Thermochimica Acta, 52 (1982) 321–332
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

INVESTIGATION OF THE IGNITION TEMPERATURE OF PYROTECHNIC SYSTEMS USING A PURPOSE DESIGNED DIFFERENTIAL THERMAL ANALYSIS APPARATUS

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(Received 10 April 1981; revised 10 August 1981)

ABSTRACT

A DTA apparatus has been developed for the routine determination of the ignition temperature of pyrotechnic systems consisting of mixtures of finely divided fuels with inorganic oxidants The effect of sample weight and heating rate on the ignition temperature has been investigated for a wide range of pyrotechnic compositions In several cases, increasing the sample weight above a certain level caused a dramatic decrease in the ignition temperature, the sample igniting at a lower-temperature exothermic reaction Small variations in the amount of an organic binder present in a pyrotechnic composition have also been shown to produce a marked change in the ignition temperature

INTRODUCTION

Pyrotechnic systems typically consist of intimate mixtures of finely divided fuels such as magnesium, titanium or boron with oxidising agents such as inorganic nitrates, dichromates or oxides [1]. They have a wide range of uses including flares or illuminants and delay compositions, the latter being designed to burn at a controlled rate.

Differential thermal analysis (DTA) has been used to characterise the behaviour of these materials under both ignition and non-ignition conditions [2]. Under ignition conditions, where the sample actually burns, a very large exothermic DTA peak is given together with a "spike" on the sample temperature curve, often corresponding to a measured temperature rise of several hundred degrees. This is illustrated in Fig. 1. The conditions required to achieve ignition will depend on the reactivity of the pyrotechnic mixture, the design of the instrument head, the sample weight, the heating rate and the atmosphere used in the sample chamber.

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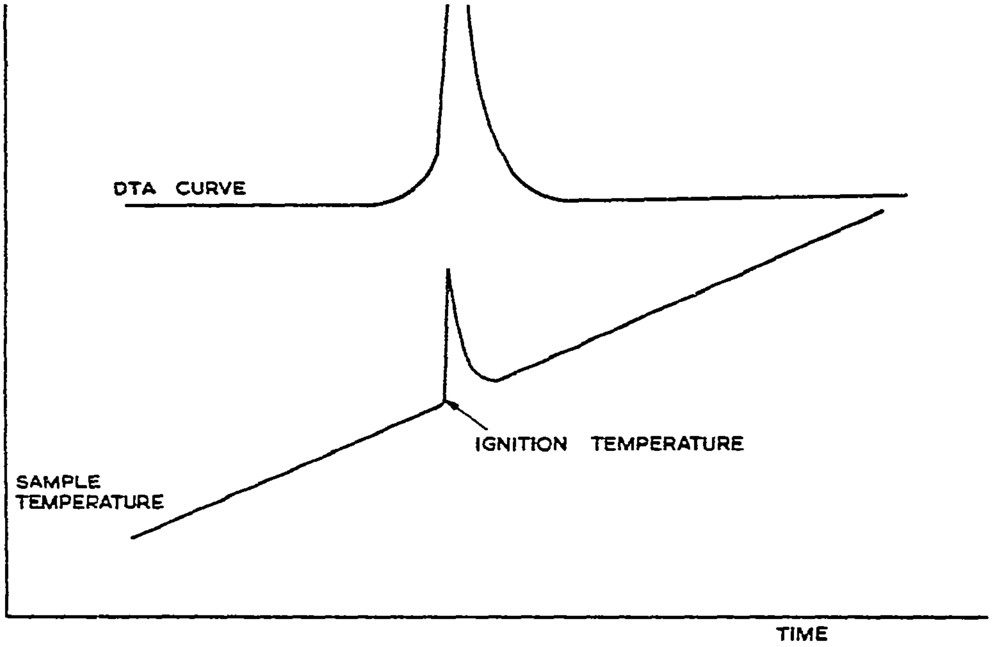

Fig 1 Schematic of ignition DTA curve

In interpreting the results of the thermal analysis experiments on pyrotechnics, it is important to distinguish between ignition reactions and non-ignition reactions, the latter normally being shown on a DTA curve as several smaller exothermic peaks with no sharp deflection on the sample temperature trace.

With a number of the so-called "gasless" delay compositions where there is little or no change in weight on ignition, the rise in temperature is proportional to the heat of reaction and the area of the DTA peak can be used to obtain an estimate of the reaction exothermicity [3].

In ignition reactions where a gaseous product is formed, large amounts of the sample may be ejected and thus the measured rise in temperature may decrease as the vigour of the reaction is increased, e.g. by increasing the weight of sample initially taken. In these cases, there is always the risk of damage to the measuring head, both from the force of the ignition and from attack by the high temperature reaction products which are ejected.

In the work carried out at Stanton Redcroft, mainly two systems have been used to determine ignition temperatures. The first is a hot stage microscope unit (Stanton Redcroft Model HSM-5) developed specifically for studies on pyrotechnic systems [4] and the second a standard DTA unit operating in the range from ambient to 1000°C (Stanton Redcroft DTA-673). Both suffer from problems due to attack by hot reaction products when a large number of pyrotechnic samples are being examined. The aim of the present work was to develop a head assembly which (a) would minimise heat losses from the sample and hence promote ignition, (b) provide reproducible temperature measurements over a large number of experiments without the need for frequent recalibration and (c) resist attack from ignition products.

DESCRIPTION OF THE APPARATUS

The ignition DTA head, designed to replace the standard DTA-673 head, is shown in Fig. 2. The sample and reference materials are contained in flat-bottomed quartz crucibles, C, 6 mm in diameter and 20 mm in length. The crucibles are supported by plate-type chromel–alumel thermocouples, P, fitted with locating ears and having 0.5 mm diameter wire leads. The latter replaced the 0.25 mm diameter wires originally used, which were not found to be sufficiently robust. The thermocouples are supported in short lengths of twin bore alumina rods, A, and passed into a four-bore alumina rise rod, R, on which the DTA block assembly is supported. The DTA block, B, is made from stainless steel and has wells 8 mm in diameter. The removable lid, L, made from the same material, serves to locate accurately the crucibles and to protect the thermocouples from attack by reaction products. It also ensures that the crucibles are effectively isolated from the block, thereby minimising heat losses.

The signal from the sample thermocouple is fed to a temperature indicator (Stanton Redcroft Model 9812) which provides a digital display of the temperature accurate to one degree centigrade and a linearised temperature output which is recorded on one channel of a two pen strip-chart recorder, the other channel recording the DTA signal. The standard DTA 673 programmer was replaced by a Model 683 unit and transformer, giving linear rates of up to 60°C min^{-1} in normal use, compared with maximum standard rate of 20°C min^{-1}. Experiments are normally carried out in static air as these conditions are used in an existing MOD ignition test, covering the range from ambient to 400°C [5]. For research purposes, when experiments in argon may be required, it is necessary to ensure that the air trapped by the lid does not cause oxidation of the fuel. Although this was initially achieved by evacuation of the unit, followed by flushing with argon, it was later

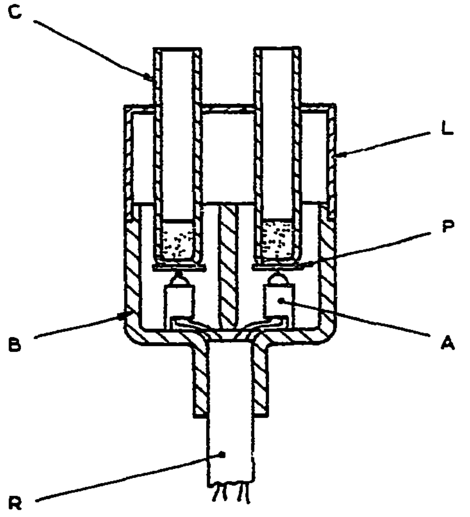

Fig. 2 Cross section of ignition DTA head

found to be equally effective to place a shallow crucible containing titanium powder on top of the lid and pass argon through the apparatus, at 400 ml min^{-1}, in the normal way.

INSTRUMENT PERFORMANCE

The performance of the head is illustrated in Fig. 3 by a run at a typical heating rate of 40°C min^{-1} on a 30 mg sample of a high purity aluminium. The head has shown good baseline stability even at the faster heating rates, together with sufficient sensitivity to enable it to be used for characterisation of pre-ignition reactions of pyrotechnic systems, in addition to its main function in the determination of ignition temperatures The temperature programme is controlled from the furnace thermocouple and at a heating rate of 50°C min^{-1}, linear heating of the sample is achieved at about 275°C, which is substantially below the ignition temperature of most pyrotechnic systems.

The performance of the head was evaluated initially using the fusion endotherms of high purity zinc, aluminium and A.R. grade potassium dichromate together with the ignition reaction of a mixture of 50% tungsten and 50% potassium dichromate* which is used as a gasless delay composition [3]. The zinc and aluminium runs were carried out in argon and the remaining runs in static air using 30 mg samples. Calibration checks were also carried out at regular intervals with either zinc or aluminium approximately every 20 runs and with the tungsten–potassium dichromate mix approximately every 30 runs. The results are summarised in Table 1 and represent means of values obtained during a period in which over 1500 runs on pyrotechnic systems were carried out. During this period, a major head rebuild has only been required once, demonstrating the suitability of this unit for pyrotechnic studies. The results in Table 1 show that the head calibration is well maintained over long periods and that replacing the head has not significantly altered the calibration values

Work has also been carried out to evaluate the effect of sample weight and also of heating rate on the temperature of a transition as determination by the extrapolated onset temperature of the DTA peak. The fusion of zinc and the phase changes in the ICTA Standards potassium perchlorate and potassium chromate have been used to cover the main temperature range of interest.

Sample weights of 10–100 mg were taken using a heating rate of 50°C min^{-1}, the zinc being run in an atmosphere of argon as before and the two salts in static air. The results are summarised in Table 2 and show that the extrapolated onset temperature is independent of sample weight, while the peak temperature increases in an approximately linear manner with sample weight.

In order to study the effect of heating rate, 50 mg samples were heated at rates from 5 to 50°C min^{-1}. The results are summarised in Table 3 and show that the

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* Throughout this paper, % = 100× weight of the component/weight of the mixture

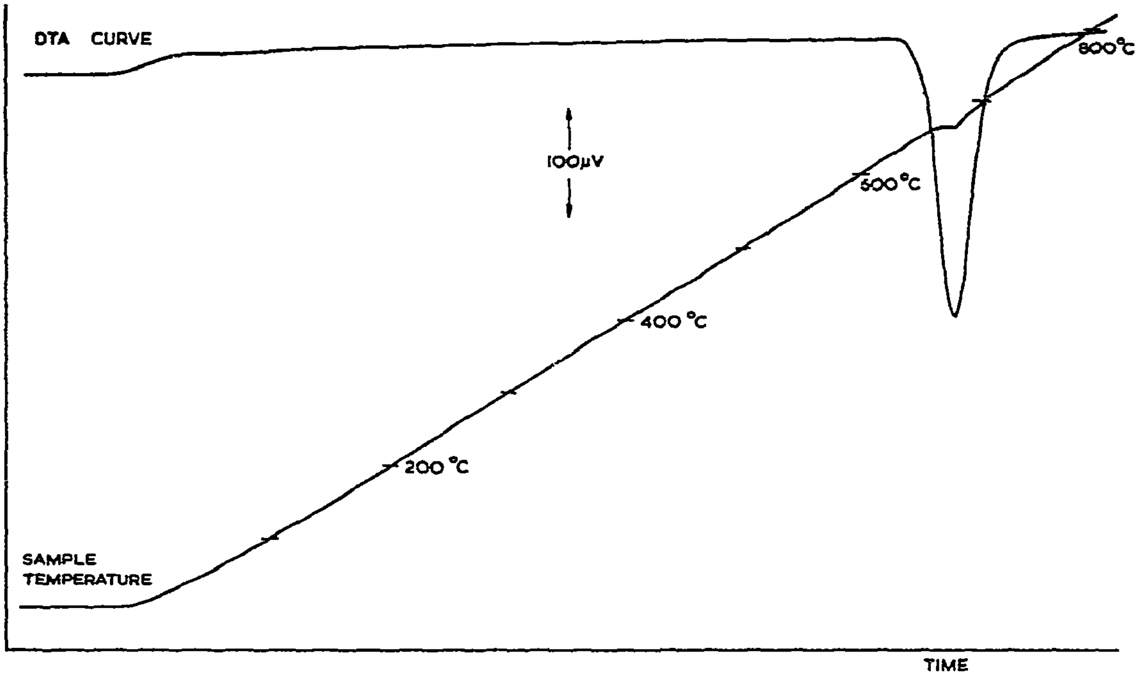

Fig 3 30 mg sample of high purity aluminium heated at 40°C min^{-1} in an argon atmosphere

TABLE 1

Calibration runs Mean extrapolated onset temperatures (°C)

The number of runs is shown in parentheses

Sample	Initial values	Overall values[a]
Tungsten–potassium dichromate	377±2 (9)	377±5 (54)
Potassium dichromate	400±2 (10)	
Zinc	422±2 (3)	419±4 (32)
Aluminium	661±1 (3)	663±3 (34)

[a] Obtained during period of 1500 experiments

TABLE 2

Variation of extrapolated onset and peak temperature with sample weight in the range 10–100 mg

Heating rate 50°C min^{-1}

	Potassium perchlorate	Zinc	Potassium chromate
Mean extrapolated onset temp. (°C)	302 ±3	421 ±2	674 ±1
Peak temperature (°C)	315 3+0.19W[a]	433.4+0 19W[a]	684 9+0 04W[a]
(Correlation coefficient)	(0 90)	(0 82)	(0 83)

[a] W=sample weight in mg

TABLE 3

Variation of extrapolated onset and peak temperatures with heating rate in the range 5–50°C min^{-1}

Sample weight 50 mg

	Potassium perchlorate	Zinc	Potassium chromate
Mean extrapolated onset temp (°C)	301 ±1	418 ±1	673 ±1
Peak temperature (°C)	$309.0+0.36H$ [a]	$424.0+0.31H$ [a]	$674.0+0.26H$ [a]
(Correlation coefficient)	(0.98)	(0.98)	(0.97)

[a] H = heating rate in °C min^{-1}

extrapolated onset temperature is not altered by increasing the heating rate, while the peak temperature increases in a linear manner.

STUDIES ON PYROTECHNIC SYSTEMS

It can be seen from Table 1 that the unit enabled the ignition temperature of the tungsten–potassium dichromate mix to be measured with good precision; 9 runs giving a standard deviation of 2°C. The ability to measure ignition temperature reproducibly was confirmed by runs on a further 7 pyrotechnic compositions heating 50 mg samples at 40°C min^{-1}, 9 runs being carried out on each composition. An average deviation of 5°C in the ignition temperature was measured. The experiments also showed that the most satisfactory method of packing the samples was to use a tamping rod under a dead-load of 1 kg.

In order to investigate the effect of sample weight and heating rate on the ignition temperature, 16 different pyrotechnic compositions were studied at sample weights ranging from 10 to 100 mg at a heating rate of 50°C min^{-1} and at heating rates from 5 to 60°C min^{-1} at a sample weight of 50 mg.

All of the compositions studied showed an approximately linear decrease in the ignition temperature with increasing sample weight. The rate of decrease ranged from 0.16 to 0.91°C for a 1 mg increase in sample weight. Figure 4 shows the DTA curve for the ignition of a 50 mg sample of a pyrotechnic composition based on a mixture of boron, silicon and potassium nitrate, while Fig. 5 shows the linear variation of ignition temperature with sample weight for this composition.

In 4 cases, a dramatic drop in ignition temperature was given when the weight was increased above a certain level. An example of this is the pyrotechnic composition containing magnesium, barium peroxide and acaroid resin. Selected DTA curves for this material are shown in Fig. 6. At the lower sample weights, the sample ignited in the region of 550–600°C. However, as the sample weight was increased, the exothermic reaction in the region of 300°C (barely observed with a 10 mg sample) increased in magnitude until with a 60 mg sample, ignition took place at this

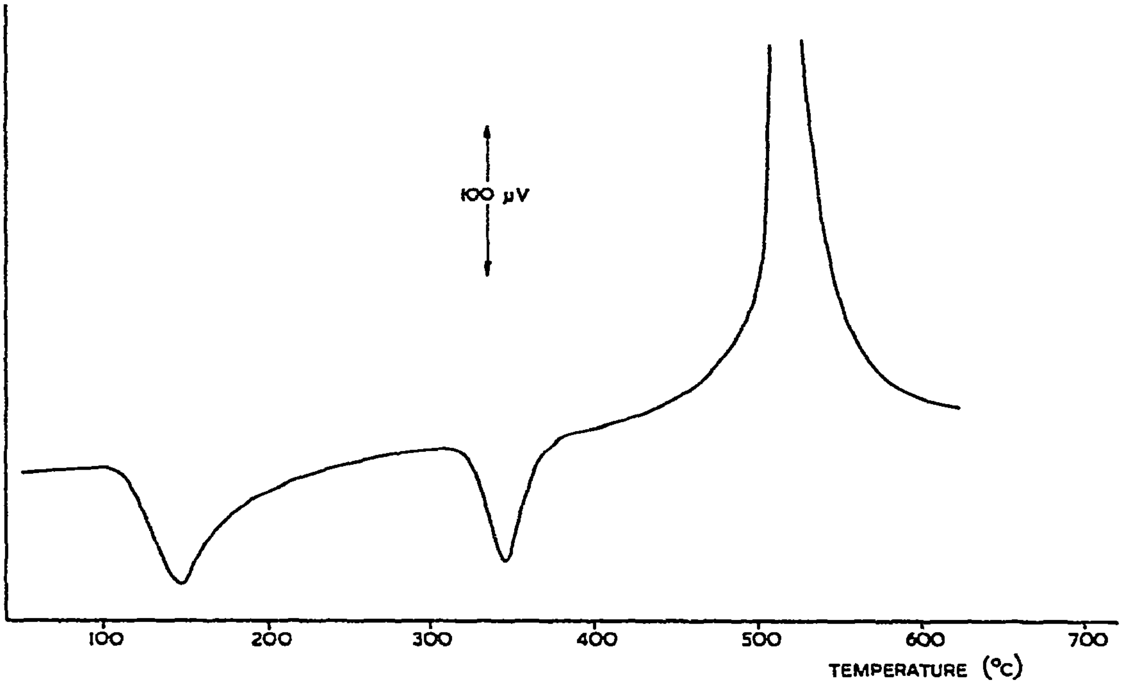

Fig 4 DTA curve for a boron–silicon–potassium nitrate composition Sample weight, 50 mg, heating rate, 50°C min^{-1}, static air

exotherm. The variation of ignition temperature with sample weight is plotted in Fig. 7.

Work currently in progress on the effect of organic materials used as binders in pyrotechnic systems has shown that the first exotherm is due to a reaction involving the acaroid resin. The binary mixture of magnesium and barium peroxide does not give an exotherm in this region (Fig. 8) and the plot of ignition temperature versus

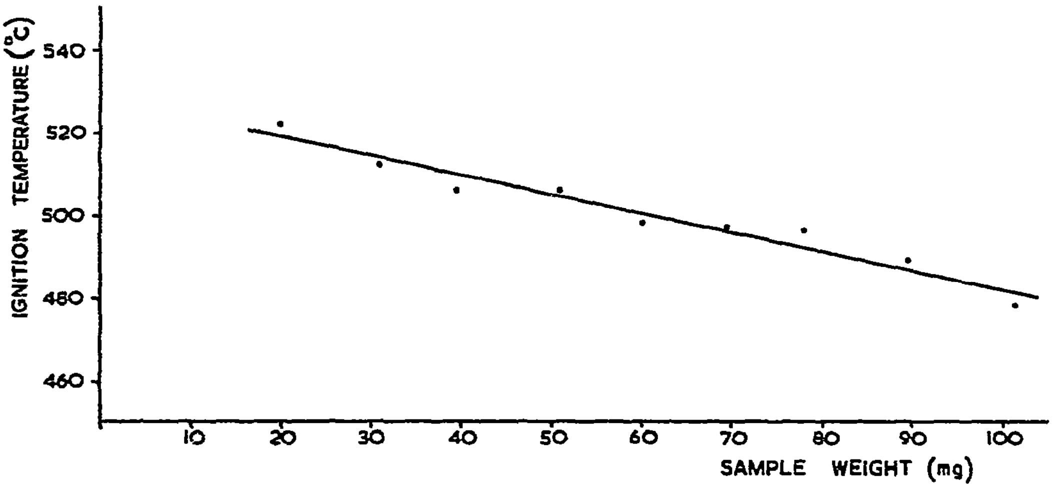

Fig 5. Plot of ignition temperature vs sample weight for a boron–silicon–potassium nitrate composition

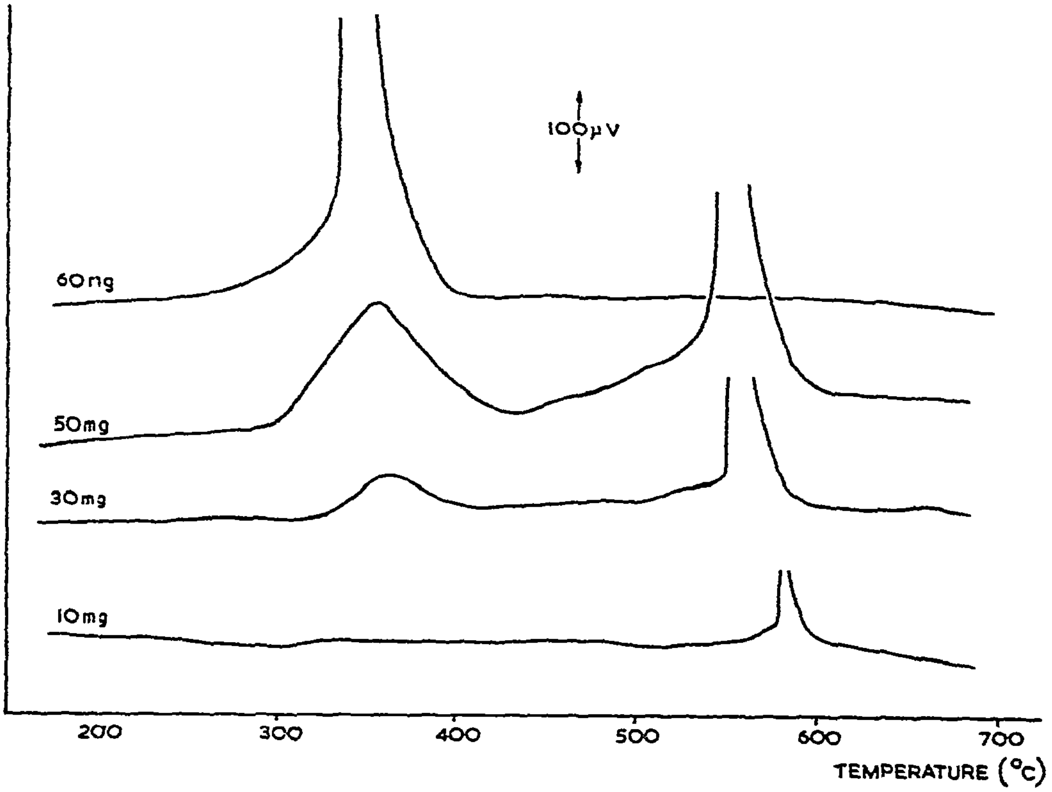

Fig 6 DTA curves for different sample weights of a magnesium-barium peroxide-acaroid resin composition

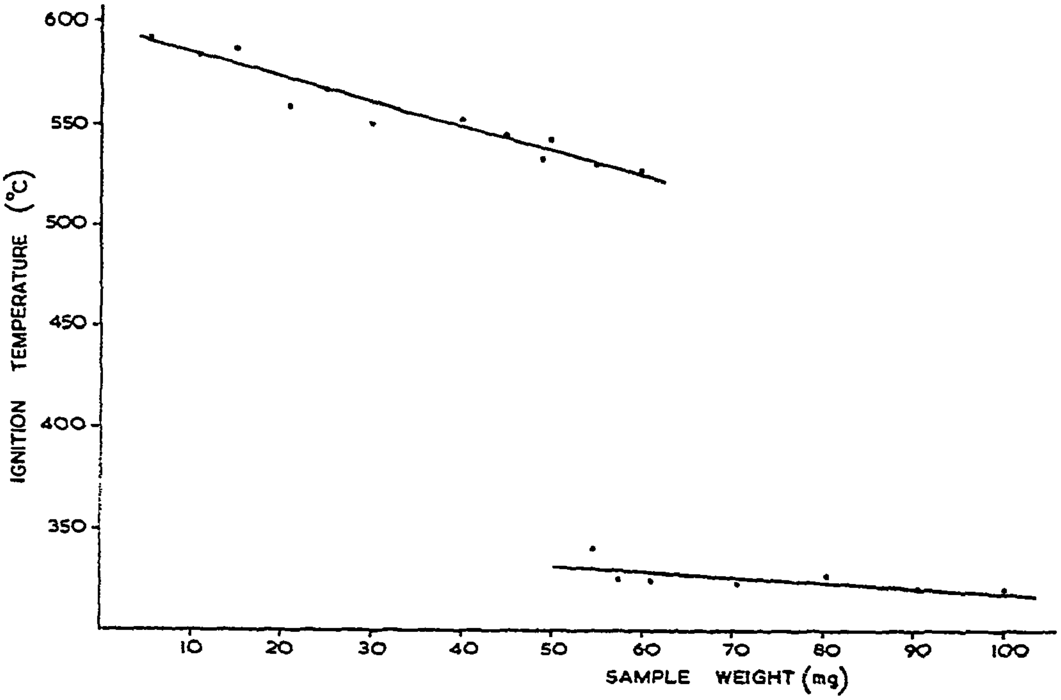

Fig 7. Plot of ignition temperature vs sample weight for a magnesium-barium peroxide-acaroid resin composition

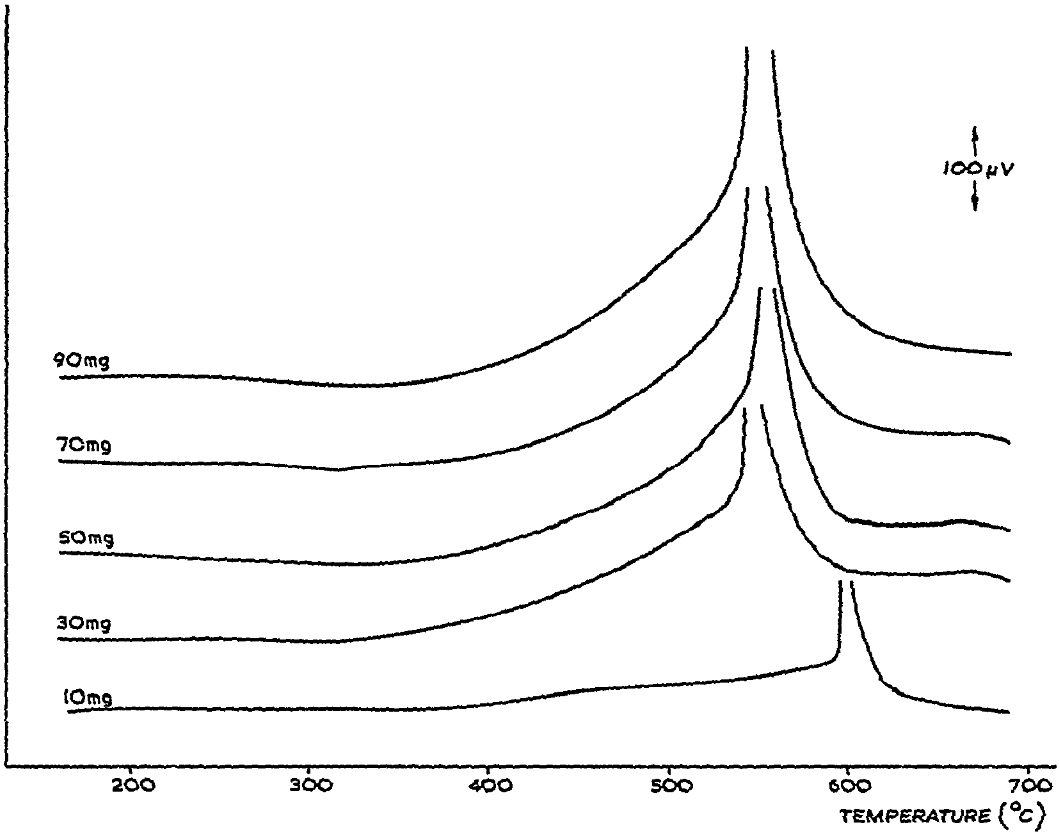

Fig 8 DTA curves for different weights of a binary magnesium–barium peroxide composition Heating rate, 50°C min^{-1} static air

sample weight (Fig. 9) shows that the sample always ignited above 500°C. The results show greater scatter than those obtained when the acaroid resin is present.

Small changes in the binder concentration itself can have a marked effect on the ignition temperature. In the ternary system under discussion, 2% by weight of acaroid resin is present. Table 4 illustrates the effect of varying the binder concentration from 0 to 6% on the ignition temperature of samples weighing 10–100 mg heated at 50°C min^{-1}. It can be seen that with the binary mix and the mix containing 1% resin, ignition will only take place at the second exotherm. As the binder level is increased, for a given sample weight there is a corresponding increase in the magnitude of the first exotherm. The transition from ignition at the higher temperature exotherm to ignition at the lower temperature exotherm will therefore occur at a lower sample weight when there is a higher percentage of resin present. Under the procedure that has now been adopted as standard for comparative ignition DTA studies using a 50 mg sample and heating at 50°C min^{-1}, an increase in the resin concentration from 2 to 3% can lower the ignition temperature by some 200°C.

A number of the compositions studied have also shown a decrease in the ignition temperature with increasing heating rate. In general, a smaller decrease in ignition temperature was observed for a unit change in heating rate than for a unit change in weight. Some of the compositions showed no trend with heating rate, while in the

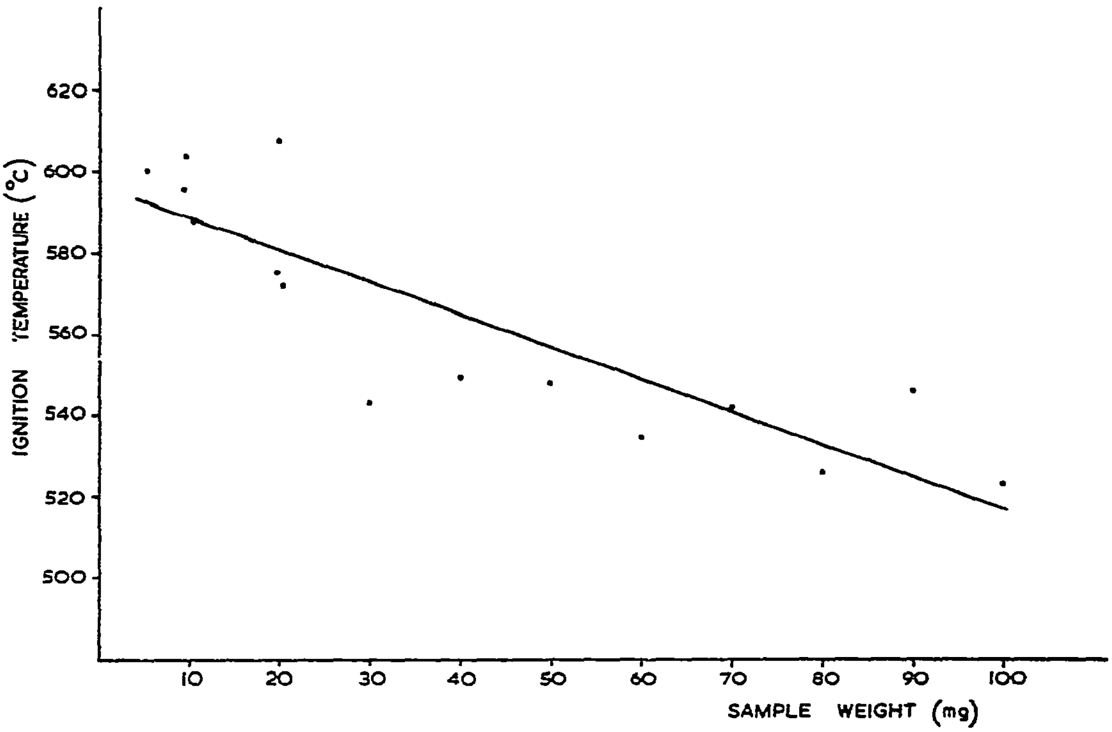

Fig 9 Plot of ignition temperature vs sample weight of a binary magnesium–barium peroxide composition

case of a 50% magnesium–50% strontium nitrate mix, an increase of ignition temperature with heating rate was observed. This implied an induction period in the reaction leading to ignition and this was subsequently confirmed by carrying out

TABLE 4

Ignition temperatures for magnesium–barium peroxide mixes containing from 0 to 6% of acaroid resin

Wt (mg)	Ignition temperature (°C) of mixture containing						
	0%	1%	2%	3%	4%	5%	6%
10	596	584	584	607	578	589	304
20	585	599	558	595	600	609	313
30	543	606	551	603	331	335	335
40	549	607	553	336	317	323	319
50	548	560	543	332	326	321	317
60	535	536	335	300	314	313	312
70	542	559	314	315	317	313	303
80	526	526	317	303	304	308	311
90	546	522	311	309	307	308	311
100	523	523	310	305	296	306	300

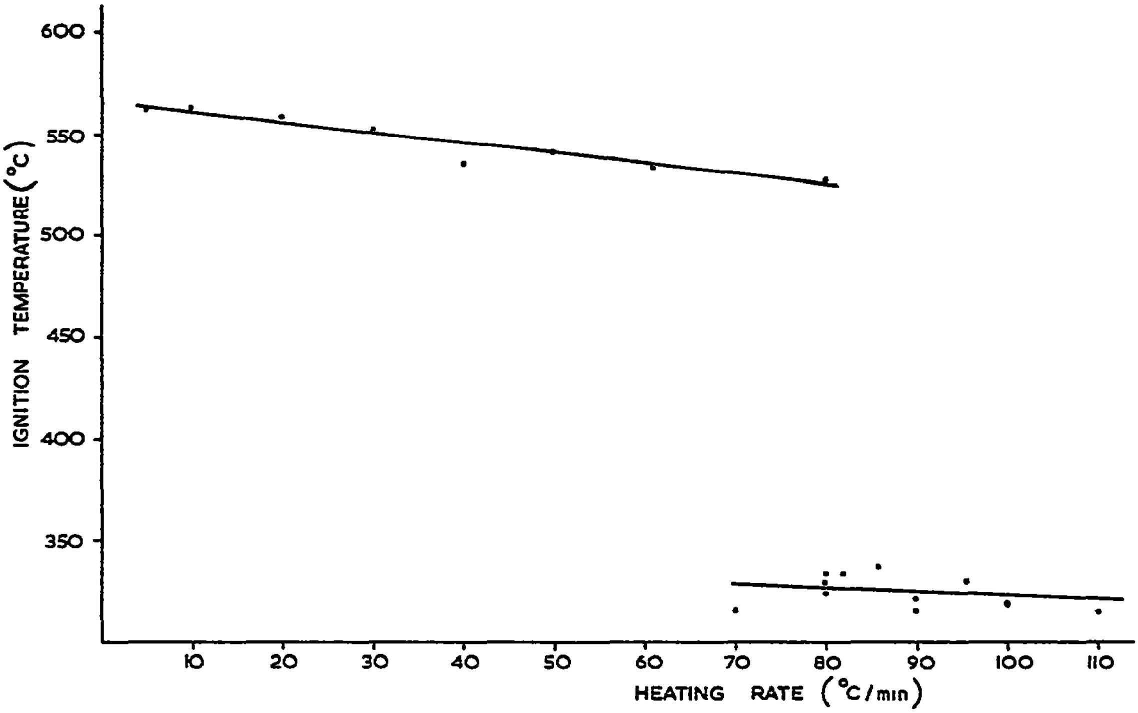

Fig 10 Plot of ignition temperature vs heating rate for 50 mg samples of a magnesium–barium peroxide–acaroid resin composition

isothermal time-to-ignition experiments. In the case of magnesium–barium peroxide–2% acaroid resin mix, it was found possible to obtain ignition at the first exothermic reaction by increasing the heating rate above 60°C min^{-1} using 50 mg samples. This is illustrated in Fig. 10.

As mentioned in the introduction, in some systems ignition may result in the ejection of large amounts of material from the crucible and this can lead to difficulties in determining the point of ignition from the temperature trace. To overcome these difficulties, a photocell detection system has been developed which on detecting the light emitted on ignition, will operate a relay to freeze the digital display at the ignition temperature [6].

CONCLUSIONS

The apparatus described has proved to be capable of determining reproducibly the ignition temperature of a large number of samples of pyrotechnic mixes without the need for frequent repair or recalibration. It has also been found to be sufficiently stable and sensitive at the high heating rates used to enable pre-ignition reactions to be studied.

The wide range of pyrotechnic compositions evaluated have all shown an approximately linear decrease in ignition temperature with increasing sample weight, ranging from 0.16 to 0.91°C mg^{-1}. The effect of heating rate is less simply described and depends on the system being studied. In one case, an increase in the ignition temperature with increasing heating rate was observed and attributed to an induction period in the pre-ignition reaction.

With some compositions, increasing the sample weight above a certain level caused a dramatic decrease in the ignition temperature. Ignition was then found to take place at a lower-temperature exothermic reaction. It was also possible to observe this effect by using faster heating rates. From the viewpoint of safety testing, any low temperature reaction should be viewed as a possible ignition hazard.

Small variations in the amount of an organic binder present in a pyrotechnic composition have also been shown to produce marked changes in the ignition temperature Thus, for the system studied, namely magnesium–barium peroxide–acaroid resin, an increase of the order of 1% in the resin content was found to reduce the ignition temperature by some 200°C.

ACKNOWLEDGEMENTS

The authors wish to thank M. Newman (Stanton Redcroft) for technical assistance. This work has been carried out with the support of the Procurement Executive, Ministry of Defence.

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