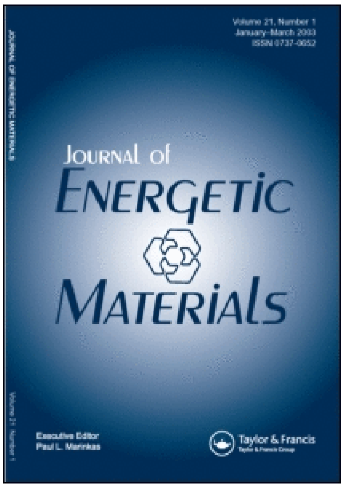

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Use of Bismuth Chromate with Antimony Trisulphide in Delay Compositions

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Antimony trisulphide is used with potassium perchlorate, barium chromate, and binder in delay compositions. The effect of substitution of barium chromate by bismuth chromate in the system barium chromate–antimony trisulphide–potassium perchlorate has been studied and reported here. These compositions contain 20% antimony trisulphide, 10% potassium perchlorate, and the remainder barium chromate/bismuth chromate. It is observed that the burning rate decreases from 0.43 to 0.23 cm/s with an increase in bismuth chromate content. The ignition temperature of these compositions determined by Differential Thermal Analysis (DTA) is found to be in the range 400 ± 10°C, the same for all compositions.

Theoretical calculations by a chemical equilibrium program (REAL) are used to discuss the possible reaction mechanism. Thermo gravimetry (TG)/Differential Scanning Calorimetry (DSC) data are reported. It is observed that the main exothermic peak of the compositions containing bismuth chromate shows at about 462°C as compared to the basic system, where it is at 498°C. These compositions are safe to handle, as suggested by sensitivity data.

Keywords: burning rate, bismuth chromate, delay composition, thermal analysis

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Introduction

Antimony trisulphide is used as a fuel in delay detonating cords. The composition based on red lead, ferrosilicon, and antimony trisulphide was studied for the burning rate, coefficient of thermal sensitivity, heat of combustion, and combustion gas pressure by Nagano et al. [1]. Xia Zhaoming et al. [2] reported a study on pyrotechnic composition containing red lead, silicon, and antimony trisulphide with 2% polyvinyl alcohol as a binder and recommended its use for a high-precision delay element. The behavior of the pyrotechnic delay composition based on antimony trisulphide, Zr, and barium chromate was studied in the temperature range −20°C to +75°C by Barisin et al. [3]. They also studied this composition at 98.5% relative humidity for a stability test and concluded that this composition has excellent storage characteristics. The reaction of red lead, ferrosilicon, boron, and antimony trisulphide was studied by Nakamura et al. [4] by employing thermal analysis, end product analysis, as well as burning rate studies.

The pyrotechnic composition based on antimony trisulphide, potassium perchlorate, and barium chromate was chosen for the present study, and the effect of substitution of barium chromate by bismuth chromate on the burning rate was studied. The decomposition of bismuth chromate takes place at a lower temperature (at about 600°C) compared to barium chromate (1450°C). The decomposition of bismuth chromate is endothermic, which absorbs the heat of the system, thereby reducing the heat flow in the reaction front, which reduces the burning rate. The burning rate, heat of combustion, ignition temperature, and sensitivity of the compositions have been studied in addition to thermal analysis. The chemical equilibrium computations have also been carried out for constant volume condition, and the results are presented in this paper. The materials studied are the following:

Chemicals	Percentage purity	Average particle size (μ)
Barium chromate	98.85	3.1
$KClO_4$	98.22	12.0
Antimony trisulphide	94.50	5.6
Bismuth chromate	98.85	3.1

Methods

Ignition temperatures of these samples were recorded on a locally fabricated DTA apparatus at a heating rate of 40°C/min using a 40 mg sample mass in air. The heat of combustion was determined in an argon gas medium using a Parr adiabatic bomb calorimeter.

TG/DSC curves were recorded on a Netzsch STA 409 EP at a heating rate of 10°C/min. The sample mass was 10 mg, and the environment was static air. Pt-Pt with 10% Rh thermocouples were employed to measure temperatures. The burning rate was measured by a lead tube method.

Impact sensitivity was determined on the Fall hammer apparatus using a 2 kg drop weight and 20 mg sample. Tetryl was used as standard material, and the figure of insensitivity was calculated. Friction sensitivity was determined on a Julius Peter friction sensitivity apparatus using a 10 mg sample.

Results and Discussion

Thermochemistry

Thermochemical performance characteristics of these compositions were calculated using a computer program. During combustion of these compositions, the main reaction is expected to be between antimony trisulphide and potassium perchlorate. Thermochemical calculations for the system antimony trisulphide 71.5% and potassium perchlorate 28.5% at constant volume ($V = 0.1\ \text{m}^3/\text{gm}$) indicated the gaseous combustion products to be S, SO_2, SO_3, Sb, Sb_2, Sb_3, Sb_4, Sb_4O_6, SbCl, SbO, SbS and solid products as K_2SO_4, Sb, Sb_2O_3 as well as unburnt Sb_2S_3. The calculated equilibrium flame temperature is 1130°C. When the mole ratio of Sb_2S_3 and $KClO_4$ is kept constant and 72 parts $BaCrO_4$ are added (that is, Sb_2S_3 20%, $KClO_4$ 8%), the flame temperature increases from 1130 to 1339°C. Similarly, bismuth chromate compositions show the flame temperature to be 1317°C. The proportion of condensed products is at a maximum with barium chromate and declines with replacement of barium chromate by more and more bismuth chromate, as shown in Tables 1 and 2. Thus compositions containing bismuth chromate are likely to be gassy even though their burning rate is less. These compositions are likely to show more variation in burning rate because of ambient pressure changes.

Thermal Analysis

The DSC curve of $KClO_4$ and thermal decomposition of bismuth chromate have been reported in [5, 6]. $BaCrO_4$ decomposes at about

Table 1
Thermodynamic data of $BaCrO_4$ (A) + $Bi(OH)CrO_4$ (B) + Sb_2S_3 (C) + $KClO_4$ (D) + NC (E)

Proportion of ingredients A + B + C + D + E	Flame Temp (°C)	Volume (m^3/gm)	Mass of condensed products	Impetus (J/g)
72-00-20-8-1	1323	0.11	89	11.15
62-10-20-8-1	1268	0.17	82	16.85
52-20-20-8-1	1266	0.22	79	20.85
42-30-20-8-1	1265	0.26	76	24.89
32-40-20-8-1	1264	0.30	72	29.00
22-50-20-8-1	1263	0.35	69	33.18
12-60-20-8-1	1262	0.39	66	37.41
02-70-20-8-1	1245	0.43	64	41.70
00-72-20-8-1	1227	0.44	63	42.51

1450°C [7]. Thermal analysis of antimony trisulphide has been carried out in air and the DSC curve (open cup) is shown in Figure 1, where there are three exothermic peaks. The first exothermic peak is due to conversion of Sb_2S_3 to SbS at about 403°C. The second exotherm at

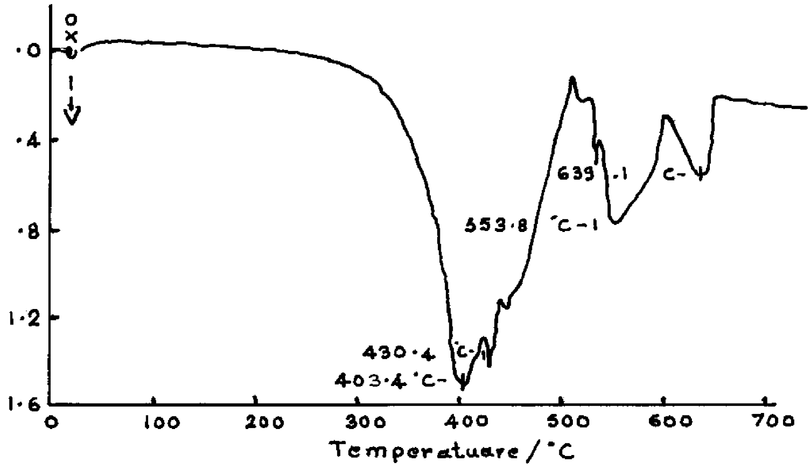

Figure 1. DSC curve of antimony trisulphide.

Table 2
Concentration of combustion products in moles per kg: $BaCrO_4$ (A) + $Bi(OH)CrO_4$ (B) + Sb_2S_3 (C) + $KClO_4$ (D) + NC(E)

Proportion of ingredients A + B + C + D + E	Sb_2O_3	KCL	SO_2	$Ba(CrO_2)_2$	$BaSO_4$	Cr_2O_3	Bi_2O_3	K_2SO_4
00-00-72-28-1	0.37	2.0	3.23	–	–	–	–	–
72-00-20-8-1	0.43	0.33	0.33	1.42	1.42	–	–	–
42-30-20-8-1	0.47	0.24	0.85	0.87	0.78	0.39	0.25	–
32-40-20-8-1	0.48	0.24	1.00	0.62	0.63	0.58	0.50	0.12
00-72-20-8-1	0.47	0.18	1.58	–	–	1.05	0.97	0.17

about 553°C corresponds to the formation of Sb_2O_3, and the third peak to the formation of Sb_2O_4 [8, 9]. The scheme of reactions can be given as;

$$Sb_2S_3 \xrightarrow{403^\circ C} 2SbS \xrightarrow{553^\circ C} Sb_2O_3 \xrightarrow{639^\circ C} Sb_2O_4.$$

This is well supported by TG data. First-stage weight loss of 9.3% occurs in the range 229–497°C, and the second step is between 497 and 630°C, which shows weight loss up to 5.6%. This is further supported by XRD data. Antimony (III) sulphide was heated in a furnace at 400, 600, and 700°C for 2 hr, and XRD data were taken at room temperature. Table 3 shows X-Ray Diffraction (XRD) data that indicate that Sb_2S_3 is converted to Sb_2O_3 at 400°C.

Comparison of experimental data with the ASTM card data file shows that the data belong to a cubic form with cell dimensions $a = 11.152$ A°, $Z = 8$, and density = 5.583. At 600 and 700°C, it is converted to Sb_2O_4, which compares well with ASTM data (Table 4). It belongs to an orthorhombic group with cell dimensions

Table 3
Comparison of reported XRD data of Sb_2O_3 and Sb_2S_3 heated to 400°C

Sb_2S_3 heated at 400°C			Reported Sb_2O_3 card no. 5-0534		
2θ	d	I/I$_o$	d	I/I$_o$	hkl
13.74	6.4393	7	6.44	12	111
27.7	3.2177	100	3.218	100	222
32.08	2.7876	43	2.788	40	400
35.04	2.5586	12	2.559	11	331
42.10	2.1444	5	2.145	3	511
46.00	1.9713	60	1.972	42	440
54.58	1.6800	58	1.681	35	622
57.28	1.6071	17	1.611	11	444
59.18	1.5599	12	1.562	7	711

Table 4
Comparison of reported xRD data of Sb_2O_4 and antimony (III) trioxide heated in air at 600°C

Sb_2S_3 heated at 600°C			Reported Sb_2O_4 Card no. 5-0575		
2θ	d	I/Io	d	I/Io	hkl
20.00	4.4357	5	4.42	6	101
25.90	3.4371	29	3.44	60	111
29.14	3.0639	100	3.07	100	112
30.40	2.9378	31	2.94	25	004
32.90	2.7200	6	2.72	3	020
33.86	2.6451	23	2.65	20	021
36.48	2.4609	10	2.46	8	022
37.46	2.4000	16	2.40	12	200
40.30	2.2360	6	2.24	3	023
45.40	1.9959	7	1.99	6	024
46.10	1.9673	7	1.97	6	115
47.40	1.9163	7	1.92	2	213
49.00	1.8574	24	1.86	20	204
51.50	1.7729	21	1.76	15	025
53.30	1.7172	38	1.72	25	116
54.10	1.6937	12	1.69	9	130
56.20	1.6303	6	1.64	12	033

$a = 4.804$
$b = 5.424$
$c = 11.76$
$d = 6.59$
$Z = 4.$

Figure 2 shows DSC curves of the mixes containing different percentages of barium chromate. It is seen from Table 5 that an endotherm appears at 307 ± 2°C corresponding to the crystalline transition of potassium perchlorate. The exothermic peak at 411–424°C is attributed to the formation of SbS. The exothermic peak at 650°C disappears as barium chromate content increases in the composition. The peak at 516°C becomes sharp for 12% and 2% barium chromate, while for 0% barium chromate the only single peak is observed at 424°C.

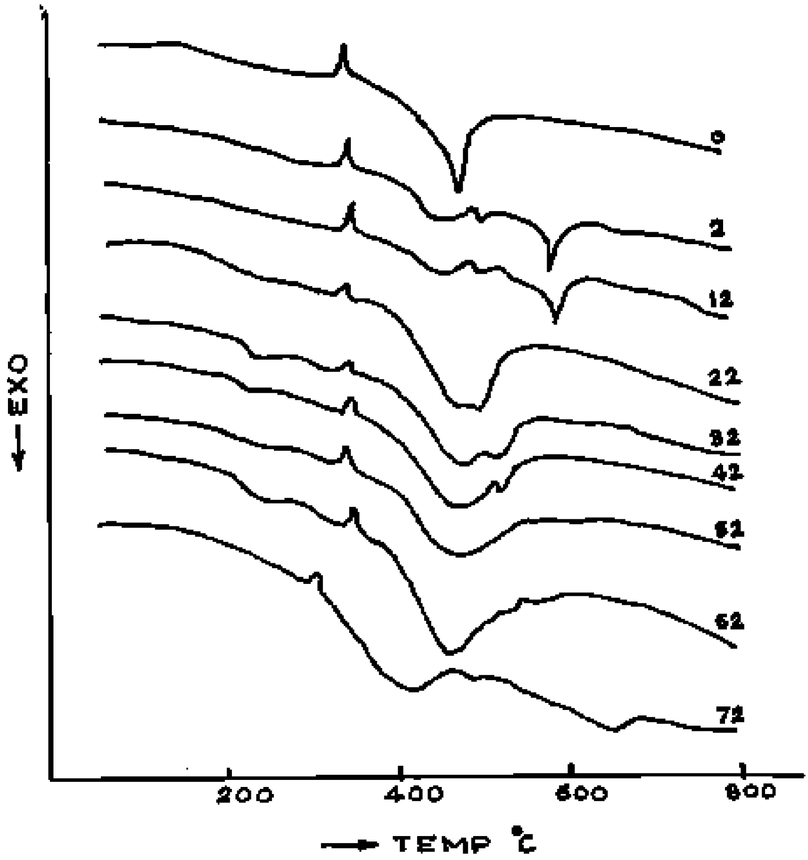

Figure 2. DSC curves of compositions containing varying percentages of barium chromate.

Thus this peak is due to the reaction between Sb_2S_3 and $KClO_4$. Further TG data show a gradual increase in weight loss as bismuth chromate increases.

Ignition Temperature

Ignition temperatures determined by heating a 40 mg sample at 40°C/min are in the range 400 ± 10°C. This suggests that the ignition reaction is between antimony trisulphide and potassium perchlorate. Therefore, a mix containing a 20:8 ratio of Sb to $KClO_4$ was prepared

Table 5
Thermoanalytical data of $BaCrO_4$ (A) + $Bi(OH)CrO_4$ (B) + Sb_2S_3 (C) + $KClO_4$ (D) + NC (E)

Proportion of ingredients A + B + C + D + E	DSC endotherm (°C)	DSC exotherms (°C) 1	2	3	TG (%)
72-00-20-8-1	305	411	498	650	−5.8
62-10-20-8-1	307	415	–	–	−5.5
52-20-20-8-1	307	415	–	–	−12.6
42-30-20-8-1	308	419	462	–	−7.8
32-40-20-8-1	307	415	–	–	−8.4
22-50-20-8-1	307	419	–	–	−5.2
12-60-20-8-1	307	412	–	516	−10.8
02-70-20-8-1	307	–	–	516	−15.1
00-72-20-8-1	307	424	–	–	−15.1

and tested under the same conditions. It also ignited at 360°C. The presence of bismuth chromate or barium chromates probably shows a slight dilution effect on the ignition temperature (Table 6).

Burning Rate

Antimony trisulphide is generally used as a secondary fuel in some ignition compositions [2]. In this work it was used as a primary fuel, and a series of compositions were made using potassium perchlorate, barium chromate, and bismuth chromate, and nitrocellulose as a binder. The original composition contains 20% antimony trisulphide, 8% potassium perchlorate, and 72% barium chromate. The barium chromate was progressively replaced by bismuth chromate, and a series of compositions were prepared. These were filled in lead tubes, and burning rates were determined. Table 6 shows the burning rate, cal-val, and sensitivity to impact and friction data.

It is seen that the burning rate decreases with increase in bismuth chromate content and is in the range 0.43–0.23 cm/s. The decrease in burning rate of the composition with the addition of bismuth chromate is attributed to the decrease in heat of combustion of the mixture. The endothermic nature of the decomposition of bismuth chromate may also contribute to this phenomenon.

Table 6
Sensitivity and cal-val data $BaCrO_4$ (A) + $Bi(OH)CrO_4$ (B) + Sb_2S_3 (C) + $KClO_4$ (D) + NC (E)

Proportion of ingredients A + B + C + D + E	Cal-val (cal/g)		Ignition temp.	Impact		Friction (kg)	BR (cm/s)
	Observed	Calculated		F of I	Energy (Joules)		
72-00-20-8-1	216	–	404	132	31.8	36	0.43
62-10-20-8-1	218	–	402	102	24.5	36	0.37
52-20-20-8-1	218	–	400	101	24.3	36	0.32
42-30-20-8-1	214	–	404	96	25.0	36	0.31
32-40-20-8-1	202	–	403	111	29.1	36	0.28
22-50-20-8-1	202	259	402	122	31.8	36	0.27
12-60-20-8-1	186	240	389	117	29.1	36	0.25
02-70-20-8-1	170	221	409	106	26.3	36	0.24
00-72-20-8-1	171	217	411	113	28.1	36	0.23

Sensitivity

The figure of insensitivity and impact energy values are given in Table 6. These values are around 100, which suggests that these compositions are safe to handle. At the same time all these compositions are insensitive up to 36 kg weight for friction sensitivity.

Conclusions

Mixtures of antimony trisulphide with $KClO_4$ and a large proportion of barium chromate give a series of slow-burning pyrotechnic compositions suitable for applications as delay compositions. The burning rate is further lowered by the replacement of bismuth chromate, mainly because of (1) decrease in flame temperature, and (2) decrease in calorimetric value. These compositions are safe to handle, as revealed by the sensitivity data.

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