Study on new gas−generating agents (II) Evaluation of deflagration properties for tetrazole-oxidizer compositions

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In order to obtain some information on the new gas generating agents for airbag systems, we have attempted to evaluate the deflagration properties of various tetrazole-oxidizer compositions using the small scale deflagration test which was reported in our previous paper.

As the results, we can say from the stand point of deflagration properties that some tetrazole-oxidizer compositions may be applicable as new gas-generating agents for airbag systems.

1. Introduction

Airbag systems are well known to be a useful tool for protecting lives in the car crash accidents. Sodium azide is now chiefly used as a base material for the gas-generating agents of airbag systems. However, as sodium azide has not only strong toxicity but also possibility for the formation of explosive materials from its reaction with heavy metals, many researches have been carried out to find out new gas-generating agents.

In order to obtain some information on new gas-generating agents, at first we have examined thermal behavior and time-pressure profiles of tetrazoles and tetrazole-oxidizer compositions by heating[1-4]. Next, in order to clarify the deflagration properties of the tetrazole-oxidizer compositions by igniting, we have devised a small scale deflagration test apparatus for a screening test and have investigated the possibility of its application to preliminary evaluation by examining the influences of testing conditions on the deflagration properties and comparing their data on the deflagration properties with those obtained from the 1 L tank test, which is a good but larger scale screening test for evaluating the deflagration properties of gas-generating agents for airbag systems.

In the previous paper[5], we reported that small scale deflagration test should be a useful screening test for evaluating the deflagration properties of new gas-generating agents.

We have then attempted to apply the test method to the evaluation of the deflagration properties for the tetrazole-oxidizer compositions, one of the most promising new gas-generating agents in the near future, by examining the time-pressure behavior obtain from the deflagration. In this paper, we report the results.

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2. Experimental

2.1 Materials

2.1.1 Tetrazole-oxidizer compositions

Tetrazoles used in the experiments are shown in Table 1. HAT was purchased from Tokyo Kasei Co., Ltd.. Other tetrazoles were kindly supplied from Toyo Kasei Co., Ltd.. These tetrazoles were used without further purification. Oxidizer used in the experiments are shown in Table 2 and were used without further purification.

Table 1 Tetrazole used (abbreviation and purity)

Tetrazoles	Abbreviation	Purity (wt. %)
Potassium 1H-Tetrazole	1HTK	99.6
5-Amino-1H-tetrazole	HAT	>98.0
Sodium 5-amino-1H-tetrazole	HATNa	93.3
Disodium 1H-tetrazole-5-carboxylic acid	TCA	97.2
Dipotassium bitetrazole	BHTK	99.5
Dimethylamine bitetrazole	BHT2MA	100.0
Diammonium bitetrazole	BHT2NH3	99.9
Diaminoguanidine bitetrazole	BHT2AGAD	99.5
Disodium azotetrazole	ZTNa	>98.0
Diguanidine azotetrazole	GZT	>98.0

Table 2 Oxidizer used

Oxidizer	Chemical formula	Purity (wt. %)	manufacture
Potassium nitrate	KNO_3	Special grade	a
Sodium nitrate	$NaNO_3$	Special grade	a
Ammonium nitrate	NH_4NO_3	Special grade	a
Barium nitrate	$Ba(NO_3)_2$	Special grade	a
Magnesium nitrate	$Mg(NO_3)_2 \cdot 6H_2O$	Special grade	b
Curic nitrate	$Cu(NO_3)_2 \cdot 3H_2O$	Special grade	b
Silver nitrate	$AgNO_3$	First class grade	b
Potassium perchlorate	$KClO_4$	First class grade	a
Sodium perchlorate	$NaClO_4$	Special grade	b
Ammonium perchlorate	NH_4ClO_4	Special grade	c
Lithium perchlorate	$LiClO_4$	First class grade	c
Magnesium perchlorate	$MgClO_4$	Special grade	a
Copper oxide	CuO	99.9%	a
Iron(II) oxide	Fe_2O_3	99.5%	a
Manganomaganic oxide	Mn_3O_4	99.0%	d

a: Wako Pure Chemical Industries, Ltd. b: Koso Chemical Co., Ltd.
c: Kanto Chemical Co.. Inc. d: Soekawa Chemical, Ltd.

Tetrazole-oxidizer powder compositions were prepared by mixing a tetrazole and an oxidizer in the V-type mixer or by mixing with a brush at zero oxygen balance. AS-82 is a commercial sodium azide type of gas-generating agents and its powder composition and pellet were supplied from Nippon Kayaku Co., Ltd. 6 ϕ of the pellet were prepared by pressing the powder compositions in the metal mold.

2.1.2 Igniting material

Pb_3O_4 and Si are of reagent grade and were purchased from Wako Pure Chemical Industries, Ltd. An igniting material was prepared by mixing Pb_3O_4 (70

Table 3 Maximum pressure rise and maximum rate of pressure rise in the deflagration of tetrazole-oxidizer compositions
Sample: 6 φ pellet of the tetrazole-oxidizer composition, 0.5 g
Igniter: 0.2 g

Composition Tetrazole (wt.%) - Oxidizer (wt.%)	Pmax (kg/cm²)	(dP/dt)max (kg/cm²·s)
AS-82	52.4	697
1 HTK (47.1) - KNO_3 (52.9)	45.2	1248
HAT (37.5) - KNO_3 (62.5)	55.9	727
HATNa (43.1) - KNO_3 (56.9)	56.1	888
TCA (56.6) - KNO_3 (43.4)	31.2	225
BHTK (51.5) - KNO_3 (48.5)	58.2	1560
BHT2MA (26.1) - KNO_3 (73.9)	42.8	142
BHT2NH_3 (34.7) - KNO_3 (65.3)	68.6	582
BHT2AGAD (32.1) - KNO_3 (67.9)	52.1	281
ZTNa (51.0) - KNO_3 (49.0)	56.2	635
GZT (34.0) - KNO_3 (66.0)	52.5	730

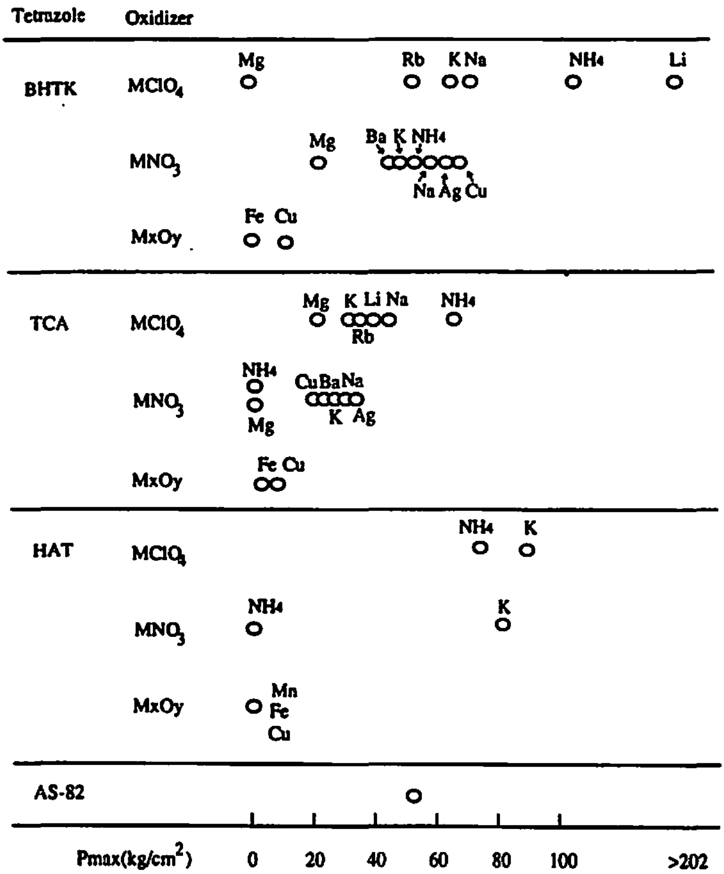

Fig. 1 Effects of tetrazoles and oxidizers on maximum pressure rise in the deflagration of the tetrazole-oxidizer composition
Sanmple: 6 φ pellet of the tetrazole-oxidizer composition, 0.5 g
Igniter: 0.2 g

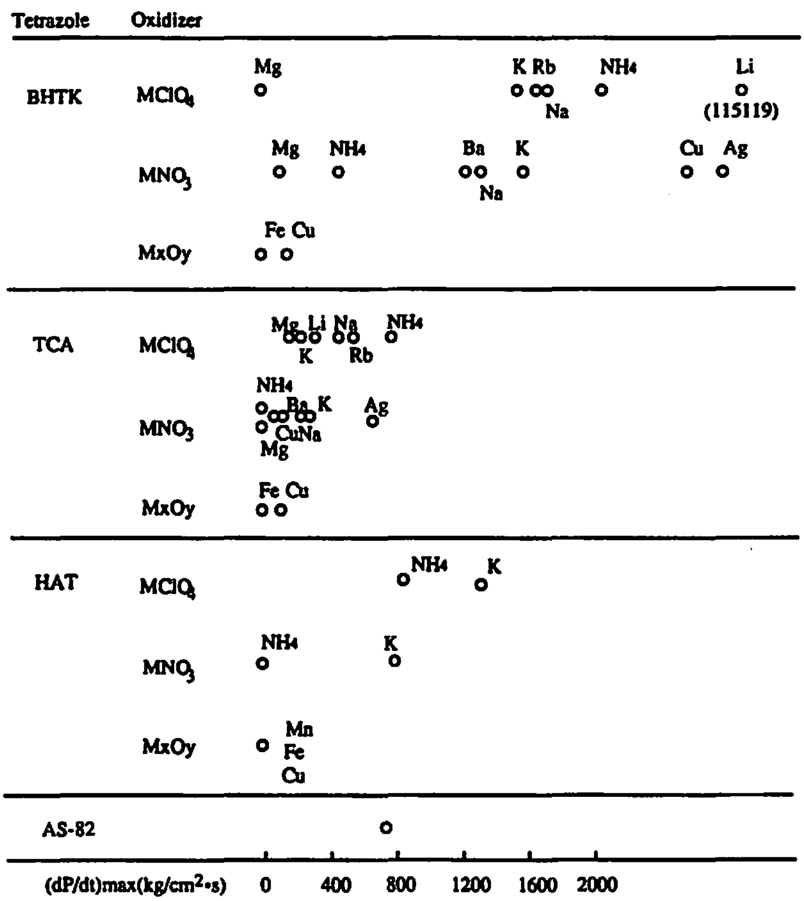

Fig. 2 Effects of tetrazoles and oxidizers on maximum pressure rise in the deflagration of the tetrazole-oxidizer composition
Sanmple: 6 ϕ pellet of the tetrazole-oxidizer composition, 0.5 g
Igniter: 0.2 g

wt.%) and Si (30wt.%) carefully with a brush.

2.2 Apparatus

Detail of small scale deflagration test apparatus was given in the previous paper[5].

2.3 Test procedure

0.5 g of a sample is introduced in the chamber and 0.2 g of the igniting material is then placed on it so as to be in sufficient contact with the nichrome wire heater. The vessel is closed and the firing leads are connected to the terminals of the electrodes. The sample is then ignited by operating the dynamo at a remote place. Time-pressure profiles by the deflagration of gas-generating agents in the chamber are measured.

3. Results and Discussion

Table 3 shows the deflagration properties of the tetrazole-KNO_3 (oxidizer) compositions. As shown in Table 3, the maximum pressure rise of the compositions using $BHT2NH_3$, BHTK, HATNa, ZTNa, HAT and GZT with oxidizer are larger than that of AS-82. The maximum rate of pressure rise of the compositions using BHTK, 1HTK, HATNa, GZT and HAT with oxidizer are also larger than that of AS-82.

Fig. 1 and 2 show the effects of tetrazoles and oxidizer on the maximum pressure rise and the maximum rate of pressure rise in the deflagration of the tetrazole-oxidizer compositions.

From Fig. 1, we can say that BHTK and HAT as tetrazoles gives a larger value of the maximum pressure rise by deflagration than TCA and that NH_4ClO_4, $KClO_4$ and $NaClO_4$ as oxidizer give larger values of the maximum pressure rise by deflagration than other oxidizers.

From Fig. 2, we can also say that BHTK as a tetrazole gives a larger value of the maximum rate of pressure rise by deflagration than TCA and HAT and that NH_4ClO_4, $KClO_4$, $RbClO_4$, $Ba(NO_3)_2$, KNO_3 and $NaNO_3$ etc. as oxidizers give higher values of maximum rate of pressure rise by deflagration.

BHTK-$LiClO_4$ composition gives too high value of the maximum pressure rise and the maximum rate of pressure rise by deflagration. Therefore the composition may be difficult to use from the stand point of safety.

4. Conclusion

In order to obtain some information on the new gas-generating agents for airbag systems, we have attempted to evaluate the deflagration properties for the tetrazole-oxidizer compositions, one of the most promising new gas-generating agents in the near future, by examining the time-pressure behavior obtained from the deflagration.

As the results, we can say from the stand point of deflagration properties that some tetrazole-oxidizer compositions may be applicable as new gas-generating agents for airbag systems.

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References

1) Jian Zhou Wu, Haruhisa Yuzawa, Toshio Matsuzawa, Mitsuru Arai and Masamitsu Tamura, Kayaku Gakkaishi, 55, 66 (1994)
2) Jian Zhou Wu, Mitsuru Arai and Masamitsu Tamura, Kayaku Gakkaishi, 55, 74 (1994)
3) Jian Zhou Wu, Mitsuru Arai, Toshio Matsuzawa and Masamitsu Tamura, "Thermal decomposition behavior of tetrazole compositions", Kayaku Gakkaishi (in contribution)
4) Jian Zhou Wu, Mitsuru Arai, Toshio Matsuzawa and Masamitsu Tamura, "Pressure release behavior of tetrazole compositions", Kayaku Gakkaishi (in contribution)
5) Jian Zhou Wu, Mitsuru Arai, Toshio Matsuzawa and Masamitsu Tamura, "Study on new gas-generating agent (I) A small scale deflagration test for evaluation of deflagration properties for tetrazole-oxidizer compositions", Kayaku Gakkaishi, 55, 96 (1994)

新規ガス発生剤に関する研究（II）
テトラゾール組成物の爆燃特性評価

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自動車エアバッグ用新規ガス発生剤として注目されているテトラゾール類－酸化剤組成物の爆燃特性を小型爆燃試験装置により調べた。

その結果，いくつかのテトラゾール類－酸化剤組成物は，爆燃特性としては，現行のアジ化ナトリウム系ガス発生剤より優れており，エアバッグ用新規ガス発生剤として適用できる可能性があると言える。

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