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THERMAL STUDIES OF PYROTECHNIC SYSTEMS

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INTRODUCTION

This paper describes the results of a collaborative study of gasless pyrotechnic delay systems using temperature profile analysis and differential thermal analysis (DTA). The work has extended over several years and has been concentrated on systems containing boron and tungsten.

BORON SYSTEMS

Temperature profile studies of mixtures of boron and potassium dichromate have shown the presence of two main exothermic stages in the pyrotechnic combustion[1]. Figure 1 shows the temperature profile recorded for a mixture containing 5% boron and 95% potassium dichromate, where the initial rate of temperature rise is 10^5 K min^{-1} and the maximum burning temperature is 1700 K. The products from the first reaction stage have been isolated using DTA under non-ignition conditions and the presence of potassium chromate has been identified by X-ray analysis. Quantitative DTA shows that the exothermicity of the first reaction stage is significantly reduced for mixtures containing less than 4% boron which is consistent with the stoichiometric amount of boron (3.5%) required by the equation $B + K_2Cr_2O_7 = K_2CrO_4 + 0.5Cr_2O_3 + 0.5B_2O_3$. In the second stage the potassium chromate reacts with excess boron. Mixtures containing less than 5% boron show only the first reaction stage and do not self-propagate the combustion. The second stage can be established independently of the first and mixtures of boron and potassium chromate may be ignited and burn smoothly.

Silicon is often added to mixtures of boron and potassium dichromate to produce a coherent glassy slag. DTA studies[2] have shown that the presence of silicon does not influence the low temperature reaction stage identified with the binary mixes, but that it increases the exothermicity of the second reaction stage. With those ternary mixtures prepared from 4% B – 96% $K_2Cr_2O_7$, where the binary mixture does

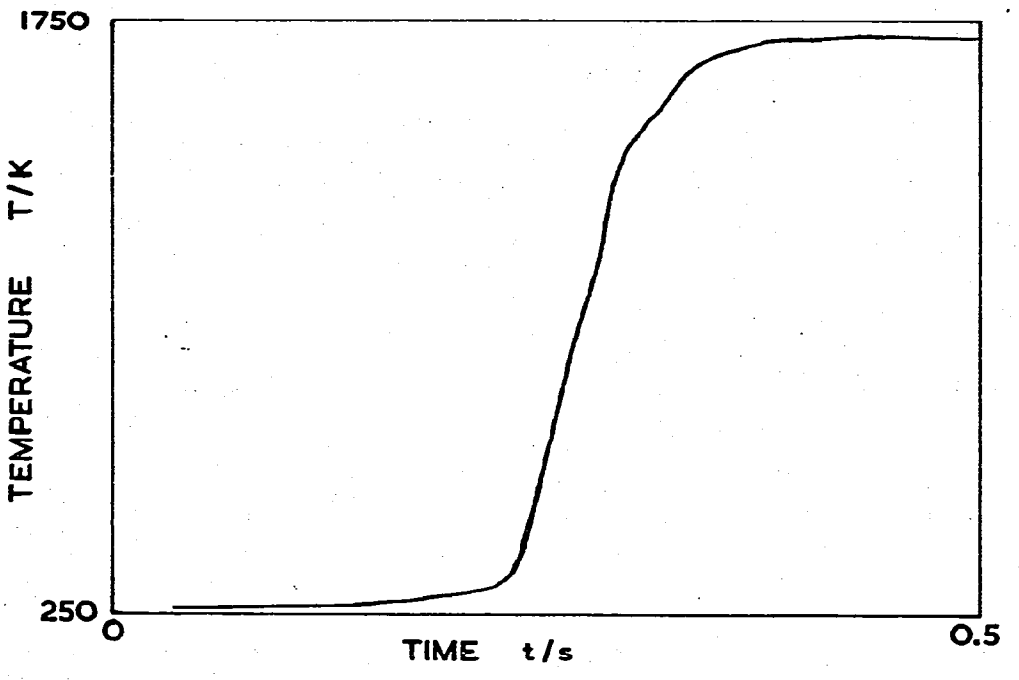

Fig. 1. Temperature profile for the mixture containing 5% boron and 95% potassium dichromate.

not give the second reaction (Fig. 2), the presence of silicon is essential for self propagation of a combustion wave. Combustion calorimetry shows that addition of 6% silicon to a binary mixture containing 5% boron and 95% potassium dichromate, increases the exothermicity by about 40%. With ternary mixtures containing 10% and over of silicon, there is evidence of complex high temperature behaviour.

DTA studies of mixtures of boron and molybdenum trioxide[3] have shown this to be a more complex system than boron and potassium dichromate. Hot stage microscopy[4] at 100 K min^{-1} has established that the mixtures ignite in the temperature range 840 - 870 K, about 200 K higher than for mixtures containing potassium dichromate. Five overlapping exotherms have been identified by DTA under non-ignition conditions and Mo_4O_{11} and MoO_2 established as reaction intermediates. The burning velocity behaviour is unusual and some measurements, as yet unconfirmed, suggest that it may be possible to establish more than one burning velocity depending on the ignition system used.

TUNGSTEN SYSTEMS

Binary mixtures with potassium dichromate are easily ignited and burn smoothly. Both temperature profile and DTA studies show the presence of two main exothermic reactions[5]. Potassium tungstate and chromic oxide have been identified in the final

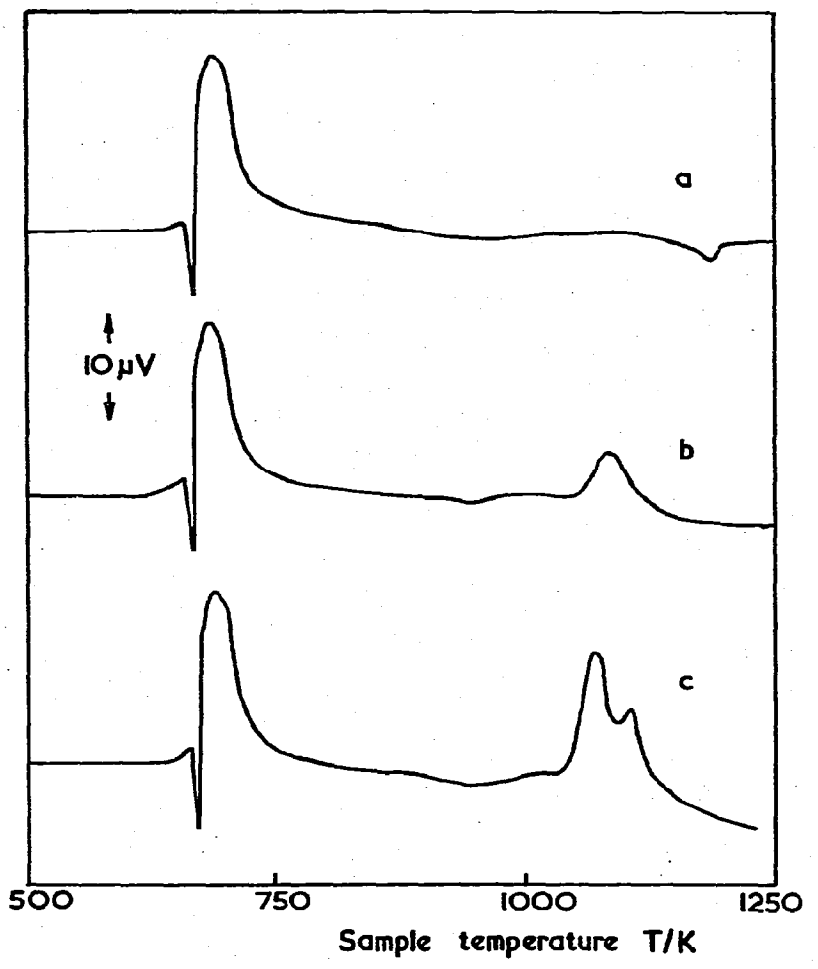

Fig. 2. DTA curves for the binary mixture (a) 4% boron and 96% potassium dichromate and ternary mixtures containing (b) 4% and (c) 10% silicon, prepared from the binary mixture, recorded under non-ignition conditions.

products and the reaction $W + K_2Cr_2O_7 = K_2WO_4 + Cr_2O_3$ in which the stoichiometric proportion of tungsten is 39%, is consistent with the maximum shown by the exothermicity data (Fig. 3). The products from the first reaction stage are not well defined and only potassium chromate has been established unequivocally. A possible representation of the reaction might be $W + 2K_2Cr_2O_7 = WO_3 + 2K_2CrO_4 + Cr_2O_3$ which leads to the reaction $W + WO_3 + 2K_2CrO_4 = 2K_2WO_4 + Cr_2O_3$ at the second stage.

Subsidiary DTA experiments have shown that mixtures of tungsten, tungstic oxide and potassium chromate give an exotherm similar to the second reaction exotherm. However, this ternary mixture does not readily self-propagate combustion and the burning velocity of the binary mixture containing 50% tungsten-50% potassium dichromate can be reduced five fold by the addition of 50% of the ternary mixture. This lack of reactivity in the second stage is reflected in a broad ill-defined DTA peak[4], in marked contrast with a well-defined peak shown in the boron system.

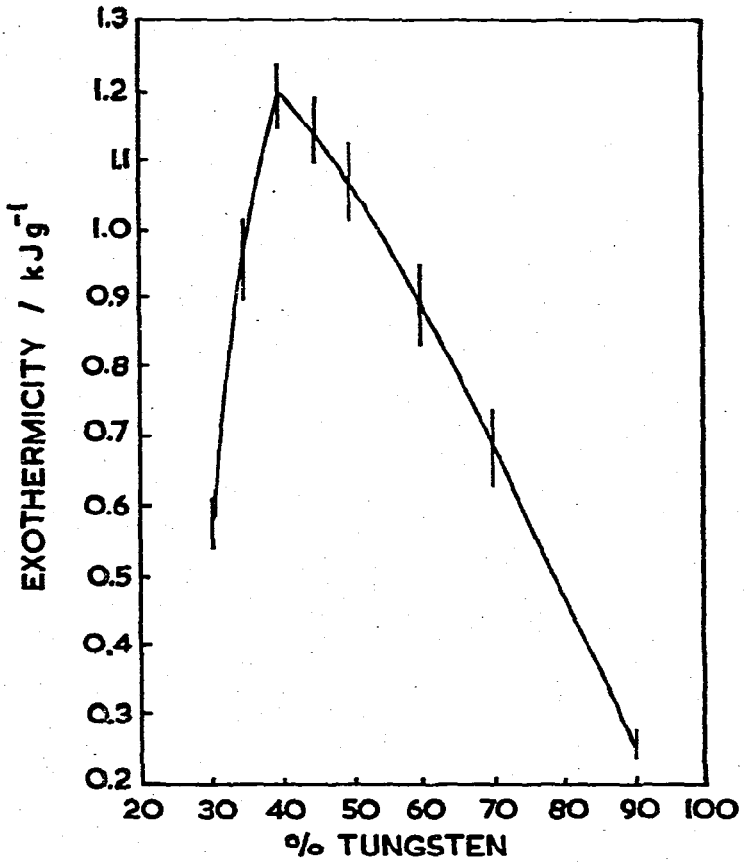

Fig. 3. Exothermicity of the ignition reaction of the tungsten-potassium dichromate system determined by quantitative DTA.

REFERENCES

1 E.L. Charsley, T. Boddington, J.R. Gentle and P.G. Laye, Thermochim. Acta, 22 (197 175.
2 E.L. Charsley, Chieh-Hua Chen, T. Boddington, P.G. Laye and J.R.G. Pude, Thermoc Acta, in press.
3 E.L. Charsley and M.R. Ottaway, Reactivity of Solids, Plenum Press, 1977, p.737.
4 E.L. Charsley and Diane E. Tolhurst, Microscope, 23 (1975) 227.
5 E.L. Charsley, M.C. Ford, Diane E. Tolhurst, S. Baird-Parker, T. Boddington and P.G. Laye, Thermochim. Acta, 25 (1978) 131.

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