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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

Twenty-seventh session, 4-8 July 2005
Item 3 (a) of the provisional agenda

EXPLOSIVES, SELF-REACTIVE SUBSTANCES AND ORGANIC PEROXIDES

Test series 8

Report of the informal Working Group on Ammonium Nitrate Emulsions (ANE), Suspensions and Gels and Tests Series 8

Transmitted by the expert from the Netherlands

1. An informal Working Group on Ammonium Nitrate Emulsions (ANE), Suspensions and Gels and Tests Series 8 met on 14 and 15 February 2005, at the invitation of the expert from Spain, at Madrid, under the Chairmanship of Mr. A. Johansen (Norway) (see also ST/SG/AC.10/C.3/52, para. 58).

2. Government and industry experts from Canada, Germany, France, Japan, the Netherlands, Norway, South Africa, Spain, Sweden, the United Kingdom and the United States of America participated.

3. The following presentations and discussion items were submitted before the meeting:

1	Alternative Series 8 Tests	Canada
2a	Test results of 8 (d) with vent pipe in Japan	Japan
2b	Development of a small scale type 8 (d) test on ANE	
3	Lecture about vent sizing	Germany
4	Modified Vented Pipe Test	Spain
5	Reference Substance for Koenen Test	France
6	Considerations on Modified Vented Pipe Test 8 (d)	France
7	UNITED KINGDOM proposals for Test Series 8	United Kingdom
8	Koushnen 2002 full scale burning test	Norway
9	Discussion on transportation of ANEs in flexible IBCs	Sweden

4. At the request of the Chairman, an expert from the Norwegian industry informed the group about an accident that happened last June in the Russian Federation with a truck carrying 12 – 15 tons of ANE matrix in steel tanks. A tyre fire started at some point and about 500 litres of hydraulic oil and fuel oil were involved in the fire as well. The fire could not be extinguished so the two persons involved set up a road block. About 40 minutes later a detonation took place. From the damage, it was estimated that 5 to 6 tons were involved in the detonation. The accident was still under investigation, but it might be possible that gassed (sensitized) material was trapped in the piping system.

5. An industry expert from the United States of America briefly informed the group about an explosion that took place in Brazil last November at a packaging plant of Division 1.1 explosives. No information on a possible cause was available yet; the investigation was still ongoing.

Item 1 Alternative Series 8 Tests (Canada)

6. The expert from Canada presented the Canadian position on the current Series 8 tests and potential future developments. The current tests, designed for molecular explosives and older products such as dynamite and black powder, are often not suitable for modern emulsions, watergels and ANFO blends, where the issue of propagation is often as important as initiation.
The current 8(a) test takes at least a week to perform and gives no indication of the margin of safety. The Accelerating Rate Calorimeter (ARC) was mentioned as an alternative.
With regard to the shock sensitiveness, the paper raised doubts as to whether test 8(b) was actually more severe than the series 1(a) test.

7. The expert from Canada found it debatable whether either Test 8(c) or 8(d) were realistic worst-case simulations of what happens when a truck carrying ANEs is engulfed in a fire. The ratio of vent area to sample volume is much greater than for a tanker truck, for example. Nevertheless, it is generally recognized that a truck fire represents a significant hazard for ANE transportation and that a test that provides useful information on the behaviour of large quantities of ANE in a fire situation is essential.

8. The expert from Canada further brought up the ignition and burning properties as can be assessed by the Minimum Burning Pressure (MBP) test and whether tests simulating multiple stimuli could be introduced.

9. A number of experts questioned whether a MBP test is relevant for transport situations. The Chairman pointed out that situations other than transport situations should also be considered since the Manual of Tests and Criteria is referred to in the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) which has a much wider implication.

10. The expert from the United States of America encouraged laboratories to run the Koenen and MBP tests and provide data which can be used for a decision in the future.

Item 2a Test results of 8 (d) with vent pipe in Japan

11. The expert from Japan presented test results of vented pipe tests performed on a military test site in Japan. For reasons of efficiency, three tests were conducted at the same time. Each test was shielded in the direction of the other tests and were about 10 metres apart. The sample were all within the composition range of Special Provision 309; all had 5% paraffin fuel and 1.5% emulsifier while the ammonium nitrate content varied from 81.5 to 71.5%, with the rest water. Thermocouples were used to measure the temperature distribution in the vessel. In all three cases, a positive result (fragmentation of the vessel) was found.

Item 2b Development of a small scale type 8 (d) test on ANE (Japan)

12. In Japan, it is very difficult to find a suitable test site to perform this test. For this reason, Japan is looking into the possibilities of a reduced version of the vented pipe test. The expert from Japan presented a research programme aimed at finding a suitable test between the current sizes of 25 g in the Koenen test and the 40 litres vented pipe test. Ideally, the size would be 1 or 2 litres. Two types of vessel were used: 100 ml and 1 l glass vessels and 200 ml and 1.5 l stainless steel vessels. In the 100 ml glass vessels, vent openings of 1 and 0.5 cm diameter are used; in the 1 l vessel a 1 cm diameter vent is used. The latter two correspond with the Australian Modified Vented Pipe Test (MVPT). The test substance consisted of: ammonium nitrate 61.5%; sodium nitrate 13%; calcium nitrate 2%; water 17%; oil 5% and emulsifier 1.5%.

13. On a 100 ml scale, no explosions were observed, regardless of vent size, heating rate and composition, and it could be concluded that at this scale no discrimination could be made.
From the experimental data, the 1 litre vessel was capable of making a distinction between a “go” and a “no go”.

14. The stainless steel vessels were equipped with a pressure transducer and thermocouple. On a 200 ml scale the obtained results were not reproducible, but on a 1.5 litre scale the reproducibility was much better. This seemed to indicate a way forward, the programme being still ongoing.

15. The question was raised how much the smaller scale tests differ from the Koenen test. The scale was somewhat larger, but especially in the steel vessels, the diagnostics were much better.
The heating rate of the different vessels was calibrated but are different for each size.

Item 3 Lecture about vent sizing (Germany)

16. The expert from Germany gave a presentation about vent sizing. The example of the vent sizing test used for organic peroxides and self-reactive substances was given. The heating rate to be used in such a test was calculated from heat input (via indirect and direct exposed surface), insulation factor and surface and volume of the actual tank and the test vehicle. If this were done for the 8(d) Vented Pipe Test (VPT) and MVPT, numbers of 0.104 m^2/m^3 and 0.192 m^2/m^3 were found respectively. For comparison: a 24 m^3 tank has a figure of about 0.03 m^2/m^3. It may be better therefore not to rely on venting but on the material of the tank as illustrated by the Scandinavian tests with aluminium tanks.

17. Furthermore, the expert from Germany had doubts about the thermal stability test which may be better replaced by the current H.2 test, the adiabatic storage test, since the emulsions are closer to a solid.

18. A number of experts pointed out that not all emulsions and suspensions could be treated as solids.

19. The expert from Canada pointed out a fundamental question: are we trying to classify the materials as they are, or as they might become during a fire?

20. The Chairman pointed out that, after the Scandinavian tests with tanks, the residue was not detonable and was to be gassed to be cleared up after the tests.

Item 4 Modified Vented Pipe Test; Spain

21. An expert from the Spanish industry presented a summary of more than 75 tests that had been performed by the Unión Española de Explosivos (UEE), taking the results obtained by two other companies (Dyno and Orica) into account. In that way, a rather good insight in the influence of several parameters could be given. Parameters like the amounts of water, emulsifier, methyl amine nitrate, sodium perchlorate, sodium nitrate, ammonium nitrate, etc. were analysed and the influence presented.

Item 5 Reference Substance for Koenen Test (France)

22. The expert from France recalled a German proposal at the July 2004 Sub-Committee meeting for a better specification of the materials used in the Koenen test. He shared the French experience that this is not an easy subject since those specifications usually define static inner pressure resistance. What is actually needed is to know the dynamic resistance at elevated temperature. It was therefore proposed to use musk-xylene as a reference substance since this material gives a very specific behaviour: 3 out of 3 tests gave positive results with an orifice of 8 mm, 0 out of 3 positives at 2 mm and 3 out of 3 positives again at 1 mm diameter.

23. Several experts expressed support for having a better specification of the Koenen tests and felt that this might be a good way forward.

Item 6 Considerations on Modified Vented Pipe Test 8 (d) (France)

24. The expert from France also presented French MVP tests, performed with wood as fuel with a fixed vent diameter of 87 mm. The wood fire had a flame temperature of 800 to 1000° C during a minimum of 25 minutes. Tests were performed with two pairs of test substances similar in composition. Three out of four samples passed the tests but substance FB ruptured the tube.

25. He also stressed the difficulties of finding a suitable test range to perform these tests, due to the amount of substance involved. He continued that the current criteria are sometimes hard to interpret in practice. He concluded that the MVPT gives no real indication of the behaviour of ANEs in tanks and he believed that properties like minimum burning pressure should be taken into account.

26. An expert from the Spanish industry stressed that the heat source was very important and that the procedure in the MVPT should be followed. Furthermore, he said that there were two types of reaction: an explosion like that found by France and a detonation. The expert from France answered that this distinction might not be so important because scaling effects could lead to more violent behaviour in practice.

27. The expert from Canada stressed that tests should be performed more than once since the reproducibility might be poor.

Item 7 Proposals for Test Series 8 (United Kingdom)

28. The expert from the United Kingdom presented some comments on the current Test Series 8. First, he pointed out a possible flaw in the flow chart, allowing substances that do not pass series 8 to be transported as non dangerous goods. Secondly, he expressed doubts about the 8(b)

test quoting an analysis by an Australian expert from industry. The expert from the United Kingdom proposes the UN Detonation Test (Test A.6 of the UN Manual). Further, it was pointed out that both the United Kingdom and Spain had presented indications that thermal cycling might lead to a degree of changes in the substances, as indicated by crystal growth. It was, therefore, recommended to introduce a requirement on thermal cycling in the test procedure.

29. Since various reports on blocking of the orifice in the Koenen test were known, the expert from United Kingdom proposed to replace the Koenen test in series 8(c) by the US Pressure Vessel Test (Test E.3 of the UN Manual).

30. Finally, the expert from the United Kingdom also had many problems performing the 8(d) test because of the scale and environmental restrictions. The expert from the United Kingdom therefore proposed, like Germany, to use a test similar to the one given in Appendix 5 of the UN Manual instead of the (M)VPT.

31. An expert from the Spanish industry stressed that the work on the (M)VPT was picked up by industry because there was a need for a sufficient scale test for cook-off behaviour. He, therefore, urged the group to be careful with scaling down tests, since the scale can have a considerable influence on the behaviour. He agreed that there are certain disadvantages to the tests, although test series 8 increased industry's confidence in the safe transport of these products.

32. On the issue of scale, the expert from Sweden pointed out that the critical diameter of ANEs could be as large as 370 mm and therefore expressed doubts as to whether the current 8(b) test were severe enough. It was felt that the tests should have more confinement to get positive results. The expert from France pointed out that there are ANEs with a much smaller critical diameter. The expert from the Netherlands said that it was felt that the dimensions of the tube were about right but that the witness plate might be too thick, since many tests ended up with a totally fragmented tube but with a dented (not perforated) witness plate.

33. The expert from Germany pointed out that a test for explosive power (like the Trauzl test) could be useful.

Item 8 Kuosanen 2002 full scale burning test (Norway)

34. An expert from the Norwegian industry presented a video from a full scale test performed in 2002 by three Scandinavian companies. In 1995, the first large scale test was performed in aluminium tanks demonstrating that the tanks would open non violently leading to only burning of the ANE. Afterwards, the companies performed the VPT with only positive results which could not be explained. This was the reason why another full scale test was performed in a superfluous aluminium ADR tank. Only the last of the four compartments, just over the wheels with the original tyres, was used and filled with 6000 kg of ANE. About 400 litres of fuel was used to start the fire. Again the test demonstrated that the aluminium would melt, leading to discharge of the tank, before a violent reaction could possibly take place.

35. The expert from Sweden asked whether VPT tests were performed in aluminium vessels and what the results were. Indeed, one test was performed in a 10 mm wall thickness aluminium vessel with an explosion as a result. It was believed that the contents of the vessel reacted before the aluminium of the vessel was weakened by the fire. The tanks should only have a 5 mm wall.

Item 9 Discussion on transportation of ANEs in flexible IBCs (Sweden)

36. The expert from Sweden explained that he had received an application for importing ANE in flexible IBCs, which had already been approved in another country. He anticipated problems in handling and environmental problems with empty, uncleaned IBCs. From a safety point of view, there was no problem in transporting ANEs in these IBCs. He asked for the views of other experts.

37. The general feeling was that such transport could be done safely, but that the other problems mentioned would generally prevent large scale transport in (flexible) IBCs.

General discussion on test methods

38. The Chairman raised the question as to whether the current 8(d) test should be abolished and, if so, whether another test was necessary and which test it should be.

39. The group felt that there was a need for a test which assesses the hazard on a larger scale. For the time being, the VPT was the only available test, but it was agreed that it needed better specified conditions regarding heating rate and vent size criterion.

40. The general feeling was also that the Japanese presentations pointed out a good way forward in finding a smaller scale test which could be an alternative to the VPT. The expert from Japan was encouraged to continue the work and to present a proposal to the Sub-Committee when appropriate.

41. The expert from South Africa had practical experience with ANEs in the ARC and this experience was that every composition failed at 250 °C and 70 bar. Usually the formulations had a much lower burning pressure.

42. The expert from Spain volunteered to submit a proposal for revision of the 8(d) test before 8 April 2005.

43. For the 8(a) test, the group felt that alternative tests, such as ARC and Series H tests, could be allowed.

44. With regard to the 8(b) test, the expert from the United Kingdom intends to perform work on the gap test, both with fresh and thermally cycled samples. The expert from the Netherlands is going to perform a comparison of the mentioned gap tests and the thickness of the witness plate in the 8(b) test.

45. The expert from France indicated that a proposal regarding a reference substance in the Koenen test for all relevant Test Series might be submitted for the July session of the TDG and GHS Sub-Committees.

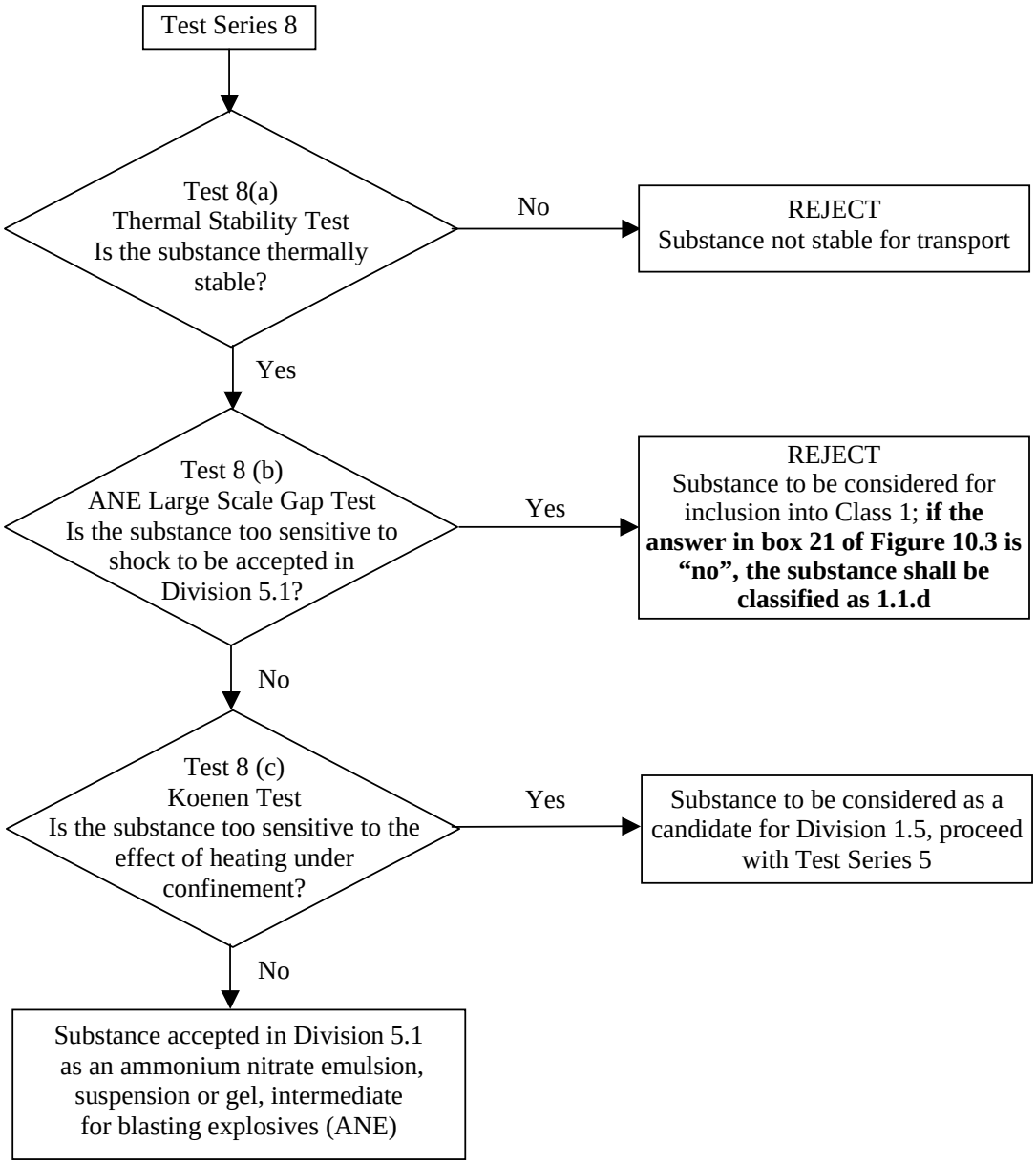
46. The expert from the United Kingdom identified a flaw in the current flow charts in Figures 10.2; 10.3 and 10.4. A substance too sensitive to meet the requirements of an ANE could end up as non dangerous goods according to the current flow charts. This could be solved by changing the wording in Figure 10.4 in the Manual of Tests and Criteria from “Substance to be considered for inclusion into Class 1” to “Substance is not an ANE and if the answer in box 21 of Figure 10.3 is “no”, it shall be classified as 1.1D”. A proposal for a revised flow chart is attached to this report (see annex).

47. In looking at the flow charts it was also noticed that the box number 19 appears twice (in Figure 10.2 and 10.3 respectively).

48. Based upon the Canadian document the Chairman remarked that the test methods for explosives may need to be revised to cover also the modern explosives and safety aspects which are not associated only with transport.

49. The Sub-Committee may wish to consider this report in the light of other proposals and test results which might be submitted in relation to it.

Annex


Test Series 8
Test 8(a)
Thermal Stability Test
Is the substance thermally stable?
No
REJECT
Substance not stable for transport
Yes
Test 8 (b)
ANE Large Scale Gap Test
Is the substance too sensitive to shock to be accepted in Division 5.1?
Yes
REJECT
Substance to be considered for inclusion into Class 1; **if the answer in box 21 of Figure 10.3 is "no", the substance shall be classified as 1.1.d**
No
Test 8 (c)
Koenen Test
Is the substance too sensitive to the effect of heating under confinement?
Yes
Substance to be considered as a candidate for Division 1.5, proceed with Test Series 5
No
Substance accepted in Division 5.1 as an ammonium nitrate emulsion, suspension or gel, intermediate for blasting explosives (ANE)