COMMITTEE OF EXPERTS ON THE TRANSPORT OF DANGEROUS GOODS AND ON THE GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION AND LABELLING OF CHEMICALS

Sub-Committee of Experts on the Transport of Dangerous Goods

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EXPLOSIVES, SELF-REACTIVE SUBSTANCES AND ORGANIC PEROXIDES

Ammonium nitrate emulsions, suspensions and gels

Proposal of a Procedure and Criterion for the Modified Vented Pipe Test to be adopted as Recommended Series 8 Type (d) Test

Transmitted by the expert from Spain

Background

In the December 2002 session, the Committee of Experts on the Transport of Dangerous Goods approved the inclusion of the Series 8 Tests in the Manual of Tests and Criteria. The Tests 8(a), 8(b) and 8(c) must be used to establish whether an ammonium nitrate emulsion, suspension or gel, intermediate for blasting explosives (ANE), can be assigned to Division 5.1 (UN 3375). Test 8(d): Vented Pipe Test was included in this series as a method of evaluating the suitability of a substance for its transport in tanks.

Test 8(d) is controversial because, amongst other things, the procedure does not specify the heating rate that the sample must be subjected to. This may explain why this test has not been reproducible or discriminatory in some instances where has been reported **(1, 2)**.

In an attempt to make this test more reproducible and less difficult, Orica Explosives and Dyno Nobel developed a new Modified Vented Pipe Test, MVPT, **(3)** in Australia. Based on this work, the Competent Australian Authority proposed a Modified Vented Pipe Test **(4)**. The ANE Working Group proposed that the future work to be carried out for the development of Test 8(d) bear in mind the guidelines prepared by the Australian Authority, with both Australia and Spain agreeing to perform further studies.

Since then, an extensive series of trials has been performed in Australia **(5)** and Spain **(6,7)** using the MVPT procedure on a wide range of emulsion and suspension compositions.

At 24th session of the Sub-Committee the expert from Australia presented a MVPT proposal **(8)**. The proposal follows the procedure already presented in session 21 **(4)**, including a period of time called "*run-time*" (2.75 times the calibration-time, approximately 66 min). Based on this time, it sets as a criterion: "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". This criterion considers irrelevant if the test ends with a venting or with an explosion.

The expert from Sweden has presented another proposal on this test **(9)** for the upcoming 25th session of the Sub-Committee that follows the same philosophy as the Australian proposal although the procedure and criterion are rather more complex. In this case, two new periods of time are defined: the "*run-time for rupture*" (2.8 times the calibration-time, approximately 67 min) and the "*run-time for venting*" (1.4 times the calibration time, approximately 34 min). This proposal considers two criteria; it is either a substance with UN number 3375 or a substance with the number "*UN 3XXX for chemically sensitised emulsions, suspensions and gels*" **(10),** also proposed by the Swedish expert. In the case of the UN 3375 number, the test candidate is suitable for transport in bulk as Class 5.1 if the vessel is not vented or ruptured within a time less than the "run time for rupture". In the case of the UN 3XXX number, the test candidate is suitable for transport in bulk as Class 5.1 if the vessel is vented within a time greater than the "run time for venting" and the vessel is not ruptured within a time less than the "run time for rupture".

Discussion

This proposal supports the proposal made by Australia at session 21 of the Sub-Committee **(4)** but keeps the basic criteria of the current Test 8(d) **(11)**, that is to say, *"the test result is considered "+" and the substance should not be transported in tank if an explosion and/or fragmentation of the pipe is observed".*

We have found that there is not sufficient technical justification for the run-time concept and is therefore recommended that it be dismissed as irrelevant to assess the behaviour of a substance as a consequence of an external fire. We found however, that the same criterion as is customary for the current VPT test provides relevant information on the behaviour of the substance.

Other than the criteria suggested, we find that the experimental procedure presented by Australia for the MVPT is adequate, and this proposal has been drawn up according to this procedure, although obviously all reference to the "run-time" concept has been eliminated. As we have mentioned, the criterion proposed by the Australian expert does not distinguish between the different candidates and, more importantly, it ignores the information necessary to determine the magnitude of the reaction of a substance to an external fire.

We cannot accept Sweden's proposal as it also includes the "run-time" concept to develop its criterion. In the case of UN number 3375, both proposals are very similar, as the "run-time" and "run time for rupture" are almost identical. In addition to the run-time concept, Sweden's proposal for a new UN number *UN 3XXX for chemically sensitised emulsions, suspensions and gels*, has an additional fundamental inconsistency: it an ANE candidate meeting the current definition of SP309 were to show a venting 50 min after the start of the test, this product could only be transported in tanks as Class 1.5. According to the criteria presented by Sweden, by simply adding 1% sodium perchlorate to its formula it may be classified under the new proposed UN number UN 3XXX and be transported in tanks as 5.1. The addition of the small amount of perchlorate (as shown in **7**) is not going to affect the outcome of the test and changes the classification dramatically without a significant change in behaviour. This is an artifact of the criteria which shows its limitations.

In the report included in document UN/SCETDG/25/INF.74 **(7)**, the reaction time is considered to be the time that it takes for the substance to react fully either with venting or explosion. This time only depends on the type of mixture in question, i.e., if it is an emulsion, or a suspension with or without thickener. Within these three types of mixture, a relation between the reaction time and the chemical and physical characteristics of the substance has not been found. However, it has been observed that the limiting vent diameter, (i.e., the maximum vent diameter at which the rupture of the vessel is observed), allows a distinction to be made between the different substances according to their chemical and physical characteristics. In addition, in light of the results in **(7)** it can be stated that in general limiting vent diameters show a logical behaviour according to the different factors considered and which may have an influence on the reaction capacity of a substance to an external fire.

The ideal MVPT procedure would be to determine the value of the limiting vent diameter in a way that substances could be compared similarly to what is currently done with the Koenen Test. The high cost of the MVPT made it practical to use a given vent diameter and look for explosion or venting effects as a means of determining whether a substance has a greater reaction capacity than the standard. The value of the vent diameter is shown in square brackets.

One modification that we find appropriate in the test is the need to carry out more than one trial with the same result to pass the test and reduce the uncertainty of the experimental errors seen during the trials. The proposed procedure includes the need to repeat the trial twice. This value is also shown in square brackets because it is open for discussion and it could be argued that three trials be carried out like in the Koenen Test. Document UN/SCETDG/25/INF.74 **(7)** shows that different results (venting and explosion) were obtained for some substances and vented diameters. Undertaking two trials of the test to obtain a negative result is not new. The Bureau of Mines (U.S. Department of the Interior) in its Large Scale vented Vessel Bonfire Test provides that "*Two trials are conducted on each sample. The test result is considered positive if the sample explodes or detonates in any trial. Explosion or detonation is evidenced by fragmentation of the vessel*" **(12)**. This condition was not applied to Test 8 (d): Vented Pipe Test. However, we believe its inclusion is appropriate in the proposed procedure.

Proposal

To adopt the Modified Vented Pipe Test as detailed in the Annex as a recommended test for Series 8 type (d) Test and an alternative to the current Test 8 (d): Vented Pipe Test.

The proposed procedure for the MVPT given in the Annex includes two parameters enclosed in square brackets, namely the vent diameter in section 18.7.2.2 (a) and the number of times that the test has to be carried out in section 18.7.2.4.8. The final values of these parameters should be set by consensus after discussion by the UNSCETDG.

This proposal also includes the amend of Table 18.1: TEST METHODS FOR TEST SERIES 8 as follows:

Test code	Name of Test	**SECTION**
8 (a)	Thermal Stability Test for ANE[a]	18.4.1
8 (b)	**ANE Gap Test[a]**	18.5.1
8 (c)	Koenen Test[a]	18.6.1
8 (d) (i)	Vented Pipe Test[b]	18.7.1
8 (d) (ii)	Modified Vented Pipe Test[b,c]	18.7.2

a This test is intended for classification.
b This test is intended for evaluating the suitability for transport in tanks.
c Recommended test.

References

1. *J. Vestre, Dyno Nobel Europe, Forcit OY and Kimit AB, "Evaluation of proposed USA Vented Pipe Test", 13 March 2002.*
2. H. Karlström, Dyno Nobel Europe, Forcit OY and Kimit AB "Further Characterisation and Development of the USA Vented Pipe Test", 13 March 2002.
3. D.L. Kennedy, Orica Explosives and Dyno Nobel, "The Modified Vented Pipe Test", 14 June 2002.
4. ANE Working Group, "Future Work. Manual of Tests and Criteria. Test 8(d) - Vented Pipe Test", UN/SCETDG/21/INF.69, Annex 1, Geneva, July 2002.
5. D.L. Kennedy, Orica Exploxives, "A Review of the Modified Vented Pipe Test", UN/SCETDG/24/INF.45, Geneva, December 2003.
6. J.R. Quintana, F. Beitia and F. Cimadevilla, UEE, "Preliminary Results of Modified Vented Pipe Test (Australian Procedure) on Ammonium Nitrate Emulsions and Suspensions (ANE)", UN/SCETDG/23/INF.32, Geneva, July 2003.
7. J.R. Quintana and F. Beitia, UEE, "Performance of Modified Vented Pipe Test (Australian Procedure) on Ammonium Nitrate Emulsions and Suspensions (ANEs)", UN/SCETDG/25/INF.74, Geneva, July

2004.

8. Expert from Australia, "Proposed Procedure and Criterion for the Modified Vented Pipe Test", UN/SCETDG/24/INF.44, Geneva, December 2003.
9. Expert from Sweden, "Proposal for the adoption of a ‘Modified’ Vented Pipe Test as the optional Test Series 8(d)", ST/SG/AC.10/C.3/2004/24, Geneva, April 2004.
10. Expert from Sweden, "Proposal for a new UN number for Sensitized Ammonium Nitrate Emulsions, Suspensions and Gels", ST/SG/AC.10/C.3/2004/24, Geneva, April 2004.
11. “Recommendations on the Transport of Dangerous Goods. Manual of Test and Criteria”, ST/SG/AC.10/11/Rev.4, Geneva 2003.
12. T.S. Bajpayee, "Comparative Evaluation of Large Scale Vented Vessel Bonfire and Deflagration-to-Detonation Transition Tests of Blasting Agents", Internal Report No. 4875, U.S. Department of the Interior, Bureau of Mines, Pittsburgh, 1991.

ANNEX: Recommended procedure for the MVPT

18.7.2. Test 8(d)(ii): Modified Vented Pipe Test

18.7.2.1 *Introduction*

This test is not intended for classification but is included in this Manual for evaluating the suitability of bulk substances to be transported in tanks.

The modified vented pipe test is used to asses 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.

18.7.2.2 *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 fillet weld with a thickness of at least 5 mm. The top plate has a vent diameter of [75 mm] ± 1.0 mm. A further two small holes are drilled in the top plate to accommodate neatly thermocouple probes;

(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 a propane flow rate of up to 60 g/min. 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 propane 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) Propane bottle(s) connected via a manifold and fed into a pressure regulator. Other fuel gases may be used providing the specified heating rate is obtained. The pressure regulator should reduce the propane bottle pressure from 600 kPa down to about 150 kPa. The gas then flows through a gas rotameter capable of measuring up to 60 g/min of propane and a needle valve. An electrical solenoid valve is used to switch the propane flow on and off remotely. Typically three 9 kg propane bottles will achieve the desired gas flow rate for the duration of up to five tests. The gas pressure and flow are regulated to give a heating rate of 3.3 ± 0.3 K/min when measured by the calibration procedure;

(g) Three thermocouples with 500 (2) and 100 (1) mm long stainless steel probes and fiber-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.

18.7.2.3 ***Calibration***

18.7.2.3.1 The vessel is filled to the 75% level (i.e. to a depth of 435 mm) with the pure water, and heated using the procedure specified in Section 18.7.2.4. Water is heated from ambient temperature up to 90 ºC, monitoring temperature by the thermocouple in the water. Temperature-time data must fit a straight line whose slope will be the "calibration heating rate" for the given combination of vessel and heat source.

18.7.2.3.2 The gas pressure and flow must be regulated to give a heating rate of 3.3 ± 0.3 K/min.

18.7.2.3.3 This calibration must be performed prior to the testing of any ANE substance, though the same calibration can be applied to any test conducted within a day of the calibration provided no change is made to the vessel construction or gas supply. New calibration has to be made every time that the burner is changed.

18.7.2.4 ***Procedure***

18.7.2.4.1 The concrete block is placed on a sandy base and levelled using a spirit level. The propane 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.

18.7.2.4.2 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 mm) with the ANE under test without tamping during loading. The initial temperature of the ANE must be recorded. The substance is carefully packed to prevent adding voids. The wind shield is positioned around the base of the assembly to protect the propane flame from heat dissipation due to side winds.

18.7.2.4.3 The thermocouple positions are as follows:

- the first 500 mm long probe (T1) in the gas flame;
- the second 500 mm long probe (T2) extending all the way into the vessel so that the tip is positioned 80 to 90 mm from the bottom of the vessel;
-the third 100 mm long probe (T3) in the headspace 20 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.

18.7.2.4.4 Propane pressure and flow is checked and adjusted to the values used during the water calibration described in Section 18.7.2.3. Video cameras and any other recording equipment are checked and started. Thermocouple functioning is checked and data logging is started, with a time set between thermocouple readings not exceeding 10 seconds, and preferably shorter. The test should not be performed under conditions where the wind speed exceeds 6 m/s. With higher wind speed, precautions against side winds are required to avoid dissipation of the heat.

18.7.2.4.5 The propane 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.

18.7.2.4.6 The gas reservoir should be large enough to bring the substance to a possible reaction and provide a fire duration lasting beyond total consumption of the test sample. If the vessel does not rupture, the system should be allowed to cool down before carefully dismantling the test set-up.

18.7.2.4.7 The test outcome is determined by whether or not a rupture of the vessel is observed when the test reaches conclusion. Evidence of test conclusion is based on:

- The visual and aural observation of vessel rupture accompanied by loss of thermocouple traces, or
- The visual and aural observation of vigorous venting accompanied by peaking of both vessel thermocouple traces and no substance remains in the vessel, or
- The visual observation of decreased levels of fuming following the peaking of both vessel thermocouple traces at temperatures in excess of 300 ºC and no substance remains in the vessel.

For the purposes of assessing results, the term “rupture” includes any failure of welds and any fracture of metal in the vessel.

18.7.2.4.8 The test is performed [two] times unless a positive result is observed.

18.7.2.5 ***Test criteria and method of assessing results***

The test result is considered “+” and the substance should not be transported in tanks as a dangerous good of Class 5.1 if an explosion is observed in any trial. Explosion is evidenced by rupture of the vessel. Once the substance is consumed in [both] trials and no rupture of the vessel is observed, then the result is considered “-“.

18.7.2.6 **Examples of results**

Substance	Result
76.0 ammonium nitrate / 17.0 water / 5.6 paraffin oil / 1.4 PIBSA emulsifier	-
84.0 ammonium nitrate / 9.0 water / 5.6 paraffin oil / 1.4 PIBSA emulsifier	+
67.7 ammonium nitrate / 12.2 sodium nitrate / 14.1 water / 4.8 paraffin oil / 1.2 PIBSA emulsifier	-
67.4 ammonium nitrate / 15.0 methylamine nitrate / 12.0 water / 5.0 glycol / 0.6 thickener	-
71.4 ammonium nitrate / 14.0 hexamine nitrate / 14.0 water / 0.6 thickener	-