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Hazard Evaluation of Raw Pyrotechnics Mixtures Regarding Cause Investigation of Explosive Incident*

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[**ABSTRACT**] In order to conduct the cause investigation of an explosive incident by raw pyrotechnics mixtures, various hazard evaluation tests were performed. Explosions occurred during manufacturing fire-works, which consisted of potassium perchlorate ($KClO_4$), aluminum (Al) powder and antimony trisulfide (Sb_2S_3). Identification of the explosive materials was conducted by sampling of soil at the explosion places including craters and analyzing them. Though we found it was very stable thermally, at least up to 500 ℃ based on the results of DSC and TG-DTA, it appeared high sensibility in friction and falling impacts. By the gap test (sympathetic detonation test), we found it was easy to develop sympathetic detonation. Therefore, more careful treatment is needed when we manufacture, treat or consume these materials.

[**KEYWORDS**] hazard evaluation test; fire-works; sympathetic explosion
[**CLASSIFICATION CODE**] X932

烟火药原材料混合物爆炸事故原因探究

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[**摘 要**] 利用几种危险性评价方法,研究烟火药剂原材料混合物引发爆炸事故的原因。爆炸事故发生于烟花制造过程中,通过采集、分析爆炸现场炸坑的土壤,发现爆炸物质由高氯酸钾($KClO_4$)、铝(Al)粉及硫化锑(Sb_2S_3)组成。尽管DSC、TG-DTA数据表明该混合物热稳定性好,分解温度高达500 ℃,但是,其摩擦感度及撞击感度却很高。间隙试验(殉爆试验)显示该混合物容易发生殉爆。因此,在制造、处理以及使用这些物质时必须格外谨慎。

[**关键词**] 危险性评估试验;烟花爆竹;殉爆

Introduction

Mixture of potassium perchlorate ($KClO_4$) and aluminum (Al) powder was used for fire-works, blasting caps widely, and it was important to study characteristics of these materials for safety treatments. And characteristics of mixture depended on the ratio of mixture and its grades[1]. $KClO_4$ was imported from Asian countries, but it might have sometimes high impurity material.

We experienced an explosive incident of these materials in Japan. Cause investigation of explosion was conducted by governments including local fire department and the National Research Institute of Fire and Disaster (NRIFD)[2-4].

1 Explosive incident

Explosive incident occurred in Kagoshima, Japan, in April 2003. Summary of incidents was reported[2]. Explosive incident occurred at a factory where they made various fire-works, and the incident killed ten workers and four workers injured. The blast of explosions damaged houses about 500 m away from the factory.

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When the explosion occurred in this factory, they were making fire-works, socalled 'Niagara fall'. Because of rain, several workers were in the mixing house where first explosion occurred, which was assured by information from witnesses who worked at the factory. So we thought that 'Niagara fall' was the most possibility material to cause the first explosion, and then several induced explosions might occur. The atmospheric vibration meter of Kagoshima Meteorological Observatory recorded four vibration waves by detonations.

In this factory, there were two storage houses for storing dangerous materials of Fire Service Law. One was for sulfur and second one was for oxidizing solids. However, fire-works (raw, products) might be also stored in the same houses, and it was against the regulation.

The explosions made at least four craters. Crater sizes (approximate value) and estimated TNT equivalence calculation results were shown in Tab. 1.

Tab. 1 Summary of craters which were made after explosion

Place	Size of crater (Diameter × Depth)/(m × m)	TNT equivalence/kg
Mixing house	2.00 × 0.50, 2.70	15.6, 10.0
Storage house A	0.80 × 0.32	11.9
Storage house B	2.20 × 0.30	20.8
Momentary magazine	4.00 × 1.00	125.0

2 Experimental

2.1 Identification of explosion material in the incidents

'Niagara fall' consisted of $KClO_4$, Al powder and about 1 % of antimony trisulfide (Sb_2S_3). And Sb_2S_3 was not used for other fire-works in this factory. Therefore existence of Sb_2S_3 at explosion places meant that exploded materials consisted of Sb_2S_3. Therefore we sampled soil at eight points including craters, that is, five places where explosion might occur and two points where no explosion occurred and a point where was very far away from explosion place.

Measurement of antimony in soil was conducted using the ICP (inductive coupled plasma) and the atomic absorption analysis with hydrogenation unit (Thermo Electron Co., Ltd.). There were of high concentration of antimony (Sb) from samples which were obtained from craters, and other places gave low concentration. The maximum value was 235×10^{-6} at the crater of mixing house. Average value of three points of no explosion was 0.6×10^{-6} (Tab. 2). Average concentration of Sb in the earth's crust was 200×10^{-9}[5]. Therefore, we concluded that it was possible material which consisted of Sb, that is, 'Niagara fall' exploded at the first stage in this incident.

Tab. 2 Sb concentration of samples taken in the factory

Sample, place	Sb concentration/10^{-6}
Crater, mixing house	30-235
Crater, Storage A	13-54
Crater, Storage B	2.3
Soil, no explosion	0.5-0.6

2.2 Samples used in the experiments

According to the recipe of the manufacturer, we prepared two samples with mixing by hands and machine. In this factory imported $KClO_4$ was used, so we used imported $KClO_4$ (KP-I), and used domestic material (KP-D) for comparison. Imported material had slightly more amount of impurity materials than domestic material. Specifications for purity of imported potassium was 99.0% though 99.6% for domestic. Major impurity material was potassium chlorate ($KClO_3$), and the difference of concertation for both materials were about ten times. Component ratio was an approximately value and details of Al powder, such as kind, grade, powder size, was unknown due to closed information of the manufacturer.

2.3 Experimental methods

2.3.1 DSC and TG-DTA

The DSC (Thermoplus DSC 8230, Rigaku. Co., Ltd.) tests were conducted with the following conditions: 1-2 mg of sample, 10 K/min of scanning rate, 50 mL/min nitrogen supply rate, and SUS closed sample cell was used, and the temperature was scanned from room temperature to 750 ℃. The TG-DTA (Thermoplus TG 8120, Rigaku. Co., Ltd.) tests were conducted with 5 mg samples, 10 K/min of scanning rate, 50 mL/min nitrogen supply rate, an SUS closed sam-

ple cell was used, the temperature was scanned from room temperature to 750 ℃.

2.3.2 Ignition tests (cerium/iron sparks test, small gas flame test)

The cerium/iron sparks test was conducted with the Standards ES—12 of the Japanese Explosives Society (JES). A pistol-shaped cerium/iron sparks gas lighter was used for ignition of 3 mL sample on asbestos sheet.

The small gas flame test was conducted using 3 mL sample by a 20 mm length flame of Bunsen burner on asbestos sheet following ES—12 of the JES.

2.3.3 Ignition temperature test (Krupp method)

The ignition temperature tests were conducted with the Standards ES—11, ignition point test method of the JES. About 20 mg sample in a steel cylinder (crucible) were heated in an electric furnace.

2.3.4 Fall hammer test

The fall hammer test was conducted following the test manual written in JIS—K 4810 (testing methods of explosives) and ES—21 (1) of the JES. A 5 kg hammer was dropped from the height between 0.05 m and 0.50 m.

2.3.5 Friction sensibility test

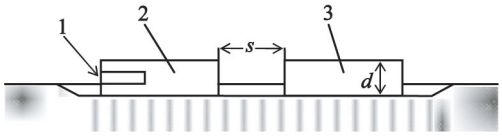
The BAM friction test was used, which was also written in JIS. Therefore tests were conducted following the test manual written in JIS—K 4810. About 0.1 g sample was used for the test.

2.3.6 Mk Ⅲ ballistic test

The Mk Ⅲ ballistic tests were conducted for evaluating explosive properties, following the Standards ES—44(2), JES. 5 g sample was placed in a 10 mL or 15 mL sample tube. A No. 6 detonator was used. TNT was used as reference material.

2.3.7 Sympathetic detonation test (gap test)

Tests were conducted following the Standards ES—32(1) of JES, and JIS K 4810—1979 (testing methods of explosives). Fig. 1 shows illustration of apparatus of the test. Two explosive materials (weight: about 100 g) were put on the dry sand, and one explosive cartridge was ignited by a detonator and then second one was detonated by sympathetically. The maximum distance between both materials, s, to induce detonation was a parameter of sympathetic detonation test.



1 – Detonator; 2 – First cartridge; 3 – Second cartridge.

Fig. 1 Set-up of experiments of sympathetic detonation test

3 Results and discussion

Summary of major test results for KP-I is shown in Tab. 3. In Tab. 3, T_{DTA} is the onset temperature measured by the DTA; ignition was defined that a fire was made in ten seconds after a sample was touched with a small burner in small gas flame test.

Tab. 3 Summary of major test results for KP- I

Method	Test results	
DSC	T_{DSC} = 402.0 ℃ (188.8 ℃) Q_{DSC} = 4 061.7 J/g (48.8 J/g)	
TG-DTA	T_{DTA} = 568.5 ℃ weight loss = 1.14%	
fall sensibility test	0/6 (height: 15 cm) 2/3 (height: 20 cm)	rank 4
BAM friction test	0/6 (weight: 78.4 N) 2/6 (weight: 156.8 N)	rank 5
ignition temperature test (Krupp method)	ignition temperature waiting 4 seconds: 507 ℃ lowest ignition temperature: 497 ℃	
ignition test	cerium/iron sparks test: 0/5 small gas flame test: 2/5	
Mk Ⅲ ballistic motor test	①116%, ②117%, ③140%; average 124%	
sympathetic detonation test	explosion at s = 150 mm no explosion at s = 180 mm	rank 5

3.1 DSC and TG-DTA

In order to know the overall properties of the mixtures and level of violence of their explosions, the DSC and TG-DTA tests were conducted. Examples of test charts of KP-I are shown in Fig. 2 and Fig. 3.

Results of the thermal analysis (DSC, TG-DTA) show that KP-I was so stable and nearly no weight loss though it gave small heat release between 190 ℃ and 280 ℃. This small heat release might be from oxidation of organic material courting the Al surface, and then large heat release was observed starting at about 450 ℃, and the peak was at about 520 ℃. Second large peak might be caused by oxidation of Al (Fig.

2). In the TG-DTA, its weight decreased very slightly until 560 ℃, and large weight decrease and large heat release were observed at 560 ℃ (Fig. 3). These results implied that the mixture was stable between room temperature and about 400 ℃.

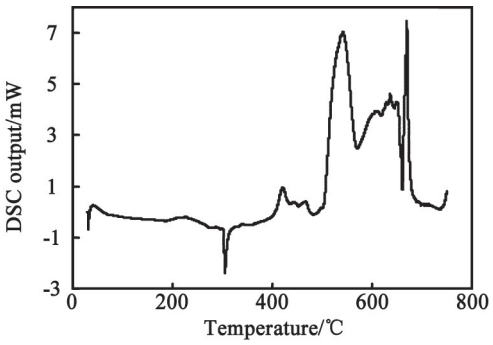


Fig. 2 Example of DSC result of KP-I

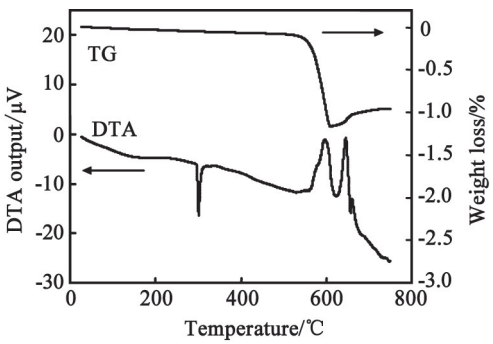


Fig. 3 Example of TG-DTA results

Therefore the fire-works composition material does not make self-reaction easily, when it is handled, stored at room temperature, and thermal decomposition of fire-works should not cause the explosion. Its SADT (self-activation decomposition temperature) was about 200 ℃. And at 300 ℃ heat absorption was observed, maybe due to change of its phase. Based on the DSC data, we obtained that 48.84 kJ/kg of heat of combustion, which was smaller compared with other popular self-reactive materials [6-8]. For example heat of combustion of 50 % hydroxylamine water solution is 2 300 kJ/kg [6]. Therefore it might release small heat when it exploded.

Tab. 4 shows the difference between domestic materials and imported materials on DTA for $KClO_4$, and Al (kind, particle size) for mixture. In regard to $KClO_4$, KP-I showed lower T_{DTA}, and more unstable. Compared with mixture, T_{DTA} of $KClO_4$ was higher, and KP-I gave lower T_{DTA} than KP-D because there was more impurity material in imported $KClO_4$. In mixture tests, we used three different samples (No. 1, No. 2 and No. 3) and the difference was Al powder [kind (ato-mized, stamped), particle size (pass through 425 μm mesh or not)]. In regard to T_{DTA}, there was not large difference among these samples, though No. 1 sample (stamped, finer particle) gave lower T_{DTA}.

Tab. 4 Test results of DTA ℃

Parameter	$KClO_4$		Mixture, KP-I base		
	KP-D	KP-I	No. 1	No. 2	No. 3
T_{DTA}	623.5	586.0	560.2	568.4	582.2

Mixtures of No. 1 and No. 2 consisted of stamped Al and No. 3 consisted of atomized Al. And No. 1 consisted of finer Al (pass through 425 μm mesh) than No. 2.

3.2 Ignition temperature test (Krupp method) and ignition test

The ignition temperature measured with the Krupp method of KP-I was about 500 ℃, and Fig. 4 shows relationship between the ignition temperature and the waiting time, τ. And result was similar with T_{DSC} of DSC, 402 ℃ and T_{DTA} of DTA, 569 ℃.

Result of ignition test data with the cerium/iron sparks test was no ignition (0/5) and the small gas flame test was partly ignited (2/5), which implies that it was less sensitive with ignition. Considering these results they were so stable thermally and had resistance to a small flame.

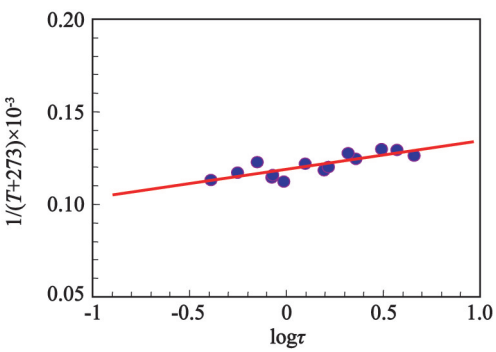


Fig. 4 Results of the ignition temperature test (Krupp method)

3.3 Fall hammer test and friction sensibility test

Result of the fall hammer test of KP-I was rank 4, and result of the friction test was rank 5, which were similar violence with industrial explosives like to dynamite and Carlit [8-10]. Therefore we had to handle this material carefully like to treatment of dynamite or Carlit.

The friction sensibility tests gave rank 5, which was middle level against impact among explosive materials. That is, both ANFO (ammonium nitrate fuel oil explosive) and watergel (or oil slurry explosive) were rank 8 [8-10].

In order to know the effect of impurity materials in the sample, KP-D was also tested. Results were similar with those of KP-I, so both materials had similar impact hazard.

3.4 MkⅢ ballistic test

The ballistic mortar values (B') is the parameter to evaluate explosive properties of sample, and defined by the following expression:

$$B' = \frac{d_1 - d_0}{d_2 - d_0} \times 100 。 \quad (1)$$

In Formula(1): d_0, the length of the swing with 5.0 g of boric acid, mm; d_1, the length of the swing with 5.0 g of the tested substance, mm; d_2, the length of the swing with 5.0 g of TNT, mm.

Results of the MkⅢ ballistic motor test are that: Ratio to TNT, B' number, was very high, 124% (average) compared with past test results of about 90% for most explosives, but dynamite had higher value[8-10].

3.5 Sympathetic detonation test

Several sympathetic detonations occurred in several seconds in the Kagoshima incident, and the possibility of these explosions was discussed with the results of sympathetic detonation tests (Tab. 5), and we compared with other popular explosives. In Tab. 5, ○, detonation; ×, non-detonation.

Tab. 5 Sympathetic detonation test results

s/d	Results	Remarks
2	○	
4	○	
5	○	
6	×	deflagration occurred
8	×	(vessel left)

When detonation occurred, small crater was created. Rankings of sympathetic detonation property were evaluated with the value of s/d. Here s is the distance between both explosives, and d is the diameter of explosives cartridge and here d is 30 mm (Fig. 1). When s/d was equal to or smaller than 5, a crater was made in our tests. Therefore degree of sympathetic detonation was rank 5, and it was higher sensitivity of sympathetic detonation than most dynamites (gelatine dynamite, rank 4-7; powdery dynamite, rank 2-3), and ANFO explosives (rank 2-3)[8-10] here, the larger number is the more dangerous of sympathetic detonation explosive makes.

3.6 Cause of explosion and sympathetic detonation

Based on the testification of witness and damage situation, first explosion occurred at mixing house. And then at least four explosions occurred. Analyzing materials at craters, we identified the material which caused first explosion. We did not have detail information when first explosion occurred because all workers at the mixing house were killed. There were seven workers in small room, and they might not start mixing work because time was just after lunch break. Therefore, one of possibility ignition was impact of metal bottle of raw pyrotechnics mixture which was done in the morning, fell from the working desk. It was rain when the incident occurred, so electrostatics might not relate with trigger of explosion.

4 Conclusions

In order to find the cause of an explosive incident with raw pyrotechnics mixtures, in Kagoshima City, various evaluation tests were conducted. Explosions were occurred when fire-works were made, which consisted of $KClO_4$, Al powder and Sb_2S_3.

1) Based on data of analysis of Sb of soil at totally eight places including craters in the factory we found that raw pyrotechnics mixture which consisted of $KClO_4$, Al powder and Sb_2S_3, was the cause material of the first explosion.

2) We found this mixture was very stable thermally, at least up to 500 ℃ based on the results of the DSC, TG-DTA tests.

3) Based on results of the falling and friction tests, this mixture had high sensibility of friction and falling impacts.

4) This mixture made sympathetic detonation easily, and this might be the reason that there were several explosions after first explosion.

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5) Considering the above results it was so dangerous to treat this kind of pyrotechnics mixture, and we should handle them with more carefully.

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