CURRENT TECHNIQUES FOR THE ASSESSMENT OF UNSTABLE SUBSTANCES

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Techniques for assessing the ignition sensitiveness, thermal stability and propensity to detonation or rapid deflagration of chemicals that react exothermically have been in use for many years. However, moves to classify substances in terms of their explosive properties in transport, storage and use, by various classification schemes (flow charts) require standardisation of existing tests, and safety assessments in terms of the manufacturing hazard also require the application of these and certain new techniques.

INTRODUCTION

A very wide range of techniques is now available to the investigator who wishes to assess the properties of energetic materials. In some ways his task is easier than in the past, due to the availability of sophisticated methods such as differential scanning calorimetry or accelerating rate calorimetry. On the other hand the interpretation of results from such small scale methods is open to question. Often it will prove necessary to perform a relatively crude, large scale test to assess the potential hazard of a real system, but these too have their drawbacks in terms of repetition to provide a suitable statistical base.

Before examining experimental techniques, we define an unstable substance according to Clancey[1] as a substance which can undergo an exothermic change by itself under conditions which are likely to occur during manufacture, processing, storage or transport. "By itself" in this context means "in the absence of any other substance with which reaction may occur" although, in many cases, an external stimulus, eg heat, is required to promote instability. The process following the onset of the exothermic reaction is well documented, with the heat of reaction pre-heating unreacted material, subsequent rate acceleration due to the heat evolved, and possible explosion if the rate of heat build-up is greater than the heat losses from the system. Some examples of chemical classes that are potentially dangerous are peroxy-, nitroso-, nitro-, azo- and diazo- compounds and nitrate esters.[2]

It is the intention in this paper to examine a wide range of tests used by the Health and Safety Executive (HSE) laboratories at Buxton and to point

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out where anomalies may exist. Mention will also be made of the progress in recent years to try to harmonise testing procedures. Finally, some new techniques will be described with an indication of how their results relate to those from more established methods.

RESPONSE TO MECHANICAL STIMULUS

Before starting to handle any potentially hazardous substance it is essential to know how sensitive it may be to rough handling. For example, it would be unwise to attempt to tamp a powder until it were known that the powder was not likely to be initiated by friction. The HSE laboratories at Buxton employ a range of tests to establish sensitiveness to friction, impact and a combination of both.

a) Friction. We use the Koenen friction apparatus[3] in which the sample is placed on a small porcelain tile and dragged under a loaded porcelain stylus. Glowing is often seen at the point of contact. The estimation of whether an ignition or decomposition has occurred is subjective. The method is not suitable for liquids since a lubricating effect occurs at the point of contact. Also only porcelain surfaces are involved and these are not commonly encountered in practice. The test is "tuned" to materials that are very sensitive, and experience with the test shows that a large majority of samples, including dinitrobenzene, give a negative result at the highest loading attainable in the machine. This test is, however, accepted internationally and appears in ADR, RID and EEC[4,5,6] legislation and in the UN explosives classification scheme[7].

b) Impact. Three types of apparatus are available at HSE, namely a version of the Woolwich drop-ball impact machine[8], the Fallhammer[9] and the Rotter[10]. The first of these is unique to Buxton and for this reason is being phased out. Hence it will not be discussed here. The Fallhammer is now widely accepted throughout Europe although the interpretation of results in terms of explosions or ignitions (positive results) and decompositions (negative results) is still open to discussion. The Rotter was developed within the Ministry of Defence for testing explosives. Like the Fallhammer it employs a falling weight with the criterion for a "fire" being the evolution of at least 1ml of gas. At present a program of work is being arranged to investigate relationships between results from these two tests, along with interlaboratory reproducibility. Also, an opinion must be evolved as to whether the minimum ignition level on a 0/6 basis (Fallhammer) or the 50% height (Rotter) is the better measure from a safety viewpoint. Furthermore, reference standards need to be better defined. Whilst the RDX which is employed as a reference standard for the Rotter is very well defined, the same cannot be said about the dinitrobenzene which is mentioned as an EEC standard, PETN (UN), and tetryl (ADR/RID). PETN, for example, depending on the source, can have a Rotter F. of I. of between 30 and 50. Clearly this is unsatisfactory if legislation is couched in terms of "less sensitive than...".

c) Impacted friction. The combination of friction and impact is likely to be encountered in practice and is simulated in a crude test whereby an experienced operator delivers a series of glancing blows to the sample on an anvil. In the "Impacted Friction Test[11]" used at Buxton, the weight and composition of the hammer may be varied as may the strength of blow and nature of anvil but we are considering rationalising the test with the "Mallet Friction Test" employed by the Ministry of Defence[12].

In this test, both the blow and the mallet head weight are kept constant and

a maximum of 50 blows is delivered in any one test. However, due to the difficulties in exactly specifying test parameters, these tests are not widely accepted. Care must be exercised in the interpretation of results when either the hammer or anvil is suspected of reacting. Such a situation arises, for example, when a wooden mallet is used to deliver blows to a mixture containing a chlorate or other powerful oxidiser.

d) In a move to give a more quantitative measure of frictional hazard for solids, the Ministry of Defence developed the Rotary Friction Machine[13]. This has been commissioned at Buxton and is still being evaluated. The machine drags a ground steel flywheel, which is at a preset (adjustable) velocity across the sample which is compressed against the flywheel by a ground steel bar at a preset (adjustable) load. A "Figure of Friction" with reference to standard RDX is obtained by the Bruceton technique as in the Rotter test. It remains to be determined whether this apparatus will replace the mallet/anvil test or prove to be more informative than the Koenen friction machine mentioned earlier.

RESPONSE TO ELECTRIC SPARKS

As in the case of sensitiveness to mechanical initiation, it is important to know, for handling purposes, whether a material is sensitive to initiation by static electricity.

The electric spark test[14] gives an indication of susceptibility to spark initiation although recent work has suggested that the absolute value of spark energy passing through the sample may be difficult to assess and that results should only be used on a comparative basis. The test employs three energy levels—4.5J, 0.45J and 0.045J. Should ignitions be observed with the lowest energy, further testing is needed to determine whether antistatic or fully-conducting conditions should be employed when handling the substance.

RESPONSE TO FLAME AND HOT SURFACES

This essentially gives an indication of ignitability although the subsequent burning behaviour of the sample may serve to highlight flammability characteristics.

a) Again, as an aid to safe handling of a material, a series of ad hoc ignitability tests, described by Koenen[15] is applied to some samples we receive. These tell us if a hazard exists from very hot surface contact, but do not predict behaviour under longer term, more gentle heating. Essentially samples of the substances are touched by a red hot rod, thrown onto a red hot dish, subjected to cerium-iron sparks and subjected to flame from a powder fuse. The Bickford fuse test[16], widely used in MoD, is used *by us in place of the powder fuse test described by Koenen. The major* difference is that in the former, the sample is confined in a test-tube, whereas in the latter the material sits as a small heap on a plate.

b) Flammability is assessed using the "train" test as required for the EEC directive 67/548/EEC[17]. Here a triangular mould of the solid sample, is subjected to the flame from a burner and the rate of flame spread or decomposition propagation is noted. This test is currently under consideration by the UN Committee for the Transport of Dangerous Goods for the classification of flammable substances. Formerly the MoD train test[18] was used by us but this is no longer the case in the interests of harmonisation and the provision of data which may be used for classification.

c) <u>Deflagration under confinement.</u> In the UK time-pressure test[19] a confined sample (5g) is subjected to the incendive flame from a pyrotechnic ignition system and the rate of pressure rise is measured. This test, which is now a UN test, requires measurement of the time taken for the pressure to rise from 100 psig (690 kPa) to 300 psig (2070 kpa). The sample is considered to present a hazard of explosion by deflagration if this time is less than 30 ms. The test is applied to both solids and liquids, the ignition system being protected by a plastic sheath in the latter case. Interlaboratory trials which we have undertaken with industry and other test laboratories in OECD-IGUS (International Group of Experts on the Explosion Risks of Unstable Substances) have given good repeatability and reproducibility.

RESPONSE TO HEATING

This section deals with indirect heating tests.

a) <u>Koenen steel tube test</u>[20]. This test is widely used in Europe and is described in ADR/RID, EEC and UN documents. The test material is held in a 24mm diameter steel tube fitted with an orifice plate, and is subjected to severe heating from four gas burners. An "explosion" occurs when the tube fragments into at least three pieces. The minimum orifice diameter to cause this is determined. We consider it important to use a "run-down" procedure whereby the orifice diameter is gradually reduced, since some materials can exhibit "explosive" behaviour at one orifice diameter, but not at a smaller diameter[21]. The reason for this anomalous behaviour is not fully understood. Harmonisation of the test method on the international level has shown up difficulties which are discussed later.

b) <u>Steel box test</u>[22]. In this test the sample is held in a 8cm cubed steel box with a crimped-on lid, and is heated with either gas burners or a wooden crib. The procedure is described in ADR/RID and specifies crib timber of 0.25m diameter and 0.5m length! We use this test when we suspect that there may be scaling problems with the Koenen Tube test eg in the testing of diluted explosives which are used as drugs.

c) <u>Dutch pressure vessel</u>[23]. This is similar in principle to the Koenen steel tube test except that as well as having an orifice plate the vessel is also fitted with a bursting disk. The Koenen critical diameter of 2mm for exhibition of explosive properties roughly corresponds to one of 9mm in the DPV test although, as would be expected, exact agreement between the two methods is not always achieved. The DPV test was originally devised for assessing the properties of organic peroxides and discussion within the UN Organic Peroxides experts group is aimed at harmonising this test with the American and Japanese pressure vessel tests which operate on similar principles.

RESPONSE TO DETONATIVE SHOCK

In the UN classification schemes for explosives, organic peroxides and self-reactive substances, the first test criterion to be applied to a substance to assess whether or not it is an explosive is that from the response to detonation test. We employ various types of test of response to detonative shock as outlined below.

a) <u>50/60 tube test</u>[24]. This well-known test is one, among others, which forms part of the UN classification schemes and consists of subjecting the sample, in a tube of 50mm internal and 60mm external diameter, to the shock from either a high explosive booster or from just a detonator. The beha-

viour of the sample is assessed in terms of the propagation of the shock as shown by the condition of the steel tube. For the UN explosives scheme only, propagation and non-propagation are considered and the result is simple to interpret, but in the organic peroxides scheme "partial propagation" is taken into account and difficulties can arise in the case of fading detonation. The test is performed in duplicate and hence a substantial volume of sample is required to fill the 0.5m long tube twice. This can be difficult for manufacturers whose product has to be tested for non-inclusion in Class 1 where the annual production of the product is far less, or not much more, than the amount needed for the test. In such cases it would be desirable to have a smaller-scale test, perhaps the NOL gap test[25], for example, but sometimes we have to rely on the Ballistic Mortar results alone (see below).

b) HSE also employs other types of tube test to quantify the extent of propagation, such as the 50/70, 4" and cap sensitivity tests[26,27,28], but these will not be discussed here.

c) Ballistic mortars[29]. We employ two types of mortar (MkIIId and MkI) to examine the effect of the shock from a detonator on a sample of an unstable substance under high and low confinement. The recoil of the mortar is used to quantify this effect relative to picric acid as a reference standard. The mortar was originally designed to replace the costly Trauzl lead block test[30] and hence good agreement is to be expected between these methods when the same type of detonator is employed. Recent research by workers in Japan has questioned the current method of treating the results and this is now under discussion at an international level. Although the ballistic mortar does not feature directly in the UN explosives classification scheme, it is required for organic peroxides which are being considered for "bulk" conveyance. Their power must be less than 10% that of picric acid.

THERMAL STABILITY TESTING

Many tests have been developed over the years to examine the behaviour of a substance under storage at a particular temperature. These tests are readily applicable to many peroxides and substances in the self-reacting class and purport to measure the Self Accelerating Decomposition Temperature (SADT). Of the tests listed in the UN "Orange Book"[31], we can carry out the following:

a) Adiabatic Storage Test[32]. Here, one litre of sample is introduced into a Dewar vessel and heated in an oven under near-adiabatic conditions. By using constant power, the specific heat can be calculated. The temperature rise of the sample caused by self-heating is monitored as a function of time and, by knowing the specific heat and mass, the heat generation can be calculated. Provision is made to cool the sample if decomposition is too rapid. The method is particularly suited to "bulk" quantities.

b) Heat accumulation storage test[33] (Wärmestaulagerung). 400ml of sample is placed in a Dewar vessel of 0.5 litre capacity which has specified heat loss characteristics. The Dewar is placed in a test chamber at a selected temperature and left for at least seven days. If no decomposition occurs the test is repeated with a fresh sample at a higher temperature. The SADT, rounded to a 5 degC interval, is reported as the minimum temperature at which self-accelerating decomposition occurs. This test is realistic in that it simulates, to a certain extent, conditions that may occur in practice and allows control temperatures for storage and transport to be established for packages. On the other hand it is extremely slow and if a

range of vessels are not available for operation at different temperatures, the determination of the SADT may take several weeks. Also, as the sample is allowed to self-heat the end event can be a mild temperature rise or a vigorous explosion, depending on the nature of the sample. Containment of the sample and reaction products could be particularly important if there are associated toxicological hazards and we have an autoclave for testing where we believe that the sample and/or products need to be retained and chemically destroyed.

TEMPERATURE RAMPING TECHNIQUES

In this type of technique the sample is heated at a prescribed rate. In general the sample sizes are small and the determination of the onset of exothermic decomposition will be affected by the heating rate.

a) Hot Stage Microscopy. We have a Stanton Redcroft HSM-5 and this apparatus is used to give a quick visual examination of the effect of heating. The sample (usually a few milligrams) is placed in a small open container and heated under a microscope. The heating rate is variable but is normally 10 or 50deg C/minute. The sequence of events is recorded on videotape and phase changes, decompositions and ignitions can be monitored as a function of temperature. Air is usually the medium surrounding the sample although other gases may be employed. A reflected light intensity probe is also fitted and serves to aid interpretation of phase changes which result from crystal modifications.

b) Differential Scanning Calorimetry (DSC). This widely used technique consists of heating a milligram-sized sample and measuring the heat input and output necessary to maintain the sample at the same temperature as a reference sample through exothermic and endothermic reactions. The heat of reaction (both exo- and endothermic) can be calculated and onset temperatures can be measured. The data acquisition package available for our Perkin Elmer DSC-2 allows us to assess order of reaction and activation energy quickly. However, the results must be very carefully interpreted. For example, exothermic decomposition of bulk quantities of material can occur at temperatures as much as 100 degC below the exotherm onset temperature indicated by DSC.

c) Accelerating Rate Calorimetry (ARC). This relatively new technique has been extensively described[34] and many claims have been made as to the information that can be obtained. We have purchased this equipment but, to date, have only limited experience in its use and in the interpretation of results. In essence, a sample of a few grams is introduced into a "bomb" whose temperature is slowly ramped up in set stages. At each temperature, the machine searches for an exotherm, as exhibited by a sample temperature rise rate of over 0.02 degC/minute. If such an exotherm is detected, it is followed under near adiabatic conditions to completion. Temperature and pressure are measured. If no exotherm is detected the temperature is raised to the next level and the process is repeated. The amount of operator time is certainly minimal, since a sample can be put on test in the afternoon and the results are ready the following morning. Exotherm onset temperatures predicted by ARC are much lower than those from DSC, and from our limited experience appear to relate well to those SADT values obtained from the Wärmestaulagerung test described earlier. For example, one material we examined gave an onset temperature of 194 degC in DSC, an SADT of 120 degC in the Dewar vessel and a lowest detectable exothermic onset temperature of 117 degC in the ARC. Further work is continuing with ARC to evaluate the data that it gives.

d) EEC auto-flammability test[35]. For this test a *temperature-programmed* oven of about two litres capacity is fitted with natural air circulation and explosion relief. The sample is held centrally in the oven in a very fine-meshed cube of 20mm side and the oven temperature is raised from ambient at a rate of 0.5 degC/minute. The temperature of the sample is monitored. The temperature of the oven at which the temperature of the sample reaches 400 degC by self-heating is called the self-ignition temperature. This test is suitable for finely divided materials and is not suitable for liquids or pastes that lose their viscosity on heating. It is a comparative test and gives an indication of oxidative self-heating characteristics. We found it particularly useful in determining how these are altered by variations in the constituents of a mixture, in particular how the ignition temperature of an organic based drying agent was lowered by contamination with inorganic nitrates and nitrites carried over from a salt bath[36].

CONCLUSIONS

With many types of testing in the field of hazard assessment it is particularly important not to base an assessment on the results from only one test. This is especially true in the assessment of energetic substances since so many tests exist, utilising different sample sizes and measuring different properties. The tests outlined in this paper are those in use in our laboratory. They represent a fraction of those that have been devised, many of which are in extensive use and which appear in standards and testing manuals. In general, therefore, it is necessary to perform a number of tests on a material to assess its potentially hazardous nature starting with sensitiveness to mechanical initiation. If any one test appears at a decision point in a classification flow chart, then it is essential that the test be specified in absolute detail and that all users are operating to the same protocol. A good example is the Koenen steel tube test described earlier, the result of which determines whether a thermally stable energetic material would be a candidate in the UN classification scheme for explosives and whether an organic peroxide or self-reactive substance be assigned an "E-mark" in the UN "Orange Book". Similarly, in EEC Directives it determines whether a substance be notified and labelled for use as "explosive". Fragmentation of the steel tube into three or more pieces at an orifice diameter of 2mm or more is the deciding factor. Many criticisms can be levelled against this test. For example, the criterion of three or more tube pieces would appear, at first sight, to be quite arbitrary. What is the significance of three pieces?--is not an explosive effect also shown if the tube violently ruptures but only two pieces are produced? Furthermore, the specification of this very important test differs in various standards as tabulated below:

Authority	Jet	Gas Press	Flow Rate	Method	Filling
EEC	0.6mm	500mbar	3.2 l/min	N/A*	3 inc-80N
UN	0.6mm	50mbar	3.2 l/min	Run-down	3 inc-80N
ADR	0.8mm	500mm wg	1.7 l/burner/min	Unspec	Light tamp
RID	0.8mm	500mm wg	1.7 l/burner/min	Unspec	Light tamp

1 bar = 10200 mm water gauge (wg)
1 mbar = 10.2 mm water gauge (wg)
* 3 trials at 2mm dia, then 3 at a larger dia eg 6mm.

Not only do these anomalies exist, but it is still not certain whether the currently specified UN and EEC filling method whereby three equal volume increments are tamped with a load of 80N, gives a uniform pressing density of the sample within the tube which can be repeated between laboratories. OECD-IGUS has been examining these anomalies and hopes to resolve them by a test program involving several of the major test houses throughout Europe.

The Koenen test should also not be considered in isolation since recent experience has shown that a plastic high explosive (PE4) can pass the UN test by rapid extrusion through the orifice; the tube peels open and does not fragment. This raises the question as to whether the Pass/Fail criterion of such an important test should not simply be the ability or otherwise of the tube to maintain its physical integrity as opposed to the fragmentation into three or more pieces.

Not only that, but substances may exhibit explosive behaviour in the Koenen steel tube test but not in another test and vice versa. For example, musk xylene gave a limiting diameter of 12mm but did not ignite in the UK time-pressure test, whereas a different material had a Koenen limiting diameter of less than 1mm but exhibited a pressure rise from 100 to 300 psig in 24msec.

This may seem to be singling out one test for harsh criticism but similar comments can be made about many of our other well-accepted tests. For example, most flammability tests can give rise to misleading results because the sample size is low and a completely different effect could be observed with a large sample under conditions of high heat flux; the Koenen friction test is unrepresentative of surfaces met in practice; the impacted friction test is crude and operator dependent; the 50/60 tube test does not have the steel specified to the necessary quality (St 35) etc.

Despite these comments, the basic framework for testing and classification of explosives, organic peroxides and self-reactive substances is now well established. However, many more problems would exist in the mutual acceptance of data were it not for the, perhaps little recognised, co-operation between the testing laboratories who comprise OECD-IGUS, wherein the fine detail of test methods can be critically examined. Such detailed argument is not suited to the UN groups who often have vast agendas on wide-ranging topics related to the conveyance of dangerous goods. As can be seen, much still has to be done in the field of harmonisation of the test methods for the assessment of the explosive and self-heating hazards of

unstable substances before we can be sure that we are all testing to an agreed protocol and interpreting results to common standards.

The views expressed in this paper are those of the author, and not necessarily those of the Health and Safety Executive.

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