The reactivity of manganese – lead chromate – barium chromate delay composition

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The thermal analyses, the analyses of combustion residue, and the combustion characteristics measurements such as burning rate or combustion temperature were carried out to clarify the thermal and combustion reaction mechanisms of the manganese – lead chromate – barium chromate delay composition. The following results were obtained.

The main reaction of the manganese – lead chromate – barium chromate delay composition was the oxidation of manganese by lead chromate. Barium chromate acted as a burning rate modifier, i.e. the larger its content, the less its burning rate. The thermal analyses of manganese – lead chromate binary mixture and manganese – lead chromate – barium chromate ternary mixture showed a broad exothermic peak over 200 to 750 ℃ in atmospheric condition, but under reduced pressure, it showed an intense exothermic reaction. The heat of combustion of the delay composition had a maximum value at the composition of manganese/lead chromate = 30/70 by weight without barium chromate, but the compositions which contained a larger percentage of manganese than this showed a larger linear burning rate. The pressure index of combustion is small, indicating that a solid state reaction played an important role in the combustion.

1. Introduction

There are two types of delay compositions, one is gassy compositions which produce gases upon ignition having a significant dependence of burnung rate on external pressure and the other is gasless. The latter is preferred as a requirement for low pressure dependent combustion characteristics. The manganese (Mn) – lead chromate ($PbCrO_4$) – barium chromate ($BaCrO_4$) delay composition is one of the typical gasless compositions and has been used in various pyrotechnic devices because of its precise delay time [1),2)]. Manganese is an attractive fuel for pyrotechnic engineers, because it reacts in several different ways depending on its proportion in the mixture; that is, there exist three types of oxidation state such as MnO_2, Mn_2O_3 and MnO [3)]. However, this composition has disadvantage of high sensitivity to moisture which may cause aging during storage if it processed under humid conditions, due to the high reactivity of manganese powder with water.

The combustion of gasless delay compositions usually proceed through solid state reactions. Solid state reactions are significantry affected by the surface properties of the ingredients such as surface area, the degree of surface oxidation, and so on. In this study, the thermal analyses, the analyses of the combustion residue, and the burning rate and combustion temperature measurements were carried out to clarify the thermal and combustion reaction mechanisms of the manganese – lead chromate – barium chromate delay composition.

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2. Experimental

2. 1 Materials

Manganese powder obtained from a commercial supplier, RARE METALLIC CO., LTD., had an average particle diameter of 13.3 μ m and purity of 99.9%. Lead chromate was reagent grade with an average diameter of 3.0 μ m and had purity of 96%. Barium chromate was reagent grade with an average diameter of 4.8 μ m and had purity of 95%.

The delay powders were prepared using an ordinary ball-mill mixer after properly weighing the ingredients.

2. 2 Analyses

Thermal analysis was performed using a RIGAKU DTA-TG simultaneous analyzer in which the sample weight was 5 mg and the heating rate was 20 K/min. in atmospheric condition, under argon gas stream, or under reduced pressure.

Qualitative analysis of the reaction residue were performed using common X-ray powder diffraction.

2. 3 Combustion experiments

The delay compositions were burnt in an aluminum cylindrical tube, and the time for a 10 mm burning was recorded using a Digital Stragescope from the Iwasaki Tuusinki Co., LTD. with optical fiber signals. The mixtures divided into equal nine part was loaded nine times in one aluminum tube. Preliminary experiments showed that the linear burning rate decreased with increase in loading density, but that the mass burning rate was constant within a loading of 50 ~ 65% of the theoretical maximum density. With regard to the diameter of the delay tube, the linear burning rate was constant at inside diameter of 4 ~ 7 mm. From the above results, the combustion experiments were carried out using a delay tube with diameter of 6 mm and a loading of 65% of the theoretical maximum density.

A "Shimadzu auto calculating bomb calorimeter" was used to measure the heat of combustion of the delay composition for a 1 g sample in an argon gas atmosphere, and the combustion products were analyzed by the method described above.

The combustion temperature was measured using a W/W-Re thermocouple connected to a Digital Scope DL708 from the Hokushin Denki Co., Ltd. The thermocouple was inserted into the center of the delay powder perpendicular to the direction in which combustion wave proceeded.

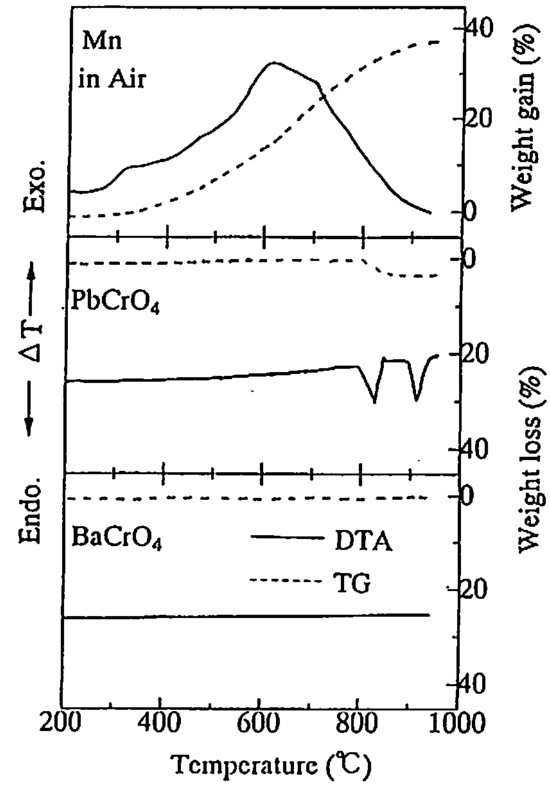

Fig. 1 Thermal analyses of Mn, $PbCrO_4$, and $BaCrO_4$ in air

3. Results and discussion

3. 1 The thermal reaction of manganese, lead chromate, barium chromate and their mixtures

Fig.1 shows the thermal analysis results of manganese, lead chromate, and barium chromate in atmospheric condition. The DTA and TG curves of manganese in air showed a gradual and step-wise oxidation which started at 250 ℃. The oxidation seemed to continue up to 950 ℃, and the final weight increase was about 37 %. X-ray powder diffraction patterns of the reaction residue at 950 ℃ showed the existence of manganese oxide (Ⅱ) (MnO) and manganese (Ⅱ) manganese (Ⅳ) oxide (Mn_3O_4). The DTA and TG curves of lead chromate showed two endotherms of melting and decomposition at about 800 ℃ and about 900 ℃. Barium chromate did not undergo physical and chemical changes below 1000 ℃, but showed a melting at 1450 ℃ followed by decomposition.

Fig.2 shows the results of the thermal analyses of various mixtures of manganese with lead chromate in air. The mixtures of manganese with lead chromate underwent an exothermic reaction over the wide temperature range between 250 and 800

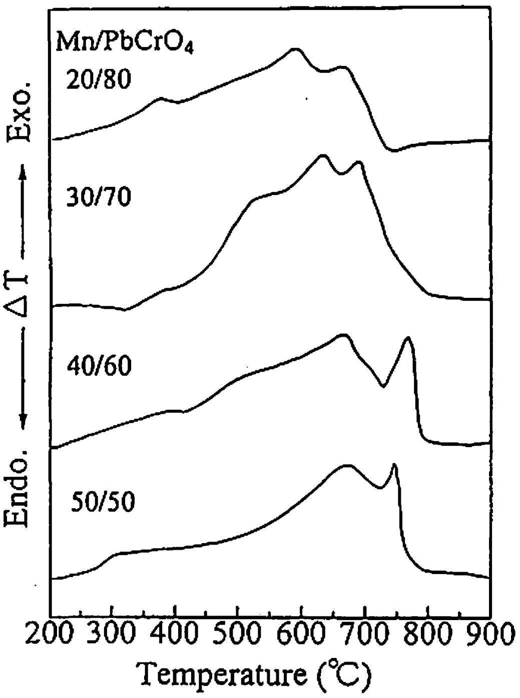

Fig. 2 DTA curves of various mixtures of Mn with $PbCrO_4$ in air

℃ in air. As the decomposition of lead chromate occurred above 800 ℃, it can be concluded that oxygen in air also reacted. The reaction residue contained manganese oxide (Ⅱ), manganese (Ⅱ) manganese (Ⅳ) oxide, lead oxide (Ⅱ), manganese, lead, and chromium (Fig.3). Fig.4 shows the DTA curves of various mixtures of manganese with lead chromate under reduced pressure. The mixtures of manganese with lead chromate under reduced pressure below 0.1 Torr underwent an intense exothermic reaction at temperatures of 475 ~ 520 ℃, which is different from the result in air. The reaction temperature was 520 ℃ for the composition of manganese/ lead chromate = 20/ 80, and the larger the content of manganese, the lower the reaction temperature. The difference in reactivity in air and under reduced pressure are considered as follows. Manganese was easily oxidized by oxygen in air. In the case of the experiments in air, manganese in the mixture was gradually oxidized before its reaction with lead chromate and an oxide layer was formed on its surface. This oxidized layer acted as a resistance to the reaction. In contrast to air, manganese in an atmosphere free from oxygen was scarcely oxidized before the reaction and can cause a violent reaction.

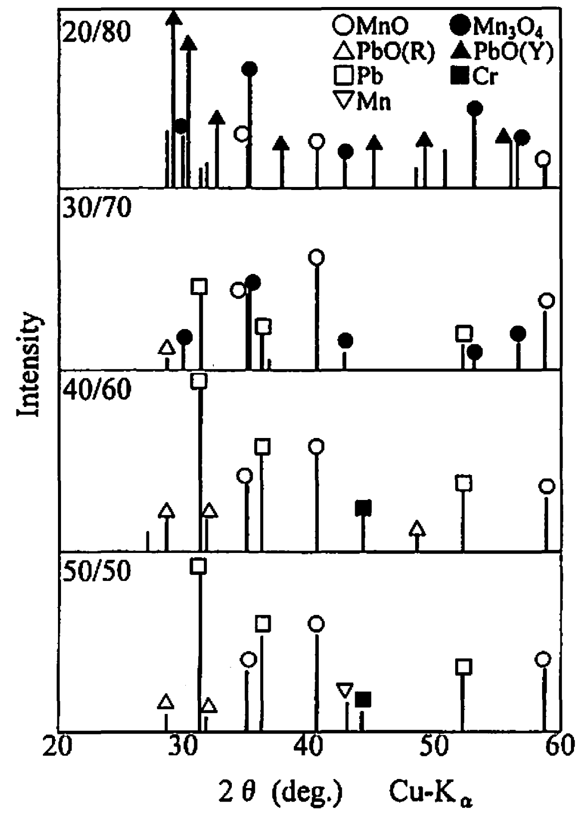

Fig. 3 X-ray powder diffraction patterns of the reaction residue of various mixtures of Mn with $PbCrO_4$ in air

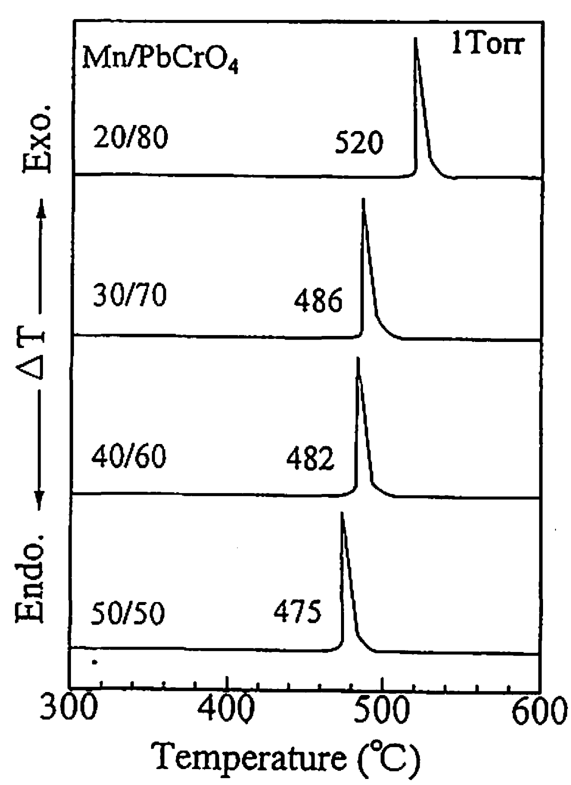

Fig. 4 DTA curves of various mixtures of Mn with $PbCrO_4$ under reduced pressure

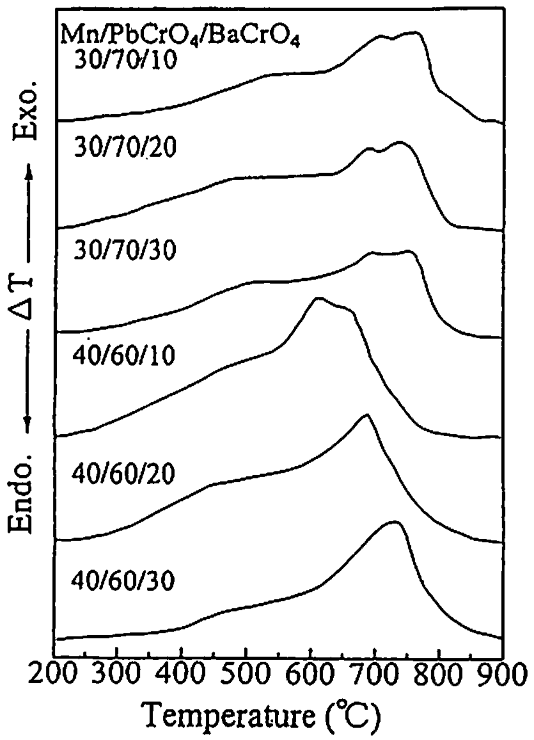

Fig. 5 DTA curves of various mixtures of Mn, $PbCrO_4$, and $BaCrO_4$ in air

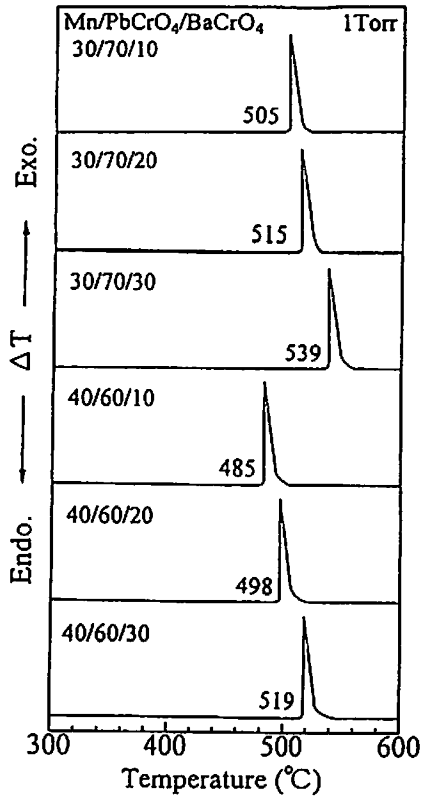

Fig. 6 DTA curves of various mixtures of Mn, $PbCrO_4$, and $BaCrO_4$ under reduced pressure

Fig.5 shows the DTA curves of various mixtures of manganese, lead chromate, and barium chromate in air. The results were very similar to that of the binary mixture, and it was concluded that barium chromate did not play such important role. The ternary mixtures of manganese, lead chromate, and barium chromate also underwent a violent reaction at reduced pressure below 0.1 Torr (Fig.6). This was interpreted as the same reaction in the case of the binary mixture. With regard to the role of barium chromate, it had a restraining effect on the reaction.

3. 2 Combustion reaction of manganese – lead chromate composition and manganese – lead chromate – barium chromate composition

Fig.7 shows the results of the linear burning rate measurements of various mixtures of manganese with lead chromate under atmospheric conditions. The binary mixtures were combustible within a manganese content from 20 to 50 wt.%. The linear burning rate increased with increasing manganese content up to 40 wt% and showed a constant value above 40 wt%. This is ascribed to the higher thermal conductivity with increasing metal contents.

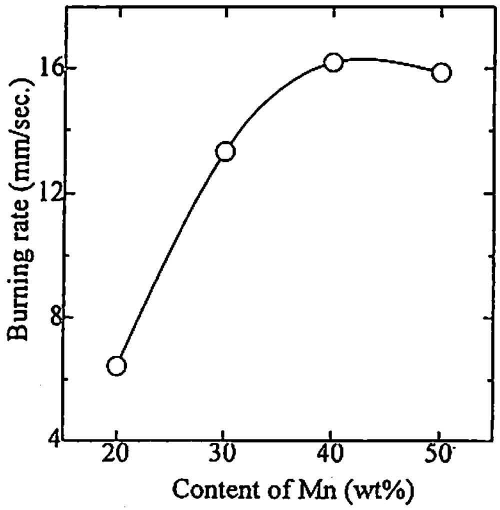

Fig. 7 Limear burning rate of various mixtures of Mn with $PbCrO_4$

Fig.8 shows the results of the linear burning rate measurements of various mixtures of manganese with lead chromate under pressurized nitrogen. The linear burning rate showed a slight increase with increasing ambient pressure for every composition. For propellant combustion, the linear burning rate under pressurized conditions, V, is represented by

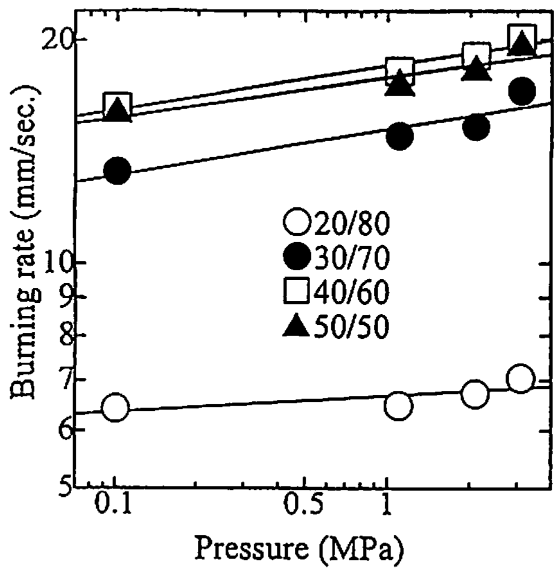

Fig. 8 Limear burning rate of various mixtures of Mn with $PbCrO_4$ under pressurized nitrogen

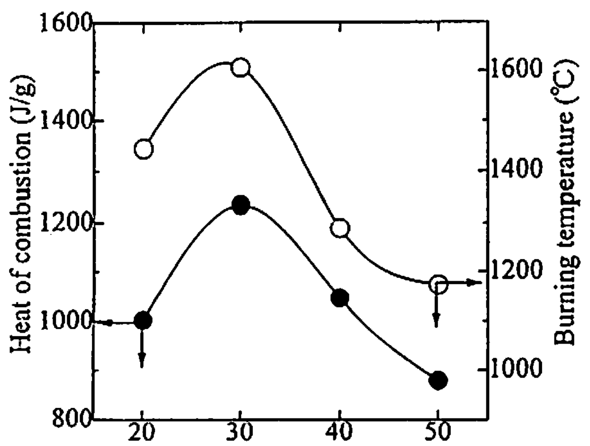

Fig. 9 Heat of combustion and combustion temperature of various mixtures of Mn with $PbCrO_4$

the following Vieille's equation:

$$V = bP^n \quad (3)$$

where P is the pressure, n is the pressure index and b is a constant. The pressure index n was very small for every composition and had a value from 0.02 to 0.06. This small pressure index might be ascribed to the fact that the main combustion reaction is a solid-state reaction.

Fig.9 shows the results of the measurements of the heat of combustion and combustion temperature of various mixtures of manganese with lead chromate under atmospheric pressure. Both the heat of combustion and combustion temperature had

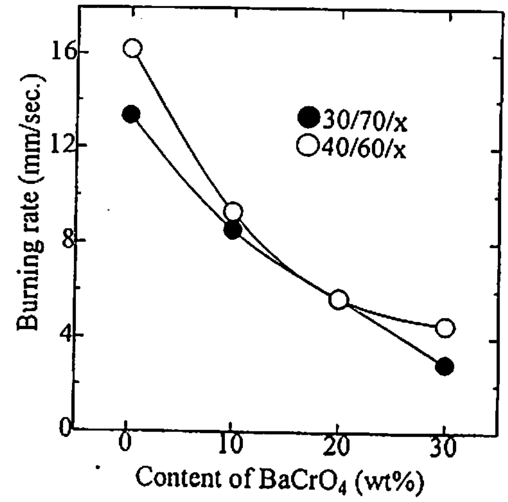

Fig. 10 Linear burning rate of various mixtures of Mn, $PbCrO_4$, and $BaCrO_4$ under atmospheric pressure

maximum values at the composition which contained 30 % manganese, which was a smaller manganese content compared to that of maximum burning rate. Stoichiometry and heat of combustion are usually interrelated, but in these cases, stoichometric composition of the binary mixture could not determined due to the existence of two kinds of manganese oxides and no detected chromium compounds.

Fig.10 shows the results of the linear burning rate measurements for various mixtures of the manganese - lead chromate - barium chromate delay composition under atmospheric conditions. As the linear burning rate of this delay composition decreased with increase in barium chromate content, barium chromate could be used as a burning rate modifier when a lower burning rate preferred. Fig.11 shows the results of the linear burning rate measurements of various mixtures of the manganese - lead chromate - barium chromate delay composition under pressurized nitrogen. The linear burning rate of this delay composition showed only a small increase or was constant for every composition. This again suggests that the main combustion reaction is a solid-state reaction.

Fig.12 shows the results of the heat of combustion and combustion temperature measurements of various mixtures of the manganese - lead chromate - barium chromate delay composition under atmospheric pressure. The effect of barium chromate on

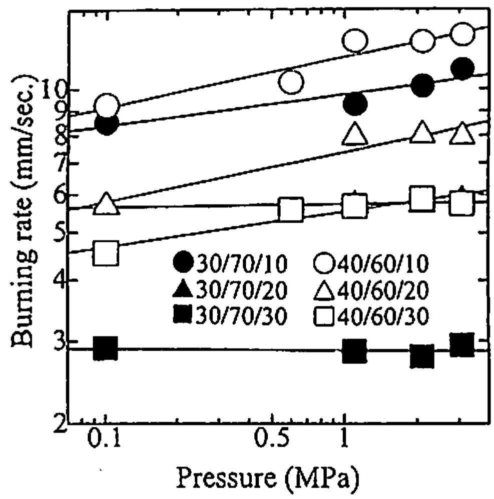

Fig. 11 Linear burning rate of various mixtures of Mn, $PbCrO_4$, and $BaCrO_4$ under pressurized conditions

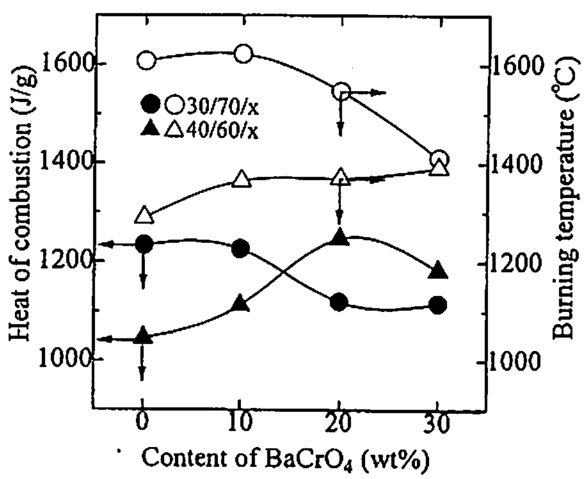

Fig. 12 Heat of combustion and combustion temperature of various mixtures of Mn, $PbCrO_4$, and $BaCrO_4$ under atmospheric pressure

the heat of combustion and combustion temperature varied with the composition of manganese and lead chromate. That is, the composition of manganese/ lead chromate = 30/70 (by wt.) (practical stoichiometric composition because this composition had the maximum heat of combustion) showed a decrease in the heat of combustion and combustion temperature with increasing barium chromate content. On the other hand, the delay composition of manganese/ lead chromate = 40/60 (by wt.) had an increased heat of combustion and combustion temperature up to a 20 wt% manganese amount. This suggests that barium chromate acts as an oxidizer for a fuel rich condition.

4. Conclusion

Because manganese was easily oxidized in air and barium chromate had a high decomposition temperature, the main reaction of manganese - lead chromate - barium chromate delay composition was the oxidation of manganese by lead chromate. Barium chromate acted as a burning rate modifier, and the smaller the content, the larger the burning rate. However, it acted as an oxidizer under fuel rich conditions. The thermal analysis of a manganese - lead chromate binary mixture and a manganese - lead chromate - barium chromate ternary mixture showed a broad exothermic peak ranging from 200 to 750 ℃ in air, but under reduced pressure, they underwent an intense exothermic reaction.

The heat of combustion of the delay composition had a maximum value at the composition of manganese/ lead chromate/ barium chromate = 30/70/0 (by wt.), but the manganese rich compositions than this showed a larger linear burning rate. The combustion temperature had the same tendency with the heat of combustion. The pressure index of combustion was small, indicating that the solid state reaction might play an important role in the combustion.

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マンガン－クロム酸鉛－クロム酸バリウム系延時薬の反応性

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熱分析，燃焼残留物の分析，燃焼速度や燃焼熱などの燃焼特性の測定により，マンガン－クロム酸鉛－クロム酸バリウム系延時薬の反応性を検討し，次の結果を得た。

この延時薬系の主反応は，クロム酸鉛によるマンガンの酸化であり，クロム酸バリウムは燃焼を抑制する。大気中でのこの三成分延時薬の熱分析では，200～750℃で幅広い発熱反応を示すが，減圧中では激しい反応を引き起こす。延時薬の燃焼熱は，マンガン/クロム酸鉛＝30/70で最大値を持つが，燃焼速度はこれよりマンガン過剰の領域で最大値をとった。圧力指数が小さいことから，この系の燃焼には固相反応の寄与が大きいと考えられる。

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