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AGING EFFECTS ON THE DETONATION VELOCITY OF XTX-8003.*

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ABSTRACT

In this work we measured the effects of time and temperature on the detonation velocity of XTX-8003. We found an initial increase in velocity, followed by a total decrease of 2% after 48 months at the highest temperature. At the lower storage temperatures, the changes in velocity were only slight. Five batches of XTX-8003 were used in the study and each batch was significantly different in a statistical sense. However, all five batches performed satisfactorily. This data was best described by H. Eyring's model for uncased charges, which also can give us calculated values for h, an effects parameter. In general, with increasing exposure in the time-temperature matrix, h initially decreases up to about two years then increases non-linearly in the logarithmic time domain. Projections from our response surface analysis predict that the batches would function after storage of more than 30 years at room temperature (20°C). We established an empirical relationship between service life and storage temperature (°C):

Service life (years) = 147 $e^{(-.0268)x\ (T°C)}$.

INTRODUCTION

XTX-8003 is a Los Alamos Scientific Laboratory (LASL) extrudable explosive composed of 80 wt% of pentaerythritol tetranitrate (PETN) and 20 wt% of Dow Corning Sylgard 182, a silicone resin. It is prepared by first mixing the dry PETN with the silicone resin/curing agent mixture and then it is processed through a three-roll point mill for 25 passes.

The purpose of this test was to establish the aging characteristics of this explosive formulation. As a measure of its aging characteristics we studied the change in detonation velocity as a function of track width. Our ultimate goal is to mathematically describe the data using a model that has a theoretical basis. This model could then be used as a prediction tool for new production batches.

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RESULTS

Experimental Design

Since the response we wished to measure in this test was the detonation velocity, we designed a special velocity block (Fig. 1). Made of polycarbonate, it is 12.5 mm (0.5 in.) thick, 127 mm (5 in.) wide by 254 mm (10 in.) long, and contains four parallel square channels with widths of 0.38 mm (.015 in.), 0.508 mm (.020 in.), 0.889 mm (.035 in.), and 2.032 mm (.080 in.). The four parallel channels are connected by an 0.889 mm channel as shown in Fig. 1. The spacing between the channels on the block is sufficient to prevent shock interaction between adjacent channels. These blocks were loaded with the XTX-8003 by extrusion through an orifice plate. Sixty blocks were loaded for each of the five batches, giving us a total of 300 blocks. After loading and curing, each block was wrapped in aluminum foil for exposure to isothermal storage. Our test matrix for this study, Table 1, included three temperatures at six periods; three blocks were fired for each data point.

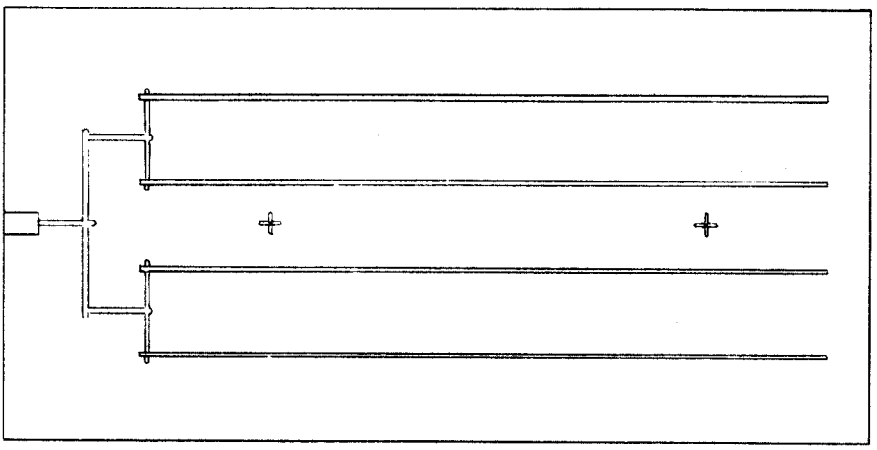

Fig. 1. Velocity test plate.

Table 1. Experimental matrix.

Temp. (°C)	Time, mos.						
	0	3	6	12	24	38	Total
20	15	3	3	3	3	3	30
50		3	3	3	3	3	15
70		3	3	3	3	3	15
				60 x 5 (batches)			300

For test fire, a switch plate containing eight ionization switches spaced one inch apart along each tract was clamped to the surface (Fig. 2). A single detonator simultaneously initiates all four channels. As the detonation velocity proceeds down the track, each swtich is successively shorted and the time is recorded on an oscilloscope.

Fig. 2. Detonation velocity block test fire assembly.

Data Reduction

After studying the time-distance data, we concluded that we should assume a constant velocity down the track. There were numerous instances where we found a switch reporting very late and usually this was followed by a very early switch.

We believe that this is due to an electronic problem. When this occurred in the middle of the track it was readily apparent. However, at either end of the track interpretation was more difficult. To resolve these problems we first estimated the detonation velocity from the slope of a least squares (LSQ) fit to the time-distance data. We found that the LSQ value usually agreed with the average velocity determined by measuring the elapsed time between the second pin switch and the seventh pin switch.

Another problem in reducing the data was due to a change in the firing procedure during the four-year test period. All of our test fire data was normalized to 20°C. Initially, we fired these blocks in an indoor facility with a known, controlled temperature. Firing was subsequently transferred to an outdoor firing table. The blocks were placed in styrofoam boxes to maintain a constant temperature, but their temperatures were not recorded. This procedural change was discovered in reviewing the 24-month data. For the 48-month test fire samples, we installed thermocouples and so determined the firing temperature. The net effect is that there is an uncertainty of ~0.2% in the temperature corrections for the 6-, 12-, and 24-month data. This temperature correction proved to be significant only for the 12-month data. The overall test error is also 0.2%.

Discussion

The average velocities with their 95% confidence limits (n = 4) for each channel diameter, representing each point in the time-temperature matrix, are present in Table 2 and Figs. 3-6. Figures 7 and 8 are plots of velocity vs. 1/W, the reciprocal of the channel width at 0 and 48 months, to show the channel size effect on the detonation velocity. H. Erying's[1] model for an uncased charge, which adequately describes the data, is:

$$\frac{D}{D_i} = 1 - \frac{a}{W} \qquad (1)$$

where D is the measured velocity, D_i is the infinite track width velocity, a is a reaction zone length, and W is the track width. We also tried to fit the data to the modified Eyring equation[2] which is given by:

$$\frac{D}{D_i} = 1 - \frac{a}{W-W_c} \qquad (2)$$

where W_c is a critical width. This approach appealed to us because the Eyring model is not valid at very small values of W since in the limit of $W \to 0$ the equation diverges. However, when we applied our data to the modified model it yielded numerous negative coefficients, which made use of the equation impractical. One

Table 2. Average detonation velocity of XTX-8003.

Channel diam	T°C	Time (mos.) 0	3	6	12	24	48
		V (mm/μsec) 95% C.L.*	V (mm/μsec) 95% C.L.	V (mm/μsec) 95% C.L.	V (mm/μsec) 95% C.L.	V (mm/μsec) 95% C.L.	V (mm/μsec) 95% C.L.
2.03 mm	20	7.284 ± .025	7.292 ± .023	7.285 ± .007	7.281 ± .020	7.296 ± .013	7.290 ± .069
	50		7.298 ± .017	7.297 ± .023	7.289 ± .027	7.305 ± .025	7.305 ± .045
	70		7.310 ± .035	7.313 ± .023	7.288 ± .023	7.255 ± .020	7.166 ± .075
0.89 mm	20	7.261 ± .019	7.265 ± .025	7.261 ± .010	7.254 ± .008	7.270 ± .008	7.269 ± .037
	50		7.269 ± .023	7.267 ± .016	7.258 ± .023	7.280 ± .026	7.257 ± .050
	70		7.282 ± .022	7.288 ± .017	7.257 ± .018	7.220 ± .029	7.112 ± .082
0.51 mm	20	7.219 ± .030	7.223 ± .013	7.222 ± .034	7.211 ± .019	7.232 ± .024	7.223 ± .098
	50		7.217 ± .031	7.213 ± .042	7.207 ± .034	7.234 ± .044	7.217 ± .067
	70		7.235 ± .021	7.257 ± .033	7.218 ± .011	7.162 ± .052	7.029 ± .143
0.38 mm	20	7.183 ± .046	7.191 ± .025	7.192 ± .052	7.170 ± .039	7.196 ± .041	7.196 ± .133
	50		7.171 ± .069	7.170 ± .092	7.159 ± .067	7.197 ± .065	7.192 ± .076
	70		7.203 ± .032	7.237 ± .029	7.182 ± .015	7.104 ± .080	6.937 ± .141

*C.L. = confidence limit

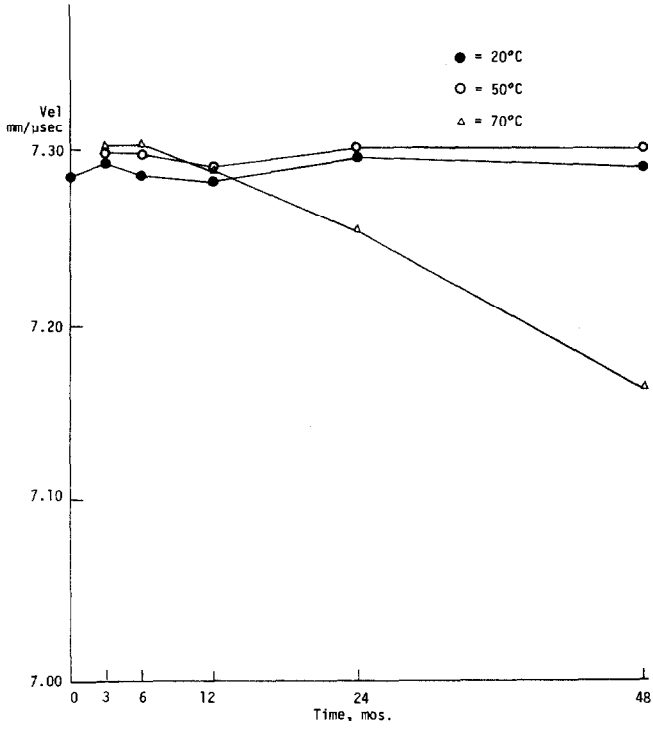

Fig. 3. Detonation velocity in 2.03 mm track.

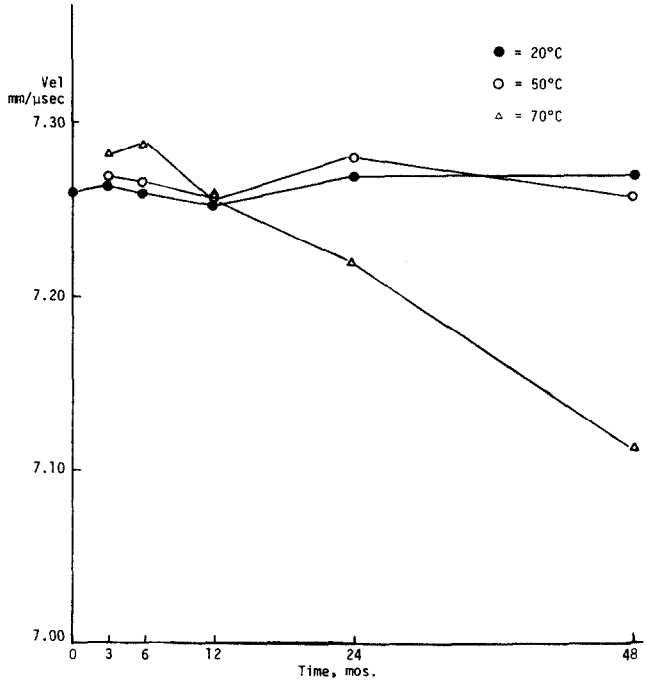

Fig. 4. Detonation velocity in .89 mm track.

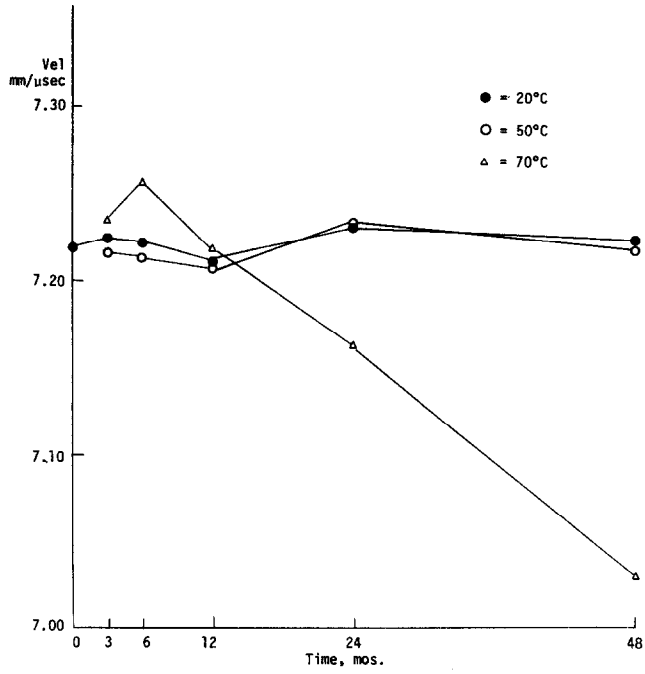

Fig. 5. Detonation velocity in .51 mm track.

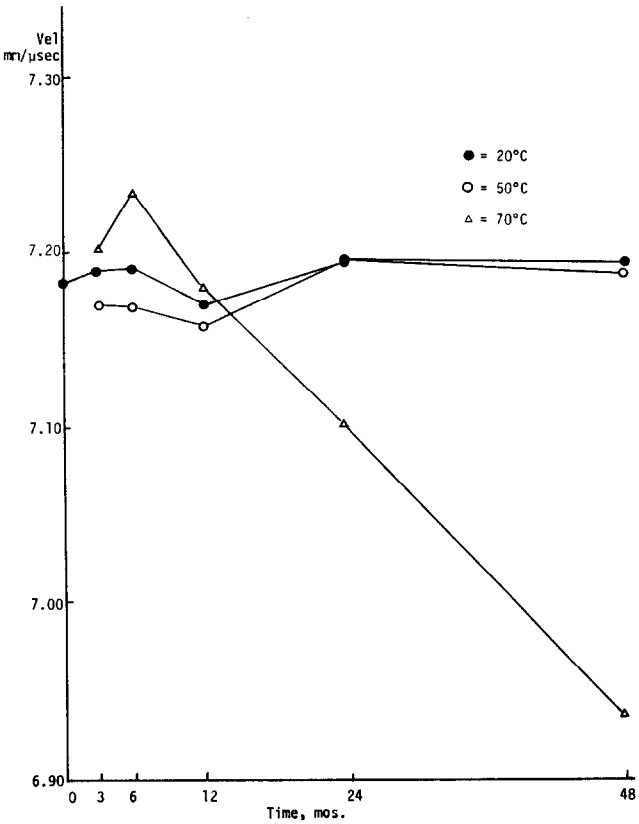

Fig. 6. Detonation velocity in .38 mm track.

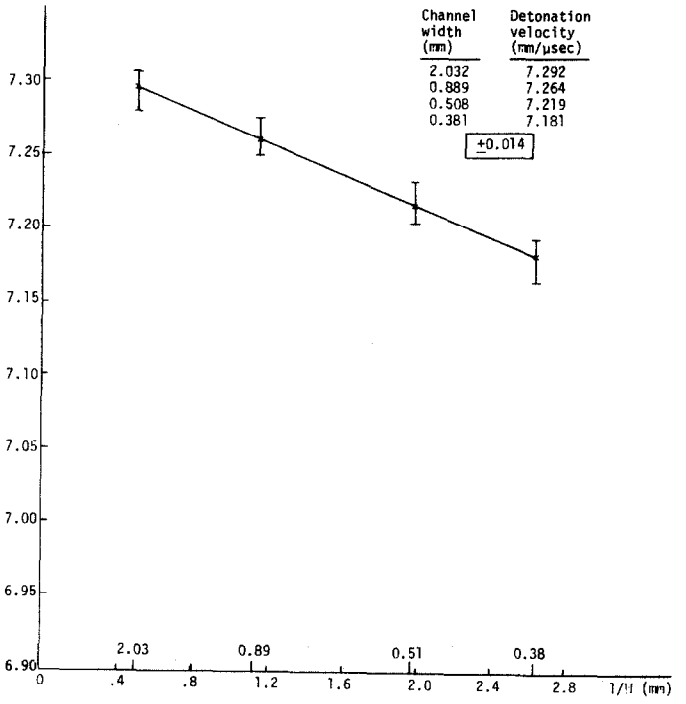

Fig. 7. Baseline data.

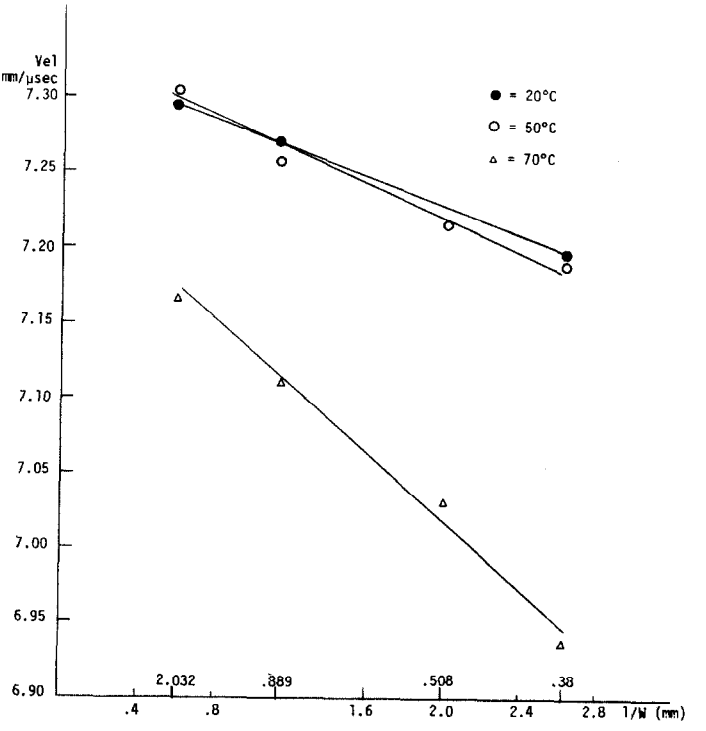

Fig. 8. 48-month data.

big advantage in using Eyring's theory is that we can reduce the numerous experimental data into simple meaningful parameters.

Our data shows that during the aging process the detonation velocity initially increases in time and then begins to decrease. An analysis of variance shows that this is real and not an artifact. At the lower temperatures (20-50°C), the velocity changes are statistically insignificant. At 70°C the effects of aging are much more dramatic and are statistically significant. We have some concern that there may be a different aging mechanism at 70°C than at temperatures below 50°C. Nevertheless, we treated the data as a continuum, including the 70°C data.

According to Eyring's absolute rate theory:[1]

$$\frac{a}{a_i} = \left(\frac{D_i}{D}\right) e^{\frac{\Delta H^{\ddagger}}{T_i R}\left[\left(\frac{D_i}{D}\right)^2 - 1\right]} \qquad (3)$$

where: a = the reaction zone length for a given track size.

a_i = the reaction zone length at the infinite track width.

D = the velocity for a given track size.

D_i = the velocity for an infinite track width.

$\Delta H^{\ddagger}$ = heat of activation for the reaction, cal $mole^{-1}$.

T_i = detonation temperature in the reaction zone.

R = gas constant, 1.986 cal deg^{-1} $mole^{-1}$.

Therefore, the reaction zone and the velocity parameters are dependent on the heat of activation. To simplify the following discussion, we define $h = \frac{\Delta H^{\ddagger}}{T_i R}$ as a calculated effects parameter. As shown in Fig. 9, h initially decreases with time up

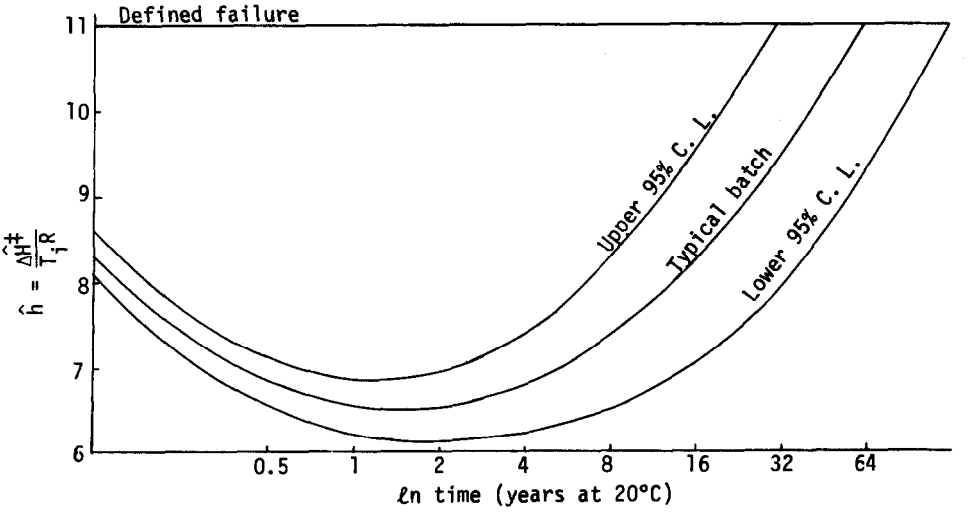

Fig. 9. Changes of h with time.

to ∿2 years and then increases non-linearly in the logarithmic time domain. In this study we use temperature to accelerate the aging properties. This permits us to apply the Arrhenius law for chemical reaction rate, i.e., we assume that the following general model is valid:

$$\ell nh = f\left(\frac{1}{T}, \ell nt\right). \tag{4}$$

This unknown function is expanded into a Taylor series:

$$\ell nh(T,t) = \beta_0 + \beta_1(\ell nt) + \beta_2\left(\frac{1}{T}\right) + \beta_3(\ell nt)^2 + \beta_4\left(\frac{1}{T}\right)^2 + \beta_5\left(\ell nt \cdot \frac{1}{T}\right) \tag{5}$$

The response surface methodology[3,4] was then used to express the effect parameter h as a function of the experimental temperature and time variables. The outcome of this process is a response surface equation:

$$\ell n\hat{h} = \ell n\left(\frac{\Delta\hat{H}^{\ddagger}}{T}\right) = 9.38 + 0.58(\ell nt) - 5.22\left(\frac{10^3}{T}\right) + 0.04(\ell nt)^2 + 0.89\left(\frac{10^3}{T}\right)^2 - 0.24\left(\frac{10^3 \ell nt}{T}\right) \tag{6}$$

where ℓnt is the natural logarithm of time in months and T is the temperature in

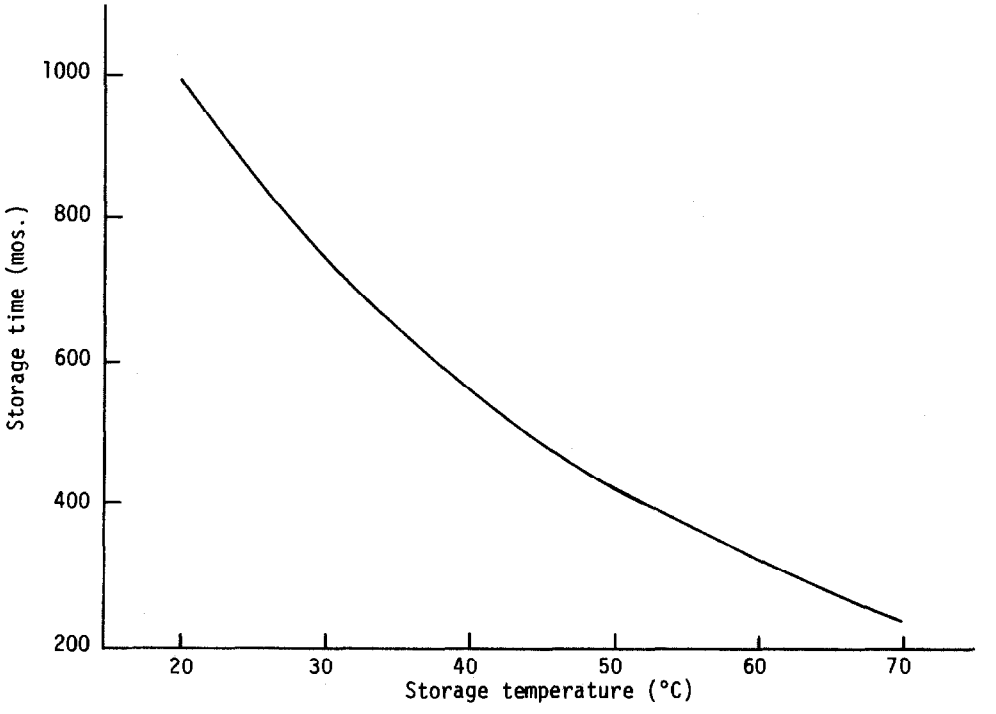

Fig. 10. Service life.

°K. This equation adequately describes the data (σ = .04). To use this equation for the prediction of service life, we must first establish a failure criterion. We define failure as the inability of a given track size to support a steady detonation velocity. Our analysis of this data indicates that we would expect failure if the Eyring parameters approach a detonation velocity of 6.1 mm/sec. in a track width of 0.318 mm. This corresponds to a value of h = 11 for the failure criterion. Using this criterion and the response surface equation, we calculated an empirical equation relating service life with surface temperature (°C):

$$\text{Service life (years)} = 147\, e^{(-.0286)(T)} \quad (20°C \leq T \leq 70°C). \tag{7}$$

This relationship is shown in Fig. 10 and indicates that these batches of XTX-8003 would function for more than 30 years when stored at 20°C.

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