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Thermal Stability of PBX 9501

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by

M. L. Matuszak and E. D. Loughran

ABSTRACT

Compression buttons of PBX 9501 were stored in a helium atmosphere at 35, 40, 45, and 50°C. The limiting compressive strength of 9501 was ~1700 kPa. Plots of ln (compressive strength) vs time gave the rate constant for the degradation process at each temperature. An Arrhenius plot of the rate constant data gave a value of 22.4 kcal/mol for the apparent activation energy, E_a, and 1.17×10^7 s^{-1} for the pre-exponential. The Arrhenius plot was extrapolated to 25°C and a rate constant of 5.03×10^{-10} s^{-1} was obtained. With this rate constant, the following relationship between compressive strength and time at 25°C was formulated.

$$\ln(\text{compressive strength}) = 8.792 - 5.03 \times 10^{-10}t.$$

The constant 8.782 was the Y-axis intercept in a plot of ln (compressive strength) vs time at 50°C. It was assumed to have the same value at 25°C. According to the above equation, the time required for 9501 to reach the limiting compressive strength will be 85 yr.

I. INTRODUCTION

Earlier studies[1] demonstrated the usefulness of elevated-temperature storage experiments for obtaining kinetics data and constructing lifetime predictive models. Previous work[2] on the effects of long-term storage of PBX 9501 at 60 and 74°C showed that the change in compressive strength was the most useful property in obtaining kinetics data. The compressive strengths of the 75°C samples decreased from an initial value near 6900 kPa to a constant value of 1700 kPa. The results indicated that the rate of compressive strength loss is a function of storage conditions. A lower limit of loss eventually is reached, regardless of storage temperature or cover-gas composition, thereby providing one measure of system lifetime. However, unless the explosive's compressive strength is critical to the weapon design, the limiting value achieved upon aging does not necessarily provide a useful lifetime criterion for the system. The limiting value does, however, provide a reference time. Whether or not this decrease in compressive strength is detrimental depends on the application of the explosive. The small amount of gas evolved and the lack of significant change in the chemical composition of 9501 would not serve as useful criteria for lifetime predictions. Even the molecular weight of the degraded polymeric binder was sufficiently large to preclude problems from material migration.

II. EXPERIMENTAL METHOD

A. Material

Cylindrical 3.6-kg billets of PBX 9501 were prepared by standard pressing procedures from a special lot of Los Alamos Scientific Laboratory (LASL) molding powder. The compression buttons were 1.27 cm in diameter and 2.54 cm long. The tensile specimens were standard 10.2-cm-long "doggie bones." Both types of specimen were wet-machined from billets and air-dried at room temperature. The sample density, determined by a water-immersion technique, was 1.84 g/cm^3.

B. Sample Preparation

During the study, compression and tensile specimens (five of each type) were stored in sealed stainless steel containers (Fig. 1) equipped with copper O-ring seals and Nupro SS-4BK sampling valves for gas analyses. The specimens were inserted into polyethylene blocks (Fig. 2) before being placed in the stainless steel containers. Each container was sealed by a remote welding technique.[3] The containers were evacuated and backfilled with helium at 85.1 kPa.

C. Surveillance Conditions

Samples were stored in electrically heated, explosion-proof, forced-draft ovens, which were equipped with both control and safety thermostats. Temperature control was maintained to ±2°C.

D. Postsurveillance Examination

Samples were removed from the ovens every 3 months. After being cooled to room temperature, the containers were opened on the inlet system of a DuPont 21-104 mass spectrometer. Gas volumes were determined by expansion into a calibrated volume, and a mass spectrum of each sample atmosphere was obtained. Only small amounts of gas were evolved, and the data could not be used for kinetics calculations.

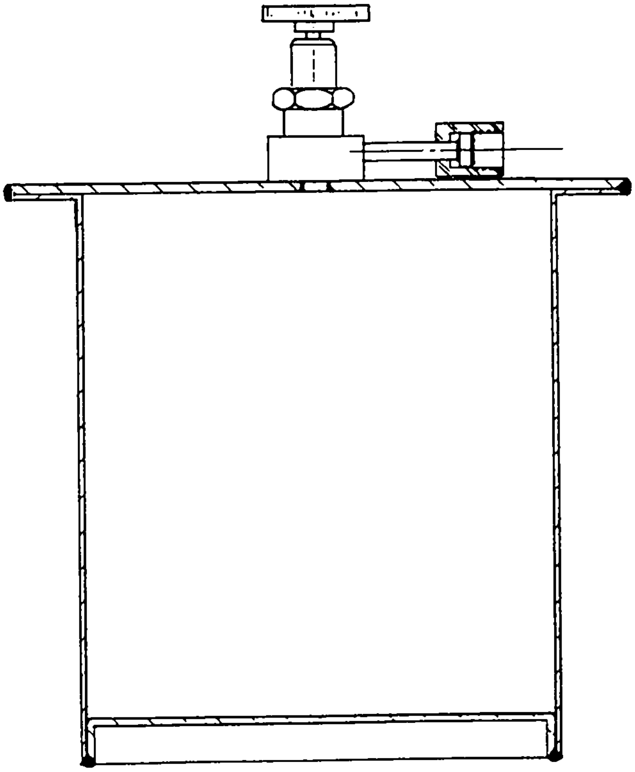

Fig. 1.
Stainless steel storage cylinder.

Chemical analyses were performed on the PBX samples, but little change in composition was observed. Sample compressive and tensile strengths were measured with an Instron tester at a load rate of 0.05 cm/min according to ASTM procedures D595 and D638.

Degradation of the PBX 9501 binder system during storage was measured by following changes in the molecular-size distributions of the binder components as a function of storage time. These distributions were determined with a Waters Model 440 gel-permeation chromatograph (GPC); tetrahydrofuran (THF) was the elution solvent. The GPC column set consisted of four 30-cm columns arranged in series and having respective maximum pore sizes of 10^5, 10^4, 10^3, and 500 Å. A solvent flow rate of 2 mℓ/min was used throughout the study.

The binder components were solvent-extracted from the surveillance samples before GPC analysis by the procedure described in Ref. 2.

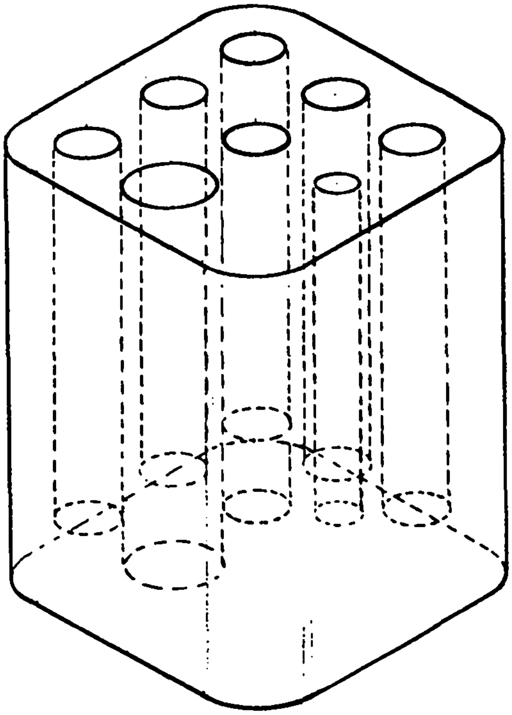

Fig. 2.
Polyethylene block.

III. RESULTS AND DISCUSSION

A. Density, Weight, and Dimensional Changes

The densities, weights, and dimensions of the PBX 9501 cylinders were not followed as a function of temperature. In a previous study[2] performed at higher temperatures, the magnitudes of the changes were within the experimental error of the measurements.

B. Gas Evolution

Little gas was evolved and the data were not useful for constructing a predictive lifetime model.

C. Compressive and Tensile Strengths

The compressive and tensile strengths of the PBX 9501 samples examined in this study are shown in Tables I and II. Because of the lower test temperatures employed (and concomitant slower degradation rates), the compressive strengths did not reach the limiting value found in Ref. 2.

TABLE I

PBX 9501 COMPRESSIVE STRENGTH (kPa)
(Average of five specimens)

Aged Sample Time (Months)	Temperature 35°C	40°C	45°C	50°C
3	6433	6264	6371	6522
6	6267	6267	6116	6054
9	6295	5867	6026	6129
12	6536	6550	6467	6072
15	6012	5805	5399	5619
18	6509	6240	6302	5812

D. Binder-Degradation Studies

The earlier work on 9501 stability[2] showed a direct relationship between the decrease in sample strengths and the degradation of the polymeric component, Estane 5703. Because of the lower temperatures involved in the present experiments, significant changes in peak molecular weight of the polymer were not observed, although a trend was apparent at 50°C. The GPC data are given in Table III. The compressive strength values were more useful than the GPC data in obtaining kinetics data.

E. Predicted Storage Lifetime of PBX 9501

Storage-stability data were analyzed by standard kinetics methods. First-order plots of the data—ln (compressive strength) vs t—were reasonably linear, and rate constants k could be calculated (Table IV). These rate constants were used to construct the Arrhenius plot shown in Fig. 3, from which the activation energy E_a and the pre-exponential factor A in the expression, $k = Ae^{-E_a/RT}$, were calculated. Extrapolation of the Arrhenius plot to 25°C gave the

TABLE II

9501 TENSILE STRENGTH (kPa)
(Average of five specimens)

Aged Sample Time (Months)	Temperature 35°C	40°C	45°C	50°C	Ambient (°C)
3	1469	1407	1455	1365	
6	1455	1262	1455	1365	
9	1331	1441	1682	1641	
12	1620	1620	1586	1434	
15	1551	1510	1462	1538	
18	1524	1427	1448	1186	1138

TABLE III

POLYMER MOLECULAR WEIGHT PBX 9501

Aged Sample Time (Months)	Temperature 35°C	40°C	45°C	50°C	Ambient (°C)
6	85 600	86 550	83 000	85 200	
12	83 200	63 250	79 800	74 200	
15	91 300	85 000	77 000	78 000	
18	91 300	85 000	77 000	65 300	92 400

value of k at that temperature. From the kinetic treatment, the following predictive model was formulated: $S_t = S_o e^{-kt}$, where S_t is compressive strength at any time, S_o is the initial strength, and k is the rate constant at the temperature of interest. This equation expresses the first-order rate dependence of the compressive strength loss. However, the equation is valid only for compressive strength values >1700 kPa, the limiting compressive strength. Using the Arrhenius equation to calculate a rate constant at a given temperature, one can predict the time required to reach limiting compressive strength at that temperature. Storage lifetimes estimated for different temperatures and based on limiting compressive strength were calculated with the model equation (see Fig. 4).

IV. CONCLUSIONS

The temperature range of degradation measurements for PBX 9501 has been extended downward. The activation energies and pre-exponential factors agree with those of Ref. 2. The same mechanism operates throughout the temperature range. Compressive strength loss is a useful parameter for the prediction of stockpile lifetimes of 9501.

TABLE IV

PBX 9501 KINETIC DATA

	Temperature					
	25°C	35°C	40°C	45°C	50°C	60°C[a]
k (s^{-1})	5.03×10^{-10}[b]	1.89×10^{-9}	3.31×10^{-9}	5.91×10^{-9}	1.03×10^{-8}	2.56×10^{-8}
A (s^{-1})	1.17×10^{7}[c]	1.17×10^{7}	1.15×10^{7}	1.17×10^{7}	1.18×10^{7}	1.20×10^{7}
E_a (Kcal/mol)	--- ←		22.4		→	21.4
Correlation coefficient	---	0.98	0.92	0.99	0.92	---

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[a] Previously published data.

[b] Extrapolated value.

[c] Assumed to be this value.

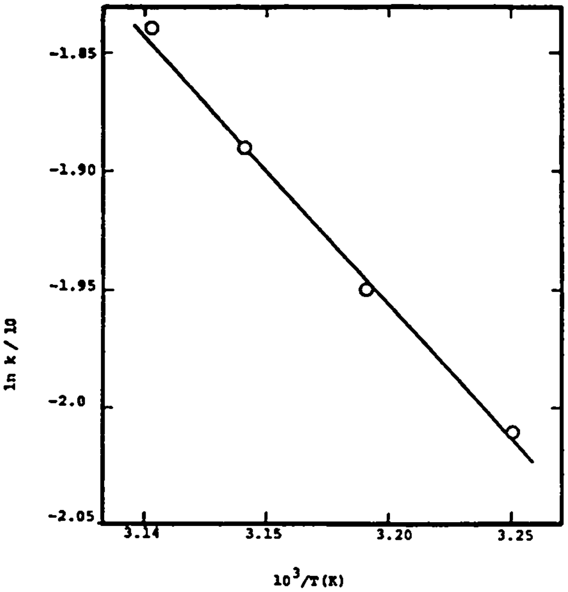

Fig. 3.
Arrhenius plot for degradation of PBX 9501.

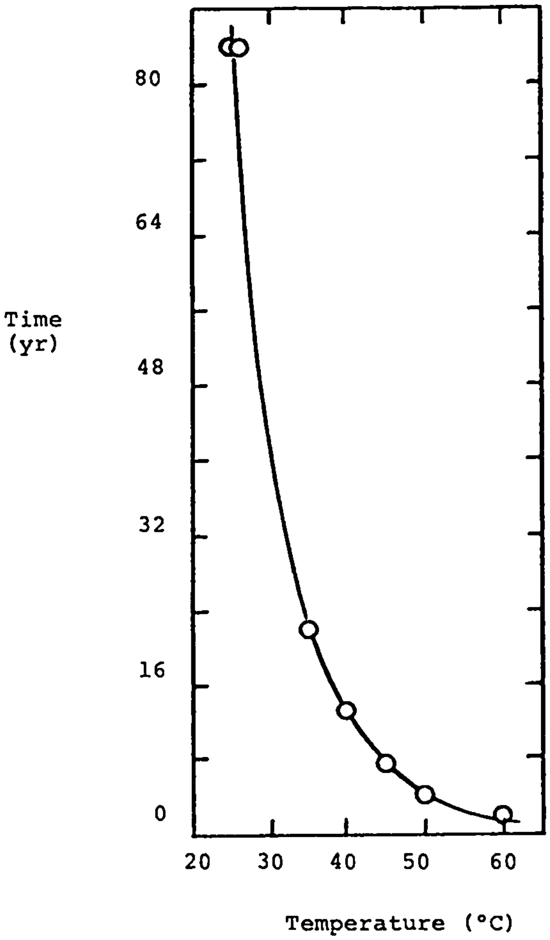

Fig. 4.
Estimated time required for PBX 9501 to research the limiting compressive strength at six temperatures.

ACKNOWLEDGMENTS

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