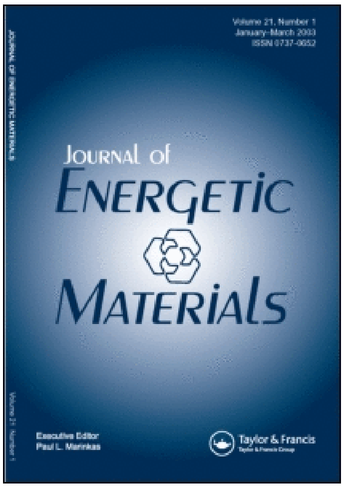

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Pressure effects on pyrotechnic delays of the molybdenum family

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To cite this Article Tsai, L. M. , Wang, S. J. and Lin, K.(1992) 'Pressure effects on pyrotechnic delays of the molybdenum family', Journal of Energetic Materials, 10: 1, 17 — 41
To link to this Article: DOI: 10.1080/07370659208018633
URL: http://dx.doi.org/10.1080/07370659208018633

PRESSURE EFFECTS ON PYROTECHNIC DELAYS OF THE MOLYBDENUM FAMILY

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ABSTRACT

The effects of ambient pressure, from 22800 down to 27 mm of Hg, on molybdenum delay mixes of high, medium and low burning rates have been investigated. As is typical of most gasless delay compositions, rather small pressure coefficients are obtained. Discontinuity of ignition propagation at reduced pressure is only observed in delay mixes of slow burning rate, or low molybdenum content. It is attributed to the diminution of rate of heat release. Molybdenum content has been recognized as the dominant factor, for increasing it will reduce the pressure effects significantly. On the other hand, the variation of burning process with ambient pressure is not

Journal of Energetic Materials vol. 10, 017–041 (1992)
Published in 1992 by Dowden, Brodman & Devine, Inc.

associated with the degree of compaction of the delay mixes. It is found that the pressure coefficients of molybdenum delay mixes can be further diminished by the addition of metal fluorides. Among the fluorides employed, lithium fluoride results in better performance at the moderate quantity of 3% by weight.

INTRODUCTION

Gas producing delay mix has long been used as the main component of pyrotechnic delay elements. From experience, several drawbacks have been recognized, such as the burning rate alteration due to gas pressure, and the emission of gas products which are harmful to other components of a system. The limitations of gas producing delay mixes and the disadvantages they bring to the design of delay elements have led to the development of gasless delay compositions. However, there are still some constraints that must be taken into account in the use of gasless compositions. The constraints include limits on modification of burning rate, critical diameter, sensitivity to ignition, dependence on ambient pressure and availability of raw materials.

For many years, studies have been conducted to address these deficiencies. Nakahara[1] reported in his study that the burning rate equation, $v=a\times p^n$, can be used to describe the relationship between burning rate, v, and pressure, p, for the burning of delay mix, in which n is the pressure coefficient and a is constant. The value of the pressure coefficient is affected by composition, particle size of the metal fuel and the initial ambient temperature. Comparative tests with different compositions of delay mixes give results that indicate, in general, that metal fuel of finer size or higher initial temperature will result in increased pressure coefficient.

The influence of ambient pressure on the burning rates of gasless delay compositions has been shown to be unimportant over broad ranges of pressure by Kristal and Kaye[2]. Two factors have been recognized in their study to be of importance in sustaining the flame propagation of the delay element: (a) The decomposition temperature of oxidant should be lower than the reaction temperature. (b) Rate of heat output should exceed that of heat loss. A propagation index, P_i, was defined by Rose[3], by $P_i=\Delta H\rho v/T$, where ΔH,ρ,v and T stand for heat of reaction, density, burning rate and ignition temperature respectively. A large value of P_i indicates a better flame propagation in the delay composition; at reduced pressure the burning rate and Pi are diminished. Analysis by Conkling[4] verified that the pressure effect on burning rate for gasless delay powder is not large. He also pointed out that the participation of ambient oxygen in the burning process will lead to the possibility of disrupting the ignition propagation at low pressure. This is an undesirable situation because the disruption could cause failure of the main charge.

In the tactical application, there exists a broad range of pressure. The delay element in a HESD (High Explosive Self Destruction) projectile may experience a reduced pressure at high altitude, while very high pressure may be exerted on it in a gun barrel or in a rocket motor. To maintain its delay function as intended, an ideal delay mix is one with steady burning rate which will not be affected by the pressure change from ambient. Unfortunately, this kind of composition has not been found. Delay mixes of the molybdenum family are often chosen as the alternative. For compositions of this family it has been shown that the content of molybdenum is the dominant factor in controlling the burning rate[5]. In this study, a variety of molybdenum compositions have been studied to investigate the burning behavior of delay mix at different ambient pressures. It turns out the burning rate equation can be used to interpret the relationship between burning rate and ambient pressure. It is also found that compositions with low molybdenum content, (30%), are inclined to show a discontinuity in ignition propagation at reduced pressure (less than 320 mm of Hg). The lowest pressure at which the delay mix would ignite could be extended to 27 mm of Hg as the molybdenum content was increased to 72%. Additives that can lower the pressure coefficients have also been examined. Fluorides were selected for this study. At the optimum content, lithium fluoride and sodium fluoride are found to be superior to calcium fluoride in this respect, while in Rose's study[6] calcium fluoride was found to be the best additive for the tungsten family of delay mixes. Finally, comparing the physical properties of fluorides with the performance of those fluorides in delay mixes, it seems there are some correlations between the ability of fluorides to suppress the pressure effects and their melting points, or boiling points.

EXPERIMENTAL

Specifications of components used to prepare delay mixes are listed in Table 1. Three types of molybdenum family delay mixes, i.e., fast, medium and slow burning rates, have been prepared. Their compositions are as follows:

burning rate	Mo(%wt)	$BaCrO_4$(%wt)	$KClO_4$(%wt)
fast	72	10	18
medium	48	40	12
slow	30	58	12

All chemicals were used as received without further treatment. Delay elements were made by pressing the mixture into a brass tube of 4 mm ID, 8 mm OD and 16 mm length. Three loading pressures, namely 32, 80, and 110 kpsi, were chosen to consolidate the delay mixes. In the loading process, the mix was added as four increments for each delay element, to reduce density gradients. Unless specified otherwise, a quantity of 0.05 gram ignition powder was introduced to initiate the delay mix. The ignition powder is a mixture of zirconium powder with ferric oxide (72/28).

Gas products generated from the burning of delay mix were collected with an apparatus specially made for determining the quantities of gases. This apparatus was manufactured by Julius Peters K. G., Berlin, Germany. The gas volume was obtained in terms of gas pressure.

Heat of reaction of delay mixes was obtained with a model 1241 adiabatic calorimeter together with a model 1720 calorimeter controller from Parr Instrument Company Inc., Illinois, U.S.A. Sample pellets for this measurement were consolidated at 110 kpsi. Measurement was carried out in a calorimeter bomb pressurized with nitrogen or helium gas to 25 atm.

A delay element is characterized by its burning time. To learn the changes of the burning time under various ambient pressures, an apparatus of one liter volume was designed as shown in Figure 1. An initiation circuit and photo sensor are part of the ignition device, which can be bolted to the pressure chamber with a flange and gas sealed with a rubber o–ring. A tungsten bridgewire of 0.2 mm diameter is employed to set off the delay mix (the bridgewire is arranged to contact the ignition powder once the delay element being fired is in position). At the bottom of the apparatus is a second photo sensor. Light emitted from the burning delay mix at its final stage can be detected through a Lucite plate positioned underneath the delay element. Output from these two photo sensors is used to trigger a digital counter. The time span measured by the counter represents the burning time of the delay element.

RESULTS AND DISCUSSION

Combustion of Delay Mix in Nitrogen Environment

It is obvious that the oxygen from the air will take part in the combustion of delay mix in its gaseous phase. It would be interesting to examine the behavior in an inert atmosphere. Variations of heat of reaction for delay mixes of the same composition in nitrogen gas or in helium gas are listed in Table 2. Slight changes of heat of reaction indicate the inert property of nitrogen and helium gases for molybdenum family delay mixes. It is for this reason, nitrogen gas was chosen as the gas medium to pressurize the test sample.

Effects of Ambient Pressure on Burning Rate and Propagation of Ignition

Molybdenum family delay mixes give off small amounts of gas products during their burning. Gas volumes of 1.02±0.22, 3.47±0.65, and 4.62±0.64 ml/gm are measured for fast, medium and slow burning delay mixes of the molybdenum family, respectively, which all amount to aboout 1% that of gaseous delay mixes. For instance, a gas volume of 271 ml/gm is obtained for black powder composed of potassium nitrate/sulfur/charcoal (74.0/10.4/15.6).

Burning rates for the molybdenum family at different ambient pressures are summarized in Table 3. For the measurement of burning rate, eight to ten runs are made for each sample. The standard deviation is expressed as coefficient of variation (figures in parentheses) which is the percentage of total burning time. It shows that, in the pressure range considered (from 27 to 22800 mm of Hg), the burning rate is inclined to increase in accordance with the increase in ambient pressure. However, at reduced ambient pressure, discontinuity of ignition propagation is observed, but only for delay mixes of low molybdenum content or slow burning rate. This happens at 114 mm of Hg for composition (48/40/12) and 320 mm of

Hg for composition (30/58/12). It is a result owing to the diminution of the rate of heat release. In Table 4, the rate of heat release for the molybdenum family delay mixes is calculated from the measured total heat divided by the burning time under various ambient pressures. It shows the dependence of heat release rate on the ambient pressure. At reduced ambient pressure the rate of heat release is so low for low molybdenum content delay mixes (30/58/12) and (48/40/12) that the heat loss is no longer compensated, and will interrupt the ignition propagation.

Degree of Compaction and Its Effects

Conditions of consolidation for delay mix can be expressed as degree of compaction. This is shown in Table 5, in which degree of compaction is defined as:

$$\text{degree of compaction} = \frac{\text{loading density}}{\text{theoretical density}}$$

The theoretical density is calculated with the following equation, in which weight percentages of molybdenum, barium chromate and potassium perchlorate are designated as x_1, x_2, x_3 respectively, and 10.2, 4.498 and 2.524 are the densities in gm/ml for molybdenum, barium chromate and potassium perchlorate respectively.

$$\text{theoretical density} = \frac{100}{\frac{x_1}{10.2} + \frac{x_2}{4.498} + \frac{x_3}{2.524}}$$

The results of Table 5 indicate that values of degree of compaction ranging from 0.76 to 0.94 are obtained as the delay mixes are pressed from 32 kpsi up to 110 kpsi. Data of pressure coefficient, n, for each composition of the molybdenum family at different consolidation pressures are given in Figures 2, 3 and 4, where burning rate, v, is plotted vs ambient pressure, p, on a logarithmic scale. The fairly good linearity of the plot demonstrates the validity of the burning rate equation. It also shows that the way the pressure coefficients change does not coincide with the variation in compaction. Small values of n only are found in compositions of fast burning rate (72/10/18), which means the molybdenum content is the dominant factor in controlling the n value. On the other hand, the degree of compaction does have some effect on the stability of ignition propagation. Delay mix consolidated under lower pressure shows better behavior in ignition propagation. For instance, in slow burning composition (30/58/12), the minimum reliable ignition pressure can be extended to 281 mm from 372 mm of Hg, once the consolidation pressure goes down to 32 kpsi from 110 kpsi.

The Performance Change of Delay Mix by the Addition of Fluorides

It is known that the addition of calcium fluoride to the delay mix reduces the effects of pressure. Hence it is worthwhile to investigate the performance change resulting from the addition of different fluorides, especially to the molybdenum family of delay mixes. The effects of calcium fluoride on slow burning composition are illustrated in Figure 5, together with Table 6. They point out that the effect of stabilizing the ignition propagation by the addition of calcium fluoride reaches its maximum at a CaF_2 content of 1%. The ignition propagation for calcium fluoride at 3% returns to the same value as that without calcium fluoride and is even worse at 5%. On the other hand, the smallest value of the pressure coefficient is found at calcium fluoride contents above 3%, if the pressure influence is the main concern. Also shown in the same figure and table, an improvement of ignition stability at reduced ambient pressure from 372 mm to 320 mm of Hg has been achieved, due to a larger amount of ignition powder being introduced. Nevertheless, more ignition powder also leads to the increase of pressure coefficient, making it necessary to balance these two factors in order to achieve a desirable combination of effects.

To study the effects of fluorides on slow delay mixes, 3% of sodium fluoride and lithium fluoride were added separately. The results are shown in Figure 6. Rather small values of pressure coefficients are obtained for delay mixes with 3% of lithium or sodium fluoride, which shows a better performance than that of calcium fluoride, but the ignition propagation is just as poor as that of the latter. Examining the physical properties of these three fluorides reveals that the burning process is related to some extent to their melting and boiling points. This is illustrated in Table 7. As the melting point and boiling point of the fluorides are arranged in decreasing order, the same trend appears for the pressure coefficients. Furthermore, the small difference in pressure coefficient between delay mixes with sodium fluoride and lithium fluoride corresponds to the small differences of physical properties that these two fluorides possess. It has been proven that for slow burning delay mix a formulation with fluoride will materially lower its sensitivity to ambient pressure. The effect of fluoride on medium and fast burning delay mixes is then explored. Lithium fluoride of 3% is selected for its extraordinary performance in the slow burning composition. Pressure coefficients shown in Figures 7 and 8 verify the effects of lithium fluoride on fast burning delay mix (72/10/18) and medium burning delay mix (48/40/12).

CONCLUSIONS

The burning phenomena of molybdenum family delay mixes follow the burning rate equation in principle, and the low pressure coefficients demonstrate dependence on ambient pressure only to a slight degree. Unfavorable performance has been observed in slow burning delay compositions of the molybdenum family; they exhibit relatively high pressure coefficients and may lose their ignition propagation ability at reduced ambient pressure. Fluoride can be added to the delay mix to reduce the burning rate fluctuation caused by the variation of ambient pressure. Quantities of fluoride up to 5% have been introduced into delay mixes, resulting in significant reduction of pressure coefficients, but this jeopardizes ignition propagation at reduced ambient pressure. Among the fluorides employed, lithium fluoride shows better performance than calcium fluoride, at the moderate quantity of 3%. Reducing the fluoride content to 1% only slightly alters the pressure coefficients.

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TABLE 1

Specification of Components in Delay Mixes

Chemical	Purity	Size	Manufacturer
Molybdenum powder	99.9%	1.35μm(mean)	CERAC
$BaCrO_4$	99.9%	<63μm	Riedel–De Haen
$KClO_4$	99.9%	<44μm	Fluka
Zirconium power		<40μm(mean)	Merck
Fe_2O_3	99.9%	10μm(mean)	CERAC
CaF_2	99.9%	<44μm	Fluka
NaF	99.9%	<44μm	Merck
LiF	99.9%	<44μm	Fluka

TABLE 2

Values of Heat of Reaction for Metal Fuel and Oxidizer($Mo/KClO_4$) of Different Compositions in Inert Gas Media

Composition	Heat of Reaction (cal/g)	
($Mo/KClO_4$)	in Nitrogen	in Helium
80/20	338	335
70/30	415	434
60/40	611	608
50/50	754	753
40/60	743	726
30/70	543	546
20/80	348	354

TABLE 3

Burning Rates (cm/sec) of Molybdenum Family Delay Mixes under Different Ambient Pressures

Ambient Pressure (mm of Hg)	Composition($Mo/BaCrO_4/KClO_4$)[b]		
	30/58/12	48/40/12	72/10/18
22800[a]	0.23 (2.2)[c]	0.61 (1.4)	5.02 (2.6)
2206	0.17 (1.8)	0.46 (2.5)	4.88 (2.7)
736	0.15 (1.6)	0.41 (3.0)	4.71 (3.7)
372	0.14 (2.1)	0.39 (2.7)	4.71 (3.4)
152	N.I.[d]	0.36 (3.9)	4.68 (1.9)
27	N.I.	N.I.[e]	4.54 (2.1)

a. The pressure of 22800 mm of Hg (or 31kg/cm^2) is an averaged pressure the delay element experienced when the primer is used as ignition source in practical application. The measurements were carried out in a close vessel equipped with a pressure gauge.

b. Consolidation pressure for all composition is 110 kpsi, and the ignition mixture introduced is 0.05 gram.

c. Coefficient of variation, a standard deviation calculated as the percentage of total burning time.

d. No ignition, actual pressure is 320 mm of Hg.

e. No ignition, actual pressure is 114 mm of Hg.

TABLE 4

Rates of Heat Release and Other Burning Properties of Molybdenum Family Delay Mixes.

Composition[a] ($Mo/BaCrO_4/KClO_4$)	Weight (g)	Heat of Reaction (cal/g)	Total Heat (cal)	Ambient Pressure (mm Hg)	Burning Time (sec)	Rate of Heat Release (cal/sec)
30/58/12	0.61	345	210	22800	4.46	47.1
				2206	6.04	34.8
				736	6.84	30.7
				372	7.33	28.6
				152	N.I.[b]	——
48/40/12	0.69	324	224	22800	1.69	132
				2206	2.24	100
				736	2.51	89.2
				372	2.64	84.8
				152	2.86	78.3
				27	N.I.[b]	——
72/10/18	0.79	363	287	22800	0.201	1428
				2206	0.207	1386
				736	0.214	1341
				372	0.214	1341
				152	0.216	1329
				27	0.222	1293

a. All compositions were consolidated at 110 kpsi.
b. No ignition.

TABLE 5

Relationship Between Degree of Compaction and Consolidation Pressure

Consolidation Pressure(kpsi)	Composition ($Mo/BaCrO_4/KClO_4$)		
	30/58/12	48/40/12	72/10/18
32	0.79	0.78	0.76
80	0.86	0.86	0.85
110	0.90	0.91	0.94

TABLE 6

The Effects of Ignition Mixture and Calcium Fluoride on the Burning Rate and Pressure Coefficients of Slow Burning Delay Mix $Mo/BaCrO_4/KClO_4$[a]

Ambient Pressure (mm of Hg)	Ignition Mixture (g)		Calcium Fluoride[b] (%wt)		
	0.20	0.05	1%	3%	5%
22800	0.32	0.23	0.25	0.22	0.21
2206	0.22	0.17	0.20	0.18	0.17
736	0.20	0.15	0.19	0.17	0.16
372	0.18	0.14	0.18	0.16	N.I.[c]
320	0.18	N.I.	0.17	N.I.	N.I.
281	N.I.	N.I.	0.17	N.I.	N.I.
Pressure Coefficient	0.127	0.096	0.084	0.069	0.067

a. All compositions were consolidated at 110 kpsi, and the composition is $Mo/BaCrO_4/KClO_4$, 30/58/12.

b. The composition for calcium fluoride containing delay mixes is $Mo/BaCrO_4/KClO_4/CaF_2$, 30/58/12/X, and the ignition mixture used is 0.05 gram.

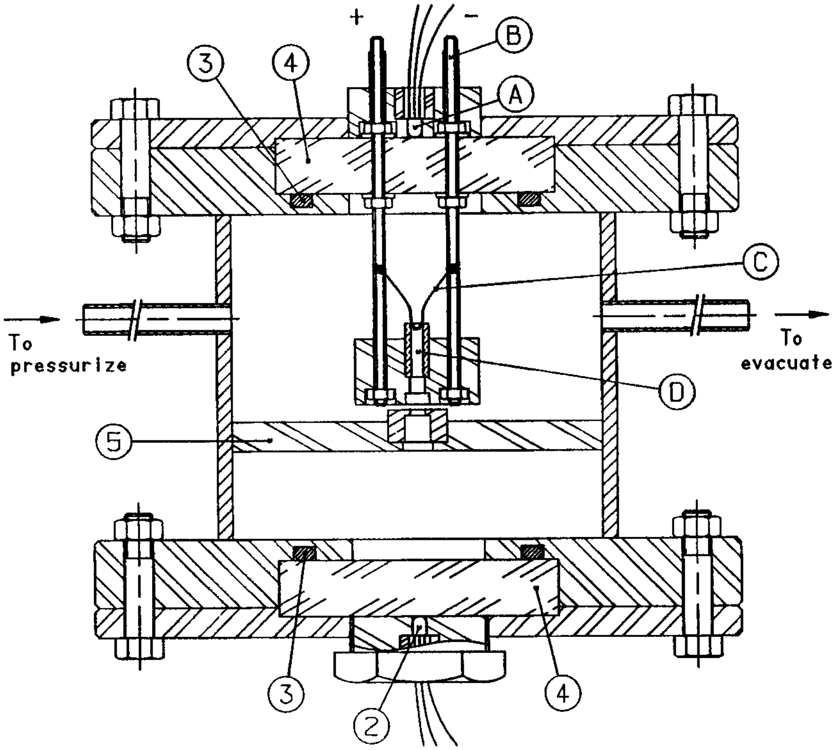
c. No ignition.

TABLE 7

Relationship of Pressure Coefficient and Physical Properties of Fluorides for Delay Mix of Slow Burning Rate[a]

Fluorides Additives	Boiling Point(°C)	Melting Point(°C)	Pressure Coefficient of Delay Mix
CaF_2	2500	1403	0.069
NaF	1704	993	0.042
LiF	1681	848	0.036
no additive	——	——	0.096

a. The composition for delay mix of slow burning rate is $Mo/BaCrO_4/KClO_4$ /fluoride(30/58/12/3). All compositions were consolidated at 110 kpsi.



1. Ignition device
   A. Photo sensor
   B. Electrode
   C. Tungsten wire
   D. Delay element
2. Photo sensor
3. Rubber O-ring
4. Lucite plate
5. Metal plate with a small hole at the center.

FIGURE 1
Drawing of the design for the measurement of pressure effects on the burning time of delay elements. The volume designed for the pressure chamber is one liter and the metal plate in the chamber is placed to block the light from the early stage of combustion.

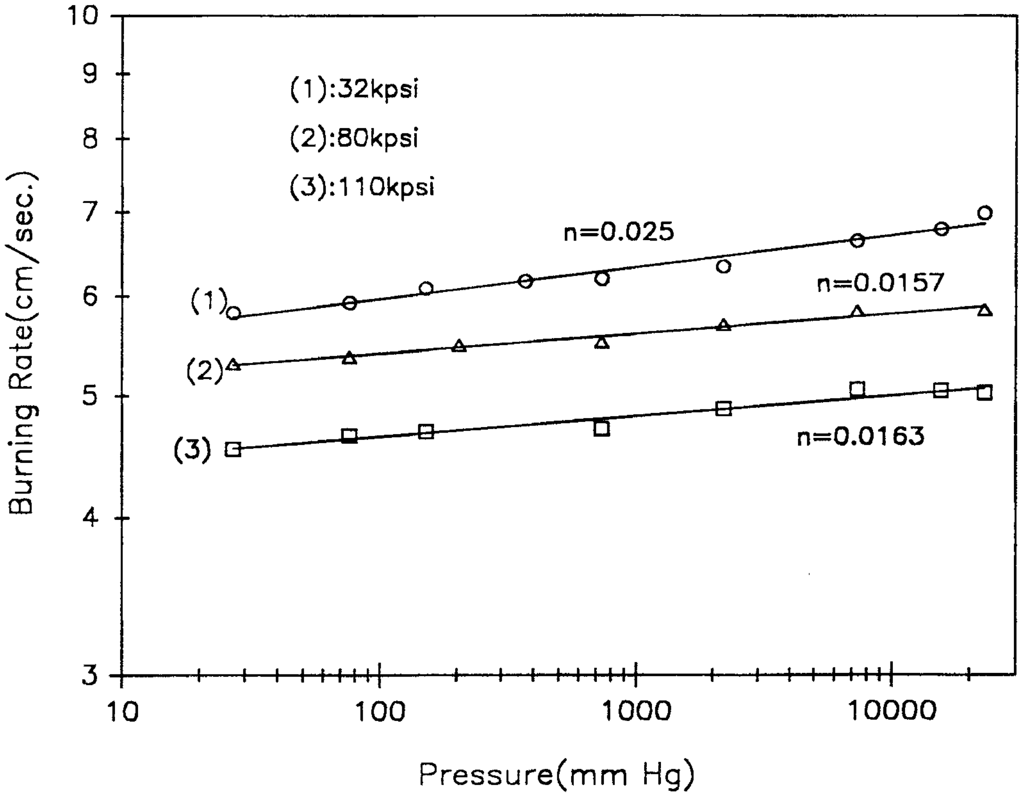


FIGURE 2

Pressure coefficient, n, calculated according to burning rate equation, $v=a \times p^n$, v for burning rate, p for ambient pressure, for fast burning rate composition (72/10/18) at different consolidation pressures.

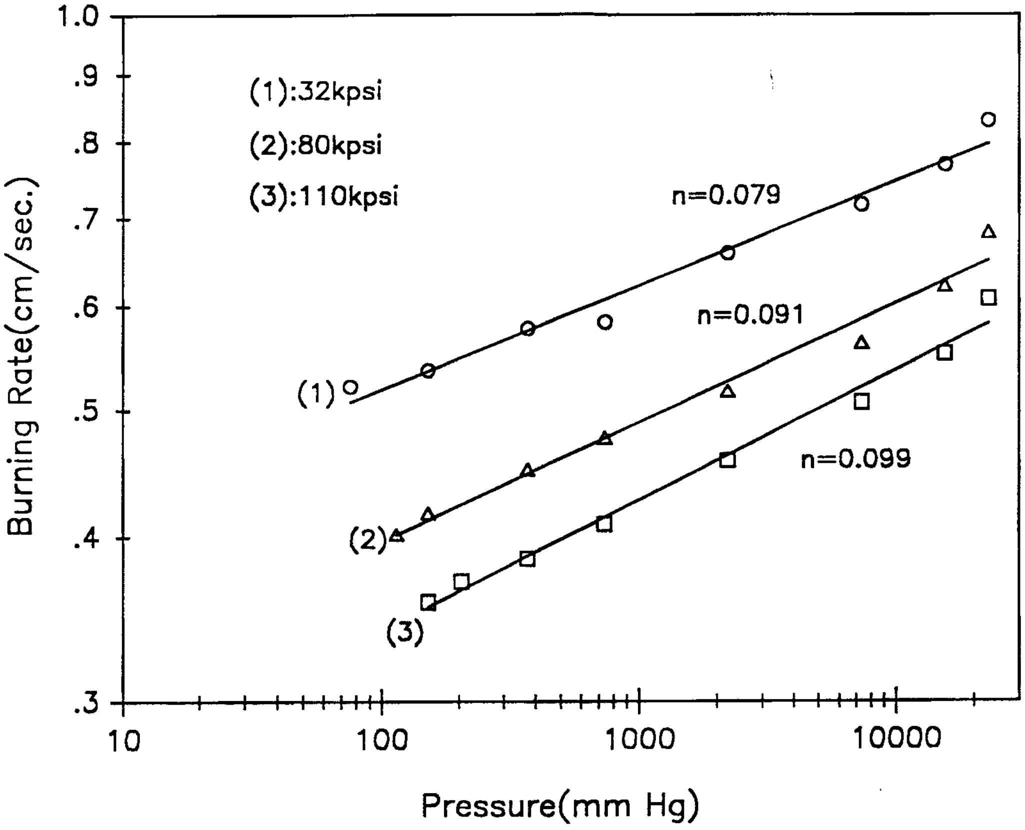


FIGURE 3
Pressure coefficient, n, calculated according to burning rate equation, $v=a \times p^n$, v for burning rate, p for ambient pressure, for medium burning composition (48/40/12).

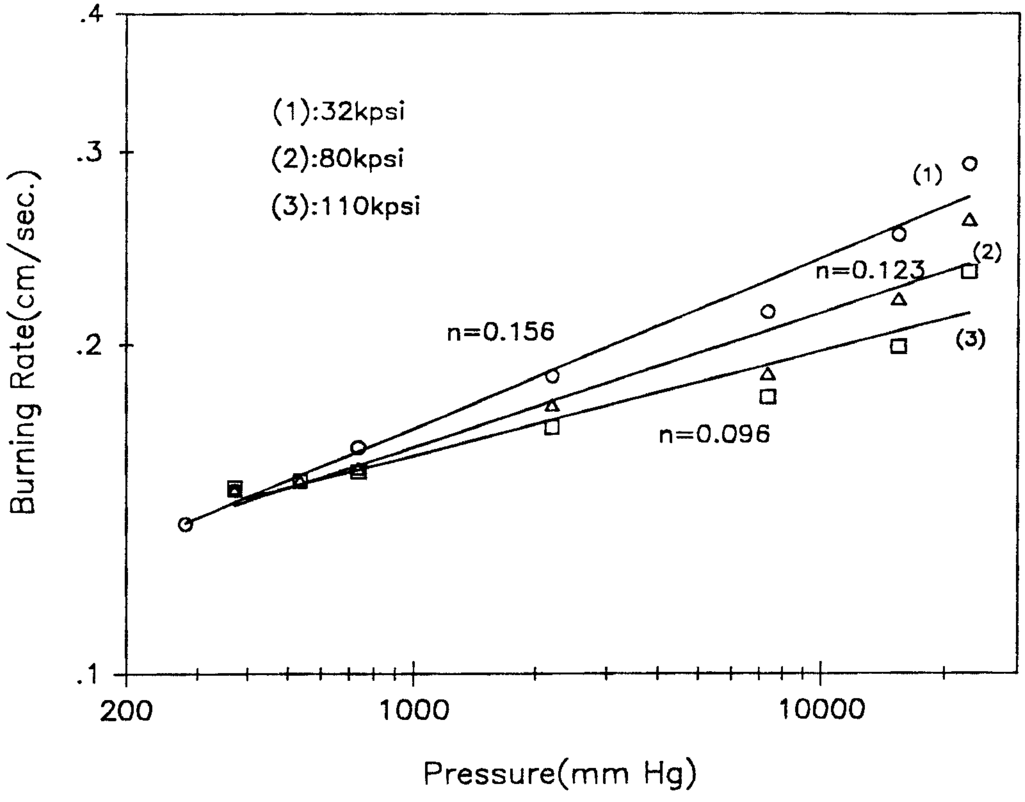


FIGURE 4
Pressure coefficient, n, calculated according to burning rate equation, $v=a\times p^n$, v for burning rate, p for ambient pressure, for slow burning composition (30/58/12).

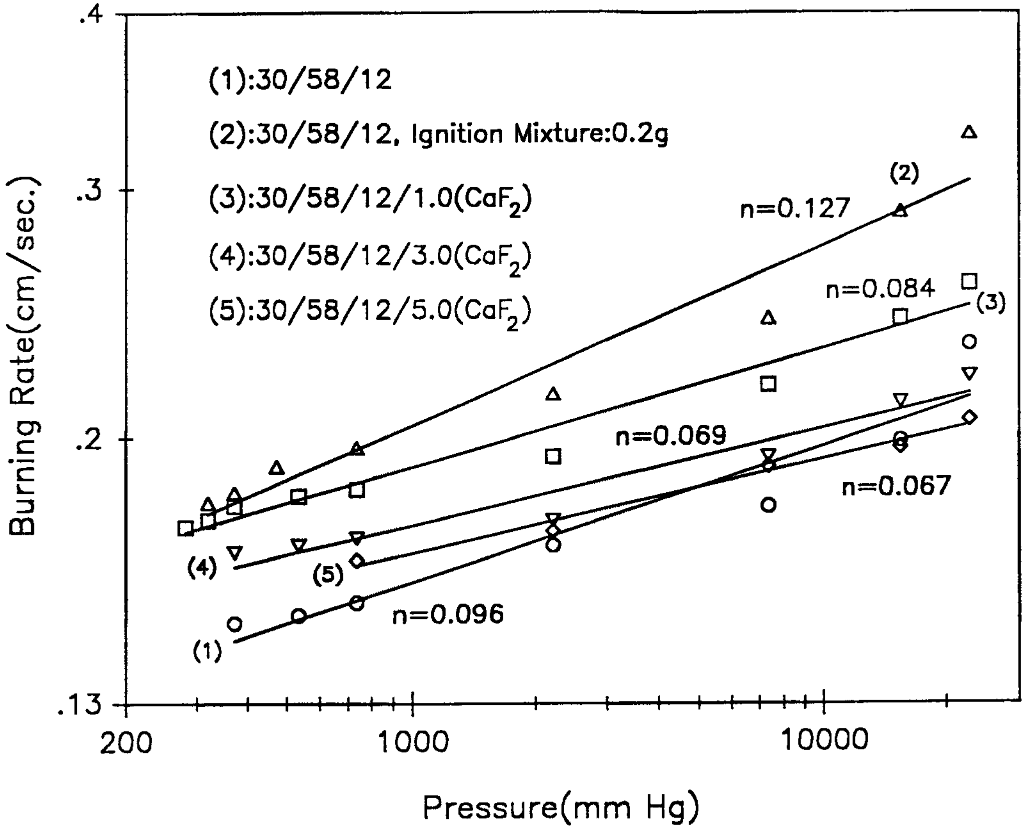


FIGURE 5
Effects of ignition powder and calcium fluoride on slow burning composition (30/58/12) under different ambient pressures.

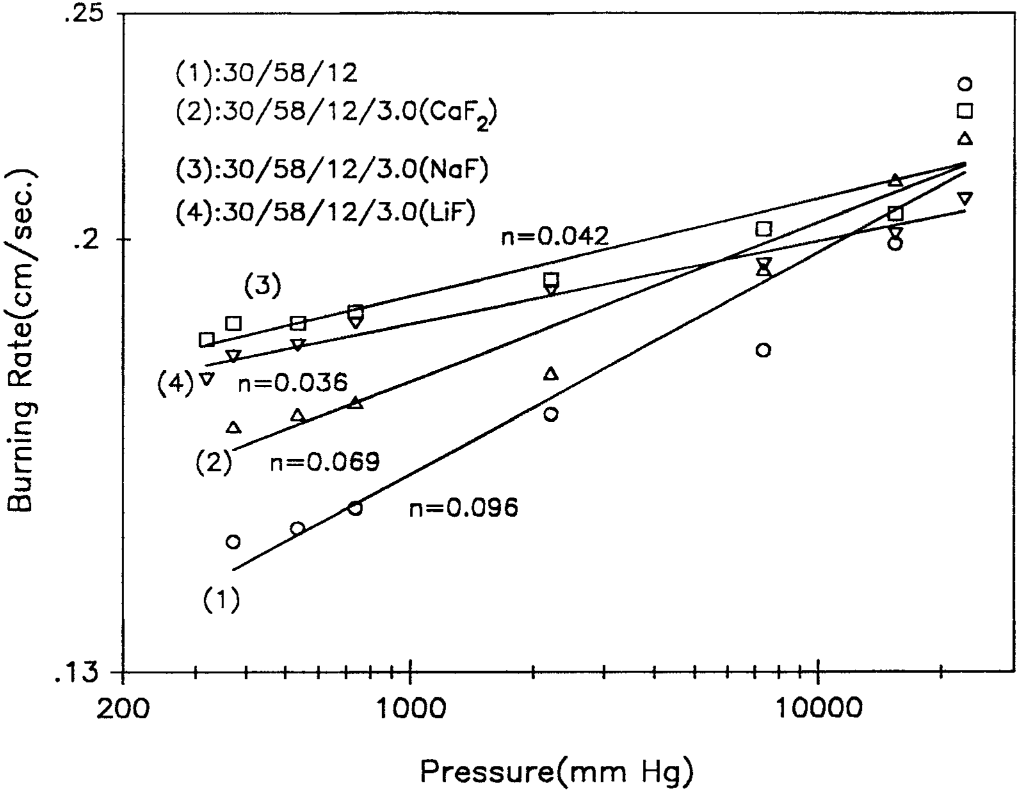


FIGURE 6
Effects of fluorides on slow burning delay mix under various pressures. The consolidation pressure is 110 kpsi.

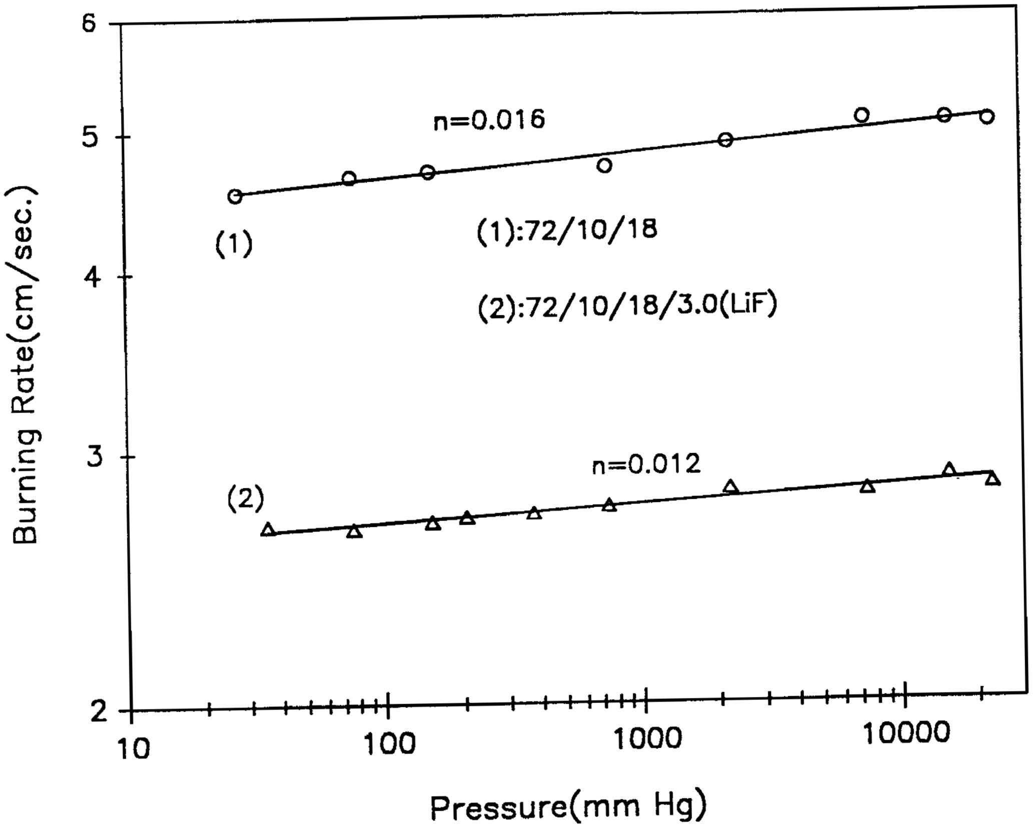


FIGURE 7
The effect of LiF on pressure coefficient of fast burning delay mix consolidated at 110 kpsi.

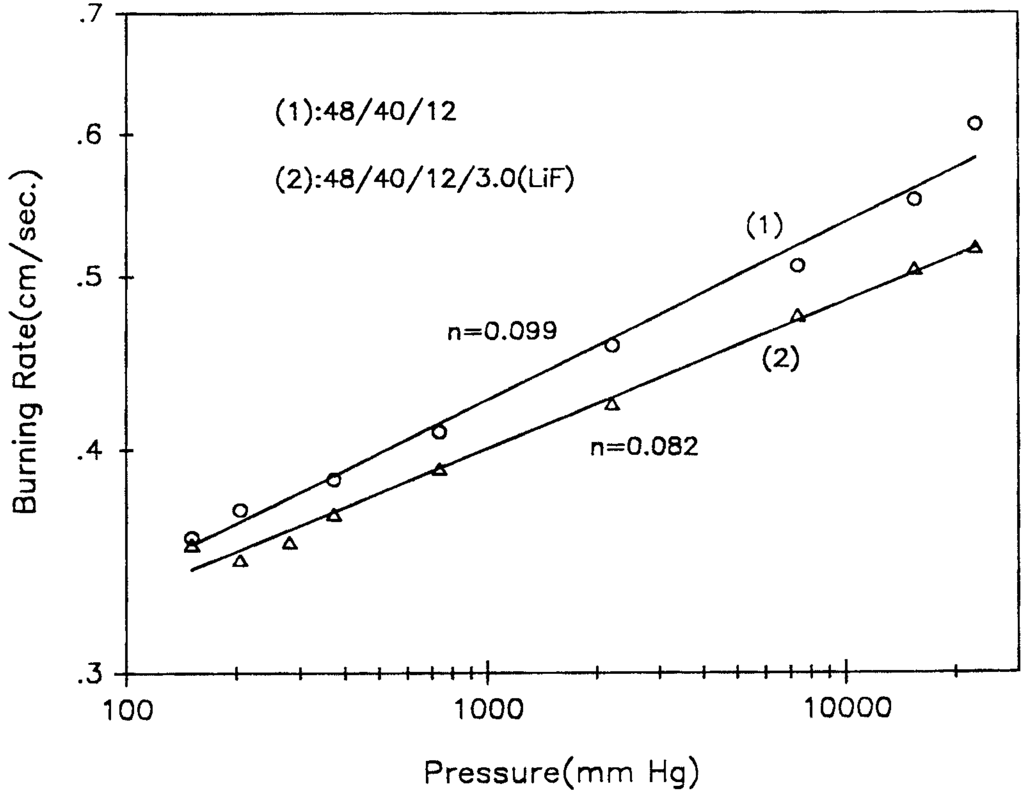


FIGURE 8
The effect of LiF on pressure coefficient of medium burning delay mix consolidated at 110 kpsi.