The Safe Storage Life Estimation for Energetic Materials

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Abstract. In the present study, the safe storage life prediction of gun-propellant in different temperature mode were calculated by the dates of stabilizer content under thermal accelerated aging at temperature of 95°C, 90°C, 85°C, 75°C and 65 °C via Berthelot equation and Arrhenius equation. In order to demonstrate these predictions, all the estimation results have been compared with the real experimental results. Presented results indicate that the prediction via Arrhenius equation is consistent well with real storage experimental results at shallower reaction depth of stabilizer (α = 6.6%). Furthermore, predicting by shallower Berthelot equation is available at deeper reaction depth (α = 50%).

1. Introduction
It is well known that nitrocellulose-based propellants may decompose slowly, which may lead to decreasing of their chemical stability and directly related to the storage life of the whole product [1, 2]. At present, accelerated aging test is a common life test method, which is to establish a suitable aging model according to the high temperature test data, so as to predict the safe storage life of Energetic Materials.

Life assessment involves the following aspects: 1. Selection of test conditions; 2. Determination of failure judgment basis; 3. Time relationship between extrapolation to normal temperature and degradation of failure parameters and temperature relationship of degradation rate. This paper only comments on the third item, the mathematical model and calculation method of predicting the life temperature relationship.

2. Experimental sections

2.1. Accelerated Aging Test
A kind of triple based propellant (contains RDX, NG, NC, the stabilizer etc.) were used for the experiments. The propellant was synthesized about 24 years ago and some of the samples were aged at 95, 90, 85, 75 and 60 °C at the same year, then the remainder of the stabilizer content under thermal aging at different temperature were measured by brominating method according to GJB 770B-2005.
2.2. Storage Life Prediction Methods

Safe storage life prediction using accelerated ageing data mainly needs scaling up of shelf life from elevated temperature to that at reference temperature. The Arrhenius and Berthelot approaches are mostly used for such correlations.

2.2.1. Arrhenius Approach. Based on the Arrhenius equation, the logarithm of the conversion rate $\frac{d\alpha}{dt}$ as a function of the reciprocal temperature at any conversion $\alpha$

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot f(\alpha)$$  \hspace{1cm} (1)

Where $A$ = pre-exponential factor (1/s), $k(T)$=rate constant, $E$ = activation energy (kJ/mol), $T$ = temperature (K), $t$ = time (s), $R$= the universal gas constant,$\alpha$= reaction progress and $f(\alpha)$ = kinetic model function[3];

Roduit et al. [2] applied the modification introduced by Pérez-Maqueda et al. [4] who proposed the use of the following algebraic expression for $f(\alpha)$ (called throughout this study as PM-model):

$$f(\alpha) = (1-\alpha)^m \alpha^n$$  \hspace{1cm} (2)

known as a modified Prout-Tompkins (PT) equation discussed in detail by Brown. It follows that the general expression describing the rate of reactions has the form [5, 6]:

$$\frac{d\alpha}{dt} = k(T) f(\alpha) = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot (1-\alpha)^m \alpha^n$$  \hspace{1cm} (3)

Thus, the general expression given by Eq. (3) allows describing the rate of the reactions. In AKTS-Thermokinetics Software, the kinetic parameters are calculated using the PM approach. Therefore, the safe storage life $t_{\alpha}$ under certain reaction progress can be rearranged to:

$$t_{\alpha} = \int_{\alpha_s}^{\alpha} \frac{d\alpha}{A \cdot \exp\left(-\frac{E}{RT}\right) \cdot (1-\alpha)^m \alpha^n}$$  \hspace{1cm} (4)

2.2.2. Berthelot Approach. The Berthelot equation is approach to predict the storage life of propellants. This approach is applied to develop curves reflecting the variation in the reaction rate with temperature [5-6]. In this case, log of time to base 10 is directly proportional to temperature as follows:

$$\log k = aT + b$$  \hspace{1cm} (5)

The slope of this line can be defined by $\gamma_{10}$ corresponding to the increase of the reaction rate for a temperature change of 10 K. Therefore, to determine $\gamma_{10}$, it is sufficient to take the duration $t_1$ and $t_2$ corresponding to temperatures of $T_1$ and $T_2$. Mathematically, it could be shown that the following equation was derived by subtracting $T_1$ from $T_2$ in Equation (6):

$$\log \left(\frac{t_1}{t_2}\right) = \gamma_{10} \left(\frac{T_2}{T_1}\right)$$  \hspace{1cm} (6)

Generally $10 \degree C$ is taken as a standard and for every $10 \degree C$ rise or fall in temperature, the propellant properties changes by the same fraction, defined by $\gamma_{10}$. The shelf life prediction correlation is given as Eq. (7):

$$t_{1/2} = (\gamma_{10})^{\frac{1}{10}} x$$  \hspace{1cm} (7)

3. Results and Discussions

3.1. Storage Life Prediction by Arrhenius Approach

Figure 1 shows the stabilizer depletion vs. time (days) under thermal aging at 95, 90, 85, 75 and 60 $\degree C$. Apparently, the decreasing trend of stabilizer is approximately linear. Usually, the decomposing depth of nitrocellulose-based propellant during thermal aging experiment is no more than 1–2%, so the propellant sample is still in the decomposition delay period and the zero-order reaction is a suitable rate equation. Therefore, $m=0$ and $n=0$ can be set in Equation (2) and predictions for the safe storage life of the propellant based on the dates of stabilizer depletion have been simulated by AKTS Thermokinetics software in Arrhenius approaches, which can be described by the following equation
\[ k(T) = \exp(29.388) \cdot \exp \left(\frac{-132100}{8.314 \cdot T(t)}\right) \]  

(8)

According to Equation (2), the stabilizer concentration as a function of time which gives a straight line with a slope of the reaction rate constant. Figure 1 shows the variation of the stabilizer concentration as a function of time at 95, 90, 85, 75 and 60 °C. The safe storage life of the propellant based on the dates of stabilizer depletion under thermal aging have been simulated by Prediction line in Figure 1.

Fig.1 Prediction line of attenuation of stabilizer concentration in triple base gun-propellant at different temperature calculated by equation (5).

For zero order reactions, equation (1) can be rearranged to

\[ \frac{d\alpha}{f(\alpha)} = k(T) dt = A \cdot \exp \left( -\frac{E_a}{RT} \right) \cdot dt \]  

(9)

\( f(\alpha) \) can be written in integral form:

\[ g(\alpha) = \int \frac{1}{f(\alpha)} \]  

(10)

By substituting Equation (10) in Equation (9) it follows:

\[ g(\alpha) = k(T) = A \cdot \exp \left( -\frac{E}{RT} \right) \cdot t \]  

(11)

For zero order reactions,

\[ g(\alpha) = \int \frac{1}{f(\alpha)} = \alpha = kt \]  

(12)

Then

\[ t = \frac{\alpha}{k} \]  

(13)

By substituting Equation (13) in Equation (8), the time of stabilizer decomposes to a certain depth at the specific temperature can be calculated as follow:

\[ t = \frac{\alpha}{k} = \frac{\alpha}{\exp(29.388) \cdot \exp \left(\frac{-130700}{8.314 \cdot T(t)}\right)} \]  

(14)

Equation (14) can be used to calculate the storage life of the triple based propellant samples under different temperature conditions. It is generally accepted that the stabilizer depletion in the aging process could be taken as judgment basis in evaluating of safe storage life. At 95% confidence, reaction progress of the decomposition of stabilizer as a function of time under isothermal conditions calculated via Equation (14) is shown in Fig. 2 and safe storage life calculated by equation (14) depicted in Table.2. It can be conclude that the safe storage life of the triple based propellant samples at 25°C is about 391.7y. If the storage temperature is increased to 30°C, the safe storage life will be shortened to 162.5y. At 95%
With high confidence, the safe storage life of propellant samples is 276.7–678.0 y at 25 °C and 117.6–280.8 y at 30 °C.

![Figure 2](image)

**Fig. 2** Reaction progress of the decomposition of stabilizer as a function of time under isothermal conditions calculated by equation (12): (a) 25 °C, (b) 30 °C.

**Table 1.** The safe storage life calculated by equation (12) under isothermal conditions.

| T/°C | T/K | α  | k (T) /S⁻¹ | τ₀.5/y |
|------|-----|----|------------|--------|
| 30   | 303 | 0.5| 9.75663E⁻¹¹| 162.5038167 |
| 25   | 298 | 0.5| 4.04753E⁻¹¹| 391.7178882 |

3.2. Storage Life Prediction by Arrhenius Approach

According to Berthelot’s mathematical expression in Equation (5), T and lg τ represent a straight line functional relationship. Using these values of the times required for the depletion of 50% for stabilizer, the Berthelot plot of the degradation reaction is shown in Figure 3.

![Figure 3](image)

**Fig. 3** Berthelot plot of stabilizer (R²=0.9994)

By using Berthelot plot, the storage life at each temperature was calculated. Table 2 shows the predicted storage life in the temperature range 20-30°C (293–303 K).

**Table 2.** Comparison of the fuel shelf life predicted using Arrhenius and Berthelot approaches.

| T/K | T/°C | Storage Life by Berthelot Plot/y |
|-----|------|----------------------------------|
| 303 | 30   | 104.8                            |
| 298 | 25   | 55.5                             |

3.3. Comparison and Verification of Arrhenius and Berthelot Prediction Model

Using different evaluation models to calculate, there will be a certain gap in the results. Therefore, the life prediction results of different algorithms should be verified by natural storage dates in a certain period of time. After 24 years storage in the semi underground warehouse, the content of stabilizer was reduced to 1.4%, that is to say, the decomposition depth of stabilizer (α) is 6.6% in the actual storage
process. According to Fig. 1, the storage life ($\tau_{0.066}$) at 95, 90, 85, 75 and 60 °C is 0.6d, 1.2d, 2.4d, 8.2d and 30.2d respectively when $\alpha$ is 6.6%. Using Berthelot formula for linear regression as follows:

$$T = 454.4 - 18.1 \log \tau$$  \hspace{1cm} (15)

**Table 3.** The safe storage life calculated by different aging model under isothermal conditions.

| Evaluation Model | $\tau_{0.066}$/y | Exuviated Temperature Calculated by different model when $\alpha=0.066$ /℃ |
|------------------|-----------------|----------------------------------|
| Arrhenius        | k=exp(29.388)*exp(-132100/8.314T) | 51.7    21.5    26.3 |
| Berthelot        | $T=454.4-18.1\log t$           | 13.9    7.3    20.6 |

Analysis of Table 3 shows that when the decomposition depth of stabilizer is 6.6%, the exuviated temperature calculated is 26.3℃ by Arrhenius approach and 20.6℃ by Berthelot approach. Compared with the natural storage date, the prediction result of Arrhenius model is closer to the actual situation.

In fact, the temperature environment of semi underground warehouse fluctuates to certain extent near the room temperature with the alternation of seasons and days and nights. The annual temperature profile of storage site is shown in Fig. 4.

![Fig. 4](image)

**Fig. 4** The annual temperature profile of storage site.

Analysis of Fig. 4 shows that the average value of the annual temperature profile is about 23.5℃. Therefore, the temperature profile is substituted into Equation (14), and the decomposition depth of stabilizer changes with storage time is calculated, as shown in Fig. 5. It can be seen from the figure that, in the temperature profile depicted in Fig. 4, the time required for the decomposition depth of stabilizer to 6.6% is about 26.1y, which is close to the result of natural storage. This is because a series of temperature shock models are formed in the temperature difference cycle of day, night and seasons, which results in alternating stress, resulting in a ladder like cumulative loss of stabilizer content of the sample. Combined with the predicted date at room temperature, the results of storage life assessment with Arrhenius approach are closer to the natural storage date when the consumption of stabilizer is low.

![Fig. 5](image)

**Fig. 5** Reaction progress of the decomposition of stabilizer as a function of time under temperature profile depicted in Fig. 4 calculated by equation (14).

In fact, although the safe storage life of propellant sample is based on the change of stabilizer content, during the long-term storage process, the impact of a series of changes on the storage reliability, such as decrease of mechanical properties, loss of mass, and the damage of structural integrity, should also
be considered. The change of stabilizer content is not necessarily the only failure mode, and the safe storage life evaluated by stabilizer is not exactly equal to the reliable life. However, the safe storage life estimated by Berthelot approach is shorter, which can avoid neglecting the risk of failure caused by other modes when calculating the storage reliability based on a single failure mode. At the same time, because it is more accurate to use a model to predict when the stabilizer is consumed in a small amount, so Arrhenius and Berthelot approach should be used for comprehensive evaluation in product finalization.

4. Conclusion
1. When the decomposition depth of the stabilizer in the propellant is shallow (e.g. \( \alpha = 6.6\% \)), the time required for aging prediction by using Arrhenius approach is closer to the natural storage results. At the same time, the closer temperature function is to real situation of storage location, the higher reliability of estimated value is.

2. When the decomposition depth of stabilizer is deep (e.g. \( \alpha = 6.6\% \)), a series of performance changes such as mechanics, quality and structural integrity should be considered. As the storage life calculated by extrapolation of Berthelot approach is far lower than that calculated by Arrhenius approach, so Berthelot approach prediction results are more reliable in the process of new product development and finalization.

3. Arrhenius and Berthelot approach should be used for comprehensive evaluate the remaining storage life of inventory products.

References
[1] X. P. Fan, Z. R. Liu, L. X. Sun, A Prediction on the Physical Aging Life of NEPE-5 Propellant (in Chinese), Chin. J. Explos. Propellants 2003, 26, 43 – 46.
[2] M. Liu, L. Du, J. Su, Current Research Situation of Stabilizer for NEPE Propellant (in Chinese)s, Chem. Propellants Polymeric Mater. 2009, 4, 31 – 33.
[3] Prout EG, Tompkins FC. The thermal decomposition of potassium permanganate, Trans Faraday Soc [M] 40:488–498. 1944.
[4] M.E. Brown, Thermochim. Acta, 300 (1997) 93.
[5] K. C. Raha, S. S. Adhav, N. M. Bhide, A. D. Yewale, G. K. Gupta, J. S. Karir, Thermal Stability and Shelf-life of High Energy Fuel for Torpedoes, Def. Sci. J. 2002, 52, 165.
[6] N. S. Garman, J. P. Picard, S. Polakoski, J. M. Murphy, Prediction of Safe Life of Propellants, Report AD 763879, United States Army Armament Research, Development and Engineering Center, Picatinny Arsenal, Dover, NJ, USA, 1973.