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The thermal behaviour of porous residual ammonium perchlorate

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Abstract

Differential scanning calorimetry (DSC), thermogravimetry (TG) and differential thermogravimetry (DTG) measurements show that the thermal decomposition temperature of porous residual ammonium perchlorate is up to 50 °C lower than that of normal ammonium perchlorate. Their thermograms are different in appearance, but the same heat is released. The first weight-loss stage of the decomposition of residual ammonium perchlorate on the DTG curve occurs about 40 °C below that of normal ammonium perchlorate. A catalytic effect was observed in the decomposition of pure normal ammonium perchlorate when mixed with residual ammonium perchlorate.

INTRODUCTION

The thermal decomposition of ammonium perchlorate (AP) has been studied by many investigators [1]. Bircumshaw and Newman [2] found that the decomposition of ammonium perchlorate in vacuuo at 220–280 °C was typical of many solid decompositions in that it spread throughout the crystals from surface nuclei yielding gaseous products. The decomposition left a residue which was still almost pure ammonium perchlorate and amounted to about 70% by weight [2,3]. This is the so-called low-temperature decomposition reaction. Klager et al. [4] named the residue PAP (porous ammonium perchlorate). At temperatures above 350 °C, the high-temperature decomposition reaction occurs. It was also found that the residual ammonium perchlorate obtained from the low-temperature decomposition did not decompose further at the assigned decomposition temperature; however, when it was exposed to water vapour the ammonium perchlorate rejuvenated and when re-heated, started to decompose again. The rejuvenation could also be accomplished by exposure to the vapours of those solvents in which ammonium perchlorate is soluble [2,5]. There is no further information concerning the thermal properties of residual porous ammonium perchlorate.

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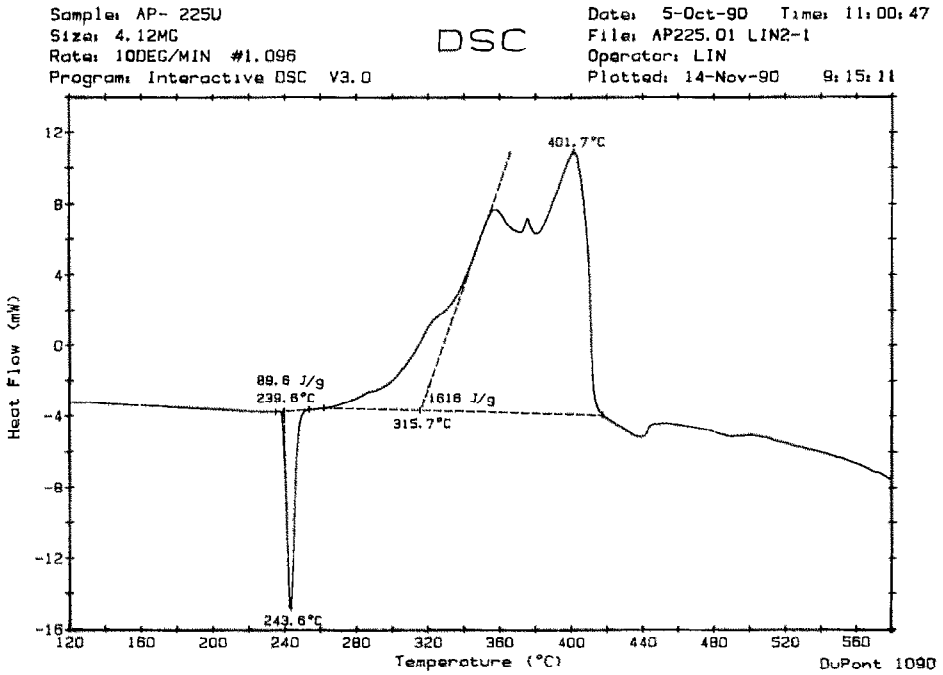

Fig. 1. DSC curve of ammonium perchlorate of particle size 225 μm.

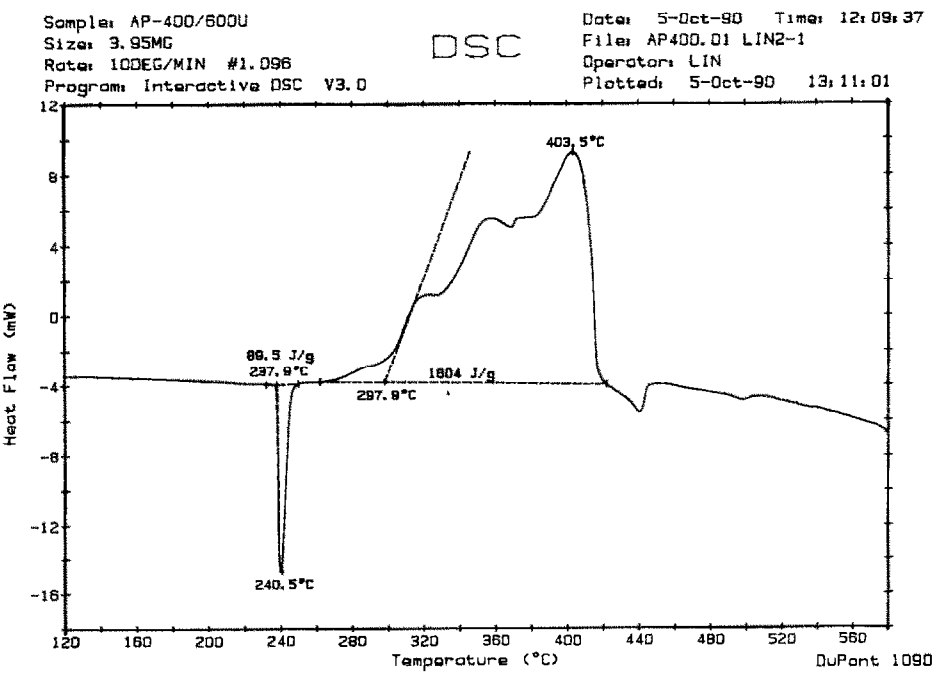

Fig. 2. DSC curve of ammonium perchlorate of particle size 400–600 μm.

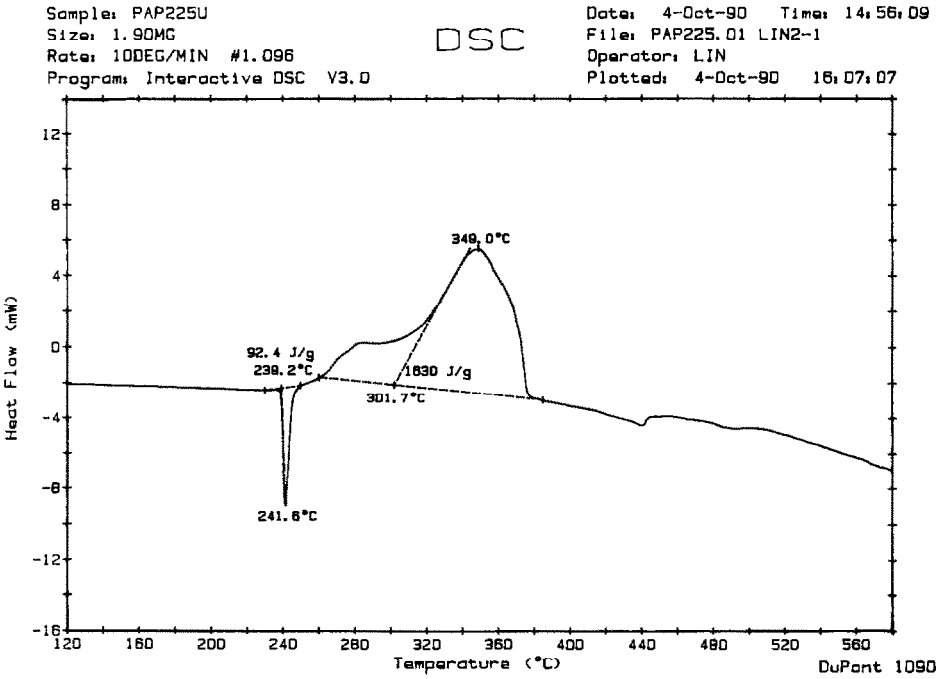

Fig. 3. DSC curve of porous residual ammonium perchlorate of particle size 225 μm.

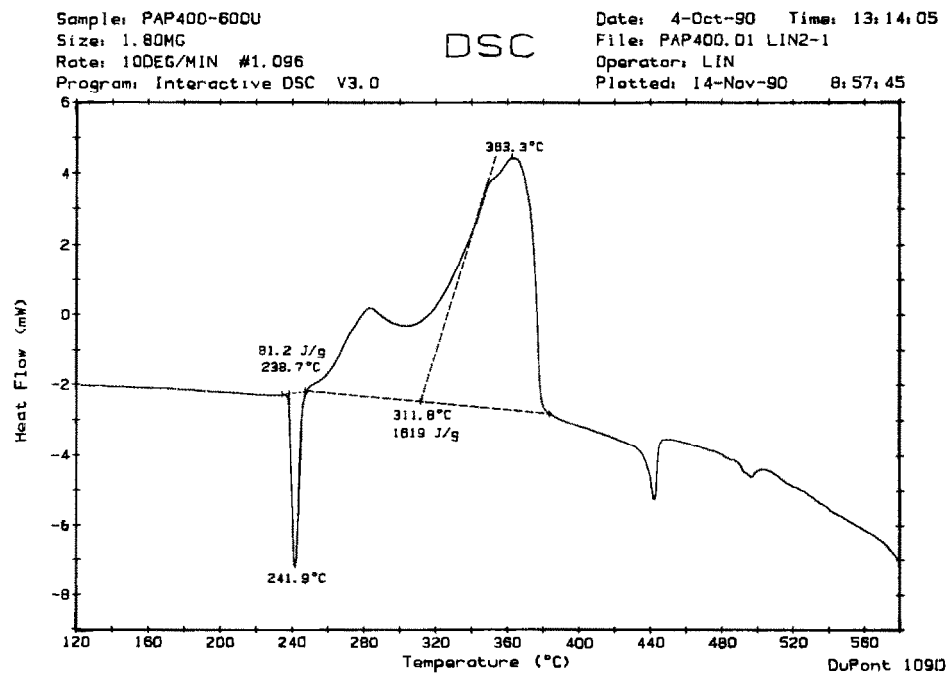

Fig. 4. DSC curve of porous residual ammonium perchlorate of particle size 400–600 μm.

In most solid composite propellants, ammonium perchlorate is employed as an oxidiser. Many investigators have tried various ways of increasing the burning rate of solid composite propellants. Of these, porous ammonium perchlorate has proved to be effective in yielding a high burning rate when it was partially substituted for the ammonium perchlorate in the propellant [4,6–8]. The burning rate of the propellant increased up to 130% when 20% PAP was substituted for the same amount of AP [7]. The role of the residual ammonium perchlorate in the burning of the propellant is unclear although researchers have proposed some explanations. Klager et al. [4] believe that the increase in propellant burning rate is attributable to the surface properties and void mechanism of porous ammonium perchlorate. The thermal properties of the residual ammonium perchlorate must be understood in detail in order to interpret its role in solid propellants.

In this paper, differential scanning calorimetry (DSC), thermogravimetry (TG) and differential thermogravimetry (DTG) measurements are employed to study the thermal behaviour of the above-mentioned residual porous ammonium perchlorate and the results are compared to those of ammonium perchlorate.

EXPERIMENTAL

Sample preparation

Ammonium perchlorate of propellant grade was obtained from Carlit Co., Japan (JCC). Three particle sizes (400–600, 225 and 50 μm) were used in this study.

Porous residual ammonium perchlorate was manufactured according to the fluidisation process developed by Leu and co-workers [6,8,9]. In this process, the thermal decomposition of ammonium perchlorate takes place in a fluidised bed reactor at 230 °C for 120 min until there is no further discernible decomposition reaction. The products are then transferred to a vacuum oven and degassed in vacuuo for 7 days and stored under a nitrogen atmosphere at room temperature. In this study, the porous residual ammonium perchlorate used had two particle sizes (400–600 and 225 μm) and the AP had three particle sizes as mentioned above.

DSC, TG and DTG measurements

The DSC, TG and DTG measurements were performed on a Du Pont 1090 thermal analyser. For the DSC measurement, samples weighing about 2–4 mg were placed in an aluminium sample cell and covered with an aluminium cap using a crimping press. For the TG and DTG measurements, samples weighing about 4 mg were used. All the DSC, TG and DTG

measurements were recorded under nitrogen flowing at 80 ml min^{-1} using a heating rate of 10 °C min^{-1}.

RESULTS AND DISCUSSION

The DSC results for porous residual AP and normal AP are shown in Figs. 1–5. In the DSC thermograms, the heat flow is expressed in mW. Figures 1 and 2 show the DSC curves for normal ammonium perchlorate with particle sizes of 225 and 400–600 μm, respectively. Figures 3 and 4 show the DSC curves for porous residual ammonium perchlorate with particle sizes of 225 and 400–600 μm, respectively. From these figures, it is obvious that different thermal decomposition mechanisms are observed for porous residual AP and normal AP.

DSC results (Figs. 1–5 and 9) show an endothermic valley at around 240 °C in both the porous residual AP and normal AP thermograms; this has been assigned to the transformation of the crystal structure from orthorhombic to cubic [10]: this shows that the porous residual AP and the normal AP in this study have the same crystal structure. From Figs. 3 and 4, it can be seen that the thermal decomposition of porous residual ammonium perchlorate takes place immediately after the crystal transformation and that it is completely decomposed at about 350 °C, which is about 50 °C lower

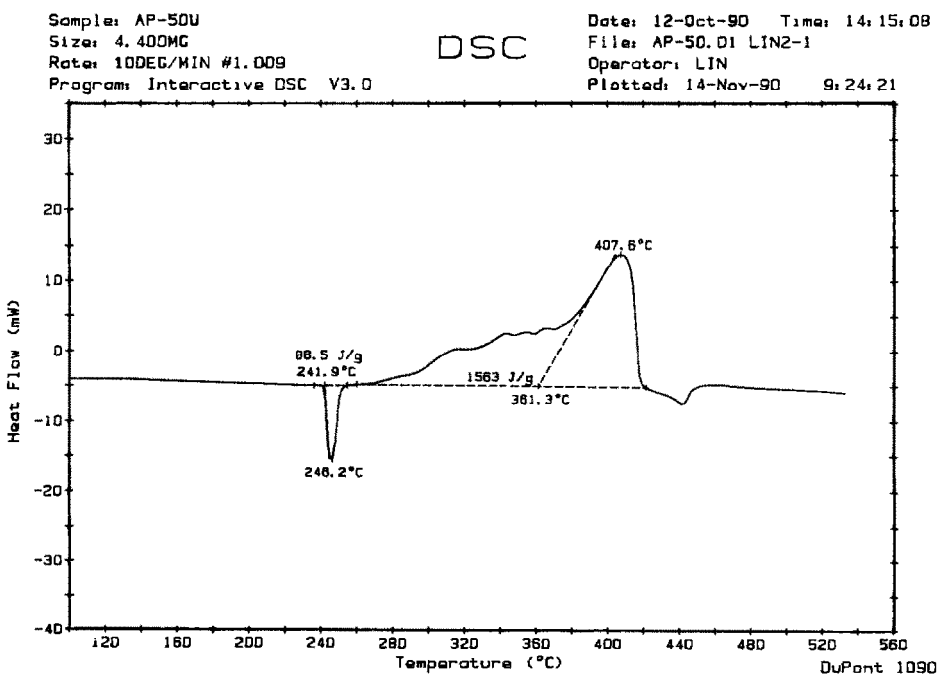

Fig. 5. DSC curve of ammonium perchlorate of particle size 50 μm.

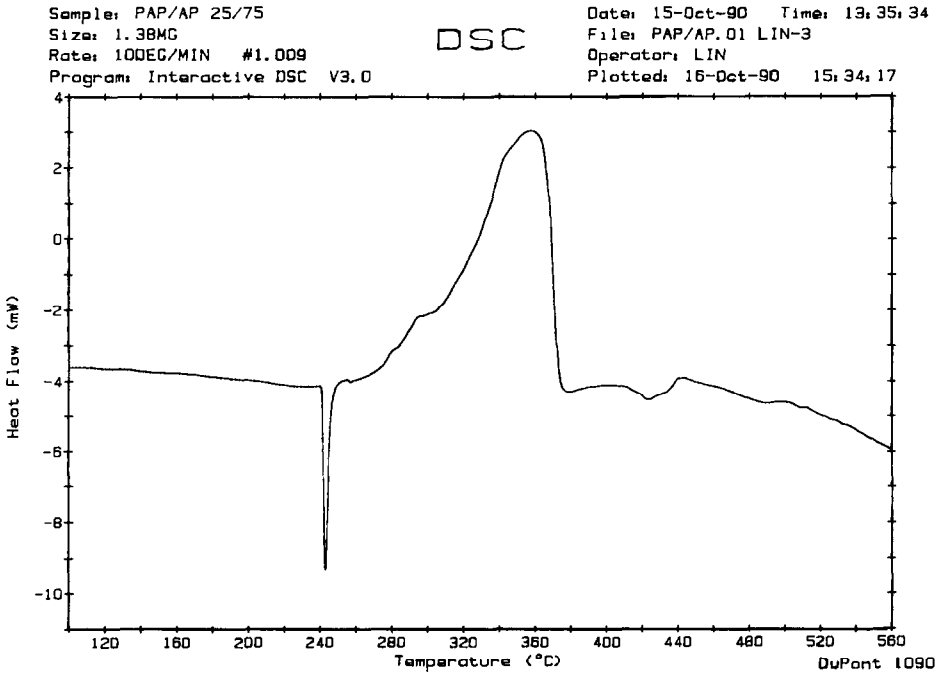

Fig. 6. DSC curve of a mixture of ammonium perchlorate and porous residual ammonium perchlorate in the ratio of 75/25 wt.%.

than for normal AP. In addition, the decomposition time of porous residual ammonium perchlorate is about 20% shorter than that of normal AP. The decompositions of both porous residual AP and normal AP release almost the same amount of heat but with different thermograms; this means that different mechanisms are occurring, possibly with the same final products being obtained. An earlier report stated that the high-temperature decomposition occurs at temperatures in excess of 350 °C. For residual AP, the decomposition is complete at about 350 °C. Thus the earlier report would imply that there is no high-temperature decomposition for residual ammonium perchlorate.

The effects of a wide variety of additives on the thermal decomposition of ammonium perchlorate have been studied by many researchers [1,11]. It is well known that the oxides and some other compounds of transition metals catalyse the AP decomposition [11]. The results of this study show that the thermal decomposition behaviour of porous residual ammonium perchlorate is similar to some extent to that of pure ammonium perchlorate under the effect of catalytic additives.

The DSC trace for the ground mixture containing 25 wt.% porous residual AP and 75 wt.% normal AP is shown in Fig. 6: it is almost the same as that of porous residual AP. The presence of residual AP lowers both the decomposition temperature and the decomposition duration of normal AP.

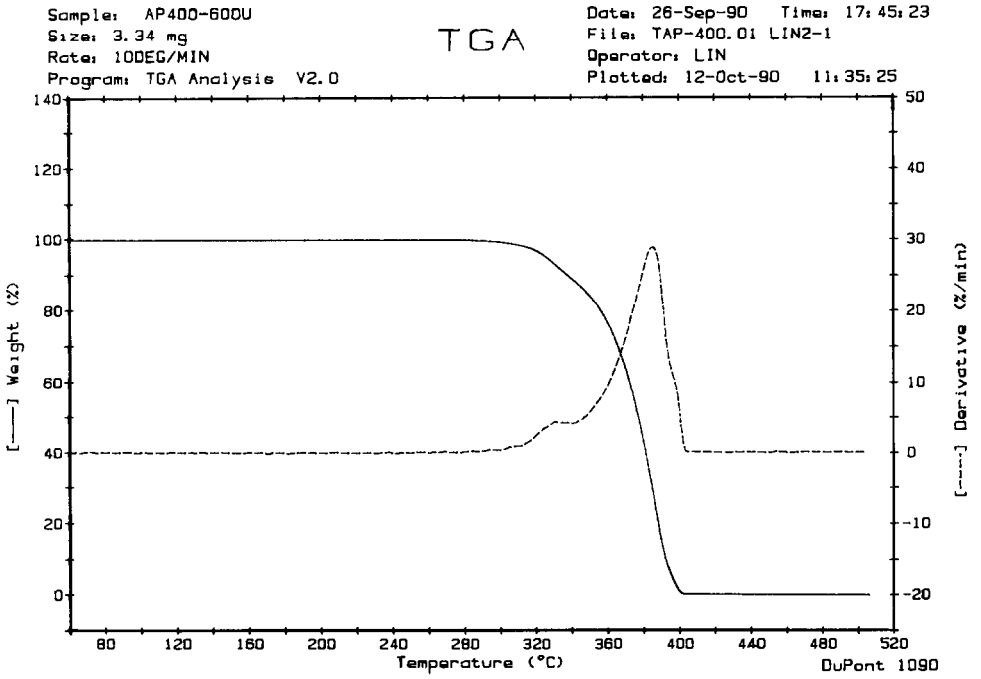

Fig. 7. TG and DTG curves of ammonium perchlorate of particle size 400–600 μm.

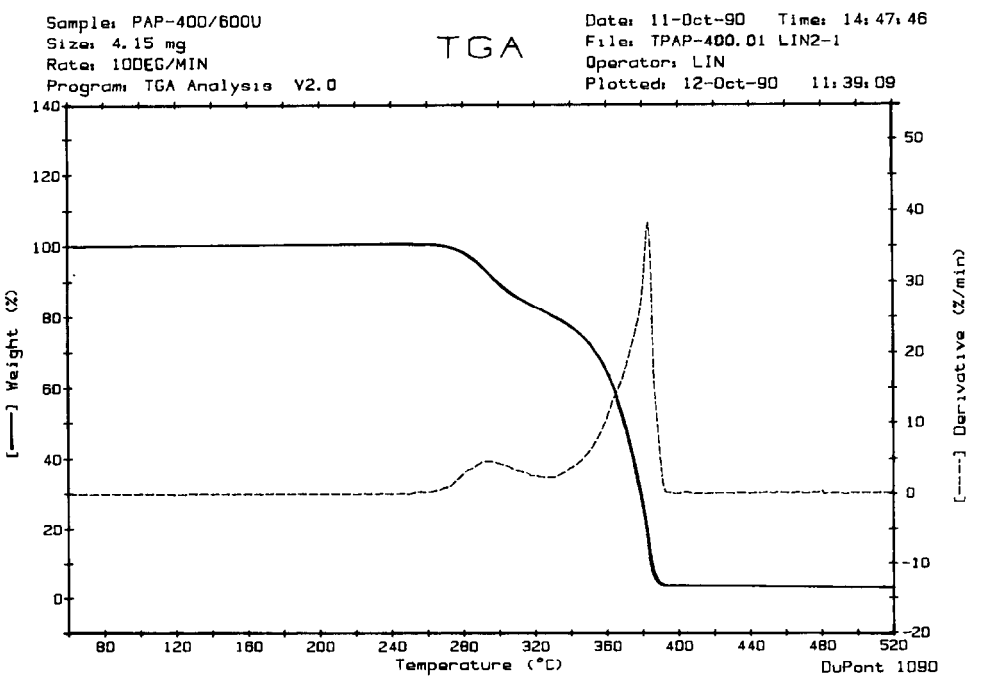

Fig. 8. TG and DTG curves of porous residual ammonium perchlorate of particle size 400–600 μm.

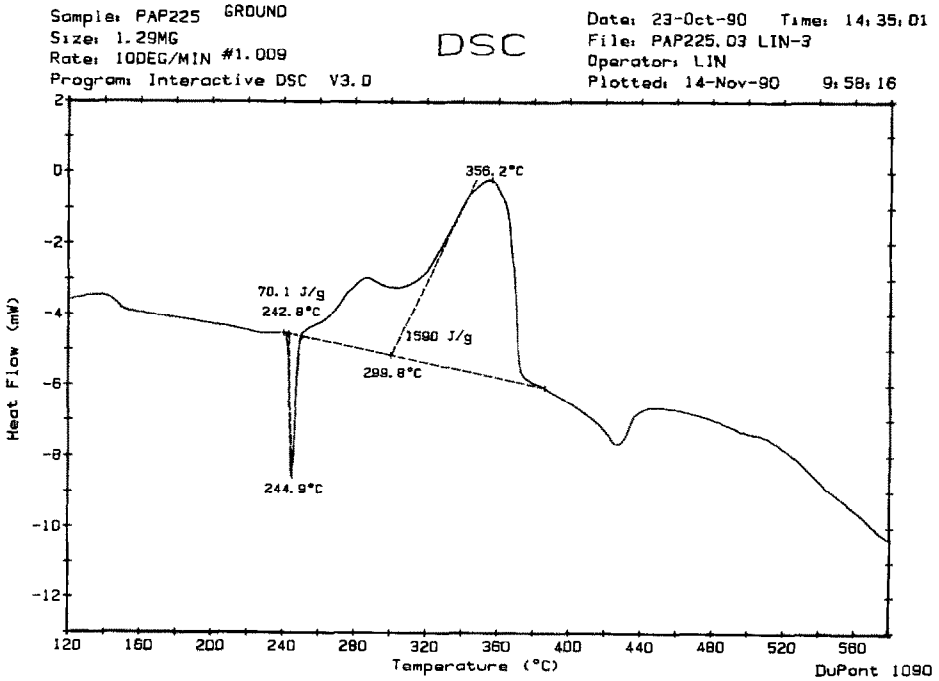

Fig. 9. DSC curve of ground porous residual ammonium perchlorate.

This result proves that the residual AP has catalysed the decomposition of normal AP.

The TG and DTG curves (Figs. 7 and 8) show that the first weight-loss stage for residual ammonium perchlorate occurs about 40 °C lower than that of normal AP, with the same weight-loss rate. The decomposition rate of the second weight-loss stage is much sharper and narrower for residual AP than for normal AP. Both residual AP and normal AP decompose completely.

Figure 9 shows the DSC curve of ground porous residual AP; it is the same as that of porous residual AP, as shown in Figs. 3 and 4. Earlier studies reported that the reactivity could be restored by grinding or by exposure of the residual ammonium perchlorate to solvent vapours [12]. But the results of this study show that there is no effect on the reactivity of the residual AP as a result of grinding.

In this study, the measured surface area for 225 μm normal AP and residual porous AP are 0.0473 and 47.3441 $m^2\ g^{-1}$, respectively; the porosity within the particles leads to a 1000-fold increase in the surface area. Figures 1, 2 and 5 show that the DSC results for normal AP of various particle sizes are the same, even when the surface area was increased about 100 times as a result of the particle size being decreased to about one tenth. This shows that the particle size or surface area of ammonium perchlorate has no effect on the DSC measurement. Therefore, it can be concluded that the difference

in the DSC curves of residual AP and normal AP is not due to the surface area.

CONCLUSIONS

DSC, TG and DTG measurements proved that the decomposition temperature of residual ammonium perchlorate (RAP) is much lower than that of normal AP. A catalytic effect appeared when residual AP was added to pure normal AP. This effect is not due to surface area or crystal structure. It would be interesting to investigate in detail the mechanisms taking place.

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