Safety assessment of material incompatibility in formulations for pyrotechnic manufacture.

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Introduction

The introduction of new pyrotechnic systems requires a structured and progressive safety assessment throughout the initial research then development process. For new composition formulations an initial rapid and cost effective chemical compatibility screening process is required to act as a 'first sift' to accept formulations for further development. Full energetic material qualification testing is generally applied much later in the development cycle when a formulation is close to being introduced into an 'in-service' status.

The first experiment with a new pyrotechnic formulation could be a simple ignition pile test to establish if a new pyrotechnic powder actually burns. However, in order to mix a new pyrotechnic formulation that may contain new or different ingredients it is necessary to investigate if any chemical compatibility problems exist between fuels, oxidisers and binder systems. Since a large number of formulation variants and perturbations could be under investigation a rapid screen was thought to be a suitable substitute to full STANAG compliant testing.

If no adverse reaction is evident when comparing individual chemicals with binary and tertiary mixtures small scale mixing can progress for initial trials such as a pile test or small scale burn rate test which can act as a 'second sift'. A successful candidate formulation may be required to undergo a pressing compaction test followed by a burn rate test ('fourth sift') or larger scale mixing process once a 'third sift' sensitiveness testing has been completed.

Experimental

Raw materials for safety testing experiments were provided by DSTL. Samples of various fuels (magnesium powder, potassium benzoate), Oxidizers (sodium nitrate, potassium nitrate, potassium perchlorate) were used as received. A sample of red phosphorus, a further common ingredient in pyrotechnic formulations, was also used since its chemical reactivity is prone to

degradation reactions during storage, which potentially can make it more difficult to ignite, reduce its burn rate and lead to the evolution of toxic phosphine.

Many binder systems used in pyrotechnic compositions negate combustion efficiency and can lead to difficulties to incorporate sufficient oxidant into a formulation to achieve stoichiometric combustion, without compromising physical properties. There is potential to mitigate this problem through the use of energetic polymers such as Poly NIMMO (Poly(3-methyl-3-nitratomethyl oxetane) and Poly GLYN (Polyglycidylnitrate), samples of these materials were obtained from QinetiQ (UK).

The samples were prepared using the incipient wetness technique. The base material was dried for at 110°C to remove all water. The sample was then wetted with acetone to determine the volume of water adsorbed per gram of support. Once this had been determined, a solution of the energetic binder in acetone of the appropriate molarity was produced. A second dried sample of support material was then wetted using this solution and then dried in-vacuo for 24 hours at 70°C.

The materials were tested using a new calorimeter system, the Rapid Screening Device (RSD) from Thermal Hazard Technology. This, ramped heating, instrument is designed to identify exothermic reaction hazards and it can rapidly determine differential temperature and differential pressure data, a feature which is which is unique to this system. Examples of these data can be seen in figures 1 and 2 which show data from the decomposition of 20% di-tertiary butyl peroxide (DTBP) in toluene solution.
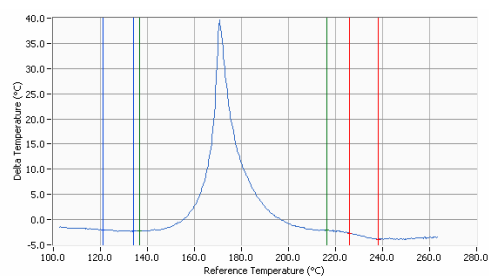

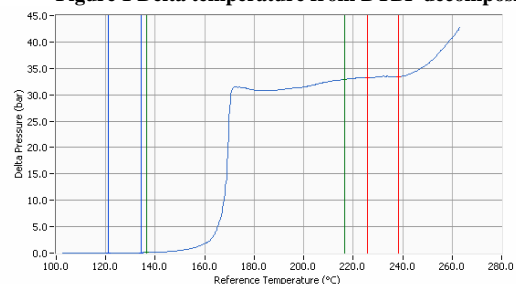**Figure 1 Delta temperature from DTBP decomposition.**

Figure 2 Delta pressure from DTBP decomposition.

The RSD is a Ramped Passive-mode Calorimeter, which depends on the principles of heat flow and transient heat accumulation. The key to this technique is a very stable heat transfer coefficient. The heat transfer capacity can thus be modelled successfully during the entire reaction period. The RSD measures temperatures and pressures, and as such is capable of providing a real-time basis for determining the partial pressures resulting from condensable vapours and non-condensable gases.

Ramped Passive-mode Calorimetry successful implementation requires an environment whereby small control changes are applied over relatively long (with respect to a system's time constant) periods. This ensures smooth transitions to the heat transfer capabilities of each particular test-cell and allows predictions to be made regarding the nature of heat accumulation and heat flow to and from the sample under investigation. Understanding the test-cell thermal transfer behaviour provides the basis for the determination of process heats (melting, boiling, reaction, etc.) as well as the determination of thermal transfer based kinetics.

It is also imperative that the heat flow to the sample during the inert pre-process and post-process phases is also quantified successfully. Ramped Passive-mode Calorimetry may also be used to determine heat capacities of unknown samples when referenced against known standards. For a successful data analysis, certain physical data must be known. The mass and heat capacity of the sample, as well as the test-cell must be known. An air reference temperature is also a prerequisite. This provides a means of calibrating the test-cell during a temperature ramp.

During an exothermic process, three distinct regimes exist when studied by a Ramped Passive-mode Calorimeter. These are illustrated in figure 3 (below)

1. **Heat supplementation phase.**

   Here heat is constantly added to the sample from the external temperature. Heat accumulation is due in part to the reaction in progress as well as the power being supplied to maintain the ramp. The power supplied is gradually lessening due to a decreasing temperature difference between the sample and environment.

2. **Heat overload phase.**

   At this stage the heat being produced exceeds the capacity of the test-cell to loose it to the environment resulting in an accumulation of heat within the sample. The amount of heat lost

to the environment controlled by the heat transfer characteristics of the test-cell: environment interface.

3. **Heat dissipation phase.**

   With the reaction complete, all that remains is the measurement of the accumulated heat to the environment. This provides the basis of determining when exactly the reaction ceased during the heat overload phase. When the temperature of the calorimeter and test-cell cross over, the sample is being heated externally once again.
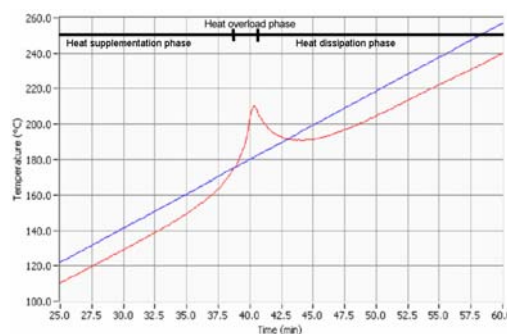

Figure 3 Heat transfer diagram for a typical exothermic reaction in the RSD.

During the pre-process and/or post-process stages the heat transfer capability of test-cell i may be defined by equation 1. UA may be assumed static or dynamic (the latter case may be modelled to vary from the pre-process to the post-process value on the basis of conversion). Typically values vary by 2% to 3% and is considered to be mainly due to the effect of changes to the sample.

$$UA_i = \frac{mCp_i \frac{dT}{dt}_i}{\Delta T_{air}}$$

Equation 1 – RSD Calculation of Heat Transfer

With UA established, it is then possible to determine a total power balance over the entire experiment (see equation 2) providing reference subtractions are performed. This use of a reference also provides the basis for establishing the point at which exothermic (if present) behaviour ceases.

$$\dot{q}_{pi} = UA_i \frac{d(\Delta T)}{dt}_{pi} + \dot{q}_{ramp}$$

Equation 2 – calculation of power balance

It is therefore possible to determine the total heat consumed or generated by a process from equation 3.

$$Q_{Pi} = \int \dot{q}_{pi} dt$$

Equation 3 – Total Heat generation calculation

Having determined the specific heat of a process, it is possible to use the temperature rates with knowledge of excess power added or deficit power lost to determine the process kinetics. Essentially equation 4 may be used, such that a linearly corrected Wilson plot for reaction order may be used to establish kinetic parameters.

$$Q_{Pi} = \Delta H_{Pi} \frac{dC}{dt}_i$$

Equation 4 derivation of kinetic parameters

One of the main features of the RSD is that a wide range of different sample containers can be used for measurements. The arrangement of two such systems is shown in figure 4.
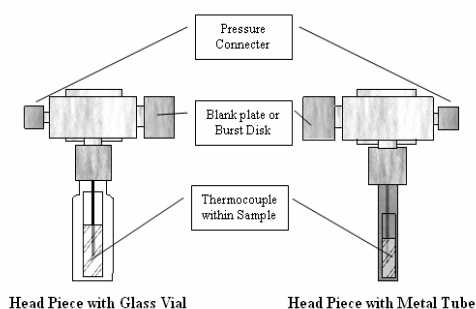

Figure 4 Test cell configurations

Initial screening experiments were first conducted in Glass Vials however these were abandoned as ignition events could give rise to cell rupture. The samples were mounted in small glass ignition tubes within the test cell to avoid the influence of metal on the tests.

Identical conditions have been utilised for all the tests conducted here with a sample mass of 0.15g. The tests were conducted from room temperature to 400°C* at a scan rate of 4°C/min.

Results

The effect of Poly NIMMO on Sodium Nitrate

Initial experiments were performed to test the effect of coating the base material with an energetic binder. The data below show the temperature (1) and pressure (2) responses from sodium nitrate as received from DSTL.
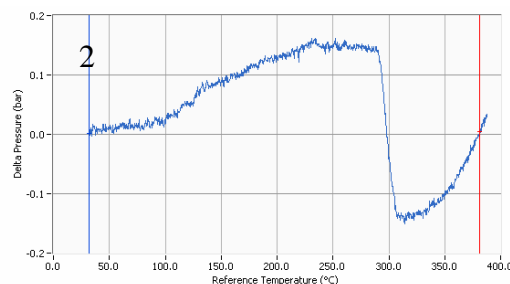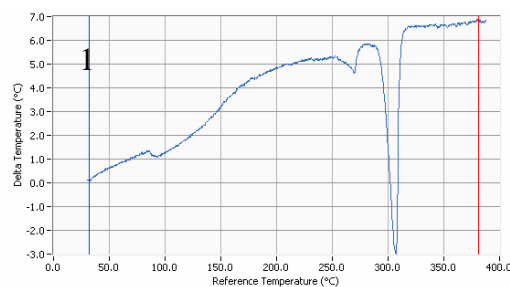
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* Several experiments terminated early as ignition events caused the temperature to rapidly increase beyond the final experiment temperature

Figure 5 Temperature and pressure responses from pure NaNO₃

As can be seen there are small endothermic transitions visible in the temperature curve with peak temperatures of 95°C and 273°C. A major melting endotherm is visible with a peak temperature of 304°C. These transitions agree with literature data for this material.

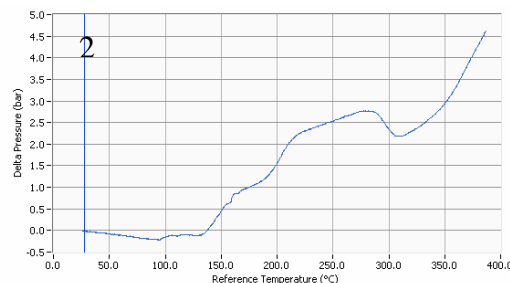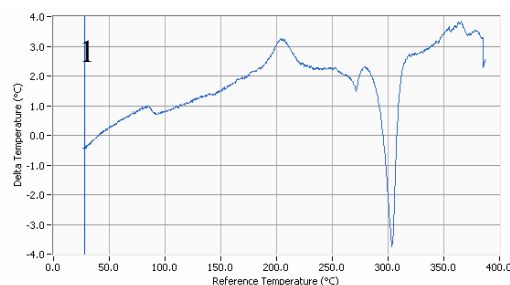The pressure data supports this with a very small deflection in the pressure visible when the material melts.

Figure 6 Temperature and pressure responses from Poly NIMMO coated NaNO₃

The temperature data from the binder coated material shows the same general features as the uncoated material with the crystal transitions at 95°C and 273°C and the melting transition at 303°C.

The main difference in the thermal signal is a broad exotherm centred at 205°C. Upon inspection of other materials this is found to be consistent with the decomposition of the Poly NIMMO.

The pressure data show a slightly different response with two pressure rises, the first from 135°C and a second congruent with the thermal decomposition peak. There is then a fall in the recorded pressure which matches that observed for the melting of the uncoated material.

Possible Incompatibility Reactions in Mixed Systems

Having previously established that none of the materials are incompatible with the poly NIMMO binder material it is then important to look at the binary and tertiary mixtures of the materials from our chosen composition. To this end, poly NIMMO coated mixtures of magnesium powder and sodium nitrate, magnesium powder and phosphorus, phosphorus and sodium nitrate and a mixture of all three materials were tested under the same conditions. The temperature data for all 4 of these compositions is shown in figures 7-10.
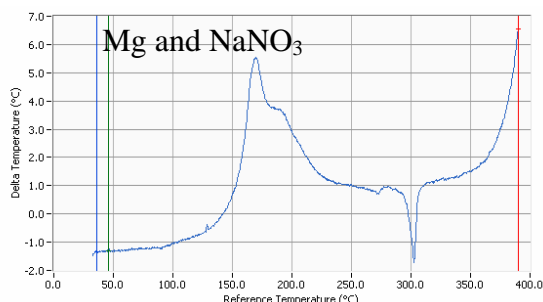
Figure 7 Temperature responses from a Poly NIMMO coated mixture of Mg & NaNO₃

The mixture of sodium nitrate and magnesium gave rise to a larger than expected decomposition reaction with a peak maximum of 160°C and a ΔT of almost 6°C. This was accompanied by a secondary peak at 190°C. The transition of sodium nitrate at 273°C and the melting at 305°C persist at half their previous intensity (accounting for the change in concentration to 50% of the mixture). This would suggest that the previous peaks, whilst obviously promoted by the presence of the NaNO₃ seems to not change this constituent
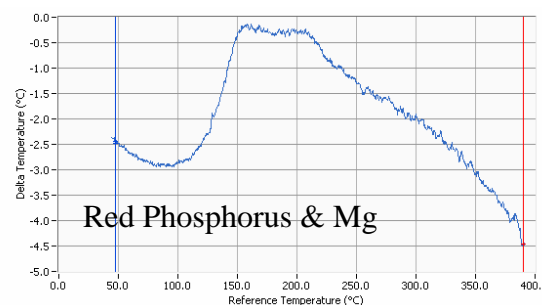
Figure 8 Temperature responses from a Poly NIMMO coated mixture of P & Mg

The results from the mixture of red phosphorus and magnesium show a more consistent behaviour. The sample shows a dual peak at 155°C and 205°C with a maximum delta temperature of around 2.5°C. These results suggest that the system is a simple additive mixture of the components with the two observed responses being the additive of the two individual samples.
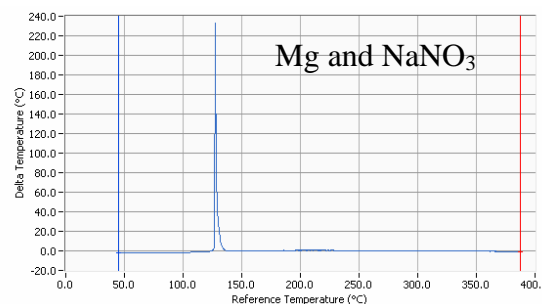
Figure 9 Temperature responses from a Poly NIMMO coated mixture of NaNO₃ & Mg

The results from the mixture of magnesium and sodium nitrate are the most worrying and potentially dangerous of all the data presented here. These data show a sudden and rapid rise in temperature (and not shown in pressure) at a temperature of 128°C, with a delta temperature of over 220°C. This is the only temperature effect visible within the sample (the usual transitions of sodium nitrate and poly NIMMO have disappeared) which suggests that this reaction consumes the sample.
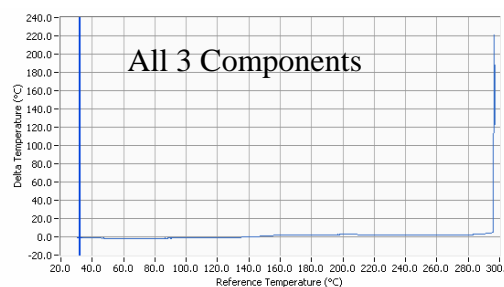
Figure 10 Temperature responses from a Poly NIMMO coated mixture of P, Mg and NaNO₃

As can be seen from these 4 figures the mixture of all three components had a gross incompatibility

reaction at around 295°C. A larger scale view of this data shows that there is the expected decomposition of the poly NIMMO at 205°C which suggests that this is not involved in the final incompatibility reaction however decomposition products for the poly NIMMO could be a factor in this incompatibility.

Conclusions

The use of the RSD as a rapid screen for material compatibility in pyrotechnic formulations has been well established. A simple description of results should mean that in a compatible mixture the sum of the curves from the individual materials is equal to those of the mixture whilst in an incompatible system this is not the case. The ability of the system to measure both temperature and pressure differential data is unique and highly useful as it allows two separate material responses to be correlated.

The data from the coated/uncoated sample of sodium nitrate with poly NIMMO shows that there is no incompatibility between these two materials. The transitions, melting and decomposition events which occur in the mixed sample are a simple summation of the individual components.

The low temperature of the incompatibility reaction in the phosphorus / $NaNO_3$ (128°C) is concerning as this is in the order of temperature used for curing processes within preparation of final mixtures. The change in the onset of this incompatibility between the full mixture and the one where the magnesium is omitted is in the order of 180°C this has significant implications in manufacturing safety – both in terms of the order in which materials are added and ensuring that the magnesium is added.

The origin of this incompatibility issue is of great interest and importance and further experiments must be conducted to elucidate the cause. Experiments will be made in the absence of the binder and with alternative binders to verify if the poly NIMMO is a contributory factor. Experiments will also be conducted in different atmospheres (in the absence of oxygen, in the absence of moisture and in moisture rich conditions) to provide further information on the observed reaction.