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DIFFERENTIAL THERMAL ANALYSIS OF PRIMARY EXPLOSIVES

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ABSTRACT

A description is given of modifications which have been made to the remote cell used in conjunction with a DuPont 900 DTA such that the possibility of explosion is minimized. Using lead azide to evaluate the technique it is shown that complete curves for the exothermic decomposition

$$PbN_6 \rightarrow Pb+3N_2$$

are reproducibly obtained. The endotherm in the curve corresponding to the fusion of the product lead serves as a confirmation of the reaction. Illustrations are given to show extensions of the system to other sensitive compounds, namely lead styphnate, mercury fulminate, and potassium dinitrobenzfuroxan.

INTRODUCTION

The application of thermal analysis to decomposition studies of very sensitive materials, such as primary explosives, has been hindered by the possibility of explosions of samples within the apparatus. Although specimens can be sufficiently small to ensure little risk of instrument damage this is an undesirable situation since the amount of significant data which can be extracted from such a curve is minimal.

Krien[1] investigated the application of combined differential thermal analysis and thermogravimetry (DTA–TG) to the decomposition of explosives. Problems associated with this TG apparatus restricted him to slow heating rates (5 °C/min or less) and as a consequence the DTA peaks obtained were spread out.

In more recent work PaiVerneker and Maycock[2,3] described the application of simultaneous DTA–TG to lead azide. They were able to observe thermal decomposition which they attributed to the reaction

$$PbN_6 \rightarrow Pb+3N_2 \tag{1}$$

Since the DTA and TG traces are recorded from the same sample it is correct to assume that analysis obtained for the TG will also be incorporated in the DTA

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results. The nitrogen content of lead azide is 28.8%; therefore it would be expected that if this reaction were to take place the weight loss recorded by thermogravimetry would be 28.8%. The curves which they obtained show very slow thermal decomposition over a wide temperature range with loses of 21.9–27.5%. Thus the decrease in weight found experimentally could indicate that the products of reaction consist of a mixture of metallic lead and its oxide. If this is so, then the results can be more adequately explained from a consideration of reactions of the type

$$PbN_6 \xrightarrow{\text{trace } O_2} PbO + 3N_2 \qquad (2)$$

or formation of higher oxides of lead depending on oxygen concentration. The weight losses predicted for reactions of this type would be 23.4% for the formation of PbO or less for a mixture of PbO plus higher oxides of lead. The experience of the present investigators has been that such slow reactions invariably yield oxide mixtures, or, at best, metal plus oxide mixtures. It is more tenable to propose that the decomposition which was reported was not the formation of metal plus gaseous nitrogen but decomposition in the presence of trace amounts of oxygen to yield an ill defined product consisting of a variable mixture of metal plus oxides with no assurance that the same reaction path will be followed in any two experiments.

Lead azide is of interest because of its wide use. A study of the decomposition reaction (Eqn. 1) is most suitable since it is known to occur in the detonation process[4] yielding basic lead and nitrogen and therefore can be easily characterized using DTA techniques. Thus, it was considered ideal to use this reaction for the evaluation of the modified cell.

EXPERIMENTAL

Remote cell modifications

A typical remote cell as currently supplied by E.I. DuPont (Fig. 1) differs from earlier models in that the heating block has been raised and is separated from the thermocouple connections by a large insulating disk of pressed asbestos. Experience with earlier designs of the cell had shown that it is imperative to protect these connections from exposure to stray thermal currents. The need to protect samples from the slightest oxidizing environment necessitated the cell being evacuated to 10^{-6} torr. This required removal of the porous disk and redesign of the support. It was also necessary to seal the electrical connectors, relocate the gas inlets, and modify the base plate and locking clamps.

The modified cell is shown in Figs. 2 and 3, where Fig. 2 shows an overall view and Fig. 3 gives the dimensions. It was necessary to reconstruct the original cell starting with a new base having four holes to accomodate vacuum tight cartridge bushings, supplied by Glass Tite Industries [A-2622], which were in turn soldered into the base. The pins from the original plug were soldered into the new cartridges to adapt them to the existing thermocouple and heater connections. The new heating block holder and support consisted of a single unit fabricated from heavy walled

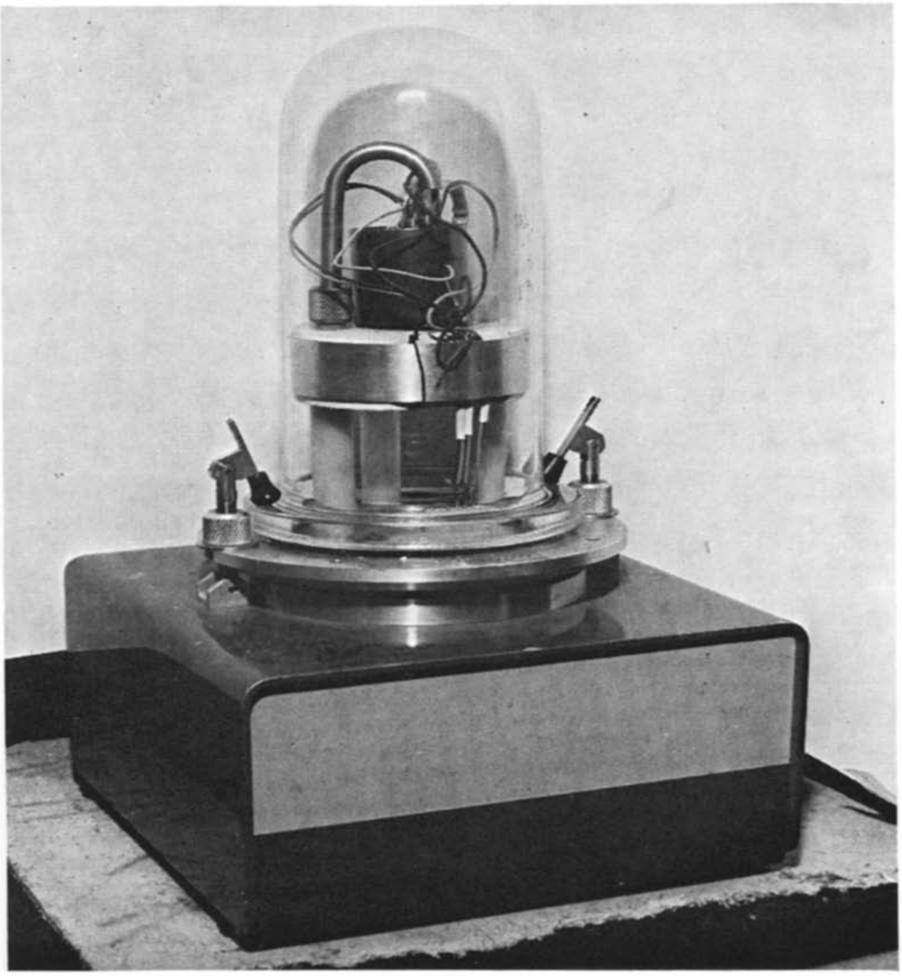

Fig. 1. Remote cell as supplied by E. I. DuPont.

glass and silver coated to minimize thermal losses. The thermocouple connections were further protected from the development of thermal gradients by shielding with glass tubing. Evacuation and gas flow was effected through two pressure-vacuum stopcocks attached to the top of the pyrex dome. The pyrex dome was made vacuum tight by fastening it to the base with a ring seal and metal ring clamp.

DTA procedures

Samples investigated were in the form of fine crystalline powders. Glass beads were used as reference materials and in the tube containing the heater control thermocouple. Standard heating blocks of silver or aluminum were used with specimens contained in either 2-mm or 4-mm capillary tubes. With 2-mm tubes the sample weight was approximately 0.5 mg, in 4-mm tubes a maximum of 2.5 mg was used; however, the weight could be increased to 5 mg if the sample were diluted with an equal volume of glass beads[5]. In all cases samples were compacted by mild tapping.

Fig. 2. Modified remote cell.

The cell was evacuated to 10^{-6} torr for several minutes before backfilling and purging with dried helium gas. A flow rate of 400 ml/min was maintained throughout the experiment. Standard chromel-alumel thermocouples were employed. Heating rates up to 10°C/min and maximum differential temperature sensitivity, 0.1°C/in. could be used.

Fischer Scientific "Thermetic" standards and high purity lead (99.999%) supplied by Electronic Space Products, Inc. were selected for instrument calibration. Lead azide of high purity was prepared by reaction of lead nitrite with hydrozoic acid[6]. Other explosive samples were of commercial or military production grade stock.

RESULTS AND DISCUSSIONS

The instrument was calibrated through the lead azide temperature range using m.p. standards and was in agreement with the old cell. The results of pure lead melting at 318 C under the high helium flow rate is shown in Fig. 4a. The lead fusion peak is indicated as an exotherm at 318 C in Fig. 4b when lead is placed in the reference tube and analyzed simultaneously with lead azide in the sample tube. The differences in the peak sizes of the product lead from that of the added lead is due to differences in amount.

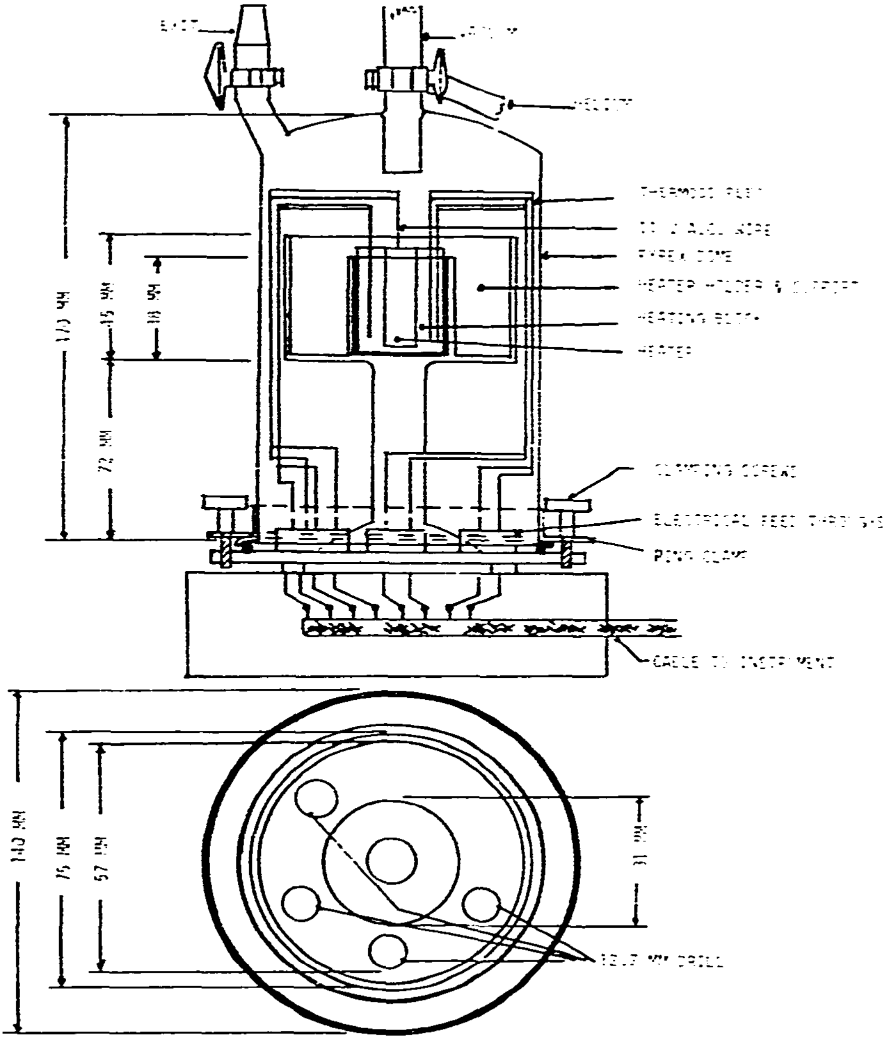

Fig. 3. Schematic diagram of components in the modified remote DTA cell.

DTA curves for lead azide obtained prior to cell modifications are shown in Fig. 5. Two unacceptable curves, sample detonation (Fig. 5a) and sample oxidation (Fig. 5b) are shown.

The presence of trace amounts of oxygen causes non-reproducible distortion of the decomposition exotherm. Depending on the oxygen concentration this distortion can range from gross deformation and extended tailing of the peak to a reduction in peak area in the presence of extremely minute traces of oxygen. When lead azide specimens were placed in the modified cell at varying vacuum pressures before backfilling and purging with helium it was found that the exotherm trace configuration was a function of pressure becoming constant at 10^{-6} torr. Although the peak height and shape is affected, this treatment did not influence either the onset or peak temperature except in cases of gross deformation of the trace. It is readily apparant that very little information other than onset temperature can be extracted from those curves in which high order detonation or sample oxidation occured.

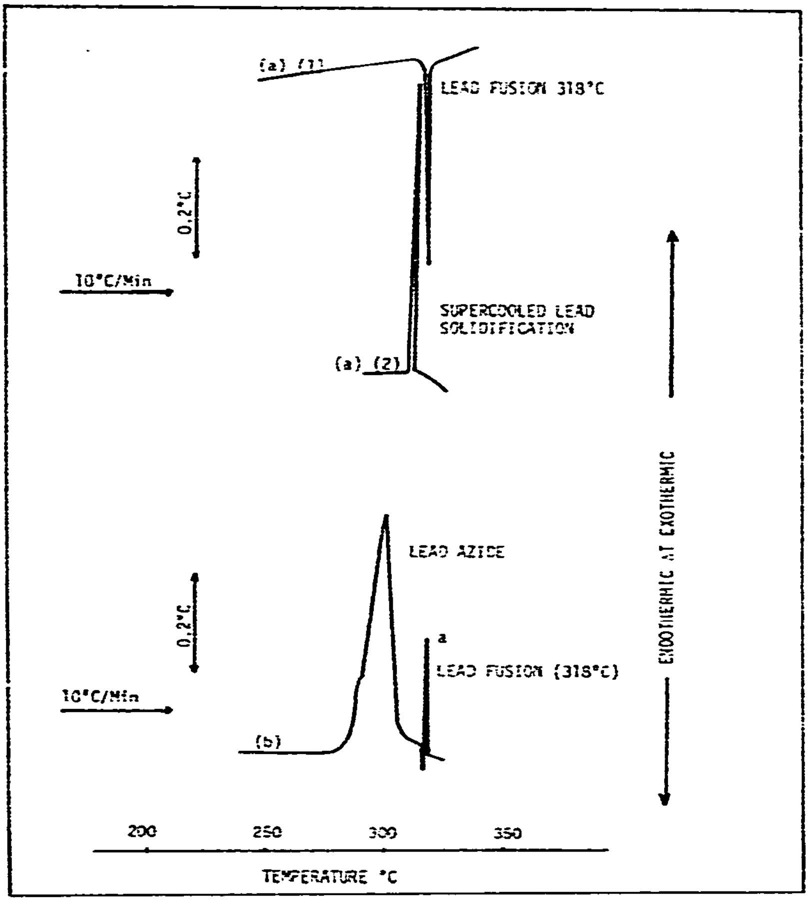

Fig. 4. DTA curves showing the position of the lead m.p. (a) (1), lead fusion; (a) (2), supercooled solidification of lead (cooling curve). (b), lead metal in reference tube + PbN_6 in sample tube.

Fig. 6 shows decomposition of high purity lead azide to metallic lead as obtained in the modified system. Features of importance are the decomposition exotherm in the region 287–302 °C and the lead fusion endotherm at 318 °C. Subsequent cooling of the sample gives the exothermic solidification of lead supercooled to 315 °C. The products of reaction (Eqn. 1) are confirmed by the lead fusion. The extent to which the fusion point is displaced at a constant heating rate depends on the amount of azide used.

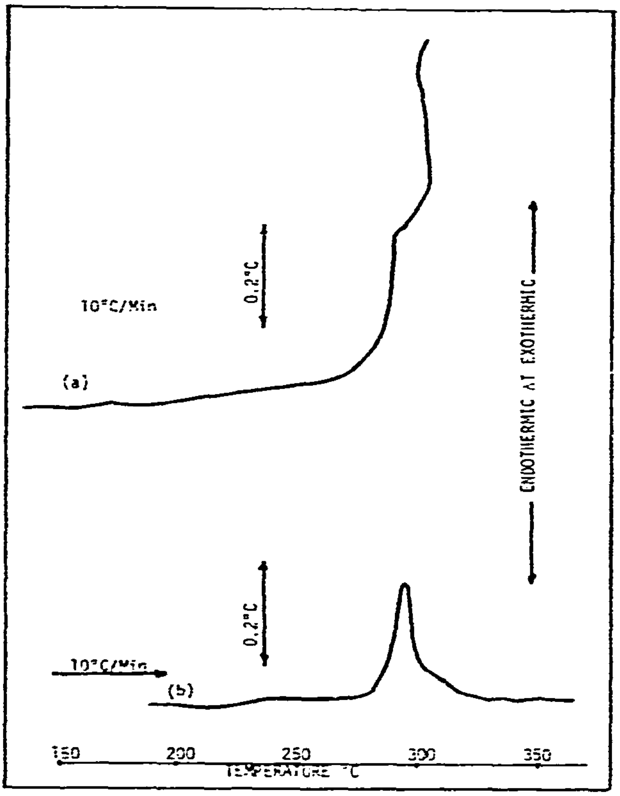

Fig. 5. DTA curves for lead azide. (a), sample detonated. (b), sample decomposed in the presence of trace amounts of oxygen.

TABLE I

RESULTS OF THERMAL DECOMPOSITION OF LEAD AZIDE UNDER VARIOUS EXPERIMENTAL CONDITIONS

$T_{(onset)}$ (°C)	$T_{(max)}$ (°C)	*Lead m.p. (°C)*	*Sample weight (mg)*	*ΔT (°C/in)*	*Glass beads*	*Size of capillary tube (mm)*
287	305	317	2.4	0.5	No	4
289	305	316	2.6	0.5	No	4
288	305	320	1.1	0.2	No	4
293	305	320	1.0	0.2	No	4
294	306	321	0.8	0.2	No	4
290	304	320	0.5	0.2	No	4
288	304	320	0.4	0.2	No	2
290	304	316	0.4	0.2	No	2
287	302	316	0.5	0.2	No	2
290	303	320	0.3	0.2	No	2
287	302	320	0.3	0.1	No	2
288	300	316	3.0	0.5	Yes	2

Using varying quantities of lead azide to check out the cell the average deviation of the lead fusion was ±1.9 °C at 318 °C. This could be significantly reduced by use of a constant mass of sample. Similarly values of the decomposition onset and apex temperatures could be obtained with greater accuracy if all experimental parameters were held constant during a set of experiments. It would also be desirable to sieve samples for constant particle size but with sensitive materials such as lead azide; this proves to be extremely time consuming. The onset and peak temperatures are used for trace description. These values are given in Table I and were obtained from experimental curves using various instrument settings and sample size. This data gave an average $T_{(\text{onset})}$ 287 °C with a deviation of ±1.0% and an average $T_{(\text{max})}$ 302 °C with a deviation of ±0.8%.

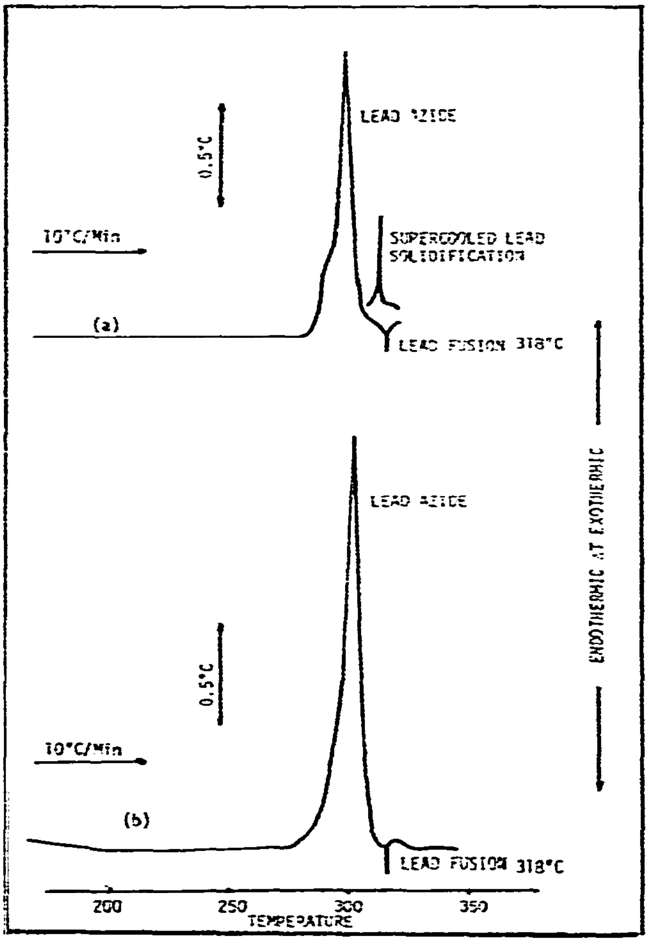

Fig. 6. DTA curves for lead azide using modified remote cell. (a), 2.6 mg lead azide. (b), 3.1 mg lead azide diluted with glass beads.

It can be seen from the table that considerable flexibility in choice of instrument settings and sample configuration is possible. It was found essential to provide for efficient conduction of heat away from the sample area since the reaction is highly exothermic and can result in detonation. Helium was employed as the preferred carrier gas. When the sample size was increased to the point where helium gas alone was not sufficient, dilution of the sample with glass beads, commonly used for reference material, provided a heat sink. This use of glass dilution affects peak magnitude but not position as shown in Figs. 6a and b.

The new cell and the experimental procedure were evaluated further using doped lead azide samples and other primary explosives. From another study[7] it is known that lead azide prepared in the presence of various dopants has related defect structure. Fig. 7 shows curves for a series of lead azide samples doped with ferric halide salts.

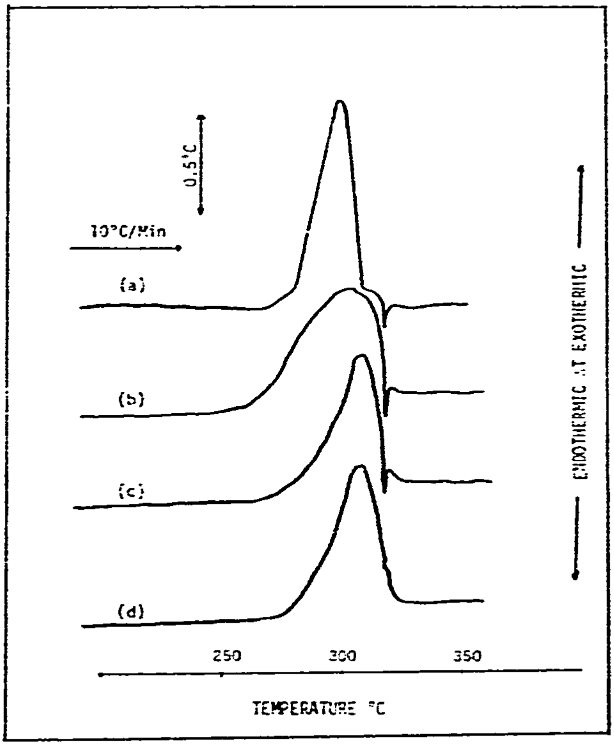

Fig. 7. DTA curves for iron-doped lead azide. (a), $PbN_6 + FeI_3$. (b), $PbN_6 + FeBr_3$. (c), $PbN_6 + FeCl_3$. (d), $PbN_6 + FeF_3$.

Work is in progress to interpret these results in terms of observed electron spin resonance phenomena. In general, initiating compounds were difficult to analyze without the modification of the remote cell. Fig. 8 shows some results of the extension of the method to several other meta-stable compounds. In all instances complete curves are obtained and it appears that the method can be successfully applied to other sensitive materials.

Effort is currently being directed to modifying the accessory DuPont 950 T.G. apparatus to enable equivalent thermogravimetric data to be obtained.

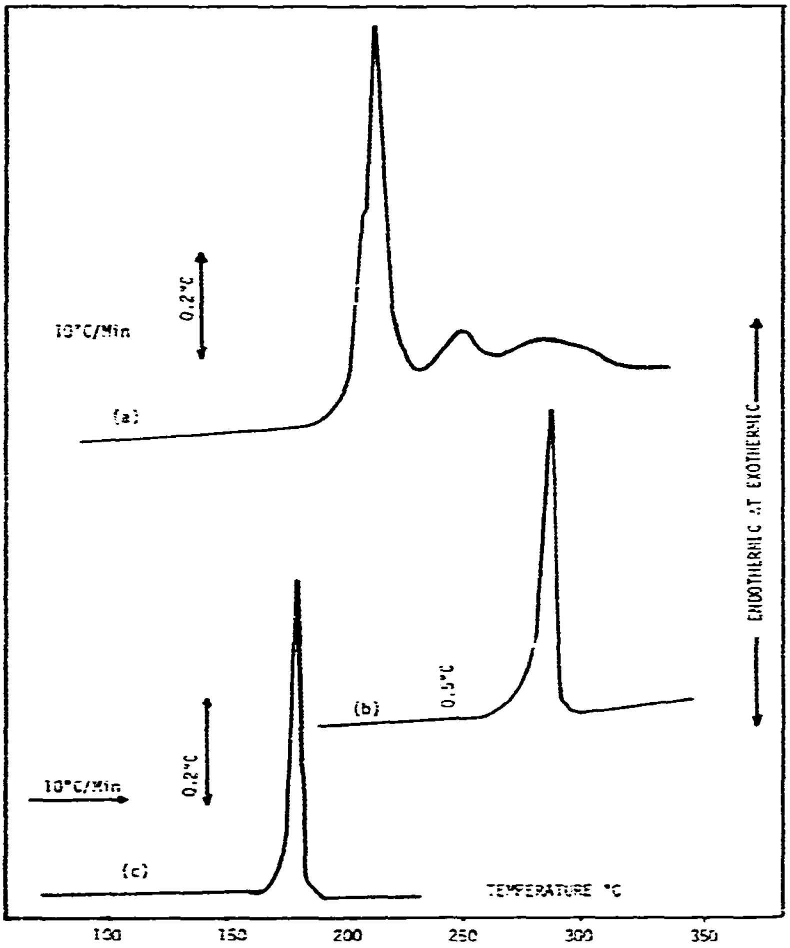

Fig. 8. DTA curves for other primary explosives. (a), potassium dinitrobenzfuroxan (KDNBF). (b), lead styphnate. (c), mercury fulminate.

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