LA-UR- 09-05057

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Title:	PBX 9404 Detonation Copper Cylinder Tests: A Comparison of New and Aged Material
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Intended for:	Proc. APS Topical Group on Shock Waves in Condensed Matter---2009

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Form 836 (7/06)

PBX 9404 DETONATION COPPER CYLINDER TESTS: A COMPARISON OF NEW AND AGED MATERIAL

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Abstract. We present detonation copper cylinder test results on aged PBX 9404 (94 wt% HMX, 3 wt% CEF, 2.9 wt% NC, 0.1 wt% DPA) explosive. The charges were newly pressed from 37.5 year-old molding powder. We compare these results to equivalent data performed on the same lot when it was 3.5 years old. Comparison of the detonation energy inferred from detonation speed to that inferred from wall motion suggests that the HMX energy is unchanged but the NC energy has decreased to ~25% of its original value.
Keywords: PBX 9404, Cylinder Test, HMX, Binder, Aging
PACS: 82.33Vx

INTRODUCTION

The degradation of explosives and their binders is a subject of continual interest. Secondary explosives such as HMX are sufficiently stable near room temperature that they do not measurably degrade over a period of at least several decades. For formulated systems the bigger concern is binder degradation, for which the three main issues are strength, initiation safety, and (if the binder is energetic) energy content.

In this paper we examine the detonation energy of new and aged PBX 9404 (94 wt% HMX, 3 wt% tris-β chloroethylphosphate (CEF), 2.9 wt% nitrocellulose (NC), 0.1 wt% diphenylamine (DPA) [1, 2]), measured via the detonation copper cylinder test.

In 1959, two independent PBX 9404 accidents [3] raised serious concerns about the safety of the formulation. Over about a decade's time, Los Alamos pursued a safer, energetically equivalent replacement, which ultimately became PBX 9501.

In order to accurately compare the performance of the PBX 9404 and PBX 9501 formulations, W. Campbell and R. Engelke (C&E) developed a stringent cylinder test protocol that they called the *Los Alamos Precision Cylinder Test* [4]. The present aging study is possible because excellent PBX 9404 data from those qualification tests endures.

TEST MATERIAL

PBX 9404 is a legacy explosive that was manufactured to Los Alamos specification [5] by the Holston Army Ammunition Plant. Immediately after formulation the molding powder was off-white; however, reaction of the DPA stabilizer with NC decomposition products caused the material to turn various colors. These apparently varied with lot and storage conditions, but the nominal progression was: blue (which occurred by the time the molding powder was dried), sage green, dirty brown, light tan, and finally (in at least a few cases) bright yellow [1, 6].

The lot fired by C&E and in this study was HOL 620-5, which Los Alamos designated #43 (and which is often referred to as 620-5(43)). This lot was produced in December 1971. It was apparently the last one made and the only one that remains. It was 3.5 years old when C&E tested it in 1975, and 37.5 years old when we tested it in 2009.

The molding powder was stored in an unheated magazine at Los Alamos for its entire lifetime. The magazine temperature varied between ~40 F in the winter to ~70 F in the summer [6]. Presently, the molding powder color varies from blue to green. Rather than use old pressed charges, we pressed "fresh" charges from old molding powder.

EXPERIMENTS

We fielded two standard 1-inch diameter cylinder tests as pictured in Fig. 1, and compared the data with those of two C&E legacy tests [7]. The two sets of tests are closely comparable because our modern cylinder test protocol (essentially as described in [8]) is nearly identical to that developed by C&E. Here we shall only note special features, as well as deviations from, or enhancements to, the norm.

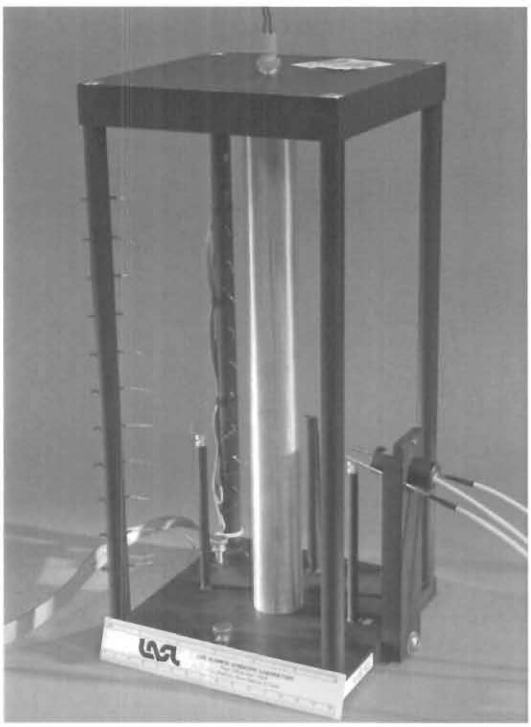

FIGURE 1. Photo of one of the PBX 9404 cylinder tests.

In order to obtain a good value of the detonation energy from wall motion measurements, it is necessary that the tube expand to a sufficiently large diameter before breaking. The target large expansion limit is $R - R_0 = 30$ to 40 mm, where R is the outer radius at the measured axial measurement location, and R_0 is the corresponding pre-detonated radius.

In an effort to promote large tube expansions, a small amount of grease was used to fill any internal air space. A careful procedure was developed to fill all void spaces without adding any excess grease. We also observed the shot with a Cordin 550 framing camera, which clearly showed that the tube held together to 30-mm expansion and beyond.

Streak camera records were obtained in the standard manner, with the slit located 2/3 of the way down the tube. The shot was fired in a helium atmosphere to mitigate the optical aberration caused by the gas shock. While there is some question, Engelke believes that their tests were also fired in helium [9].

We used photon doppler velocimetry (PDV) as a backup and to compare with the streak records. The PDV probe, its holder, and two fiber optic x-t fiducial pins are seen in Fig. 1. Although the PDV data was excellent, the purpose of this paper is to compare our results to the legacy experiments, which used only streak camera. Consequently we defer discussion of the PDV data to a future publication.

DETONATION SPEED MEASUREMENTS

Detonation speed measurements for the new and aged materials are listed in Table 1. The first two rows are nominally identical tests fired by C&E, and the second two rows are nominally identical tests fired in this study.

The four speeds in Table 1 are plotted versus pressed density in Fig. 2. C&E's plane wave speed (ideally the Chapman-Jouguet, or CJ) speed, which was extrapolated from diameter effect measurements [10], is plotted for comparison. From this we see that 1-inch-diameter copper-confined PBX 9404 detonates at virtually the CJ speed.

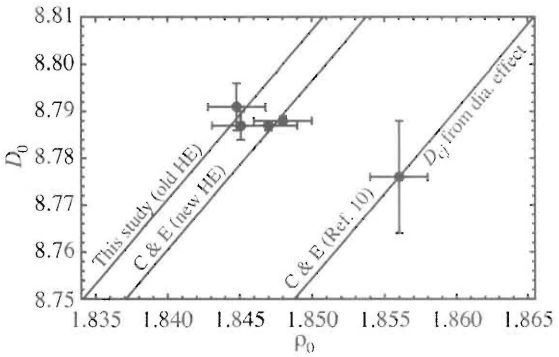

FIGURE 2. Detonation speed data.

Each of the three data sets is fit by a line with the handbook slope of 3.6 m/s per mg/cc [2]. The linear fits indicate the trend with density. They also serve to illustrate that, on an equal density basis, the speed of the aged material errs on the large side. As we shall argue in the following sections, this result indicates that the HMX component has not degraded.

TABLE 1. Summary of Cylinder Test Results

Pressed Density (g/cc)	Phase Speed (m/s)	Energy by D_0 (kJ/g)	Energy by Wall (kJ/g)	Shot No. (—)
1.847	8787 ± 1	5.37	5.48	C-4526
1.847	8783 ± 1	5.36	5.43	C-4527
1.845	8791 ± 5	5.37	5.37	8-1292
1.845	8787 ± 3	5.38	5.37	8-1293

ENERGY FROM THE DETONATION SPEED

The specific energy q of a CJ detonation given by Zel'dovich/Neumann/Doering (ZND) theory [11] is:

$$q = \frac{D_{cj}^2}{2(\gamma_{cj}^2 - 1)}, \tag{1}$$

where D_{cj} is the CJ detonation speed and γ is the generalized isentropic exponent [11]. ZND goes a step beyond CJ theory in assuming that *in the reaction zone only*, γ is constant and equal to γ_{cj}.

W. Davis [12] has proposed the following empirical formula for γ_{cj}:

$$\gamma_{cj} = a + b\rho_0, \tag{2}$$

where ρ_0 is the pre-detonated bulk density in g/cc. Davis used $a = 1.6$, $b = 0.8$, whereas we shall use $a = 1.2$, $b = 0.9$. Combining Eqs. 1 and 2, one may express q in terms of D_{cj} (which we assume to be equal to the measured detonation speed D_0) and ρ_0.

The calculated q-values are listed in Table 1. For our purposes the absolute energies—which depend on one's choice of a and b—are less important than their differences. The energy of the aged material exceeds that of the new material by 0.23%. Because there is no way for the energy to increase over time, the difference must be caused by experimental error. However, this error is rather small compared to the $\pm 0.7\%$ maximum energy variation associated with the constituent concentration tolerance [5].

ENERGY FROM THE WALL MOTION

Another way to infer the detonation energy is by the Gurney method [13], which calculates the combined kinetic energy of the HE products and a metal case. Gurney assumes that 1) the material motion is strictly radial, 2) the HE product density is spatially uniform, and 3) the case stretches without breaking. Each assumption requires a sufficiently large metal/HE mass ratio, which the cylinder test satisfies.

In the large expansion limit the product gas pressure is so small that it no longer pushes the wall, which coasts at constant speed v_∞. Likewise the product gas temperature is so small that its internal energy may be neglected. Thus, kinetic (Gurney) energy accounts for nearly all the system energy. Because very little energy leaks to the surroundings, the asymptotic Gurney energy may be equated to the initial system energy, which is the detonation energy.

Expressing these concepts mathematically yields

$$q = \frac{v_\infty^2}{2}\left(\frac{1}{2} + \frac{\rho_w}{\rho_0}\left(\left(\frac{R_0}{r_0}\right)^2 - 1\right)\right), \tag{3}$$

which is the cylindrical Gurney formula evaluated at v_∞, ρ_w is the wall density, and r_0 is the HE radius.

We fit a smooth curve to the streak camera expansion data, and differentiate it to obtain radial speed. There are several considerations in choosing a fitting form, many of which pertain to equation of state (EOS) determination [14]. For Gurney, the most important curve attribute is how it extrapolates to large expansions beyond those that are measured.

In this and in EOS studies we have used the form

$$R - R_0 = \frac{v_\infty(t - t_0)\left((1 + \alpha(t - t_0))^{2/3} - 1\right)}{\frac{4\alpha v_\infty}{3a_0} + \left((1 + \alpha(t - t_0))^{2/3} - 1\right)}, \tag{4}$$

where v_∞, a_0 (the initial wall acceleration), t_0 (the virtual time origin), and α are fitting parameters.

The wall speed fits for a new and aged data set are plotted in Fig. 3, and the associated detonation energies are listed in Table 1. As in the previous section, the important quantity is the energy *difference* between new and aged materials, which is 1.5%.

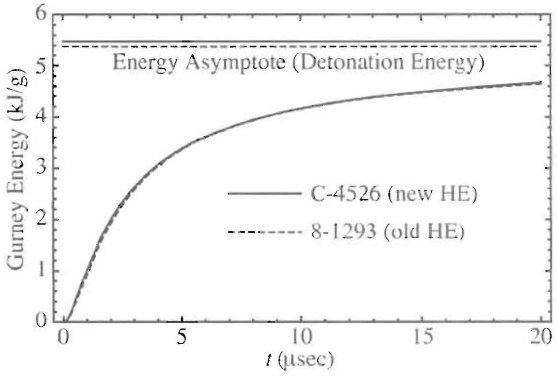

FIGURE 3. Gurney energy versus time.

AN ESTIMATE OF BINDER DEGRADATION

The consistency of repeat tests for new and aged materials suggests that the energy difference deduced in the previous section is trustworthy. One may then sensibly explain our observations by considering the detonation reaction zone structure, as follows.

Figure 4 illustrates the reaction zone structure of a cylinder test detonation wave in a wave-fixed coordinate system. The lead shock is followed by a sonic surface, which is followed by the more nebulous (because reactions tend to asymptotically complete, or else "freeze") end of reaction. Energy released upstream of the sonic surface drives the shock; whereas, energy released downstream does not influence the shock speed but is imparted to the wall.

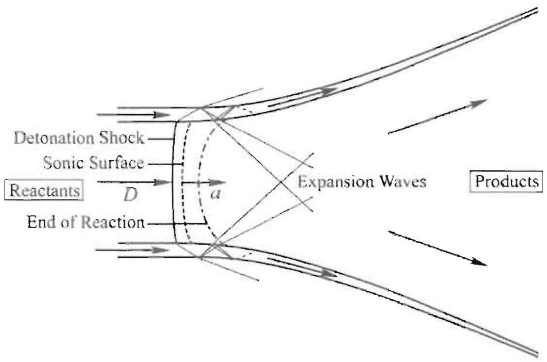

FIGURE 4. Cylinder test detonation wave structure.

Consider the likely scenario that HMX reaction is mostly complete at the sonic surface, but that NC reaction, retarded by its intimate mixture with non-energetic CEF plasticizer, reacts mostly after the sonic surface. Then, the detonation energy computed from D_0 is due to HMX only; whereas, the energy computed from the wall motion is due to HMX and binder combined. Thus, any difference in the wall energy of new and aged materials is attributed to binder degradation, and to NC degradation in particular.

Under the stated assumptions, the change in NC energy is related to the change in total energy by:

$$\frac{\delta q_{nc}}{q_{nc}} = \left(\frac{q}{q_{nc}\,\chi_{nc}} \right) \frac{\delta q}{q}, \qquad (5)$$

where $\chi_{nc} = 0.029$, $q = 5.45$ kJ/g, and $q_{nc} = 3.66$ kJ/g. Inserting these values into Eq. 5 predicts that the NC energy has degraded by ~75%. If NC degradation is assumed to proceed exponentially with time, its half life is estimated at ~19 years.

CONCLUSIONS

Our results indicate that the HMX has not degraded over the ~37.5 year life span of the considered PBX 9404 material, but that the binder energy has degraded significantly. Making sensible assumptions based on established detonation theory, we estimate that the NC energy has decreased to ~ 25% of its original value. Additional confirmation would require chemical analysis. These results also identify a potential disadvantage of energetic binders: they may burn much slower than the explosive, thereby introducing a small non-ideal component to the behavior.

ACKNOWLEDGEMENTS

We thank L. Vaughan, J. Morris, and S. Hare for help in fielding the shots, L. Hatler, B. Olinger, and A. Montano for researching material lots, and S. Larson and T. Zocco for their program management. This work was funded by the LANL enhanced surveillance program under U.S. Department of Energy.

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