

Study on estimation of aging behavior of explosives

Hidetsugu NAKAMURA*, Miyako AKIYOSHI*, and Yasutake HARA*

The aging of explosives because of low temperature reactions during long-term storage causes a change in the practical performance or an incidental explosion. In this paper, typical aging mechanisms of explosives are discussed. Selected model samples of a low temperature reaction were a delay composition of red lead/ ferrosilicone/antimony trisulfide, nitrocellulose in acid mixtures and a composite solid propellant consisting of ammonium nitrate, aluminum and a GAP binder. As an experimental method, accelerated aging tests carried out at a temperature slightly higher than room temperature were adopted. The results obtained are as follows.

The delay composition of red lead/ ferrosilicone/ antimony trisulfide caused a decrease in the burning rate due to aging, which involved the low temperature reaction of red lead with antimony trisulfide. On the other hand, the burning rate of a composite solid propellant consisting of ammonium nitrate, aluminum and a GAP binder increased after aging due to the formation of a water soluble intermediate. Last, nitrocellulose in acid mixtures underwent autocatalytic degradation after a long induction period, which was ascribed to the formation of a reactive intermediate. From the mechanisms and the temperature dependence of aging, a general idea will be presented to predict the aging behavior of explosives at normal temperatures.

1. Introduction

Explosives are one of the most reactive chemicals. In practical use, these rapidly produce large amounts of energy, which is utilized by engineers to do various kinds of work. Because of this reactive nature of explosives, the aging of explosives during long-term storage causes a change in the practical performance or an incidental explosion. So, many data for the aging of explosives have been reported from the viewpoint of safety in manufacturing, storage and use, or operational reliability¹⁾⁻⁷⁾. We have also studied the aging problem with regard to propellants, explosives and pyrotechnic mixtures.

In this paper, three types of explosives were selected as model samples of aging of explosives in order to present a general idea of estimation of aging behavior of explosives. First, the aging behav-

ior of a composite solid propellant consisting of ammonium nitrate, aluminum and a glycidyl azide polymer (GAP) binder was studied as a model of propellants aging. The second type is the delay time prolongation of a red lead (Pb_3O_4)/ ferrosilicone (FeSi)/ antimony trisulfide (Sb_2S_3) delay composition after long-term storage as a model of delay composition aging. Last, nitrocellulose (NC) in acid mixtures, which were repeatedly reported to cause firing or explosion in manufacturing and storage, were selected as model samples of aging.

Because the aging study under ambient temperature normally requires a long period to obtain evidence of aging, accelerated aging tests are effective for easily estimating changes in explosives properties during long-term storage at ambient temperature. In this paper, accelerated aging experiments were carried out at a temperature slightly higher than room temperature, and the aging behavior of explosives and their mechanisms were elucidated to predict the practical aging behavior at ambient temperature.

Received on September 3, 1999

*Department of Applied Chemistry, Faculty of Engineering, Kyusyu Institute of Technology
Sensui, Tobata, Kitakyusyu, 804-8550 JAPAN
TEL 093-884-3319
FAX 093-884-3300

2. Experimental

2. 1 Materials

Delay powder is prepared by ball-mill mixing of red lead (reagent grade, mean particle diameter; $2.9 \mu\text{m}$, purity; 98.6 wt.%), ferrosilicone (industrial grade, content of silicone; 95 wt.%, $3.3 \mu\text{m}$) and antimony trisulfide (industrial grade, content of antimony; 62.7 wt.%, $4.0 \mu\text{m}$). Its formulation is $\text{Pb}_3\text{O}_4/\text{FeSi}/\text{Sb}_2\text{S}_3 = 57/6/37$ by weight.

NC is an industrial grade supplied by Asahi Chemical Industry Co., Ltd., and its nitrogen content is 11.6 %.

The propellant composition contains 59 % ammonium nitrate, 13 % aluminum and 28 % GAP binder (by weight), respectively.

2. 2 Analysis

Thermal analysis was performed using a RIGAKU DTA-TG simultaneous analyzer and high pressure DTA, in which the sample weight was 5 mg and the heating rate was $20 \text{ }^\circ\text{C}/\text{min}$ under an argon gas flow.

Exothermicity in the isothermal decomposition of NC was examined using a handmade DTA apparatus (abbreviated as microcalorimetry) which can detect the temperature rise of $0.01 \sim 1^\circ\text{C}$ under an argon gas atmosphere⁹⁾.

2. 3 Combustion experiment

Propellant strands for the linear burning rate measurement were formed in a $6 \text{ mm} \times 6 \text{ mm} \times 60 \text{ mm}$ shape and the side of each strand was inhibited by silicone resin. Time needed for the 40 mm burning of the strand piece was measured by means of a chimney-type strand burner under pressurized nitrogen 5 MPa.

The delay compositions were burnt in an aluminum cylindrical tube, and the time for 10 mm burning was recorded using a Digital Stragescope from the Iwasaki Tuusinki Co., LTD. with optical fiber signals. The mixtures were loaded nine times, and the bulk density was 65% of the theoretical maximum density.

2. 4 Accelerated aging tests

Accelerated aging tests were carried out at temperatures ranging from $60 \sim 98 \text{ }^\circ\text{C}$ for the $\text{Pb}_3\text{O}_4/\text{FeSi}/\text{Sb}_2\text{S}_3$ delay powder and $60 \sim 80 \text{ }^\circ\text{C}$ for the solid propellant. The isothermal decomposition of NC in

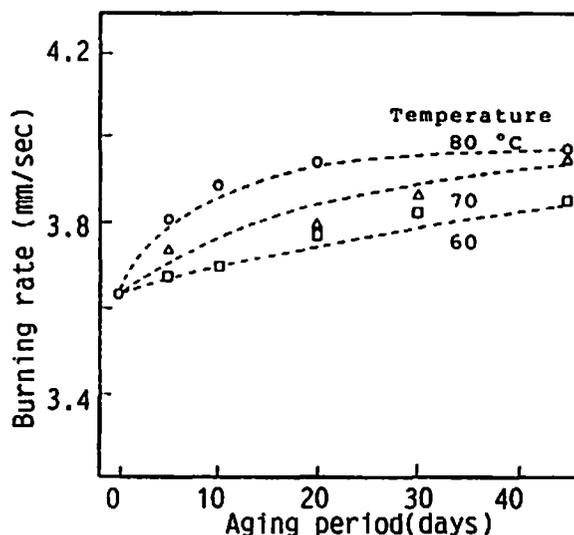


Fig. 1 Burning rate (R) of solid propellant after storage at $60 \sim 80 \text{ }^\circ\text{C}$

mixed acid ($\text{H}_2\text{SO}_4/\text{HNO}_3/\text{water} = 60/22/18$) was carried out at temperature ranging from $50 \sim 75 \text{ }^\circ\text{C}$.

3. Results

3. 1 The enhancement in burning rate of a composite solid propellant consisting of ammonium nitrate, aluminum and a GAP binder after aging

Figure 1 is the result of the accelerated aging tests for a composite solid propellant consisting of ammonium nitrate, aluminum and a GAP binder. This propellant has a linear burning rate of 3.63 mm/sec under 5 MPa. After aging at $60 \sim 80 \text{ }^\circ\text{C}$, the linear burning rate increased with storage time. Burning rate also increased with the aging temperature, but has a maximum value of about 3.95 mm/sec at $80 \text{ }^\circ\text{C}$. Let the fractional change in burning rate $x(t)$ for storage time t be shown in equation (1).

$$x(t) = (r(t) - 3.63) / (3.95 - 3.63) \quad (1)$$

The burning rate vs. aging period curves showed a monotonous decrease with aging period. Therefore, the first order rate equation (2) was applied to represent the relation between the fractional change in burning rate $x(t)$ and the storage time. The $\ln 1/(1-x)$ vs. time plots gave a straight line for every temperature, though some plots vary widely.

$$\ln 1/(1-x) = kt \quad (2)$$

An Arrhenius plot of rate constant k gave an activation energy of 87 kJ/mol . Moreover, the prolonged

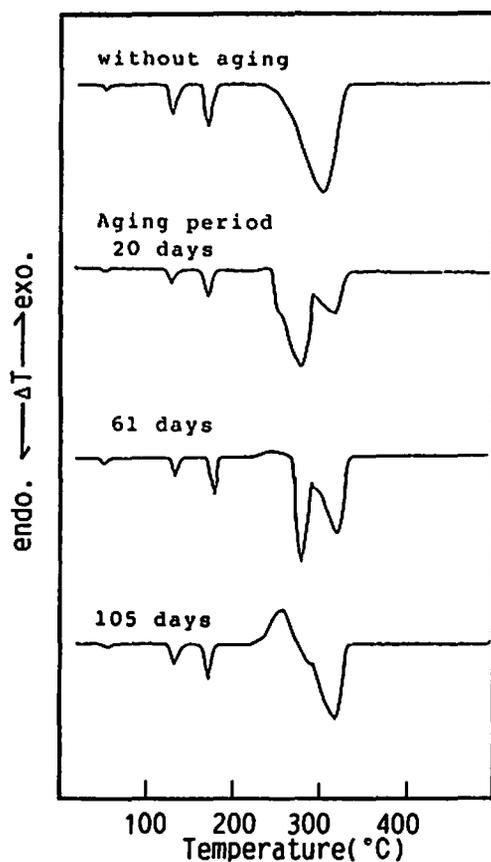


Fig. 2 DTA of water-soluble components in solid propellants heated at 80 °C

burning rate $x(t, T)$ can be estimated using this value of activation energy and first order rate equation.

In order to examine the reaction residue after aging, water-soluble components were extracted with distilled water by filtration and evaporated. Almost all of the water-soluble components was ammonium nitrate. Fig. 2 shows the thermal analysis of the evaporated water-soluble components from aged propellants at 80 °C. The water-soluble components without aging showed only an endothermic peak caused by evaporation or decomposition of ammonium nitrate, but the aged one showed a small exothermicity before the endothermic reaction. Based on elemental analysis, the amount of carbon increased and that of nitrogen decreased. However, a water-soluble intermediate formed during aging could not be specified.

3. 2 The delay time prolongation of a $Pb_3O_4/FeSi/Sb_2S_3$ delay composition after aging

The linear burning rate of a $Pb_3O_4/FeSi/Sb_2S_3$ de-

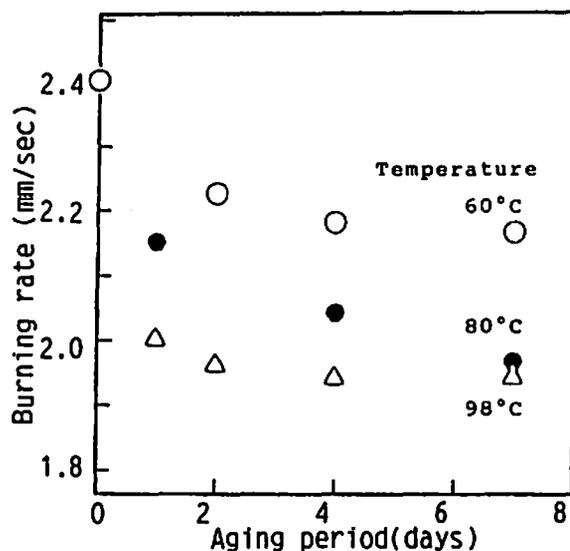


Fig. 3 Burning rate (R) of $Pb_3O_4/FeSi/Sb_2O_3$ delay composition after storage 60 ~ 98 °C

lay composition after aging decreased with increasing storage temperature and storage period (Fig. 3). However, its delay time prolongation was concentrated during the initial stage of storage. Especially, the burning rate changed to 2.00 mm/sec from initial 2.40 mm/sec after 1 day storage at 98 °C and underwent little change thereafter, showing a constant value.

The mixture of $Pb_3O_4/FeSi$ was preheated at 98 °C for 4 days, and the delay powder was then prepared by adding Sb_2S_3 without preheating. The burning rate of this powder was 2.36 mm/sec, the same value as that without aging in Fig. 3. On the other hand, if the delay powder was prepared by adding Sb_2S_3 to the mixture of Pb_3O_4/Sb_2S_3 which was preheated at 98 °C for 4 days, the burning rate decreased to 2.13 mm/sec. Moreover, sulfate formation was recognized in the above Pb_3O_4/Sb_2S_3 mixture preheated at 98 °C for 4 days. From the above results, the reason for the burning rate prolongation of Pb_3O_4/Sb_2S_3 mixture in storage is considered to be the formation of sulfate due to the reaction of the oxidant Pb_3O_4 with Sb_2S_3 . The facts of initial large burning rate prolongation and cessation of this prolongation thereafter is ascribed to the restraining effect of sulfate formed on further reaction after the advancement of the reaction to some extent.

Let the fractional change of the burning rate $x(t)$ for storage time t be as shown in equation (3).

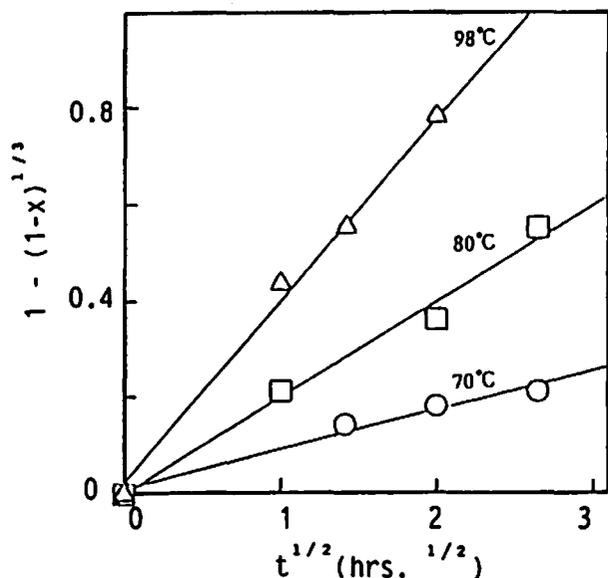


Fig. 4 Applicability of Jander's equation to the change in burning rate of an aged $\text{Pb}_3\text{O}_4/\text{FeSi}/\text{Sb}_2\text{O}_3$ delay composition (Fraction $x = R_t/R_{t=0}$)

$$x(t) = (r(t) - 1.91) / (2.40 - 1.91) \quad (3)$$

The relation between the fractional change in burning rate $x(t)$ and the storage time was represented well by Jander's rate equation (4) (Fig. 4)⁹. This rate equation was derived from a postulation of a surface reaction followed by a diffusion-limited reaction proceeding in spherical particles.

$$1 - (1-x)^{1/3} = kt^{1/2} \quad (4)$$

3. 3 The isothermal decomposition of nitrocellulose in mixed acids

NC caused exothermic decomposition in mixed acids at temperatures ranging from 50 ~ 75 °C. Fig. 5 shows the result of isothermal decomposition of NC (36 mg) in mixed acids (864 mg, $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{water} = 60/22/18$ by weight) obtained by microcalorimetry. NC decomposition in mixed acids had an induction period, and this induction decreased with increasing reaction temperature. Moreover, the induction period decreased with the increasing NC / mixed acid ratio. An increase in the content of nitric acid in the mixed acid then had a decreasing effect on the induction period. Plots of the logarithm of the induction period t vs. the inverse of reaction temperature showed good linearity according to the following Arrhenius-type equation (5).

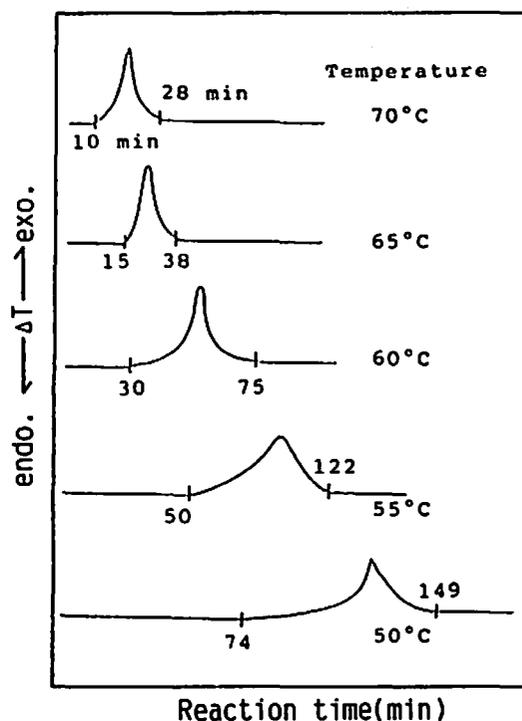


Fig. 5 Exothermicity obtained by microcalorimetry for the isothermal decomposition of NC in mixed acids

$$\ln t = E_a / RT + \ln A \quad (5)$$

The obtained E_a was 76 kJ/mol with regard to the results of Fig. 5.

Once the decomposition was initiated, the rate increased with the reaction time and reached a maximum in the middle of exothermicity. This exothermic reaction rate increased with the increasing NC / mixed acid ratio and the content of nitric acid in the mixed acid also had the same effect on the reaction rate. The fractional decomposition (x) at time t was determined by a graphical integration, in which the area of exothermic peak up to time t was divided by total area of exothermic peak. A curve of the fractional decomposition (x) vs. time (t) obtained from Fig. 5 had a s-shape (Fig. 6). Fig. 7 shows the applicability of the results of Fig. 5 to the autocatalytic rate equation (6).

$$\ln(x/(1-x)) = kt \quad (6)$$

Arrhenius plots of k obtained from Fig. 7 gave an activation energy of 39 kJ/mol.

Many experiments which were devoted to the NC decomposition reported that due to the catalytic action of the reaction product as oxides of nitrogen,

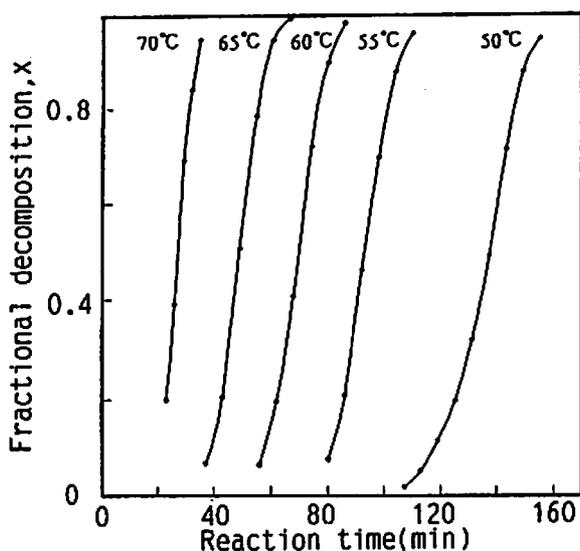


Fig. 6 Fractional decomposition x vs. time t curves for NC decomposition in mixed acids

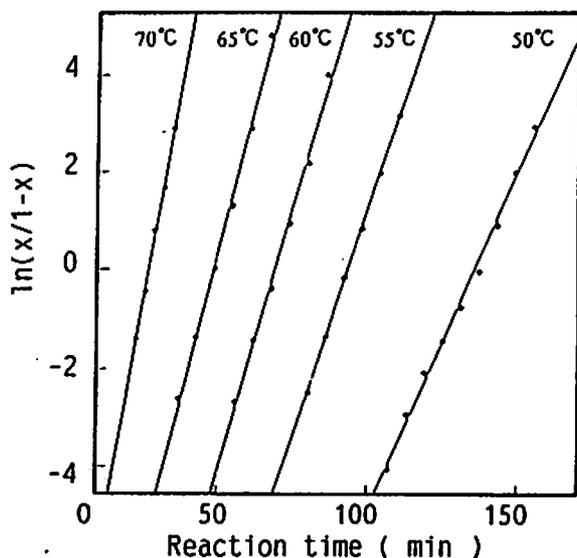


Fig. 7 Applicability of autocatalytic rate equation to the isothermal decomposition of NC in mixed acids

the decomposition in the atmosphere proceeded obeying the autocatalytic rate equation¹⁰⁾. Our experiments in mixed acid also showed the same rate equation, but with a long induction period and a smaller activation energy.

4. Discussion

Because the aging study at ambient temperature normally requires a long period, accelerated aging tests are effective for easily estimating the change in the explosive properties during long-term stor-

age at ambient temperature. Usually, from the accelerated aging experiments which were carried out at several temperatures slightly higher than room temperature, the temperature dependence of the change in chemical and physical quantities is determined to predict the practical aging behavior at ambient temperature.

As stated above, explosives because of aging cause a change in the practical performance such as the burning rate, sensitivity, explosives strength and mechanical strength et. al. In some cases, explosives become unstable during long-term storage, showing an change in chemical or physical properties and combustion characteristics. In order to estimate the aging behavior quantitatively, it is necessary to know that how these properties and characteristics change with time (rate equation) and temperature (kinetic parameter; activation energy and pre exponential factor).

Due to chemical reaction, many types of aging behavior exist in which the chemical and physical quantities of the explosives change with time. If the reaction of aging occurs everywhere in equal probability, it will proceed obeying the first order. On the other hand, a large aging rate will be recognized at the initial stage, when the kinetic course is dominated by a solid-solid surface reaction. If a reaction intermediate serves a very important role, there may be an autocatalytic course.

First order rate equation is a typical equation and is used to represent chemical phenomena as a first approximation. In aging of explosives, however, there were many types of aging. Propellant aging in this paper was described by a first order rate equation. Therefore, once the rate equation determined, the burning rate change caused by aging can be estimated by calculation using the first order rate equation and the temperature dependence. However, delay powder aging occurred according to Jander's equation. Therefore, the burning rate will be underestimated, if the estimation is carried out by a first order assumption and the obtained temperature dependence. On the other hand, NC degradation in mixed acids will be overestimated using a first order equation and the obtained activation energy. From these results, it is necessary to know how the properties and characteristics of explosives

change with time (rate equation) and temperature (kinetic parameter) in order to estimate the aging behavior quantitatively.

5. Conclusion

There are many types of aging behavior, in which the chemical and physical quantities change with time. Because the aging behavior is caused by some chemical reactions, it is affected by the temperature and its reaction mechanisms. If we predict the aging behavior, how the physical quantity in question changes with time is very important as well as its temperature dependence.

References

- 1) F. Volk, M. A. Bohn and G. Wunsh, Propellants. Explos. Pyrotech., 12, 81(1987)
- 2) J. M. Bellerby and M. H. Sammour, Propellants. Explos. Pyrotech., 16, 235, (1991), 16, 273(1991)
- 3) G. Om Reddy and A. Srinivasa, Propellants. Explos. Pyrotech., 17, 307(1992)
- 4) D. Mark Husband, Propellants. Explos. Pyrotech., 17, 196(1992)
- 5) M. A. Bohn and F. Volk, Propellants. Explos. Pyrotech., 17, 171(1992)
- 6) Ines B. H. Dubravkac B. Ivan S. and Zoran V. Prop. Explos. Pyrotech., 17, 10(1992)
- 7) A. Chen and D. S. Ellison, Proceedings of Twentieth International Pyrotechnics Seminar, Colorado, p203(1994)
- 8) The Chemical Society of Japan, Zikkenkagaku-kouza 5, Maruzen (1963) P.172
- 9) W. Jander, Z. Anorg. Allg. Chem., 163, 1(1927)
- 10) J. Kimura and H. Hayashi, Proceedings of Annual Meeting of Japan Explos. Soc., p85(1995)

火薬類の経時変化の予測に関する研究

中村英嗣*, 秋吉美也子*, 原 泰毅*

火薬類は長期間貯蔵すると、通常の温度でもその経時変化により、純度の低下、性能の劣化、感度の変化および物性の変化を引き起こす。本研究では、これらの火薬類のうちで特徴的な経時変化を示す例について検討した。選ばれた反応系は、鉛丹-ケイ素鉄-三硫化アンチモン系延時薬、酸溶液中のニトロセルロースおよび硝酸アンモニウム-アルミニウム-GAPバイндаから成る固体推進薬系である。実験方法として、実際の貯蔵温度より若干高い温度での加速老化試験法を採用した。

鉛丹-ケイ素鉄-三硫化アンチモン系延時薬は、成分中の鉛丹による三硫化アンチモンの酸化のために、低温での経時変化により延時秒時の伸びを引き起こした。これに対して、硝酸アンモニウム-アルミニウム-GAPバイндаから成る固体推進薬は長期間の貯蔵では燃焼速度は増加した。これは水溶性の活性な中間体の生成による。酸溶液中でのニトロセルロースは温度に依存する誘導期を経て発熱分解した。一旦、分解が開始したら分解は自触的に進行した。

以上の結果から、火薬類の長期間貯蔵による性能の変化の推定には、変化の温度依存性(活性化エネルギー)と同様に、変化の機構(速度式など)の知見を得ることの重要性が指摘された。

(*九州工業大学・工学部・応用化学教室 〒804-8550 北九州市戸畑区仙水町1-1)