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Thermal Response of Spherical Explosive Charges Subjected to External Heating

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by

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ABSTRACT

A series of one-dimensional heating experiments was performed with selected high explosives (HEs) in unconfined spherical geometries. The purpose of the program was to observe experimentally the thermal behavior of HE specimens near their ignition temperature and also to examine the accuracy with which the Arrhenius kinetics models can simulate the ignition process.

All test samples were instrumented with thermocouples and the time-temperature data were recorded on a flexible disk. Comparisons between analytical predictions and test data show that (1) the explosives go through a solid-state induction process before the Arrhenius models describe their behavior effectively, (2) the explosives have a "memory" of the induction process, and (3) the Arrhenius model can accurately predict the critical temperature but not necessarily the time to ignition.

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I. INTRODUCTION

Chemical explosives are metastable materials that decompose exothermally at all temperatures. If the high explosives (HEs) decompose according to a known law (such as that of Arrhenius[1]) and the kinetics constants are known, then it should be possible to compute accurately the temperatures and time to ignition as a function of the time-dependent boundary conditions. The Arrhenius heat generation term has the form

$$F = \rho Q (1 - W)^N Z e^{-E/RT} \quad ,$$

where ρ is the density, Q is the heat of reaction, W is the decomposed mass fraction, N is the reaction order, Z is the frequency factor, E is the activation energy, R is the gas constant, and T is the temperature.

The ability to compute the ignition characteristics of HEs with confidence is important in all aspects of operational safety, including the manufacture, storage, and delivery of explosive ordnance. For instance, accidental ignition of explosives by mechanical impact is, in the limit, a problem of thermal ignition followed by growth to detonation. The storage lifetime of explosive mixtures is a second problem related to thermal decomposition. Explosive ordnance exposed to various thermal environments, in particular aerodynamic heating in supersonic flight, represents a third important area dealing with thermal ignition.

Previously published papers[1-7] have noted the strong dependence of time to ignition on such explosive variables as size, composition, geometry, and boundary conditions. Several computer codes, such as EXPLO,[8] have been written to perform the complex calculations required to model the explosive thermal-ignition process. A comparison of experimental test results with analytical models plays a key role in the eventual understanding of the decomposition process.

Large samples were selected for the test program to study the response of HEs to predetermined, time-dependent boundary conditions. The large dimensions insured that the critical temperatures of these samples would be much lower than those for samples previously studied. In this report, "critical" or "ignition" temperature is defined as that surface temperature at which the internal energy generated by chemical decomposition is greater than that which can be removed through the surface by thermal conduction.

Our earlier work concentrated on slab geometry.[9] That work showed reasonable agreement between experiment and calculation for most explosives. However, relatively high heating rates were used, and the HE samples were ignited by an external heat source at the source-HE interface rather than by heat generated within the HE.

II. DESCRIPTION OF TEST ASSEMBLY

Many experimental test configurations and geometries were considered. To investigate sensitivity to Arrhenius kinetics constants, we constructed analytical models for each configuration. The models were used to calculate pressure ruptures for closed systems and thermal ignitions for open systems. Two important facts came out of the analytical studies. First, the most sensitive test of the thermal kinetics is one in which the boundary temperature is raised to a value slightly above the critical temperature, for the particular size and geometry, and the HE is ignited by its own internally generated heat. Second, sealed systems are ruptured by evolved gases at a time that does not necessarily correspond to the time to ignition.

Because the time to an event (thermal ignition or pressure rupture) varies among unconfined and con-
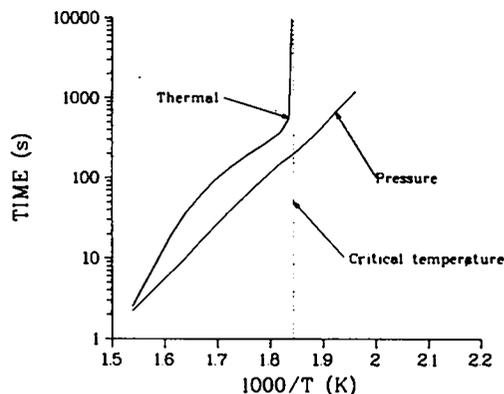
Fig. 1.
Time to explosion for thermal events shows a different characteristic than that for pressure events.

fined tests, care must be exercised when data from different tests are compared. As an example of the difference, consider two 25-mm-diam spheres, each with its surface temperature initially brought to a predefined value. In the analysis of these spheres, the calculation may stop when thermal deflagration or a pressure rupture occurs. The results of several analyses may be plotted (Fig. 1) to show the shape of the time-to-event versus temperature curve for each occurrence. Each analysis is based on a conventional first-order Arrhenius model. The results for unconfined spheres, which terminate in a thermal event, show the characteristic "S"-shaped curve with a well-defined critical temperature. However, the results for confined spheres, terminated by a pressure event, show a straight-line characteristic, with no definite critical temperature.

We decided to test instrumented, unconfined HE samples in a spherical geometry. The spherical test specimens were suspended in a test chamber that provided forced circulation of heated air (Fig. 2). The surface temperature of the HE sphere was controlled according to a prescribed temperature-time profile. The internal duct work was designed to ensure a uniform surface temperature by providing good turbulent mixing of the boundary-layer air on the surface of the sphere.

Because relatively large samples (up to 250 g) were to be tested in the test chamber and because there is always a danger of the explosive detonating
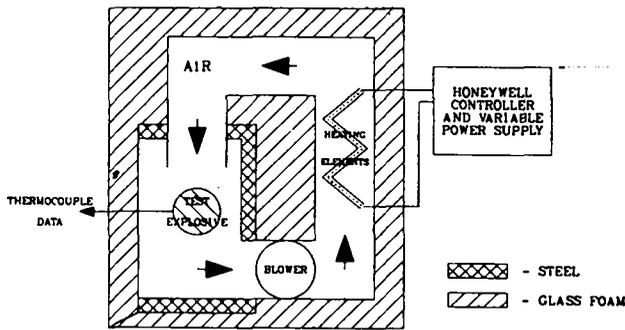
Fig. 2.
Critical-temperature test chamber for unconfined spheres up to 80 mm in diameter.
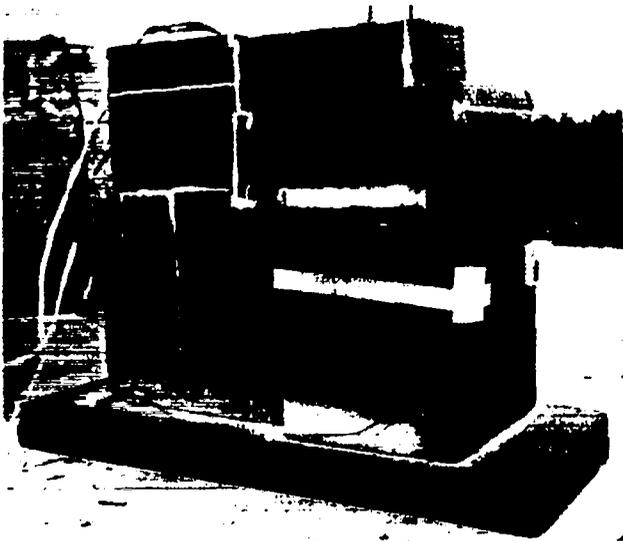
Fig. 3.
Test chamber for unconfined spherical samples.

(although none have in these experiments), the test chamber was designed to be relatively inexpensive and easy to rebuild. The frame was angle iron, the base and back were steel, and the chamber was surrounded with 50-mm-thick glass foam (Fig. 3). To heat the chamber, hot air was circulated through it from an external, insulated duct system equipped with a squirrel-cage blower. Electric heaters, capable of delivering 4500 W, were located in the duct. Temperature of the air entering the upper portion of the chamber was controlled with a Honeywell

time-proportioning temperature controller, Model R7350A.* A wooden box was placed over the entire assembly (Fig. 4) to reduce transient convection and thus improve the control-system stability. One of several Chromel-Alumel** thermocouples attached to the outer surface of the test specimen was used as the control. The test samples were fabricated as hemispheres, either pressed or machined to shape. Thermocouples with 0.125-mm-diam lead wires were glued on the equatorial surface of one hemisphere (Fig. 5), and the second hemisphere was glued to the first to complete the spherical sample (Fig. 6). The samples were suspended in the turbulent air stream for testing (Fig. 7).

A Hewlett-Packard Model 3052A† data acquisition system recorded the thermocouple signals and provided the temperature-time control signal to the Honeywell controller. The system controlled the oven temperature, monitored all thermocouple data channels, and turned off the power at a prescribed time or at the loss of a control signal.
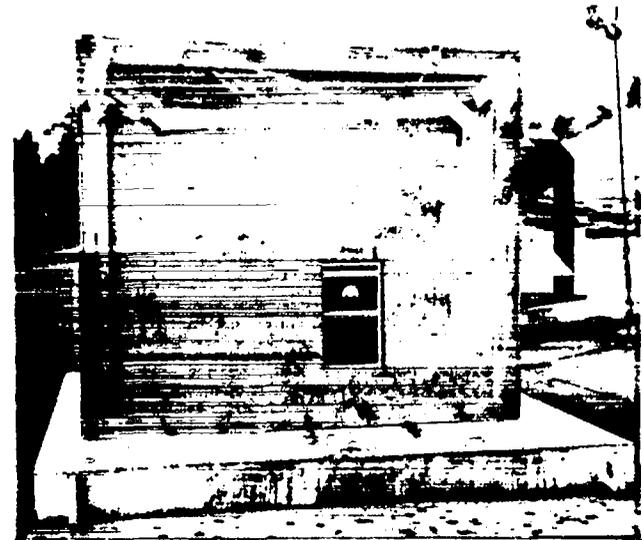
Fig. 4.
Protective cover installed over the test chamber to reduce transient convection.
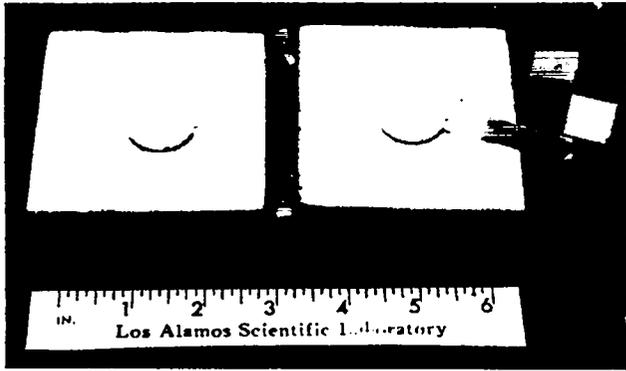
Fig. 5.
Thermocouple installation for a 25-mm sphere.
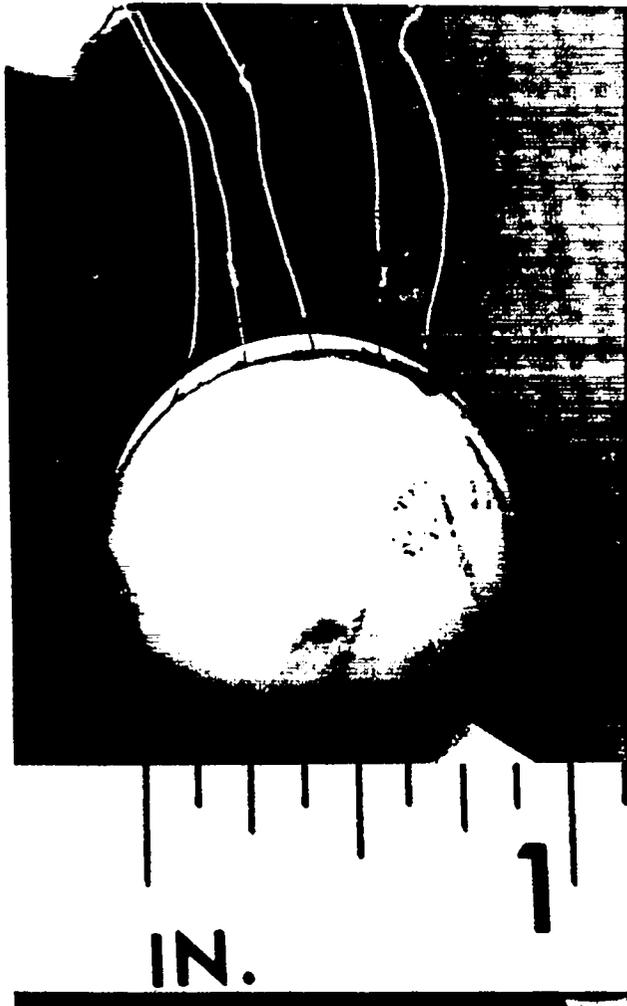
Fig. 6.
A 25-mm sphere ready for testing.

Fig. 7.
A 76-mm sphere installed in the test chamber.

III. TESTING FOR AN INDUCTION PROCESS IN EXPLOSIVES

The term induction process, as used in this report is defined as any process, whether mechanical or chemical, that must be completed before the explosive is capable of releasing energy. To understand the effect of an induction process on the transient thermal response of the HE, let us consider an example in which an induction process is not present. Analytical models using the Arrhenius heat-generation function were constructed to compare the transient response of two 25-mm-diam spheres, one with a surface temperature just below the critical temperature and the other with a surface temperature just above the critical temperature. For the

analysis, the surface was considered to be subjected to a transient temperature history similar to that it would have encountered in the test chamber. The calculated temperature at the center of the sphere was chosen to represent the response of the sphere. The results of the analysis indicated that, if the initial surface temperature is above the critical temperature, the center of the sphere ignites shortly after the center equilibrates with the surface (Fig. 8). If, on the other hand, the initial surface temperature is below the critical temperature, the center decomposes instead of igniting. The decomposition is rapid enough to release most of the sphere's energy over several hours, after which the temperature of the center of the sphere decreases. We conclude that, in the absence of an induction process, material obeying an Arrhenius decomposition law will either ignite or rapidly decompose.

To test the validity of the analysis, we heated a 25-mm-diam PBX 9502* sphere to just above its predicted critical temperature; the test results showed that the center of the explosive responded to the surface temperature change as expected (Fig. 9). However, upon reaching an equilibrium temperature, the explosive did not generate the amount of heat the Arrhenius model predicted. (The material properties and decomposition kinetics constants used for the analytical models are shown in Table I.) When the surface temperature of the ex-

*95 wt% TATB, 5 wt% Kel-F 800.

Fig. 9.
Comparing the test data with the analytical model for PBX 9502 shows that an induction process is impeding the reaction.

plosive was held constant over a period of 20 000 s (5.5 h), the explosive began generating a measurable amount of energy. Then, after approximately 50 000 s (14 h), the explosive generated sufficient energy to ignite. A similar test was performed using PBX 9501* (Fig. 10) with consistent results. Both explosives exhibit an induction process; that is, their behavior is controlled by an energy-generation function that is both time- and temperature-dependent, instead of by the solely temperature-dependent function assumed in the conventional Arrhenius model.

IV. TESTING THE "MEMORY" OF EXPLOSIVES

We investigated memory by preheating spheres through a predetermined temperature cycle and then comparing the response of these spheres to that of previously unheated spheres (control). The preheat cycle consisted of heating the spheres to 10 K below their calculated critical temperature, holding their surface temperature constant for 24 h, cooling them to ambient temperature, and allowing them to stay at that temperature for a minimum of 12 h. The preheated and control spheres were then

Fig. 8.
Analysis of spheres near critical temperature shows that spheres either ignite or rapidly decompose.

*95 wt% HMX, 2.5 wt% nitroplasticizer, 2.5 wt% Estane.

TABLE I

ARRHENIUS KINETICS AND MATERIAL PROPERTIES
USED FOR ANALYTICAL MODELS

Property	Temp (K)	PBX 9502	PBX 9501
Density (g/cm³)	293	1.89	1.84
Specific Heat (cal/g·K)	293	0.239	0.238
	373	0.287	
	446		0.359
	554		0.441
Conductivity (cal/cm·s·K)	293	0.00132	0.00108
	446		0.00073
Heat of Fusion (cal/g)	446		9.8
	554		50.0
	693	50	
Heat Release (cal/g)		716	505
Activation Energy (cal/mole)		59885	52700
Frequency Factor (1/s)		3.18E19	5.02E19
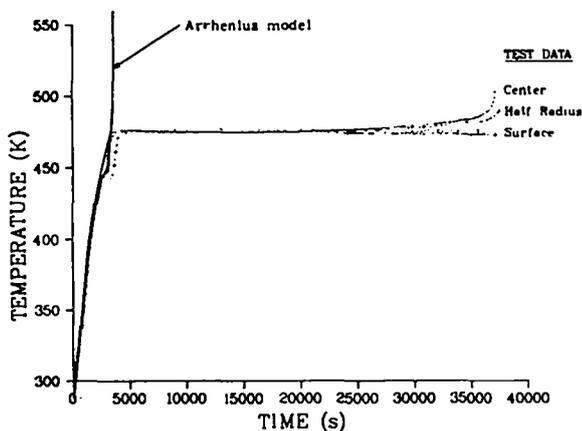
Fig. 10.

Comparing the test data with the analytical model for PBX 9501 shows that an induction process is impeding the reaction.

heated to a temperature slightly above the critical temperature.

The test results for PBX 9502 spheres (Fig. 11) show that the time to ignition for the preheated sphere is only 5% of that of the control. When the same test was performed on PBX 9501, the time to ignition was 33% of that of the control (Fig. 12).

In a different type of test, PBX 9502 again showed a strong memory characteristic. A 25-mm-diam sphere was heated to within 1 K of its critical temperature. After 110 000 s (28 h), the induction process had proceeded to the point that the sphere was generating energy. The power was then removed and the sample was held at ambient temperature for 2 days. The sample was again heated, keeping the surface temperature to within 1 K of what it was in the initial portion of the test. At this time, the explosive "remembered" the rate at which it should
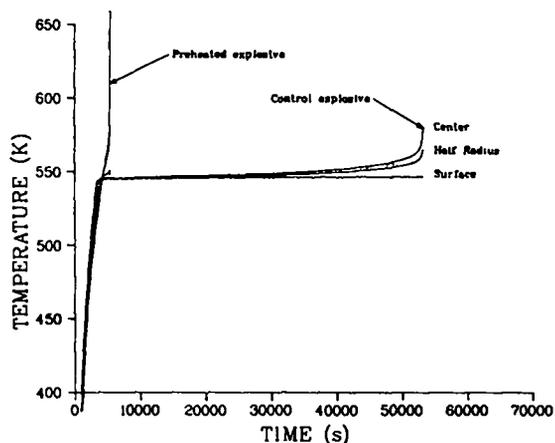
Fig. 11.

A PBX 9502 sample that was previously heated shows a memory when compared with an unheated sample.
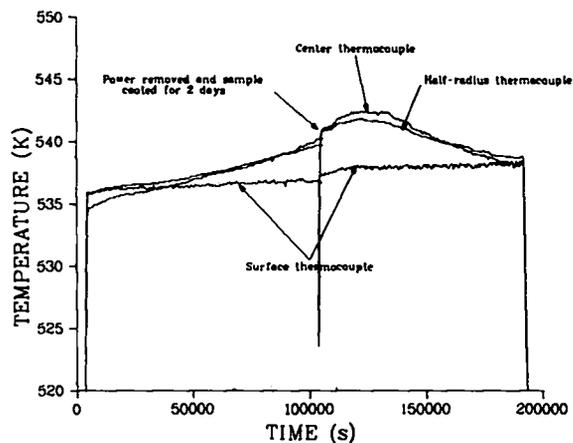
Fig. 13.

The memory characteristic of PBX 9502 can also be seen in an extended-term test of a 25.4-mm sphere.
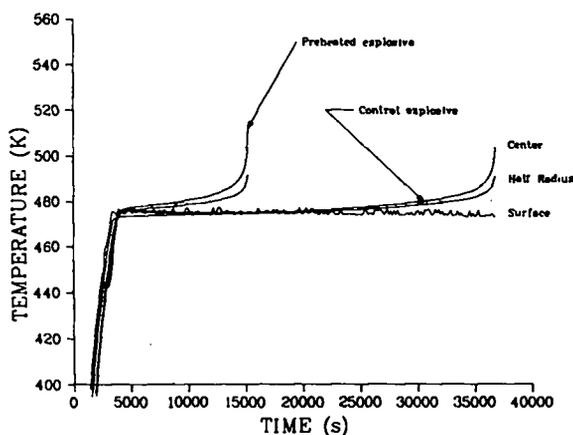
Fig. 12.

A PBX 9501 sample that was previously heated shows a memory when compared with an unheated sample.

continue to produce energy. The heat generation rate, measured by the temperature difference between the center and surface thermocouples, was an extension of the previously exhibited rate (Fig. 13).

An approximate calculation (based on the observed temperature gradient and time), in which constant material properties and steady-state conditions were assumed, showed that the energy liberated by the sphere during this entire test was approximately 850 cal/g, which is most of the chemical reaction energy normally released in a burning reaction. The weight of the sphere before the test was 15.8 g; after the test, it was 5.5 g. Following the test, the sphere looked like a slightly charred version of the original, with a somewhat rubbery, "orange peel" surface texture. In spite of the large energy expenditure and weight loss, the sphere remained intact.

V. TESTING HOW WELL THE ARRHENIUS MODEL PREDICTS CRITICAL TEMPERATURES

Four tests were conducted with PBX 9502 to determine the critical temperature (Fig. 14). A comparison of the critical temperature calculated by the EXPLO computer code and the measured critical temperature shows that the critical temperature can be accurately calculated by using the Arrhenius kinetics model. The analytical models can also accurately simulate the heat transfer aspects of the problem. A similar series of tests was conducted with PBX 9501 (Fig. 15) with consistent results.

VI. CONCLUSIONS

The unconfined spherical tests proved to be our most useful tests performed to date on large-scale
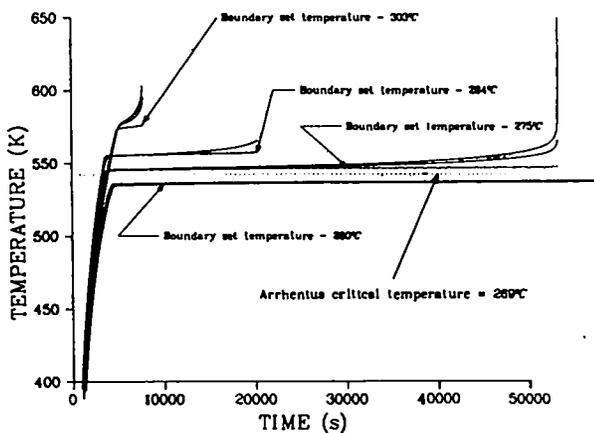
Fig. 14.
The Arrhenius function can accurately calculate the critical temperature of PBX 9502.
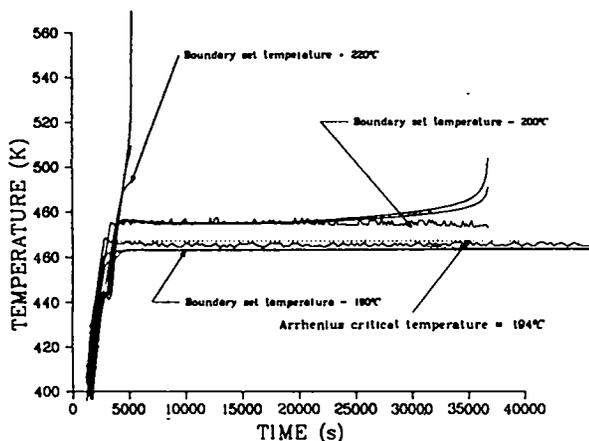
Fig. 15.
The Arrhenius function can accurately calculate the critical temperature of PBX 9501.

samples. The test results show that the temperature of test explosives can be controlled to approximately 1 K for several days in an inexpensive, expendable test chamber.

Tests on PBX 9502 and PBX 9501 demonstrate that both explosives display an induction process. Correlations between test data and computer codes using the Arrhenius model indicate that the induction process prevents the conventional Arrhenius model from accurately predicting the time to explosion. However, the tests show that the Arrhenius model can predict the critical temperature of large-scale charges. The large-scale verification is important, because the kinetics constants used in the Arrhenius model are derived from the results of very small scale tests made in a differential scanning calorimeter.

ACKNOWLEDGMENTS

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