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EXPLOSIVES, SELF REACTIVE SUBSTANCES AND ORGANIC PEROXIDES

Proposed Procedure and Criterion for the Modified Vented Pipe Test

Transmitted by the expert from Australia

Introduction

The first agenda item discussed by the ANE Working Group at the UNSCETDG in Geneva July 2002 [1] was the Vented Pipe Test (VPT), intended to examine the response of ammonium nitrate (AN) based emulsions and suspensions to prolonged heating in a large scale test. Both the Scandinavians [2, 3] and the South Africans [4] presented their results from wood-fired tests, recommending that such wood-fired tests not be adopted as part of a classification method. The Australians [5] presented test results from a modified procedure using a gas burner as the heat source, calibrated to standardise the effects. The Working Group decided that this Modified Vented Pipe Test (MVPT) [6] should be developed further over the next biennium, with both Australia and Spain agreeing to perform further studies.
Since then, Spain has performed an extensive series of tests using the MVPT procedure on a variety of suspensions and emulsion compositions [7, 8 and 9]. Further testing in Australia has yielded MVPT results for a variety of proprietary emulsion compositions and for suspensions [10].

A recent review [11] has been performed of all 87 MVPT trials conducted prior to September 2003 in Australia and in Spain on a variety of compositions including pure AN prill and AN-based emulsions and suspensions. Based on detailed analyses of the thermocouple traces, of video records, of the phase and vapour pressure diagrams of AN/water systems, and of the known decomposition reactions of AN, the review provided interpretations of all key stages throughout MVPT trials of pure AN, of a typical emulsion and of a typical suspension. The analyses highlighted that the production of toxic fume from various decomposition pathways became a definite hazard at lower temperatures and at earlier times in the heating process than did the possible risk of explosion.

The review discussed how a revised criterion for the MVPT could account for the dual hazards represented by the generation of toxic fume and by possible explosion.

Proposal

Based on this review of the past MVPT test results and past USA VPT test results, it is recommended that a revised criterion and set of procedures for the MVPT be adopted for the Series 8(d) test. The recommended revised criterion and procedures are attached here in the Appendix.
In particular, it is proposed that the acceptance criterion be based on whether or not a trial of the candidate ANE concludes within a defined run-time, which while defined explicitly in the procedure from the heating

rate of water, has been based implicitly on the time measured to completely decompose pure ammonium nitrate prill under identical heating conditions [11].

Justification

This proposed MVPT procedure fulfils many of the requirements for a large scale test intended to delineate the response of candidate ANE to prolonged heating in accidental fires during transport.

The procedure is robust. The test apparatus has been assembled in two different countries, and has given reproducible results as exemplified by similar heating conditions, similar thermocouple traces and similar observed behaviours over a range of compositions. Corrections can be made for differences in heating rate and sample initial temperature. The thermocouple traces and video records can be analysed jointly to give considerable insight into the physical processes occurring during the breakdown, boiling, concentration and decomposition of ANE.

The test heat source and geometry appears to provide a realistic yet conservative simulation of the conditions during a “typical” road tanker fire. The prolonged and constant heat flux into the base of the vessel [5] exceeds by about 25% the peak heat flux measured during experimental tests of pool fire engulfment of LPG tanks [12]. The duration of the MVPT (ie the run-time) is roughly twice the duration of a “typical” road tanker fire where the diesel was assumed to pool under the vehicle [13], and roughly twice the minimum duration specified for the wood-fired USA VPT. The ratio of heated surface area to ANE volume in the MVPT [5] closely matched that of the Kuosanen full-scale burning test [14].

The criterion is an inclusive and all embracing one, in that a trial can finish prematurely not only in explosion (producing blast and shrapnel), but also as the result of prolonged decomposition (forming toxic fume) or of prolonged vessel overflow (intensifying the fire and producing toxic fume).

The criterion allows quantitative assessments to be based on the experiences gained historically from a much wider base of transport accidents. Ammonium nitrate has been transported in much greater quantities for a longer period of time, and has as a consequence been involved in many more transport fires than has ANE. It is presumed that inspection of historical data could be used to estimate what fraction of AN transport loads have been involved in accidental fires, and of those fires, what fraction have been of sufficient intensity and duration to completely empty the tanker of AN. It is the latter case that represents the minimum fire conditions necessary to bring an ANE approved for bulk transport by the proposed MVPT to the stage where major decomposition may commence and, at a still later time again, where explosion becomes possible.
The criterion delineates the time-scale over which these hazards develop, and hence the time-scale available to the authorities to respond to any accidental fire involving ANE approved for transport in bulk. This time-scale is in excess of one hour under heating conditions that match those of the MVPT.

Results

Application of the revised criterion to the existing set of data generated during past MVPT trialing leads to negative outcomes being observed for the majority of the emulsion compositions that lay within Special Provision 309 for UN3375 ANE [15], thus deeming them suitable for transport in bulk.

On the other hand, an emulsion composition that lay outside the UN3375 definition due to the inclusion of sodium perchlorate gave two positive outcomes in Australian trials, with a similar composition giving one positive and one negative outcome in Spanish trials. Hence the proposed MVPT appears to discriminate between emulsions that have traditionally been judged suitable for bulk transport and those that have not.

References

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14. 14. H. Karlström, "Full-scale burning test of a tank loaded with emulsion matrix, Kuosanen 2002", report by Dyno Nobel, Forcit OY and Kimit AB, 21 May 2002.
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APPENDIX: Recommended procedure for the MVPT

EXPLOSIVES, SELF-REACTIVE SUBSTANCES AND ORGANIC PEROXIDES.

Classification of Ammonium Nitrate Emulsions, Suspensions and Gels.

Manual of Tests and Criteria. Test 8(d) – Modified Vented Pipe Test

1 *Introduction*

The vented pipe test is used to assess the effect of exposure of a candidate for "ammonium nitrate emulsion or suspension or gel, intermediate for blasting explosives" to a large fire under confined, vented conditions. It will determine whether or not an ANE can be transported in tanks as a dangerous good of Class 5.1.

The ANE is subjected to this test only after it has passed Test 8(a), Test 8(b) and Test 8(c) and deemed to be a dangerous good of Class 5.1.

2 *Apparatus and materials*

The following items are needed:

(a) A vented vessel consisting of mild drawn steel pipe with an inner diameter of 265 ± 10 mm, a length of 580 ± 10 mm and a wall thickness of 5.0 ± 0.5 mm. Both the top and the base plates are made from 300 mm square, 6.0 ± 0.5 mm thick mild steel plates. The top and base plates are fixed to the pipe with a single 5 mm fillet weld. The top plate has a central vent diameter of 87 ± 1 mm. A minimum of three, and preferably up to five, small holes are drilled in the top plate to accommodate neatly thermocouple probes, these holes being equally spaced around a circle of radius 90 ± 5 mm concentric with the vent;

(b) A concrete block about 400 mm square and 50 to 75 mm thick;

(c) A metal stand for supporting the vessel at a height of 150 mm above the concrete block;

(d) A gas burner capable of accommodating an LPG flow rate of up to 35 ± 2 litres per minute. This rests on the concrete block under the stand. A typical example of a suitable burner is a 32-jet Mongolian wok burner;

(e) A sheet metal shield to protect the LPG flame from side winds. This can be fabricated from approximately 0.5 mm thick galvanised sheet metal. The diameter of the wind shield is 600 mm and the height is 250 mm. Four adjustable vents 150 mm wide and 100 mm high are spaced equally around the shield to ensure adequate air reaches the gas flame;

(f) LPG bottle(s) connected via a manifold and fed into a pressure regulator. The pressure regulator should reduce the LPG bottle pressure from 650 kPa down to about 250 kPa. The gas then flows through a gas rotameter capable of measuring up to 40 litres per minute of LPG gas. An electrical solenoid valve is used to switch the LPG flow on and off remotely. Typically four 9kg LPG bottles will achieve the desired gas flow rate for the duration of up to five tests.

(g) One thermocouple with 600 mm long stainless steel probe and a minimum of three, though preferably five, thermocouples with 500 mm long stainless steel probes and fibre-glass coated lead wires;

(h) A data-logger capable of recording the output from the thermocouples;

(i) Cine or video cameras, preferably high speed and normal speed, to record events in colour.

(j) Pure water for calibration.

(k) The ANE to be tested.

Blast gauges, radiometers and associated recording equipment may also be used.

3 *Calibration*

3.1 The vessel is filled to the 75% level (ie to a depth of 435 ± 10 mm) with the pure water, and heated using the procedure specified in Section 4. The time taken to reach the boiling point of the water is recorded, and is used to define the "calibration-time" for the given combination of vessel and heat source. The boiling point has been reached when all thermocouple traces converge at approximately 100°C (or lower if at altitude).

3.2 If the initial temperature of the water was not 25°C, corrections to the calibration-time must be made based on the measured mean heating rate, $\dot{T}_{cal}$, over the temperature interval between 40°C and 80°C as recorded by the thermocouple T3 in the water.

3.3 The calibration-time, t_{cal}, is defined as the corrected time taken to heat water from 25°C to boiling point within the test equipment, and must be 24 minutes ± 2 minutes 30 seconds. If t_{cal} lies outside this time window, the calibration must be repeated from step 3.1 with a fresh sample of water making appropriate adjustments to the gas flow. If sufficient adjustment is not available from the gas flow, it may be necessary to alter the height of the metal stand supporting the vessel above the gas burner.

3.4 This calibration must be performed prior to the testing of any ANE substance, though the same calibration-time, t_{cal}, and mean heating rate, $\dot{T}_{cal}$, can be applied to any test conducted within a week of the calibration provided no change is made to the vessel construction, LPG burner type or gas supply.

4 Test Procedure

4.1 The concrete block is placed on a sandy base and levelled using a spirit level. The LPG burner is positioned in the centre of the concrete block and connected to the gas supply line. The metal stand is placed over the burner.

4.2 The vessel is placed vertically on the stand and secured from tipping over. The vessel is filled to 75 % of its volume (to a height of 435 ± 10 mm) with the ANE under test. The substance is carefully packed to prevent adding voids. The wind shield is positioned around the base of the assembly to protect the LPG flame from heat dissipation due to side winds. The test should not be performed under conditions where the wind speed exceeds 6 m/s.

4.3 The thermocouple positions are:

- the first 500 mm long probe (T1) in the LPG flame;
- the second 500 mm long probe (T2) in the headspace 20 ± 5 mm into the vessel;
- the third 500 mm long probe (T3) in the sample 175 ± 5 mm into the vessel;
- the 600 mm long probe (T4) in the sample 570 ± 5 mm into the vessel;

If used, the extra two thermocouples are placed

- the fourth 500 mm long probe (T5) in the sample 360 ± 5 mm into the vessel;
- the fifth 500 mm long probe (T6) in the headspace 100 ± 5 mm into the vessel.

The thermocouples are connected to the data-logger and the thermocouple leads and data-logger are adequately protected from the test apparatus in case of explosion.

4.4 LPG pressure and flow rate are checked and adjusted to the values used during the water calibration described in Section 3. Appropriate values for the pressure and the flow rate at which to conduct the first water calibration procedure are 250 kPa and 35 litres per minute respectively. Thermocouple functioning is checked and data logging is started, with a time step between thermocouple readings not exceeding 20 seconds, and preferably shorter. The initial temperature of the ANE must be recorded. Video cameras and any other recording equipment are checked and started.

4.5 The LPG burner may be started locally or remotely and all workers immediately retreat to a safe location. Progress of the test is followed by monitoring thermocouple readings and closed circuit television images. The start time of the trial is defined by the time at which the flame thermocouple trace T1 first begins to rise.

4.6 The “run-time” t_{run} for the ANE is calculated as 2.75 times the calibration-time t_{cal} for water, adjusted by a suitable correction based on the measured heating rate $\dot{T}_{cal}$ for water if the initial temperature of the ANE is below the normal shipping temperature. The ANE should not be tested at an initial temperature above the normal range of shipping temperatures.

4.7 The ANE is heated for this run-time or longer. At the end of this run-time, or earlier if the test is deemed to have reached its conclusion according to section 4.9, the LPG supply may at the discretion of the workers be switched off remotely using the solenoid valve. Alternatively, the ANE may continue to be heated until the test is deemed to have reached its conclusion according to section 4.9. The choice as to how long to prolong heating past the run-time should be based on a detailed risk assessment of the relative hazards and environmental impacts of handling and disposing of hot degraded ANE versus the generation of toxic fume and the possible projection of hot metal shrapnel.

4.8 Once the vessel and any remaining ANE have cooled to a safe handling temperature, the vessel and any remaining ANE should be disposed of in an environmentally responsible manner and according to local statutory requirements.

4.9 The test outcome is determined by whether or not the test reaches a conclusion prior to the run-time. Evidence of test conclusion is based on:

- The visual and aural observation of vessel rupture accompanied by possible loss of thermocouple traces, or
- The visual and aural observation of vigorous venting accompanied by peaking of two or more vessel thermocouple traces, or
- The visual observation of decreased levels of fuming following the peaking of two or more vessel thermocouple traces at temperatures in excess of 300ºC.

In all cases, the conclusion time is taken as the time at which the maximum temperature was recorded inside the vessel.

5 *Test criteria and method of assessing results*

The ANE is heated under the set test conditions for its run-time or longer.

If the test concludes within the run-time, the outcome of the test would be recorded as being positive (+) and the ANE is not suitable for transportation in tanks as a dangerous good of Class 5.1.

If the test does not conclude within the run-time, the outcome of the test would be recorded as being negative (-) and the ANE is suitable for transportation in tanks as a dangerous good of Class 5.1.

6 *Examples of results*

Example of calibration calculation:

Calibration for water:

Initial temperature of water = 32°C.

Time to heat water from 32°C to 100°C = 21 minutes 30 seconds.

Mean heating rate between 40°C and 80°C $\dot{T}_{cal}$ = 3.50°C/minute.

Calibration-time t_{cal} = 21 minutes 30 seconds + (32 -25)/3.50 minutes = 23 minutes 30 seconds.

Example of run-time correction:

Example run-time correction for Test Substance 2:

Initial temperature of substance = 21°C.

Normal shipping temperature = 60°C.

Run-time = 2.75×(23 minutes 30 seconds) + (60-21)/3.50 minutes = 75 minutes 46 seconds.

Observed conclusion time = 109 minutes 48 seconds.

Test outcome: Negative

Example run-time correction for Test Substance 5:

Initial temperature of substance = 6°C.

Normal shipping temperature = 60°C.

Run-time = 2.75×(23 minutes 30 seconds) + (60-6)/3.50 minutes = 80 minutes 3 seconds.

Observed conclusion time = 58 minutes 35 seconds.

Test outcome: Positive

Example run-time correction for Test Substance 6:

Initial temperature of substance = 37°C.

Normal shipping temperature = 40°C.

Run-time = 2.75×(23 minutes 30 seconds) + (40-37)/3.50 minutes = 65 minutes 29 seconds.

Observed conclusion time = 23 minutes 59 seconds.

Test outcome: Positive

Example of typical results:

	Substance	**Result**
1.	76.0 AN / 17.0 Water / 5.6 paraffin oil / 1.4 emulsifier	-
2.	82.1 AN / 12.3 Water / 4.2 diesel oil / 1.4 emulsifier	-
3.	82.1 AN / 12.3 Water / 4.2 paraffin oil / 1.4 emulsifier	-
4.	68.3 AN / 17.6 SN / 6.5 Water / 5.7 diesel oil / 1.9 emulsifier	-
5.	74.9 AN / 9.7 SP / 9.0 Water / 3.7 paraffin oil / 2.7 emulsifier(1)	+
6.	60.5 AN / 17.0 HMN / 12.0 Water / 10.0 EG / 0.5 guar gum(1)	+
7.	60.5 AN / 17.0 MAN / 12.0 Water / 10.0 EG / 0.5 guar gum(1)	+
8.	Dense AN prill(1)	-

(1) *Composition lies outside definition of UN3375 ANE.*