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A study of some factors that affect the impact sensitiveness of liquids determined using the BAM Fallhammer apparatus

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Abstract

We report the results of a systematic investigation of the effect of two experimental parameters on the results obtained using the BAM Fallhammer test for liquids. We demonstrate that the impact sensitiveness of liquids can be highly dependent on the initial gap set between the impact surfaces and also on the position occupied by the test material. From pressure measurements taken in the reaction chamber, a relationship is derived between the pressure generated on impact and the likelihood of ignition. The findings of our study, particularly the dependence of sensitiveness upon the initial gap, will have implications to schemes that employ the BAM Fallhammer test as part of the determination of hazardous properties (e.g. UN Test Series 3). Some recommendations are therefore made concerning changes to published impact test procedures for liquids.

1. Introduction

The sensitiveness of energetic materials, which is defined by Bailey and Murray [1] as "a measure of the relative ease with which an explosive may be ignited or initiated by a particular stimulus", is an important parameter in hazard evaluation. Tests for sensitiveness are given in the UK's Sensitiveness Collaboration Committee (SCC) Manual [2] (to assess safety for UK Military Service use) and also in the UN Tests and Criteria Manual [3] (to assess safety in relation to transportation). European Community (EC) legislation [4] also requires sensitiveness information in relation to the notification, supply and use of bulk chemicals.

Sensitiveness tests are available to measure the response of solids and liquids to impact and friction stimuli. For impact, the BAM Fallhammer is probably the most

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widely used apparatus: it appears in both the UN Manual and in the EC requirements.

Examination of the BAM Fallhammer test procedures given for liquids in these two sources indicates that, whereas the UN Manual specifies where the liquid sample should be located for the test (Fig. 1), the EC document does not. Tests done at HSE's Explosion and Flame Laboratory with the energetic liquid nitromethane placed centrally on the upper surface of the lower cylinder (as permitted by the EC test scheme) gave a value of 40 J for the limiting impact energy required to induce ignition. It has previously been incorrectly reported that the UN test procedure was used [5]. In contrast, experiments at the TNO Prins Maurits Laboratory [6] which employed the UN method of placing the nitromethane liquid in the groove between the lower cylinder and the guide ring gave a limiting impact energy of $\leqslant 1$ J.

The experiments with nitromethane indicated that large differences in results could arise from relatively minor changes in the test procedure, and this could clearly have implications to the determination of the hazard presented by a liquid material. We therefore undertook a series of experiments to obtain information on the effect of sample placement in the BAM Fallhammer on the impact sensitiveness of a limited range of liquids. The investigation also examined the dependence of the result on the gap between the upper and lower cylinders. Although both the UN and EC tests specify a 1 mm gap, it was important to examine whether any variation in this (through, for example, poor setting prior to test) could affect the test result.

We believe that information of this type forms useful technical input to discussions on revision of the UN Tests and Criteria Manual.

2. Experimental

The present study examined seven liquids, which could be broadly classified as energetic, explosive or flammable (Table 1).

Table 1
Test liquids

Energetics	Explosives	Flammables
Nitromethane UN Round Robin sample [6]	Casting liquid 76% Nitroglycerine 23% Triacetin 1% 2-Nitro diphenylamine	Methanol Rathburn Chemicals Ltd. HPLC grade
Isopropyl nitrate Fluka cat. no. 59640 >98%	Methylamine nitrate 78% solution	Dodecane Fluka cat. no. 44020 >98%
2-Butanone peroxide Methylethylketone peroxide Fluka cat. no. 04390 Contains approx. 50–60% plasticiser (phosphoric acid + phthalic acid ester)		

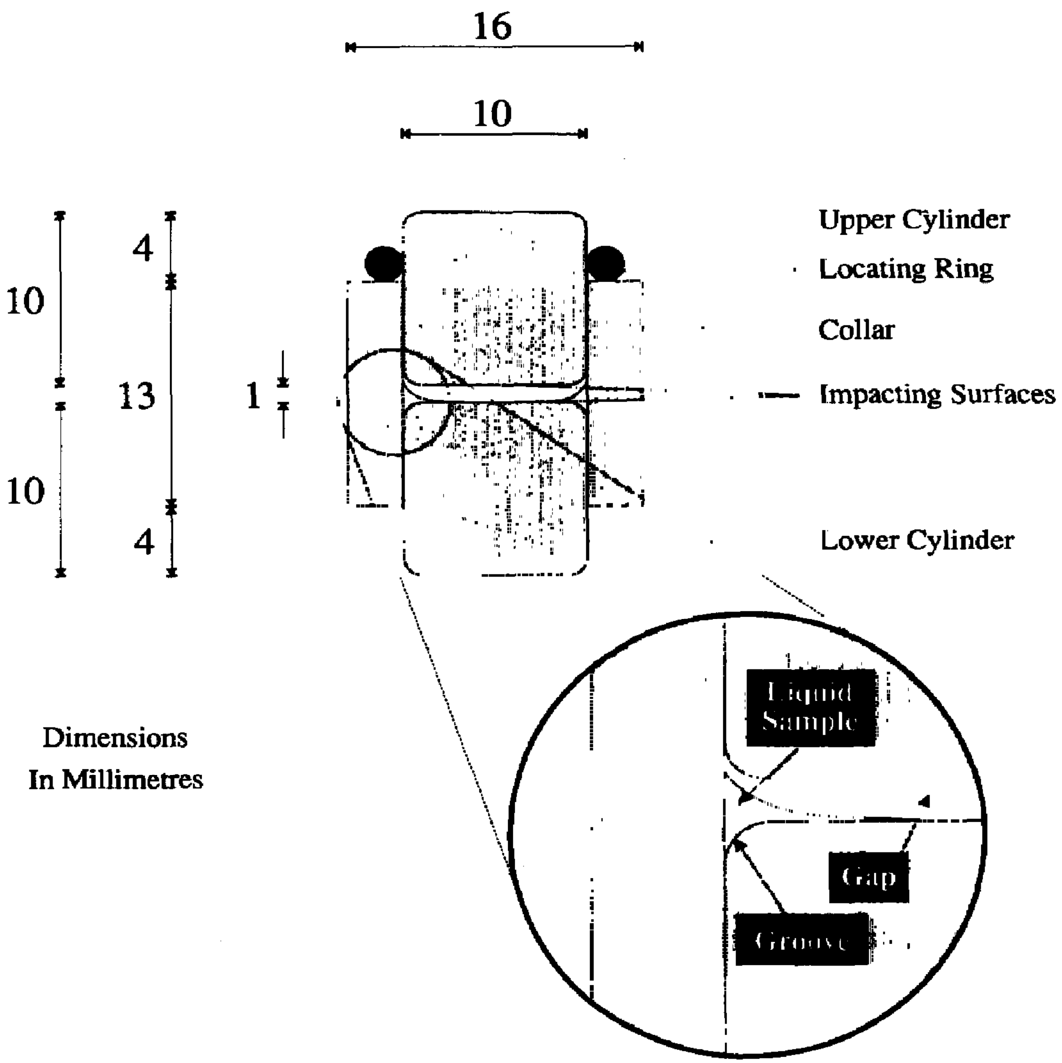

Fig. 1. United Nations experimental arrangement for determination of the sensitiveness of liquids using the BAM Fallhammer apparatus [3].

Full details of the BAM Fallhammer impact test procedures for liquids are given in the published literature [3, 4].

The UN scheme employs a 1 mm gap between the upper and lower cylinders and requires 40 mm^3 of the liquid to be placed in the groove between the collar and the lower cylinder (Fig. 1).

In order to examine the effects of variations in both the placement of the sample and the gap between the cylinders, experiments were performed using the following procedures:

(i) A standard UN test with a 1 mm gap between the cylinders, and 40 mm^3 of liquid pipetted around the edge of the lower cylinder. Koenen et al. [7] have reported

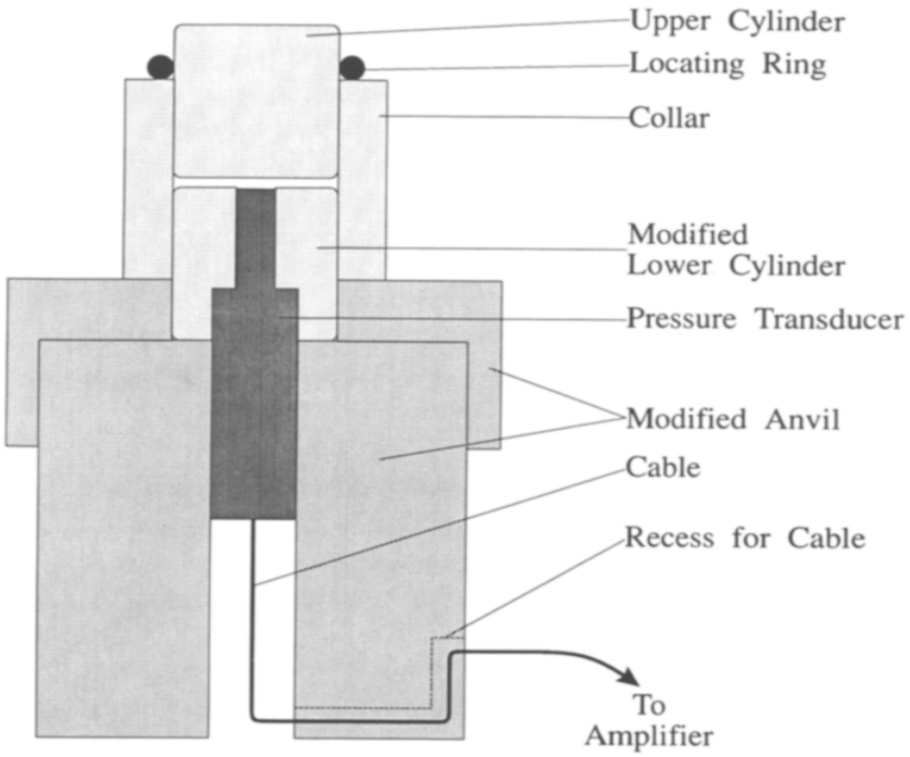

Fig. 2. Modified housing used to determine pressures generated in the BAM impact test.

that in this configuration the test sample occupies a layer 0.5 mm deep on the top of the cylinder.

(ii) A standard UN test, except the gap between the upper and lower cylinders was 2 mm.

(iii) A standard UN test, except the gap between the upper and lower cylinders was 0.5 mm. In this configuration the sample occupies virtually all the free volume in the test chamber.

(iv) A standard UN test, except the 40 mm^3 of liquid sample was pipetted into the centre of the upper surface of the lower cylinder.

Steel shims of thicknesses 0.5, 1.0 and 2.0 mm were manufactured to a tolerance of $\pm$0.02 mm. To set the gap between the cylinders, a shim of the appropriate thickness was placed on the lower cylinder, the upper cylinder pushed down and the locating ring placed in position at the base of the exposed barrel of the upper cylinder. We consider that this provided a more accurate method than using a depth gauge as suggested in the UN Manual [3], provided that care was exercised to ensure that the locating ring was not disturbed when removing the shim.

A modified cylinder and anvil were manufactured from stainless steel to permit measurement of typical pressures generated in the vicinity of the sample during testing. This unit enabled a Kistler type 601H piezo-electric pressure transducer to be incorporated in the lower cylinder (Fig. 2). The diaphragm of the transducer was positioned parallel to the face of the cylinder but 0.02 mm below the surface to avoid the effect of direct impacts: this arrangement limited the maximum increase in test volume to <1.5%. The amplified signal from the pressure transducer (which had a linearity of 0.3%) was digitally recorded with a logging frequency of 1 MHz.

Since in conventional experiments the presence of the liquid at the interface between the collar and the lower cylinder effectively produces a seal, this was reproduced in the pressure measuring experiments by ensuring that the modified lower cylinder was manufactured to be a very tight fit within the collar.

The modified assembly was used to record the pressure generated in the apparatus with impact energies of 1.0 and 1.5 J and initial gap settings of 0.5, 1.0 and 2.0 mm. Experiments could not be done with impact energies in excess of 1.5 J because of the distortion caused to the modified lower cylinder. Three experiments were done for each set of experimental conditions.

3. Results

Limiting impact energies (LIEs) for the liquids tested using each of the four methods outlined above are given in Table 2. By assigning values of 0.5 and 51 J to results recorded as ≤1 J and >50 J, respectively, it was possible to present these data graphically as in Fig. 3. It is apparent that the LIE values of some of the liquids tested change significantly as the gap setting is varied.

Comparison of the data obtained from tests with a 1.0 mm gap, and the liquid sample placed either centrally or in the outer groove, indicates that nitromethane is the only one of the liquids tested for which sample location was important. Varying the sample position with this liquid can exert a dramatic effect on the numerical result, and therefore on the overall result of the test.

Table 2
Impact sensitiveness results determined using the BAM Fallhammer apparatus

Liquid	Sample around edge: 0.5 mm gap LIE (J)	Sample around edge: 1.0 mm gap[a] LIE (J)	Sample around edge: 2.0 mm gap LIE (J)	Sample in middle: 1.0 mm gap LIE (J)
Nitromethane	>50	5	≤1	>50
2-Butanone peroxide	>50	2	≤1	—[b]
Isopropyl Nitrate	>50	>50	2	>50
Casting liquid	≤1	≤1	≤1	≤1
Methylamine nitrate	>50	>50	10	>50
Methanol	>50	>50	>50	>50
Dodecane	>50	>50	50	>50

[a] Standard UN test procedure.
[b] 2-Butanone peroxide was not tested in this instance because the sample would not remain on the upper surface of the lower cylinder. Instead, it flowed into the groove formed between the collar and lower cylinder (as required for the standard UN Test 3 (a) (ii) procedure).

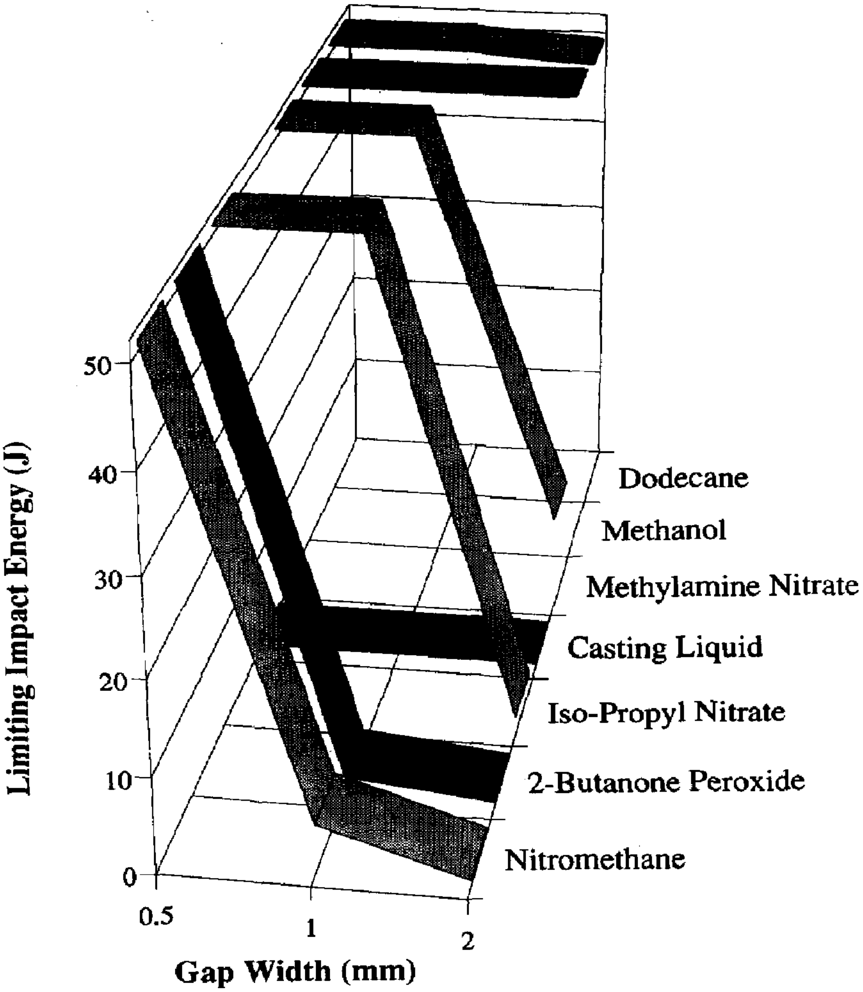

Fig. 3. The dependence of the LIE values for a range of liquids on the gap width used in the BAM Fallhammer test.

The results obtained for pressure measurements within the test chamber (Table 3) indicate that, over the limited range of gaps and impact energies examined, the peak pressure is directly proportional to the gap width (Fig. 4).

Apart from methanol and casting liquid, which had sensitivenesses beyond the limits of measurement of the test, all the liquids displayed LIE values that decreased as the gap increased. Since the likelihood of obtaining an ignition increases as the gap increases, this suggests that the occurrence of a positive event is directly dependent on the pressure generated within the system.

4. Discussion

The mechanism of ignition in liquid impact test methods has been investigated by several workers. Berthelot [8] thought that solid or liquid explosives ignited when,

Table 3
Results of pressure measurements in the BAM Fallhammer test chamber

Gap (mm)	Peak pressure for 1.0 J impact energy (kPa)	Mean peak pressure for 1.0 J impact energy (kPa)	Peak pressure for 1.5 J impact energy (kPa)	Mean peak pressure for 1.5 J impact energy (kPa)
0.5	370	360	470	510
	360		530	
	360		540	
1	640	610	1110	1190
	570		1260	
	610		1190	
2	1330	1350	1790	1700
	1390		1670	
	1330		1630	

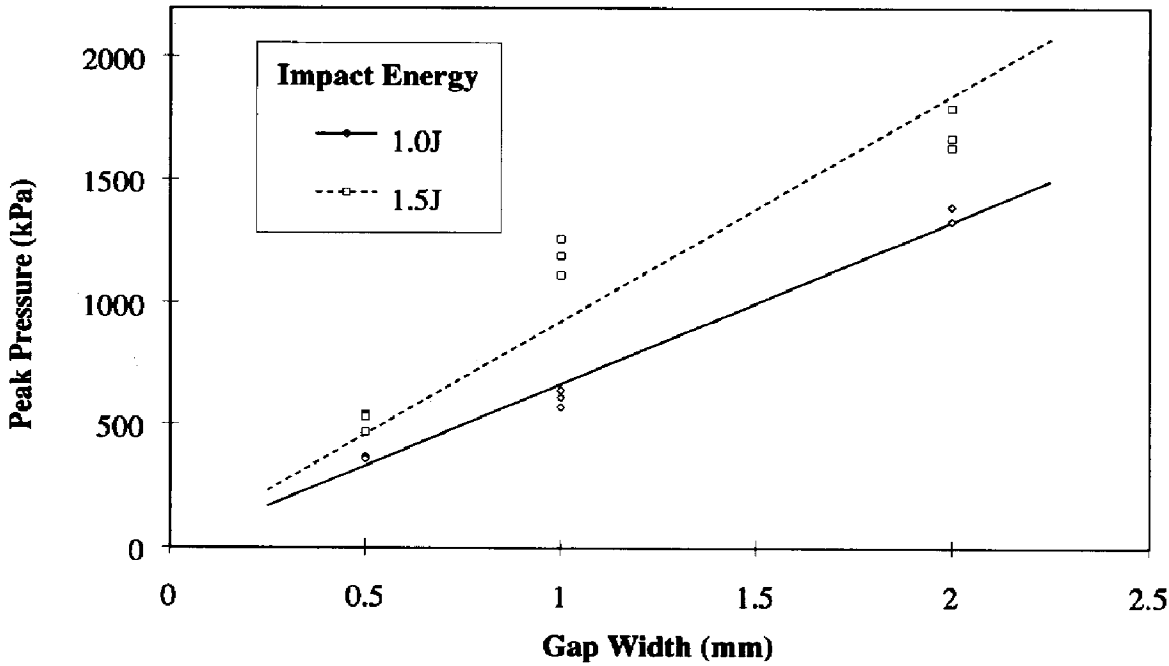

Fig. 4. The dependence on gap width and impact energy of the peak pressure generated within the BAM Fallhammer apparatus.

somewhere within the mass, the temperature was raised above the deflagration point. Thus, he proposed a mechanism for explosion induced by impact that involved conversion of the mechanical energy stimulus into heat which was capable of raising the substance to the temperature at which it explodes. Bernal [9] pointed to the heat energy being localised at specific locations within a sample that has been subjected to impact, a concept that was developed further by Bowden and Yoffe [10], who developed the hot-spot theory to explain explosions initiated by friction or impact stimuli.

The main source of hot-spots in liquid impact tests that are based on closed systems is the adiabatic compression of an air void above the sample or bubbles of dissolved air in the explosive during application of the falling weight. Initiation can start, for example, as burning in the vapour phase inside a hot bubble and then spread to the bulk liquid.

Brower [11] has also shown that ignition of liquid explosives can be caused by transient exposure to adiabatically compressed inert gas if a sufficient temperature rise occurs in the bulk gas above the liquid.

Bowden and Yoffe [10] were able to demonstrate the critical role of trapped air bubbles in impact tests with liquids by employing a striker with a cavity at the impact surface. For degassed samples of the liquid explosive nitroglycerine, an impact energy of 50 J caused no explosion in the absence of the cavity, whereas explosions were obtained at less than 0.01 J in the presence of an air bubble.

More recently, Field's group [12] has confirmed the role of air bubbles in a series of experiments with small hollow microspheres placed in liquid explosives.

Bowden and Yoffe have also shown that the distribution of the liquid explosive is important. Afanas'ev and Bobolev [13] have reported similar results for a range of energetic substances, indicating that a significant difference in Fallhammer results can be obtained by altering the position of the sample from an even distribution on the top surface of the lower cylinder to a central location.

Since there is a significant reduction in the energy required for initiation in the presence of an air space, the design of many impact test methods for liquids has included the compression of a void above the sample. It is for this reason that the BAM method employs a rubber ring to ensure that the upper cylinder is initially retained above the liquid surface. Similarly, the SCC method for liquids [2] ensures that compression and adiabatic heating of an explosive vapour/air mixture can occur by incorporating a space above the sample. The Guillet–Meyer apparatus for liquid organic peroxides also employs a similar system [14].

From our work it is apparent that liquid impact tests that utilise a void above the sample can give different rankings for sensitiveness. The results from the standard UN test in Table 2 imply that casting liquid is more sensitive than nitromethane which is more sensitive than isopropyl nitrate, whereas the SCC test [2] suggests that casting liquid is more sensitive than isopropyl nitrate which is more sensitive than nitromethane.

Other test methods have employed different means of sample containment: for example, Stull [15] refers to a drop-weight impact test that uses 40 mm^3 of liquid sealed in a glass tube, the Bureau of Mines test requires the liquid to be tested on a filter paper, and in the Picatinny Arsenal method the liquid is held in a cup [16].

Our work has shown that in the BAM Fallhammer test the likelihood of ignition is critically dependent on the gap between the impacting surfaces, i.e. on the volume of gas being compressed. Bowden and Yoffe [10] have suggested that explosion can take place when the minimum compression ratio is ca. 20:1, and also that a temperature rise in the compressed gas of ca. 450 °C is necessary for initiation to occur: both values are significantly exceeded even in light impact. We have clearly demonstrated that an increase in the gap produces an increase in the peak pressure attained on impact with a given weight. Thus, the dependence reported in Fig. 3 reflects the increased energy available for reaction when larger gaps are employed.

Ide et al. [17] have previously reported that 80 mm^3 of nitromethane in the presence of 240 mm^3 of air exploded on every occasion when tested in the BAM impact machine with an energy of 1 J. In general agreement with the above, we obtained an LIE of $\leqslant$1 J when testing 40 mm^3 of this liquid with a 2 mm gap (conditions that produce a void above the sample prior to test of approximately 120 mm^3).

However, nitromethane may exhibit a different general mechanism for initiation in the impact test since Ide et al. report that in experiments giving an explosion result, undecomposed nitromethane was left behind. This suggests that the explosion was primarily in the bulk air/nitromethane vapour mixture rather than in a dissolved gas bubble. This was confirmed by the fact that no reaction was observed when the tests were repeated with nitrogen replacing air.

It has been reported [18] that oxidising gases such as O_2 and N_2O give bubbles that have a greater sensitising effect than nitrogen, probably because of the ability to enter into an oxidation reaction with the decomposition products of the explosive vapour. It has also been suggested [18] that the role of inert versus oxidising gas may become particularly important if the energetic liquid is oxygen deficient, such as nitromethane.

Nitromethane was the only liquid of those investigated for which the measured LIE was affected by sample location. The large difference found between the results obtained using edge and central placement could have potential safety implications. Since the EC scheme gives no instruction on where to place the test sample, a value of $>$50 J would be obtained with a centrally positioned sample, whereas a value of 5 J would be found with the same gap setting and the sample pipetted around the edge of the top of the lower cylinder. The EC screening test, which reports the occurrence of any positive events at input energy levels of 40 and 7.5 J, would therefore give a different overall assessment of nitromethane depending on which test procedure was used.

The present study has shown that variation in the gap setting or in the location of the liquid sample can give rise to different results for the same material. In terms of improving the standard tests that are based on the BAM Fallhammer apparatus, increasing the separation between the two cylinders to 2.0 mm would improve the accuracy with which the gap can be set and should, therefore, enable more consistent results to be obtained. However, this would decrease the measured LIE for many liquid samples, and would result in more liquids failing the current UN Series 3 Test for which LIE $\leqslant$2.0 J currently determines a need for further testing.

The experimental data obtained with a 2.0 mm gap indicate that a modified test, although more stringent, would still permit the transport of flammable liquids such as methanol and dodecane which have been shown, historically, to be safe to transport. Alternatively, if a 2.0 mm gap was adopted, the LIE value that is used to identify liquids that are too sensitive for transport could be amended.

Currently, the UN scheme [2] assigns 2.0 J as the pass/fail criterion for both solids and liquids. This implies that the LIEs obtained for solids and liquids are directly comparable, which is unlikely because the test uses different methods of sample containment, and different ignition mechanisms may apply. We suggest that the test method could be usefully divided into two parts (one for liquids, and one for solids) and also that the 2.0 J pass/fail limit for liquids is examined further. One approach would be to identify a solid and a liquid substance that have impact sensitivenesses which are deemed to be at the pass/fail limit. These materials could then be specified as the reference standards which are used with the BAM Fallhammer test. The EC procedure already recommends 1,3-dinitrobenzene and RDX as materials for comparison purposes.

General revision of the UN BAM Fallhammer test scheme, and any clarification of the procedures to be adopted for an EC test on liquids, should also consider two effects that were noted during the present study:

(i) When attempting to test samples placed in the groove formed between the lower cylinder and the collar using gaps of 1.0 and 0.5 mm, a capillary action sometimes occurred. This caused some of the liquid sample to flow between the upper cylinder and the collar until liquid was visible at the top of the upper cylinder. With nitromethane the result “explosion” was obtained only when the capillary effect did not occur. The capillary effect was not observed when testing with a gap of 2.0 mm, and we recommend that, in order to obtain consistent results, testing should not proceed in those instances where this effect is manifest.

(ii) In tests with gaps of 1.0 and 0.5 mm where the liquid samples were placed in the groove between the lower cylinder and the collar, it was often difficult to press the upper cylinder to the correct depth in the impact assembly. This effect was attributed to the liquid seal between the lower roller bearing and collar, which prevented the displacement of air from the impact device. The liquid seal effect was not encountered as frequently when testing with a gap of 2.0 mm. In those experiments where this effect was manifest, the apparatus was reconfigured using new collars and cylinders until the gap could be set correctly. During routine testing, however, there is clearly a danger of such effects being overlooked. We suggest that it would be useful to mention specifically this effect in the description of the test method.

In our work the liquid seal effect was not apparent in any tests with centrally positioned liquid samples. However, in these experiments there will be some loss of pressure on compression of the system because of the ineffective seal, and a consequent reduction in the peak level attained. It is possible that this reduction in pressure could exert an effect on the measured LIE.

We note that the LIEs determined from our tests with a 0.5 mm gap and an edge sample and those obtained when using a 1.0 mm gap and a central sample are identical, which suggests that in these cases the magnitude of the effects caused by pressure leakage and gap size may be similar.

5. Conclusions

This study has shown that the likelihood of ignition of liquids in the BAM Fallhammer test is critically dependent on the gap set between the impacting surfaces. The results indicate that the likelihood of ignition could also be dependent on the location of the sample. We conclude, therefore, that inaccurate setting of the gap and variation in the position occupied by the sample are factors that could result in significantly different impact sensitiveness values being obtained for the same material. This could account for the difference in the LIEs reported in the literature [5, 6] for nitromethane.

Pressure measurements have indicated that a direct relationship exists between the magnitude of the gap and the peak pressure attained in the BAM Fallhammer test. It follows that the likelihood of ignition of a liquid in the BAM Fallhammer test is proportional to the peak pressure attained in the vicinity of the sample. A likely mechanism for ignition in systems where this relationship exists, involves the temperature rise which accompanies compression being sufficient to cause ignition.

We consider that there is scope for further work in this area. The BAM Fallhammer test currently quantifies impact sensitiveness by determining the minimum impact energy (LIE) required to cause ignition. The figure obtained does not, however, account for energy losses, e.g. in the generation of noise. Quantification of the minimum pressure to cause ignition of a liquid explosive or an energetic liquid measured in a modified sample housing may provide a more direct measure of the energy required to cause ignition.

We can make several recommendations for improvements to the BAM Fallhammer test method for liquids:

(i) The gap between the impacting surfaces should be increased to 2.0 mm since this would enable more accurate setting and hence yield more consistent results.

(ii) The test method should highlight factors that may influence the experimental result: inaccurate setting of the gap; variation in the location of the sample; capillary action; the liquid seal effect.

(iii) The UN BAM Fallhammer test method should be divided into two sections (one for solids, and one for liquids) in order to distinguish clearly the different operating arrangements. Division in this manner would also enable the use of different threshold values to define the LIE of solid and liquid substances that are too sensitive for transport.

(iv) Reference substances to define the pass/fail criterion of the test methods would be a useful improvement.

(v) The BAM Fallhammer test procedures used for UN classification [3] and EC notification [4] purposes should be harmonised in order to eliminate the potential for generating dissimilar test results since our work has clearly shown that for some liquids the position occupied by the sample can be critical. This would involve providing clearer and more detailed instructions on the experimental procedures in the EC method, principally adoption of the UN arrangement for sample location.

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