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## Stability Predictions for the Autocatalytic Decomposition of Nitrocellulose in Toluene

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**Instrument:** *2277 Thermal Activity Monitor*

**Field of Application:** *Material Science*

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### INTRODUCTION

Nitrocellulose with toluene diluent, is preferred for the manufacture of furniture coatings and printing inks. However, it is known that replacing the normal alcohol diluent with toluene decreases stability. A number of warehouse fires occurred during storage of the toluene-wet material. Programmed DSC and DTA experiments are normally used to obtain stability data for such energetic materials. However these techniques cannot be used to evaluate the reaction hazard of this system. The use of highly sensitive isothermal microcalorimetric methods were necessary to determine the exact nature of the reaction at close to normal storage conditions.

### EXPERIMENTAL

A 2277 Thermal Activity Monitor (TAM) was used for isothermal microcalorimetric measurements between 60 and 75°C. DSC runs were also made on the samples.

### STABILITY CALCULATIONS

Plots of times-to-peak and maximum heat rates versus  $1/T$  allowed the calculation of the Arrhenius activation energy,  $E_a$ . The maximum safe reactant dimensions ( $r$ ) for various ambient temperatures ( $T$ ) and related peak heat rates ( $q$ ) were then determined using values for  $E_a$ , critical shape factor ( $\delta$ ), concentration ( $C$ ), and thermal conductivity ( $K$ ), in a form of the well known Frank-Kamenetskii heat balance equation:

$$r^2 = (\delta K R T^2) / (C q E_a)$$

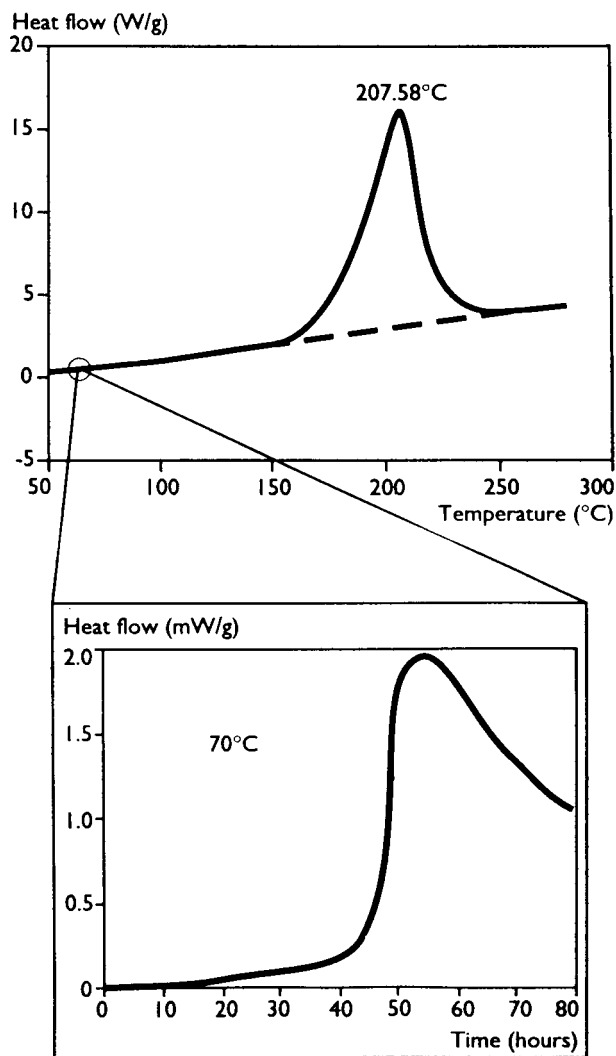
where  $R$  is the gas constant.

### RESULTS AND DISCUSSION

DSC experiments showed single, high temperature decomposition exotherms which could not be related to storage stability (fig 1). In contrast, isothermal microcalorimetric data showed the presence of a low temperature autocatalytic reaction (fig 1). The times to peak height at different temperatures are shown in

table 1. The sudden release of the autocatalytic reaction heat was enough to trigger a runaway of the high temperature decomposition reaction. Additional experiments showed that water was not tightly bound to the nitrocellulose and that the water readily migrated from warmer to cooler zones in the container. This subsequently would tend to keep the preparation safe. However, in production lots with higher water and acidity levels, the autocatalytic rate could exceed the water loss rate and the migration mechanism would no longer be protective.

Fig. 1. A high temperature DSC curve together with an isothermal plot of nitrocellulose in toluene revealing the autocatalytic activity at lower temperatures.



Temperature	mWatts/g	Peak Times, Hours
60 °C	880	118.00
65 °C	1500	70..25
70 °C	2600	41.25
75 °C	4500	24:00

\* Average of four runs

Table 1. Peak times and maximum heat rates versus temperature\*.

## CONCLUSION

DSC experiments, while showing the main decomposition exotherm, could not be used to study the autocatalytic reaction responsible for nitrocellulose instability. Indeed data from isothermal heat conduction microcalorimetry were necessary for determining the product specifications leading to safe storage of toluent-wet nitrocellulose.

## NOTE

This application note is written by A. Duswalt (Hercules Inc) and M. Shafiq (Thermometric AB).