Effect of barium peroxide activity on the reactivity of barium peroxide - lead chromate - dinitronaphthalene - chlorinated rubber delay composition

Hidetsugu NAKAMURA*, Yuuzi TOMIOKU*, Miyako AKIYOSHI* and Yasutake HARA*

Some kinds of barium peroxide were prepared by pulverizing with a vibro-mill, and their properties and the reactivity were estimated. Moreover, the linear burning rate of delay powder containing milled barium peroxide was measured to clarify the effect of the activity of barium peroxide on the burning characteristics. The results obtained are as follows:

The mean particle diameter and active oxygen content of barium peroxide decreased with increasing milling time. In addition, the size of the crystallite became smaller and an effective lattice distortion constant increased with milling time. Although barium peroxide without milling caused only melting, the milled one caused melting and the formation of carbonate on heating in air. Barium peroxide - lead chromate - dinitronaphthalene - chlorinated rubber delay composition also exhibited different thermal reactivity by pulverization of barium peroxide. The milling over 72 hours caused a decrease of about 60 ℃ in the temperature at which an intense exothermic reaction commenced. With regard to combustion characteristics, a decrease of 100℃ in the ignition temperature was observed compared to the case without milling, and pulverization caused a six fold increase in the linear burning rate.

1. Introduction

Barium peroxide - lead chromate - dinitronaphthalene - chlorinated rubber mixture (abbreviated as BaO_2 delay composition) is used as a delay composition in a Ms or DS detonator. Ordinarily, a delay composition consisted of an oxidizer and reducing agents as fuel, such as metallic powder, in order to avoid producing of gaseous products. However, the BaO_2 delay composition is somewhat different from the usual formulation with respect to containing organic compounds. Nevertheless, the delay time is quite precise, though it produces somewhat gaseous products. Its reactivity and combustion characteristics have been known empirically to be affected especially by the activity of barium peroxide.

In this study, some kinds of barium peroxide were prepared by pulverizing by a vibro-mill, and their properties and reactivity were measured in order to evaluate the effect of the activity of barium peroxide on the reactivity of the BaO_2 delay composition. Moreover, the burning rates of the delay compositions containing milled or unmilled barium peroxide were measured in order to clarify the effect of the property of barium peroxide on the burning characteristics.

Received on September 7, 1999

*Department of Applied Chemistry, Faculty of Engineering, Kyusyu Institute of Technology
Sensui, Tobata, Kitakyusyu, 804-8550 JAPAN
TEL 093-884-3319
FAX 093-884-3300

2. Experimental

2.1 Materials

The sample barium peroxide (BaO_2) was reagent grade and had an average particle diameter of 3.42 μm. Its purity was 95.7wt.% determined from chemical analysis. Pulverization was performed using a laboratory vibro-mill (Tutui Scientific Instrumentation Co., Ltd.), using a stainless container and 50 stainless grinding balls (10mm ϕ). One batch treatment was performed for a 20 g sample dipped in toluene. The vibration frequency was 100 rpm, and its running time ranges from 24 to 96 hours. After

pulverization, toluene was washed out by ethanol and dried in a vacuum.

The lead chromate ($PbCrO_4$) was reagent grade and had a content of 98wt.%. Its average particle diameter is under 106 μ m. Dinitronaphthalene (DNN) was industrial grade and supplied by Japan Carlit Co., Ltd. It had an average particle diameter of 106μm and contained a 37～38wt.% 1,5-DNN, 55～56 wt.% 1,8-DNN, 0～0.3wt.% 1,3-DNN and 1-nitronaphthalene. The industrial grade chlorinated rubber CR-150 supplied by Asahi Denka Kougyou KK. was poly isoprene rubber and contained 65wt.% chlorine.

The delay powder was prepared using an ordinary ball-mill mixer. The composition was BaO_2/$PbCrO_4$/DNN/chlorinated rubber = 90/10/2.5/0.3 by weight.

2.2 Analysis

The purity of barium peroxide was determined by a oxidation - reduction titration of potassium permanganate in hydrochloric acid solution. Particle size was measured using a Horiba Centrifugal Particle Size Analyzer CAPA-500. Thermal analysis was performed with a Rigaku DTA - TG simultaneous analyzer TAS - 200 in argon flow with a heating rate of 20 K/min. X-ray powder diffraction was performed using a Rigaku Roter Flex RU-200. The particle morphology was observed using a JEOL Ltd. Scanning Electron Microscope JSM-2.

2.3 Combustion experiment

The delay compositions were burnt in an aluminum cylindrical tube, and the time required for burning was recorded using a digital memory with optical fiber signals. The sample of the delay powder used in one combustion experiment was loaded nine times in order to obtain a homogeneous loading, and its density was 60% of theoretical maximum density.

The ignition test was carried out according to the Krupp method under argon. After the mixture of 100 mg was pressed at 588MPa, the pellet obtained was divided into 5mg pieces for the use of ignition test.

2.4 Sensitivity tests

Friction sensitivity was measured using the BAM Friction Sensitivity Tester according to the Japanese Industrial Standards JIS K 4810[1]. Electrostatic sensitivity test was carried out using an electrostatic sensitivity tester having a fixed electrode according to the Japan Explosives Society Standard ES-25[2].

3. Results and Discussion

3.1 Effect of milling on the property and reactivity of barium peroxide

Fig. 1 shows the effect of milling on the mean particle diameter and the purity of barium peroxide. The mean particle diameter of unmilled barium peroxide was 3.42 μ m. The milled barium peroxide decreased in size with increasing milling time and became about half after milling for 92 hours. Fig. 2 shows SEM photographs of unmilled (a) and milled for 92 hours (b) barium peroxide. From observation of the SEM photographs, unmilled barium peroxide which had an average particle diameter of 3.42 μ m was like a single crystal and consisted of 0.3～5 μ m particles. On the other hand, milled barium peroxide became smaller in size, and its crystallite at the surface was disordered with milling time. Barium peroxide milled for 92 hours consisted of opaque polycrystalline particles and some dozens of primary particles of about 0.01～0.5 μ m aggregate to form a secondary particles of several or several ten microns in size. Therefore, it is concluded that the actual surface area of the milled sample was several tens of times larger than the surface area of the milled sample calculated by the mean particle diameter obtained from the particle size analyzer.

The purity of barium peroxide without milling was 95.7% and decreased with milling time to 70.0% after milling for 92 hours. This decrease in the amount of

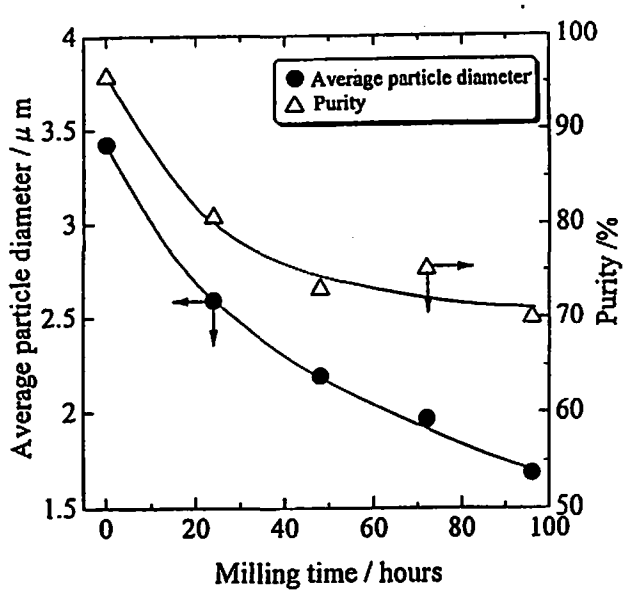

Fig. 1 Effect of milling on mean particle diameter and purity of barium peroxide

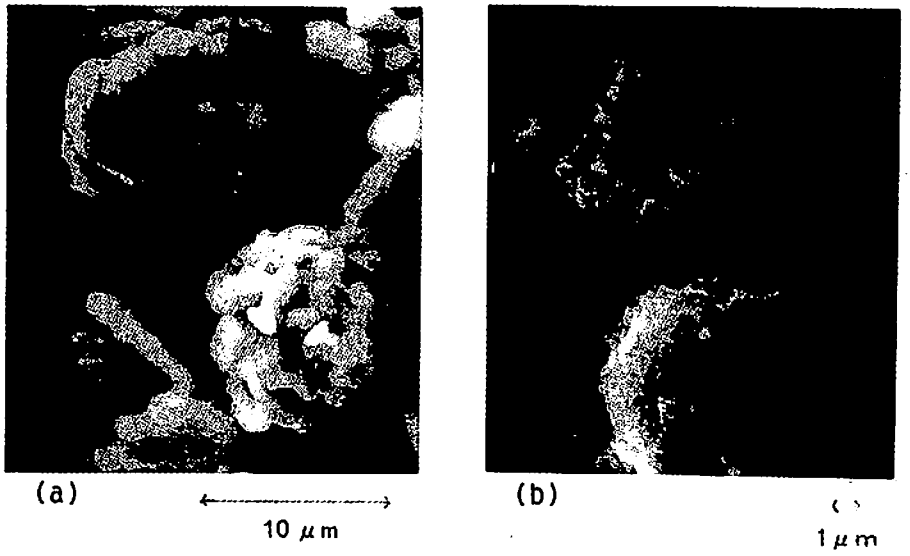

Fig. 2 SEM photographs of unmilled (a, X4000) and milled (b, X6000) barium peroxide

active oxygen was caused by accumulation of mechanical energy on the surface and in the bulk decreased by pulverization.

Fig. 3 shows the X-ray powder diffraction of barium peroxide. Barium peroxide without milling (Fig. 3-a) showed none of the peaks of impurities. On the other hand, the one milled for 92 hours (Fig. 3-b) contained barium carbonate, but the existence of barium oxide could not be confirmed because the diffraction peaks of barium oxide overlapped with that of barium carbonate. Moreover, precise observation of X-ray powder diffraction data indicated that milling over 24 hours caused an increase in the half-width (β) of the diffraction pattern and the formation of barium carbonate. The diffusion of the peak in the diffraction pattern depends on the crystallite which is the minimum unit of the crystal. That is, the wider the diffusion, the smaller the crystallite and the relationship between these is designated by the following equation[3]:

$$L = K\lambda / \beta \cos\theta \qquad (1)$$

where L is the size of the crystallite, K is a constant, λ is the wave length of the Cu-Kα line, β is the half-width of the diffraction peak and θ is the diffraction angle. Moreover, the diffusion of the peak also depends on the disorder of the crystal lattice. The disorder of the crystal lattice is described by the following equation[4]:

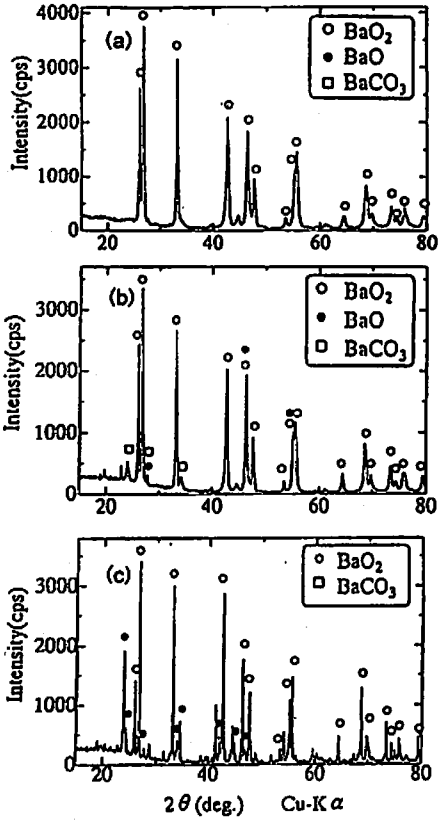

Fig. 3 X-ray powder diffraction patterns of milled barium peroxide (a), without milling (b) and milled barium peroxide after heating up to 450℃ (c)

$$\beta \cos\theta = K\lambda / L + \eta \sin\theta \qquad (2)$$

where η is an effective lattice distortion constant. Table 1 shows the calculated values of L for the barium peroxide obtained by milling for various times.

Table 1 Effect of milling on the size of crystallite and the effective lattice distortion constant of barium peroxide

Milling time/hours	0	24	48	72	96
L	1136	700	572	589	499
$\eta \times 10^3$	2.25	4.33	7.65	6.85	6.36

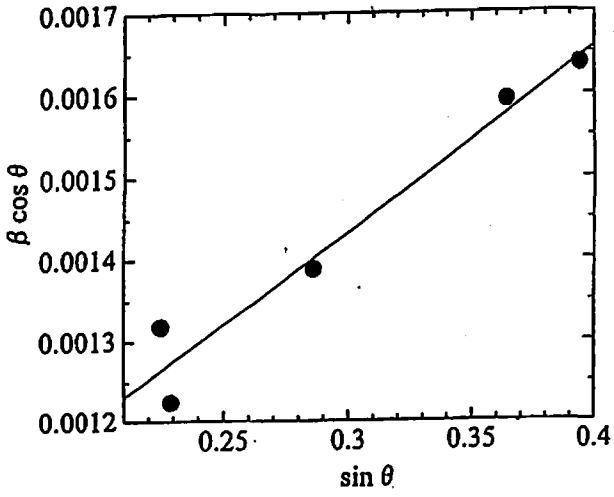

Fig. 4 $\beta \cos\theta$ vs. $\sin\theta$ plot for milled and unmilled barium peroxide followed by Sherrer and Stokes equation

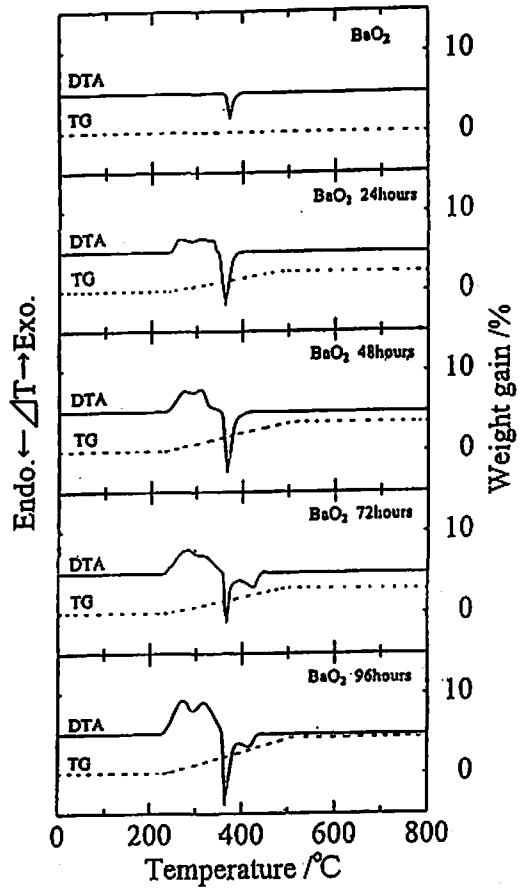

Fig. 5 DTA and TG curves of milled and unmilled barium peroxide in air

Using these L values, an effective lattice distortion constant η can be obtained by plotting a $\beta \cos\theta$ vs. $\sin\theta$. Fig. 4 shows the relationship between the $\beta \cos\theta$ vs. $\sin\theta$ plot for milled and unmilled barium peroxide followed by equations 1 and 2, and the obtained η values are shown in Table 1. The calculated values of the size of crystallite L became smaller with milling time to below half with milling for 92 hours. According to the decrease in the size of the crystallite, the extent of lattice distortion η values became greater.

3.2 Thermal reactivity of barium peroxide and delay composition containing barium peroxide

Fig. 5 shows the results of the thermal analysis of milled and unmilled barium peroxide in air. The DTA trace of unmilled barium peroxide showed an endothermic peak ranging from 365 to 395℃ with no weight increase. It is caused by melting, but this temperature was about 100℃ lower compared to the literature data [5]. In this paper, we did not investigated why the melting point dropped. But, it can be considered that comelting of barium peroxide with barium carbonate or barium oxide formed on the surface is one of the reasons. The DTA and TG of milled barium peroxide showed quite different features from that of unmilled. The DTA traces of milled barium peroxide showed exothermic peaks before melting and a weight increase. Moreover, the endothermic peak caused by melting became larger or occurred stepwise for the barium peroxide milling for over 72 hours. The X-ray powder diffraction patterns for the samples which were heated up to just before the temperature of melting of about 365℃ and up to 450℃ showed the far larger peaks of barium carbonate (Fig. 3-c). Therefore, we conclude that the active barium oxide forming on the surface because of pul-

verizing causes an exothermic reaction with carbon dioxide in air to form carbonate.

Fig. 6 shows the DTA curves of the BaO_2 delay composition under argon atmosphere. The delay composition containing milled barium peroxide caused two-step exothermic reactions ranging from 235℃ to 440℃. The temperature at which the exothermic reaction commenced became lower for the delay composition which contains milled barium peroxide. Delay compositions which contained barium peroxide milled over 72 hours showed an intense exothermic reaction at 178℃. The purity of barium peroxide milled over 72 hours decreased up to about 70wt.%, but was more reactive compared to the unmilled one.

3.3 Combustion characteristics of barium peroxide - lead chromate - dinitronaphthaleine - chlorinated rubber mixture

Fig. 7 shows the effect of milling time of barium peroxide on the ignition of the BaO_2 delay composition. The delay composition containing unmilled barium peroxide shows the minimum ignition temperature of 296℃. On the other hand, the ignition temperature of the delay composition containing milled barium peroxide decreased with increasing milling time and dropped up to 195℃ for a sample which contained barium peroxide milled for 92 hours.

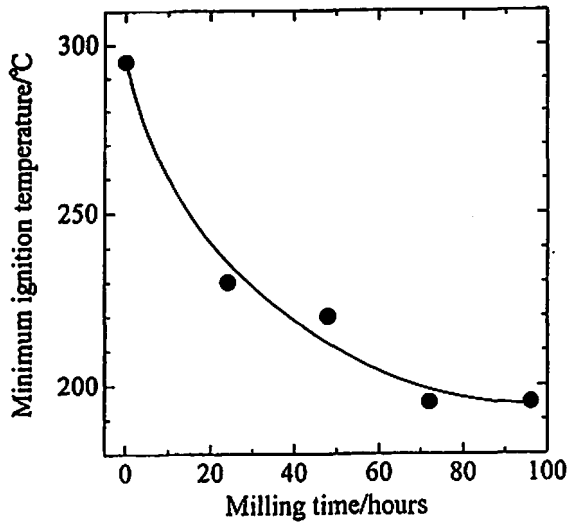

Fig. 7 Effect of milling of barium peroxide on the ignition of the barium peroxide - lead chromate - dinitronaphthalene - chlorinated rubber delay composition

The linear burning rate in Fig. 8 increased with increasing milling time. That is, the delay composition containing unmilled barium peroxide had a linear

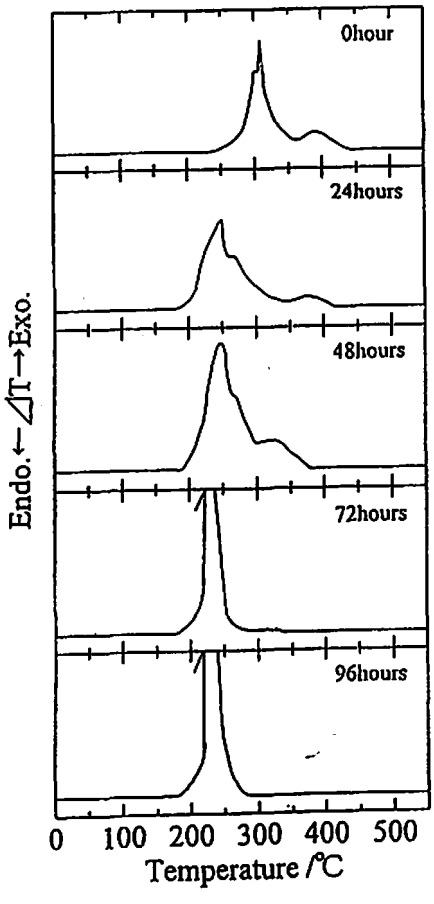

Fig. 6 DTA curves of barium peroxide - lead chromate - dinitronaphthalene - chlorinated rubber delay composition containing milled and unmilled barium peroxide

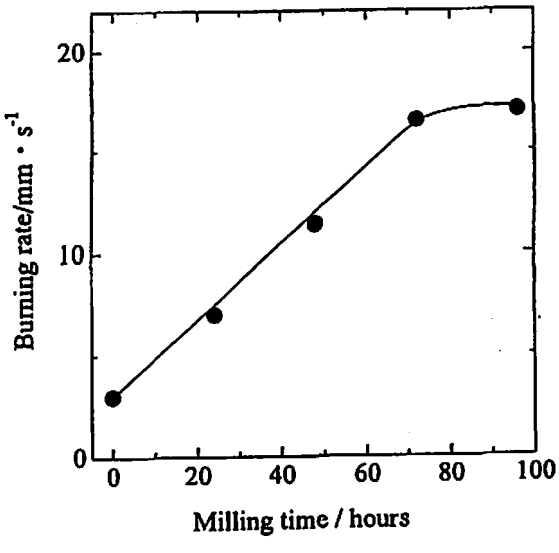

Fig. 8 Effect of milling of barium peroxide on the linear burning rate of barium peroxide - lead chromate - dinitronaphthalene - chlorinated rubber delay composition

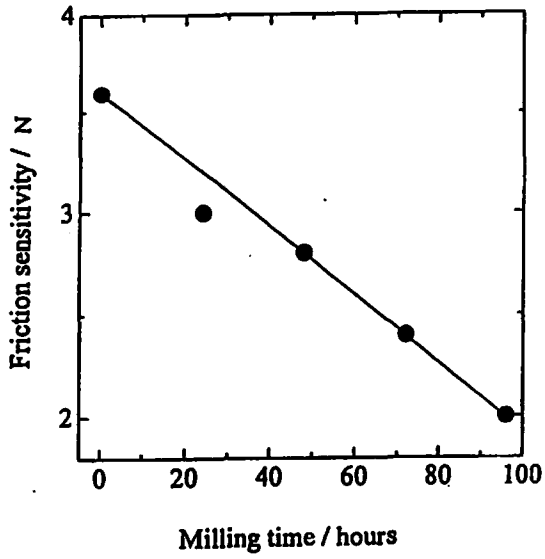

Fig. 9 Effect of milling of barium peroxide on the friction sensitivity of the barium peroxide - lead chromate - dinitronaphthalene - chlorinated rubber delay composition

burning rate of 2.99mm/sec. On the other hand, every composition which contained the milled one showed a increase in linear burning rate, and the one milled for 92 hours reached a about six times larger value of 17.0 mm/sec compared to the delay composition containing unmilled one. From these results, it is concluded that the burning characteristics of this delay composition were affected by the activity of barium peroxide.

Friction and electrostatic sensitivities are especially important factors for a safe production of delay composition. Every composition was insensitive in the electrostatic sensitivity test, although the electrode gap length, capacitance of condenser and resistance of discharge circuit were changed. However, in friction sensitivity test, ignition occurred accompanied by noise and light. The results of the friction sensitivity test for the BaO_2 delay compositions are shown in Fig. 9. The vertical axis is the load which causes one firing among 6 trials of the test. The results resemble the other reaction characteristics, and the friction sensitivity became more sensitive with increasing milling time.

4. Conclusions

The surface and bulk properties of barium peroxide changed by pulverization using a laboratory vibromill. That is, the mean particle diameter and its active oxygen content of barium peroxide decreased with increasing milling time. In addition, the size of the crystallite became smaller, and an effective lattice distortion constant increased with increasing milling time. By pulverization, the thermal reactivity of barium peroxide changed and partially the decomposition of barium perchlorate occurred to form barium oxide and carbonate. Although the unmilled barium peroxide caused only melting, milled barium peroxide caused the formation of carbonate on heating in air, because of its activeness. The BaO_2 delay composition also shows quite different thermal reactivity, and the pulverization over 72 hours caused a decrease in the temperature at which an intense exothermic reaction commenced.

The combustion characteristics of the delay compositions were also affected by pulverization. A decrease of 100℃ in the ignition temperature was observed compared to the case without milling. Every composition which contained the milled one showed an increase in the linear burning rate, and the one from 92-hours milling reached a six times greater value of 17.0mm/sec compared to unmilled case.

References

1) Japanese Industrial Standards, JIS K4810, Japanese Standards Association (1979)
2) Japan Explosives Society Standards, ES-25, Japan Explosives Society (1988)
3) A.R.Stokes, A.J.C.Wilson, Proc. Camb. Phil. Soc., 38, 313 (1942)
4) W.H.Hall, Proc. Phys. Soc., A62, 741 (1949)
5) The Chemical Society of Japan, "Kagakubinran (Kisohen I), 3rd Ed.", Maruzen (1984) p. 67

過酸化バリウムークロム酸鉛ージニトロナフタレンー塩化ゴム系延時薬の反応に及ぼす過酸化バリウムの活性の影響

中村英嗣*，富奥祐二*，秋吉美也子*，原　泰毅*

ボールミルで粉砕することにより，数種の活性の異なる過酸化バリウムを調整して，その物性と反応性を検討した。また，この過酸化バリウムを含む延時薬を調整し，その物性が反応性や燃焼特性に及ぼす影響を検討した。

過酸化バリウムを粉砕すると，粉砕時間に対応して粒子径は減少し，純度も低下した。また，粉砕により結晶の歪みが増加して，放置時または加熱時には空気中の炭酸ガスと反応した。これらを含む過酸化バリウムークロム酸鉛ージニトロナフタレンー塩化ゴムの四成分系延時薬を調整した場合の反応性はその物性に大きく影響されて，燃焼速度は粉砕により粉砕しない場合の約6倍増加し，熱反応の反応開始温度や発火温度は低下し，熱反応性や着火性は著しく活性化した。

(*九州工業大学工学部応用化学教室　〒804-8550 北九州市戸畑区仙水町1-1)