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Applications of thermal analysis to development of gas generant formulations used to inflate automobile airbags[1]

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Abstract

Differential scanning calorimetry and modulated differential scanning calorimetry were used to understand the decomposition mechanism of a developmental gas generant formulation. A eutectic mixture was formed by two fuels in the formulation. Differential scanning calorimetry data was used to construct a phase diagram. The low melting point of the eutectic mixture explains why the formulation undergoes exothermic decomposition at a lower temperature than expected. Accelerating rate calorimetry was used to determine the temperature at which exothermic decomposition of the formulation occurs. A significant decrease in exotherm onset temperature occurred when fuel from a new supplier was used. This was detected by the accelerating rate calorimeter and the fuel was rejected.

Keywords: TA; Automobile airbag; Gas generant

1. Introduction

Pyrotechnic formulations contain a mixture of fuels, oxidizers, and processing aids, designed to decompose energetically when exposed to a stimulus (usually heat) and produce light, sound, smoke, heat, or gas in the case of inflatable restraint systems. Performance, thermal stability, and manufacturing safety are all critical parameters that must be evaluated and understood prior to continuous production of large scale batches. An un-

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derstanding of the decomposition mechanism of the generant allows the formulation chemist to tailor the composition in order to achieve optimal performance and minimize output of undesirable gases. A common method for production of gas generant is to make an aqueous slurry of the dry ingredients followed by homogenization and drying by one of several methods. The thermal stability of the mixture must be well defined so that the drying stage of the process can be properly designed to assure manufacturing safety. Once produced, the gas generant must be able to survive rigorous heat accelerated aging tests without a loss of performance or mechanical properties.

The objective of this paper is to highlight applications of thermal analysis techniques to the development of a gas generant used to inflate automobile airbags. All of the experiments presented herein were performed on the same formulation. Because of the competitive nature of this business, we cannot publish the identity of the components in the formulation or their concentrations. However, for purposes of discussion the formulation contains two fuels (Fuel A and Fuel B), and a primary and co-oxidizer. Since this paper focuses on the thermal analysis of this formulation, the authors feel that maintaining secrecy of the formulation identity will not detract from the usefulness of the document.

2. Experimental

DSC (TA Instruments Model 2910 DSC) was used to determine the thermal behavior of the formulation. Important information such as melting temperature, and temperature of decomposition can be observed as the extrapolated onset temperature. Five milligrams of sample are normally used. Non-hermetic aluminum sample pans were used. The heating rate used depends on the particular application but when transition temperatures are the measurement of interest, a heat rate of 5°C min^{-1} is used. In all DSC experiments a 99% nitrogen purge at a rate of 60 ml min^{-1} was employed.

Modulated DSC (TA Instruments Model 2910 MDSC) is a thermal analysis technique where an oscillating temperature is superimposed on a linear heat ramp. The data obtained undergoes Fourier transformation to produce a reversible and non-reversible heat flow versus temperature curve. This allows separation of reversible processes (e.g. melts, glass transitions) from irreversible processes such as decomposition reactions. For these experiments, the MDSC was operated at 5°C min^{-1} heat ramp with a temperature oscillation of ±0.5°C and a period of 80 s. A 99% nitrogen purge at a rate of 60 ml min^{-1} was employed. This technique was used to increase our understanding of the decomposition mechanism.

Accelerating rate calorimetry (ARC, Columbia Scientific Industries) is a thermal analysis technique designed to study the behavior of materials in an environment where heat transfer is minimal (e.g. large scale batch processing). Typically, 5 g of material are placed in a spherical titanium bomb. The calorimeter heats the sample up to temperature and then monitors the sample for self heating. If no self heating is detected, the calorimeter heats the sample up to the next programmed temperature (in 5°C increments). When self heating is detected (usually at a self heat rate of >0.01°C min^{-1}), the calorimeter heats up with the sample to maintain the sample in an adiabatic environment as the self heat rate versus temperature is recorded. The ARC data are obtained for a development formulation before any scale up to a production size batch is attempted.

3. Results and discussion

Fig. 1 shows the heat flow versus temperature curve of a lab produced mixture of the gas generant obtained by DSC. The presence of two exotherms indicates that the gas generant decomposes in a two step process. However, the information in Fig. 1 is not sufficient to elucidate the mechanism by which the gas generant decomposes. Figs. 2–5 show the heat flow versus temperature curve for each of the ingredients in the formulation. Fuels A and B (Figs. 2 and 3) have distinct melting points at approximately 199 and 204°C, respectively. These values agree well with those reported in the literature. The co-oxidizer melts at approximately 298°C (Fig. 4) and the oxidizer shows small endothermic transitions between 225 and 275°C (Fig. 5). However, since none of the ingredient transitions are observed in Fig. 1, it is still difficult to determine the mechanism by which the gas generant undergoes exothermic decomposition. Fig. 6 shows the total heat flow and reversible heat flow versus temperature curves of the gas generant obtained by MDSC. The presence of endothermic events in the non-reversing curve that were not visible in the total heat flow curve show what a powerful tool MDSC is for interpretation of complex mechanisms. As the sample is heated, a component melts at approximately 133°C. This event leads to some departure from baseline in the total heat flow curve and initiates exothermic activity. At approximately 200°C, heat is absorbed by the system due to melting of a component and the exothermic reaction is quenched until the melt is com-

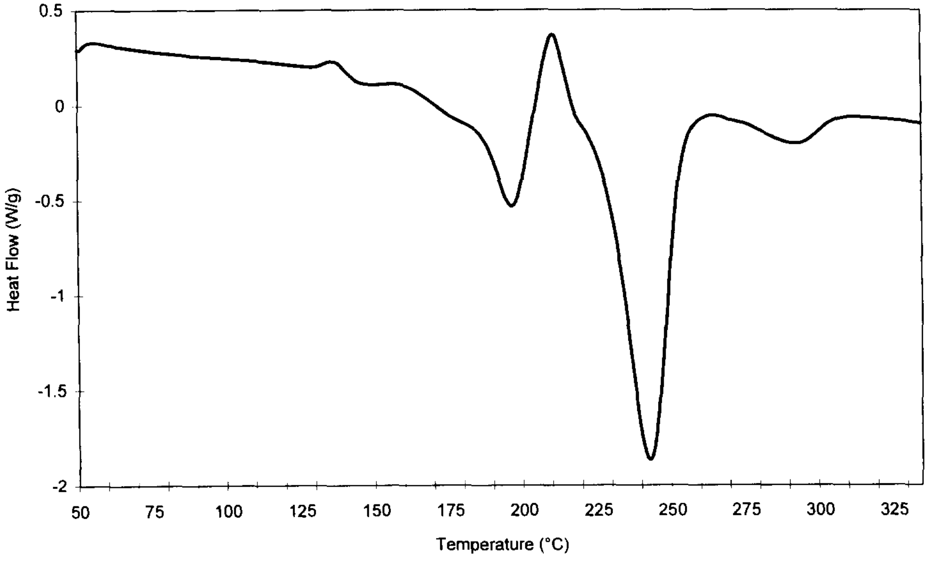

Fig. 1. Total heat flow versus temperature curve as obtained by DSC for gas generant formulation.

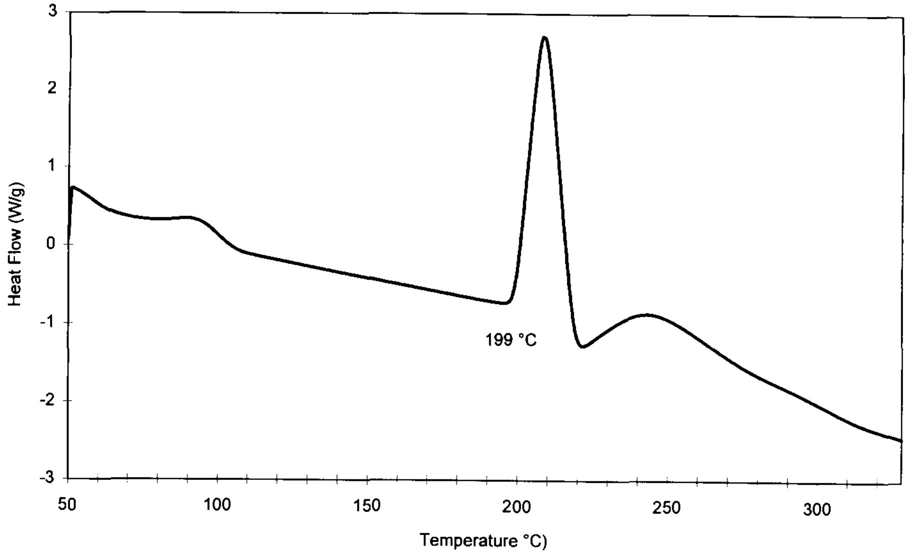

Fig. 2. Total heat flow versus temperature curve as obtained by DSC for Fuel A.

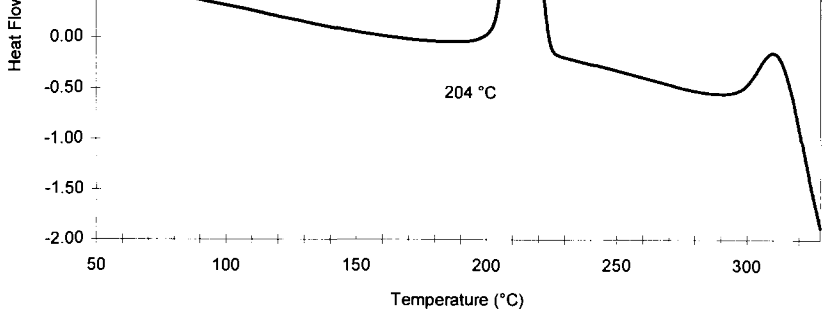

Fig. 3. Total heat flow versus temperature curve as obtained by DSC for Fuel B.

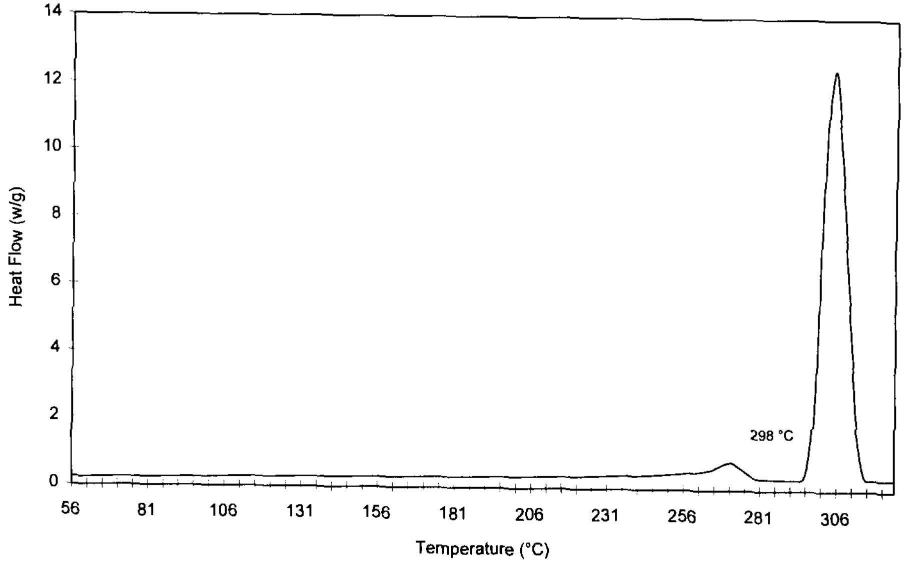

Fig. 4. Total heat flow versus temperature curve as obtained by DSC for co-oxidizer.

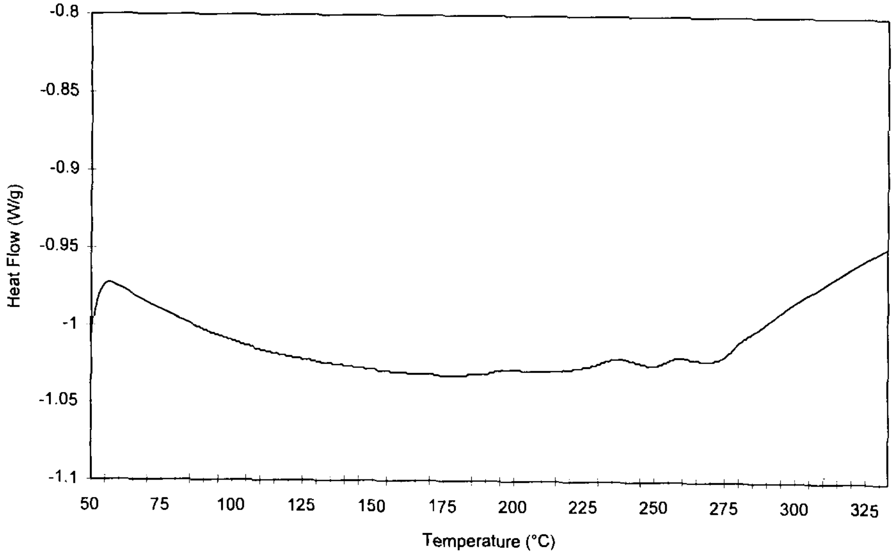

Fig. 5. Total heat flow versus temperature curve as obtained by DSC for oxidizer.

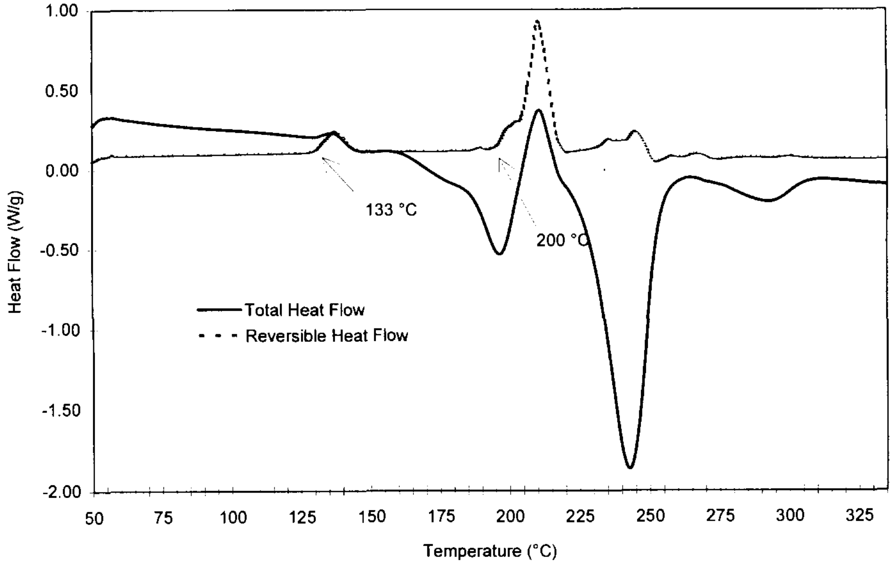

Fig. 6. Total and reversible heat flow versus temperature curves as obtained by MDSC for the gas generant formulation.

plete at which time the formulation decomposes exothermically. The presence of a liquid fuel at temperatures where sufficient lattice vibration of the solid oxidizer is occurring results in intimate contact between fuel and oxidizer and is a well known mechanism for initiation of a reaction in pyrotechnic mixtures [1]. Fuel A has a melting point of 201°C and melting of this component with subsequent diffusion into the lattice of the oxidizer is probably responsible for initiation of the second exotherm shown in Figs. 1 and 6. One complication with explaining the mechanism is that the onset of the endothermic event in Fig. 6 at 130°C does not correspond to known melting points of the remaining components in the mixture. A possible explanation for the melt at 130°C is that Fuels A and B form a eutectic mixture. This theory was tested using mixtures of Fuels A and B with the mole fraction of Fuel A varying from 0.1 to 0.9. The mixtures were prepared by slurrying with 50% water at 60°C and oven drying at 90°C for 4 h. Figs. 7–9 show the MDSC curves of the mixtures containing 0.1, 0.5 and 0.9 mole fraction of Fuel A, respectively. DSC curves of eutectic mixtures are characterized by a relatively sharp endothermic peak with an onset temperature that is independent of the component concentrations [2]. The onset of this endotherm is the melting point of the eutectic. At higher temperatures an endotherm with a gradually sloping onset and a sharp endpoint is present in Figs. 7 and 9. This corresponds to melting of excess Fuel B and Fuel A, respectively, in equilibrium with the eutectic mixture. This endotherm is absent in Fig. 8 indicating that a mole fraction of 0.5 is the eutectic composition. A phase diagram can be constructed by plotting the peak temperature of the broad endotherm versus the mole fraction of the components as shown in Fig. 10. The onset of the melt would be preferable to the peak temperature but due to the difficulty in selecting the onset we chose to plot the peak temperature. The

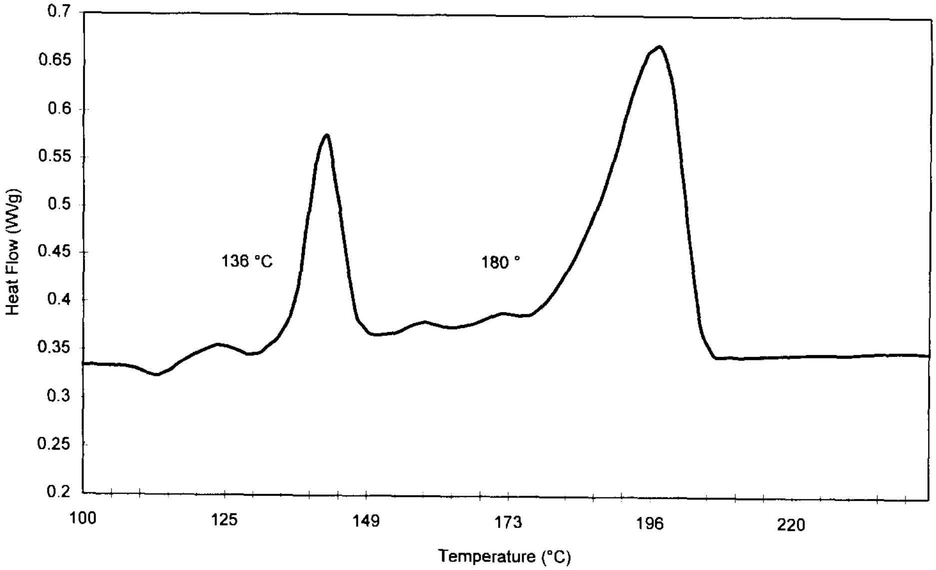

Fig. 7. Total heat flow versus temperature curve as obtained by DSC for a 0.1 mole fraction Fuel A, 0.9 mole fraction Fuel B mixture.

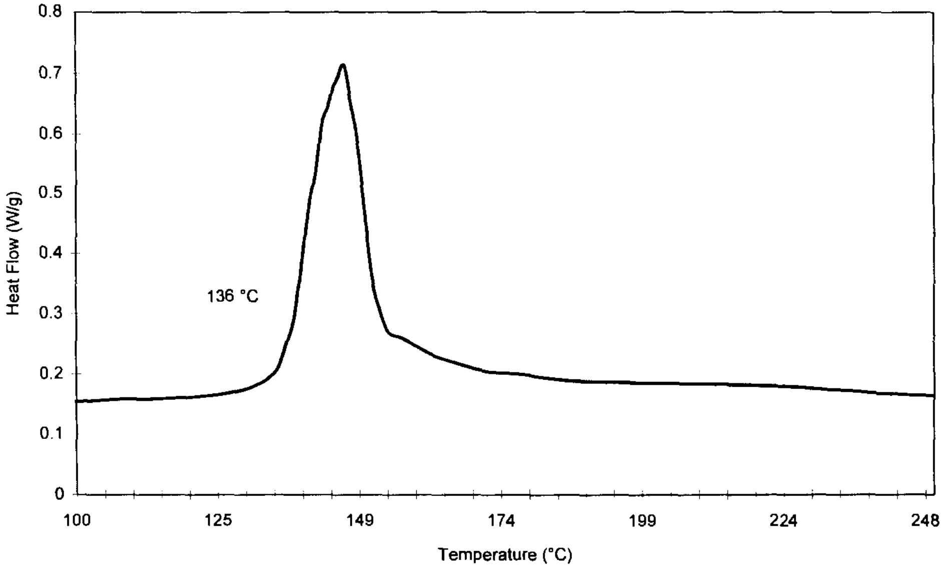

Fig. 8. Total heat flow versus temperature curve as obtained by DSC for a 0.5 mole fraction Fuel A, 0.5 mole fraction Fuel B mixture.

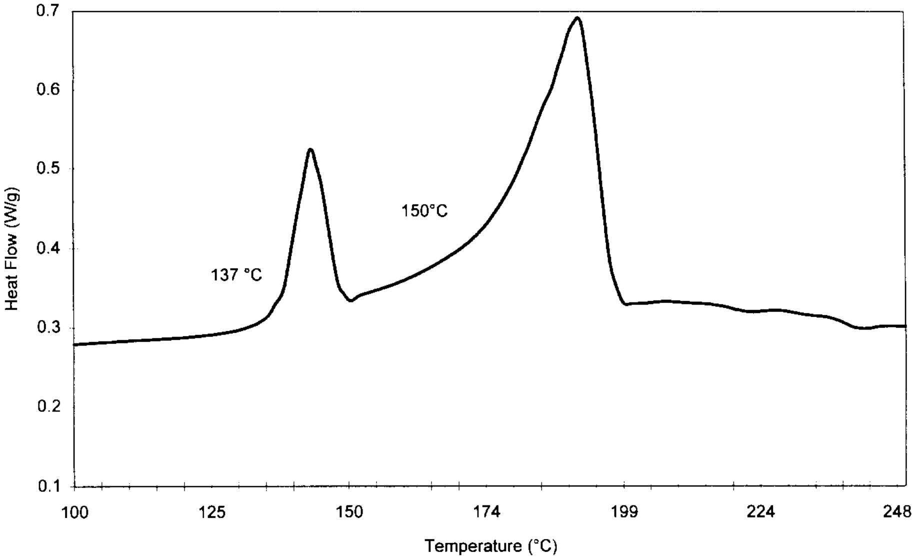

Fig. 9. Total heat flow versus temperature curve as obtained by DSC for a 0.9 mole fraction Fuel A, 0.1 mole fraction Fuel B mixture.

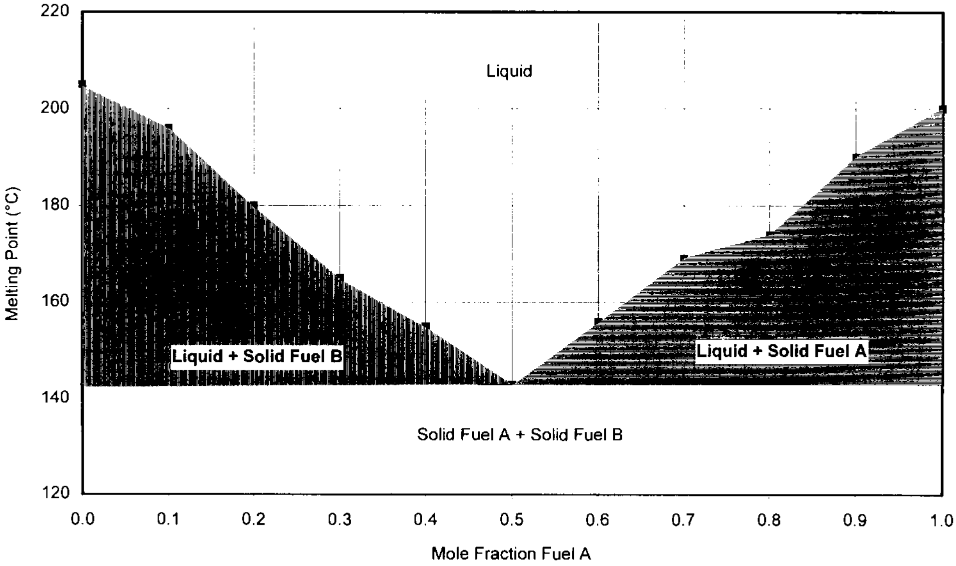

Fig. 10. Phase diagram: peak temperature is mole fraction of components.

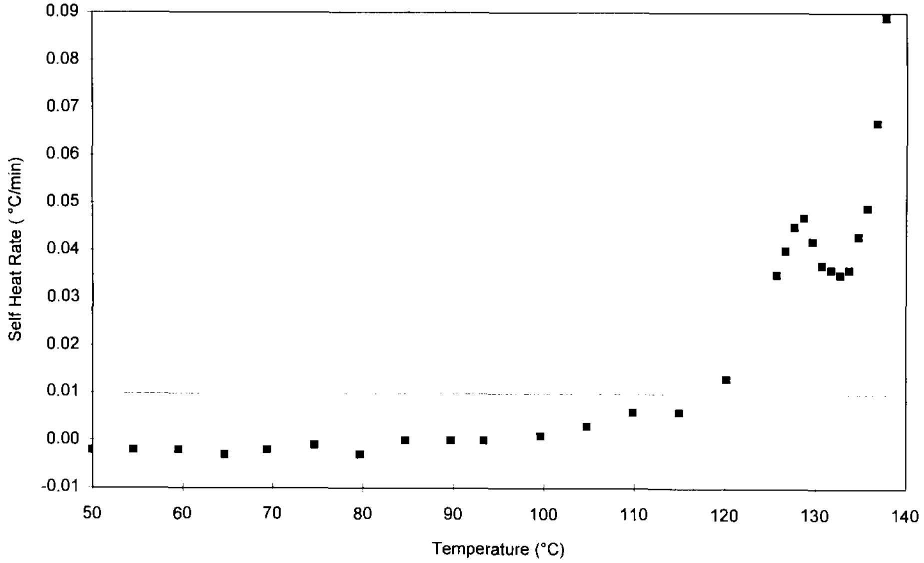

Fig. 11. Self heat rate versus temperature curve as obtained by the ARC for the gas generant formulation.

lowest point on the diagram will be the freezing point of the eutectic. Fuel A is present in the formulation at a higher concentration than Fuel B. Fuel A is also sparingly soluble while Fuel B is readily soluble. For these reasons we believe that the component melt at approximately 200°C in Fig. 6 is due to a combination of excess Fuel A in equilibrium with the eutectic mixture and possibly some insoluble Fuel A that does not participate in

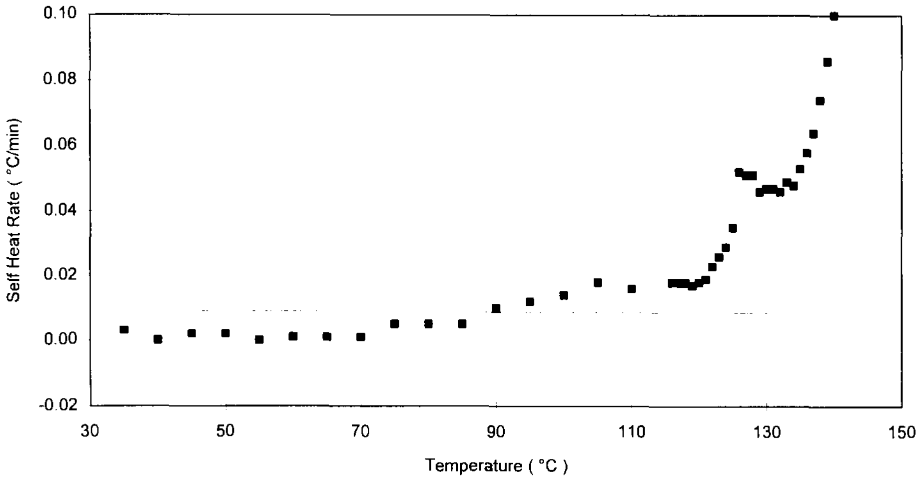

Fig. 12. Self heat rate versus temperature curve as obtained by the ARC for the thermally unstable gas generant formulation.

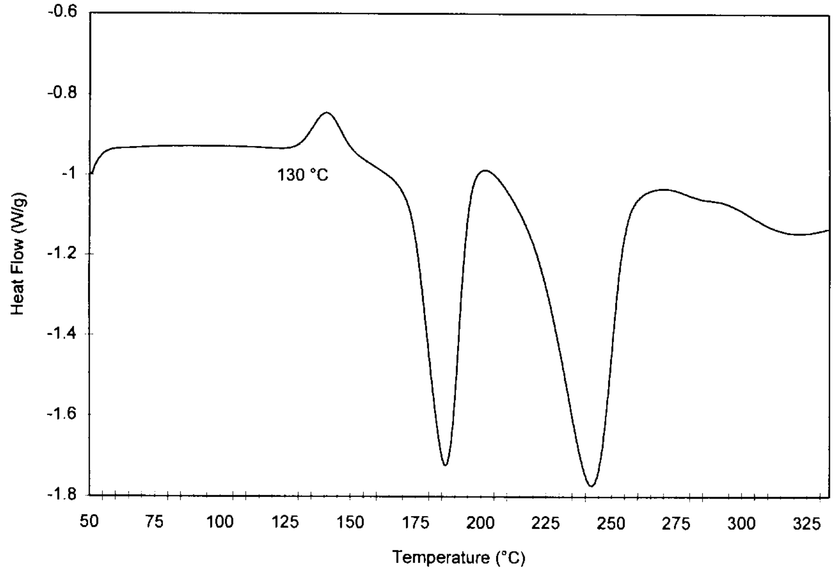

Fig. 13. Total heat flow versus temperature curve as obtained by DSC for the thermally unstable gas generant.

eutectic formation. The low melting point of the eutectic explains why the formulation is able to undergo exothermic decomposition at temperatures lower than the melting point of the pure fuels. We are currently performing experiments to determine if the low melting point of the eutectic composition can result in fuel loss during drying of the formulation under vacuum and explain observed performance losses in the burn rate.

The onset of decomposition for the formulation is 120°C as determined by ARC (see Fig. 11). During the development of the formulation, alternate suppliers for Fuel A were evaluated. We discovered that when Fuel A was manufactured by one of two possible processes, an impurity produced by the process formed an unstable intermediate with Fuel B during slurrying of the gas generant. When the formulation was drying, ignition occurred at approximately 85–90°C. A small handmix of the formulation was prepared in the laboratory and ARC analysis was performed. The onset of decomposition occurred at approximately 90°C (see Fig. 12), a significant loss of thermal stability compared to the formulation used to generate Fig. 11. The heat flow versus temperature curve for the thermally unstable formulation shows some differences from the curve in Fig. 1. For example, the size of the first exotherm relative to the second is much larger in Fig. 13 than in Fig. 1. However, it is difficult to show any difference in thermal stability by DSC. This shows the sensitivity of the ARC for determination of thermal stability. ARC analysis of a hand mix formulation is now standard practice when new sources of raw materials are evaluated.

4. Conclusions

Since initiation of decomposition in this gas generant formulation is dependent on melting of components and these melts are overlapped by exothermic peaks, the traditional DSC was of limited use in elucidating the decomposition mechanism of the formulation. The ability of MDSC to separate reversible and irreversible transitions allowed the component melts to be visualized as the formulation underwent exothermic decomposition and proved invaluable for determining the decomposition mechanism.

The sensitivity of the ARC allowed us to detect thermal instability in the formulation when a new supplier of Fuel A was used. ARC is now used as a screening test for thermal stability whenever formulation or supplier changes are made.

References

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