Article

Reactivity and burning rate of manganese-barium chromate-lead chromate delay composition

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As for a Mn-$BaCrO_4$-$PbCrO_4$ system delay, the combustion characteristics and the lifetime vary depending on the surface condition and particle size of Mn used.

The Mn delay as well as tungsten delay is important for the defense industry from flexibility to control the burning rate widely. The Mn delay does not generate gaseous products during burning fundamentally, but tungsten delay does. Therefore, the Mn delay is useful for the delay in closed burning system or in a sealed container.

Generally, the metallic Mn is oxidized in air gradually, and the oxidized surface has Mn oxides such as MnO and Mn_2O_3. The oxidized surface remarkably reduces the reactivity of Mn remarkably. So a heating deterioration and an accelerated aging test for Mn were carried out to examine the progress of oxidation on the surface of Mn powders. We have confirmed that Mn increased in weight in this deterioration test.

Finally, we knew that the Mn used in the delay composition has to satisfy the following conditions from this new finding:

(1) The oxidizer of the Mn-$BaCrO_4$-$PbCrO_4$ delay composition is $PbCrO_4$, while $BaCrO_4$ acts as a burning rate modifier.

(2) Burning rate becomes slower as the particle size of Mn is increased. On the other hand, burning rate increased as the one decreased. However, the particle is too fine, the combustion reaction is interrupted, since the thickness of preheating area becomes extremely narrow.

(3) Mn powders after grinding should be treated to prevent the surface from oxidation.

Moreover, we had found out the following facts.

(1) The delay composition does not become to react at last, as the surface of Mn in the composition is gradually oxidized with aging.

(2) Grinding of Mn must be carried out in an inert atmosphere.

(3) The delay composition must be designed to increase the heat of combustion especially for the delay composition with low burning rates.

(4) The coefficient of the variation which is the percentage of value divided standard deviation by average burning rate must have the value less than 5% for the delay composition for low burning rate types.

1. Introduction

Mixtures of manganese (Mn) - barium chromate ($BaCrO_4$) - lead chromate ($PbCrO_4$), hereinafter are called as Mn-$BaCrO_4$-$PbCrO_4$ delay composition, or Mn delay composition, which are being widely used as a delay composition for the defense industry due to the flexibility to control the burning rate. Many investigators have made efforts to investigate the burning characteristics and to elucidate the combustion mechanism of the delay compositions. For example, Nakamura et al. reported the

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approach based the combustion theory of these compositions[1] and Shibata discussed the effect of some factors on the burning characteristics of these compositions[2) 3) 4)].

The delay compositions consist of the mixture of oxidizer and metallic powders as reducing agent. Generally, the burning characteristics of the delay compositions are affected by many factors: the particle size of ingredients, especially the surface condition of reducing agent, mixture ratios, loading densities, burning conditions. It is also well known that the degree of these factors on burning rate characteristics was affected by the mechanisms of thermal reaction and combustion. In order to clarify the relationships between the burning rate and the heat of combustion for the mixture ratio, thermal analysis and other instrumental analysis for the raw materials and the compositions were carried out in this study. The burning rate measurements and the combustion calorimetric measurements were also conducted for the compositions. Experimental results described on the triangle coordinates are discussed from the viewpoints of the burning rate theory and the combustion reaction thermodynamics.

2. Experimental

2.1 Materials

A manganese powder obtained from a commercial grade had purity higher than 98.5 wt% and its average particle size was 14.2 μm. The barium chromate was a reagent grade, which had purity higher than 99.0 wt% with an average particle size of 2.4 μm. The lead chromate was a reagent grade having purity higher than 98.5 wt% and an average particle size of 1.65 μm. These ingredients used in the delay compositions are listed in Table 1.

The ignition powder to ignite these delay compositions consists of ferrosilicon and trilead tetroxide, in which the ferrosilicon was a commercial grade with an average particle size of 13.0 μm, and the trilead tetroxide was a reagent grade with an average particle size of 3.5 μm. Both the ignition powder and the delay composition were prepared by manual mixing in wet condition. The ratio of ferrosilicon to trilead tetroxide was 25/75% by weight. The Mn delay compositions were varied widely the burning characteristics by the mixture ratio. The properties for the ignition powder and some delay compositions are shown in Table 2.

2.2 Grinding of Mn powder

The Mn powder was further ground in nitrogen or in air by ball-mill, jet-mill and other techniques depending on the purpose of tests. For example, the Mn with an average particle size of 17.6 μm was ground to a small size with an average particle size of 8.7 μm for 3 hours in 40 rpm. If the average size of Mn particle is too small, the delay

Table 1 Properties of ingredients used in the experiments

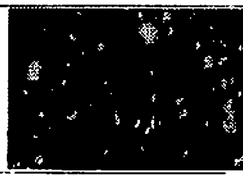
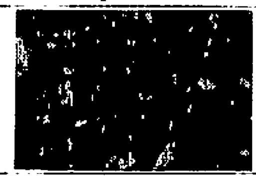
Ingredient	Particle size	Purity(%)	Delivers
Mn	14.2μm	98.5	ASAHI Metal Refining Co., Ltd.
$BaCrO_4$	2.4μm	99.0	KANTO Chemical Co., Ltd.
$PbCrO_4$	1.65μm	98.5	YONEYAMA Reagent Co., Ltd.

Table 2 Ignition powder and the examples of delay compositions

Type	Ingredient & Ratio (%)	C. H.(J/g)	DSC(℃)	W. C.(%)
Ignition Powder	$FeSi/Pb_3O_4$=25/75	996	563	0.05
Delay Mixture	$Mn/BaCrO_4/PbCrO_4$ = 37/22/41	1189	627	0.06
〃	$Mn/BaCrO_4/PbCrO_4$ = 38/40/22	866	612	0.05
〃	$Mn/BaCrO_4/PbCrO_4$ = 34/44/22	946	622	0.05
〃	$Mn/BaCrO_4/PbCrO_4$ = 30/48/22	1009	611	0.05
〃	$Mn/BaCrO_4/PbCrO_4$ = 34/46/20	912	613	0.08
〃	$Mn/BaCrO_4/PbCrO_4$ = 34/48/18	921	635	0.06

C. H. ··· Heat of Combustion, W. C. ··· Water Content

Table 3 Characteristics of Mn particles ground by different pulverization system

Machine	Pulverizer in air	Jet mill in N_2	Ball mill in N_2
Size	11.32μm	8.87μm	16.03μm
S. S. A.	$0.326 m^2/g$	$0.312 m^2/g$	$0.287 m^2/g$
Particle feature	squarish	squarish	spherical without squarish
Photo			

S. S. A. ··· Specific Surface Area ($Mn/BaCrO_4/PbCrO_4$ = 34/44/22)

composition may cause the burning interruption. This phenomenon will be explained later. The material characteristics of ground Mn are listed in Table 3.

2.3 Apparatus and Analytical Methods

Thermal analysis was performed by using a SEIKO TG/DTA320 Simultaneous Analyzer, in which the sample weight was about 10 mg and the heating rate was 10°C/min in air flow of 300 ml/min. The particle size was determined with a HORIBA Centrifugal Particle Size Analyzer CAPA-300, a MICROTRAC FRA Laser Diffractive Particle Size Analyzer and others. The surface appearances of ground Mn particles were observed using a KEYENCE High Precise Digital Microscope VH7000. The surface area of Mn particles was measured by using a NIKKISO Automatic Surface Area Analyzer Model-4232. Moreover, the heat of combustion of each delay compositions was measured by using a YOSHIDA Automatic Digital Calorimeter 1013-H.

2.4 Burning Rate and Combustion Experiments

The ignition powder about 0.1g was used to ignite each delay mixture in the burning experiments. The burning time of this ignition powder was about 60 μs. The delay compositions were pressed at a pressure of 157 MPa in a stainless cylindrical tube (O.D. 7.9 mm, I.D. 4.9 mm, and 23 mm in length) and measured the burning time for 10 mm length between the onset of ignition battery and solar cell signal by using a digital analyzing recorder Model 3655 made by YOKOGAWA HOKUSHIN Electronic Co. The delay mixture was pressed four times to become the ratio of length to diameter about 0.5. An average loading density of the samples was about 66.5% of the theoretical maximum value. Sample amount in each calorimetric measurements was about 2 g and the amount of ignition powder was 0.1 g, which was ignited by electronic wire made of pure nickel.

3. Results and Discussions

3.1 Oxidation of the Mn

Fig. 1 shows an example of mass increase of the Mn with an average particle size of 14.2 μm by heating at 130 ℃ in the Muffle Furnace FP-31 made by YAMATO Co. From this figure, we knew that the Mn was oxidized in air during long-term storage. Both the fact that the delay composition using the heat-treated Mn exhibited a slow burning, and that the heat of combustion also became small are indicating that surface of the Mn was oxidized.

If the heating time of the Mn were less than 4

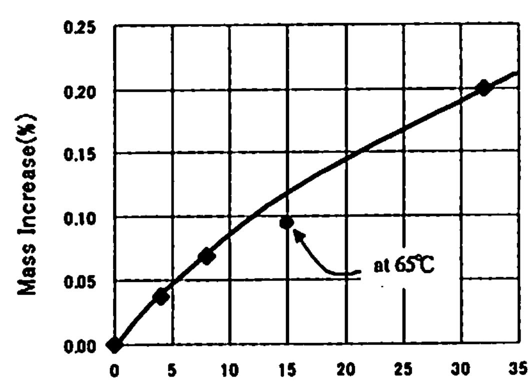


Fig. 1 Relationship between oxidation degree of Mn and heating time

hours at 130 ℃, the weight change was not large. The burning characteristics of the delay mixture remained almost unchanged. If it exceeded 8 hours, the burning continuity of the delay was deteriorated and the heat of combustion decreased. However, the heat of combustion is decreased at higher temperatures even if it is dried for less than 4 hours. This is ascribed to that the Mn had received some deterioration in the drying processes. Therefore, it is necessary for the Mn to carry out drying less than 4 hours at 130 ℃. Thereafter, the drying process is carried out at 65 ℃ within 4 hours.

3.2 Burning characteristics

The repeating number of measurements was 10 for each composition in the burning rate measurements. From Table 3, the Mn ground by the ball mill was spherical, and the one by the pulverizer was squarish. Although the jet mill was expected to have the largest pulverizing performance from the viewpoint of the surface area, the average size of the Mn particles was exceedingly small.

Fig. 2 shows the relationships between the average size of the Mn particles and the burning rate against the loading pressures. Although the influence of the loading pressure on the burning rate was not large, the influence of average size of the Mn particles on the burning rate was large. Also, the burning rate became faster as the average size of the Mn particle decreased. As the average size of Mn particle was too small, the delay composition caused the burning interruption. It can be thought that the rate of the surface oxidation per unit mass is quick when the average size of Mn particle becomes small. Then, Mn is easily oxidized in air and its reactivity gradually decreases.

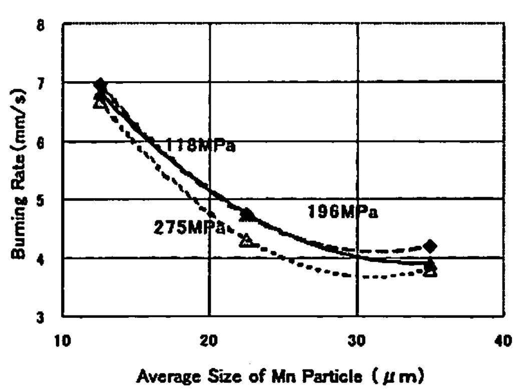


Fig. 2 Relationship between particle size of Mn and burning rate ($Mn/BaCrO_4/PbCrO_4$ =37/22/41)

Fig. 3 also shows the relationships between the burning rate or the heat of combustion and composition of delays, in which Mn or lead chromate is kept constant. The burning rate and the heat of combustion will increase with the increasing amount of lead chromate under condition of a constant content of Mn 34% by weight. On the other hand, the burning rate increased, but the heat of combustion decreased with the increasing amount of Mn under condition of constant content of lead chromate 22% by weight. It is better to control the burning rate by the amount of Mn rather than by the amount of lead chromate, when you design the delay

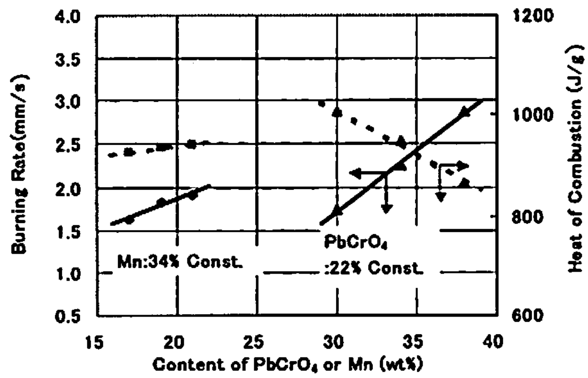


Fig. 3 Relationship between burning rate or heat of combustion and composition

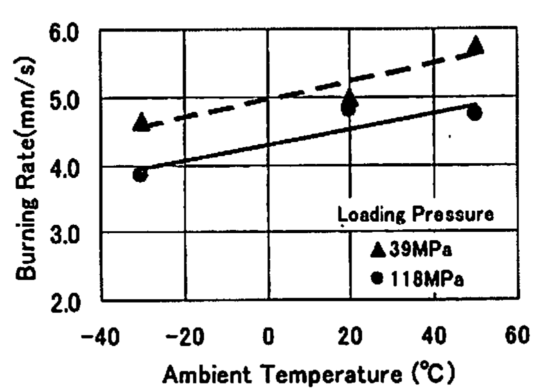


Fig. 4 Relationship between sample temperature and burning rate ($Mn/BaCrO_4/PbCrO_4$ =37/22/41)

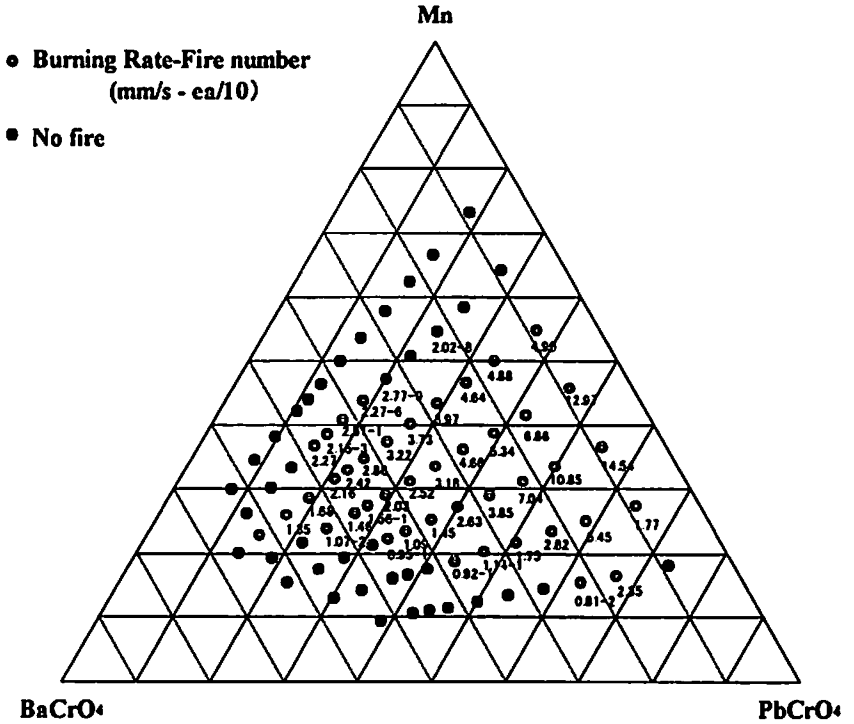


Fig. 5 Relationship between burning rate and its composition

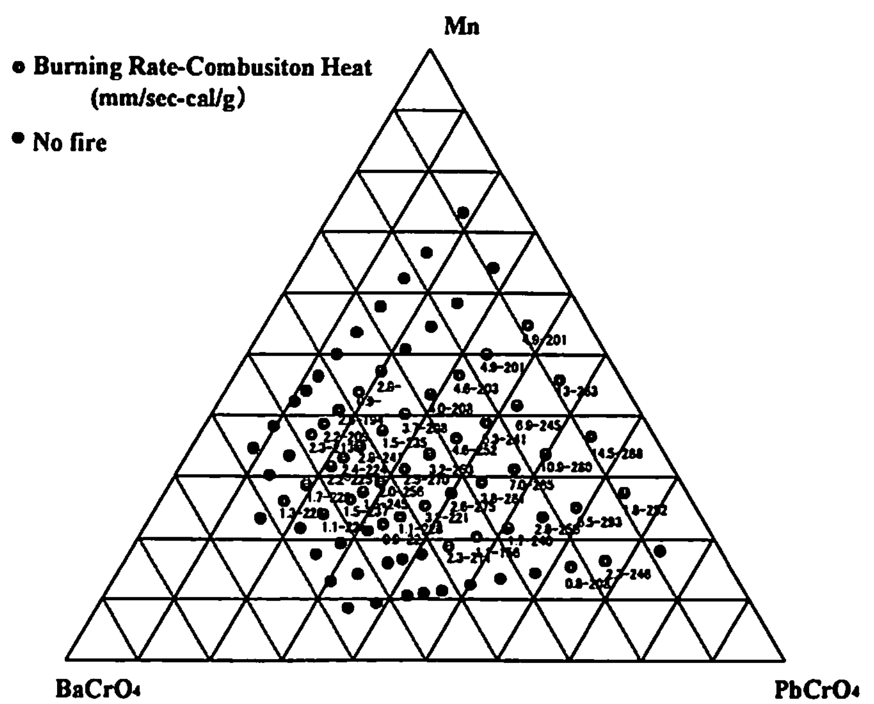


Fig. 6 Relationship between heat of combustion and its composition

composition for the same low burning rate.

Fig. 4 shows the relationship between the ambient temperature and the burning rate at a constant mixture ratio and loading pressure. The temperature dependence of the Mn delay composition was small and had the same slope, even if the loading pressure were varied.

Fig. 5 shows the relationship between the mixture ratio and the burning rate of the Mn delay composition on the triangle coordinates. From this figure, it could be estimated that the combustion reaction area and their burning rates for the ternary delay compositions.

Fig. 6 also indicates the heat of combustion for the each composition on the same triangle coordinates.

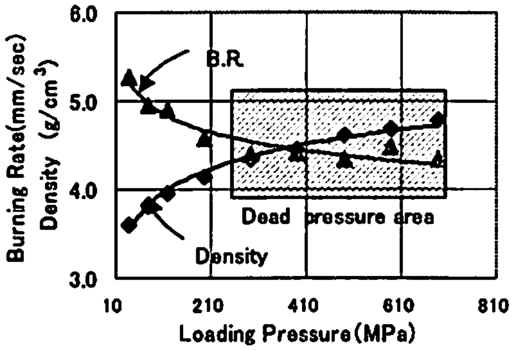


Fig. 7 Relationship between loading pressure and density or burning rate ($Mn/BaCrO_4/PbCrO_4$ =37/22/41)

Fig. 7 shows the relationship between the burning rate or the loading density and the loading pressure of the ternary delay composition ($Mn/BaCrO_4/PbCrO_4$ = 37/22/41 by weight). As the loading density increased, the burning rate decreased. It is easy to define or accept the dead pressure to be above 210 MPa, as the result of the burning interruption for the delay composition. We supposed that the combustion reaction collapsed in the reaction area, because the porosity in a pressed delay composition decreases, and the heat flux generated from the chemical reaction area becomes hard to penetrate into the non-reacting area. Finally, the pre-heating area will be lost, and the chemical reaction will cease at last.

When the Mn is ground before mixing, the burning rate increases with decreasing the average size of Mn particle. A delay composition using ground Mn powders, which were prepared just before mixing, usually deteriorates faster than a delay composition using un-ground Mn powders. Mn powder could cause a high reactivity immediately after grinding, because the burning rate is higher compared to that for un-ground one, even if the average size of Mn particle is equivalent. That is, the ingredients in the composition can easily oxidize the reactive Mn, because the oxidation of Mn is increasingly accelerated due to the improvement of its reactivity and increase in the specific surface area by grinding.

Several surface processing by using hydrazine hydrate, chromic acid solution and other treatments were tried in order to restrict the influence of Mn deterioration on the burning rate during long-term storage.

Fig. 8 shows several microscopic pictures of the surface of surface-treated Mn particles. Fig. 9 shows the relationship between the burning rate and coefficient of variation for the delay composition constituted $Mn/BaCrO_4/PbCrO_4$ ratio of 34/44/22 by using these surface-treated Mn particles. We understood that the surface treatment by potassium dichromate solution, and the coating of the surface of Mn particle with stearic acid are the most effective treatment for storage stability of this type of delay compositions.

Since the frictional heat on grinding may oxidize the surface of Mn particle, the grinding of Mn should be carried out in an inert atmosphere such as nitrogen and argon.

In the Mn delay composition of the low burning rate, the burning stability gradually deteriorates, and at last the burning interruption may take place since the heat loss to the circumference is large during combustion. In order to prevent this phenomenon, the delay composition for low burning rate should be designed to become the heat of

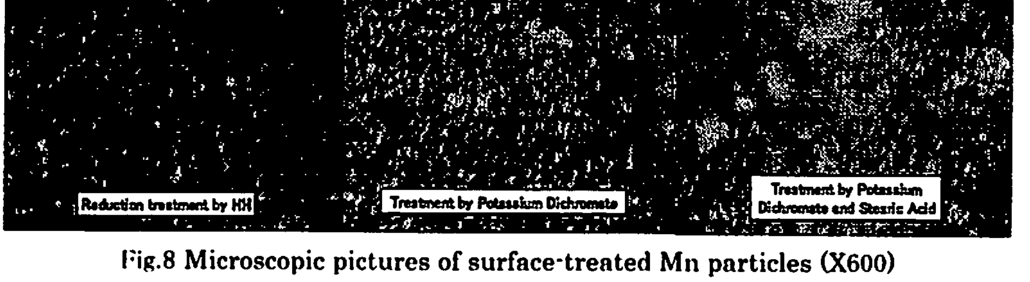


Fig.8 Microscopic pictures of surface-treated Mn particles (X600)

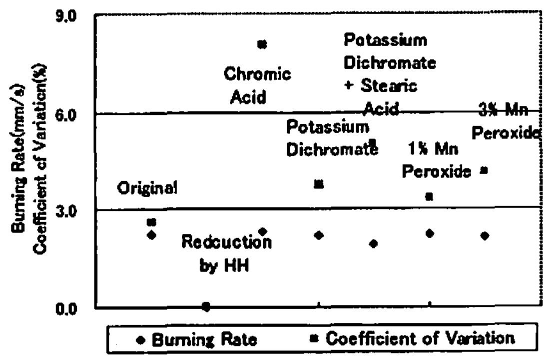


Fig. 9 Relationship between burning rate and coefficient of variation of delay composition using surface-treated Mn ($Mn/BaCrO_4/PbCrO_4$ = 34/44/22)

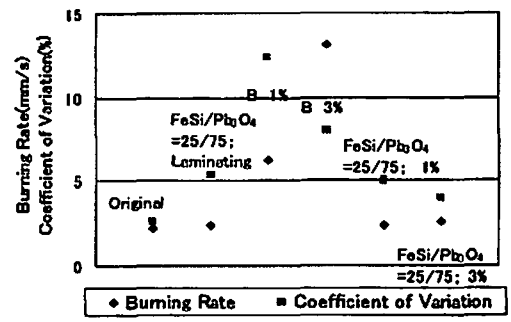


Fig. 10 Effect of additives on the burning rate and coefficient of variation ($Mn/BaCrO_4/PbCrO_4$ = 34/44/22)

combustion as much as possible. As the result, the burning stability of the composition was improved and the variation in burning rates became smaller. This procedure led to the reduction of the coefficient of variation to be less than 5% for the Mn delay compositions.

The relationship between the burning rate and the mixture ratio, and the relationship between the heat of combustion and the mixture ratio are shown in the triangle coordinates in Fig. 5 and Fig. 6 for the Mn delay compositions, respectively. We can estimate the reaction area, the burning rate and the heat of combustion for the Mn delay composition from these figures. We can also obtain information on the high burning rate area or the low burning rate area. These figures suggest that the mixture ratio for the delay composition with the low burning rate had high values of the heat of combustion.

3.3 Addition effect of boron or others on the burning characteristics

Very small amount of metallic boron or ignition powders with the delay composition which is constituted $Mn/BaCrO_4/PbCrO_4$ ratio of 37/22/41 was mixed in order to maintain the burning continuity or to improve the ignitability. Fig. 10 shows the relationship between the burning rate and the coefficient of variation of the delay. In any compositions, the burning rate became high and the coefficient of variation became large, depending on the amount of addition boron or ignition powders. Addition of boron caused an increase in the heat of combustion on the burning rate, because it has a relatively low specific heat capacity and a large thermal diffusivity. The increase in the heat of combustion of the delay took place by including these additives with a high reactivity in the composition. Thus, these methods have some merits such as the improvement of reactivity and burning continuity, but have a great demerit to increase in the burning rate and the coefficient of variation.

4. Summary

The main reaction of the Mn delay composition is the oxidation of Mn by the lead chromate, and the barium chromate is not related to the oxidation of Mn in low reaction temperature range.

The burning rate of the delay compositions is affected by the surface properties of the Mn, the mixture ratio and the loading pressure, but not by the surrounding temperatures. It is suggested that the loading pressure may affect the length of pre-heating area in combustion. Therefore, if the loading pressure is high, the length of pre-heating area will become thin resulting in decrease of the burning rate. As the result burning will be interrupted.

We also investigated many relationships both between the mixture ratio and the burning rate, and between the mixture ratio and the heat of combustion for Mn delay compositions. These results are plotted on the triangle coordinates. The several conclusions were obtained about the burning rate and the heat of combustion for the ternary delay composition of the Mn system. In order to restrict the influence on the burning rate by deterioration of Mn with the long-term storage and grinding, the surface treatment of Mn particles by potassium dichromate solution and surface coating by the stearic acid are the most effective for improvement in the storage stability of the Mn delay composition. Research on the surface treatment of Mn is still undergoing.

Boron and ignition powders improved the burning continuity and ignitability if added to these delay compositions, but the coefficient of variation became large. Thus, this concluded us that this method is not effective.

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