

Bismuth Chromate in Delay Compositions

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ABSTRACT

Barium chromate is used as a secondary oxidiser in delay compositions which slows down the rate of the reaction. The composition containing barium chromate, potassium perchlorate and sulphur along with the binder, gives inverse burning rates up to 4.5 s/cm. If barium chromate is substituted by bismuth chromate hydrate, the rate of reaction is slowed down further to 11.8 s/cm. Various compositions were prepared by changing the percentage of barium chromate and bismuth chromate. The energy of activation was determined to be 14.5 kcal/mole for the composition with 40 per cent bismuth chromate. The explosion temperature for a delay of 5 s was observed as 480 °C. These compositions were subjected to impact and friction sensitivity tests to determine the safety aspects. This paper presents the results of burning rate, calorimetry, explosion temperature and the sensitivity data of some delay compositions containing bismuth chromate.

1. INTRODUCTION

Pyrotechnic compositions containing potassium perchlorate as oxidiser are widely used as delay compositions. Since potassium perchlorate is a powerful oxidiser, the overall reaction is very vigorous with metal powders and hence barium chromate is used as a secondary oxidiser. The composition containing sulphur, potassium perchlorate and barium chromate is one such composition. It is interesting to study the effect of bismuth chromate on the characteristics of the composition containing barium chromate, potassium perchlorate and sulphur. A number of compositions have been prepared by changing the percentages of bismuth chromate and barium chromate.

2. EXPERIMENTAL

2.1 Materials

Bismuth chromate hydrate is prepared by the usual method reported in the literature^{1,2}. A solution of bismuth nitrate pentahydrate (58.2 g in 450 ml of 2N HNO_3) is kept in a flask at 80 °C. Potassium dichromate (26.47 g) dissolved in 600 ml water, is added dropwise

with constant stirring to the bismuth nitrate solution. Addition is completed in 30 min and it is further stirred for 15 min. Chemical analysis is carried out by determining bismuth as bismuth phosphate. The bismuth value corresponds to the formula $Bi_2O_3 \cdot 2CrO_3 \cdot H_2O$ or $Bi(OH)CrO_4$.

Potassium perchlorate of average size (11 μm) and barium chromate (1.0 μm) have been used. The sulphur has an average particle size (125 μm) and nitrocellulose lacquer is used as the binder. The mixing is carried out by sieving the ingredients together through an appropriate sieve behind a safety screen.

2.2 Measurements

Thermal analysis was carried out on SETARAM TG-DTA Model 92 in air employing 10 °C/min heating rate and maximum temperature up to 1000 °C. About 50 mg sample was loaded in alumina crucible. Reaction exothermicities were determined in air using Parr adiabatic automatic bomb calorimeter Model 1240.

The burning rate of these mixtures was measured by firing the compositions pressed in lead tubes with

bunsen burner and the time was recorded using an electronic timer.

X-ray diffraction patterns were recorded on Philips x-ray diffractometer using *Cu-K* radiations and *Ni* as filter at room temperature. Infrared spectra were recorded in *Nujol Mull* at room temperature, on Perkin Elmer spectrophotometer Model 693. Ignition delay time was measured with the help of the apparatus described earlier³.

3. RESULTS AND DISCUSSION

3.1 Characterisation of Bismuth Chromate

Thermal analysis of potassium perchlorate is described earlier⁴ and that of barium chromate is given by Clement Duval⁵.

Figure 1 shows DTA, TG and DTG curves of bismuth chromate. DTA curves show four endothermic peaks at 332, 520, 868 and 938 °C. The first endotherm appears to correspond to dehydration and the second peak corresponds to the loss of half molecule of oxygen. The third endotherm is also due to the loss of second half molecule of oxygen, while the fourth peak is due to fusion. On further heating up to 1000 °C, the material decomposes into two different products, one red Bi_2O_4 and the other Cr_2O_3 green in colour. The probable course of reaction is given as

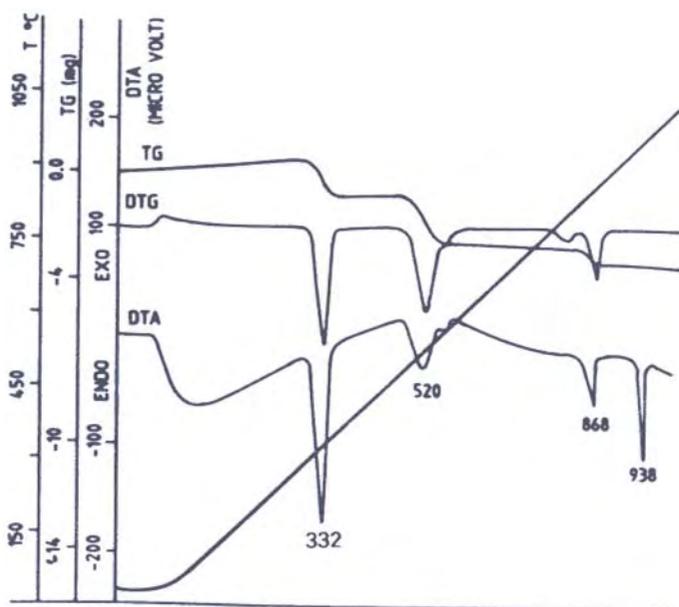
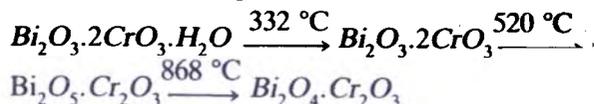


Figure 1. Thermoanalytical curves of bismuth chromate.

The above stages are supported by TG data as shown in Table 1. For further confirmation, about 3 g bismuth chromate was kept at 350, 550 and 820 °C for 2 hr and

Table 1. Thermoanalytical data of bismuth chromate hydrate

| DTA endo-thermic peak temp (°C) | TG % loss | | DTG peak temp (°C) | |
|---------------------------------|------------------|----------|--------------------|------------|
| | Temperature (°C) | Observed | | Calculated |
| 332 | 310 | 2.06 | 2.6 | 332 |
| 520 | 480 | 5.77 | 5.0 | 520 |
| 868 | 851 | 7.42 | 7.3 | 868 |

1 g residue was taken out at each stage. X-ray diffraction patterns of these different slags are given in Fig. 2. At 350 °C, bismuth chromate loses water of crystallisation

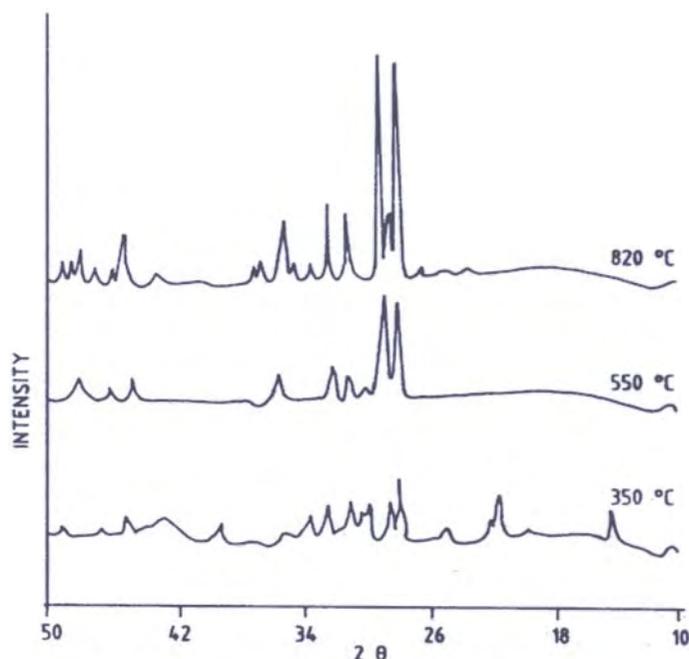


Figure 2. X-ray diffraction patterns of bismuth chromate slags.

but the crystalline form remains the same. On further heating at 550 and 820 °C, it loses half molecule of oxygen at each step, without change in its crystalline nature. The data for *d* values and *I/I*₀ is given in Table 2. Infrared spectra of bismuth chromate and its slags at different temperatures are shown in Fig. 3. It is seen that the tetrahedral symmetry of chromate group is not observed in the infrared spectrum of bismuth chromate. In addition, there is a peak at 730 cm^{-1} which indicates *Cr-O-Cr* linkage. Thus, it appears that the material must be a dichromate.

Table 2. X-ray diffraction data of decomposition products of bismuth chromate

| 350 °C | | | 550 °C | | | 820 °C | | |
|-----------------|---------|-------|-----------------|---------|-------|-----------------|---------|-------|
| $d \text{ \AA}$ | I/I_0 | hkl | $d \text{ \AA}$ | I/I_0 | hkl | $d \text{ \AA}$ | I/I_0 | hkl |
| 6.1456 | 44 | 111 | 3.1728 | 100 | 310 | 3.1728 | 100 | 310 |
| 4.0733 | 72 | 211 | 3.0972 | 100 | 311 | 3.0578 | 100 | 311 |
| 4.0008 | 33 | 210 | 2.9760 | 15 | - | 2.8464 | 30 | 222 |
| 3.5309 | 22 | 220 | 2.8732 | 30 | 211 | 2.7592 | 32 | 320 |
| 3.1728 | 100 | 310 | 2.7859 | 36 | 320 | 2.6649 | 35 | 321 |
| 3.0972 | 66 | 311 | 2.5224 | 30 | 400 | 2.5474 | 28 | 400 |
| 2.8642 | 66 | 222 | 2.0204 | 26 | 422 | 2.4531 | 12 | 410 |
| 2.7592 | 44 | 320 | 1.9664 | 15 | 431 | 1.9959 | 25 | 430 |
| 2.6649 | 33 | 321 | 1.8863 | 29 | 432 | 1.8862 | 15 | 432 |

Simple cubic - $a = 10.03 \text{ \AA}$, $n = 8$, $v = 1003.027 \text{ \AA}^3$, $d = 5.31192 \text{ g/cm}^3$

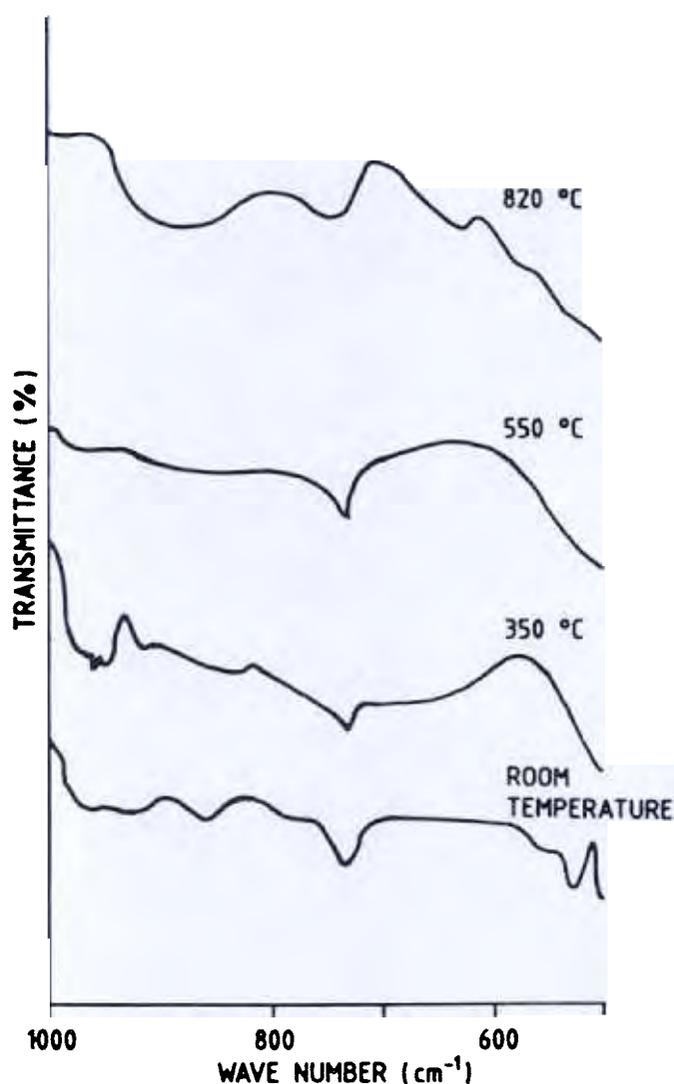


Figure 3. Infrared spectra of bismuth chromate.

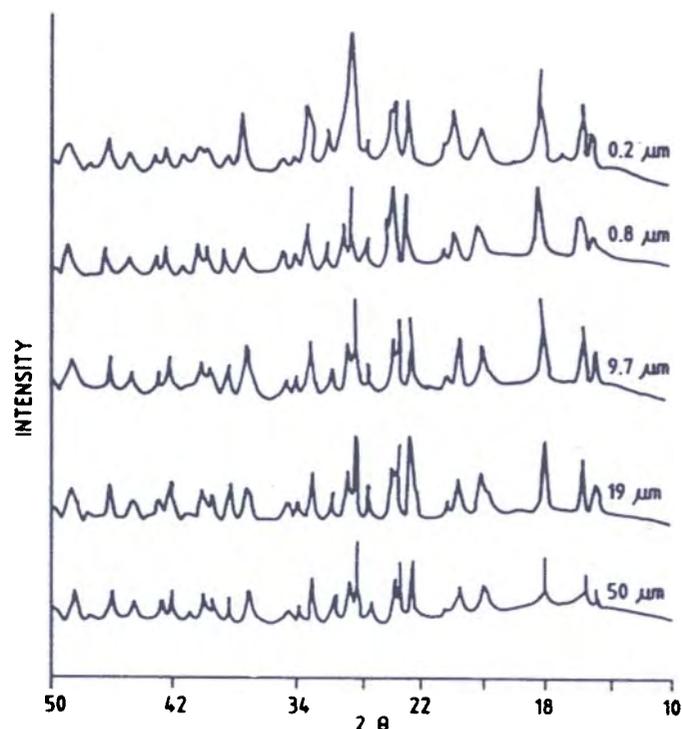


Figure 4. X-ray diffraction patterns of bismuth chromate.

The bismuth chromate prepared under different temperature conditions was studied by x-ray diffraction as shown in Fig. 4. In all the cases the same monoclinic crystals have been obtained.

3.2 Delay Compositions

3.2.1 Burning Rate

Using the above bismuth chromate, several compositions were prepared. The system containing 8

Table 3. Data on compositions containing sulphur (8%), potassium perchlorate (8%) and nitrocellulose (2 parts).

| Composition no | Bismuth chromate (%) | Barium chromate (%) | IBR (s/cm) | Cal-val (cal/g) | Impact (2 kg) (cm) | Friction (kg) |
|----------------|----------------------|---------------------|------------|-----------------|--------------------|---------------|
| | 0 | 84 | 4.56 | 268 | 38 | 21.6 |
| | 14 | 70 | 7.92 | 296 | 136 | 21.6 |
| | 24 | 60 | 9.0 | 249 | 107 | 19.2 |
| | 34 | 50 | 8.88 | 270 | 91 | 21.6 |
| | 40 | 44 | 7.45 | 258 | 79 | 16 |
| | 54 | 30 | 9.27 | 272 | 97.5 | 16.8 |
| | 64 | 20 | 9.0 | 274 | 92 | 24 |
| | 74 | 10 | 8.6 | 247 | 101 | 19.2 |
| | 84 | 0 | 11.8 | 240 | 98 | 19.2 |

per cent potassium perchlorate, 8 per cent sulphur and 84 per cent barium chromate was chosen for the study. The barium chromate was progressively substituted by bismuth chromate. The compositions were granulated using 2 parts of nitrocellulose as binder. Table 3 shows the data on inverse burning rate, calorific value in air, height of 50 per cent explosion and friction sensitivity for these compositions. As barium chromate is substituted by different percentages of bismuth chromate, the composition becomes slower and slower. When barium chromate is completely replaced by bismuth chromate, the composition has an average inverse burning rate of 11.8 s/cm. However, ignition of this composition is difficult and the composition does not propagate in lead tube for lengths of more than 5 cm.

Compositions 2 to 8 show almost same inverse burning rate of about 8.5 ± 0.5 s/cm, while composition 5 shows a burning rate of 7.45 s/cm. Table 4 shows the

Table 4. Effect of particle size

| Composition no | Particle size (μm) | BR (cm/s) | IBR (s/cm) | Impact 50% height (cm) | Friction (kg) |
|----------------|---------------------------------|-----------|------------|------------------------|---------------|
| 10 | 0.2 | 0.18 | 5.6 | 96 | 16 |
| 11 | 0.8 | 0.16 | 6.3 | 88 | 24 |
| 12 | 2.5 | 0.13 | 7.5 | 79 | 16 |
| 13 | 8.0 | 0.11 | 8.7 | 102 | 36 |

Composition : bismuth chromate 40% ; barium chromate 44% ; sulphur 8% ; potassium perchlorate 8% ; nitro cellulose 2 parts over the dry mix.

burning rate, impact and friction sensitivity data of the compositions containing bismuth chromate of different particle sizes. It is observed that as the particle size of bismuth chromate increases the burning rate decreases. Inverse burning rates show clear variation from 5.6 to 8.7 s/cm. The impact sensitivity data shows marginal variation in the height of 50 per cent explosion. The composition is reasonably safe for handling. Friction sensitivity data indicates that these compositions are sensitive to friction, but the sensitivity is not very high. Composition 13 is insensitive to friction up to 36 kg.

3.2.2 Bomb Calorimetry

The heat of combustion is determined in air. The composition containing only bismuth chromate gives 240 cal/g, while the composition containing only barium chromate gives 268 cal/g. The composition which gives less heat output burns slowly. Other compositions containing both the chromates show variation in heat of combustion from 296 to 247 cal/g.

3.2.3 Sensitivity

The results of impact and friction sensitivity measurements are presented in Table 3. Composition 1 is very sensitive to impact and the addition of bismuth chromate reduces the impact sensitivity considerably as seen from the table. The friction sensitivity of these mixtures is found in the range of 16 to 24 kg. It is seen that these compositions are not very sensitive to friction and can be used with reasonable precautions.

3.2.4 Time to Ignition

Table 5 shows the data for energy of activation and explosion temperature for delay time of 5 s. These values are obtained by plotting log of time to ignition against reciprocal of absolute temperature⁷. Energy of activation of the composition containing only barium chromate is found to be 3.2 kcal/mole. It increases with increase in bismuth chromate up to 24 per cent and suddenly decreases to 8 kcal/mole for 34 per cent bismuth chromate. It increases to 21 kcal/mole up to 64 per cent bismuth chromate and then a decrease to 17 kcal/mole for 84 per cent.

Table 5. Time to ignition data

| Composition with bismuth chromate (%) | Energy of activation (kcal/mole) | Explosion temperature for 5 s (°C) |
|---------------------------------------|----------------------------------|------------------------------------|
| 0 | 3.20 | 490 |
| 14 | 13.60 | 484 |
| 24 | 16.70 | 467 |
| 34 | 8.03 | 513 |
| 40 | 14.52 | 480 |
| 59 | 16.70 | 458 |
| 64 | 21.64 | 457 |
| 79 | 16.00 | 452 |
| 84 | 17.12 | 476 |

It can be seen that the substitution of barium chromate by bismuth chromate results in sudden increase in the activation energies of these compositions which may at least partly explain the slower burning rates of these compositions.

Explosion temperatures data for a delay of 5 s have been computed from the same plot of logarithm of time to ignition against reciprocal of absolute temperature. It is seen that the substitution of barium chromate by bismuth chromate does not affect the explosion temperature to an appreciable extent.

4. CONCLUSIONS

(a) It is noticed that bismuth chromate shows three endotherms at different temperatures. This

absorption of heat will lead to reduction in burning rates which is also reflected in the heat of combustion data. Bismuth chromate decomposes at around 1000 °C. The slags show the formation of Bi_2O_4 and Cr_2O_3 .

- (b) The compositions containing bismuth chromate are reasonably safe for handling.
- (c) From time to ignition data, it can be concluded that these compositions containing mixtures of barium chromate and bismuth chromate can be easily ignited and give sustained burning.
- (d) The system gives a fairly constant rate of burning over a wide range of proportion of bismuth chromate and barium chromate and can be easily adopted for practical application.

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