Research paper

New lift powder for fireworks

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Abstract

New lift powder which is composed of poly (oxymethylene), calcium peroxide and aluminum powder was studied.

It was suggested that the performance of the lift powder was attributed to the high pressure product gases evolved from the rapid thermal decomposition of poly (oxymethylene) activated by the thermite reaction between calcium peroxide and aluminum.

The lifting test of an aerial shell (dia.=83mm and weight=20g) was carried out using the mixture of poly (oxymethylene), calcium peroxide and aluminum loaded at the bottom of a fireworks mortar . The initial velocity of the shell was 96 to l07 $ms^{-1}$and the pressure in the mortar was 52 to 82 kPa, which showed the same potential as black powder with the initial velocity of 124 ms^{-1} and 62kPa under the same conditions.

Keywords : fireworks, lift powder, calcium peroxide, poly (oxymethylene), aluminum

1. Introduction

In fireworks, black powder has been playing two important roles, one as a lift powder, the other as a bursting powder for aerial shells. We have not yet invented an alternative lift powder like black powder which has been exclusively used as both lifting and bursting aerial shells in fireworks. The role of lift powder is to lift an aerial shell and to burst it in the sky simultaneously. It is said in fireworks that they can not find alternative lift powder like black powder which has these functions as long as they use the present fireworks mortar[1]). Black powder has been widely used in the world, but there are few reports concerning its combustion characteristics in particular applications[2,3,4]), especially in fireworks[5,6,7]).

In consumption of black powder, there may be three problems to be solved ; the first is evolution of toxic gas like SO_2 or NO_x, the second, bad view of the sky covered with smoke or unburned gases, and the third, the high risk of fire accidents on lifting. In this research, we try to replace black powder with a new lift powder because of above mentioned limitations.

For this purpose, the mixture of calcium peroxide, aluminum and poly (oxymethylene) was adopted, and time pressure measurement and burning test for practical use was carried out.

2. Experiments

2.1 Sample

Calcium peroxide was synthesized from 10ml of 30wt% calcium chloride solution adding 30ml of 5wt% hydrogen peroxide solution under controlling reaction time (10minutes) and temperature (30℃). Calcium peroxide was obtained with the purity of 50 or 80% by chemical analysis. Aluminum and poly (oxymethylene) were the same as those reported in the literature[10]).

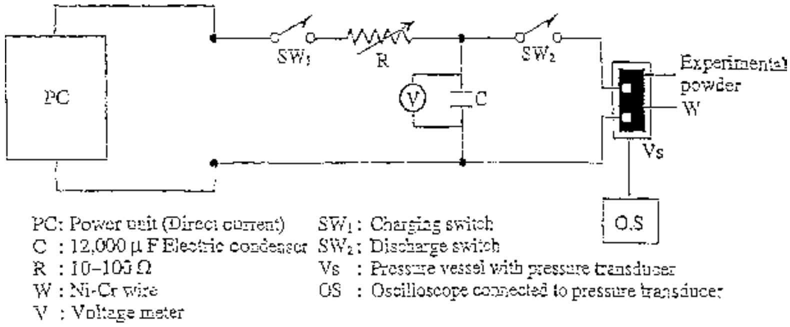

Fig. 1 Pulse discharge circuit for time pressure measurement.

2.2 Time pressure measurement

As a lift powder, mixture of thermite composition (Calcium peroxide/Aluminum=6/4 in mole ratio) with poly (oxymethylene) was used to measure combustion pressure. Thermite composition A is made of 80% purity calcium peroxide and aluminum, the composition B, of 50% purity calcium peroxide and aluminum. Nichrom wire was mounted in the mixture to ignite by electric discharge circuit as shown in Fig. 1.

2.3 Burning test of the lift powder

Choosing the 100 parts of composition A mixed with 40 parts of poly (oxymethylene) as a lift powder, burning test was carried out to pre-check practical use.

The experimental setup is shown in Fig. 2. Hi−vision digital camera was used to observe combustion of the lift powder. To measure the lifting velocity of a dummy aerial shell at the exit of the fireworks mortar, the motion pictures were taken by using high speed camera with 2000 frames per second.

The dummy shell has the size of 83 mm in diameter. Two pressure sensors were placed at the fireworks mortar to measure the burning pressure. The dimensions of the tools or instruments used in this test are as follows ;

Fireworks mortar : inner diameter of 91 mm and 650 mm long made of stainless steel

Dummy aerial shell : outer diameter of 83 to 84 mm and weight of 200 g (clearance of the mortar is 7 mm.)

Electric detonating fuse : made of Asahi chemicals with 0.9ohm

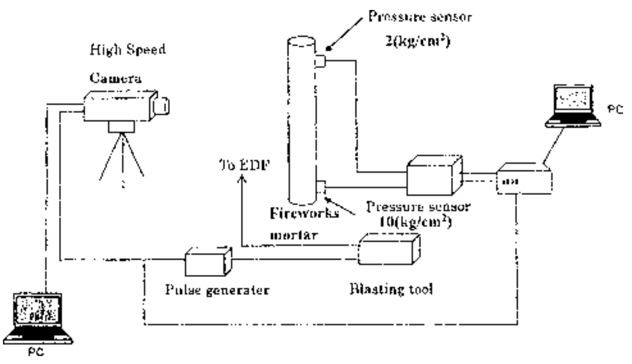

Fig. 2 Experimental setup for the measurement of pressure inside the firework mortar, and exit velocity of aerial shells by framing camera.

Hi−vision digital recorder : HDR−HCR video made by Sony Co. Ltd.

High speed digital camera : Phantom−V5.0 made by Vision research

Pressure sensor : PGM−2KC and PGM−10KC made by Kyowa Electrics

2.4 Lifting and bursting tests for aerial shells

To confirm suitable height and good bursting of stars, the lifting test for composition A with 40wt% poly (oxymethylene) was carried out using three sizes of aerial shells (No.3 to No.5 shells).

3. Results and discussions

3.1 Time pressure measurement

Figure 3 shows the relation between poly (oxymethylene) contents and pressure for the mixture of the composition A or the composition B with poly (oxymethylene). Without poly (oxymethylene), pressure is higher for the composition B than for the composition A. This is due to the fact that the amount of gas is more evolved for the composition B because calcium peroxide of the composition B contains calcium hydroxide which decomposes to calcium oxide and water vapor as well as thermite reaction. The maximum pressure is higher by 3.5 times for the mixture of the composition A than for the mixture of the composition B. This figure suggests that as the purity of calcium peroxide becomes high, the combustion limit and the pressure increase. The pyrolysis pattern of poly (oxymethylene) is known to be the gas production type (main-chain cutting type or zippering one), and a typical depolymerization type as well, which the cutting of main-chain is occurred from chain ends[8]. From the CEA program[9], the adiabatic flame temperature of poly (oxymethylene) is calculated as 871K, and main combustion products are hydrogen (29%), C (graphite, 26%), water vapor (16%), carbon dioxide (15%), carbon monoxide (9%) and methane (5%). Average molecular weight is 17g/mol. The calculation supports that poly (oxymethylene) can be used as gas generating agent. It was suggested[10] that after firing the mixture of the composition A with poly (oxymethylene), the first step of the combustion reaction is the thermite reaction between aluminum and calcium peroxide, and then its exothermic reaction initiates the decomposition of the polymer to produce large volume of gases which generates high pressure. Formaldehyde was tried

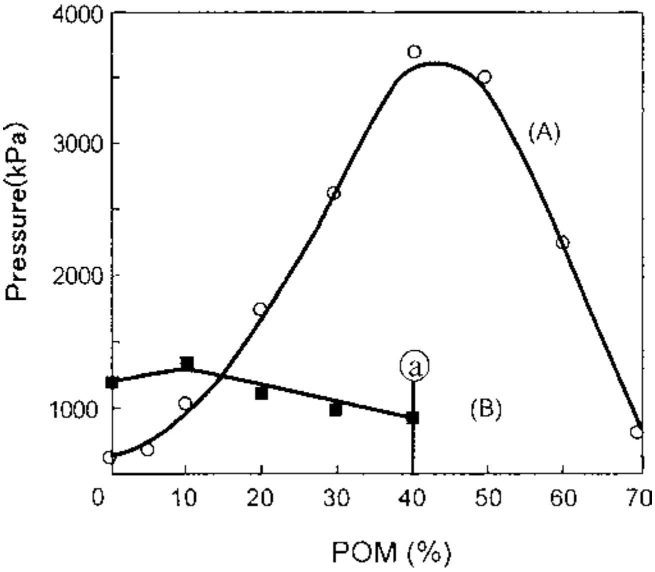

Fig. 3 Relation between poly (oxymethylene) content (%) and maximum pressure.
(A) Composition A with poly (oxymethylene)
(B) Composition B with poly (oxymethylene)
ⓐ Combustion limit

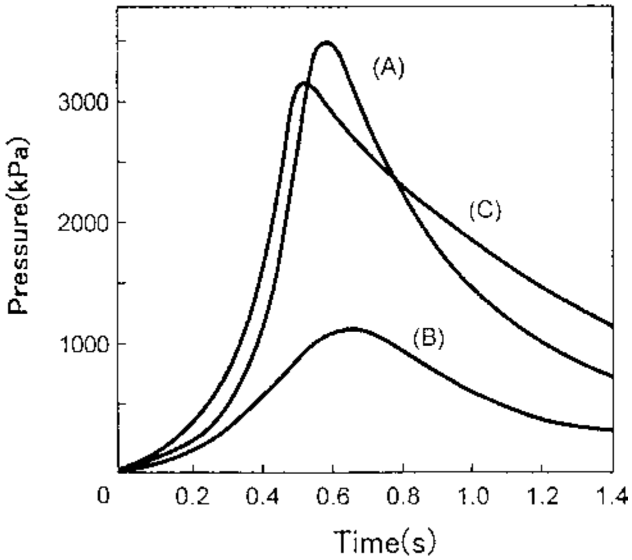

Fig. 4 Time histry of pressure for the mixtures of composition A with poly (oxymethylene) and black powder.
(A) Composition A with 40% poly (oxymethylene)
(B) Composition B with 40% poly (oxymethylene)
(C) black powder

to measure as a decomposition product but we could not detect it, for its concentration was very low.

Figure 4 shows the time history of pressure for three samples. It must be noticed that the pressure curves of the mixture of composition A with 40wt% poly (oxymethylene) is very similar to that of black powder. This suggests that as a lift powder like black powder, the mixture of composition A with 40wt% poly (oxymethylene) may be an alternative lift powder in fireworks.

The adiabatic combustion temperature is calculated by the CEA computer program. The results is summarized in Table 1. There are many products, but the main products higher than 1% in mole fraction are only shown. The combustion temperature of the mixture is higher and the average molecular weight is smaller than those of black powder.

The calculation also confirmed that as a lift powder, the mixture of composition A with 40wt% poly (oxymethylene) may be used practically in fireworks.

3.2 Burning test of the lift powder

The result of burning test of the lift powder is summarized on Table 2 containing the result of black powder. Figure 5 (a) ~ (c) shows the pressure profiles with different amount of the mixtures and black powder (d). The maximum pressure and the exit velocity of the dummy shell at the mortar are resemble to those of black powder. It was also confirmed that the on-set of burning was 0.01 to 0.02 second and the time interval on shooting the shell after firing were close each other for these mixtures. From figure 5 (b), the duration of pressure (Δt) at the bottom is estimated as 0.013 s and the exit velocity, V of the dummy shell is measured as $107.3 ms^{-1}$. Using the equation,

$$mV - mV_0 = f\Delta t \quad (1)$$

where V_0 is the initial velocity equal to $0 ms^{-1}$ the weight of the shell equal to 200 g and f the force of lift, the lift is calculated as 1613N. In case of black powder (20 g), the lift is calculated as 1924N.

From these facts we can conclude that as a lift powder, the mixture of composition A with 40wt% poly (oxymethylene) has equal performance to black powder. It is noticed that the pressure profiles of the mixture of composition A with 40wt% poly (oxymethylene) is different from black powder. The former has two peaks, while the latter has one peak. The exit velocity seems to be independent on the amount of powder in case of the mixture of composition A with 40wt% poly (oxymethylene). These facts

Table 1 Flame temperature, average molecular weight and products of poly (oxymethylene), the mixture of composition A with poly (oxymethylene) and black powder by CEA calculation.

Sample	Pom*	Mixture**	Black powder***
Flame tem.(K)	871	2347	1827
Avg. molecular weight (g/mol)	17	33	64
Products	CH_4, CO, CO_2, H_2, H_2O, C(grphite)	CO, H_2, H_2O, Al_2O_3, CaO	CO, CO_2, K, N_2, SO_2, K_2SO_4

*poly(oxymethylene)
**the mixture of composition A with 40wt% poly (oxymethylene)
***KNO_3/S/C=80/10/10(weight%)

Table 2 Summary of lifting test of dummy aerial shells by the mixtures of composition A with poly (oxymethylene) and black powder.

Exp. No.	Lifting power	Weight (g)	Pressure in mortar (kPa)		Exit velocity (m/sec)
			Bottom area	Upper area	
1	mixtures*	20	52	20	97.1
2	mixtures*	30	82	20	107.3
3	mixtures*	40	58	22	95.6
4	B.P	20	35	18	96.2
5	B.P	30	62	28	124.0

*the mixtures of composition A with 40wt% poly (oxymethylene)

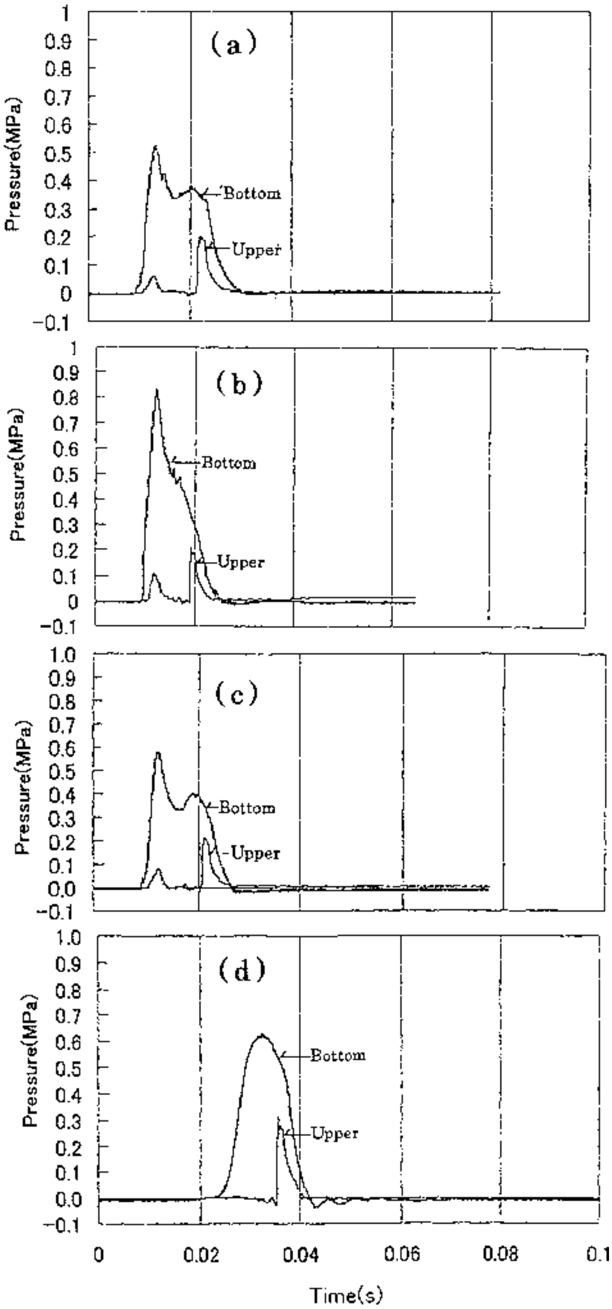

Fig. 5 Pressure profile of of various compositions.
(a) Composition A with 40% poly (oxymethylene) (20g)
(b) Composition A with 40% poly (oxymethylene) (30g)
(c) Composition A with 40% poly (oxymethylene) (40g)f
(d) Black powder (30g)

means that the altitude at which a firework shell reaches may not be predicted from the amount of lift powder used. Improvement is necessary for reliable lift powder.

3.3 Lifting and bursting tests for aerial shells

The result of lifting and burning tests by aerial shells is summarized in Table 3. As expected from the Table 2, the lift altitude were sufficiently high and it was shown that the mixture of composition A with poly (oxymethylene) had the applicability to the practical use like black powder. Figure 6 shows the fireworks mortar for lifting an aerial shell with the diameter of 10 cm.

Figure 7 shows aerial shells used in this experiment. The shell is ignited by the fuse on lifting. Figures 8 and 9 are fireworks flowers lifted by the mixture of composition A with 40wt% poly (oxymethylene) as a lift powder. The altitude of explosion seems sufficient high. As lift powder, the mixture of composition A with 40wt% poly (oxymethylene) can be used like black powder. On lifting, black powder is known to produce black smoke like lamp black, and a lot of burning gases, but the mixture of composition A with 40wt% poly (oxymethylene) does not produce black smoke and a small amount of gases after burning as expected from the Table 1.

However, there are several problems to be solved, one of which is that the reuse of a mortar is difficult because there remains sticky unburned organic substance inside the mortar after firing. Another one is that the exit velocity or the altitude of explosion of aerial shells may not be predicted by the amount of lift powder. These troubles will be solved by the lifting and burning tests under various conditions.

4. Conclusions

New lift powder which is composed of poly (oxymethylene), calcium peroxide and aluminum powder was studied.

Fig. 6 Firework mortars.
Left : for No.5 aerial shells
Right : for No.3 aerial shells

Table 3 Results of lifting and bursting tests for aerial shells.

Size of aerial shell in diameter (mm)	Amount of lifting power (g)	POM ratio*	Shot No 1	2	3	4	5	Lifting altitude (m) by glance
90 (No3)	20~30g	40%	△	○	○	○	—	120~130
		30%	—	—	—	—	○	
120 (No4)	50~55g	40%	○	○	○	▲	—	160~170
		30%	—	—	—	—	○	
150 (No5)	75~80g	40%	○	○	▲	○	—	190~200
		30%	—	—	—	—	○	

*mixed with comosition A
○ : Good. △ : Low. ▲ : High

Fig. 7 Firework aerial shells (No.3 shells).

Fig. 9 Flower of aerial shell, No.5.

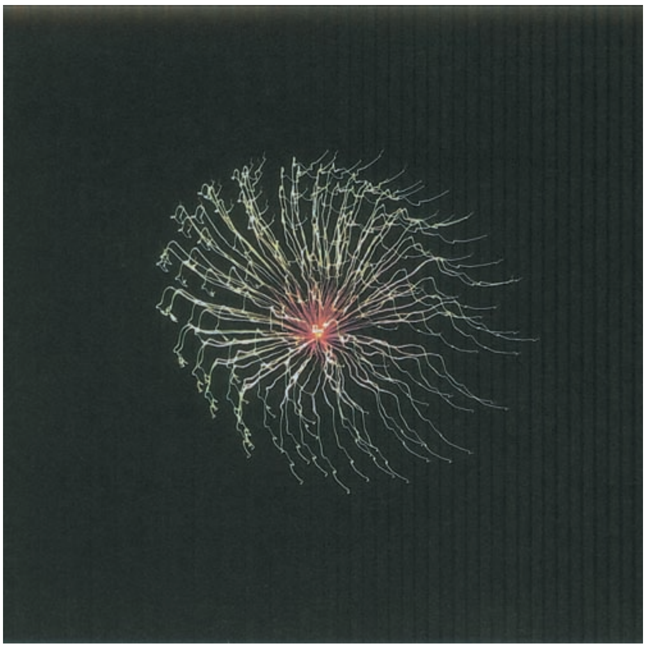

Fig. 8 Flower of aerial shell, No.3.

Time pressure measurement, burning test of the lift powder and lifting tests for aerial shells were carried out. It was suggested that after firing the mixture of the composition A with poly (oxymethylene), the first step of the combustion reaction is the thermite reaction between aluminum and calcium peroxide, and then its exothermic reaction activates the decomposition of the polymer to produce large volume of gases which generates high pressure.

It is concluded that as a lift powder, the mixture of composition A with 40wt% poly (oxymethylene) has equal performance to black powder .

5. Acknowledgment

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煙火用新規打ち上げ薬

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過酸化カルシウム，アルミニウムおよびポリオキシメチレンの混合物について圧力試験，模擬の打揚花火の打揚試験および３号玉や五号玉を使った打揚試験をおこなった。

この混合物の反応はまず，過酸化カルシウムとアルミニウムのテルミット反応が起こり，それによってポリオキシメチレンの分解が開始し多量のガスを発生することにより推進力が得られると考察した。

三号玉や五号玉を使った打揚試験において打揚花火の出口速度は95~107ms^{-1}で打揚筒内の圧力は52~82kPaとなり，黒色火薬を用いた場合とほぼ同じであった。

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