

# Mixtures of phase-stabilized ammonium nitrate containing 10 wt% potassium nitrate and tetrazoles as gas-generating agents

Kazuo Hasue<sup>\*†</sup> and Makoto Matsukawa<sup>\*\*</sup>

<sup>\*</sup>Department of Applied Chemistry, School of Applied Sciences, National Defense Academy (ret.)  
1-10-20, Hashirimizu, Yokosuka-shi, Kanagawa 239-8686, JAPAN

Phone : +81-46-841-3810

<sup>†</sup>Corresponding author : khasue@hotmail.com

<sup>\*\*</sup>The Kure Ammunition Storehouse and Maintenance Depot, Japan Maritime Self-Defense Force  
Kirikushi, Etajima-cho, Etajima-shi, Hiroshima 737-2111, JAPAN

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## Abstract

In this study, phase-stabilized ammonium nitrate and tetrazoles mixtures were investigated as gas-generating agents for air bags. Ammonium nitrate does not give off harmful gases or solid burning residues but goes through contraction and expansion during a series of phase transitions that cause structural damage to the grains. In this study, phase-stabilized ammonium nitrate containing 10 wt% of potassium nitrate was prepared by a nonhazardous aqueous method. Phase-stabilized ammonium nitrate based propellants have been known to show low burning rates. Tetrazoles were selected as they have a large heat of formation and can be used as fuel components for phase-stabilized ammonium nitrate-based gas-generating agents. In this study, the burning rate, gas generation ability by means of 4 L tank test, the mol% and wt% of each generated product, efficiency of gas evolution, wt% of solid products, number of moles of generated gas per 100 g of gas-generating agent, wt% of solid products, calorific value of per mole of gas generated, sensitivities, and thermal stability were studied on the phase-stabilized ammonium nitrate and tetrazoles mixtures to evaluate their application as gas-generating agents.

**Keywords** : phase-stabilized ammonium nitrate, tetrazole, gas-generating agent, burning rate, 4L tank test

## 1. Introduction

Air bags are vehicle safety devices that are designed to inflate rapidly during an automobile collision. Their purpose is to cushion the occupants during a crash and provide protection to their bodies. At the onset of a crash, signals from the impact sensors are fed into the air bag control unit that trigger the ignition of a gas-generating agent to rapidly inflate a fabric bag in 25-50 ms. Once an air bag deploys, deflation begins within 80-100 ms as the gas escapes through vents in the fabric. Deployment is frequently accompanied by the release of dust-like particles, and gases in the vehicle's interior.

Some of the desirable characteristics of gas-generating agents for air bags are as follows<sup>1)</sup>. The detailed discussion of each item is given in Reference 2.

(1) Gas-generating agents generally require a burning rate of at least  $10 \text{ mm}\cdot\text{s}^{-1}$  or more at  $7 \text{ MPa}^3$ . The pressure exponent of the burning rate of approximately 0.30 or less is desirable over the operating pressure of the inflator<sup>4)</sup>.

(2) Gas generation ability, which is generally measured by a 60 L tank test<sup>5)</sup>, was investigated using a 4 L tank test in this study<sup>6)</sup>.

(3) The calorific value per gram of gas-generating agent should not be more than  $4000 \text{ J}^7$ . The calorific value per mole of gas generated is set to be in the range of 95 to  $105 \text{ kJ}^7$ . The adiabatic flame temperature ( $T_f$ ) of the gas agent should be  $2273 \text{ K}$  or less<sup>8)</sup>.

(4) Concerning 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 mass<sup>3</sup>. The number of moles of gas generated is adjusted to not less than 2.70 mol per 100 g of gas-generating agent<sup>7</sup>.

(5) Concerning the thermal stability, the desirable melting point of PSAN-nonazide fuel mixture is higher than 388 K<sup>3</sup>.

(6) It is preferable that the gas-generating agents produce no harmful gasses. The molar percentage of H<sub>2</sub>O is lower than 50 mol%<sup>9</sup>.

(7) The air bag system should be inexpensive as to keep the cost of the car down. Thus, an inexpensive chemical such as AN is appropriate<sup>1</sup>.

(8) It is necessary to avoid material that may cause detonation or spontaneous combustion during the manufacturing process.

As a potential oxidizer for gas-generating agents, Ammonium nitrate (AN) have favorable features which does not give off harmful gases or solid burning residues. These advantages generally fulfill the strict requirements imposed on gas-generating agents for vehicle air bag systems. However, AN has the disadvantages of being hygroscopic (which becomes a problem during manufacture and storage) and undergoing contraction and expansion during a series of phase transitions<sup>10</sup>. The phase transformation around room temperature results in crack formation in the propellant grain. The phase-stabilization of AN has been achieved using additives such as potassium nitrate (KN)<sup>10-13</sup>, CuO<sup>10,14,15</sup>, and KF<sup>10,16</sup>.

In previous studies, AN-based gas-generating agents prepared by mixing with organic fuels had poor combustion reactivity compared to some metal perchlorates<sup>17-19</sup> or nitrates mixtures<sup>20-22</sup>. To achieve the desirable characteristics, the combination AN and tetrazoles are expected to be suitable as safe, easy-to-handle gas-generating agents<sup>23</sup>. Tetrazoles with a high heat of formation<sup>24</sup> can be used as a fuel component to improve the burnability of AN-based gas-generating agents. It was reported that aminoguanidinium 5,5'-azobis-1H-tetrazolate (AGAT)<sup>25-27</sup> and 1H-tetrazole (1HT)<sup>28,29</sup> can be used as a fuel to mix with AN. Bis (1H-tetrazoly) amine ammonium salt was used as a fuel of phase-stabilized ammonium nitrate<sup>30</sup>. The gas-generating ability of tetrazoles such as AGAT, 5-amino-1H-tetrazole (5-ATZ), 5,5'-Bis-1H-tetrazole diammonium salt (BHT·2NH<sub>3</sub>), 1HT, and 5-methyl-1H-tetrazole (M5T) with phase-stabilized ammonium nitrate containing 5 wt% KN (PSAN<sub>KN5</sub>) mixtures were investigated<sup>31</sup>.

It was found that the tetrazole/PSAN<sub>KN5</sub> mixtures needed some improvements to satisfy the desired values mentioned above<sup>31</sup>. In this study phase-stabilized ammonium nitrate containing 10 wt% KN (PSAN) was examined as an oxidizer to improve the performance of the tetrazole/PSAN<sub>KN5</sub> mixtures.

The phase-stabilized ammonium nitrate was prepared by a nonhazardous aqueous method in which KN was added to AN. Since the composition of the solid crystallized from AN-KN solution at approximately 363 K was reported to be almost the same as that of the solution<sup>11</sup>; therefore, AN-KN solutions were evaporated to dryness at 363 K and then ground to obtain PSAN.

In this study commercially available energetic tetrazoles such as AGAT, 5-ATZ BHT·2NH<sub>3</sub>, 1HT, M5T, and 1H-tetrazole-5-acetic acid (TAA)<sup>24</sup> were examined as a fuel to mix with PSAN.

## 2. Experimental

### 2.1 Materials

To obtain PSAN, 190 g of AN and 10 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 thermostatic oven at 363 K until completely dried. PSAN and each tetrazole were milled with a vibration ball mill and sieved and then dried in a vacuum dryer. The particle sizes of PSAN and each tetrazole were in the range of 75-150 μm. Each tetrazole was mixed with PSAN at the stoichiometric ratios shown in Table 1. For the burning rate test and 4 L tank test, guanidine nitrate (GN), strontium nitrate (SrN), and copper nitrate basic (BCN) were mixed in a ratio of 56.05 : 19.45 : 24.50 (w/w). The mixture is one of the gas-generating agent candidates<sup>7</sup>.

### 2.2 Burning rate test

One and half grams of the stoichiometric tetrazole/PSAN mixtures were uniaxially pressed at approximately 300 MPa for 3 min to form cylindrical pellets (diameter 10 mm, thickness 11 mm). 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 N<sub>2</sub> atmosphere in the range of 3-10 MPa. The initial temperature was set to 296 K. Ignition of the pellet was carried out with an electrically heated nichrome wire (diameter 0.6 mm) by means of a regulated

**Table 1** Values of  $a$  and  $n$  for each mixture.

Mixture	Mixing ratio [wt%]	$a$ [mm·s <sup>-1</sup> ·MPa <sup>-1</sup> ]	$n$ [-]	Correlation coefficient
AGAT/PSAN	22.3/77.7	2.52	0.919	0.972
5-ATZ/PSAN	25.0/75.0	2.94	0.774	0.958
BHT·2NH <sub>3</sub> /PSAN	22.79/77.21	1.80	0.990	0.899
1HT/PSAN	24.3/75.7	2.08	0.932	0.830
M5T/PSAN	16.1/83.9	2.84	0.703	0.873
TAA/PSAN	22.6/77.4	6.69	0.336	0.602
GN/SrN/BCN	56.05/19.45/24.50	1.91	0.809	0.996

DC power supply. The pressure in the chamber was measured with a pressure sensor and after amplification through a signal amplifier, the data was 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 end of burning. All measurements were conducted once at each pressure.

### 2.3 Four L tank test

Gas generation ability was investigated using a 4 L tank test<sup>6</sup>. Four grams of dried mixture was uniaxially pressed at approximately 200 MPa for 3 min to form cylindrical pellets (diameter 14.7 mm, thickness 13.5–14.5 mm). The pellet was uniformly coated with epoxy resin to achieve cigarette burning. The 4 L chimney-type strand burner that had been used for the burning rate measurements was also used for these experiments with no modification other than closing the gas flow exit. The 4 L 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 nichrome wire. 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,  $\Delta P$  (which is the net pressure increase between the initial pressure and maximum pressure) and  $\Delta t$  (which is the time from the onset of pressure increase to when the pressure reaches its maximum) were calculated to determine the rate of pressure increase ( $\Delta P/\Delta t$ ).

### 2.4 Chemical equilibrium calculations

Chemical equilibrium calculations were conducted using Fraunhofer institute for chemical technology thermodynamic code (Ver. 23.09.96)<sup>32</sup>.

### 2.5 Sensitivity

In order to evaluate the safety of each tetrazole/PSAN mixture, a drop hammer tests was conducted according to the regulations of the Industrial Explosives Society<sup>33</sup>.

### 2.6 Thermal analysis

Thermogravimetry (TG) and differential thermal analysis (DTA) were conducted at the heating rate of 5 K·min<sup>-1</sup> in a He atmosphere (flow rate 20 mL·min<sup>-1</sup>) using an aluminum cell (DTG-50H, Shimadzu Corp.). The melting point was determined by the cross point between a line extended from the baseline and a tangent line drawn at the maximum inclination point on the lower temperature side of a fusion peak. The decomposition start temperature ( $T_{TG}$ ) was determined by the cross point between a line extended from the baseline at the lower temperature side and a tangent line drawn at the maximum inclination point of the weight loss line.

## 3. Results and discussion

### 3.1 Burning rate

The results of the burning rate test for each tetrazole/PSAN mixture at 296 K are presented in Figure 1. It was confirmed that the burning rates of the mixtures followed Vieille's law given by  $r = a \cdot P^n$ , where  $a$  is a constant dependent on the chemical composition and initial propellant temperature, and  $n$  is the pressure exponent of the burning rate<sup>34</sup>. The burning rate of each tetrazole/PSAN mixture was higher than that of the GN/SrN/BCN mixture<sup>35</sup>.

The  $a$  and  $n$  values of each mixture are shown Table 1. It was found that the burning rate of each mixture at 7 MPa was higher than the desirable burning rate of 10 mm·s<sup>-12</sup>. The burning rate of each tetrazole/PSAN mixture was 1.3–1.8 times larger than that of the tetrazole/PSAN<sub>KN5</sub> mixture.

And the order of the burning rate of the tetrazole/PSAN mixture at 7 MPa were AGAT>5-ATZ>1HT=TAA>BHT·2NH<sub>3</sub>>M5T>10 mm·s<sup>-1</sup>>GN/SrN/BCN.

The pressure exponent of the burning rate  $n$  of the mixtures were higher than the desirable value of 0.30<sup>4</sup>.

Some discrepancy was observed for TAA/PSAN mixture and unstable burning phenomena were observed under 3 MPa.

### 3.2 Four L tank test

The results for the 4 L tank tests are shown in Figure 2 and Table 2. Each sample was ignited and burned completely (except for TAA/PSAN). The rate of pressure increase ( $\Delta P/\Delta t$ ) for each mixture was larger than that for the GN/SrN/BCN mixture (0.16 MPa·s<sup>-1</sup>).  $\Delta P/\Delta t$  of each tetrazole/PSAN mixture was approximately 2 times larger than the tetrazole/PSAN<sub>KN5</sub> mixture.  $\Delta P$  for each mixture was also larger than that for the GN/SrN/BCN mixture. It was found that the tank test result of each mixture (except TAA/PSAN) was an acceptable value for a practical gas-generating agent. The unstable burning of TAA/PSAN would contribute to the ignition difficulty of the mixture at 2 MPa.

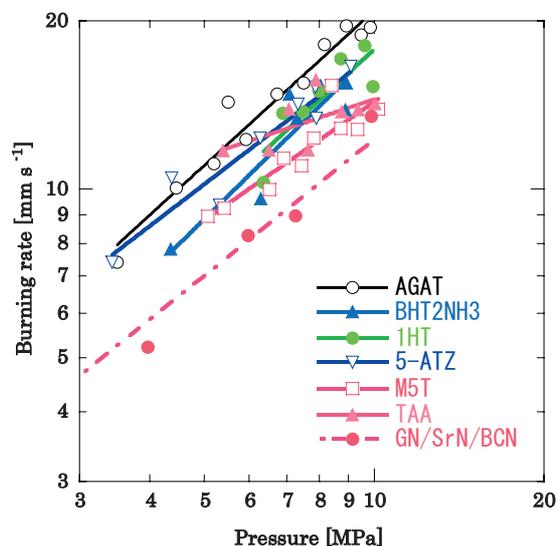


Figure 1 Burning rate for each tetrazole/PSAN and GN/SrN/BCN.

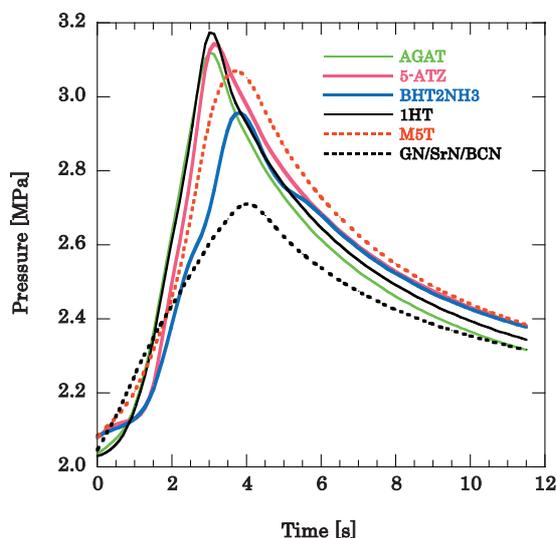


Figure 2 Pressure-time histories of each tetrazole/PSAN and GN/SrN/BCN from 4 L tank test.

The  $\Delta P/\Delta t$  increase was caused mainly by the increase of the burning rate. Although, the number of moles of generated gas per 100 g of gas-generating agent of each tetrazole/PSAN mixture decreased (Table 3) compared with that of the tetrazole/PSAN<sub>KN5</sub> mixture,  $\Delta P$  of tetrazole/PSAN mixture increased.

The burning rate increase decreased  $\Delta t$ . The increase of the inside temperature of the 4 L tank increased the temperature, the volume of gas, and  $\Delta P$ , and consequently the number of  $\Delta P/\Delta t$  increased.

### 3.3 Chemical equilibrium calculation

Chemical equilibrium calculations were conducted to obtain the mol% and/or wt%, the total amount of generated gases, heat of explosion, and  $T_f$  of each mixture (Table 3).

It was found that the generated gaseous products were harmless CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub> for each mixture. Negligible amounts of CO and NO (less than 0.002 mol%) were found in some mixtures. The molar percentage of H<sub>2</sub>O was slightly higher than the acceptable value of 50<sup>9)</sup>. The calorific value per gram of each mixture was lower than

the desirable value of 4000 J·g<sup>-1 7)</sup>. The  $T_f$  for each mixture was higher than the desirable value of 2273 K<sup>8)</sup>.

The following was inferred based on the results shown in Table 3. It was found that the calculated results of each mixture were generally acceptable values for a practical gas-generating agent.

The adiabatic flame temperature  $T_f$  of each tetrazole/PSAN<sub>KN5</sub> mixture was higher than the desirable 2273 K<sup>8)</sup> and the value of each tetrazole/PSAN decreased slightly but still much higher than the desirable value.

The calorific value per gram of gas-generating agent (water gaseous) of each tetrazole/PSAN<sub>KN5</sub> mixture was lower than the desirable 95-105 kJ·mol<sup>-1 7)</sup> and the value of each tetrazole/PSAN increased 1-4 % but only AGAT/PSAN and BHT·2NH<sub>3</sub>/PSAN mixtures satisfied the desirable value.

The molar percentage of H<sub>2</sub>O of each tetrazole/PSAN was 2-6 % lower than that of each tetrazole/PSAN<sub>KN5</sub> mixture but the value was still higher than the desirable 50 wt%<sup>9)</sup>.

The number of moles of generated gas per 100 g of gas-generating agent of each tetrazole/PSAN was 2-4 % lower than that of the tetrazole/PSAN<sub>KN5</sub> mixture but the value was higher than the desirable 2.70 mol·(100 g)<sup>-1 7)</sup>.

The wt% of solid products of each tetrazole/PSAN increased approximately two times but still satisfied the desirable 10 wt%<sup>3)</sup>.

The efficiency of gas evolution of each tetrazole/PSAN decreased approximately 5 % but still satisfied the desirable 90 %<sup>3)</sup>.

### 3.4 Sensitivity

The results of the 5 kg drop hammer test were shown in Table 3. M5T, 5-ATZ, and TAA/PSAN mixture did not ignite at a drop height of 50 cm (highest point of 1/6 ignition point). By replacing PSAN<sub>KN5</sub> with PSAN, the drop hammer sensitivity class of AGAT and BHT·2NH<sub>3</sub>/PSAN changed from class 8 to 7 (1/6 ignition point was more than 40 and less than 50 cm) and the other mixtures' sensitivity class stayed 8. The 1/6 ignition point of AGAT and BHT·2NH<sub>3</sub>/PSAN mixture was 45 cm. These mixtures

Table 2 Gas generation ability for the mixtures.

Mixtures	Starting pressure [MPa]	Maximum pressure [MPa]	Pressure increase $\Delta P$ [MPa]	Elapsed time $\Delta t$ [s]	Rate of pressure increase $\Delta P/\Delta t$ [MPa·s <sup>-1</sup> ]
AGAT/PSAN	2.04	3.12	1.08 (0.91)	3.04 (5.82)	0.356 (0.16)
5-ATZ/PSAN	2.08	3.13	1.05 (0.76)	3.12 (4.16)	0.337 (0.18)
BHT·2NH <sub>3</sub> /PSAN	2.08	2.97	0.89 (0.78)	3.86 (7.38)	0.23 (0.11)
1HT/PSAN	2.03	3.17	1.14	3.02	0.378
M5T/PSAN	2.08	3.06	0.98	3.90	0.25
TAA/PSAN	—	—	(—)	(—)	(—)
GN/SrN/BCN	2.05	2.72	0.67	4.10	0.16

—: not available, ( ): phase-stabilized ammonium nitrate containing 5 wt% KN<sup>31)</sup>

**Table 3** Results of chemical equilibrium calculation for tetrazole/PSAN.

Tetrazole		Desirable values	AGAT	5-ATZ	BHT-2NH <sub>3</sub>	1HT	M5T	TAA
Heat of formation of tetrazole [kJ·mol <sup>-1</sup> ]		–	782.1	238.5	422.0	301.6	235.8	–86.28
Nitrogen content of tetrazole [wt%]		–	80.22	82.33	81.36	79.98	66.64	43.74
Mixing ratio Tetrazole/PSAN [wt%]			22.32/	25.00/	22.79/	24.26/	16.12/	22.65/
Adiabatic flame temperature [K]		≤2273 <sup>7)</sup>	2826 (2850)	2864 (2885)	2824 (2847)	3024 (–)	2838 (2862)	2786 (–)
Calorific value per gram of gas-generating agent (water gaseous) [J·g <sup>-1</sup> ]		≥4000 <sup>6)</sup>	3787 (3799)	3804 (3815)	3787 (3798)	4136 (–)	3093 (3884)	3700 (–)
Generated products [mol %]	CO <sub>2</sub>	–	6.036	6.375	5.542	7.776	8.516	12.678
	H <sub>2</sub> O(l)	≥50 <sup>8)</sup>	54.986 (56.20)	52.683 (55.96)	55.254 (57.39)	51.508 (–)	56.420 (53.76)	53.855 (–)
	N <sub>2</sub>	–	38.018	40.000	38.255	39.759	34.016	32.469
	CO	–	0.000	0.000	0.001	0.001	0.001	0.002
	NO	–	0.001	0.001	0.000	0.001	0.001	0.000
	KOH(s)	–	0.028	0.027	0.030	0.025	0.025	0.021
	K <sub>2</sub> CO <sub>3</sub> (s)	–	0.928	0.905	0.916	0.928	1.019	0.973
Generated products [wt%]	KOH(s)	–	0.065	0.062	0.068	0.056	0.056	0.045
	K <sub>2</sub> CO <sub>3</sub> (s)	–	5.229	5.048	5.191	5.105	5.664	5.227
Number of moles of generated gas per 100 g of gas-generating agent [mol·(100 g) <sup>-1</sup> ]		<2.70 <sup>6)</sup>	3.999 (4.165)	4.040 (4.120)	4.061 (4.183)	3.940 (–)	3.980 (4.115)	3.847 (–)
Calorific value per mole of generated gas [kJ·mol <sup>-1</sup> ]		95–105 <sup>6)</sup>	95.12 (91.23)	93.74 (92.59)	93.26 (90.80)	104.96 (–)	97.37 (94.38)	96.18 (–)
Wt% of solid products [wt%]		≥10 <sup>3)</sup>	5.110 (2.665)	5.294 (2.576)	5.259 (2.649)	5.161 (–)	5.720 (2.873)	5.272 (–)
Efficiency of gas evolution [%]		≤90 <sup>3)</sup>	94.71 (99.52)	94.89 (99.53)	94.74 (99.53)	94.84 (–)	94.28 (99.48)	94.73 (–)
Burning rate at 7 MPa [mm s <sup>-1</sup> ]		<10 <sup>2)</sup>	15.0 (9.2)	13.3 (8.68)	12.3 (6.81)	12.8 (–)	11.2 (8.60)	12.8 (–)
Melting point [K]		>388 <sup>3)</sup>	382	385	393	371	385	368
Melting point of tetrazole [K]	Observed by DTA	434 (PSAN)	–	482	–	432	421	405
	Reported <sup>24)</sup>		488–490	480–482	507–510	423–430	416–420	395–400
Decomposition start temperature [K]		>473 <sup>1)</sup>	428	480	510	460	480	470
Decomposition start temperature of tetrazole [K]		500 (PSAN)	495	480	553	450	493	480
Drop hammer test, 1/6 ignition point [cm]			45 (<50)	<50 (<50)	45 (<50)	– (<50)	<50 (<50)	<50 (–)

(s): solid, (l): liquid, (–): phase-stabilized ammonium nitrate containing 5 wt% KN<sup>31)</sup>.

can be treated as insensitive mixtures.

### 3.5 Thermal analysis

Figure 3 gives the TG and DTA curves of AN, PSAN, each tetrazole, and each tetrazole/PSAN mixture.

AN showed two endothermic peaks at 326 and 400 K corresponded to phase transitions. An endothermic peak at 443 K corresponded to the melting of AN. An endothermic decomposition peak temperature was 533 K.

Endothermic peaks of PSAN at 395 and 403 K corresponded to the phase transitions and that at 434 K corresponded to the melting, and an endothermic peak at

535 K corresponded to the decomposition. No phase transition near room temperature was observed.

The melting point and  $T_{TG}$  of each mixture and tetrazole are shown in Table 3.

It is reported that the burning rate control zone may be located either in the condensed phase or in the gas phase<sup>36)</sup> and the increased heat release in the condensed phase increases the burning rate of AGAT/AN mixture<sup>24)</sup>.

It is assumed that the amount of heat released in the condensed phase controls the burning rate for the AN-tetrazole system.

It was found that there was some correlation between

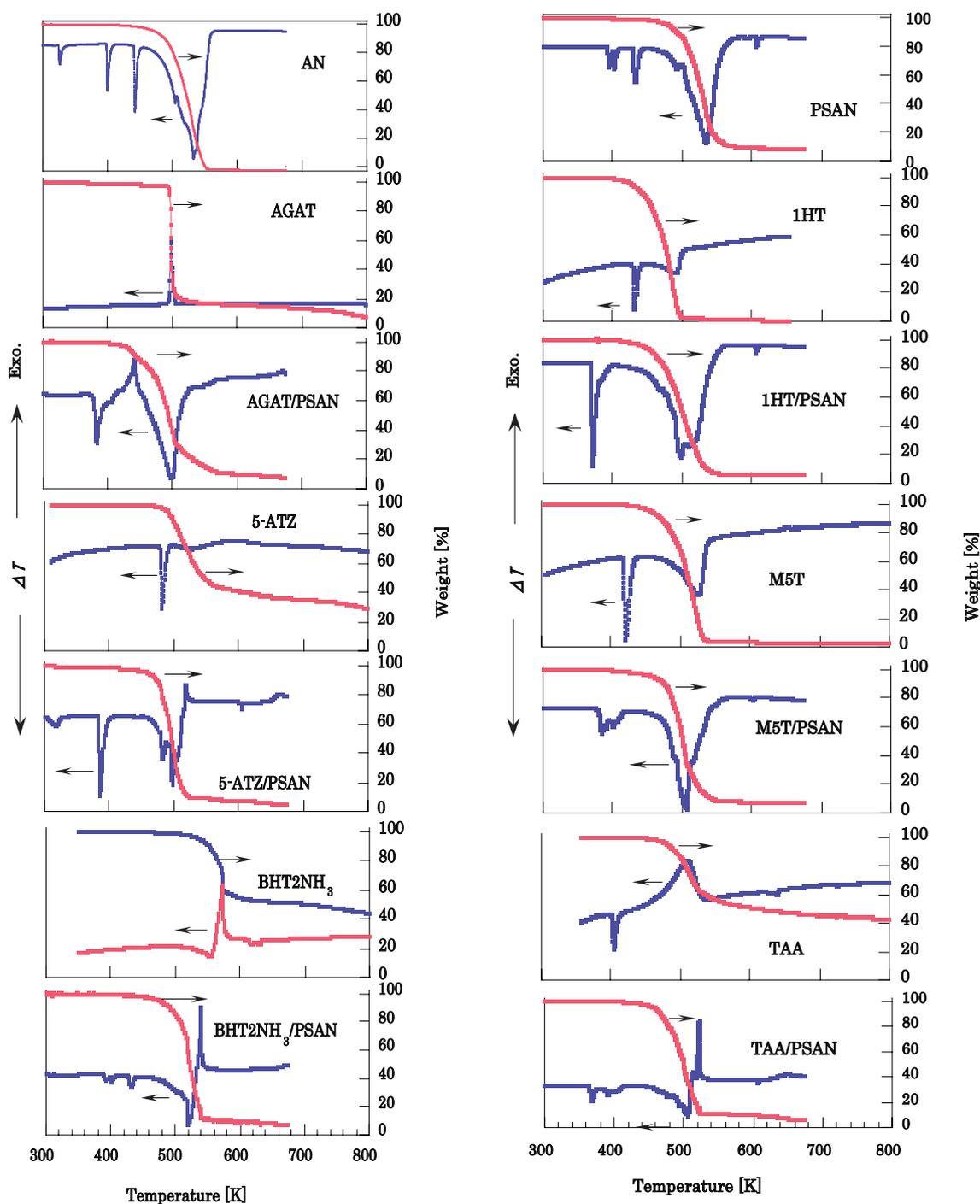


Figure 3 TG and DTA curves of AN, PSAN, tetrazole, and tetrazole/PSAN mixtures.

the burning rate at 7 MPa and the  $T_{TC}$  of each mixture and the correlation coefficient was 0.74 (the correlation coefficient is 0.669 at the 0.1 significance level<sup>37</sup>). There was no relation among the burning rate, melting point, and  $T_f$ .

The low  $T_{TC}$  means that the chemical reaction starts at a low temperature and results in a high burning rate with all other factors equal. According to the TG and DTA curves, generally tetrazoles decomposed almost immediately after the melting except M5T and TAA. And the reaction between PSAN and tetrazole might start.

It was found that there was some correlation between the melting point of tetrazole and that of the mixture but no correlation between the melting point of tetrazole and

$T_{TC}$  of the mixture.

According to the TG and DTA curves, AGAT exothermically decomposed at a lower temperature compared to PSAN that might increase the heat release in the condensed phase and contribute to the high burning rate of the mixture.

The burning rate of AGAT/PSAN was the fastest ( $15.0 \text{ mm}\cdot\text{s}^{-1}$ ) among the mixtures because the  $T_{TC}$  (428 K) was the lowest.

The burning rate of 5-ATZ/PSAN came next ( $13.3 \text{ mm}\cdot\text{s}^{-1}$ ). The  $T_{TC}$  of the mixture (480 K) was a medium level. But 5-ATZ decomposed exothermically and the amount of heat released in the condensed phase would be relatively high. According to the TG and DTA curves, 5-ATZ/PSAN

might decompose exothermically.

The  $T_{TC}$  of 1HT and TAA were 460 and 470 K, respectively. The burning rate of TAA and 1HT were 12.8 mm·s<sup>-1</sup>. TAA melted at 405 K and decomposed at 480 K and the reaction between TAA and PSAN started at 470 K that suggested the temperature of the condensed phase increased gradually. On the contrary, 1HT melted at 432 K and decomposed endothermically at 450 K but the reaction between 1HT and PSAN started at 460 K. The short reaction time suggested the amount of heat produced in the condensed phase might be almost the same as that of TAA/PSAN.

The  $T_{TC}$  of BHT·2NH<sub>3</sub>/PSAN was highest (510 K) among the mixtures but BHT·2NH<sub>3</sub>'s exothermic decomposition made the amount of heat produced in the condensed phase large and the burning rate faster than expected (12.3 mm·s<sup>-1</sup>).

The burning rate of M5T/PSAN was the lowest (11.2 mm·s<sup>-1</sup>). In spite of intermediate  $T_{TC}$  (480 K), M5T decomposed endothermically that caused less amount of heat released in the condensed phase.

The  $T_{TC}$  of 5-ATZ and M5T were 480 K but the burning rate of 5-ATZ/PSAN (13.3 mm·s<sup>-1</sup>) was larger than that of M5T/PSAN (11.2 mm·s<sup>-1</sup>) that might be caused by their decomposition behavior, namely, the former decomposed exothermically and the latter decomposed endothermically.

It is reported that the decomposition start temperature of gas-generating agents observed by differential scanning calorimetry (DSC) of 473 K is acceptable for the automobile air bag gas-generating agents<sup>1)</sup>.

Based on the value of  $T_{TC}$ , 5-ATZ, M5T, and BHT·2NH<sub>3</sub>/PSAN mixtures might be acceptable for the gas-generating agents.

The melting point of each tetrazole/PSAN mixture was slightly lower than the desirable value of 388 K<sup>3)</sup>, except BHT·2NH<sub>3</sub>/PSAN mixture which might be acceptable for gas-generating agents.

#### 4. Conclusions

The following conclusions were obtained for tetrazole/PSAN mixtures.

- 1) The burning rate of each mixture at 7 MPa was higher than the desirable value of 10 mm·s<sup>-1</sup>.
- 2) The gas generation ability of each mixture which was measured by the pressure increase rate of the 4 L tank test was higher than that of the practical gas-generating agent.
- 3) The melting point of each mixture was slightly lower than the desirable value of 388 K, except BHT·2NH<sub>3</sub>/PSAN.
- 4) Based on the chemical equilibrium calculation, each mixture generally produced harmless gases. The efficiency of gas evolution, the wt% of solid products, and the number of moles per 100 g of gas-generating agent, were better than the desirable values. The calorific value per mole of generated gases was close to the desirable value. However, the  $T_f$  and mol% of H<sub>2</sub>O were higher than the desirable values.

5) Each mixture was determined to be insensitive from the drop hammer test.

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