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HENKIN ONE-SHOT TEST - A STATISTICAL APPROACH FOR ESTIMATING CRITICAL TEMPERATURES

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ABSTRACT

The Langlie one-shot experimental design has been used to estimate the critical temperature of seven explosives in the Henkin test configuration. This test procedure is compared to the standard Henkin test method. More time is required to run the one-shot design, but the additional information obtained justifies the efforts. Analysis of the data collected using the one-shot design allows confidence limits to be placed on the estimated critical temperatures. The standard Henkin test usually only gives relative thermal stability of explosives.

SUMMARY

The Henkin time-to-explosion test is a standard method for evaluating the thermal stability of explosives. The test as it is normally performed only allows the relative thermal stability of explosives to be determined. No information about the distribution of sample response is obtained unless many tests are performed. If the Langlie one-shot experimental design is used, it is possible to analyze the Henkin data to obtain a statistical description of the sample response.

Seven explosives have been tested using the Langlie one-shot experimental design applied to the Henkin test. Analysis of the data using the ASENT computer code gave mean critical temperatures for each explosive as well as upper and lower confidence limits. The relative thermal stability of the seven explosives agree with the standard Henkin test results. In addition, the confidence intervals show that three explosives, PBX 9501, LX-09 and RX-26-AF, do not have significantly different thermal stabilities as measured by this test. The thermal stability of the seven explosives tested are PBX 9404 < (PBX 9501, LX-09, RX-26-AF) < LX-10 < HNS < PBX 9502.

INTRODUCTION

An understanding of the thermal stability of explosives is necessary for establishing safe operating conditions during the pressing of large billets. One method for evaluating thermal stability is the Henkin Test (ref.1). Basically this test consists of measuring the time-to-explosion as a function of temperature for small confined samples. The data are normally plotted as ln (time) versus the reciprocal absolute temperature. The relative thermal stability can then be obtained by

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inspection. Explosives whose data lie to the right or lower temperatures are less thermally stable than those whose data lie to the left or higher temperatures.

Another way of evaluating thermal stability using the Henkin Test is to determine the critical temperature of the explosives (ref.2). The critical temperature is defined as the lowest temperature at which an explosive of a given size and shape will self-heat to explosion. The relationship between the critical temperature, T_c, and the physical and kinetic parameters for the sample are given by the heat balance equation. Solution of this equation for steady-state conditions gives the equation commonly known as the Frank-Kamenetskii equation (ref.3). This equation is written as follows:

$$E/T_c = R\ln\left[a^2\rho QZE/T_c^2\lambda\delta R\right] \qquad (1)$$

where, a = critical dimension (i.e. radius of a sphere or cylinder or the half thickness of a slab); E = Arrhenius activation energy; Q = heat of reaction; R = gas constant; Z = Arrhenius pre-exponential factor; δ = shape factor (0.88 for infinite slab, 2.0 for infinite cylinder and 3.32 for sphere); λ = thermal conductivity; and ρ = density.

If the parameters for an explosive are known or can be determined by other experiments, this equation can be used to calculate a critical temperature which can be compared to the experimental value determined in the Henkin test. The experimental critical temperature is determined by successively lowering the temperature in the Henkin test until a point is reached where the sample will not explode in a selected time. As in any experiment there are errors associated with the Henkin test. Also each sample will react differently at a given test temperature because of sampling errors. Since each sample can be tested only once, many must be tested to determine the critical temperature with confidence.

The Langlie One-Shot Experimental Design (ref.4) has been used for testing explosives exposed to stimuli such as spark or impact (ref.5). This experimental design is based on the assumption that the response of the samples to a stimulus follows a normal distribution. Each sample can be tested only once with either a positive or negative response to the stimulus. In the Henkin test the stimulus is temperature and the sample responds by either exploding or not exploding depending on whether the temperature is above or below the critical temperature.

This paper describes the application of the One-Shot Experimental Design for estimating the critical temperature of explosives using the Henkin Test.

EXPERIMENTAL

Time-to-explosion apparatus

The Henkin test apparatus used in this study is similar to that described by Rogers (ref.2). Two methods for confining the samples were used. Empty blasting caps (DuPont #8) were used in both methods. The first method has been described by Myers and Schuldt (ref.6). After the sample (40 to 80 mg) is weighed into the blasting cap it is covered with a 6.5 mm diameter gas check (Hornady) followed by a 14 mm long by 6.4 mm diameter lead plug. A punch and die are then used to press the assembly to 135 MPa. This presses the sample into a thin slab configuration with a thickness between 0.5 and 1.0 mm. The lead plug is also expanded to seal the cap.

The second method for confining the sample uses a hollow aluminum plug (The Lee Company, Westbrook, CT) over the sample as described by Rogers (ref.2). To improve the seal, a ferrule (8 mm ID Swagelok) is swaged on the outside of the blasting cap at the Lee Plug (ref.7).

Since the diameter is much greater than the thickness of the explosive charge, both sample configurations approximate infinite slabs. It is assumed that the time for heat to conduct through the blasting cap is short compared to the total time-to-explosion.

An isothermal test temperature is achieved using a molten Wood's metal bath in a heated metal container. The temperature is regulated using a proportional controller (Omega Model 52).

Explosive samples

The seven explosives tested are all for use in nuclear ordnance. One of the explosives, 2,2', 4,4', 6,6'-hexanitrostilbene (HNS), is used primarily in small explosive devices. The other six are used in large charges. These materials are all plastic-bonded explosives (PBXs). The compositions of all except one of these PBXs are given in the LLNL Explosives Handbook (ref.8).

The explosive not given in the handbook is RX-26-AF. It is composed of 49.3% (wt) of 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX), 46.6% (wt) of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) bound with 4.1% (wt) Estane 5702, a poly-(urethane-ester-MDI).

Four of the PBXs (LX-09, LX-10, PBX 9404 and PBX 9501) have HMX as the explosive component. The LX-09 is bound with poly(2,2-dinitropropyl acrylate) and also contains 2.4% (wt) of bis(2-fluoro-2,2-dinitroethyl) formal (FEFO). LX-10 is HMX bound with Viton A, a vinylidine fluoride-hexafluoropropylene copolymer. PBX 9404 has nitrocellulose plasticized with tris-beta chloroethyl-phosphate as a binder. The PBX 9501 has the Estane binder and the eutectic mixture of bis(2,2-dinitropropyl) acetal and bis(2,2-dinitropropyl) formal. The PBX 9502 has TATB bound with Kel-F 800, a chlorofluoroethylene polymer.

All samples used were from production or development lots. They had previously been run on the standard Henkin test. This consists of running three or four samples at three or four temperatures selected to give explosions in 20 to 900 seconds.

Langlie one-shot experimental design

A detailed description of the application of the Langlie one-shot experimental design to sensitivity experiments is given by Mills (ref.9). The main feature of this design is that testing levels are determined by the design and not before the experiment is started. A testing interval must be estimated and the first test is conducted at the midpoint of the interval. Each future testing level is then determined by the response at the previous levels.

A computer program, ASENT, for the Hewlett-Packard 9845 desktop computer (ref.10) was used to analyze the data. This program is based on the Golub and Grubbs method (ref.11).

Since analysis of the one-shot data depends only on the success or failure at each stimulus level, it is necessary to define a failure for the Henkin test. According to theory, if the test temperature is above the critical temperature the sample will explode after some time. The time-to-explosion depends on the rate of heat generation and loss; therefore, if sufficient time is allowed for the exothermic reaction to be completed and no explosion has occurred, the test is a failure. For the Henkin test, 900 seconds is considered sufficient time for completion of the reaction. This same time was used in this study.

RESULTS AND DISCUSSION

The estimated critical temperatures for the seven explosives are given in Table 1. The upper and lower limits at a confidence level of 0.05 are used to give the 95% confidence interval. These values are calculated by the ASENT computer program in the analysis of the Henkin one-shot data.

The confidence limits tell us how well the Henkin test can distinguish between explosives with different thermal stabilities. As can be seen from the values in Table 1, three of the explosives (PBX 9501, LX-09 and RX-26-AF) have 95% confidence intervals that overlap; therefore, the Henkin test does not distinguish between the thermal stabilities of these explosives.

Also given in Table 1 are the critical temperatures calculated using the Frank-Kamenetskii equation. The kinetic constants and thermal properties for all of the explosives except the RX-26-AF are given in the LLNL Explosives Handbook (ref.8). The values used for RX-26-AF were those suggested by Jaeger (ref.12) and are as follows:

$Q = 505 \text{ cal g}^{-1}$
$E = 52{,}700 \text{ cal mole}^{-1}$
$Z = 5.02 \times 10^{19} \text{ s}^{-1}$
$\lambda = 13.2 \times 10^{-4} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ deg}^{-1}$
$\rho = 1.89 \text{ g cm}^{-3}$

TABLE 1

Comparison of the Henkin one-shot critical temperature estimates with the theoretical critical temperature

	(°C)		
Explosive	One Shot T_c	95% Confidence Interval	Calculated[a] T_c
PBX 9404	204.5	202.5 to 206.4	194
PBX 9501	221.1	217.9 to 224.4	251
LX-09	222.6	219.3 to 225.8	258
RX-26-AF	223.6	222.2 to 225.0	258
LX-10	228.0	225.9 to 230.1	258
HNS	313.7	309.9 to 317.5	319
PBX 9502	344.3	342.8 to 346.3	336

[a] For a = 0.35 mm.

All of the samples are assumed to be infinite slabs ($\delta = 0.88$) with a half thickness of 0.35 mm.

As can be seen, the one-shot critical temperatures for all of the explosives except PBX 9404 and PBX 9502 are significantly less than the calculated critical temperatures. Some difference could be expected due to variations in sample thickness which was not measured for the test samples. Other sample thicknesses in the range expected for this experiment were also used, but the critical temperatures calculated using these values gave no better agreement with the one-shot critical temperatures.

There are other explanations for the disagreement between the one-shot and calculated critical temperatures. The Henkin test does not actually measure the thermal runaway reaction. The criterion used to define an explosion in the Henkin test is an audible report resulting from the rupture of the blasting cap or the blowing out of the plug. This could result from the pressure buildup of the decomposition gases and not from a thermal runaway. This explanation, however, is not consistent with the results for the two samples that show higher one-shot critical temperatures than calculated critical temperatures.

Another explanation is that the kinetic constants and model used in the calculation of the critical temperature do not accurately describe the reaction observed in the Henkin Test. Most of the kinetic constants used are the values determined by Rogers (ref.2) for pure explosives (i.e., no binders). In the calculations it is assumed that the binders in the PBXs do not effect the decomposition kinetics of the explosive. Roger's values were also measured using a vented system at one atmosphere. The kinetic constants would therefore not reflect changes in the decomposition mechanism due to increases in concentration of the decomposition gases or to changes in the decomposition rate with confinement.

CONCLUSIONS

Use of the one-shot experimental design for the Henkin Test enables more information to be derived from the data than can be obtained using the standard test. The one-shot design not only allows the relative thermal stability to be determined, but also enables confidence limits to be placed on the estimated critical temperatures. Although this can be accomplished with no more samples than are required for the standard test, more time is required to complete a series. This is because more samples are tested at longer times or below the critical temperature. The additional information obtained using the one-shot design justifies the additional effort.

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