

REACTIVE CHEMICAL SCREENING

- A WIDESPREAD WEAK LINK?

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ABSTRACT

It is an accepted practice in the fine chemical industry that feeds, products and intermediates for which thermal stability data is unavailable, are first “screened” and depending on the results, might then be subjected to a more detailed evaluation (typically involving adiabatic calorimetry). The reason for this two-stage approach is economic – the costs of subjecting all chemicals to detailed scrutiny would be prohibitive.

It is frequently not appreciated, however, that this places a tremendous importance on the screening test – if this allows potentially hazardous materials to slip through undetected, the availability of more accurate downstream techniques is of no use.

This paper will present a critical review of the screening methods most widely used and also describe some industrial accidents that have arisen despite such testing. The basis of a more reliable screening method will then be presented as well as results from a recently produced instrument, the TS^U (Thermal Screening Unit), that incorporates these features.

1. INTRODUCTION

Virtually all large, multi-national chemical companies are involved with some form of hazard assessment program. An important element of this is reactive chemical testing, incorporating the assessment of feeds, intermediates and products for thermal stability so that hazards during storage, manufacture and transportation can be accurately assessed. In recent years, even medium and small companies have had to including such testing in the route from R&D to full-scale production. Regardless of the size of corporation, the evaluation procedure will frequently include a screening step aimed at separating the innocuous materials from the potentially hazardous ones.

Thermal screening is typically performed in two ways:

- (a) Theoretical evaluation of the potential energy release on the decomposition of the study material into smaller more stable species, and
- (b) Thermal scanning experimentally, where a small (few milligrams) of sample is heated over a temperature range to examine whether exothermic activity is detected.

The limitations of theoretical calculations are widely recognised (ref. 1). These include:

- The limited number of predictable reactions that can be easily assessed.
- The difficulty of unpredictable side reactions that can not be predicted and included in the calculation.
- The lack of information on the rate of heat release.
- The absence of pressure data.
- The considerable experience required to perform a reliable assessment.

It is commonly accepted that a theoretical assessment alone is rarely sufficient to permit scale-up. However, the limitations of experimental methods are not always recognised as readily and this can lead to potentially disastrous interpretations.

Experimental thermal screening methods primarily involve the use of techniques such as DSC (differential scanning calorimetry) and DTA (differential thermal analysis). These test methods have numerous shortcomings that are not always recognised, and many chemical systems are scaled-up on the basis of this data even though it is not always appropriate to do so. Some organisations will supplement this data with a reaction calorimeter, which provides information about the normal (or desired) reaction – however, this will still not make up for the shortcomings of the DSC/DTA.

2 DIFFERENTIAL SCANNING METHODS

2.1 Features of DSC/DTA Testing (ref. 1, 2)

In these tests a few milligrams of sample (often in a sealed metal pan) and an inert reference material, are heated together at a defined rate of typically 10 degree Celsius per minute. If the temperature of the sample starts to diverge from that of the reference, clear evidence of thermal activity is inferred. Using this data, it is possible to determine an "onset" temperature for the thermal event and measure the amount of heat released.

Using this information the "onset" temperature can be compared with the materials proposed operating or storage temperature. If these are similar, it might represent a potential problem. In a similar manner the information relating to energy release can be used to estimate the likely temperature and pressure rise if the exothermic reaction did occur. It is through this type of comparative analysis that DSC/DTA data can be used to estimate the severity of a possible hazard.

The benefit of this type of testing is that it can be conducted in just a few hours, requiring limited operator skill. When low running cost is also taken into account, the widespread use of DSC/DTA methods can be easily appreciated. In practice, however, these aspects should be weighed against the many disadvantages that relate to the reliability of the data and the potential problems that can ensue from not screening reactions properly.

2.2 Limitations of Differential Scanning Data

The differential thermal instruments described above are used for a wide range of analytical determinations in addition to hazard screening. In fact most DSC/DTA applications do not relate to hazard assessment at all and the comments mad in this paper will not be concerned with these alternative functions.

A design feature that contributes significantly to the ease of use and low running cost of DSC/DTA is the small mass of sample required. From a hazard evaluation perspective, this can be a serious disadvantage due to the increased uncertainty in experimental reproducibility. Whilst the testing of pure materials presents no problems, taking a representative sample of a mixture on such a small scale can be difficult. For example, in order to evaluate process intermediates (and sometimes, even products), it is frequently necessary to draw a "live" sample from a reactor. The extraction of such low sample masses that are wholly representative of the system under study can be difficult.

One of the most important piece of information obtained from thermal scanning devices is the so-called "onset" temperature for exothermic activity. However, it is important to realise that this "onset" threshold is not a fundamental property of a reaction and the measured value depends very much on the instrument sensitivity. In figure 1, the onset temperature determined by DSC is compared with that from an adiabatic instrument (using approximately 5g of sample). This information was reported by the Dow Chemical Company (ref. 3) from their historical data bank. It shows that in many cases, the "onset" temperature detected by DSC can be as much as 50 °C higher than that reported from adiabatic instruments. In fact in a substantial number of instances the difference between to two methods is as much as 100 °C. (There are also several cases where the DSC determined "onset" temperature is lower

than that reported by the adiabatic testing, but this can be attributed to the study of non-representative DSC samples).

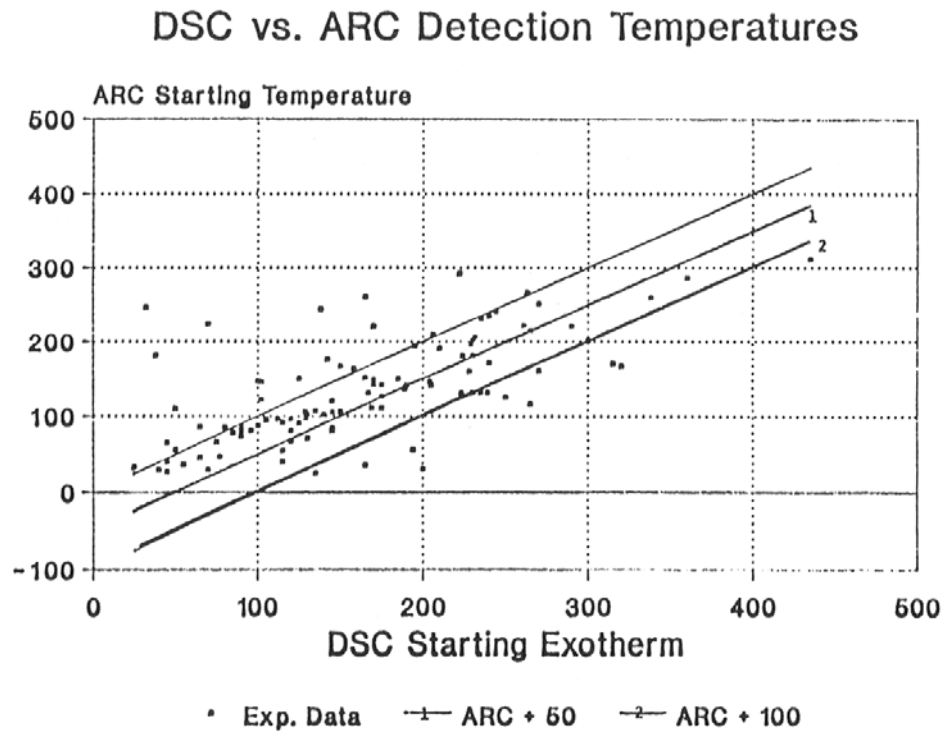


Figure 1: A comparison of “onset” temperatures between DSC and ARC data.

Most importantly the DSC/DTA type instruments do not provide any information at all regarding the pressures generated in a test. For accurate hazard assessment this information is crucial, since the extent of thermal hazard will be directly represented by the pressure generated during the reaction. It is after all the excessive pressure that causes catastrophic damage to plant and equipment.

Another important factor to consider when examining hazard potential is the aspect of time. It is vital to understand not only the amount of energy released in a process but also the rate at which energy release occurs (i.e. the reaction kinetics). Although DSC scans partially reflect the kinetics of the chemical system they do so in a very indirect and qualitative manner. The time scales determined bear almost no relation to the real life incident and unless considerable effort and rigour is put into the kinetic analysis, it is not possible to estimate the rate at which events might occur on the plant.

Taking into account all the above points, it is clear that choice of DSC/DTA, as the primary, or worse still only, method of thermal screening can be misleading and potentially dangerous.

3 PRACTICAL CASES OF HAZARDS UNDETECTED BY DSC/DTA

There are at least three incidents known to the authors, over the last few years, where major accidents have resulted, in spite of DSC/DTA data being available. For reasons of confidentiality, it is difficult to give very much detail of these cases but they all resulted in serious accidents.

The first was a fine chemicals plant in New Jersey, USA, where the mixture in a distillation column underwent violent runaway. This material had been thoroughly tested using a DSC; in this case by the operating chemical company themselves and this had revealed no signs of a potential hazard. The company was experienced in the use of calorimetry and relied on differential scanning techniques for hazard screening followed by reaction calorimetry to check the “desired” reaction. Subsequent to the accident, which caused catastrophic damage to the column plus substantial damage to neighbouring equipment, samples (around 5 to 10g) were tested in an adiabatic calorimeter where the runaway incident was readily reproduced and repeated.

The second case occurred in the Middle East, this time in a reactor vessel. The process had been run for some time on pilot plant scale without any problem. When it was due to be transferred to the commercial scale plant, three thermal evaluations were performed, two on separate DSC devices (run by two different companies) and one on the Mettler RC-1 reaction calorimeter (ref. 4). The DSC tests were performed to determine the likelihood of a thermal runaway and the reaction calorimetry test was used to confirm the heat release during a normal, controlled batch. When the process was transferred to the large scale, a violent runaway reaction occurred totally overwhelming the relief vent on the reactor. This led to an over-pressurisation of the vessel resulting in large quantities of reactants being discharged as the vessel cover was lifted under pressure. Subsequently the hot vapours released ignited and caused further damage.

The incident in the final example was less dramatic but illustrates an important point. It involved a small company that had recently acquired a DSC as its first hazard evaluation tool. The process required the mixing of two liquids at room temperature, followed by heating to 85 °C before the slow addition of the final reactant. Tests had been performed with a mixture of the two reagents added at the start and with samples of the three reactants together. No problem was detected in the first test but the second test indicated some exothermic heat release.

Based on results of the first test, it was decided that the two starting ingredients could be safely pre-mixed in drums ready for charging. However, when this was actually done, the drums started to rupture after about 2 hours of being filled. Subsequent testing with an adiabatic device (in which pressure data was measured) revealed that while the DSC had correctly reported a lack of exothermic activity, it had failed to register the fact that, even at room temperature gas was being generated at a slow rate.

4 THE TS^U AS A SCREENING TOOL

4.1 Essential Features

The TS^U (Thermal Screening Unit) has been developed to replace the DSC as the primary method of thermal screening.

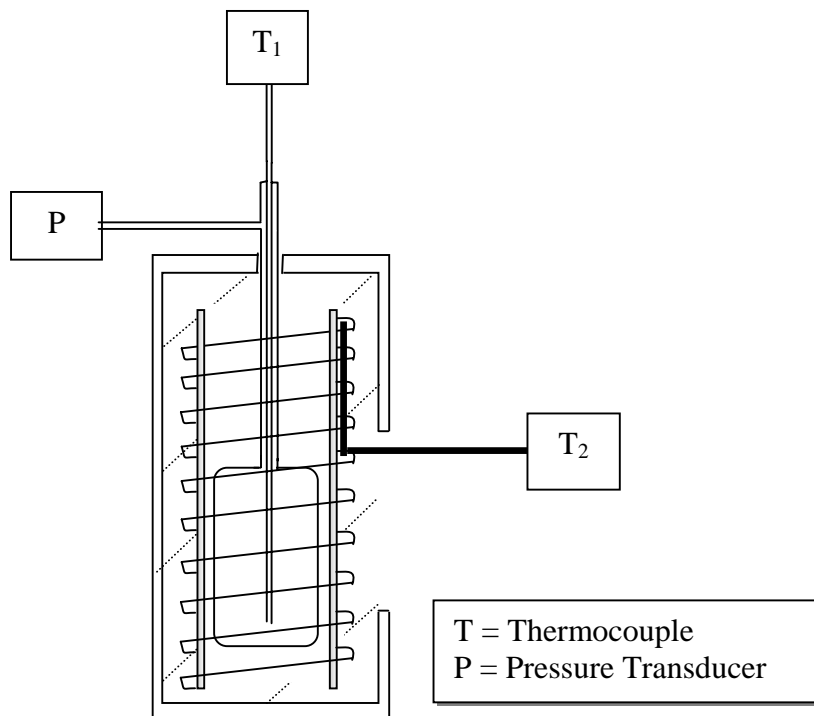


Figure 2: Schematic diagram of Thermal Screening Unit (TS^U)

Figure 3: Photograph of Thermal Screening Unit (TS^U)

A diagram of the TS^U is shown in figure 2 and a photograph is reproduced in figure 3. The sample is contained in a metal (or glass) test cell, suspended in the middle of an “oven”. The oven, essentially a metal cylinder with a heating coil wrapped around the outer surface, is heated at a user defined rate. The sample temperature follows at the same rate with a slight “offset” (which will dependant on the exact nature of the material). When an exotherm is detected, the sample temperature deviates from the background heating rate identifying the “onset” temperature. The rate of rise in sample temperature and the maximum value reached (before returning to the background rate) reflects important characteristics of the exotherm. In addition to temperature the sample pressure is also measured.

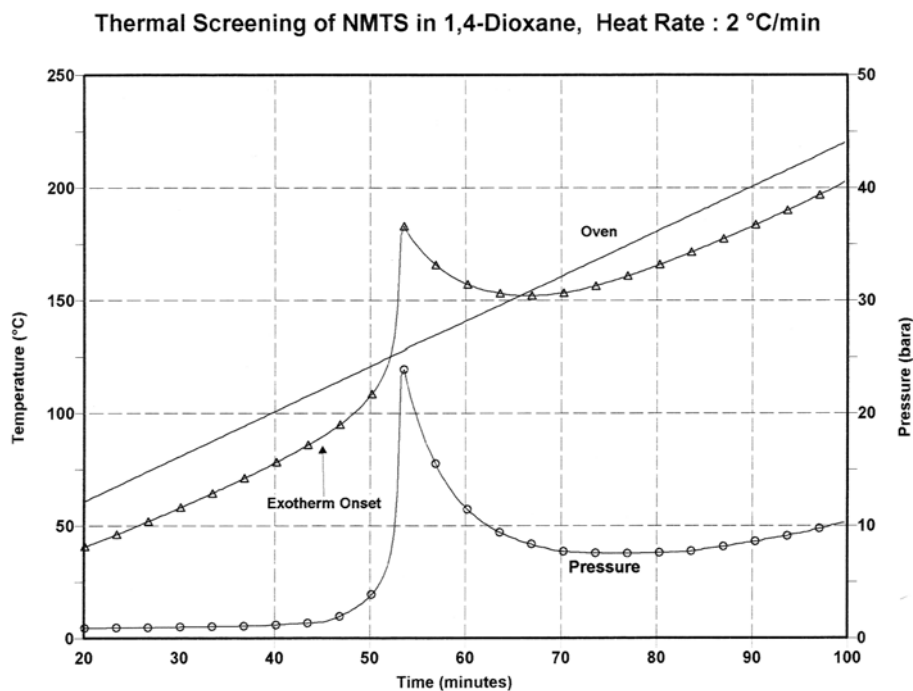


Figure 4: Thermal Screening of NMTS

An example is shown in figure 4. This is a test with NMTS (N-nitrosol-N-methyl-*p*-toluenesulfonamide) and shows the “oven” and sample temperatures and the sample pressure. The two temperatures are parallel until the sample reaches approximately 85 °C, where it begins to converge upward, indicating the “onset” of exothermic activity. Eventually after reaching a maximum the sample temperature returns to its “baseline” value and this gives a clear indication of the time-scale involved in the process.

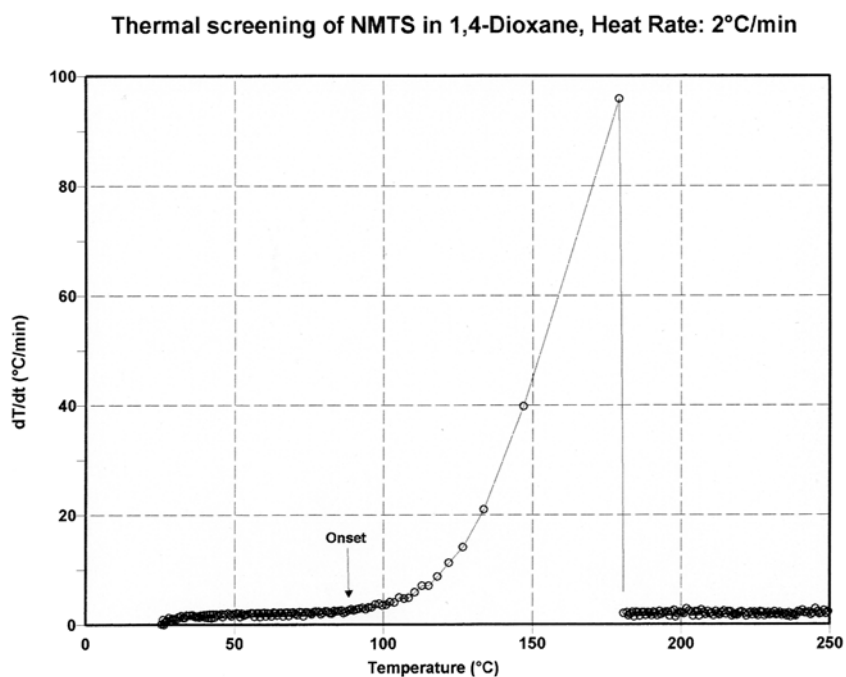


Figure 5: Thermal screening of NMTS

In figure 5, data from the above test is plotted in terms of rate of temperature rise (dT/dt) against temperature, which gives a very clear indication of the exotherm detection point. The rate of temperature rise at different temperatures is also easily obtained and provides an unambiguous measure of the rate of runaway.

While the TS^U figures are not to be extrapolated directly they are sufficiently accurate to permit a decision regarding whether the chemical presents a possible hazard potential (in which case further testing should be done) or if it is safe to proceed.

System	t_{ONSET} (°C)	t_{MAX} (°C)	$t_{MAX}-t_{ONSET}$ (°C)	$(dT/dt)_{MAX}$ (°C/min)	P_{MAX} (bar)
20% NMTS in 1,4-dioxane	85	182.9	97.9	95.8	23.9
20% DTBP in toluene	152	285.8	133.8	68.4	47.5
Crude oil*	237	321	84	9.29	105
2,4-dinitrotoluene	218	335**	117	36.7	N/A

* = Start pressure of 60 bar in pad.

** = Detonation event at 335 °C.

Table 1 – TS^U Results from Recent Studies

In table 1, data from several chemical systems, solids, liquids and mixtures, is presented. In each case the data was in line with more detailed predictions obtained from adiabatic calorimeters.

The TS^U also possesses the following additional characteristics that are important in determining its commercial viability:

- It is inexpensive, both to purchase and to operate.
- It permits the easy “set up” and “running” of tests.
- The unit uses a larger sample size than its DSC/DTA counterpart of around 1 to 5g, large enough to be representative of a plant process.
- The unit is compact enough to safely run in a standard fume hood.
- The unit directly provides pressure data.
- The unit produces data that is easy to interpret in terms of the hazard potential presented by a sample.

4.2 Comparison of the TS^U with Adiabatic Calorimeters (ref. 1, 5, 6)

Adiabatic calorimeters are traditionally regarded as the most reliable method of exotherm detection and of generating quantitative data about reaction severity. Adiabatic conditions are achieved by taking a sample cell similar to that used in the TS^U and placing it between a set of guard heaters that precisely match the sample temperature. Tests are often performed by heating the chemical in steps, holding it at each temperature until an exotherm is detected. Subsequently, as the sample temperature rises due to heat release, the guard heaters follow and thus maintain an adiabatic environment.

Data from such tests is much more reliable and representative of the large scale reactors. This is particularly true of so called low phi-factor devices, where the thermal mass of the test cell (relative to the chemicals being tested) is reduced to match plant conditions. However, tests can take longer than TS^U experiments and the instruments are more expensive to buy and run.

4.3 Operator Safety with TS^U

The containment vessel (essentially shield) that surrounds the test cell has a volume of approximately 300 cm^3 and made of heavy walled stainless steel. It is not a pressure vessel and purposely has a 1" diameter vent at the rear. The unit measures only 25 cm by 10.5 cm including the electronics. It should always be used within a fume hood with the sash lowered. If detonating explosives are tested, it should be placed in a more remote location.

To test the integrity of the enclosure, 5g of 2,4-dinitrotoluene were purposely exploded inside a 10ml stainless steel test cell. The test cell was known to withstand at least 200 bar pressure. A photograph of the test cell (before and after the explosion) is shown in figure 6.

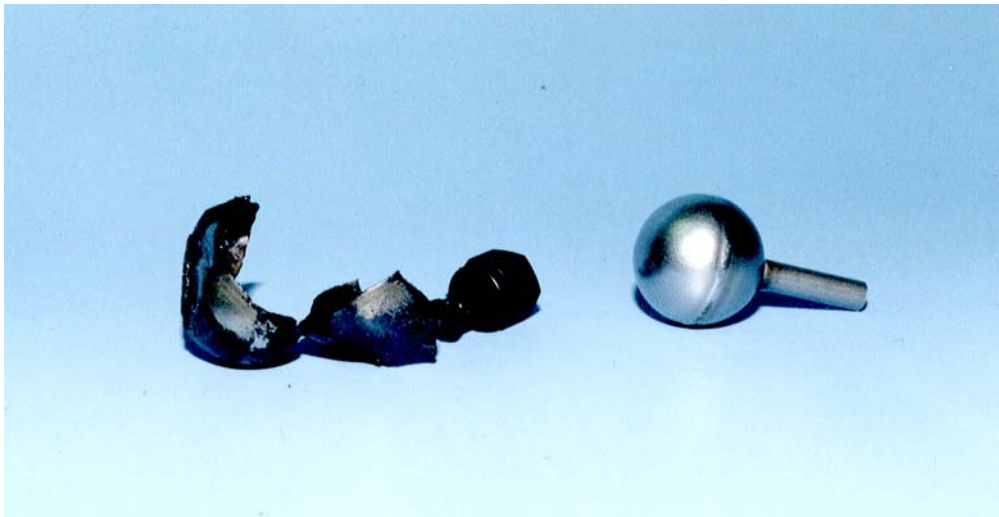


Figure 6: Test cell before and after explosion.

5 CONCLUSIONS

The use of the DSC as the main tool for thermal hazard screening represents a dangerous trend. It certainly has its application and performs a valuable function when used as part of a comprehensive testing program. However, the increasing tendency for quick, single tests possibly in combination with reaction calorimetry, does not provide a sufficient guarantee that hazardous processes will not slip through the net.

Hazard screening is erroneously seen as an activity where accuracy and reliability are unimportant, which to a limited extent is true. In the case of DSC, there are too many compromises which can (and has) led to accidents.

The TS^U has been developed as a preferred alternative to the DSC, being no more expensive but just fast and easy to use. Turnaround time between experiments is fast, requiring only removal of the used test cell and insertion of a new one. It also importantly provides data that is more reliable and in a form that is easy to interpret. Pressure data accompanies the temperature data and the sample sizes are large enough to be representative of large scale process.

6 REFERENCES

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