Article

Study on the reduction of possible harmful gases from gas generating agents (I):

Effect of addition of organic compounds

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Abstract

Various organic additives to the gas generating agent composition were tested as an attempt to prevent possible harmful gases caused by the deflagration of gas generating agents of airbag inflators. The organic additives chosen in this study were classified into two categories: 1) compounds that thermally decompose to generate NH_2 radicals; and 2) compounds that thermally decompose to generate HNCO. Quantitative analyses of product gases were conducted after deflagration tests inside a calorimeter bomb and a 60 liter tank. As a result of the addition of organic compounds to guanidine salt of 1,5'-bi-1H-tetrazole (15 BG) / $KClO_4$ stoichiometric ratio mixture in calorimeter bomb test, approx. 80 % reduction in ($NO+NO_2$) and over 95 % reduction of Cl_2 have been achieved when 5 wt% of urea or guanidine carbonate (GC) was added, although there was generally an increase in CO concentration. In 60 liter tank test, an addition of 5 wt% urea resulted in 67.5 % reduction in ($NO+NO_2$), 50 % reduction in HCN and almost 100 % reduction in HCl, together with a reduction in maximum temperature of approximately 100 K inside the tank, when 60 mg lead trinitroresorcinate (tricinate) pellet was used. When 40 mg tricinate pellet was used, an addition of 5 wt% cyanuric acid or 5 wt% GC, together with an addition of 5 wt% urea also resulted in reductions in ($NO+NO_2$) concentration and temperature inside the tank.

1. Introduction

Gas generating agent for an automobile airbag inflator is required to, other than generate a large amount of gas within a short period of time, generate gas that is non-toxic and is of relatively low temperature, in order to protect the safety of the passengers.

Table 1 shows the list of recommended values of occupational exposure limits[1] for harmful gases that could be generated during the deployment of the airbags when non-azide gas generating agents are to be used. Non-azide gas generating agents, whose fuel components are composed of tetrazole compounds, are susceptible to producing harmful nitrogen oxides (NOx) because of high nitrogen atom content in tetrazole compounds. Even more NOx are likely to be produced when oxidizers are composed of metal nitrates, e.g. strontium nitrate ($Sr(NO_3)_2$). Meanwhile, harmful gaseous chlorine compounds, e.g. HCl and Cl_2, are likely to be produced when oxidizers composed of metal perchlorates, e.g. potassium perchlorate ($KClO_4$), are used. Even though the generated gas will be diluted upon release into the compartment of an automobile, concentration of gases, e.g. HCl and Cl_2 need to be kept low because of their low exposure limit, which are 5 ppm and 0.5 ppm respectively[1].

Selecting guanidine salt of 1,5'-bi-1H-tetrazole (15 BG) (Fig. 1) as a fuel and $KClO_4$ as an oxidizer of a simulated gas generating agent composition, the authors have attempted to, through the addition of organic solid additives, reduce the toxicity and the temperature of generated gas that could be caused by the deflagration of 15 BG/$KClO_4$ stoichiometric ratio mixture (mixing ratio: 37.5 wt% / 62.5 wt%), a mixture which has previously shown highly energetic behaviors[2].

Table 1 Occupational exposure limits in Japan (Japan Society for Occupational Health[1)]).

	CO [ppm]	CO_2 [ppm]	NO_2 [ppm]	NH_3 [ppm]	HCN [ppm]	HCl [ppm]	Cl_2 [ppm]	HNO_3 [ppm]
Exposure limits	50	5000	(Pending)	25	5	5 (Ceiling)	0.5 (Ceiling)	2

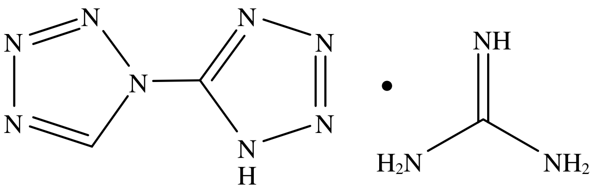


Fig. 1 Chemical structure of guanidine salt of 1,5'-bi-1H-tetrazole (15 BG).

2. Additives examined

The candidate organic additives for the reduction of harmful gas products could be divided into two categories:

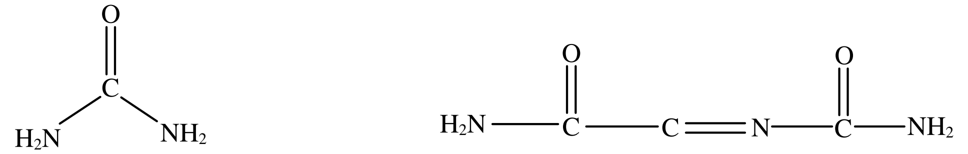
1) Organic compounds that thermally decompose to release NH_2 radicals. Urea, azodicarbonamide (ADCA), aminoguanidine bicarbonate (AGBC) and guanidine carbonate (GC), as shown in Figs. 2 (a) - (e), have been selected as the compounds in this category. NH_2 radicals produced from decomposition are estimated to reduce nitrogen monoxide (NO) through the mechanism[3)] displayed in Fig. 3 (a).

Urea (Fig. 2(a)) is a widely used additive for reduction of NOx in exhaust gases of industrial combustion systems. As for the application as NOx reducing agents of energetic materials, Pesce-Rodriguez *et al.*[4)] have found that an addition of urea powder to a solid gun propellant has resulted in a significant reduction in NOx production during pyrolysis, together with a reduction in calculated adiabatic flame temperature. A proposed decomposition mechanism for urea[5)] is given in Fig. 4 (a).

As an alternative attempt for toxic gas reduction, Maeno *et al.*[6)] have reported that an addition of vaporized ADCA (Fig. 2 (b)), an energetic material mainly used as a foaming agent, has achieved up to nearly 100 % decrease in NO concentration in simulated exhaust gases at 1023 K. Waki *et al.*[5)] proposed a decomposition mechanism of ADCA, as shown in Fig. 4 (b).

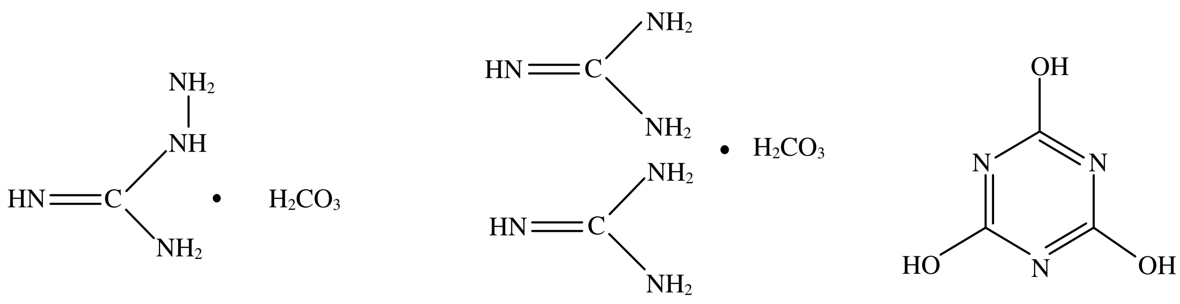
In this study, besides testing the effectiveness of the addition of urea and ADCA powders to 15 BG/$KClO_4$ stoichiometric ratio mixture, we have proposed AGBC and GC as new candidate materials in this category, since they are suggested, from the chemical structures as shown in Figs. 2 (d) and (e), to release NH_2 radicals upon decomposition.

2) Organic compounds that thermally decompose to release HNCO, which is suggested to reduce NO through subsequent chemical reactions. Cyanuric acid, as shown in Fig. 2 (c), was selected as a candidate material in this category. Siebers *et al.*[7)] have reported that an addition of vaporized cyanuric acid have resulted in up to nearly 100



(a) Urea

(b) Azodicarbonamide (ADCA)



(c) Aminoguanidine bicarbonate (AGBC)

(d) Guanidine carbonate (GC)

(e) Cyanuric acid

Fig. 2 Chemical structures of organic additives examined in this study.

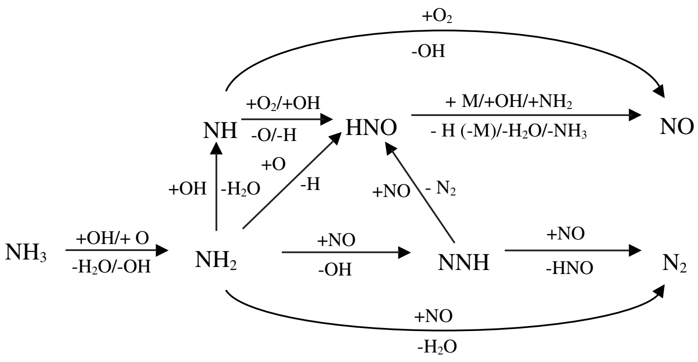


Fig. 3 (a) Schematic diagram of estimated NO reduction mechanism[3] in which NH_2 radical is involved.

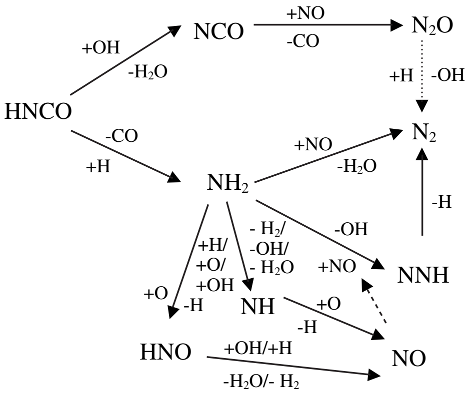
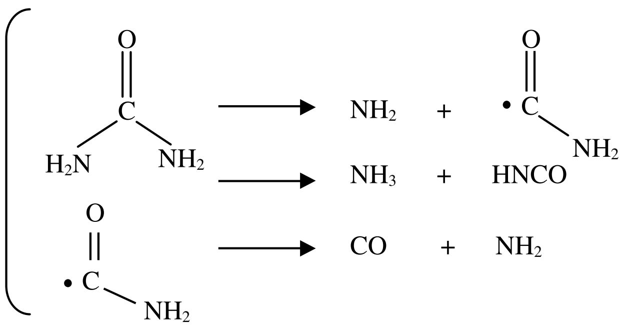
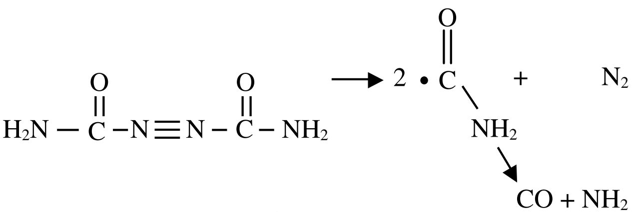


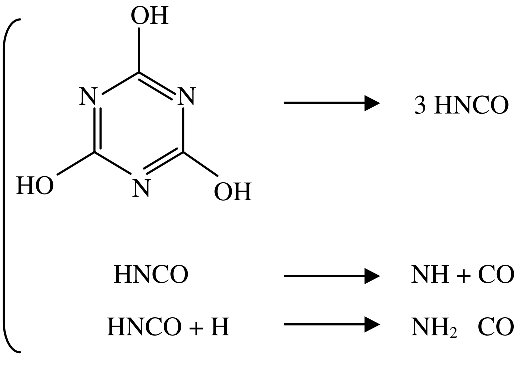
Fig. 3 (b) Schematic diagram of estimated NO reduction mechanism[3] in which HNCO radical is involved.



(a) Urea



(b) ADCA



(c) Cyanuric acid

Fig. 4 Initial decomposition mechanisms of organic additives.

% reduction of NO in exhaust gases under the presence of CO and H_2O, at a temperature of approx. 973 K. They have also reported that the addition of vaporized cyanuric acid in the presence of Fe_2O_3 have resulted in the lowering of temperature. A proposed initial decomposition mechanism[5] is given in Fig. 4 (c). Produced HNCO reacts further to form NH and NH_2 radicals, which will then reduce NO, according to the proposed mechanism[3] as given in Fig. 3 (b). In this study, a small portion of cyanuric acid powder was added directly to 15 BG/$KClO_4$ stoichiometric ratio mixture.

3. Experimental

3.1 Reagents used

15 BG was selected as the fuel component of gas generating agent mixture and $KClO_4$ was selected as the oxidizer. Additives examined were urea, cyanuric acid, ADCA, AGBC, and GC. All of the powder reagents were first ground by using separate porcelain ball mills, sieved through Japanese Industry Standard (JIS) 100 mesh (149 μm pass) sieve, dried *in vacuo* at 318 K for 24 hours through evacuated dryer and finally stored in desiccators for more than 24 hours.

3.2 Closed bomb test

Measurements of heat of explosion and the quantitative analyses of product gases during small-scale deflagration tests were conducted by using a vacuum adiabatic bomb calorimeter.

Selecting 15 BG/$KClO_4$ stoichiometric ratio mixture as a standard sample mixture, one of the additives was added in small portion (within the range of 0.5 - 10 wt%). Then, 1 g of a given sample mixture was hand-pressed into a cylindrical pellet, together with a nichrome wire embedded in the sample. The pellet was then installed inside the 100 ml calorimeter bomb. After the content of the bomb was purged twice by helium gas (purity > 99.99 %), the pellet was ignited under 3 MPa helium atmosphere. Following

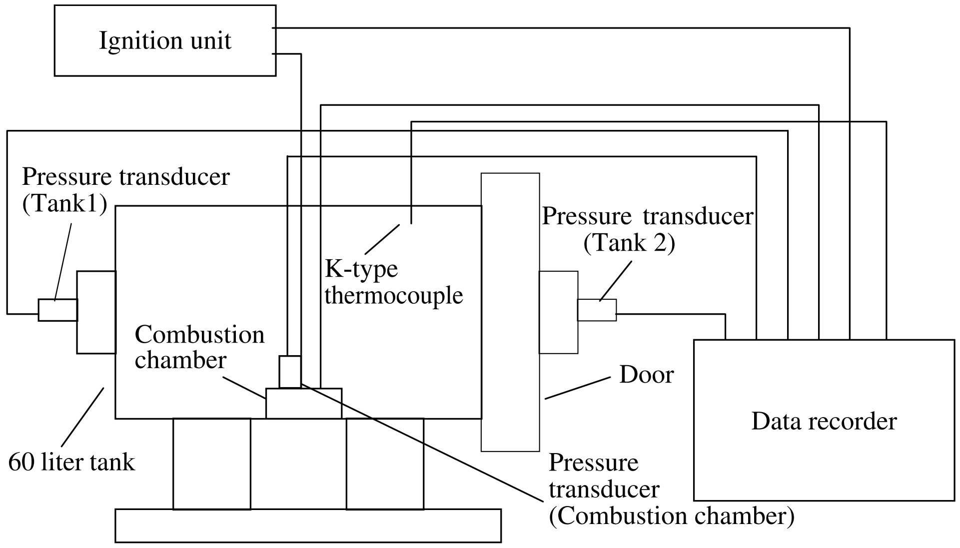


Fig. 5 Schematic diagram of the 60 liter tank test system.

the measurement of the heat of explosion, the product gas was collected into a 7 liter tedlar bag, and the concentrations of product gases, i.e. CO, CO_2, NO_2, $(NO+NO_2)$, NH_3, HNO_3, HCN, HCl and Cl_2 were measured by using gas detector tubes (Gastec Co., Ltd.).

3.3 60 liter tank test

The schematic diagram of the 60 liter tank test system is given in Fig. 5. The compositions of the mixtures examined in this study are listed in Table 2. For each set of mixture, 15 of 1 g cylindrical pellets (diameter: 14.7 mm, height: 3 - 4 mm each) were prepared by using a hydraulic press. The pressure applied was 10 MPa for each pellet. The pellets were then inserted into a combustion chamber. A donut-shaped space filler (diameter: 36 mm (outside), 19 mm (inside); height: 10 mm) was inserted beforehand into a combustion chamber for each set of experiment, in order to compensate for the lack of volume occupied by the pellets. After installing the combustion chamber inside the 60 liter tank, the pellets inside the closed combustion chamber were ignited by using a set of B/KNO_3 and lead trinitroresorcinate (tricinate) igniters. The weight of B/KNO_3 igniter was 1 g for each test, but the weight of tricinate pellet varied: 60 mg in trial 1 and 40 mg in trial 2.

Measurements were conducted with regard to the following items:

1) Changes in pressures at two locations inside the tank, $\Delta P_{\mathrm{tank1}}$ and $\Delta P_{\mathrm{tank2}}$, and the change in pressure inside the combustion chamber, ΔP_{Comb}, through pressure transducers (Kyowa Dengyo, Co. Ltd.; PGM-10KC for $\Delta P_{\mathrm{tank1}}$ and $\Delta P_{\mathrm{tank2}}$, and PGM-500 KE for ΔP_{Comb});
2) Temperature inside the tank, through K-type thermocouple; and
3) Quantitative analyses of product gas inside the tank, i.e. H_2O, CO, CO_2, NO_2, $(NO+NO_2)$, NH_3, HNO_3, HCN, HCl and Cl_2, through detector tubes (Gastec, Co. Ltd.), after collecting product gas into a 7 liter tedlar bag.

As for items 1) and 2), the data were recorded on DL-708E data recorder (Yokogawa Denki, Co. Ltd.) in trial 1, and AR-4800 data recorder (Yokogawa Denki, Co. Ltd.)

Table 2 Mixing ratios of simulated gas-generating agents for 60 liter tank test.

No.			Test 1		Test 2			
			1-1	1-2	2-1	2-2	2-3	2-4
Amount of Tricinate pellet used as igniter [mg]	(B/KNO_3 fixed at 1 g)		60		40			
Fuel	15 BG	[wt%]	37.5	37.5	37.5	37.5	37.5	37.5
Oxidizer	$KClO_4$	[wt%]	62.5	62.5	62.5	62.5	62.5	62.5
Organic	Urea	[wt%]	–	5	–	5	–	–
Compounds	Cyanuric acid	[wt%]	–	–	–	–	5	–
	GC	[wt%]	–	–	–	–	–	5

4. Results and discussion

4.1 Closed bomb test

Figure 6(a) shows the effect of organic additives on $(NO+NO_2)$ concentrations in product gases during closed bomb tests. In this study, mean concentration of $(NO+NO_2)$ was approx. 120 ppm for standard 15 BG/$KClO_4$ stoichiometric ratio mixture. There were increases in $(NO+NO_2)$ concentrations with the addition of urea, cyanuric acid or GC, when the weight contents of the additives were within the range of 0.5 - 2 wt%. However, concentrations of $(NO+NO_2)$ began to decrease when the weight contents of the additives were approx. 3 wt%, and the addition of 5 wt% urea or GC has resulted in approx. 80 % reduction in $(NO+NO_2)$ concentration. This may be due to the presence of NH_2 radicals, although up to 200 ppm of $(NO+NO_2)$ was observed when 5 wt% cyanuric acid was added. Approx. 50 % reduction in $(NO+NO_2)$ concentration was achieved when 5 wt% AGBC was added, but an addition of ADCA resulted instead in a slight increase in $(NO+NO_2)$ concentration. The fact that $(NO+NO_2)$ concentrations have increased when oxygen balance positive compounds such as urea, cyanuric acid or GC was added in a very small amount (0.5 - 2 wt%), may suggest that the reduction in NOx concentration could not simply be

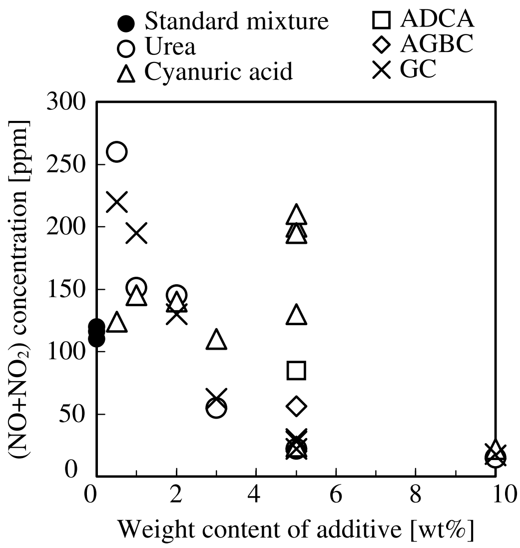


Fig. 6 (a) Experimental result of $(NO+NO_2)$ concentration in closed bomb test- Effect of organic additives.

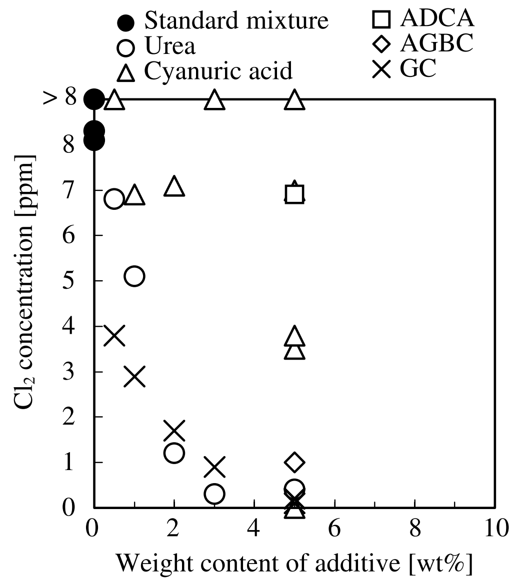


Fig. 6 (b) Experimental result of Cl_2 concentration in closed bomb test- Effect of organic additives.

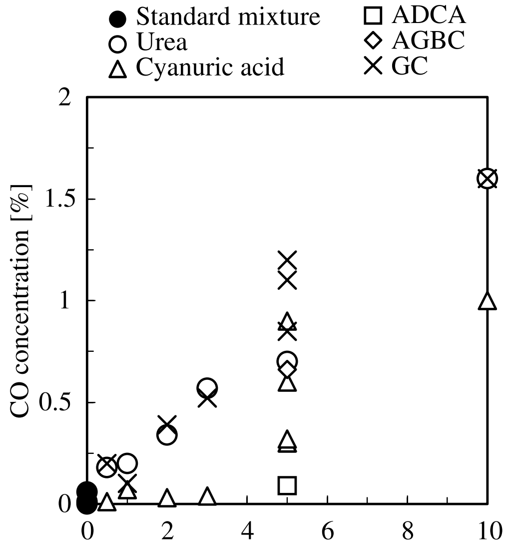


Fig. 6 (c) Experimental result of CO concentration in closed bomb test- Effect of organic additives.

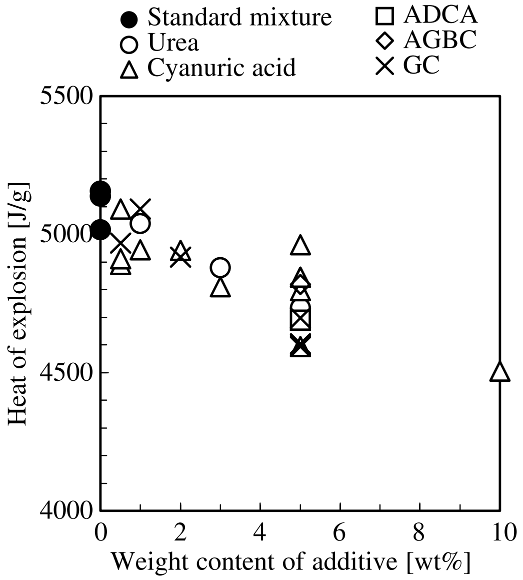
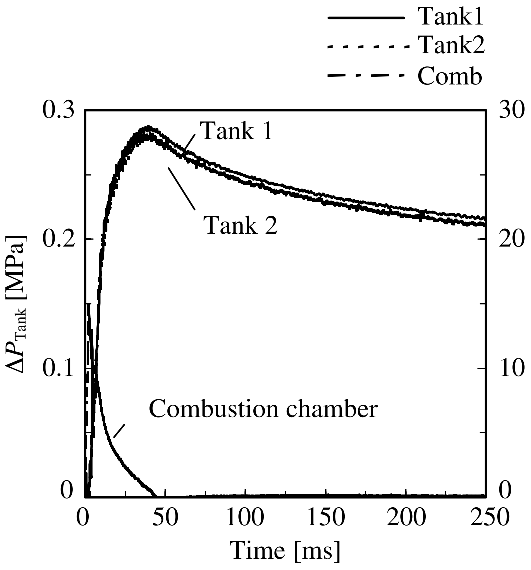


Fig. 6 (d) Experimental result of heat of explosion in closed bomb test- Effect of organic additives.

explained in terms of oxygen balance.

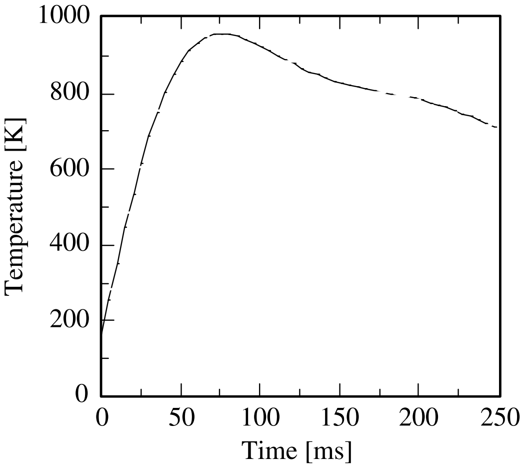
Figure 6(b) shows the effect of organic additives on Cl_2 concentrations, and Fig. 6(c) shows the effects of organic additives on CO concentrations. Over 95 % reduction in Cl_2 concentration has been achieved when only 5 wt% of urea, GC or cyanuric acid was added, which could not be explained simply by the addition of inert chemical compound.

Figure 6(d) shows the effect of organic additives on heats of explosion. Heats of explosion have decreased for all the additives examined, which suggests the possibility of reduction in flame temperature and consequently the reduction in temperature of product gas.



(a)

Fig. 7 (a) Pressure-time curve of 60 liter-tank test for 15 $BG/KClO_4$ mixture at stoichiometric ratio (igniter: B/KNO_3 1 g, tricinate 60 mg).



(b)

Fig. 7 (b) Temperature - time curve of 60 liter tank test for 15 $BG/KClO_4$ mixture at stoichiometric ratio.

Table 3 Peak change-in-pressure and temperature reached and concentration of gases inside the combustor and the tank for the 60 liter tank test (igniter: B/KNO_3 1 g, tricinate pellet 60 mg).

No.	1 - 1		1 - 2	
Mixture examined	15 $BG/KClO_4$ (Standard mixture)		15 $BG/KClO_4$/urea	
ΔP_{Comb} (peak) [MPa]	14.9		15.0	
(Time required [ms])	(2.2)		(2.5)	
ΔP_{Tank} (peak) [MPa]	Tank 1	Tank 2	Tank 1	Tank 2
(Time required [ms])	0.287	0.282	0.240	0.238
	(39.5)	(36.8)	(46.8)	(47.9)
Peak temperature (Tank) [K]	953.6		853.1	
(Time required [ms])	(59.6)		(69.9)	
CO [%]	0.55		1.00	
CO_2 [%]	2.2		2.1	
NO_2 [ppm]	380		60	
$NO+NO_2$ [ppm]	400		130	
NH_3 [ppm]	Below detection-limit		1.5	
HNO_3 [ppm]	Not available		Not available	
HCN [ppm]	8.0		4.0	
HCl [ppm]	>20		Below detection-limit	
Cl_2 [ppm]	Not available		Not available	

4.2 60 liter tank test

Figure 7(a) shows the pressure-time curves within the combustion chamber and at two locations within the tank, and Fig. 7(b) shows the temperature curve within the tank during the 60 liter tank test (trial 1) for 15BG/KClO$_4$ stoichiometric ratio mixture. ΔP_{Comb} has reached its maximum at approx. 15 MPa after 2.2 ms; and $\Delta P_{\mathrm{tank1}}$ and $\Delta P_{\mathrm{tank2}}$ have reached maximum values at approx. 0.29 MPa within 40 ms. Meanwhile, the temperature within the tank has reached its maximum at approx. 953 K after 60 ms.

Table 3 shows the results of trial 1. The mixture with 5 wt% urea have also shown high performance in $\Delta P_{\mathrm{tank1}}$ and $\Delta P_{\mathrm{tank2}}$. It was also shown that the peak temperature inside the tank has decreased by approx. 100 K, which may probably be due to the reduction in flame temperature with the addition of urea. According to quantitative gas analyses in trial 1, addition of urea have led to 67.5 % reduction in measured (NO+NO$_2$) concentration, 50 % reduction in HCN concentration and almost 100 % reduction in HCl concentration. Meanwhile, there were increases in the measured concentrations of CO and NH$_3$, which may probably be due to the decomposition of urea.

Table 4 shows the results of trial 2 of the 60 liter tank test. Comparing the results with trial 1, there was a tendency of a delay in the time taken for maximum pressure inside the combustion chamber and the tank. There was also a tendency of increases in CO, (NO+NO$_2$), HCl and Cl$_2$ concentration, together with a reduction in maximum temperature inside the tank. In this trial, addition of urea has led up to approx. 75 % reduction in (NO+NO$_2$) concentration in product gas. Addition of cyanuric acid or GC has also led to the reduction in (NO+NO$_2$) concentration, especially for GC-added mixture which displayed nearly 50 % reduction. HCN concentration also decreased especially when urea was added, with 90 % reduction in (NO+NO$_2$) and 85 % reduction in HCN, although HCl concentrations did not decrease for all mixtures in this trial. Peak temperatures inside the tank also decreased for all the mixtures with organic additives as compared to the standard mixture. Especially for the urea-added mixture, temperature inside the tank decreased by approx. 150 K in this trial.

5. Conclusions

To prevent possible harmful gases caused by the deflagration of gas generating agents during deployment of the airbags, each organic additive out of urea, azodicarbonamide, cyanuric acid, guanidine carbonate, or aminoguanidine bicarbonate was added separately to a stoichiometric 15 BG/KClO$_4$ mixture. Quantitative analyses of product gases were conducted after deflagration inside a 100 ml closed bomb and the combustion chamber of a 60 liter tank. The results have indicated the effectiveness of adding 5 wt% of urea, guanidine carbonate, or cyanuric acid for the reduction of (NO+NO$_2$) concentration and HCN concentration, together with the reduction in temperature of exhaust gases.

Table 4 Peak change-in-pressure and temperature reached and concentration of gases inside the combustor and the tank for the 60 liter tank test (igniter : B/KNO$_3$ 1 g, tricinate pellet 40 mg).

No.	2 - 1		2 - 2		2 - 3		2 - 4	
Mixture examined	15 BG/KClO$_4$ (Stoichiometric)		15 BG/KClO$_4$/ Urea		15 BG/KClO$_4$/ Cyanuric acid		15 BG/KClO$_4$/GC	
ΔP_{Comb} (peak) [MPa]	14.3		13.9		13.3		13.9	
(Time required [ms])	(3.9)		(4.8)		(4.5)		(4.5)	
ΔP_{Tank} (peak) [MPa]	Tank 1	Tank 2	Tank 1	Tank 2	Tank 1	Tank 2	Tank 1	Tank 2
(Time required [ms])	0.289	0.292	0.247	0.254	0.248	0.251	0.260	0.260
	(46.8)	(47.0)	(58.5)	(58.6)	(58.6)	(58.6)	(56.6)	(56.4)
Peak temperature (Tank) [K]	883.2		735.2		847.2		780.5	
(Time required [ms])	(105.2)		(147.3)		(124.5)		(149.1)	
CO [%]	0.70		1.15		0.95		1.00	
CO$_2$ [%]	2.8		2.4		2.7		2.5	
NO$_2$ [ppm]	680		20		370		200	
NO+NO$_2$ [ppm]	780		180		450		400	
NH$_3$ [ppm]	Below detection limit		30		Below detection limit		Below detection limit	
HNO$_3$ [ppm]	Below detection limit		Below detection limit		Below detection limit		Below detection limit	
HCN [ppm]	100		10		$> 7^*$		$> 7^*$	
HCl [ppm]	2.5		4.0		2.5		4.5	
Cl$_2$ [ppm]	> 8		> 8		> 8		> 8	

* Maximum detection concentration: 7 ppm

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ガス発生剤より発生しうる有害ガスの防止に関する研究（第一報）

有機化合物の添加効果

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エアバッグ展開用ガス発生剤の爆燃により発生しうる有害ガスの防止を目的として，種々の有機化合物系添加物を検討した。この研究において選択した添加物は2種類に分類される。即ち，１）熱分解してNH_2ラジカルを発生する化合物，及び２）熱分解してHNCOを発生する化合物である。熱量計ボンブ内及び60 リットルタンク内においてガス発生剤混合物を爆燃後，生成ガスの定量分析を行った。熱量計ボンブ内において，化学量論比の1,5'-ビ-1H-テトラゾール・グアニジン塩（15 BG）/$KClO_2$混合物に有機化合物を添加した結果，一般的にCO濃度測定値が増大する傾向が見られたものの，尿素またはグアニジン炭酸塩（GC）を5 wt％添加した場合に（$NO+NO_2$）濃度測定値の80 %の低減及びCl_2濃度測定値の95 %以上の低減が達成された。60 リットルタンク試験においては，点火薬としてトリニトロレゾルシン鉛（トリシネート）のペレットを60 mg用いた場合に，尿素を5 wt％添加したことにより，（$NO+NO_2$）濃度測定値の67.5 %の低減，HCN 濃度測定値の50 %の低減及びHCl濃度測定値のほぼ100 %の低減と同時に，タンク内において約100 Kの低下が見られた。トリシネートのペレットを40 mg用いた場合，尿素の5 wt％添加のほか，シアヌール酸またはGCを5 wt％添加した場合でも，（$NO+NO_2$）濃度測定値の低減及びタンク内温度の低下が見られた。

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