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Journal of Energetic Materials

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713770432

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To cite this Article Tsai, L. M., Wu, B. H. and Lin, K.(1992) 'Spin effects on pyrotechnic delays of the molybdenum family', Journal of Energetic Materials, 10: 4, 267 – 285 To link to this Article: DOI: 10.1080/07370659208018926 URL: http://dx.doi.org/10.1080/07370659208018926

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SPIN EFFECTS ON PYROTECHNIC DELAYS OF THE MOLYBDENUM FAMILY

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ABSTRACT

The alteration of the burning rate for delay elements of the molybdenum family under various spin rates was investigated. A detailed description of the apparatus for the spin effects study is given. Since chemicals are added to the delay mixes to improve their performance, experiments were undertaken to learn the influence of additives (e.g., binder or lithium fluoride) on the spin effect.

> Journal of Energetic Materials Vol. 10, 267-285 (1992) Published in 1992 by Dowden, Brodman & Devine, Inc.

INTRODUCTION

In projectiles, the delay element experiences very severe environments. The high temperature and pressure caused by the deflagration of propellant in the barrel are the first, followed by a tremendous setback force. There is also a huge pressure change once the projectile leaving the muzzle. Then comes the reduced pressure owing to the high altitude, and the gas flow from supersonic flight. Spin is another factor; hence its effect on the burning behavior of the delay elements cannot be ignored.

In his studies, Shulman¹ pointed out that the burning rate increase of small arms tracer is in accordance with the increase of spin rate; and the experimental results are in good agreement with those from field tests. Puchalski² showed that for tracer containing magnesium and strontium nitrate the burning rate increases as the spin rate increases. This spin effect is proportional to the diameter of the pyrotechnic but inversely proportional to the content of magnesium. He related these phenomena to the condensed phase, which is the rate determining phase in the overall reaction process. In the reaction zone of the condensed phase, the particle mobility is highest and therefore is most susceptible to the radial effects of spin. This will imply reaction and heat transfer as well. At the same time, the normal flat or concave burning surface for the pyrotechnic column will become convex in shape. As a result, all these factors will inevitably lead to the increase of the burning rate. The work of Izod and Eather³ on tracer compositions can be summarized as follows: (a) Burning rate increases with the spin rate. (b) The spin effect is suppressed by using finer metal fuel and oxidizer. (c) The aperture of the tracer retaining washer plays a major role in pressurizing the burning surface and consequently reducing the burning time. (d) The throttle formed by the slag after spinning results in the increased burning rate. In attempts to modify the nature of the slag, experiments were undertaken to verify that the burning rate could be altered by altering the flow properties of the slag.

In general the tracers burn with a flat or slightly concave burning surface which will become convex under spin. This has been proved by Barton and Bibby⁴ by using an x-ray method. Under spin the slag produced by combustion is centrifuged to the side of the tracer capsule, increasing the heat flow at the edge, leading to a convex burning surface. This convex surface has a larger area than a flat one would and thus feeds more energy into the unburnt layer. This should account for the observed increase in burning rate. Briere^{5,6} agrees with this convex burning surface postulate and verified the reduction of trace duration with the increasing spin rate.

The pronounced effects of spin on illuminant was studied by Dillehay⁷. The net overall effect is a reduction in the burning time and a loss in candle power output. This is from shear caused by differential rotation rates between the burning surface and the gases above the surface. This leads to increased heat transfer, which increases the rate of surface regression and shortens the burning time.

Although considerable work has been done on characterizing the spin effect on tracers and illuminants, very little has been published pertaining to the performance change of the delay element under spin. This paper describes the investigation conducted on delay elements of the molybdenum family under various spin rates. The influence of additive (e.g., binder or lithium fluoride) on spin effect has also been examined.

Experimental

Preparation of the Delay Element

Molybdenum delay mixes of fast, medium and slow burning rates (Mo/BaCrO₄/KClO₄, 72/10/18, 48/40/12, and 30/58/12 in %wt) were prepared. Specifications of the chemicals used are listed in Table 1.

The delay elements were made by pressing the delay mixture into a brass tube of 6 mm ID, 10 mm OD and 20 mm length, with a consolidating pressure of 64 kpsi. For each delay element, the mix was added as four increments to diminish the density gradients. A quantity of 0.1 gram ignition powder was then introduced for initiation of the delay mix. The ignition powder is a mixture of zirconium powder with lead dioxide (70/30). It is set off with an electric squib.

Apparatus

The test apparatus consisted of a sample holder placed on a high- frequency motor, a group of photo-sensors, a counter and a spin rate detecting system. The schematic diagram of instrumentation setup for the spin effects study is given in Figures 1 and 2.

For spinning the rotor at very high speed, compressed air is a very convenient source of very high rotational speed up to 300 krpm. This is suitable for the study of small caliber tracer projectile. For delay elements in larger caliber projectiles the rotational speed seldom exceeds 20 krpm, which is too slow to be maintained steadily by the air-driven spinner. After careful comparison and trials, a motor with an inverter unit was employed to construct the spinning rotor.

To measure the burning time, photo sensors were used to sense the combustion light emitted from the both ends of the delay element. Owing to the spin of the delay element, it takes a number of windows and sensors to facilitate the alignment of the window and the sensor for the light measurement of the lower end. In this experiment, six light windows were arranged at the lower end of the sample holder, and around the windows, eight photo sensors were placed to sense the output of the delay element. Figure 2 is the schematic representation of the design. The durability and accuracy of this apparatus have been demonstrated by a spin rate error less than 1% after more than seven hundred tests.

Test Procedure

In carrying out the test, the delay element was fixed in the sample holder on the rotating axis. The electric squib was adjusted to a distance of 8 ~9 mm away from the surface of the delay element. When the rotor achieved the preset spin rate, the squib was set off. The light emerging from the ignition powder triggers the counter, which times till the photo sensor at the lower end stops it. This gives the burning time of the delay element; thereby the burning rate can be calculated. At each spin rate, results were averaged from at least 12 runs for each sample.

RESULTS AND DISCUSSION

Spin Effects on the Burning Rate of Delay Element

The results of spin on the burning rate are given in Table 2. The spin effect on the slow burning delay element (Mo/BaCrO₄/KClO₄, 30/58/12) is obvious at high spin rates; while at low spin rates, pronounced effects are found on the medium (48/40/12) and fast (72/10/18) burning delay elements. Data in Table 2 are also plotted as in Figures 3, 4 and 5. Figure 3 shows that the burning rate of fast burning delay element increases with a linear rate of 0.4%/krpm as the spin rate reaches 25 krpm from zero. Figure 4 shows that the increasing rate for medium burning delay element is 0.23%/krpm when the spin rate is less than 15 krpm; a high rate of 0.86%/krpm is found for spin rate in between 15 and 20 krpm; the rate then turns to 0.11%/krpm, once the spin rate surpasses 20 krpm. The burning rate variation for the slow burning delay element (30/58/12) is shown in Figure 5. It maintains an almost steady burning rate until the spin rate hits 15 krpm, then the burning rate goes up with a rate of 1.48%/krpm. All these experimental results have indicated an increase of the burning rate with the spin rate for delay elements of the molybdenum family.

The Influence of the Binder on the Spin Effects

Binders in small quantity are always added to delay elements to enhance the column strength; this enables the delay element to survive the high setback force in the gun barrel. Vinyl alcohol acetate resin (VAAR) is one of the most important binders used in the pyrotechnics⁸. It contains oxygen through its alcohol and ester functional groups which can react with some ingredients in the pyrotechnics to produce energy. In addition, the gas pressure generated from the decomposition of VAAR may also affect the burning rate. To learn the influence of the binder on the spin effects, 0.5% VAAR was introduced into the slow burning delay mixture. The experimental results are tabulated in Table 3. It shows significant changes in the burning rates at low and medium spin rates; but the change is suppressed as the delay elements are spun at high speed. When the burning rate is plotted versus spin rate as shown in Figure 6, a burning rate increment of 0.16%/krpm is found if the spin rates

are kept less than 20 krpm. Above this spin rate, the increasing rate turns to 1.26%/krpm. It gives a distinctive curve when compared with the one in Figure 5. In other words, with binder in its composition, the delay element exhibits different burning characteristics.

The Influence of LiF on the Spin Effects

Our previous study⁹ has shown that the addition of LiF (3% by weight) to the delay mixes can reduce the pressure coefficient effectively. It also pointed out that the delay mix of slow burning rate is the one affected most significantly by LiF. It is for this reason that slow burning delay element of the molybdenum family was studied to learn the spin effect. Comparative results of the slow burning delay elements with and without added LiF at various spin rates are collected in Table 4. There is impressive rate change when the burning rate is plotted versus the spin rate as shown in Figure 7, in which the slope changes at 15 krpm from 0.38%/krpm to 3.64%/krpm. This large increase of the burning rate is probably due to the low melting point of LiF. It is also recognized in the same study that the reactions in the condensed phase dominate the combustion process. With LiF, the absorption of the latent heat will lower the reaction temperature and consequently reduce the reaction rate in the gaseous phase. Furthermore, considering the convex burning surface resulting from the centrifuge of the combustion slag at spinning, LiF with its low melting point will contribute to the fluidity of this slag. Therefore,

the convexity of the burning surface increases, which inevitably leads to a drastic alteration of the burning rate.

CONCLUSIONS

Using a high speed spinner, the spin effects on the combustion behavior of pyrotechnic delays is examined. It is found that the burning rate increases with the spin rate. For fast burning delay elements of the molybdenum family, the burning rate increases at a constant rate with respect to the increment of spin rate, while the burning rates of slow and medium delay elements increase irregularly. At a high spin rate (25 krpm), the slow burning delay elements exhibit significant changes in burning rate resulting from the spin effects; and the obvious burning rate changes are only found in the medium and fast burning delay elements at spin rates ranging from 5 to 20 krpm.

Investigation of the additive effects show that the binder (VAAR) in delay mixes will suppress the spin effect to a large extent when the spin rates are above 20 krpm. A large increase in burning rate is found for the delay elements containing LiF, which is adverse to the performance of the delay elements.

TABLE 1

Specifications of the Chemicals Used in Delay Mixes

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Chemical	Purity	Size	Manufacturer
Molybdenum Powder	99.9%	$1.35 \mu m(mean)$	CERAC
BaCrO ₄ KClO ₄ Zirconium Powder	99% 99%	<63μm <44μm 40μm(mean)	Riedel–De Haen Fluka Merck
PbO2 LiF VAARa	99% 99%	<63μm <44μm	CERAC Fluka

a. VAAR(polyvinyl acetate-alcohol resin) is the product of partial hydrolysis of PVAc. The solid content of the VAAR solution prepared for this experiment is 30% by weight. The percentage of polyvinyl alcohol in this solid is 18% by weight.

TABLE 2

Change of Burning Rates(cm/sec) of Molybdenum Delay Elements (Mo/BaCrO₄/KClO₄) Under Various Spin Rates

Spin Rate (krpm)	72/10/18	48/40/12	30/58/12
0 5 10 15 20 25	$\begin{array}{c} 4.385()\\ 4.398(+0.3\%)^{a}\\ 4.473(+2\%)\\ 4.618(+5.3\%)\\ 4.686(+6.9\%)\\ 4.786(+9.1\%)\end{array}$	$\begin{array}{c} 0.502()\\ 0.504(+0.4\%)\\ 0.511(+1.8\%)\\ 0.519(+3.4\%)\\ 0.540(+7.6\%)\\ 0.543(+8.2\%)\end{array}$	$\begin{array}{c} 0.208()\\ 0.208(0)\\ 0.205(-1.4\%)\\ 0.205(-1.4\%)\\ 0.221(+6.2\%)\\ 0.237(+13.9\%)\end{array}$

a. Percentage changes of burning rates under various spin rates.

TABLE 3

The Influence of the Binder on the Spin Effects for Slow Burning Delay Elements

Spin Rate	30/58/12/X(VA/	AR)
(krpm)	X=0	X=0.5
0 5 10 15 20 25	$\begin{array}{c} 0.208^{a}()\\ 0.208(0)\\ 0.205(-1.4\%)\\ 0.205(-1.4\%)\\ 0.221(+6.2\%)\\ 0.237(+13.9\%)\end{array}$	$\begin{array}{c} 0.215()\\ 0.218(+1.4\%)^{b}\\ 0.221(+2.8\%)\\ 0.223(+3.7\%)\\ 0.221(+2.8\%)\\ 0.237(+10.2\%)\end{array}$

a. Burning rates in cm/sec.

b. Percentage changes of burning rates under various spin rates.

TABLE 4

The Influence of LiF on the Spin Effects for SlowBurning Delay Elements

Spin Rate (krpm)	30/58/12/X(LiF) X=0	X=3
0 5 10 15 20 25	$\begin{array}{c} 0.208^{a}()\\ 0.208(0)\\ 0.205(-1.4\%)\\ 0.205(-1.4\%)\\ 0.221(+6.2\%)\\ 0.237(+13.9\%)\end{array}$	$\begin{array}{c} 0.199()\\ 0.202(+1.5\%)^{\rm b}\\ 0.204(+2.5\%)\\ 0.211(+6\%)\\ 0.248(+24.6\%)\\ 0.284(+42.7\%)\end{array}$

a. Burning rates in cm/sec. b. Percentage changes of burning rates under various spin rates.



FIGURE 1 The block diagram of the spin effect tester



FIGURE 2 Drawing of the design for the measurement of spin effects



FIGURE 3 Spin effect on the fast burning delay element (Mo/BaCrO4/KCl04, 72/10/18)



FIGURE 4 Spin effect on the medium burning delay element (Mo/BaCrO4/KCl04, 48/40/ 12)



FIGURE 5 Spin effect on the slow burning delay element (Mo/BaCrO4/KCl04, 30/58/12)



FIGURE 6 The influence of the binder (0.5% VAAR) on the spin effect for slow burning delay element



FIGURE 7 The influence of LiF on the spin effect for slow burning delay element

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