Burning Characteristics of the Molybdenum - Potassium Perchlorate - Barium Chromate Delay Compositions

by Long-Ming Tsai*, Chii-Horng Liaw*, and Yeong-Jgi Chen*

The ignitibility, burning rate and its reproducibility for different compositions of Mo-$KClO_4$-$BaCrO_4$ delay elements are studied. It is observed that the compositions in certain region of triangular diagram are not ignitible, and for reliable performance the content of $KClO_4$ in the mixtures should not exceed 40%. With proper selection of formulation, delay element having a burning rate from 0.027 to 7.5sec/cm can be readily achieved. The experimental results also show that the burning rate can be made more precise by vacuum annealing of pellet or by pressing an acceleration cavity at the input end of pellet. Data from heat of reaction, autoignition temperature and X-ray powder diffraction have been collected and discussed.

1. Introduction

Since delay composition play an important role in the development of explosive trains, its quality and reliability have strong effect on the performance of the whole system. Although a large number of delay compositions have been evaluated for certain purposes (1)(2), in general, the molybdenum delays were found to have a wider range of burning rate (3)(4)(5). However, the ignitibility and reliability of molybdenum delays have not yet been thoroughly investigated. In this study, the ignitibility, burning rate and reproducibility of the Mo-$KClO_4$-$BaCrO_4$ delay compositions are investigated. In addition to formulation study, two processing techniques namely vacuum annealing and acceleration cavity are applied to improve the precision of burning rates. Finally, thermal and chemical data are collected to reveal with the variation of performance quality.

2. Experimentals

2.1 Raw Materials

(1) Molybdenum, 99.9% pure powder, Z. Bruton AG reagent, with average particle diameter 1.6μm. (2) Barium Chromate, 99% pure powder, Riedel De Haen reagent, <63μm after grinding and sieving. (3)Potassium Perchlorate, 99% pure powder, Fluka AG reagent, <44μm after sieving.

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2.2 Preparation of Delay Element

The manufacturing process of the delay elements is schematically described in Fig. 1. The delay powder is pressed in increments under 110,000 psi into a 10㎜ long copper tube, 4㎜ I. D. and 8㎜ O. D.. A 3.0㎜ primer cap is used as igniter. The primer time is less than 1.5msec (6). A 0.05gm weight of Zr/Fe_2O_3 (72/28) ignition mixture is pressed on top of the delay pellet. The burning time of this ignition mixture is about 3.5msec.

2.3 Burning Rate Measurement

A schematic drawing of experimental apparatus is shown in Fig. 2. The burning rate is measured with an HP-5315A universal counter. Timing starts when the hammer hit the firing pin, and stops when the photocell is actuated by the flash of the delay pellet. Fifteen runs are fired for each tested composition.

2.4 Vacuum Annealing and Acceleration Cavity

Two processing techniques are applied in an attempt to improve the performance of the delay mixtures, namely, by vacuum annealing of pellet or by pressing an acceleration cavity at the input end of the pellet. A schematic drawing of acc-

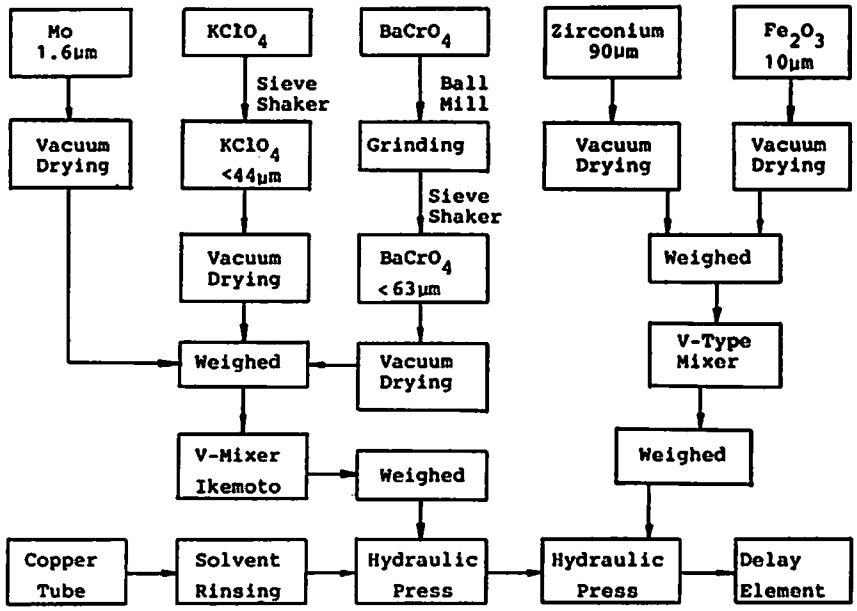

Fig. 1 Manufacturing process of delay element.

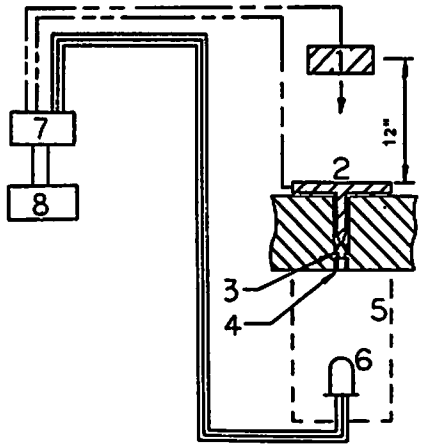

Fig. 2 Apparatus for delay time measurement.
1;hammer, 2;firing pin, 3;primer, 4;delay element, 5;dark chamber, 6;phototransistor, 7;interface, 8;counter.

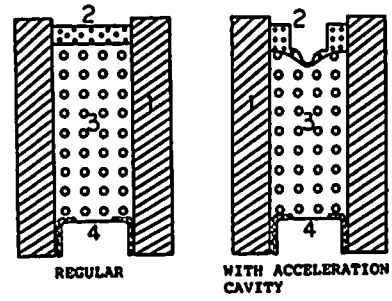

Fig. 3 Schematic drawings of delay elements.
1;body, 2;ignition mixture, 3;delay composition, 4;contraction hole.

eleration cavity configuration is shown in Fig. 3. For the case of vacuum annealing, the delay mixtures are heated under vacuum at 130℃ for 64 hours.

2.5 Thermal and Chemical Analysis

Parr bomb calorimeter and autoignition temperature tester have been employed for the measurement of heat of reaction and autoignition temperature of the delaymixtures respectively.

Heat of reaction of Mo-$KClO_4$ binary mixtures are measured under 25 atm argon. Each test sample weigh 10gms is pressed to form a thin disc at 110,000 psi which can be ignited by the tungsten wire assembled inside the bomb. The autoignition temperature tester was supplied by Julius Peter Company, Germany. In which, 0.5gm of the delay mixture is loosely packed in a test tube immersed in Wood's metal bath. The temperature of the bath is controlled to keep at a 5℃/min increment. When the delay mixture sample reaches its auto-ignition temperature, it will ignite with a sudden puff. Precision of the measurement is about ±2℃. Gas evolution tester was supplied by Haake Company, Germany. The sample used for total

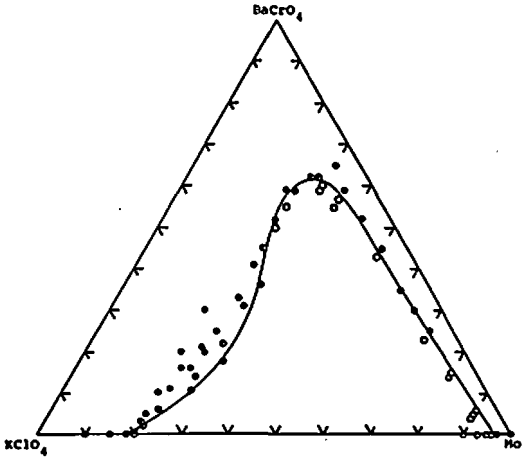

Fig. 4 Boundary of ignitible compositions of Mo $-BaCrO_4-KClO_4$ mixtures.
○;may or may not ignite, ●;not ignitible, ○;ignitible.

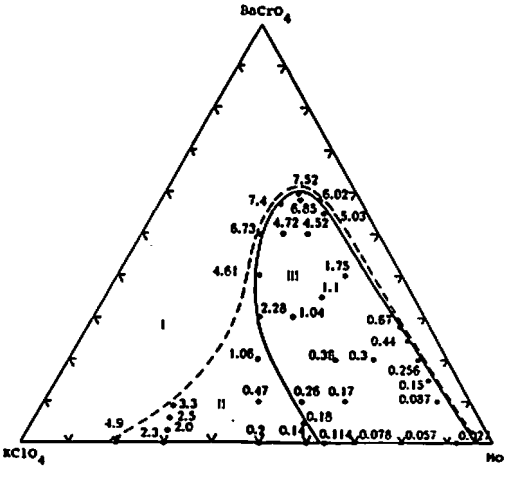

Fig. 5 Burning time (sec/cm) of Mo-$BaCrO_4$ $-KClO_4$ mixtures.

gas evolution test is prepared as those for Parr bomb calorimeter. Ignition proceeds in a 50 cc thick wall bomb furnished with tungsten wire heating device. Before the test, the bomb is connected to a 3 liter flask which is under nearly vacuum condition. After ignition, the gas pressure inside the flask is measured, the total gas volume is then converted to 0℃, 1 atm.

Philips PW1050/71 X-ray powder diffractometry is used for the analysis of the residue after burning of the delay elements. The gaseous combus tion product from the bomb used in gas evolu-

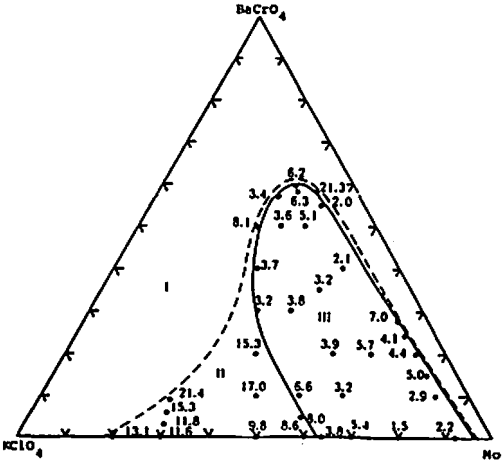

Fig. 6 Coefficients of variation of burning time of Mo-$KClO_4$-$BaCrO_4$ mixtures.

tion test is connected to sample inlet system of Finigan 4023 GC/mass spectrometer for the identification of the presence of Cl_2 gas.

3 Results and Discussions

3.1 Ignitibility, Burning Rates and their Coefficients of Variation

In the study of the combustion behavior of Mo $-KClO_4-BaCrO_4$ mixtures, we found that some of the compositions could not be burned completely and some of them could even not be ignited. The results are summerized in Fig. 4. Fig. 5 and Fig. 6 are the inverse burning rates (sec/cm) and their coefficients of variation of Mo-$KClO_4$-$BaCrO_4$ delay compositions respectively. The coefficient of variation is standard deviation expressed as a percentage of the mean value. The non-ignitible compositions are designated as region I in Fig. 5 and Fig. 6. In region II, the mixtures have inflammability with relativey large amount of gas evolution, and the coefficients of variation for burning rate are significantly higher than those in region III. It can be realized that the delay mixtures will not have good performance quality if the content of $KClO_4$ exceeds 40%. For reliable performance, delay element compositions can be selected from those in region III where the burning time varies 0.027 sec/cm to 7.52 sec/cm.

3.2 Effect of Vacuum Annealing

Table 1 shows the examples that vacuum annealing treatment affects the performance quality of Mo-$KClO_4$-$BaCrO_4$ mixtures. It can be seen that

Table 1 Effect of vacuum annealing on the performance quality of Mo-$KClO_4$-$BaCrO_4$ mixtures

Formulations Mo/$KClO_4$ wt. ratio / Results		20/80	30/70	30/70 + 6wt. % $BaCrO_4$	30/70 + 9wt. % $BaCrO_4$	40/60	50/50	50/50 + 10wt. % $BaCrO_4$	50/50 + 20wt. % $BaCrO_4$	60/40
Burning time (sec/cm) & Coefficient of variation (%) in parenthesis	untreated	4.9 (13.1)	2.3 (11.6)	2.5 (15.3)	3.3 (21.4)	1.26 (18.1)	0.2 (9.8)	0.47 (17.0)	1.06 (15.3)	0.14 (8.6)
	Vaccum* Annealing	2.17 (5.3)	1.07 (9.2)	1.21 (11.7)	1.68 (16.0)	0.86 (12.5)	0.29 (8.4)	0.72 (11.8)	1.27 (15.3)	0.13 (8.8)

* Evacuated under 130℃ for 64 hours.

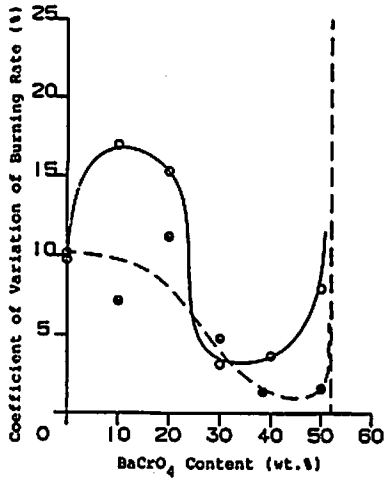

Fig. 7 Effect of acceleration cavity configuration on the performance quality of Mo-$KClO_4$-$BaCrO_4$ mixtures. Mo/$KClO_4$=50/50, ——regular type, ……with acceleration cavity.

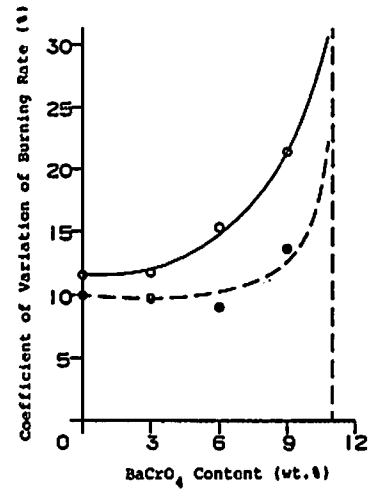

Fig. 8 Effect of acceleration cavity configuration on the performance quality of Mo-$KClO_4$-$BaCrO_4$ mixtures. Mo/$KClO_4$=30/70, ——regular type, ……with acceleration cavity.

after vacuum annealing, the burning time of the mixtures are changed and the coefficients of variation are reduced. The compositions listed in Table 1 are those selected from the region II of Fig. 5 &6. Whereas the delay compositions inside region III which already have satisfactory quality, the vacuum annealing treatment does not give significant change or improvement in the consistency of their burning rates.

3.3 Effect of Acceleration Cavity Configuration

Fig. 7 and Fig. 8 show the effect of acceleration cavity configuration (7) on the performance quality. It is recongnizable that the burning time of delay pellet can be made more precise by this design. Some U. S. military explosive devices have adopted this design. According to their report, acceleration cavity configuration is attempted to reduce the variation of burning rate due to high thermal conductivity (8) and the inconsistency of roughness of the delay tube wall (7).

3.4 Heat of Reaction and Autoignition Temperature

Fig. 9 shows the heat of reaction and autoignition temperature of Mo-$KClO_4$ binary mixtures. For those molybdenum content higher than 80% or lower than 18%, their autoignition temperature are higher than our experimental limit 400℃, and the heat of reaction are found to be lower that 350 cal/gm. For these compositions, the low heat of reaction may not provide enough energy as required for successive ignition to sustain flame propagation. This argument may explain qualitatively the ignitibility of Mo-$KClO_4$ mixtures shown in

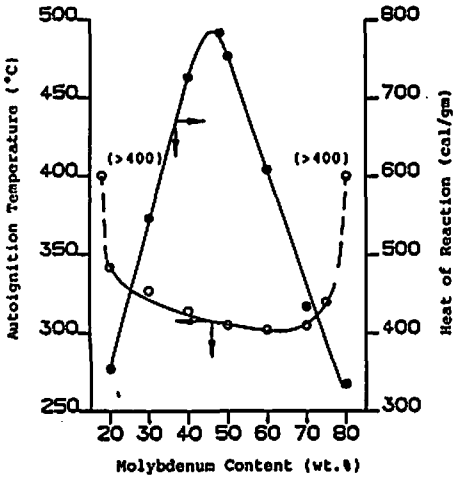

Fig. 9 Heat of reaction and autoignition temperature of Mo–$KClO_4$ binary mixtures.

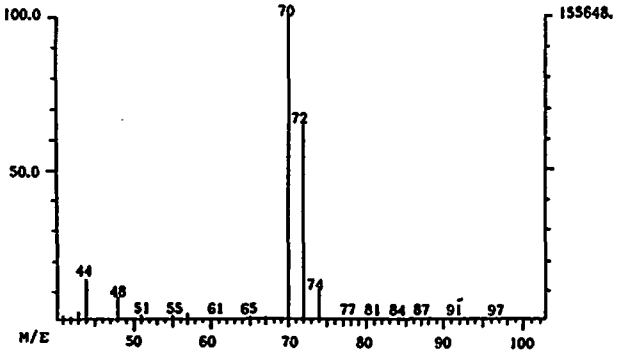

Fig. 10 Identification of Cl_2 in the burning products of Mo/$KClO_4$(30/70)mixture by GC/MS analysis.

Fig. 4. That is, for those molybdenum content higher than 95% and lower than 18%, the delay columns are not able to burn through. We have noticed that for the excess fuel compositions whose molybdenum content varied from 80wt% to 95wt% are combustible. The explanation is that the large percentage of molybdenum acts as a good heat conductor, the unburnt column prior to the flame front is preheated and therefore its ignitibility is enhanced. In this system, the heat of reaction reaches a maximum at approximately 48wt percent molybdenum content. Therefore this result qualitatively may agree with the following stoichiometric relation suggested by other investigators (4)

$$4Mo+3KClO_4 \longrightarrow 4MoO_3+3KCl \quad (1)$$

But, from the results that certain amount of MoO_2 and $K_2Mo_4O_{13}$ have been found in the combustion residue, and that Cl_2 gas has been found in gaseous combustion products as shown in Fig. 10, it indicates that only considering equation (1) is not enough to understand the detail combustion mechanism, some other chemical reactions must be taken into account. In other respect , the weight burning velocity increases monotonically with the molybdenum content (Fig. 11). These results suggest that the burning rates of molybdenum delay compositions can not be correlated with their caloric output, but appear to be a function of the thermal conductivity of the mixtures (9)(10).

3.5 Gas Evolution

Fig. 12 shows that the amount of gas evolution of Mo–$KClO_4$–$BaCrO_4$ mixtures in region II is much larger than that in region III. Free oxygen is concerned as the major component in gaseous products, because free oxygen may be released if the potassium perchlorate is stoichiometrically excess with respect to molybdenum (9). Our observation also concludes that larger amount of gas evolution for the compositions in region II of Fig. 12 are due to higher

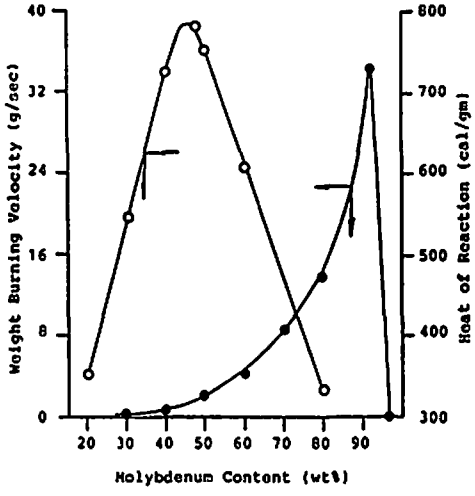

Fig. 11 Heat of reaction and weight burning velocity of Mo–$KClO_4$ binary mixtures. delay tube:brass tube of 4㎜Φ and 10 ㎜ length.

Table 2 Relative diffraction intensity of the combustion residue of $Mo/KClO_4$ mixtures from X-ray powder diffraction data.

Combustion Residue / Mo/$KClO_4$ (by wt.)	Mo $2\theta = 40.4$	KCl (Cubic) $2\theta = 28.2$	MoO_3 (orthorhombic) $2\theta = 39.2$	MoO_3 (hexagonal) $2\theta = 19.2$	MoO_2 (monoclinic) $2\theta = 36.7$	$K_2Mo_4O_{13}$ $2\theta = 25.3$
70/30	1	0.754	0.033	0.043	0.156	0.08
50/50	0.33	0.58	0.036	0.06	0.101	0.094
48/52	0.32	0.57	0.029	0.192	0.062	0.043
40/60	0.38	0.86	0.058	0.275	0.029	0.123
20/80	0.70	2.59	0.101	0.138	0.036	0.326

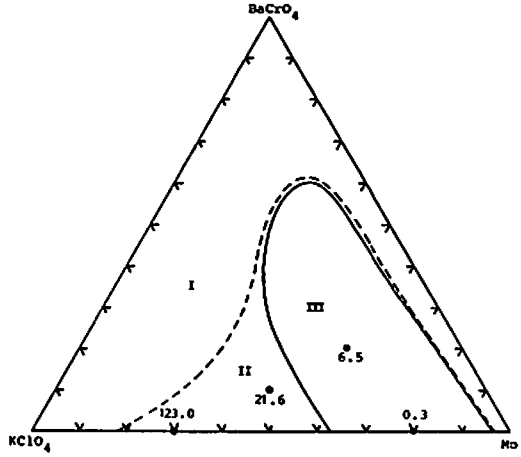

Fig. 12 Gas evolution (ml/gm) of Mo-$BaCrO_4$-$KClO_4$ mixtures.

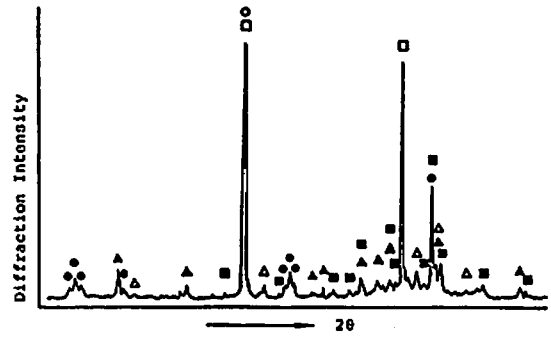

Fig. 13 X-ray powder diffraction spectrum of the reaction products of $Mo/KClO_4$ (70/30) mixture.
○ ; Mo, △ ; MoO_3(othorhombic), ▲ ; MoO_3(hexagonal), □ ; KCl, ■ ; $K_2MO_4O_{13}$, ● ; MoO_2(monoclinic).

$KClO_4$ content in this region. Furthermore, presence of free chlorine in burning products also gives indication that violent oxidation reaction can be occurred. Although no attempt was made in this study to include the detail quantitative analysis of gaseous products, our experimental results suggest that the chemical reactions associated with the combustion process are quite complicated.

3.6 Analysis of Combustion Residue

Fig. 13 shows a typical X-ray powder diffraction spectrum of the reaction products of Mo-$KClO_4$ binary mixtures. The components of combustion residue are identified as KCl, MoO_3, MoO_2, $K_2Mo_4O_{13}$, Mo, etc. Table 2 lists their relative diffraction intensity of several binary mixtures. The results indicate that the molybdenum can not react completely even with very high oxidizer content ($KClO_4$). Riffault (11) pointed out that the temperature of ignition of Mo-$KClO_4$ mixtures varied for different compositions and the oxidation of Mo would give MoO_2, MoO_3, Mo_4O_{11}, and Mo_9O_{26} etc. Bernard et al (12) proposed that the combustion residue might include MoO_2, MoO_3, Mo_4O_{11}, and Mo_8O_{23} and Mo_9O_{26}. Their revised model of solid propagation rate has been found quite successful for many pyrotechnic mixtures, but does not fulfil the reaction of Mo-$KClO_4$ system. Obviously, the detail mechanism of reaction for molybdenum delay composition need to be carefully studied.

4. Conclusion

(1) The combustion behavior of Mo-$KClO_4$-$BaCrO_4$ delay compositions in obturated system are investigated. Reliable performance can be obtained for the range of burning time from 0.027 sec/cm to 7.52 sec/cm by proper

selection of formulation, while the content of $KClO_4$ are confined not to exceed 40%.

(2) The burning rates of delay elements can be made more precise by vacuum annealing of pellet or by pressing an acceleration cavity at the input end of pellet.

(3) The combustion residue of Mo-$KClO_4$ binary mixtures consist of MoO_2, MoO_3, $K_2Mo_4O_{13}$ and KCl, their relative content varies with the ratio of Mo/$KClO_4$ before firing. Further study is needed for the better understanding of reaction mechanism.

5. References

1) Ellern, H., "Military and Civilian Pyrotechnics" Chemical Publishing Company Inc., N. Y. (1968) P383
2) Engineering Design Handbook: "Explosive Trains" AMCP 706-179, Headquarters, U. S. Army Material Command (1974) P6-7
3) Hsu, Y. E., Proc. 7th Int. Pyrotech. Semin. (1980) P771
4) Olander, D. E., U. S. patent 3,028,229 (1962)
5) Ellern, H., "Military and Civilian Pyrotechnics" Chemical Publi hing Company Inc., N. Y. (1968) P385
6) Tsai, L. M., Liaw, C. H., Chen, Y. J., 工業火薬協会昭和60年度年会講演要旨集(1985) P91
7) Engineering Design Handbook: "Explosive Trains" AMCP 706-179, Headquarters, U. S. Army Material Command (1974) P6-4
8) Ellern, H., "Military and Civilian Pyrotechnics" Chemical Publishing Company Inc., N. Y. (1968) P205
9) Ellern, H., "Military and Civilian Pyrotechnics" Chemical Publishing Company Inc., N. Y. (1968) P203
10) Puchalski, W. J., "The Effect of Angular Velocity and Composition on Pyrotechnic Performance" Frankford Arsenal Technical Report R-74011 (1974)
11) Riffault, M. L., Proc. 3rd Symp. Chem. Probl. Connected Stab. Explos., (1973) P302
12) Bernard, M. L., Proc. 7th Int. Pyrotech. Semin. (1980) P826

Mo-$KClO_4$-$BaCrO_4$延時薬の燃焼特性

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種々の組織のMo-$KClO_4$-$BaCrO_4$系延時薬の発火性（ignitibility），燃焼速度およびその再現性について検討を行った。

発火性を三角図上に示すと，組成により，不点火の領域がみられ，混合物が確実に発火する場合の$KClO_4$の含有量は40wt%以下である結果が得られた。

再現性の良い燃焼速度の範囲は27ms/cm～7.5sec/cmであり，実験結果により燃焼速度の変動は真空アニーリングまたはペレットの初端にacceleration cavityの加圧整形を施すことにより改善されることがわかった。

なお，反応熱，自然着火点および燃焼生成物の粉末X線回折などのデータについても考察した。