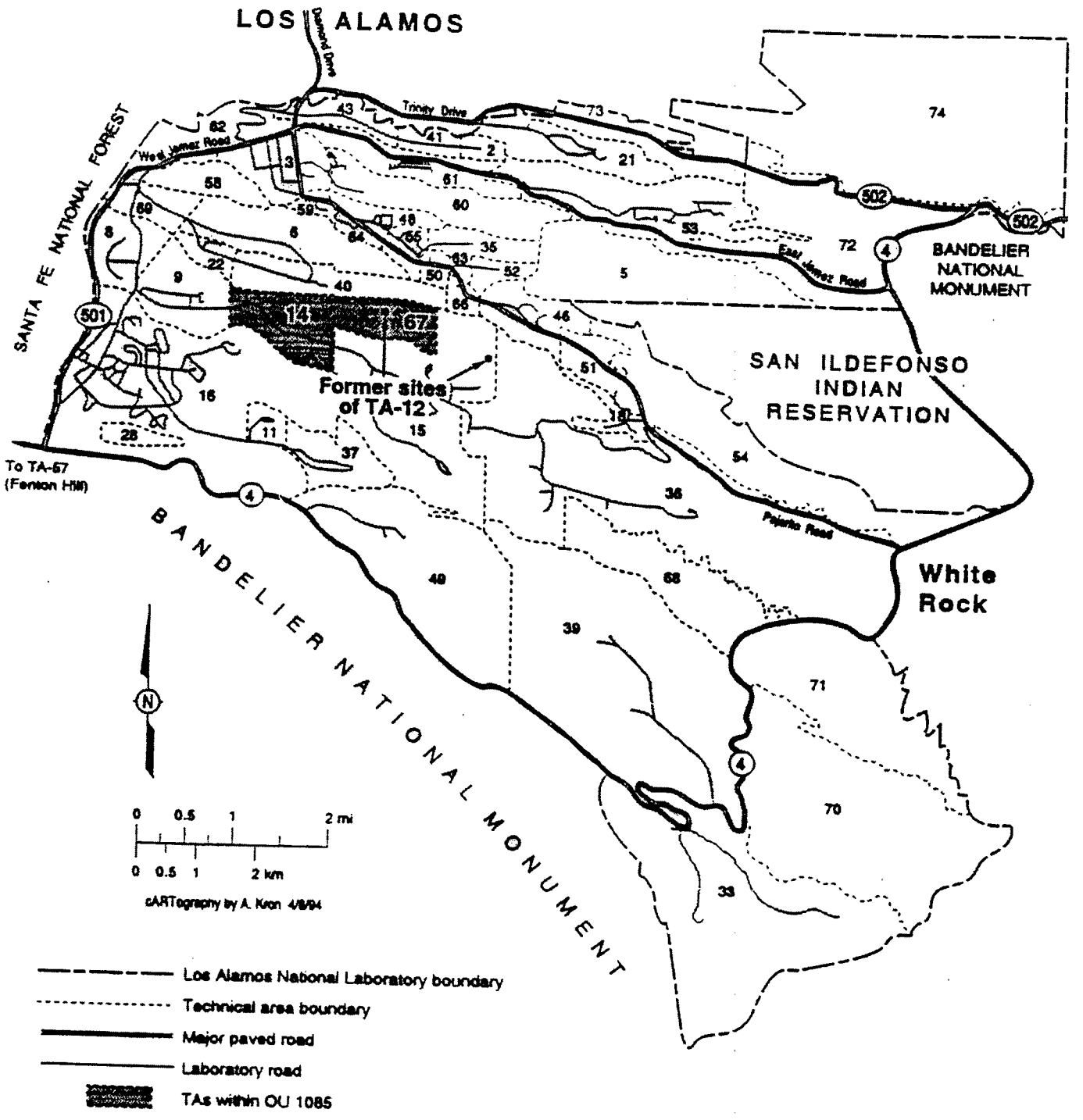


Figure 1. Location of Laboratory Technical Areas 11, 14, 16, and 67 with respect to other technical areas and surrounding landholdings.

An explosive is a pure or formulated chemical compound that possesses a tremendous amount of potential energy. It can react violently when initiated by an outside stimulus. This energy is forcefully released in the forms of heat and gaseous products. Whether the material deflagrates (burns rapidly) or detonates depends upon its confinement and the speed at which the supersonic shock wave, if produced, travels through the material.[1]

Explosive samples in this study are generally those that have been shocked and scattered during the test firing of a weapon component or during the performance and safety testing of a new explosive. In the latter, the material explodes or undergoes a partial detonation, which scatters the solid material over the grounds rather than consuming it.

In the skid and spigot tests, the explosives are dropped from a predetermined height at a given angle, and during the mechanical impact, it is possible to have shearing, heating, explosions, and detonations. Gap tests, both large and small, are examples of basic tests done on explosives to measure the transition thickness of a detonation wave. This measurement is usually reported at 50% load, i.e., the thickness at which a detonation is sustained beyond the added plates for 50% of the time.[2-5] This example is an explosive train test in which the material to be boosted is loaded, by pressing or casting, into one end of a steel tube that is mounted on a witness plate, Fig. 2.

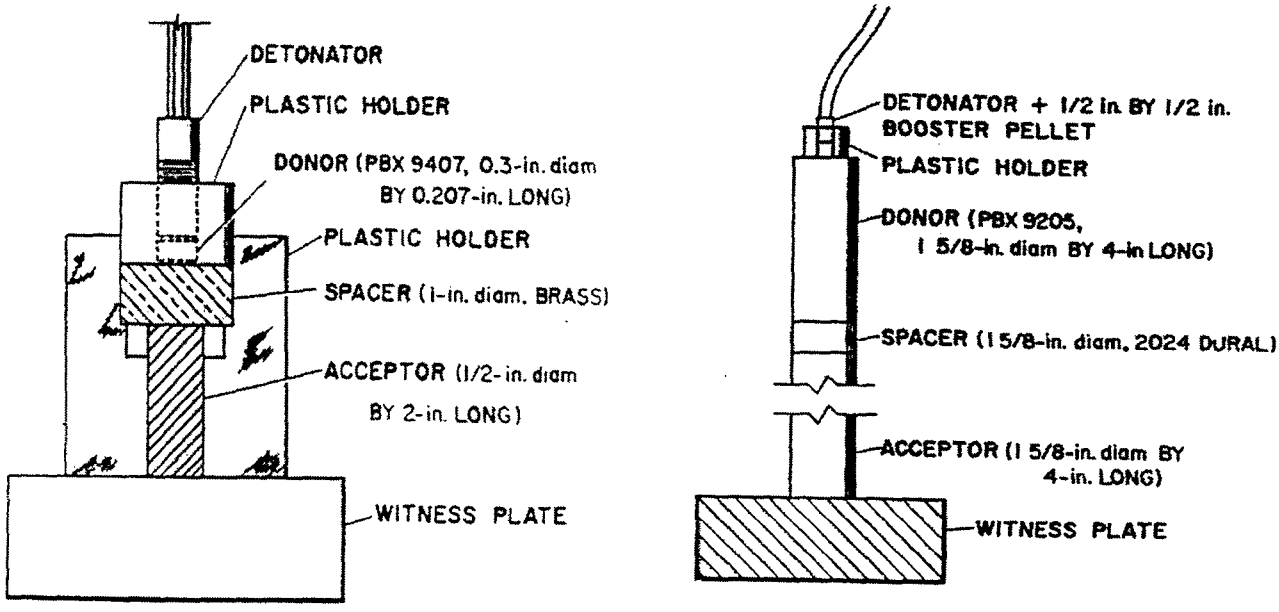


Figure 2. (Left) Small-scale gap-test assembly. (Right) Large-scale gap-test assembly.

Then, one or more disks of half-hard brass, each with a thickness of 0.017 in. and a diameter equal to that of the steel tube, are loaded into the tube and pressed against the charge. The booster explosive is placed into a plastic holder, an ellipsoid cross section, is placed on top of the plates. The assembly is exploded by means of a detonator. It is noted whether the explosive beyond the disk or disks undergoes high-order detonation. Repeat tests are made to determine the maximum number of disks necessary to prevent detonation of the booster explosive. Over the years, some phases of this experiment caused the HE to be scattered in the soil around the test pad. Partial

detonations and misfires also accounted for small amounts of the explosives being released into the soil.

All samples have been exposed to the weather and other environmental elements, and their organic structures have been altered or contaminated. This may increase their sensitivity. Also, we believe that biodegradation products can cause adverse sensitivity effects in the formulated explosive. In New Mexico, biodegradation is slower because of a lack of moisture, as compared with the rapid biodegradation in humid states such as Louisiana. Still, biodegradation does occur in New Mexico's soil, and its products are considered as sources of OSW-HE contaminants.

II. THEORY OF EXPLOSIVE INITIATION

Unexploded ordnance (UXO) also are a concern to environmentalists working in active and inactive military installations. However, UXO are not addressed in this study. The samples examined are uncased, once-shocked pressed materials.

There are several theories as to what initiates a reaction in energetic materials. The most acceptable one is that "hot spots" are created in the explosive. It either burns slowly (deflagrates) or heats up, evolving into gaseous products, building up pressure, and becoming a self-sustaining explosive reaction. Impacts, friction, heat, and electrostatic sparks have been known to create these hot spots. The theory of hot spot creation has been extensively studied.

Deflagration is believed to be the most likely response to the stimuli imposed by environmentalists. When energetic materials are subjected to heat, they reach an ignition temperature at which they begin to burn. The material first volatilizes from the surface before it reaches a temperature at which it under goes exothermic decomposition. Between 500°C and 1700°C, these materials have been shown to produce a self-sustaining reaction. Deflagration is a surface phenomenon. The reaction products flow away from the unreacted material below the surface. In finely divided explosives, deflagration of all particles can occur almost simultaneously. Confinement or low viscosity of the gaseous products may increase the pressure to the point of an explosion or, in some materials, a detonation.

A simple, easy to use method for testing the initiation of an explosive is to subject it to a blow from a falling weight. This method was developed at the turn of the century and used by the military as early as 1941, with it being standardized by the U.S. Army and Air Force in 1955. There are several types of impact machines. Until recently, the reproducibility depended upon the operator's ability to distinguish between an explosion, which is termed as a "go," and no detectable response, which is termed as a "no/go" reaction.[6]

Explosions resulting from a blow or from a sample being struck by an outside stimulus are probably caused by the development of hot spots of finite size within the material. The following items are three suggested causes for an explosion when the sample is struck: (1) small air or vapor bubbles trapped within the material are adiabatically compressed; (2) heat arises from friction between a particle of grit with a crystal of explosive under the pressure of impact; or (3) viscous heating of rapidly flowing explosive under the pressure of impact.[7]

Hot spots are generated by sudden changes in pressure and temperature. Confined gases, carbon dioxide, water, and nitrogen oxides can cause the pressure to build up to an explosion; or a shock wave is produced that initiates and sustains a detonation. The explosion or detonation occurs rapidly. The chemistry and physics of both phenomena have been explained in many ways. The behavior of the gases deviates from the simple gas law and is expressed by the van der Waals equation:

$(P + a/V^2)(V-b) = RT$ van der Waals Equation

where P = pressure,
T = temperature,
R = gas constant,
V = volume per mole,
a = attractive force between molecules, and
b = volume occupied by the molecules.

The solution to this equation is cubic in nature, making it inconvenient to use. Berthelot developed a more often used equation of state using critical temperatures, T_c, and critical pressures, P_c.[8]

This equation is shown below:

$PV = nRT [1 + 9/128 P/P_c T_c/T (1 - 6 T_c^2/ T^2)]$,

where n = no. of moles of gas.

This equation is used for a reaction with moderate pressures. M. A. Cook developed another equation of state for high temperatures and high pressures involved in explosions. [8] This equation is shown below:

$PV = nRT + a(v)P$,

where a(v) is the average covolume of the products of the explosion.

Detonations are based upon three laws: conservation of momentum, conservation of mass, and conservation of energy. Employment of these three laws can lead to an equation of state in the general form expressed by Cook.[8] Temperature, detonation rate, and transition velocity of product gaseous molecules can be derived. Many factors may cause a variance in these results, and one of these is heat. Temperature tends to increase the sensitivity of explosives. Equations of state have been used for many years in the study of the properties of explosives. Yet, there is no perfect and universal equation of state.

III. LABORATORY TESTS FOR SENSITIVITY

To measure the sensitivity of OSW-HE specimens, we used the following tests: the impact sensitivity, the hammer, the critical temperature, and the spark tests. Laboratory tests for evaluating the sensitivity hazard use small (10 to 100 mg) samples. Among these are the drop-weight impact from the hammer and a standard LANL impact machine, friction, and electrostatic sensitivity.

A. Henkin's Critical Temperature Test

When heated, confined energetic materials will decompose. In the process, a self-heating to explosion may occur. This is caused by a buildup of pressure from gases generated in the heating process. The temperature just below the self-sustaining reaction temperature is labeled the critical temperature (T_c).[9] This measurement is a good indication of the materials' reaction to gradual heating. The T_c of this reaction is expressed in relationship to other physical and chemical parameters in the Frank Kemeneneskii equation:

$$E/T_c = R\ln(a^2pQZE/T_c^2ldR),$$

where R = the kinetic gas constant (1.9872 cal mol^{-1} K^{-1}),
a = is the radius of a sphere or cylinder, or the half-thickness of the slab,
p = density,
Q = the heat of reaction during the self-heating process,
Z = pre-exponential,
E = activation energy from the Arrhenius equation,
l = thermal conductivity, and
d = the shape factor (0.88 for infinite slabs, 2.00 for infinite cylinders, and 3.32 for spheres).

B. The Hammer Test

The sensitivity of the explosives to mechanical impact was tested by hammer blow and with the LANL drop-weight impact machine. The hammer test is an initial indication of the sensitivity of the explosive to an outside impact stimulus. A few grains of explosive were placed on a clean steel surface of a witness plate and hit with a hammer. Audible responses were recorded as sensitive. A more scientific measurement of the same sensitivity was done with the drop-weight impact machine.

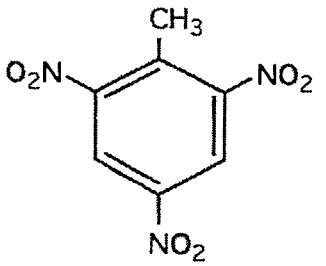
C. Drop-Weight Impact Sensitivity Test

An air-conditioned, humidity controlled room in the Dynamic Experimentation (DX) Division at Los Alamos houses the impact machines. The impact machine used was an ERL Bruceton No. 12 design developed by the U.S. Navy Surface Weapon Center-Explosive Research Laboratory at the Explosive Research Laboratory, Bruceton, Pa. The fundamental components are a 1.25-in. diameter steel anvil upon which the sample is placed, a 1.25-in. diameter steel cylinder or striker that rests on the sample, and a 2.5-kg steel weight or hammer that is dropped from various heights onto the striker.

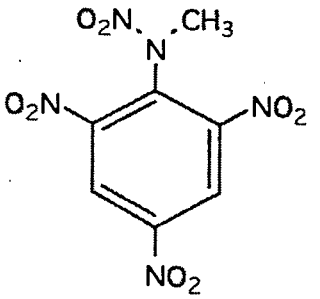
The Impact Machine is calibrated from drop heights of 0 to 320 cm with a set of standards and according to a standard procedure. The anvil is cleaned with acetone. Samples, 40 mg, are weighed on a sandpaper circle and placed upon the anvil. A 2-kg weight is raised to a predetermined height by a manual crank. The "go/no go" response is detected by two strategically placed microphones that send a signal in decibels (dB) to the corresponding readers. The sum of the two readers must equal or surpass 240 dB to yield a "go."

D. Remote Crushing, Grinding, Cutting, and Drilling

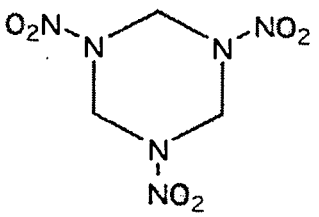
Chunks of PBX 9404, cyclotol/Composition B, PBX 9007, LX-10, PBX 9011, and PBX 900-10 were collected from the ground. The explosive components of these formulations are shown in Fig. 3.



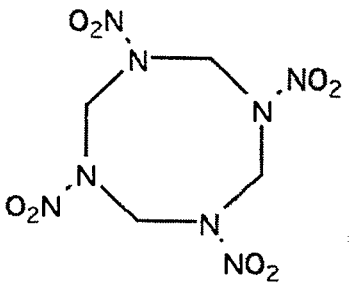
TNT FW = 227.1



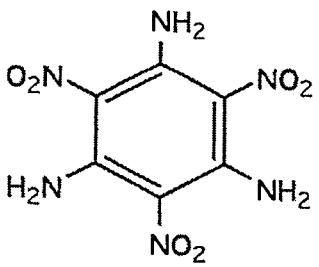
TETRYL FW = 287.1



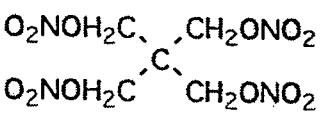
RDX FW = 222.1



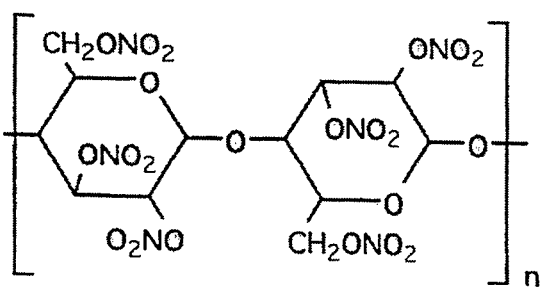
HMX FW = 296.2



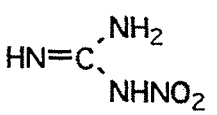
TATB FW = 258.1



PETN FW = 316.1



NC



NQ FW = 104.1

Figure 3. Common high explosives.

The HE must be in a powder form in order to run several of the other tests. Crushing and grinding apparatuses were used to prepare the samples. The response of the HE to crushing and grinding gave us an indication of its sensitivity to these operations. However, because of the manner in which these operations were made safe, they provided little or no information on a true environmental encounter with OSW-HE.

The two machines used for crushing and grinding were an electrically operated mortar and pestle manufactured by Fisher Scientific and an electrical, explosion-proof, dust-tight crusher manufactured by Masters. The chunks of HE were soaked in liquid nitrogen and placed in the crusher. After crushing, they were transferred to a liquid-nitrogen-cooled mortar and pestle. Remote, strategically located cameras monitored both operations.

Pure and formulated explosives are sometimes drilled, sawed, and cut in order to shape them into components that can be used in weapons' applications. Our weathered HE was wet-drilled and -cut to see whether or not there were visible signs of reactions from the processes. These experiments gave us an indication of the sensitivity of the weathered HE in the environment to drills and shovels that might be used in taking samples.

E. Electrostatic "Spark" Sensitivity Test

An explosive's response to an electrostatic stimulus is another measure of its sensitivity to initiation. The sample is subjected to a single discharge from a condenser that is charged to a high voltage. [10] A voltage increase and, then, decrease are used to vary the discharge for each sample until 50% of the trials produce an ignition. This test is known as the Bruceton method.

The sample is placed in a steel dowel holder with a cemented polystyrene sleeve around it. The dowel has a 3/16-in. inner diameter with a 1/4-in. opening at the top. A lead foil disk covers the sample once it is in the dowel. The foil and sample are held in place with a polystyrene ring. The dowel is then placed on the grounded plane for the electric circuit.

A variable (0-15 kV) power supply is used to charge a selected condenser in a condenser bank. Any total value of capacitance from 2×10^{-4} to 4 microfarads can be obtained by a switching arrangement that allows one to connect any of the eighteen (18) condensers in the bank in parallel. The condenser output is connected to a moving electrode device, similar to that used by the U.S. Bureau of Mines and described by Brown, Kusler, and Gibson.[11] This device operates like a spring-loaded phonograph needle or a single-stroke sewing machine. The apparatus is cocked, and a phonograph needle placed in the chuck. As the spring is released, the needle moves down and returns. The duration of the stroke is about 0.04 s. From a positively charged needle, the spark moves through the explosive material to ground. The spark energy is taken as the energy stored on the selected capacitors.

F. Other Stimuli

Another method of stimulating and evaluating weathered explosives is differential thermal analysis (DTA) that is described in the experimental section of this report.

IV. EXPERIMENTAL

Pressed, cast, or plastic bonded explosives tend to show little or no solubility in soil. Also, when exploded or busted apart, fragments tend not to be thrown very deep into the soil (less than 1 ft). Therefore, at some test facilities, pieces and chunks have remained on or near the surface for many years. We collected pieces and chunks of explosives for analysis. Results were compared to the unweathered samples. There were two types of samples collected: those that had been shocked from actual test firings and those that had been dropped from a tower during skid and spigot tests. Samples were taken from TA-67 (TA-12) near two inactive firing pits and around the TA-11 drop tower. A few samples were taken from Canyon de Valle below the tower.

A. Sample Description

PBX 9011 [HMX/Estane, (90/10 wt %)] fragments from the Los Alamos skid test were picked up from Canyon de Valle. They were estimated to have been there for more than five years. This sample of PBX 9011 appeared as a dull, grayish, hard material with little or no evidence of biodegradation. Estane is a polyester-polyurethane.

LX-10, Lawrence Livermore National Laboratory explosive No. 10 [HMX/Viton A, (95/5 wt %)], samples were collected along the canyon edge, very near the drop tower at TA-11, Fig. 4.

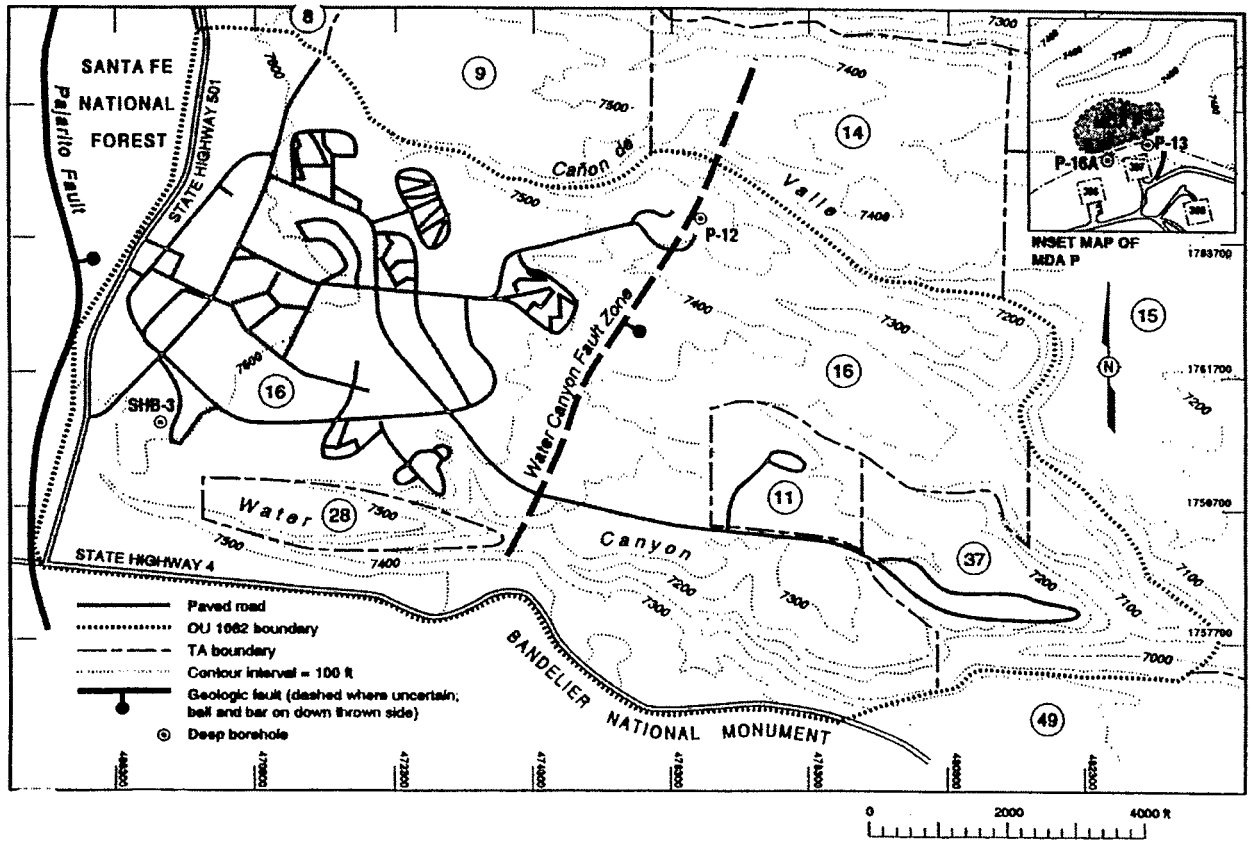
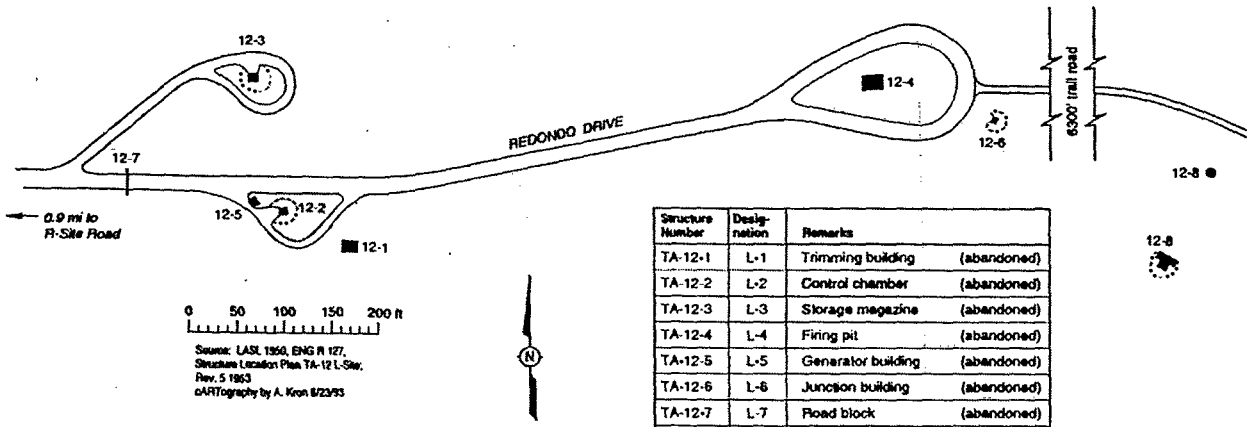


Figure 4. Structural geology and topography of the Weapons Research Area.

LX-10 is a hard, white material with green specks throughout. It has a smooth clean, fresh surface. These Livermore explosives had been on the ground for about one year. They are leftover fragments from the skid test used at Los Alamos. Viton A is vinylidine fluoride/hexafluoropylene copolymer, 60/40 wt %.

Composition B or cyclotol [RDX/TNT, (75/25 wt %)] was found as a dirty, brownish ball of material with a beady surface. These small samples were taken from TA-67 (TA-12) L-Site, Firing Pit 1, Fig. 5. Analysis showed them to be nearly 100% TNT. They had been in the area for more than 30 years.



Structure Number	Designation	Remarks
TA-12-1	L-1	Trimming building (abandoned)
TA-12-2	L-2	Control chamber (abandoned)
TA-12-3	L-3	Storage magazine (abandoned)
TA-12-4	L-4	Firing pit (abandoned)
TA-12-5	L-5	Generator building (abandoned)
TA-12-6	L-6	Junction building (abandoned)
TA-12-7	L-7	Road block (abandoned)
TA-12-8	L-8	Radiation test structure (abandoned)

Figure 5. TA-67 (TA-12) L-site, Firing Pit 1 (TA-12-4).

Another explosive from TA-67 (TA-12) L-Site was very hard and pink in color, but it was not the inert material used in an explosive test. It had a white, powdery surface. Analysis showed it to be nearly 100% RDX and a polymer. Private communication confirmed that it was PBX 9007 (90% RDX, 9.1% polystyrene, 0.5% dioctyl phthalate, 0.45% resin, and a red dye). This explosive had been the booster on the end of a 126A detonator. It measured about 1 in. in diameter and 1/4 in. thick. It had been in the area for more than 20 years.

PBX 9404 [94% HMX, 3% nitrocellulose (NC), 3% tris(beta-chloroethyl) phosphate (CEF)] was collected as a few hard, greenish-blue pieces from the bottom of Canyon de Valle near the drop tower at TA-11, where the skid test were done. The greenish color probably comes from the biodegradation or reaction of diphenylamine in the formulation to form a dye.

Pink samples identified as PBX 900-10, a mock HE, were also collected from areas around the TA-11 drop tower. We were concerned when most of the samples had other materials attached and tested positive for explosives. Later, we were told that the inert material was sandwiched in between pieces of explosive component being dropped or, sometimes, the material may have been packed around the explosive.

Tris (beta-chloroethyl) phosphate (CEF), nitrocellulose (NC), and barium nitrate, $Ba(NO_3)_2$, are components in PBX 900-10 and older versions of mock explosives. Cyanuric acid, talc, and Kel-F [a chlorotrifluoroethylene/vinylidene fluoride copolymer (3M)] are the combined ingredients in the

Tris (beta-chloroethyl) phosphate (CEF), nitrocellulose (NC), and barium nitrate, $Ba(NO_3)_2$ are components in PBX 900-10 and older versions of mock explosives. Cyanuric acid, talc, and Kel-F [a chlorotrifluoroethylene/vinylidene fluoride copolymer (3M)] are the combined ingredients in the modern day version of a mock explosive formulation. The deep pink or red color comes from the dye that is added.

B. The General Procedure

A physical description was recorded of all samples. The pH was determined. The samples were again tested for the presence of explosives with the high-explosive spot test kit. Then milligram quantities were placed in the flame of a burner, and the results recorded. This was followed by the hammer and drop-weight impact tests. Using a remote apparatus, milligram quantities of each sample were subjected to grinding and crushing. Spark and Henkin tests were also run.

C. Differential Thermal Analysis

The thermal behavior of the weathered explosives was investigated using the differential thermal analysis (DTA) technique. Weathered samples were compared with the standards. The endotherms and exotherms were recorded during a regulated heat treatment of the explosive and an inert reference. Both were heated at a constant rate in the same environment.

A DuPont instrument, the 910 Differential Scanning Calorimeter, is connected to a TA instrument, Thermal Analyzer 200, and an IBM laser printer to record data.

D. Scanning Electron Microscope

The scanning electron microscope (SEM) utilizes a collimated, focused beam of electrons to scan along the surface of a specimen to produce a secondary electron image. This three-dimensional image of the specimen surface is focused onto a cathode-ray tube, where it may be viewed and/or photographed. The spatial resolution along the scanned surface ranged from 200-300 angstroms; useful magnifications up to 30,000× are possible. The depth of the focus obtainable is on the order of tens of microns, which means a fairly rough surface will remain in focus at a high magnification. This depth of focus is illustrated in the accompanying photomicrographs.

SEM Sample Preparation

Samples were cut into small pieces to expose both smooth and weathered surfaces. The fresh cut surface is denoted "F," and the weathered surface is labeled "W." Micrographs were made for each series with magnifications from 200× to 1,000×. The photographs ranged from 500× to 10,000×.

SEM Equipment

An American Metals Research (AMR) Scanning Electron Microscope, Model 1000, was used. It had an operating voltage of 5 kV and a beam current of 25 microamperes. The working distance was 12 mm, with a specimen tilt of 25 degrees. The magnification for each series was 200× to 10,000× as indicated; the recorded film used was Polaroid Type 52.

SEM Photographs

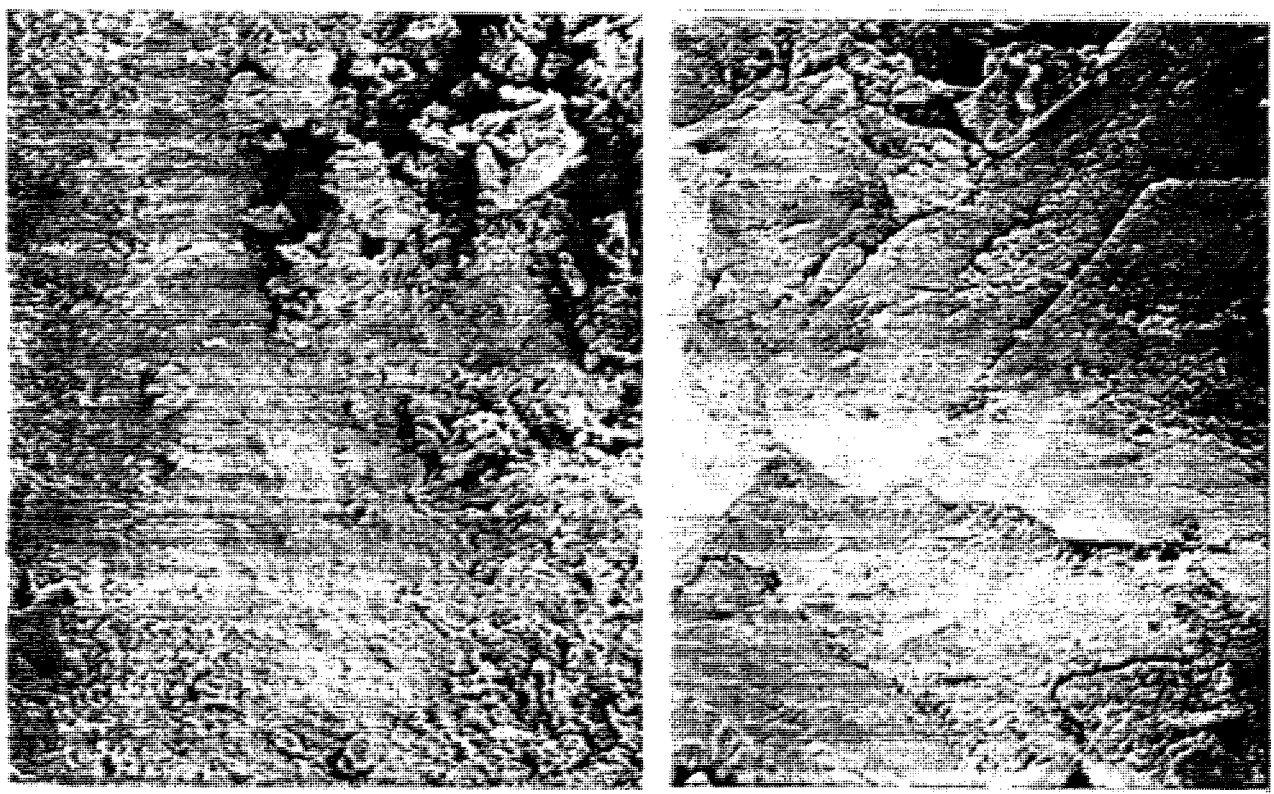


Figure 6. (Left) Weathered PBX 9404 (Specimen #1W, 1,000×). (Right) PBX 9404 fresh cut from weathered piece (Specimen #1F, 1,000×).

Specimen #1W is the weathered surface of PBX 9404, while Specimen #1F is the freshly cut surface of a weathered piece of PBX 9404, Fig. 6. By comparison, Specimen #1W is more porous and crumbly. Its biodegraded surface was more powdery than the fresh cut surface of Specimen #1F and was filled with holes, while Specimen #1F was smooth, striated, and slightly porous. We believe that the holes either are due to hot spots when the HE was shocked or are air bubbles from a portion of the material that biodegraded.

Composition B was composed of TNT and Plasterizer. Analysis of our sample showed it to be nearly 100% TNT. The holes in Composition B were very pronounced; the beady surface was well defined and degradation was extensive. Specimen #2F is shown with its holes magnified, Fig. 7. In addition, the photograph of Specimen #2F shows how deeply biodegradation has taken place in the sample.

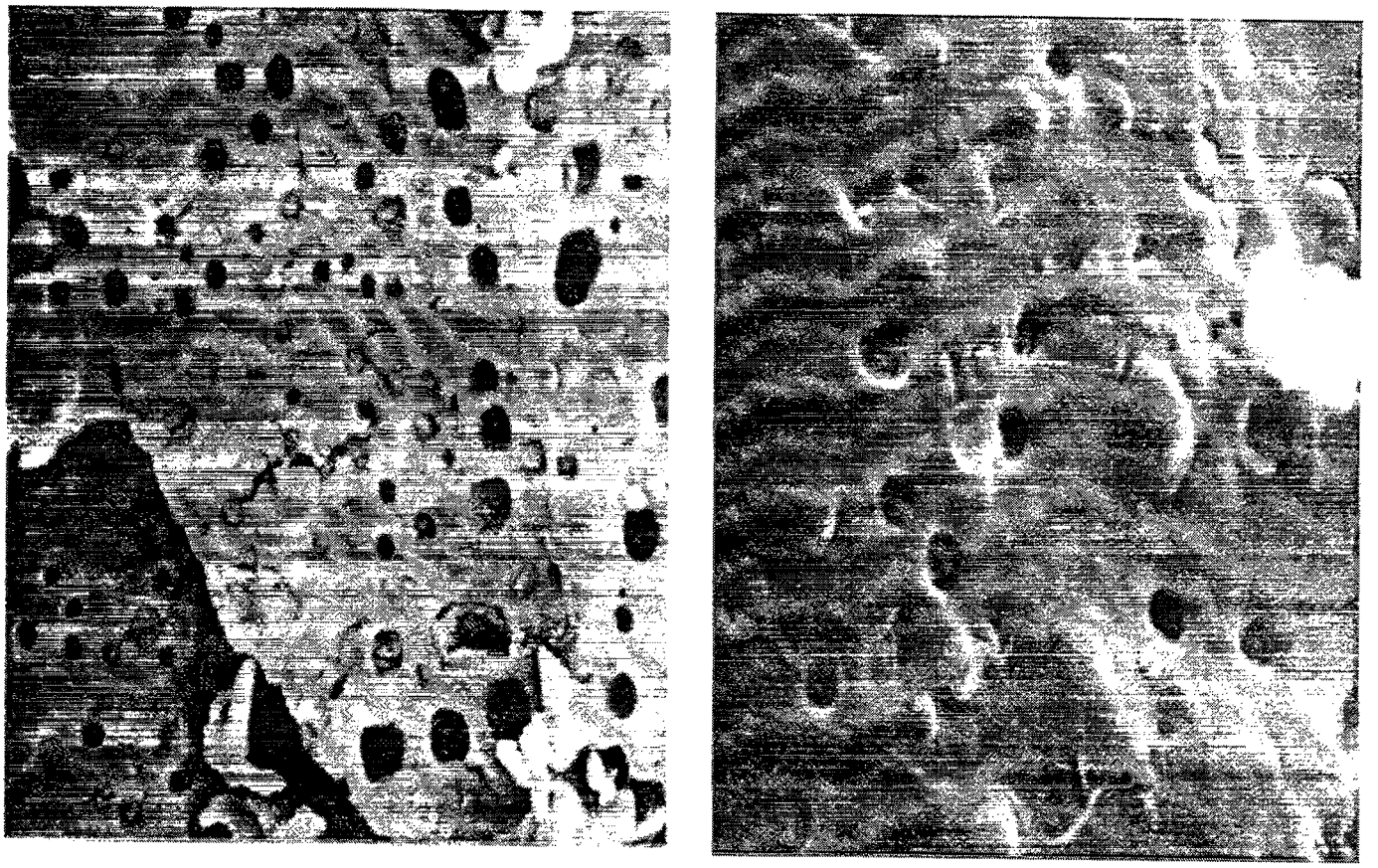


Figure 7. (Left) Composition B (Specimen #2W, 4,200×). (Right) Composition B (Specimen #2F, 10,000×).

Several photos were taken of the weathered pieces of Composition B. One photo was taken at 4,200× magnification, and this is not a fresh surface shown. At this level of magnification, the holes that are shown can be seen easily. Note the bubbles in the surface of the material. This roughness in the surface is due to the biodegradation of TNT that once was a main part of this explosive. Now only remnants remain. Another photo of the same piece, but taken at 10,000× magnification shows the same characteristics.

The surface of Specimen #3W (LX-10) shows tiny precise holes. Veins in Specimen #3F (LX-10) were an indication of stress lines, (Fig. 8). Again, the biodegradation was more pronounced on the surface.

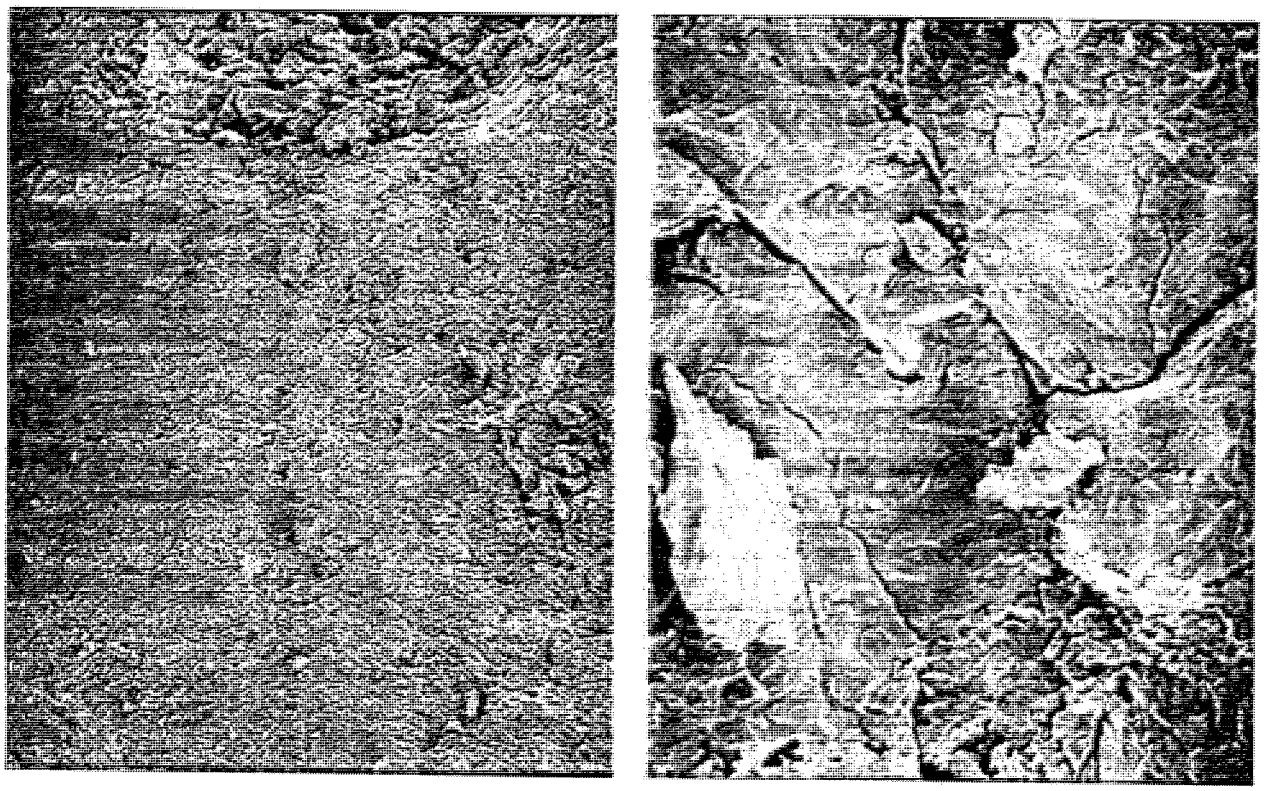


Figure 8. (Left) LX-10 (Specimen #3W, 500×). (Right) LX-10 (Specimen #3F, 1,000×).

These photos of LX-10 show the magnifications of one specimen is 500× and the other is 1,000×. On Specimen #3W, the surface is not smooth and appears crumbly. In comparison, Specimen #3F appears smooth and sharp. The wavy lines that appear in the fresh cut surface can be attributed to the shock waves or lines of stress.

The material in Specimen #4W and Specimen #4F was PBX 9011, Fig. 9. Specimen #4W has a grainy appearance and holes that were caused by biodegradation or hot spots. In comparison, Specimen #4F shows a much smoother surface. The lines are not strong enough to denote a detonation or deflagration.

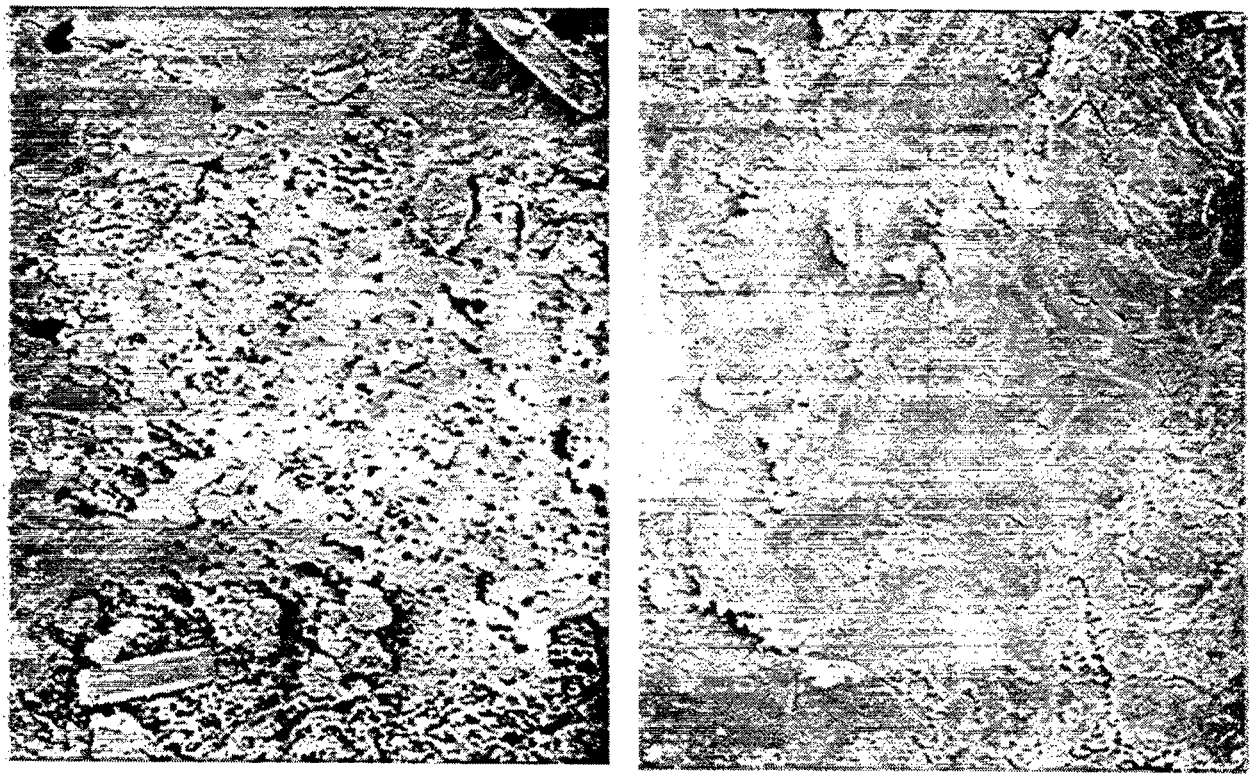


Figure 9. (Left) PBX 9011 (Specimen #4W, 1,000×). (Right) PBX 9011 (Specimen #4F, 1,000×).

These photos of PBX 9011 are the surfaces of an HMX formulation. We believe that this material started as out PBX 9011. Specimen #4W is full of holes. Even soil can be seen on the surface in this photo. In contrast, Specimen #4F is smoother, with shock waves or lines of stress. We believe the shock was not strong enough to detonate or deflagrate this material.

The inert composition PBX 900-10 gives us some indication of the degradation of polymers and other components in the explosive formulation, Fig. 10. The photograph of the weathered material (Specimen #5W) shows oxidation on the surface and a few holes. The magnification in each is 1,000×.

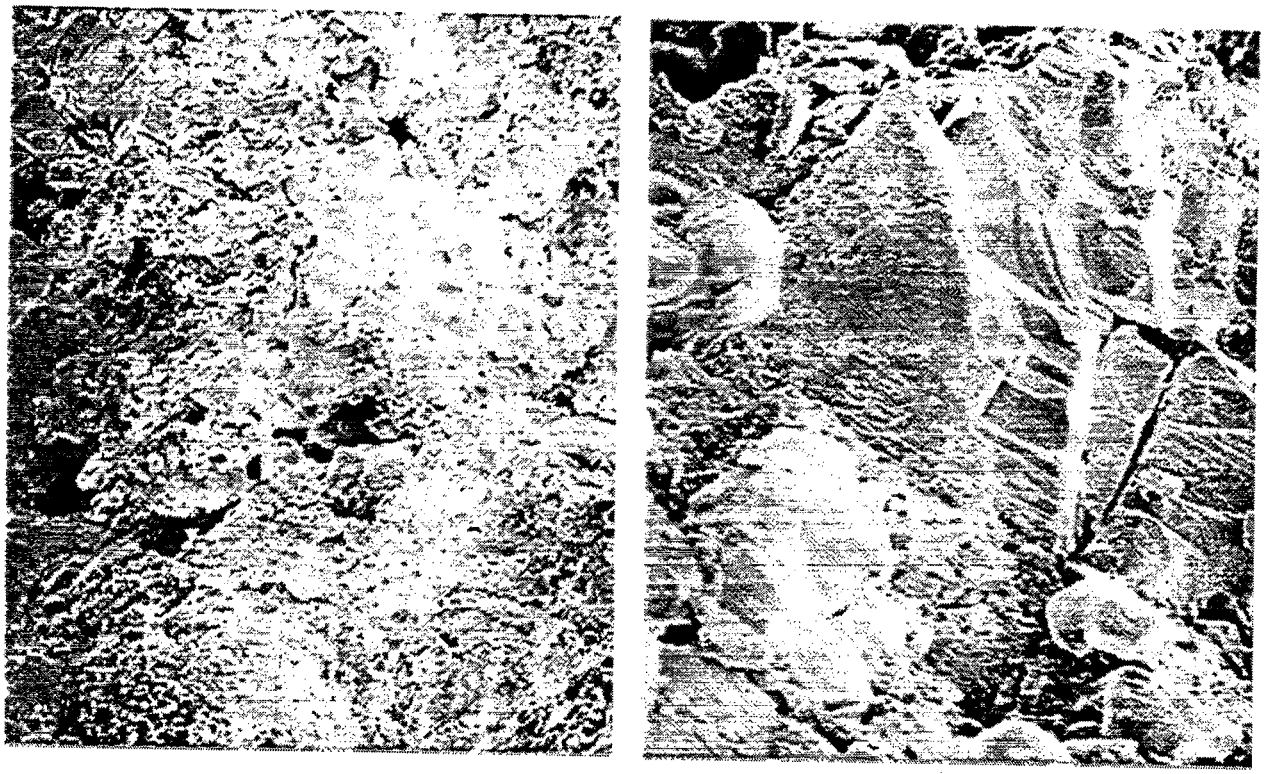


Figure 10. (Left) Inert PBX 900-10 (Specimen #5W, 1,000×). (Right) Inert PBX 900-10 (Specimen #5F, 1,000×).

Yet, these surfaces appear similar in texture. Both have grainy spots and holes in some areas. However on the fresh surface of Specimen #5F, there are smooth, sharp surfaces and edges. Even inert composition PBX 900-10 biodegrades over time.

In the photographs of PBX 9007, both Specimen #6W and Specimen #6F had granular surfaces, Fig. 11. This was an indication of a deep oxidation reaction.

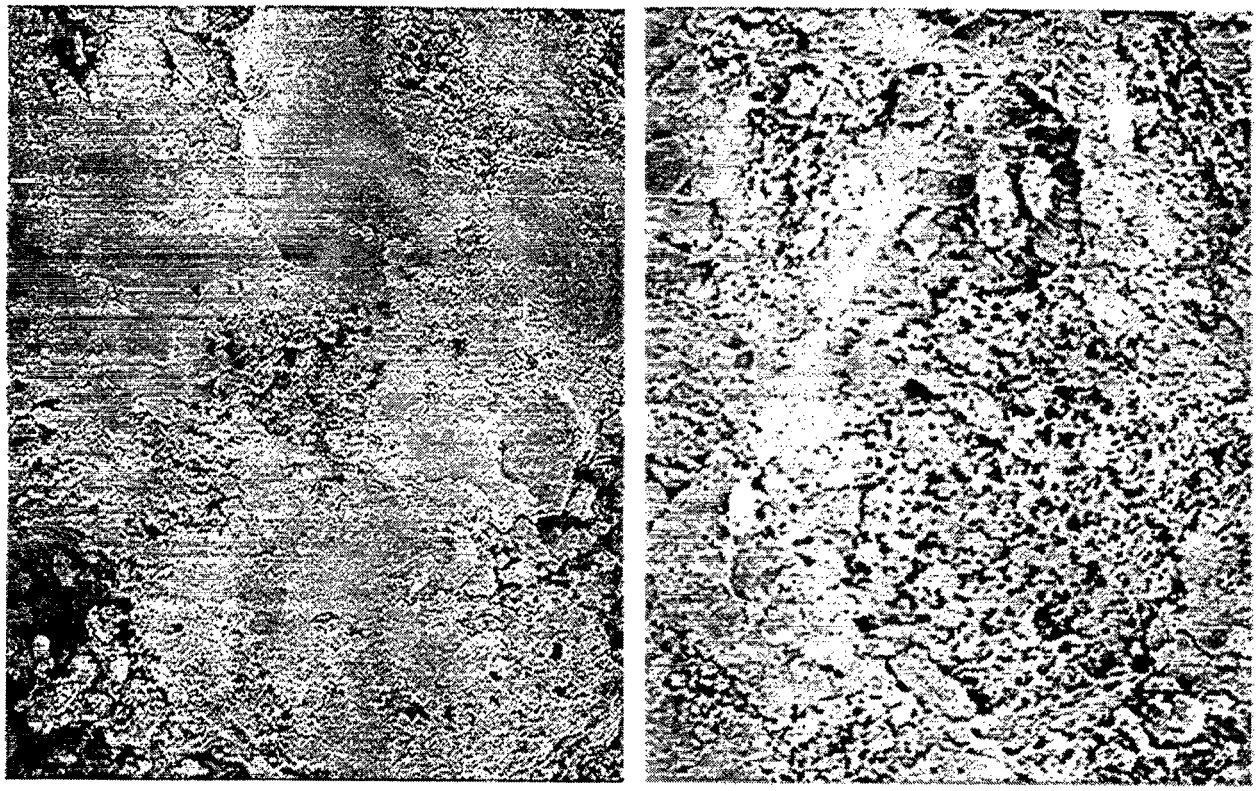


Figure 11. (Left) PBX 9007 (Specimen #6W, 500×). (Right) PBX 9007 (Specimen #6F, 1,000×).

These photos are of the fresh and weathered surfaces of PBX 9007. This particular formulation of the material was tested in the 1950s, and it contains RDX. The holes in Specimen #6W are linked with the biodegrading of RDX, and hot spots from when the material was tested. The freshly cut surface is mainly smooth and does not have any distinct features. However, there are places where some weathering may have occurred. Even though this is a freshly cut surface, we believe that over the time it has been out on the ground, the biodegradation process has continued through the material, thereby showing holes in what we are calling the fresh cut surface.

E. Henkin's Test Measurements—Critical Temperature

In the Henkin's test, explosives or propellants of a specific size and shape are lightly confined and gradually heated until a self-sustaining reaction to an explosion occurs. The temperature is then lowered until this reaction is no longer possible. This point is called the critical temperature (T_c) of the compound or composition.

The apparatus used to make the T_c determination is an in-house instrument. Los Alamos National Laboratory scientists, Howard Cady, a technical staff member, and Richard Hildner, a project engineer in Group WX-2 (now DX-2), designed and constructed it from 1975 to 1976, while technical staff-member Raymond Roger, also of WX-2 (DX-2), used it on a routine basis in his thermal analysis research. Henkin's apparatuses are also used at the Eglin Air Force Base, Pantex, and the New Mexico Institute of Mining and Technology (NMIMT).

A round, 4-in. diameter, well-insulated, single compartment bath of Wood's metal (an alloy of Pb, Sn, Bi, and Cd that melts at 70.3°C) was used to heat the samples. About 40 mg of granular or powdered sample were placed in an empty aluminum blasting cap shell (DuPont E-83, approximately 0.25 in. ID by 1.625 in. long, weighing approximately 0.719 g). The apparatus was attached to a Doric Trendicator 412A and a temperature controller manufactured by Love Control Corporation. The bath is not stirred during heating.

F. Milling, Cutting, and Drilling

Remote operations for milling, cutting, and drilling were done on small pieces of weathered explosives. A Do-All Band Saw was used to do a jaw cut, at 7 in. frames per minute, and a Maho computer numerical control (CNC) milling and drilling machine did the milling and drilling on pieces of weathered explosives, at 3 in. frames per minute.

V. RESULTS AND DISCUSSION

The explosive spot test gave definitive, positive results with all samples, Table I. Samples were identified from high-performance liquid chromatography (HPLC), infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy results. The DTA, NMR, and IR analyses were used to confirm structures of explosives in all samples. No significant evidence of foreign materials was found. The pH of the samples ranged from 7.5 to 8.0.

Table 1: Results of HE Spot Test on Once-Shocked, Weathered High Explosives

Physical description and reaction of once-shocked, weathered high explosives to reagents in the high-explosive spot test kit and to an open flame.

EXPLOSIVES	DESCRIPTION OF SAMPLE	RESULTS OF FLAME TEST	RESULTS OF SPOT TEST
PBX 9007, TA-67 (12) L-Site	Pink and hard, white, powdery surface	Burns with sparkling yellow flame	Positive for HE
LX-10, TA-11 Drop Tower	White and hard with green specks	Burns quietly with yellow flame	Positive for HE
PBX 9404, TA-11 Drop Tower	Greenish-blue and hard	Burns quietly with yellow flame	Positive for HMX
PBX 9011, Drop Tower	White to off-white	Did not burn	Positive HMX and plastic
Composition B (Cyclotol), L-Site, TA-67 (12)	Brownish-yellow with beady surface	Burns with sparkling yellow flame	Positive for TNT, RDX

When placed in an open flame, some samples burned quietly or with a sparkling, bright yellow flames, while others gave no reaction, Table I. The sparkling flames indicated a higher than normal sensitivity of the material.

Composition B, PBX 9404, PBX 9007, TNT/RDX-cast, and LX-10 gave loud pops when hit by a hammer which indicated that the materials were sensitive, Table II. PBX 9007 was noticeably sensitive. The hammer test samples were taken during the hot, dry summer months. However, when similar samples were collected during the fall and winter, the moisture was visible and the samples were not sensitive to a hammer blow. The drop-weight impact values of the weathered explosive material did not change drastically from the unweathered explosives.

Table 2: Results of Hammer and Drop Weight Impact Tests

Hammer test and impact sensitivity data from a Type 12 tool at Los Alamos National Laboratory. The 50% "go/no go" drop height in centimeters (cm) for the weathered sample is compared to the sample for once-shocked, weathered high explosives. Because of the lack of stable results on weathered samples, the values are approximations.

EXPLOSIVE	HAMMER TEST, WEATHERED EXPLOSIVE	IMPACT TEST, STANDARD EXPLOSIVE	IMPACT TEST, WEATHERED EXPLOSIVE
Composition B	No reaction	59	45
Cyclotol	Loud pop	59	48.5 to 85
TNT/RDX-cast	Loud pop	36	40.5
LX-10	Loud pop	33	28.5
PBX 9007	Very loud pop	39.1	42.3
PBX 9404	No reaction	41	43
PBX 9011	Pop and burning	55	31 to 47.8
HMX (Blend)	----	25.7	----

* Inert formulation used as reference in explosive testing.

The T_c values obtained for the weathered explosives were near the measured and predicted values obtained from the literature. However, the explosives would not stabilize as expected from the procedure. The DTA scan reached its exotherm at about 2°C below that of the pure explosive or explosive formulation, Table III.

Table 3: Predicted and Measured Critical Temperature Valves on Once-Shocked, Weathered High Explosives

Predicted and measured values for critical temperatures (T_c) from the literature compared to measured values of once-shocked, weathered high explosives collected at Los Alamos National Laboratory.

EXPLOSIVES	PREDICTED T_c (°C)	MEASURED T_c (°C)	T_c OF WEATHERED EXPLOSIVES (°C)
HMX	253	253-255	249 (varied)
RDX	217	215-217	210 (varied)
TNT	291	287-289	285 (varied)
PBX 9011	278	218	237
LX-10	256	245	268-278
PBX 9404	276	297.8	233-246
PBX 9007		215	226
Composition B or Cyclotol	----	284	273-279

No reaction was observed when the most sensitive samples were crushed, ground, drilled, or cut remotely. Although, the spark data was not reliable, it did indicate a trend toward greater spark sensitivity for the very dry weathered samples.

Surface analyses were done with the SEM and revealed a considerable amount of surface deterioration. At magnifications of 1,000× to 10,000×, the morphology of the "as collected" sample was distinctively different from the smooth, fresh cut surface. Large holes and surface modifications could be seen in the PBX 9007, Composition B/cyclotol, and in the year old LX-10. Figures 6-11 show these changes.

Specimen #1W is a weathered piece of PBX 9404, and Specimen #1F is a fresh cut section of the same sample of PBX 9404. The surface of the sample of Specimen #1W was dusty and with many holes, while the fresh cut sample of Specimen #1F had only a few visible signs of oxidation.

Two micrographs were made of the weathered Composition B, one at 4,200× and the other at 10,000×. There were numerous holes seen in the micrographs. Two micrographs of the fresh cut sample of Composition B did not have oxidation nor as many holes. PBX 9011, LX-10, PBX 9007, and the inert PBX 900-10 showed similar results.

No marked difference was seen between the weathered and unweathered samples in the drop-weight impact results (Table II). Although the drop-weight impact test is an industry-wide standard test, experimenters have differing views about its usefulness. Coffey and DeVost proclaim that this test plays a minimal role in assessing explosive sensitivity. Furthermore, they contend that the concept is seriously flawed. [12]

However, the observance of an event (pop) in the hammer or drop-weight impact tests is an indication that extreme caution must be taken because one has caused the material to react.

In previous research, flame and shock stimuli were applied to laboratory-prepared water-wet and dry samples of RDX and TNT mixed with sand. [13] The shock sensitivity tests showed that samples with 15% explosives or less would not react. In the flame sensitivity tests, samples with 12% explosives will not react. [14,15]

We could not get reproducible results with the Henkin's test. After obtaining a "go" from a given sample, we tried to repeat the results at or above the temperature but were unsuccessful. The time-to-explosion fluctuated over twenty-four hour periods and by more than 24 hours when the tests were done on different days.

The spark sensitivity data was inconclusive. Therefore, it has not been included in this report.

VI. CONCLUSIONS

The standard tests give a very good baseline for measuring the sensitivity of the laboratory samples versus the sensitivity of environmentally weathered samples. Erratic results as found in the Henkin's and spark test strongly suggest the explosive has undergone change and should be treated with care. During the hot, dry summer months, the weathered samples were more sensitive, as shown in the flame and hammer tests. If an environmentalist, using a hand tool or shovel, were to strike a sample of OSW-HE in the soil or cement, it could react. Also, if personnel are working very close to the soil to collect the sample, they would be put in a position to receive eye injuries from flying debris.

The small pops or explosions we witnessed in the laboratory from a few milligrams of weathered samples indicated that they were sensitive. However, there was no visible evidence of reactions when the samples were wetted and cut, ground, or drilled. This means that with precautions, the environmentally weathered explosive samples can be handled safely.

The surface oxidation of our weathered samples was extensive, but for a 40- to 50-year weathering period it was not unexpected. In a damp and warm climate at a lower altitude, the amount of oxygen in the air would have caused more surface corrosion.

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