Investigation Aging Behavior of High Energy Propellant Materials

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Abstract. NEPE propellants were exposed to aging at 55°C, 65°C, 70°C, and 75°C, respectively. The relative contents of stabilizer (MNA), tensile strength and are measured to analysis the aging characteristic of NEPE propellants. Based on aging mechanism of the stabilization depletion and the physical aging properties of NEPE propellants, the whole aging process can be separated into two processes: stabilizer gradual degradation at first stage (chemical aging stage) and degradation reaction of polymer at seconded stage. The stabilizer degradation occurred in the first process, therefore the storage life prediction at normal temperature for NEPE propellant ought to be based on the first process during high temperature aging stage. The storage life of the NEPE propellant at room temperature has been evaluated via Arrhenius and Berthelot approach.

1. Introduction
NEPE (Nitrate Ester Plasticized Polyether) propellants are cross-linked solid propellants, which use polyether polyurethane as binder and nitrate esters as plasticizer, filled with a large amount of high-energy oxidizer, such as HMX and AP [1]. It is well known that nitrocellulose-based propellants decompose gradually during storage, which may lead the decreasing of the chemical stability. Researches about aging process are important in evaluating the reliability and safe employability of NEPE propellants. Sometimes, hydrolysis reaction will occur when nitrate esters absorb the moisture in the air [2]. In the process of hydrolyzation, the decomposition of nitrate esters will be accelerated by NOx free radicals, which can catalyze the further decomposition. Hence stabilizers are usually employed into NEPE propellant to neutralize acid and nitric oxide. Meanwhile, the self-catalytic decomposition of nitrate esters is restrained, and the degradation of plasticizer framework is reduced [3]. Accordingly, the depravation of polymer network and stabilizer are the criterions to evaluate the safe storage life and chemical stability of propellant [4].

In this paper, the safe storage life of NEPE propellant was predicted by the Arrhenius and Berthelot equation via thermal aging storage. The aging process has been separated into three stages based on the chemical stability caused by the decomposition of nitrate esters and the mechanical aging caused by the degradation of cross-linked network structure.

2. Experimental Sections

2.1 Accelerated Aging Test
The typical composition of NEPE propellant contains of polyether, NG-BTTN and MNA. The fuel density was 0.846g/cm³. The propellant samples were cut into cubic shape (120mm×25mm×10mm). The samples were sealed and aged at 55°C, 65°C, 70°C, and 75°C for different times.
2.2. Content of Stabilizer Analysis
The relative migration ratio of stabilizer (MNA) is characterized by HPLC. NEPE propellant lamella of different aging time weighting 0.2 g were put into 20 mL Erlenmeyer flask and soaked in chromatographic acetone/H$_2$O mixture for 8 h. Afterwards the soaking liquid was detected by HPLC. The relative content of MNA is obtained by calculating the ratio of peak area.

2.3. Determination of Cross-linking Density
The variety of cross-linked densities during NEPE propellant aging process was characterized via magnetic resonance cross-linking instrument. The cross-linking density can be calculated via rubber elasticity statistics theory.

2.4. Determination of Tensile Strength
The tensile strength of NEPE propellant has been characterized via uniaxial tension test according to GJB 770B-2005. Figure 1 shows the general sample for the uniaxial tension test.

![Figure 1. Tensile specimens.](image)

2.5. Storage Life Prediction Methods
Prediction of safe storage life based on accelerated aging dates commonly needs scaling up of the storage life from high temperature to that at normal temperature. The Berthelot and Arrhenius approaches are extensively used for such extrapolation.

2.5.1. Arrhenius Approach.
Arrhenius approach has been usually used to analyse accelerated aging dates of propellants at elevated temperature, and the results can be calculated for storage predictions at any storage temperature [5]. The Arrhenius equation is given by Eq. (1):

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

Which can be rearranged in this form:

$$\ln k = \ln A - \exp\left(-\frac{E_a}{RT}\right)$$

Where $k$ represents the reaction rate constant, $a$ represents pre-exponential factor, $E_a$ represents the activation energy (kJ/mol), $R$ represents the universal gas constant, and $T$ represents the temperature (K). $t_1$ or $t_2$ is the storage life at temperature $T_1$ or $T_2$. Correspondingly, $t$ is proportional inversely to $k$.

2.5.2. Berthelot Approach.
Berthelot equation is another common approach for storage life estimation. This approach depicts curves reflecting the correlation between variation in reaction rate and temperature [6]. Thus, logarithm of time based 10 is in directed proportion to temperature in Eq. (3):

$$\log k = aT + b$$

where $k$ represents the reaction rate constant, $a$ and $b$ are constants, and $T$ represents the temperature in Kelvin (K). For zero-order reactions, the rate constant $k$ can be expressed as:

$$k = \frac{c}{t}$$

where $c$ is defined as the concentration decrease of the substrate, and $t$ represents the required time for achieving a certain change (50% of stabilizer according to GJB 770B-2005) in the concentration of substrate. By superseding expression of $k$ in Eq. (4), Eq. (3) can be written as:

$$\log \frac{c}{t_{0.5}} = aT + b$$
Therefore, \( t_1 \) or \( t_2 \) can be defined as the storage life under temperature \( T_1 \) or \( T_2 \). Correspondingly, the following equation can be deduced by subtracting \( T_1 \) from \( T_2 \) in Equation (5):

\[
\log \left( \frac{t_1}{t_2} \right) = a(T_2-T_1)
\]  

(6)

3. Results and Discussions

3.1. Aging Behaviour of Chemical Stability

Figure 2 shows the relationship of MNA stabilizer depletion and aging time under 55°C, 65°C, 70°C, and 75°C. The values of MNA depletion obtained from different accelerated aging temperatures can then be used to define the effect of temperature on the degradation rate or to predict the storage life of propellant.

According to the data in Figure 2, the trend of MNA stabilizer consumption exhibited almost linear and the concentration of MNA have independence on MNA stabilizer degradation, so the degradation of stabilizer accords with the zero-order reaction \([7]\). Concentration of MNA stabilizer has linear functional relationship with aging time and the slope of stabilizer content-time line denotes reaction rate. The degradation rate of MNA under different accelerated aging temperatures can be utilized to predict the safe storage life of NEPE propellant. Accordingly, the prediction of safe storage life at ambient temperature will be carried out via both Berthelot and Arrhenius approach.

![Figure 2. Prediction lines of degradation stabilizer (MNA) concentration based on experimental dates collected in the range of 55°C-70°C.](image)

The slope of prediction lines in Figure 2 represents the reaction rate constants (\( k \)) under 55°C-75°C (328-348k). According to Eq. (2), the plot of \( \ln k \) as a function of \( 1/T \) gives a straight line. Thus, the values of reaction rate constants at 55°C-75°C can be calculated the slope of MNA stabilizer depletion trend line under different accelerated aging temperatures in Figure 2. Meanwhile, Eq. (2) can be rearranged in this form:

\[
\frac{t_1}{t_2} = \frac{k_2}{k_1} = \exp \left( \frac{E_a}{R} (1/T_1 - 1/T_2) \right)
\]

(7)

\( T \) represents the temperature (K). \( t_1 \) or \( t_2 \) is the storage life at temperature \( T_1 \) or \( T_2 \). Correspondingly, \( t \) is proportional inversely to \( k \). Therefore, \( \ln k \) under various aging temperatures can be compute and the Arrhenius plot of the degradation reaction based on Eq. (2) is obtained, which is shown in Figure 3.
At the same time, the aging times ($t_{0.5}$) of MNA concentration decreasing to 50% also can be obtained from Figure 2. According to Berthelot’s mathematical expression in Eq. (2), $T$ and $\log(t)$ present straight line functional relationship. Then the Berthelot plot of the MNA stabilizer degradation based on Eq. (2) is shown in Figure 4.

The results of safe storage life of NEPE propellants at normal temperature calculated via Arrhenius and Berthelot approaches were compared in Table 1, which shows the safe storage life estimated by means of Arrhenius and Berthelot plots in the normal temperature range and high temperature.

Table 1. Comparison of safe storage life of NEPE propellants prediction via Arrhenius and Berthelot plots.

| T/K  | T/°C | storage life by Arrhenius plot/y | storage life by Berthelot plot/y |
|------|------|----------------------------------|---------------------------------|
| 303  | 30   | 137.9483277                      | 21.08                           |
| 298  | 25   | 263.9207194                      | 35.87                           |
| 293  | 20   | 516.2342493                      | 61.03                           |

As can be seen from Table 1, the numerical value of safe storage life at normal storage temperatures estimated by Berthelot approach is obviously lower than that calculated from Arrhenius plot; nevertheless, at high temperature, the values calculated by two approaches have proximity in number, which is accord with several former investigations \[8\]. According to the kinetic researches, the depletion of MNA stabilizer belongs to zero-order reaction. Since Arrhenius approach follow the exponential variation while Berthelot approach follow the power law variation, the reaction rate constants (K) in Berthelot and Arrhenius plot are not relevant to temperature. Besides, the Arrhenius approach is governed by the activation energy ($E_a$) while the Berthelot approach is depending on the values of 10% reaction rate factor. The storage life prediction strongly rests with the depletion of MNA stabilizer concentration. Considering the life prediction is more significant in relatively lower temperature condition, the lower storage life (predicted by Berthelot) is recommended as the storage life owing to safety aspect.
3.2. Aging Regularity of Binder Network Structure

Figure 5 show the change behaviour of MNA degradation, tensile strength and cross-linking density with aging time. The declination of tensile strength and cross-linking density are similar with the extension of storage time. Theoretically, tensile strength is given in Eq. (8) according to thermodynamics [9]:

\[ \sigma_m = 3\alpha k T \varepsilon \]  

(8)

Where \( \sigma_m \) represents the tensile strength, \( T \) represents temperature in Kelvin (K), \( \varepsilon \) represents the elongation, \( k \) represents the Boltzmann constant, and \( \alpha \) represents cross-linked density.

Equation 8 indicates the tensile strength is proportional inversely to cross-linked density, which can reflect the change of inner network system in NEPE propellant. The cross-linking network system will be reinforced on the condition of the number of hard molecular chains increase, which leads to the concentration of hard polyether molecular chain and tensile strength of NEPE propellant increase congruously.

Figure 5 also show that tensile strength and cross-linking density changed gradually with the consuming of MNA. After the stabilizer gradual decreased while the chemical aging accelerated, the network structure parameters decline logarithmically with the decreasing of the MNA content. The closer of MNA content to lowest value, the faster tensile strength and cross-linking density decrease. The network structure performance becomes worse, while the decomposition of nitrate esters speeds up and the contents of BTTN/NG have cubic function relationships with cross-linking density.

3.3. The Relationship of Chemical Stability and Network System

The aging behaviour of chemical stability can be depicted in Figure 6: In the initial stage of storage, decreasing of chemical stability is dominant. Although products of nitric esters (NG and BTTN) decomposed, stabilizers can neutralize NOx so that the tensile strength and cross-linked density of propellant decreased indistinctively. The function of the stabilizer is to neutralize free radical NOx released from the initial nitrate esters decomposition, then to prevent the auto-catalytic reaction [10]. Therefore, decomposition of molecular chain in binder network structure can be restrained in this stage. Simultaneously, the stabilizer (MNA) is consuming during the process. With MNA stabilizer consumed, the decomposition of NG and BTTN accelerated gradually.
In the second stage, the NO\textsubscript{x} concentration in propellants increases for lacking stabilizer. This progress will lead to the polymer chain decomposed in the thermal and oxidative way. The increasing of NO\textsubscript{x} accelerates the decomposition of polyether polyurethane binder structure, which leads to the rapid declining of tensile strength and cross-linking density\textsuperscript{[10]}. The aging of structural performance lagged the aging of chemical stability, the existence of MNA, effectively reduces the self-catalytic decomposition of nitrate esters, then slows down the breaking and decomposition of binder polymer chains, thereby inhibits the decreasing of cross-linking density. So MNA plays a positive role in maintaining good network structure during the process of propellant storage. The network structure parameters decrease logarithmically with the decline of the MNA content; the contents of nitrate esters have cubic function relationships with cross-linking density.

The existence of MNA effectively reduces the self-catalytic decomposition of NG and BTTN, and then restricts the degradation of binder polyether polyurethane system. Therefore, the initial stage (decreasing of chemical stability) is dominant in evaluation the storage life of the NEPE propellant sample. Thereby, the safe storage life prediction should be established in variety of MNA content.

4. Conclusions

(1) Based on change behaviour of cross-linking density, MNA degradation and tensile strength with aging time, the whole aging process of NEPE propellant can be separated into two processes: stabilizer gradual degradation at first stage (chemical aging stage) and degradation reaction of polymer at seconded stage.

(2) Degradation of polymer structure lagged decreasing of chemical stability. The function of the stabilizer is to neutralize free radical NO\textsubscript{x}, and then restrains the decomposition of binder network system.

(3) The stabilizer degradation occurred in the first stage, therefore predicting the safe storage life of NEPE propellant at normal temperature rests with the chemical aging stage during high temperature aging. Thus, the storage life of the NEPE propellant at 25°C is 35.87 years.

5. References

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