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Application of heat conduction calorimetry to high explosives[☆]

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Abstract

This paper describes some thermal analysis experiments conducted on high explosive samples. These employ differential scanning calorimetry to monitor thermal effects at elevated temperatures (around 200 °C) and heat conduction calorimetry to record thermal effects at much lower temperatures (below 100 °C).

The work shows that, due to the generally high thermal stability of many high explosive compositions, heat generation rates are very low, if detectable at all, at normal storage temperatures, even when using a very sensitive instrument. The sensitivity and reproducibility of this technique has been investigated in detail by Wilker et al. [S. Wilker, U. Ticmanis, G. Pantel, Detailed investigation of sensitivity and reproducibility of heat flow calorimetry, in: Proceedings of the 11th Symposium on Chemical Problems Connected with the Stability of Explosives, Sweden, 1998] and shown to be capable of recording heat generation rates of less than a microwatt. This allows continuous measurement of decomposition processes in nitrate ester based propellants at temperatures as low as 40 °C. However, the measurement of very low levels of heat generation is difficult, time consuming and therefore expensive. If the assumption is made that the life limiting process is invariably the slow decomposition of the energetic component, this will frequently lead to very long service lifetime predictions.

A number of possible complications are identified. Firstly, due to its low detection threshold, a heat conduction calorimeter may detect other reactions which will not lead to failure, but which may still dominate the heat flow signal. Secondly, the true failure process may generate little energy and be overlooked. In view of these considerations, at present it seems unwise to rely on heat conduction microcalorimetry as the only tool for the assessment of the life of high explosive energetic systems.

Based on examples of life terminating processes in high explosives during storage and use, it is clear that decomposition of the energetic material is not invariably the cause of system failure. It is also by no means the only reaction that may take place in, and be observed by, a heat conduction calorimeter.

Keywords: Calorimetry; Explosives; Kinetics

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1. Introduction and background

All processes (physical or chemical) are accompanied by the generation or consumption of energy, usually in the form of heat. It follows that, in principle, all processes can be studied using some sort of calorimeter. The low detection limit of modern heat conduction calorimeters means that the technique can be considered as a way to look at some very slow reactions.

Abbreviations: AP, ammonium perchlorate; PBX, polymer bonded explosive; RDX, 1,3,5-trinitro-triaza-cyclohexane; T, absolute temperature; TAM, thermal activity monitor—the commercial name for a widely used heat conduction calorimeter capable of measuring heat generation or consumption of less than a microwatt; TNT, trinitrotoluene

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For example, single, double and triple based propellants, containing nitrate esters, will undergo thermal decomposition, even at normal magazine storage temperatures, and this process can be observed directly by heat conduction calorimetry. It is known that, in addition to loss of energy leading to changes in reliability and performance, the decomposition reaction in this type of explosive is autocatalytic and can lead to self ignition in systems containing old propellant. Microcalorimetric techniques have been used increasingly over the last two decades for weapons system surveillance and lifetime prediction [2–4]. Much work has been done recently to standardise heat conduction calorimetry test procedures to allow unambiguous interpretation and pass/fail criteria to be established [5].

In addition to nitrate esters, modern weapon systems contain many other potentially unstable materials including:

- high explosives (RDX, HMX, TNT);
- composite propellants (AP/aluminium/polymeric binders);
- non-energetic materials (structural components).

In view of the success of the calorimetric approach to surveillance testing in single, double and triple base propellants [5] (i.e. those propellants containing cellulose nitrate or a combination of cellulose nitrate and glycerol trinitrate as the major explosive ingredients), it would be an attractive proposal to apply a similar approach to devices containing the materials listed above. Indeed, some countries have already proposed the use of heat conduction calorimetry in this way [6].

In the United Kingdom, at the present time, there is no rigidly defined set of procedures which are applied to all systems. Instead, the current practice is to apply past experience to decide what the failure mechanisms are likely to be on an individual, case by case, basis. A testing regime tailored specifically to observing and quantifying the critical failure process is devised [7]. Some (but by no means all) of the techniques which may be included in the test programme for a weapon system are:

Empirical full scale tests—ability to survive a feasible hazard:

- slow cook off test;
- fuel fire test;
- shaped charge attack.

Examination of physical integrity of whole device:

- dismantling/visual examination;
- X-ray, ultrasound scans.

Mechanical tests:

- dynamic mechanical analysis;
- tensile strength.

Chemical analysis of energetic components;
Vacuum stability tests;
Thermal analysis of energetic components.

Whilst clearly essential, surveillance and lifetime tests comprise a significant part of the total cost of a weapons system. Given the recent availability of sensitive heat conduction calorimeters, coupled with the fact that calorimetry is a universal technique—i.e. whatever process will eventually be life limiting will invariably be associated with *some* thermal activity, it is an attractive proposition to see if some, or even all, of the various techniques in the above list can be replaced by heat conduction calorimetry.

This paper describes some attempts to study the thermolysis reaction of an in-service PBX composition based on RDX-filled polypropylene glycol rubber by calorimetry and then discusses the results in the light of experience of processes which will limit the lifetime of systems by introducing unacceptable changes in their safety or performance characteristics.

2. Experimentation and results

Studies at elevated temperatures were carried out with a differential scanning calorimeter operated under isothermal conditions and at moderate temperatures by heat conduction calorimetry. The heat generation rate expected at moderate temperatures (60–90 °C) was found by calculation, using the high temperature data and compared with the results observed experimentally at lower temperatures.

2.1. High temperature studies

All experiments were carried out using the Mettler DSC-30 differential scanning calorimeter, using small PBX samples (<20 mg) contained in 40 μl aluminium crucibles.

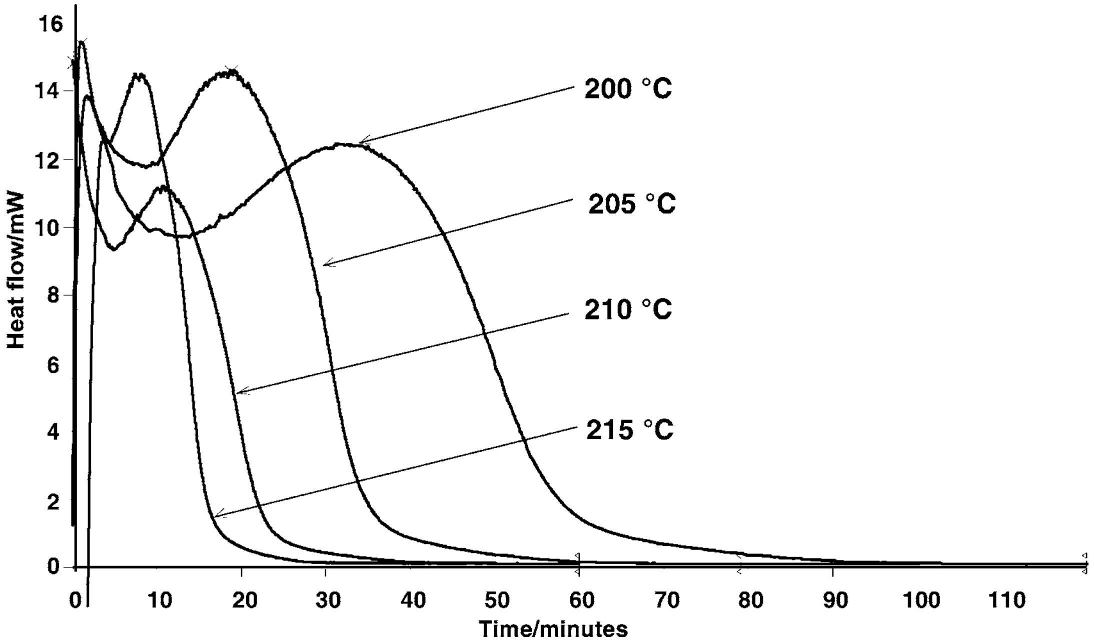


Fig. 1. Isothermal runs on PBX sample—(200 °C: 12.873 mg PBX, integral: 31.88 J, normalised integral: 2477 J g^{-1}, 205 °C: 8.995 mg PBX, integral: 23.92 J, normalised integral: 2659 J g^{-1}, 210 °C: 4.925 mg PBX, integral 12.23 J, normalised integral: 2483 J g^{-1}, 215 °C: 4.327 mg PBX, integral: 11.00 J, normalised integral: 2541 J g^{-1}).

The decomposition exotherm was recorded under isothermal conditions at temperatures of 200, 205, 210 and 215 °C. In each case the decomposition has a complicated appearance and is characterised by 2 major peaks and a total decomposition enthalpy of 2539 ± 150 J g^{-1} (Fig. 1). However, as the general shape of the curves is comparable, isoconversion techniques allow an estimate of apparent activation energy at constant degrees of advancement of the reaction [8]. The tabulated data at 50% conversion and Arrhenius plot are shown in Fig. 2 and indicate an activation energy of 174.8 ± 16.4 kJ mol^{-1} (95% confidence interval).

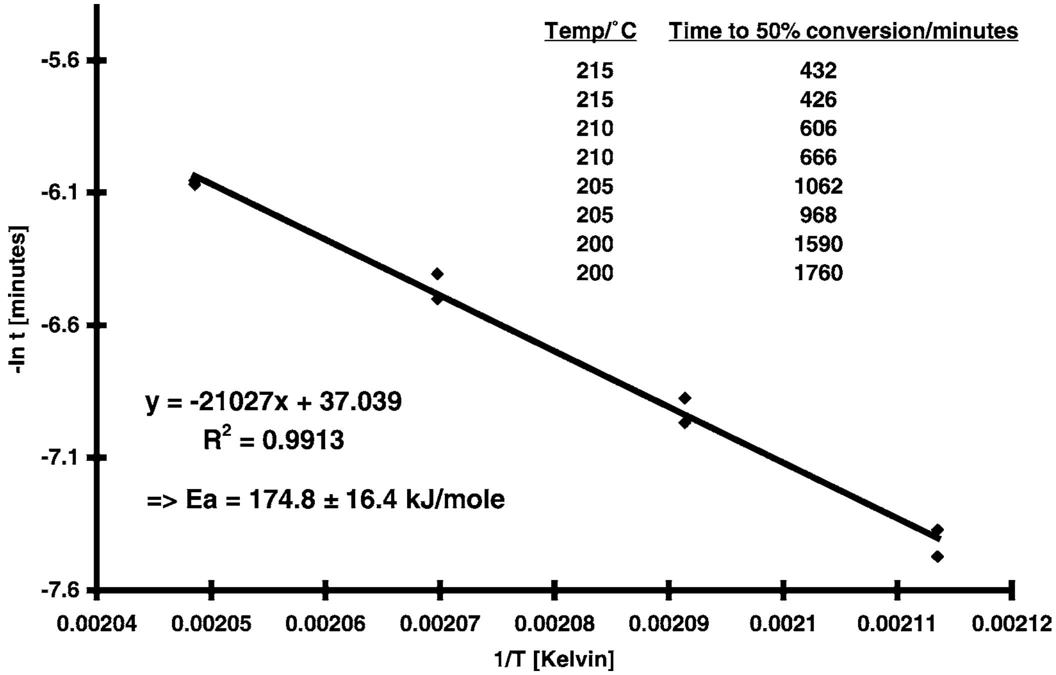
The validity of extrapolating the plot in Fig. 2 down to lower temperatures was tested as follows.

Extrapolation suggests that the time to achieve 50% extent of reaction at an isothermal temperature of 160 °C would be 1836 min. Since the instrument has an insufficiently low detection threshold to measure the anticipated exotherm at such a low temperature directly, a 'one point' ageing experiment with retrospective determination of residual energy was conducted as follows:

1. Heat a sample of known weight in the DSC-30 to 160 °C at 20 °C min^{-1}.
2. Maintain temperature at 160 °C for 1836 min.
3. Raise temperature to 210 °C at 20 °C min^{-1}.
4. Record (attenuated) exotherm while holding temperature constant at 210 °C until the signal has decayed.
5. Determine reduction in peak area resulting from earlier thermal history—i.e. storing at 160 °C for 1836 min.

The resulting differential calorimetry trace is shown in Fig. 3.

The percentage reduction was 52% compared to a PBX sample heated directly to 210 °C (very close to expected 50%) suggesting that the plot describes the temperature dependence of the decomposition from 215 down to 160 °C satisfactorily. Alternatively, using the time for a 52% reduction at 160 °C (1836 min) and to reach the same point in the reaction at 215 °C (7.4 min) suggests a similar activation energy at this stage in the reaction as found earlier in Fig. 2.



Temp/°C	Time to 50% conversion/minutes
215	432
215	426
210	606
210	666
205	1062
205	968
200	1590
200	1760

$y = -21027x + 37.039$

$R^2 = 0.9913$

=> Ea = 174.8 ± 16.4 kJ/mole

Fig. 2. Temperature dependence of PBX decomposition from isothermal calorimetry.

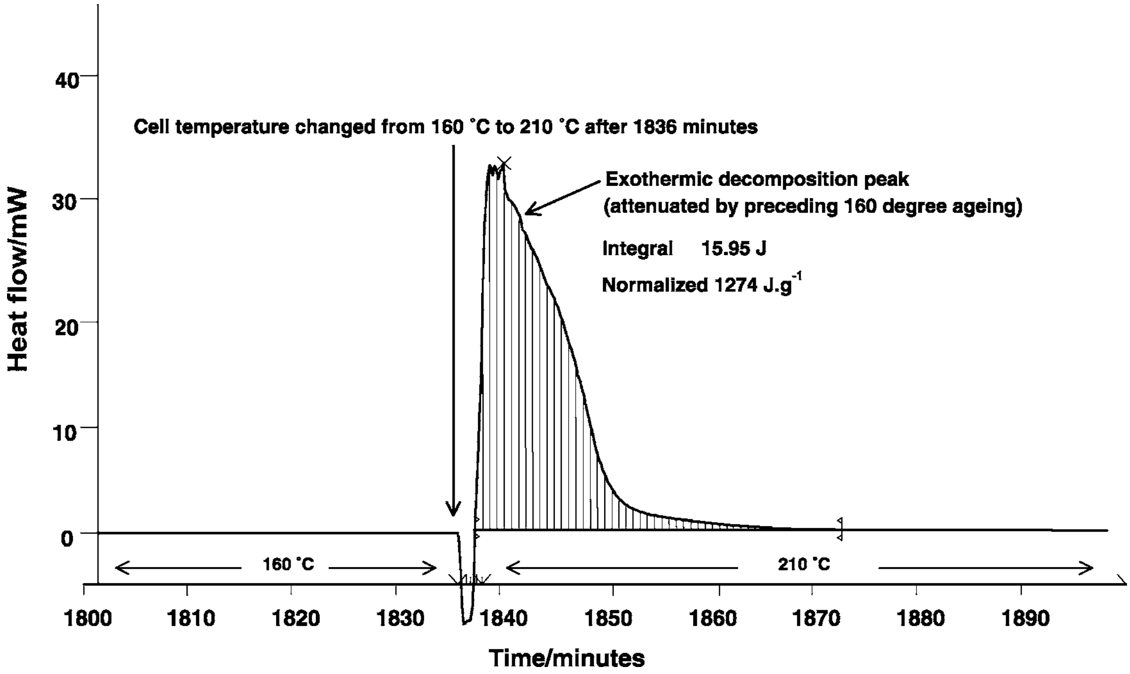


Fig. 3. Intermediate temperature ageing test to validate extrapolation of the PBX decomposition kinetics plot shown in Fig. 2.

Table 1
Anticipated maximum heat generation from heat flow calorimetry experiments at moderate temperatures

Experimental temperature (°C)	Expected heat generation rate (μW/g)	Comments
90	1.0	Should be detectable
80	0.2	Barely detectable
70	0.03	Not detectable above noise
60	0.005	Not detectable above noise

The maximum heat generation rate at 215 °C recorded was 3.23 W g^{-1}. If Fig. 2 is valid down to the temperature region generally used for heat conduction calorimetry studies, it would predict rather low values of heat generation at moderate temperatures (Table 1).

2.2. Heat conduction calorimetry studies

All heat conduction calorimetry experiments were performed on 1.5 ± 0.1 g samples of PBX sealed in 3 cm^3 glass ampoules, using a Thermometric type 2277 thermal activity monitor (TAM). Heat generation rates were recorded in duplicate on freshly prepared samples at thermostat temperatures of 90, 80 and 70 °C. In principal, it would be possible to describe the temperature dependence of simple, single, heat-generating reactions simply by determining initial rates. However, in the case of many propellant and explosive materials, the heat generation rate signal observed immediately after introducing a sample to a calorimeter may be dominated by a variety of short-term, minor effects. For example, an initial peak may be seen from polymeric materials due to rapid decomposition of accumulated peroxides which become unstable at the elevated test temperature resulting in an early, spurious peak. Therefore, when studying complex systems it is often necessary to consider heat generation rate data up to the point where the overall reaction has proceeded to a sufficient extent to ensure that these initial effects have decayed and the heat generation rate signal is due

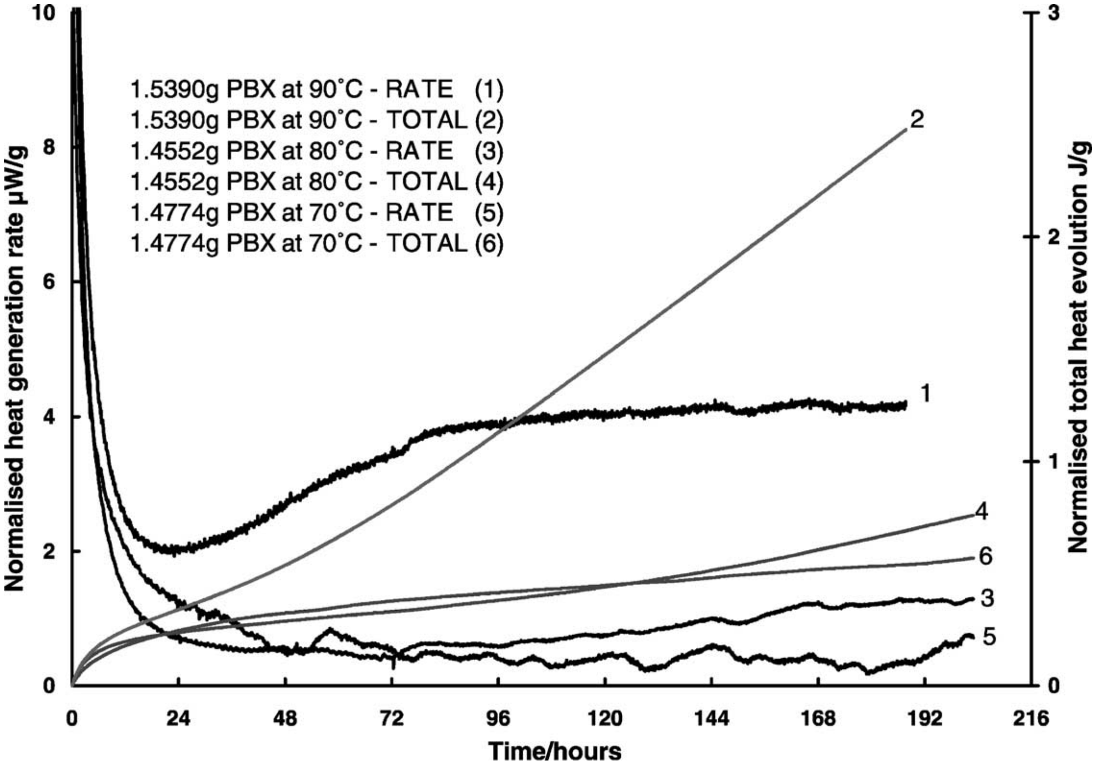


Fig. 4. Heat generation rate from PBX at 90, 80 and 70 °C.

exclusively to the thermal decomposition reaction of the main energetic component [10]. All experiments were allowed to continue until 0.5 J g^{-1} had been evolved at each temperature studied to avoid this complication. The resulting traces are illustrated in Fig. 4. In each case heat generation rate was small, but detectable. They were also higher than anticipated from a consideration of the earlier high temperature studies. Activation energy was deduced from the slope of a plot of ln(time to evolve 0.5 J g^{-1}) against $1/T$ [8]. The deduced apparent activation energy was 64 kJ mol^{-1}. However the plot was not a good fit to a straight line ($R^2 = 0.7936$). Extrapolating such data to estimate an equivalent time at room temperature would clearly give an unreliable description of the temperature dependence of the degradation process.

Based on the low heat generation rate detected at 70 °C and making the assumption that the heat generating process would exhibit a positive temperature dependence suggested that heat generation rate might be around the same order of magnitude as instrumental noise at 60 °C. Time constraints meant that leaving a PBX sample on at 60 °C for long enough to reach the equivalent degree of advancement of reaction achieved in the experiments at 70 °C and above (defined as the time after which 0.5 J g^{-1} of heat had been evolved) was not feasible and so measurements were attempted at 60 °C on the samples previously used for the TAM experiments at 90, 80 and 70 °C (i.e. their initial extent of reaction could be taken as that reached at the end of the initial, higher temperature test). If an accurate signal could be measured, this would allow activation energy in this temperature range to be determined by the 'step principle' [9].

Heat generation did appear to be just detectable above noise, although this was not easy to measure quantitatively. It has been reported that, due to the fact that the sample and reference channels thermal environment may not always be identical, the true zero point may not be exactly at apparent zero, but slightly offset by up to ±50 nW in any particular instrument [11]. For work close to the detection threshold, the application of the 'switch' technique has been

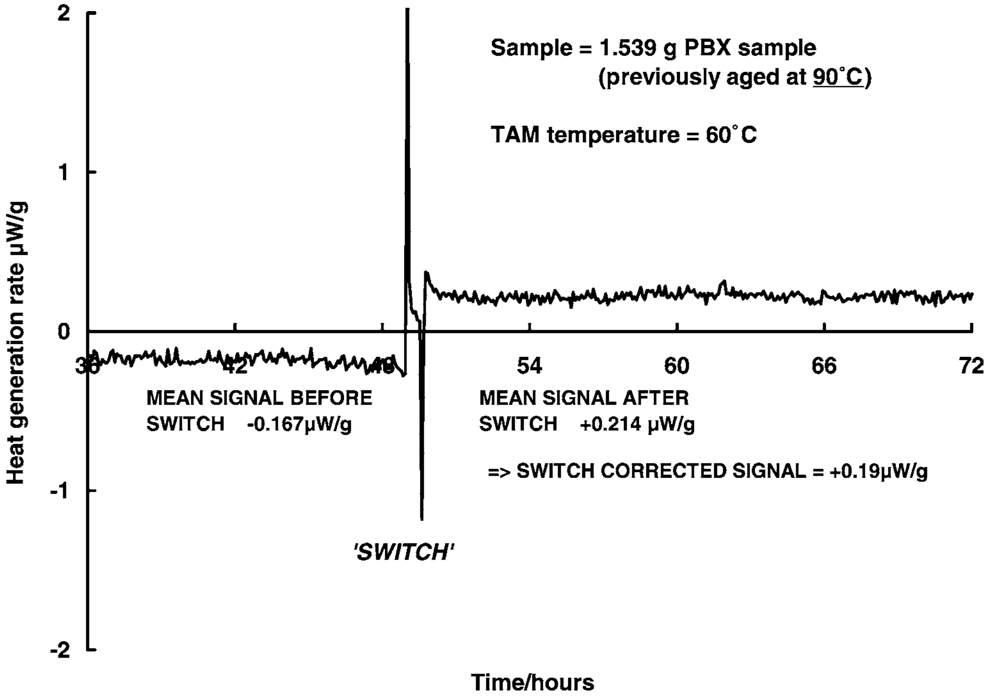


Fig. 5. Heat generation at 60 °C from PBX sample previously used for 90 °C heat conduction calorimetry experiment—'switch' technique used to confirm true baseline position.

recommended [11]. To do this, after recording a stable signal in the normal sample orientation, the sample and reference ampoules are swapped over and the heat generation signal recorded until the signal again stabilises. The true baseline may then be found from the mean of these two signals and used to correct the observed heat generation rate appropriately. A switch experiment was therefore carried out at 60 °C (e.g. Fig. 5 shows a switch experiment conducted on a sample previously monitored at 90 °C). Taking the mean values for 12 h before and after switch and deducing true baseline position to be half the difference leads to the estimates of 0.190, 0.189 and 0.124 $\mu W\,g^{-1}$ for the samples formerly measured at 90, 80 and 70 °C, respectively.

While being consistent with a rather low activation energy, since it is difficult to show that the exotherm is there at all and it would not be sensible to quote a quantitative figure.

3. Discussion

Heat generation rates at moderate temperatures from nitramine high explosives, as illustrated by the PBX composition reported here, are very low in comparison to those reported for nitrate ester based propellant compositions [1]. They become difficult to detect at all at moderate temperatures. The measurement of very low levels of heat generation close to the equipment's detection threshold ($<1\,\mu W$) has been found to be difficult, time consuming and therefore expensive.

The fact that the heat conduction calorimeter can detect low levels of heat generation rate above noise coupled with the relatively high stability of most high explosives and composite propellants will mean that other thermally-active effects may overwhelm the heat flow signal due to thermolysis of the energetic material itself. If the heat generation from another, non-life limiting process such as post curing of a polymeric binder, corrosion of a metal component or surface oxidation processes, are attributed to thermolysis of the explosive itself, this may lead to overly pessimistic forecasts.

On the other hand, some processes which could shorten the life of a device significantly may generate very small quantities of heat which are undetectable, even with a heat conduction calorimeter. For example, a small number of chain breaks in a polymer, or the formation of a small number of cross-links will represent very little chemical activity—and therefore generate very little heat. However, these may result in a major change in molecular weight and this will, in turn, have a marked effect on physical properties.

In cases where changes in physical properties could be life limiting, it appears sensible to use techniques which measure mechanical properties directly as the main tool for identifying critical age-related changes. In cases such as this, relying on calorimetric evidence too heavily might lead to overly optimistic forecasts.

If the assumption is made that the life limiting process is invariably the slow decomposition of the energetic component, this will frequently lead to very long service lifetime predictions—hundreds or even thousands of years. Any prediction that 'proves' that a complex chemical system will last virtually forever, should be treated cautiously.

4. Recommendations and conclusions

It is recommended that a critical appraisal of available data be made before reliance is made on heat flow calorimetry data when used for in-service surveillance and lifetime prediction. This is to ensure that the process responsible for any observed heat flow and the process which might lead to failure of the weapon are the same. Experiments should be examined retrospectively by asking questions such as:

- Is the kinetic evidence consistent with the reaction assumed to be taking place?
- Are the results believable in the light of experience, the results of other experiments and common sense?
- Are the results born out by any available ageing data at lower temperatures?
- Is there supporting evidence that the observed heat generation is really due to a likely lifetime limiting process at all?

Of course, for research purposes, yes or no are both useful answers to each of those questions as further critical experimentation can always follow. However, for general, standardised surveillance purposes, it is a requirement that the answer to each question is yes!

In the case of nitrate ester propellants, the situation appears promising since each of those questions can be answered with a 'yes'. Therefore the approach appears potentially very useful.

In the case of some of the more chemically stable ingredients found in weapon systems, the situation is less clear due to potential complications:

- As illustrated by the PBX measurements reported here, thermolysis of the explosive components will be more difficult to detect and therefore more time consuming and expensive than in the case of nitrate ester based systems.
- The calorimeter will detect other reactions which may dominate the heat flow signal, but be unimportant with regard to reliability and safety of the system.
- True failure process may generate little energy and remain undetected, especially in the case of failures due to changes in mechanical properties.

With the present state of knowledge, it is considered premature to rely on heat conduction calorimetry as the only tool for the assessment of the life of high-explosive energetic systems. It is proposed that the existing approach of devising a test programme tailored specifically to observing and quantifying the critical failure process should continue for the foreseeable future in the UK.

Acknowledgements

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References

[1] S. Wilker, U. Ticmanis, G. Pantel, Detailed investigation of sensitivity and reproducibility of heat flow calorimetry, in: Proceedings of the 11th Symposium on Chemical Problems Connected with the Stability of Explosives, Sweden, 1998.

[2] B. Vogelsanger, R. Sopranetti, Safety, stability and shelf life of propellants—the strategies used at nitrochemie wimmis AG, in: Proceedings of the Symposium Chemical Probability Connected Stability Explosion, Sweden, 1998, p. 361.

[3] J. Wilson, The use of heat flow calorimetry to optimize the service life evaluation of gun propellant, in: Proceedings of the Second International Workshop on Microcalorimetry, Otley, Yorkshire, UK, 17–19 May 1999.

[4] S. Wilker, P. Guillaume, International round robin test to determine the stability of db ball propellants by heat flow calorimetry, in: Proceedings of the Second International Workshop on Microcalorimetry, Otley, Yorkshire, UK, 17–19 May 1999.

[5] U. Ticmanis, S. Wilker, G. Pantel, M. Kaiser, P. Guillaume, C. Balés, N. Van der Meer, Principles of a STANAG for the estimation of the chemical stability of propellants by heat flow calorimetry, in: Proceedings of the 31st International Conference of ICT, Paper V2, Karlsruhe, Germany, 27–30 June 2000.

[6] A. Chin, Explosives Manual, Safety Assessment for Explosives (SAFE), Quality Evaluation of Explosives, Test and Evaluation Department, Ordnance Engineering Directorate, Crane, IN, 2000.

[7] Ordnance Board, in: Proceedings P 123(1) of the Scientific Basis For The Whole Life Assessment Of Munitions—Pillar Proceeding, HMSO, 1996.

[8] M. Reading, D. Dollimore, J. Rouquerol, F. Rouquerol, J. Thermal Anal. 29 (1984) 775.

[9] Swedish Defence Standard FSD 0214, Environmental Resistance Testing of Ammunition, Test Method 113.1, 1991.

[10] AC/310-D/STANAG 4582, Explosives, single, double and triple base propellants. Stability test procedure and requirements using heat flow calorimetry—final working party draft, 2002.

[11] S. Wilker, G. Pantel, U. Ticmanis, Pierre Guillaume, Microcalorimetric investigation of energetic materials—a review of methodic development at BICT, in: Proceedings of the TTCP Workshop on Calorimetry, Otley, Yorkshire, 6–8 April 1997.