Research paper

The mixture of the phase stabilized ammonium nitrate containing potassium nitrate and BTA·NH₃ as a new airbag gas generating agent

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Abstract

A new gas generating agent for airbags was investigated. Ammonium nitrate does not give off harmful gases or solid burning residues, but goes through contraction and expansion during a series of phase transitions which cause structural damage to the grains. In this study, phase stabilized ammonium nitrate containing potassium nitrate was prepared by a nonhazardous aqueous method adding 10 wt% potassium nitrate. Bis (lH-tertrazolyl) amine ammonium salt was selected as a fuel due to its high heat of formation. The burning rate, 4L tank test, amount of generated gases, efficiency for gas evolution, heat of explosion, weight percentage of solid products, melting point, and sensitivities were obtained to evaluate the characteristics that indicate a desirable gas generating agent.

Keywords : burning rate, BTA·NH₃, gas generating agent, PSAN

1. Introduction

Ammonium nitrate (AN) has attracted attention over the years as an oxidizer for environmentally friendly, clean gas generating agents, because it does not give off harmful gases or solid burning residues, advantages that could fulfill the strict requirements imposed on gas generating agents for vehicle airbag systems. However, AN has disadvantages that it is hygroscopic, which becomes a problem during manufacturing and storage, and also that it goes through contraction and expansion during phase transitions, which causes structural damage to the grains. AN shows several phase transitions such as ANv (tetragonal) \leq AN_{IV} (rhombic tripyramidal) \Leftrightarrow AN_{III} $(orthorhombic) \cong AN_{II}$ (tetragonal) $\cong AN_{I}$ (cubic) at 256, 305, 357, and 398 K, respectively. And it melts at 443 K, decomposes around 503 K at 760 mmHg, and deflagrates above 598 K¹). There have been numerous studies related to phase transitions and phase stabilization has been achieved by the addition of potassium nitrate $(KN)^{1)-4}$. In this study, phase stabilized ammonium nitrate (PSAN) was prepared by a nonhazardous aqueous method in which KN was added to AN. The AN transformation rate near room temperature is very dependent on KN concentration; the transformation rate becomes nearly indistinguishable from the others when the KN concentration is greater than $9 \text{ wt}\%^{3}$. Based on this report the 10% concentration of KN was adopted.

The AN propellants burn very slowly compared to ammonium perchlorate (AP) based systems. The low burning rate of AN propellants can be attributed to the slower reaction kinetics of the nitrogen oxides from AN and the lower enthalpy of combustion of AN with fuels. As a result, the gas phase flame in AN propellants is colder and farther from the condensed surface resulting in reduced heat feed back and lower burning rate¹⁾.

AN-based gas generating agents prepared by mixing with organic fuels have poor combustion reactivity compared to some metal perchlorates⁵⁾⁻⁷⁾ or nitrates mixtures⁸⁾⁻¹⁰⁾. It has been reported that energetic tetrazoles, such as aminoguanidinium 5,5'-azo bis-1H-tetrazolate (AGAT)¹¹⁾⁻¹³⁾ and 1H-tetrazole (1HT)¹⁴⁾ can be used as a fuel to mix with AN. In this study, Bis (1H-tertrazolyl) amine ammonium salt was selected as a fuel due to its high heat of formation (603.9 kJ-mol⁻¹).

The desirable characteristics of a gas generating agent are high burning rate, large calorific value, large amount of gaseous products, thermal stability, high ignitability, low emission of harmful gases, low emission of airborne particulates, low cost, and safety¹⁵.

Gas generating agents generally were required of burning rate of at least 10 mm·s⁻¹ or more at 7MPa, because agents with a burning rate less than this do not ignite reliably and often result in "no-fires" in the inflator¹⁶. Burning rates of energetic materials generally follow Vieille's law, given by $r = a \cdot P^n$, where *a* is a constant that depends on the chemical composition and initial propellant temperature, and n is the pressure exponent of the burning rate¹⁷). The pressure exponent should be as close to zero as possible. As n increases, a very small change in pressure will result in a large change in the burn rate, which could result in ballistic variability or overpressurization. Therefore, for automotive airbag applications, a pressure exponent n of approximately 0.30 or less is desirable over the operating pressure of the inflator¹⁸⁾.

Gas generation ability, which is generally measured by a 60 L tank test, was investigated using a 4L tank test in this study¹⁹.

The calorific value per gram of gas generating agent should not be more than 4000 J²⁰. The calorific value per mole of gas generated is set to be in the range of 95 to 105 kJ²⁰. The adiabatic flame temperature (T_i) of the gas agent should be 2273 K or less²¹.

About the amount of gaseous products, it is desirable that the gaseous products are equal to or greater than 90% of the total product mass, and that solid products are equal to or less than 10% of the total product mass¹⁶). It is desirable that the number of moles of gas generated is adjusted to not less than 2.70 mol per 100 g of gas generated²⁰.

Concerning the thermal stability, gas generating agent must be thermally stable when aged for 400 h or more at 380 K. The agents must also retain structural integrity when cycled between 233 and 380 K. Any PSAN-nonazide fuel mixture with a melting point of less than 388 K will decompose when aged at 380 K. Therefore it is desirable that the melting point of the gas generating agent is higher than 388 K¹⁶.

It is preferable that the gas generating agents produce no harmful gasses, because airbag release the combustion gases inside a vehicle after its deployment to maintain the driver's view¹⁵⁾. Airborne particulates may pass through a filter in the inflator and the fiber of the airbag. Therefore, it is necessary to restrain the passage of airborne particulate matter because they may be harmful to the respiratory organs of the human body¹⁵⁾.

The airbag system should be inexpensive to keep the cost of car down. Thus, an inexpensive chemical such as AN is appropriate¹⁵.

It is necessary to avoid using materials that may cause detonation or spontaneous combustion during the manufacturing process. In this study, drop hammer and friction tests were conducted to evaluate the safety of the gas generating agents¹⁵.



Figure 1 Structural formula of BTA·NH₃.

Table 1Some properties of BTA·NH₃/PSANKN mixture.

Mixture	Mixing ratio [parts]	Average density [g·cm ⁻³]	Theoretical maximum density [g·cm ⁻³]	Porosity [%]
BTA·NH ₃ / PSANKN	25 / 75	1.627	1.810	10.11

2. Experimental 2.1 Materials

Bis (1H-tertrazolyl) amine ammonium salt (BTA·NH₃: Masuda Chemical Industries Co. Ltd.) was used as a fuel. Figure 1 shows structural formula of BTA·NH₃. BTA·NH₃ was selected as a fuel because its high heat of formation.

A density of 1.9863 g·cm³ was measured by a specific gravity flask (055540-50, Shibata Scientific Technology Ltd.). The particle size was measeared by a particle-size distribution analyser (CAPA-300, Horiba Ltd.) using n-butanol as a solvent by gravitational and the median size was found to be 22.88 μ m.

The heats of combustion at constant pressure were 13247 and 13285 $J \cdot g^{-1}$ measured by Sumika Chemical Analysis Service, Ltd. The heats of combustion at constant volume were -2257 and -2248 kJ·mol⁻¹, and the heat of formation was obtained as 603.9 kJ·mol⁻¹.

To obtain phase stabilized ammonium nitrate containing potassium nitrate (PSANKN), 180 g of AN and 20 g of KN were dissolved in a small amount of water; the solution was then heated to let the chemicals dissolve. The solution was placed in a 363 K thermostatic oven until it was completely dry. PSANKN was milled with a vibration ball mill and sieved through JIS Z8801 sieves and dried in a vacuum dryer. The particle size of PSANKN was in the range of 75–150 μ m. The ratio of BTA·NH₃ to PSANKN was 25:75. Fuel particles and oxidizer particles were mixed at the designated mixing ratio for 30 min at 80 rpm using a rotary mixer. The composition used in this study is given in Table 1.

2.2 Thermal analysis

Thermogravimetry (TG) and differential thermal analysis (DTA) were conducted at the heating rate of 5K·min⁻¹ in a He atmosphere (flow rate $20 \text{ mL} \cdot \text{min}^{-1}$) using an aluminum cell (DTG-50H, Shimadzu Corp.). Melting point was determined using a capillary method melting point apparatus (MPA100, Stanford Research Systems, Inc.) at a heating rate of 5 K·min⁻¹.

2.3 Burning rate

A 1.5-g quantity of the stoichiometric BTA·NH₃/ PSANKN mixture was compressed at approximately 300 MPa for 3 min to form cylindrical pellets (diameter 10 mm, length 11mm). The side of the cylindrical pellet was coated with epoxy resin to ensure cigarette burning. Combustion tests were performed using a pressure- and temperature-controlled chimney-type strand burner with optical windows under a N₂ atmosphere in the range of 1-10 MPa. The initial temperatures (T_i) was 298 K. Ignition of the pellet was carried out with an electrically heated nichrome wire (diameter 0.6 mm) by means of a regulated DC power supply. The pressure in the chamber was measured with a pressure sensor. After amplification through a signal amplifier, the data were recorded using a digital data recorder. The burning rates (r) were deduced from the duration of the recorded pressure increase. The pressure began to increase as soon as the sample started to burn and stopped increasing when combustion ceased. The average internal pressure (P) was calculated by averaging the pressures at the start and the end of burning.

2.4 4 L tank test

A4g dried mixture was uniaxially pressed at approximately 200 MPa for 3 min to form a cylindrical pellet (diameter 14.7 mm, length 14 mm). The side of the cylindrical pellet was coated with epoxy resin to ensure cigarette burning. A 4L chimney-type strand burner was used as the burning test apparatus. The 4L tank tests were conducted at an initial temperature of 296 K and an initial pressure of 2 MPa. Ignition of the top surface of the sample was achieved using an electrically heated (ca. 15 V) nichrome wire (diameter 0.6 mm). The internal pressure of the vessel was monitored using a pressure transducer, and after signal amplification through a signal conditioner, the signal was recorded on a digital data recorder. From the acquired pressure-time data, as shown schematically in Figure 2, the net pressure increase (ΔP) , which is the difference between the initial pressure and maximum pressure, and Δt , which is the time duration from the onset of pressure increase to the time when the pressure reaches the maximum pressure, were calculated to determine the rate of pressure increase $(\Delta P / \Delta t)$.

2.5 Sensitivity

In order to investigate the sensitivity of the mixture, a drop hammer test²²⁾ and a friction test²³⁾ were conducted according to the Industrial Explosives Society Standard.

2.6 Chemical equilibrium calculation

Chemical equilibrium calculation was conducted using ICT-Thermodynamic code (Fraunhofer-Institut für Chemische Technologie)²⁴⁾ to obtain the amount of combustion products, heat of explosion, and adiabatic flame temperature (T_i).



Time [s]

Figure 2 Schematic diagram of 4L tank test.

3. Results and discussion

3.1 Thermal analysis

The prepared PASNKN and BTA·NH₃/PSANKN mixture were tested and compared with pure AN to determine if the undesirable phase change near room temperature had been eliminated.

Figure 3 shows TG and DTA curves of AN. AN showed phase transitions at 326 and 400 K. And it melted at 443 K and decomposed at 533 K.

Figure 4 shows TG and DTA curves of PSANKN. Endothermic peaks of PSANKN at 395 and 403 K indicated phase transitions and that at 434 K corresponded to the melting of PSANKN. It decomposed at 535 K.

Figure 5 shows TG and DTA curves of BTA·NH₃. An endothermic peak due to the melting of BTA·NH₃ was about 525 K and an exothermic peak due to the decomposition of BTA·NH₃ was about 550 K. The results



Figure 3 TG and DTA curves of AN.



Figure 6 TG and DTA curves of BTA·NH₃/PSANKN mixture.

of melting point apparatus showed that BTA·NH₃ decomposed with evolution of gas at 563 K which is relatively high among tetrazoles²⁵.

Figure 6 shows TG and DTA curves of BTA·NH₃/ PSANKN mixture. Endothermic peaks of the mixture at 396 and 402 K indicated phase transitions. An endothermic peak at 432 K corresponded to the melting of PSANKN. An endothermic peak at 499 K corresponded to the melting of BTA·NH₃/PSANKN mixture. An exothermic peak at 514 K corresponded to the decomposition of BTA· NH₃/PSANKN mixture.

The results of melting point apparatus showed that BTA·NH₃/PSANKN was partially melted in the range of 433–434 K and decomposed with evolution of gas in the range of 483–513 K. Thus BTA·NH₃/PSANKN is thermally stable¹⁶. The relatively high melting point of BTA·NH₃ may contribute to the stability of BTA·NH₃/PSANKN.

3.2 Burning rate

The results of the burning rate tests for BTA·NH₃/ PSANKN mixture are presented in Figure 7. Burning rates follow Vieille's law, given by $r = a \cdot P^n$. The values of a and n for BTA·NH₃/PSANKN were determined to be 2.23 mm·s⁻¹·MPa⁻¹ and 0.873, respectively, and the burning rate at 7MPa was 12.2 mm·s⁻¹, which was higher than the desirable 10 mm·s⁻¹¹⁶. The pressure exponent nwas larger than the desirable value of 0.3¹⁸. The burning rates of guanidine nitrate (GN) / strontium nitrate (SrN) / copper nitrate basic (BCN) mixture, which is a gas generating agent used in practical applications²⁰ are also shown in Figure 7. The burning rates of BTA·NH₃/ PSANKN mixture are approximately 1.4 times higher than those of the GN/SrN/BCN mixture.



Figure 7 Burning rates for BTA·NH₃/PSANKN and GN / SrN / BCN mixtures. GN: Guanidine nitrate, SrN: Strontium nitrate, BCN: Copper nitrate basic



Figure 8 Pressure-time histories of mixtures from 4L tank test.

GN: Guanidine nitrate, SrN: Strontium nitrate, BCN: Copper nitrate basic

3.3 4 L tank test

The results for the 4L tank test are shown in Figure 8 and Table 2. Each sample was ignited and burnt completely. The rate of gas generation $(\Delta P/\Delta t)$ for BTA·NH₃/PSANKN was 0.270 MPa·s⁻¹, which was approximately 1.7 times that for the GN/SrN/BCN mixture (0.164 MPa·s⁻¹).

The large heat of formation of $BTA\cdot NH_3$ may contribute to the large values for the burning rate, the rate of gas generation, and the adiabatic flame temperature. The relatively high percentage content of N_2 in $BTA\cdot NH_3(82.3)$ %) may also contribute to the large value of rate of gas generation.

3.4 Chemical equilibrium calculation

Chemical equilibrium calculations²⁴⁾ were conducted to obtain the mol % of each generated product, the total amount of generated gases, heat of explosion, and $T_{\rm f}$. H₂O was considered as a gas in the calculation because it is usually fed to the airbag in the form of a gas²⁰.

The results are presented in Table 3.

It was found that generated gaseous products were harmless CO₂, H₂O, and N₂.The molar percentage of H₂O was slightly higher than the acceptable value of 50^{26} , which could be improved by replacing some parts of AN

with other oxidizers that produce less water. AN is the main source of H₂O. The calorific value per gram of gas generating agent was 3990.7 $J \cdot g^{-1}$ which was lower than the desirable 4000 $J \cdot g^{-1} \cdot 20$. T_f was 2950 K which was higher than the desirable 2273 K²¹.

Based on the results in Table 3, the following results were obtained. The efficiency of gas evolution was 94.9 % which was higher than the desirable 90 %¹⁶. The wt % of solid products was 5.11 % which was less than the desirable 10 %¹⁶. The number of moles of generated gas per 100 g of gas generating agent was 4.00 mol·(100 g)⁻¹ which was higher than the desirable 2.70 mol·(100 g)^{-1 20}. The calorific value per mole of generated gas was 99.8 J·mol⁻¹ which was in the range of desirable 95 –105 J·mol^{-1 20}. It was found that the calculated results of BTA·NH₃/PSANKN were acceptable values for a practical gas generating agent.

The experimental results of BTA·NH₃/PSANKN mixture and some of the desirable values for gas generating agents are summarized in Table 3.

3.5 Sensitivity

According to the Industrial Explosives Society Standard^{22),23}, it was found that BTA·NH₃/PSANKN was classified as class 6 from the drop hammer test and as class7 from friction test; this mixture could be treated as an insensitive mixture. The high value of heat of formation gives large calorific value which may contribute to the relatively high sensitivity for drop hammer test.

4. Conclusions

The mixture of the phase stabilized ammonium nitrate containing potassium nitrate and BTA·NH₃ was tested and the following conclusions were obtained.

The burning rate at 7MPa was $12.2 \text{ mm} \cdot \text{s}^{-1}$, which was higher than the desirable $10 \text{ mm} \cdot \text{s}^{-1}$.

The rate of gas generation was approximately 1.7 times that for the guanidine nitrate / strontium nitrate / copper nitrate basic mixture, which is a gas generating agent used in practical applications.

The mixture was determined to be insensitive from drop hammer and friction tests.

The values of efficiency for gas evolution, total amount of generated gases, heat of explosion, weight percentage of solid products, and melting point were better than the desirable values for a vehicle gas generating agent.

References

1) C. Oommen and S. R. Jain, J. Hazard. Mater., A67, 253-281

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Mixture	Starting pressure [MPa]	Final pressure [MPa]	⊿P [MPa]	Elapsed time (Δt) [s]	Rate of gas generation $(\Delta P/\Delta t)$ [MPa·s ⁻¹]
BTA·NH ₃ /PSANKN	2.069	3.035	0.966	3.58	0.270
GN / SrN / BCN	2.046	2.717	0.671	4.10	0.164

GN: Guanidine nitrate, SrN: Strontium nitrate, BCN: Copper nitrate basic

		BTA·NH ₃ /PSANKN	Desirable values
Adiabatic flame temperature [K]		2950	227321)
	CO ₂ [mol%]	6.375	_
	H ₂ O (l) [mol%]	52.682	$< 50^{25}$
Amount of generated products	N ₂ [mol %]	40.007	_
	KOH (s) [mol %]	0.027	_
	KOII (s) [mol $\%$] 0.027 K ₂ CO ₃ (s) [mol $\%$] 0.905 [mol·kg ⁻¹] 40.37 [%] 94.9 [wt%] 5.11	0.905	_
Total amount of generated products	$[mol·kg^{-1}]$	40.37	-
Efficiency of gas evolution	[%]	94.9	> 90 ¹⁶⁾
Solid products	[wt%]	5.11	< 10 ¹⁶⁾
	H ₂ O(l) [mol·kg ⁻¹]	19.128	
Total amount of generated gases	H ₂ O(g) [mol·kg ⁻¹]	40.642	
	[mol·(100 g) ⁻¹]	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$> 2.70^{20}$
Heat of applacian	H ₂ O (l) [J·g ⁻¹]	5028.0	
	H ₂ O (g) $[J \cdot g^{-1}]$	3990.7	$< 4000^{20}$
Calorific value per mole of generated gas	[J·mol ^{−1}]	99.8	95-10520)
Melting point	[K]	433-434	> 38816)
Burning rate at 7MPa	$[mm \cdot s^{-1}]$	12.2	> 10 ¹⁶⁾
Pressure exponent <i>n</i>	[-]	0.879	< 0.318)

Table 3 Experimental results of BTA·NH₃/PSANKN and some of the desirable values for gas generating agents.

(l): liquid, (s): solid, <: less than, >: greater than

(1999).

- 2) J. Kim, J. Chem. Eng. of Japan, 30, 336–338 (1997).
- 3) H. H. Cady, Propellants, Explos., Pyrotech., 6, 49–54 (1981).
- H. B. Wu and C. K. Chan, Atmos. Environ., 42, 313–322 (2008).
- 5) K. Hasue, T. Akanuma, H. Hodai, and S. Date, Kayaku Gakkaishi (Sci.Tech. Energetic Materials), 60, 31–37 (1999).
- Y. Miyata, H. Kanou, S. Date, and K. Hasue, Sci.Tech. Energetic Materials, 66, 233–239 (2005).
- 7) Y. Miyata, S. Date and K. Hasue, *ibid*, 68, 125-130 (2007).
- K. Hasue, P. Boonyarat, Y. Miyata, and J. Takagi, Kayaku Gakkaishi (Sci.Tech. Energetic Materials), 62, 168–174 (2001).
- Y. Miyata, S. Date, and K. Hasue, Propellants, Explos., Pyrotech., 29, 247–252 (2004).
- K. Iwakuma, Y. Miyata, S. Date, M. Kohga, and K. Hasue, Sci. Tech. Energetic Materials, 68, 95–101 (2007).
- Y. Miyata, M. Abe, S. Date, M. Kohga, and K. Hasue, *ibid.*, 69, 117–122 (2008).
- 12) Y. Miyata and K. Hasue, J. Energ. Mater., 29, 26-45 (2011).
- Y. Miyata and K. Hasue, J. Energ. Mater., 29, 344–359 (2011).
- 14) K. Yoshitake, K. Ihoh, S. Date, and K. Hasue, Proc. of the Thirty-sixth International Pyrotechnics Seminar, 287–301, Proc. International Pyrotechnics Society, Rotterdam (2009).
- T. Yoshida and T. Hasegawa, "Application of Reactive Chemicals-From Fireworks to Airbags and Rocket-", 5–18,

Tokyo Progress System LTD, Tokyo (1996).

- 16) P. S. Khandhadia and S. P. Burns, U. S. Patent, 6306232B1 (2001).
- N. Kubota, "Propellants and Explosives-Thermochemical Aspects of Combustion", 53–54, Weinheim: WILEY-VC (2002).
- 18) S. P. Burns and P. S. Khandhadia, U. S. Patent, 6074502 (2000).
- S. Date, P. Boonyarat, T. Kazumi, and K. Hasue, Kayaku Gakkaishi (Sci. Tech. Energetic Materials) 63, 209–215 (2002).
- 20) E. Sato, D. Kubo, and K. Ikeda, U. S. Patent, 6958100B2 (2005).
- N. Katsuda, M. Yabuta, and J. Wu, U. S. Patent, 6854395B2 (2005).
- I. Fukuyama (ed.), Industrial Explosives Society Standard (2nd edition), Japan Explosives Society, 26–30 (1986).
- I. Fukuyama (ed.), Industrial Explosives Society Standard (2nd edition), Japan Explosives Society, 33–37 (1986).
- 24) F. Volk and H. Bathlet, "User's Manual for the ICT– Thermodynamic Code", Fraunhofer-Institute für Chemische Technologie, Pfinztal (1988).
- 25) M. Abe, T. Ogura, Y. Miyata, K. Okamoto, S. Date, M. Kohga, and K. Hasue, Sci. Tech. Energetic Materials, 69, 183 –190 (2008).
- 26) T. Harada, Explosion, 13, 128-133 (2003).