Research paper

Sensitivity characteristics of some guanidinium 1,5′-bis-1H-tetrazolate based mixtures

Shingo Date*†, Shizuka Nishi*, and Kazuhito Asazuki*

*Department of Applied Chemistry, National Defense Academy,
1-10-20 Hashirimizu, Yokosuka, Kanagawa 239-8686, JAPAN
Phone : +81-46-841-3810 (ext. 3561)
†Corresponding author : sdate@nda.ac.jp

Received : August 14, 2014 Accepted : December 24, 2014

Abstract

Impact sensitivity, friction sensitivity, electric spark discharge sensitivity and heat sensitivity were measured for some guanidinium 1,5'-bis-1H-tetrazolate (G15B)/ammonium nitrate (AN) based mixtures, and their results were compared with those of previously studied G15B/potassium perchlorate (KP) mixture, G15B/strontium nitrate (SrN) mixture and G 15B/metal oxide mixtures, together with commercially used guanidinium nitrate (GN)/SrN/basic copper nitrate (BCN) mixture. According to drop hammer tests, it was suggested that all G15B/metal oxides except G15B/MnO_2 mixture were more insensitive than GN/SrN/BCN mixture. Friction tests have suggested that G15B/SrN mixture, all G15B/metal oxide mixtures and G15B/AN based mixtures with non-Cu based additive were insensitive against friction. Meanwhile, electric spark discharge tests have suggested that all G15B/metal oxide mixtures and all G15B/AN/additive mixtures were equally insensitive as compared to that of GN/SrN/BCN mixture. As for ignition temperature tests, it was suggested that, in terms of 4 seconds ignition temperature, all G15B/AN based mixtures except G15B/AN/CuO mixture and G15B/AN/AC mixture were equivalent to or more insensitive than that of GN/SrN/BCN mixture. It was also found that apparent activation energies of ignition reactions for all G15B based mixtures, except G15B/AN mixture, G15B/AN/MnO_2 mixture, G15B/AN/Cu_2O mixture, G15B/AN/AC mixture and G15B/AN/SiO_2 mixture were higher than that of GN/SrN/BCN mixture. Summing up the sensitivity test results, it was found that G15B/AN/NaCl mixture has the lowest sensitivity overall among the tested G15B based mixtures that burns. Regarding correlation between different disciplines of sensitivities, it was suggested that, in general, impact sensitivity and friction sensitivity of some G15B based mixture do not necessarily correlate. As for the correlation between friction sensitivity and sensitivity to electric spark, those mixtures that were sensitive to friction were not necessarily sensitive to electric sparks. It was also suggested that heat sensitivity do not necessarily correlate with impact sensitivity and friction sensitivity.

Keywords : guanidinium 1,5'-bis-1H-tetrazolate, impact sensitivity, friction sensitivity, electric spark sensitivity, heat sensitivity

1. Introduction

There have been researches and developments of gas generating agents for automobile airbag inflators[1)-12)]. We have been studying on novel gas generating mixtures in which the fuel is guanidinium 1,5'-bis-1H-tetrazolate (G15B) (Figure 1), a double-ring tetrazole compound, and have found that the mixtures with potassium perchlorate (KP)[8)], metal oxides[9)-11)] and ammonium nitrate (AN)[12)] show high burning performances. In this study, sensitivity characteristics of G15B/AN based mixtures were studied

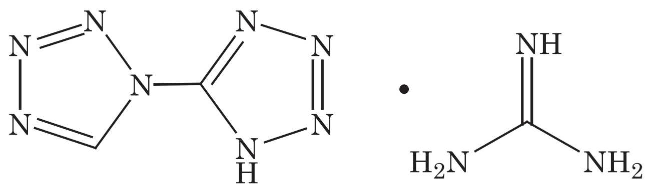

Figure 1 Chemical structure of guanidinium 1,5'-bis-1H-tetrazolate (G15B).

through drop hammer test, friction test, electrostatic discharge test and ignition temperature test, comparing with G15B/KP mixture[11], G15B/strontium nitrate (SrN) mixture[11], some G15B/metal oxide mixtures[11], together with guanidine nitrate (GN)/SrN/basic copper nitrate (BCN) mixture[13] that is currently used commercially as gas generating agents for automobile airbag inflators. Here, the additive tested on stoichiometric ratio G15B/AN mixture was: manganese dioxide MnO_2, copper Cu, copper (I) oxide Cu_2O, copper (II) oxide CuO, basic cupric nitrate (BCN), activated carbon (AC), sodium nitrate (NaCl) or silicon oxide (SiO_2), while the metal oxide[11] used as an oxidizer of G15B/metal oxide mixture for comparison was: MnO_2, CuO or iron oxide (Fe_2O_3).

2. Experimental

2.1 Reagents

G15B was purchased from Toyo Chemicals Co., Ltd. GN was purchased from Alfa Aesar. AN (purity: 99.0%), Cu_2O (purity: 99.0%), CuO (purity: 99.9%), activated carbon (AC) and NaCl (purity 99.9%) were purchased from Kanto Chemicals Co., Ltd. Cu (purity 99.9%, average particle size 10 μm) was purchased from Rare Metallic Co., Ltd. BCN was purchased from Nihon Kagaku Sangyo Co., Ltd. Silicon dioxide SiO_2 was purchased from Wako Chemicals Co., Ltd. Particle sizes of G15B and GN were controlled between 45-75 μm, and the particle sizes of AN, NaCl and SrN were controlled between 75-149 μm, each of them through milling and sieving process, but Cu, Cu_2O, CuO, BCN, AC and SiO_2 were used without milling and sieving. The powders were then dried separately under reduced pressure for a day at room temperature and they were then stored in desiccators for at least a day.

402

2.2 Preparation of the mixtures

G15B, AN and additives were mixed at one of the mixing ratios as given in Table 1, by using a V-shaped rotating mixer. Meanwhile, as a reference mixture, GN/SrN/BCN mixture based on patented composition[13] was prepared, mixing at a raio of 56.05 wt% / 19.45 wt%/ 24.50 wt%, as shown in Table 2. Here also, each mixture was then dried separately under reduced pressure for a day at room temperature and they were then stored in desiccators for at least a day. With regard to the sensitivity test data for stoichiometric ratio G15B/KP mixture, G15B/SrN mixture and G15B/metal oxide mixtures, in which their respective mixing ratios are shown in Table 2, the data of Date et al.[11] were used.

2.3 Sensitivity tests

The following sensitivity tests were conducted for G15B /AN based mixtures and GN/SrN/BCN mixtures, and

Table 1 Mixing ratios of G15B/AN based mixtures (units in wt%).

Sample	G15B/ AN	+MnO_2	+Cu	+Cu_2O	+CuO	+BCN	+AC	+NaCl	+SiO_2
G15B	20.59	20.59	20.59	20.59	20.59	20.59	20.59	20.59	20.59
GN	—	—	—	—	—	—	—	—	—
AN	79.41	79.41	79.41	79.41	79.41	79.41	79.41	79.41	79.41
SrN	—	—	—	—	—	—	—	—	—
MnO_2	—	5.00	—	—	—	—	—	—	—
Cu	—	—	5.00	—	—	—	—	—	—
Cu_2O	—	—	—	5.00	—	—	—	—	—
CuO	—	—	—	—	5.00	—	—	—	—
BCN	—	—	—	—	—	5.00	—	—	—
AC	—	—	—	—	—	—	5.00	—	—
NaCl	—	—	—	—	—	—	—	5.00	—
SiO_2	—	—	—	—	—	—	—	—	5.00

Table 2 Mixing ratios of G15B/oxidizer mixtures and GN/SrN/BCN mixture (units in wt%).

Sample	G15B/ KP[11]	G15B/ SrN[11]	G15B/ MnO_2[11]	G15B/ CuO[11]	G15B/ Fe_2O_3[11]	GN/SrN/ BCN[13]
G15B	37.5	32.9	32.3	20.7	28.1	—
GN	—	—	—	—	—	56.05
KP	62.5	—	—	—	—	—
SrN	—	67.1	—	—	—	19.45
MnO_2	—	—	67.7	—	—	—
CuO	—	—	—	79.3	—	—
Fe_2O_3	—	—	—	—	71.9	—
BCN	—	—	—	—	—	24.50

their data were compared with those of G15B/KP mixture[11], G15B/SrN mixture[11] and G15B/metal oxide mixtures[11], as mentioned in 2.2.

2.3.1 Drop hammer test

Drop hammer test of each mixture was conducted by using BAM type drop hammer test apparatus, following Japan Explosive Society (JES) regulation ES-21 (1)[14], to determine the impact sensitivity of each mixture. Mass of a drop hammer used in this study was 5 kg. Each powder mixture (0.10-0.12 ml) was placed on a small tin foil cup (diameter 12 mm) before each test. 1/6 ignition point, $H_{1/6}$ [cm], and the JES sensitivity class of each mixture was determined.

2.3.2 Friction test

Friction test of each mixture was conducted by using BAM friction sensitivity test apparatus, following the procedures of JES ES-22[15] to determine the friction sensitivity of each powder mixture. Here, 1/6 ignition point, $F_{1/6}$ [N], and the JES sensitivity class of each mixture was determined.

2.3.3 Electric spark discharge (ESD) test

Electric spark discharge (ESD) test of each mixture was conducted by using Electric Spark Sensitivity Testing Apparatus I (Hosoya Pyro-Engineering Co., Ltd.). Electric spark with energy of approximately 50 mJ was fired onto a spatula-full powder sample (approximately 20 mg) which was placed on an open polished steel plate. The test was conducted 10 times for each mixture (each sample was replaced after each trial), and the number of trials in which ignition occurred, was observed.

2.3.4 Ignition temperature test

Heat sensitivity of each mixture was evaluated by using Krupp-type ignition temperature testing apparatus, following the procedures of JES regulation ES-11(1)[16]. Starting from 673 K, a spatula-full powder mixture (approximately 20 mg) was dropped into an orifice of the testing apparatus at 5 K interval each during cooling of the furnace of the apparatus. Measuring induction time to ignition at each temperature, 4 seconds ignition temperature, T_{4s} [K], and apparent activation energy of ignition reaction, E_a [k J mol^{-1}], for each mixture were determined.

3. Results and discussion

The summary of the results of the sensitivity tests for the tested mixtures is given in Table 3.

3.1 Drop hammer test

$H_{1/6}$ for G15B/KP mixture and G15B/SrN mixture were slightly lower as compared to that of GN/SrN/BCN mixture, indicating the higher sensitivity of the former mixtures. As for G15B/metal oxides, $H_{1/6}$ for G15B/CuO mixture and G15B/Fe_2O_3 mixture were higher as compared to that of GN/SrN/BCN mixture, indicating the lower sensitivity of the former mixtures, while G15B/MnO_2 mixture was more sensitive. Meanwhile, $H_{1/6}$ for all G15B/AN based mixtures except G15/AN mixture and G 15B/AN/NaCl mixture were generally lower as compared to that of GN/SrN/BCN mixture. G15B/AN/SiO_2 mixture was especially sensitive, falling into class 2 category, being the most sensitive among all the mixtures that were tested in this study, suggesting that high melting and hard foreign object particles such as SiO_2 could, due to possible formation of hot spots, sensitize gas generating agents against impact as well as explosives[17].

3.2 Friction test

$F_{1/6}$ for G15B/KP mixture was 353.0 N, suggesting that it is more sensitive than GN/SrN/BCN mixture, while $F_{1/6}$ for G15B/SrN mixture was greater than 353.0 N, i.e. it did not ignite after 6 trials, suggesting low sensitivity against friction. Meanwhile, $F_{1/6}$ for all G15B/metal oxide mixtures were greater than 353.0 N. In contrast, $F_{1/6}$ for some G15B/AN based mixtures with Cu based additives, i.e. Cu_2O, CuO and BCN, were low, falling into class 6 category, suggesting high sensitivity against friction, while $F_{1/6}$ for other G15B/AN based mixtures were greater than or equal to 353.0 N. Meanwhile, some G15B based mixtures which indicated high sensitivity against impact were insensitive against friction, and focusing on the G15B/AN/Cu based additive mixtures, the order of impact sensitivity for (Cu ≡ Cu_2O > BCN > CuO) was not the same as that of friction sensitivity (CuO > BCN > Cu_2O > Cu), suggesting that impact sensitivity and friction sensitivity of some G15 B based mixture do not necessarily correlate. As for G15B /AN/SiO_2 mixture which had the highest sensitivity against impact, it was insensitive against friction, which did not exactly agree with the findings by Osada[15], Conkling and Mocella[18] that the presence of hard granular component can sensitize mixtures against friction.

3.3 Electric spark discharge (ESD) test

All G15B/metal oxide mixtures and all G15B/AN/additive mixtures did not ignite after 10 trials during the ESD test at approximately 50 mJ of electrical energy, indicating that they were insensitive compared to stoichiometric ratio G15B/KP mixture and G15B/SrN mixture that ignited, and they were equivalent to that of GN/SrN/BCN mixture that did not ignite. It was also shown that those mixtures that were sensitive to friction were not necessarily sensitive to electric spark, which agreed with the finding by Conkling and Mocella[19].

3.4 Ignition temperature test

While G15B/KP mixture, G15B/SrN mixture and G15B/metal oxide mixtures were lower in T_{4s} as compared to that of GN/SrN/BCN mixture, T_{4s} of all G15B/AN based mixtures except G15B/AN/CuO mixture and G15B/AN/AC mixture were equivalent or higher than that of GN/SrN/BCN mixture. As for E_a, those values of all G15B based mixtures, except G15B/AN mixture, G15B/AN/MnO_2 mixture and G15B/AN/AC mixture were equivalent or higher than that of GN/SrN/BCN mixture.

Meanwhile, regarding the G15B/AN/Cu based additive

Table 3 Summary of sensitivity test results for G15B based mixtures and GN/SrN/BCN mixture.

Mixture	Drop hammer test		Friction test		Electric spark discharge (ESD) test	Ignition temperature test	
	1/6 ignition point $H_{1/6}$ [cm]	JES Class	1/6 ignition point $F_{1/6}$ [N]	JES Class	Ignition probability(50 mJ) (number of ignitions out of 10 trials)	4 seconds ignition temperature T_{4s} [K]	Apparent activation energy E_a [kJ mol^{-1}]
G15B/KP[11)]	$20 \leq H_{1/6} < 30$	5	353.0	7	3/10	473	117
G15B/SrN[11)]	$20 \leq H_{1/6} < 30$	5	> 353.0	7	2/10	511	69
G15B/MnO_2[11)]	$10 \leq H_{1/6} < 15$	3	> 353.0	7	0/10	487	88
G15B/CuO[11)]	$30 \leq H_{1/6} < 40$	6	> 353.0	7	0/10	473	212
G15B/Fe_2O_3[11)]	$40 \leq H_{1/6} < 50$	7	> 353.0	7	0/10	498	89
G15B/AN	> 50	8	> 353.0	7	0/10	568	31
G15B/AN/MnO_2	20	5	> 353.0	7	0/10	566	38
G15B/AN/Cu	10	3	353.0	7	0/10	573	65
G15B/AN/Cu_2O	10	3	317.7	6	0/10	571	44
G15B/AN/CuO	20	5	235.4	6	0/10	543	100
G15B/AN/BCN	$10 \leq H_{1/6} < 15$	3	$235.4 \leq F_{1/6} < 247.1$	6	0/10	563	85
G15B/AN/AC	$20 \leq H_{1/6} < 30$	5	> 353.0	7	0/10	537	37
G15B/AN/NaCl	50	8	> 353.0	7	0/10	716	268
G15B/AN/SiO_2	$5 \leq H_{1/6} < 10$	2	> 353.0	7	0/10	598	39
GN/SrN/BCN	30	6	> 353.0	7	0/10	564	49

mixtures, the order of heat sensitivity based on T_{4s} (CuO > BCN > Cu ≒ Cu_2O (higher the T_{4s}, the lower the sensitivity)) was in an opposite order to that of impact sensitivity mentioned above, and in a different order to that of friction sensitivity mentioned above also, while the order of heat sensitivity based on E_a (Cu_2O > Cu > BCN > CuO (higher the E_a, the lower the sensitivity)) was also different to those of impact sensitivity and friction sensitivity, respectively. The two comparisons suggest that heat sensitivity of some G15B based mixtures do not necessarily correlate with impact sensitivity and friction sensitivity.

Summing up the sensitivity test results, it was found that G15B/AN/NaCl mixture has the lowest sensitivity characteristics overall among the tested G15B based mixtures that burns readily (stoichiometric ratio G15B/AN mixture did not burn even under an initial N_2 gauge pressure of 10 MPa during linear burning rate tests[12)]). It was also found that there were no correlations among different disciplines of sensitivity characteristics that were tested on G15B based mixtures in this study, so it is suggested that all of these sensitivity characteristics need to be measured for these mixtures.

4. Conclusions

The sensitivity characteristics of G15B based mixtures were studied through drop hammer tests, friction tests, electrostatic discharge tests and ignition temperature tests, and their respective results were compared with that of the currently-used GN/SrN/BCN mixture.

According to drop hammer tests, it was found that G15B/KP mixture, G15B/SrN mixture and all G15B/AN based mixtures except G15B/AN mixture and G15B/AN/NaCl mixture were more sensitive as compared to that of GN/SrN/BCN mixture, while all G15B/metal oxides except G15B/MnO_2 mixture were more insensitive. It was also found that G15B/AN/SiO_2 mixture was especially sensitive, suggesting that high melting and hard foreign object particles such as SiO_2 could sensitize gas generating agents against impact as well as explosives.

Friction tests have shown that G15B/KP mixture and some G15B/AN based mixtures with Cu based additives, i.e. Cu_2O, CuO and BCN, were more sensitive than GN/SrN/BCN mixture, while G15B/SrN mixture, all G15B/metal oxide mixtures and G15B/AN based mixtures with non-Cu based additive were insensitive against friction.

Meanwhile, electric spark discharge tests have shown that all G15B/metal oxide mixtures and all G15B/AN based mixtures were equally insensitive to 50 mJ of electric energy as compared to that of GN/SrN/BCN mixture.

As for ignition temperature tests, it was found that while G15B/KP mixture, G15B/SrN mixture and G15B/metal oxide mixtures were more sensitive in terms of T_{4s} as compared to that of GN/SrN/BCN mixture, all G15B/AN based mixtures except G15B/AN/CuO mixture and G15B/AN/AC mixture were equivalent or more insensitive than that of GN/SrN/BCN mixture. It was also found that the values of E_a for all G15B based mixtures, except G15B/AN mixture, G15B/AN/MnO_2 mixture, G15B/AN/Cu_2O mixture, G15B/AN/AC mixture and G15B/AN/SiO_2 mixture were higher than that of GN/SrN/BCN mixture.

Summing up the test results, it was found that G15B/AN/NaCl mixture has the lowest sensitivity overall among the tested G15B based mixtures that burns readily.

Regarding correlations between different disciplines of sensitivity characteristics of some G15B based mixtures, it was suggested that, in general, impact sensitivity and friction sensitivity do not necessarily correlate. As for the correlation between friction sensitivity and sensitivity to electric spark, those mixtures that were sensitive to friction were not necessarily sensitive to electric sparks. It was also suggested that heat sensitivity do not necessarily correlate with impact sensitivity and friction sensitivity. Therefore, it is suggested that all of these sensitivity characteristics need to be measured for these mixtures.

References

1) M. Kumasaki, R. Miyasaka, H. Kiuchi, Y. Wada, M. Arai, and M. Tamura, Kayaku Gakkaishi (Sci. and Tech. Energetic Materials), 62, 109−116 (2001).
2) Y. Miyata, M. Abe, S. Date, M. Kohga, and K. Hasue, Sci. and Tech. Energetic Materials, 69, 117−122 (2008).
3) Y. Wada, K. Hori, and M. Arai, Sci. and Tech. Energetic Materials, 71, 83−86 (2010).
4) Y. Izato, A. Miyake, and S. Date, Prop. Explos. Pyrotech., 38, 129−135 (2013).
5) K. Ikeda, Y. Shiraishi, and S. Date, Sci. and Tech. Energetic Materials, 75, 59−63 (2014).
6) K. Ikeda, A. Doi, and S. Date, Sci. and Tech. Energetic Materials, 75, 83−85 (2014).
7) Toshiaki Ohtake, Shingo Date, Ken Ikeda, and Yuji Shiraishi, Sci. and Tech. Energetic Materials, *in press*.
8) S. Date, P. Boonyarat, T. Kazumi, and K. Hasue, Kayaku Gakkaishi (Sci. and Tech. Energetic Materials), 63, 209−215 (2002).
9) S. Date, T. Sugiyama, N. Itadzu, Y. Miyata, K. Iwakuma, M. Abe, K. Yoshitake, S. Nishi, and K. Hasue, Sci. and Tech. Energetic Materials, 70, 23−26 (2009).
10) S. Date, N. Itadzu, T. Sugiyama, Y. Miyata, K. Iwakuma, M. Abe, K. Yoshitake, S. Nishi, and K. Hasue, Sci. and Tech. Energetic Materials, 70, 152−157 (2009).
11) S. Date, T. Sugiyama, N. Itadzu, and S. Nishi, Prop. Explos. Pyrotech., 36, 51−56 (2011).
12) S. Date, S. Nishi, K. Asazuki, and T. Yamamoto, Sci. and Tech. Energetic Materials, *in press*.
13) E. Satoh, K. Ikeda, and D. Kubo, International Patent WO 02/30850 A1(2002).
14) Japan Explosives Society, Regulations of the Japan Explosives Society (IV) (Sensitivity Test Methods), Japan Explosives Society, Tokyo, 60 (1995) (In Japanese).
15) Japan Explosives Society, Regulations of the Japan Explosives Society (IV) (Sensitivity Test Methods), Japan Explosives Society, 65 (1995) (In Japanese).
16) Japan Explosives Society, Regulations of the Japan Explosives Society (IV) (Sensitivity Test Methods), Japan Explosives Society,1(1995) (In Japanese).
17) H. Osada, (ed.) ; Kayaku Chemistry (Explosives Chemistry), 237, Maruzen, Tokyo (2003) (In Japanese).
18) J. A. Conkling, and C. J. Mocella, Chemistry of Pyrotechnics Second Edition, 148, CRC Press, Boca Raton (2011).
19) J. A. Conkling, and C. J. Mocella, Chemistry of Pyrotechnics Second Edition, 144, CRC Press, Boca Raton (2011).