

# UN/SCETDG/25/INF.102

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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-fifth session  
Geneva, 5-14 July 2004  
Item 3 of the provisional agenda

### Report of the Working Group on Explosives

1. The Working Group on Explosives met from 5 to 8 July 2004, under the chairmanship of Mr. A. Johansen (Norway), with the mandate to discuss the default list on fireworks, and to discuss the papers regarding ANE's including two presentations by Australia.

2. Representatives from governmental organisations and industry from Australia, Belgium, Canada, Germany, France, India, Japan, the Netherlands, Norway, Portugal, South Africa, Spain, Sweden, Switzerland, the United Kingdom and the United States of America as well as the NGO's DGAC and ICCA participated in various parts of the meeting.

*NOTE: the above listed paragraphs 1 and 2 are to replace paragraphs 1 and 2 of INF.97. The following paragraphs are to be inserted after paragraph 21 of INF.97. The thus completed documented should be considered as the complete report of the Working Group on explosives and can be annexed to the report of the Sub-Committee.*

22. The Working Group was also tasked with discussing .../C3./2004/14 and INF.92 from Germany on a better specification of the materials used in the Koenen test. The experts from Canada and the USA were supportive of a better specification of the materials, but remarked that the reference included in INF.92 was not available in North America. The expert from the Netherlands mentioned that he has made some attempts to write a European standard on the Koenen test, but was not able to find an international standard for the used materials. The expert from France recalled that not only the properties at ambient conditions were relevant, but that the behaviour at higher temperatures were equally important. He therefore suggested the possibility, as is current practice in France, to use musk xylene (dry state, melting point 113°C, > 99% purity with a specified maximum amount of isopropanol) as a reference substance to assess the correct behaviour (3 out of 3 at 1 mm orifice; 0 out of 3 at 2 mm orifice and 3 out of 3 at 8 mm orifice).

23. The expert from the USA suggested some changes to the proposed text: "To enhance reproducibility of test results, the quality of the steel tubes used need to be checked to meet the following requirements: wall thickness....etc." The expert from the Netherlands pointed out that diameter of the tubes need to be measured as well.

24. There was general support for the proposal of Germany and several experts indicated they would supply information on national steel specification to the German expert. A new proposal by Germany for the December meeting is anticipated.

### **Ammonium nitrate emulsions**

25. On Thursday the 8<sup>th</sup> of July Mr. Johansen welcomed all experts and especially those who were here only for the ANE's. He expressed the hope that the group could reach some conclusions in a co-operative spirit. Although he already expressed at the December 2003 meeting his expectation that there will not be a consensus WG view and that the decision should be left to the Sub-Committee, the number of technical details in the several proposals and information documents justified the Working Group to have a look at those technicalities.

Several national delegates indicated that representatives from industry were part of their delegation in order to allow them to join the Working Group. They would also be referred to as 'expert from ...' in this report but they do not necessarily represent the national view.

The WG was tasked to look at three different subjects:

- the question whether there should be a separate entry for ammonium nitrate suspensions and gels;
- review the proposed changes to the current SP 309; and
- to assess the proposals with regards to improving the Vented Pipe Test (test 8(d)).

#### Documents:

ST/SG/AC.10/C.3/2004/24 from Sweden was withdrawn

UN/SCETDG/25/INF.63 from Canada on the above document, is no longer relevant

ST/SG/AC.10/C.3/2004/24 from Sweden is replaced by UN/SCETDG/25/INF.73

The chairman recalled that the expert from Belgium has questioned the usefulness of having 2 separate entries for these products in the plenary meeting on Monday morning.

26. The expert from Spain introduced ST/SG/AC.10/C.3/2003/31 and .../2004/64 by recalling the history behind the documents. After having presented proposals at earlier meetings (July and December 2003), some delegations have asked to postpone a decision on these proposals to allow consultation in their respective countries. Spain agreed with these requests, since a consensus view of the Working Group was preferred. The expert from Spain stressed once again that they were convinced that both the emulsions and the suspensions are similar substances, designed for similar use, presenting similar hazards and both needing the same transport conditions. The test results should be decisive for accepting suspensions in Division 5.1 and not the ingredients.

27. During the introduction of UN/SCETDG/25/INF.73 the expert from Sweden also recalled the history starting at the first meeting of the Working Group in Engene (Norway). He was of the opinion that suspensions containing sensitizers such as perchlorates, hexamine nitrate or monomethylamine nitrate are different than ammonium nitrate emulsions and should thus have a separate UN number and connected Special Provision.

28. The expert from Spain gave a presentation to introduce UN/SCETDG/25/INF.74 and INF.84. A lot of interesting and thorough research work was presented comparing 'standard emulsions' with sodium perchlorate, hexamine nitrate or monomethylamine added in order to compare the behaviour and sensitiveness of emulsions and suspensions with Test 1(a). It appeared that the water content has a far greater influence on the shock sensitivity than the addition of the above mentioned products, sometimes referred to as sensitizers. The conclusion in the document was that test results should prevail over substance definition.

29. A long discussion took place where several questions for clarification were asked and answered. The arguments included (not exhaustive):

- filling of the test tubes
- different kinds of sensitiveness (to several stimuli)
- the fact that a substance passes a test should be the determining factor for classification
- the possibility of crystal growth and possible formation of undesired compounds

- influence of physical properties (like droplet size, etc.)
- for emulsions, the consensus was to let the test results prevail
- effect of temperature on the sensitiveness of emulsions
- promising possibilities of the Minimum Burning Pressure Test researched by Canada
- emulsions show ageing, Test Series 8(a) is meant to address that

30. The expert from Australia presented research work on modelling the 8(b) gap test and the Koenen test and comparing these results with experimental work.

Included in the work on the gap test are:

- irreversible temperature effects after passing of the shock wave of the donor,
- the influence of voids in the test substance,
- diameter effect, and
- attempts to initiate large amounts of ANE's at transport density.

The modelling work on the Koenen test resulted in prediction of behaviour under several conditions and explanation of unexpected 'strange' results. A different behaviour between emulsions and suspensions was observed experimentally.

The expert from Spain pointed out that experimental evidence in INF.74 does not agree with the above conclusion.

31. Several experts confirmed that false positive results are sometimes obtained with emulsions and suspensions and questioned the adequacy of the Koenen test for these types of substances. The presentations given confirmed once again the need to have a further examination of Test Series 8.

32. The chairman asked the Working Group whether the Swedish proposal for a new entry for sensitised emulsions, suspensions and gels could be accepted.

A majority of the delegates indicated that they did not support a new entry, neither for sensitised emulsions, suspensions and gels (.../25/INF.73), nor for a separate entry for suspensions and gels as proposed by the UK in .../25/INF.68, paragraph 12.

However, several other experts saw merits in having a new entry.

The Working Group could not reach a unanimous conclusion on the question to either expand the current SP309 (as proposed by Spain) to include suspensions with perchlorate and amines or to create a new entry as proposed by Sweden or the UK.

33. The changes to SP309, as proposed by Spain, were discussed which resulted in a slight change of the first paragraph: "... nitrate and a fuel phase intended to ..." is to be changed to "...nitrate and fuel intended to ...".

The proposal from Spain now reads:

"309 This entry applies to non sensitised emulsions, suspensions and gels consisting primarily of a mixture of ammonium nitrate and fuel, intended to produce a Type E blasting explosive only after further processing prior to use.

The mixture for emulsions typically has the following composition: 60-85% ammonium nitrate; 5-30% water; 2-8% fuel; 0.5-4% emulsifier agent; 0-10% soluble flame suppressants; and trace additives. Other inorganic nitrate salts may replace part of the ammonium nitrate.

The mixture for suspensions and gels typically has the following composition: 60-85% ammonium nitrate; 0-5% sodium or potassium perchlorate; 0-17% hexamine nitrate or monomethylamine nitrate; 5-30% water; 2-15% fuel; 0.5-4% thickening agent; 0-10% soluble flame suppressants; and trace additives. Other inorganic nitrate salts may replace part of the ammonium nitrate.

Substances shall satisfactorily pass Test Series 8 of the *Manual of Tests and Criteria*, Part I, Section 18 and be approved by the competent authority”

34. The Sub-Committee is invited to take a decision on:
- the Swedish proposal to create a new entry for sensitised emulsions, suspensions and gels in Division 5.1 as given in UN/SCETDG/25/INF.73; or
  - the proposal from the UK to amend the Swedish proposal to create a new entry for ammonium nitrate suspensions and gels in Division 5.1 and to delete suspensions and gels from the existing UN 3375 as given in UN/SCETDG/25/INF.68, paragraph 12; or
  - to change SP 309 as reflected above.

### **Improvement of test methods**

35. The expert from Spain presented .../25/INF.74, work on the characterisation of the Modified Vented Pipe Test (MVPT). Various tests on emulsions and suspensions have been performed and the results show that the earlier found differences in behaviour between emulsions and suspensions (e.g. shorter time to reaction) are caused by the thickener in the suspensions. He concluded that the modified form of the vented pipe test is reproducible and able to discriminate between substances believed to be safe for bulk transport outside Class 1 and those that are not. He advised that the test should be run until either explosion or full consumption of the tests substance with a constant heating rate and a vent diameter of 75 mm. He asked the WG to consider whether the test should be run two or three times.

36. In INF.74 a comparison between the results of the MVPT and the Koenen test was included which indicates that the results were comparable. Some experts questioned whether is it useful to continue with this type of test. It was remarked that there is only a rough similarity and that the heating rate in both tests is quite different. More work is needed to draw firm conclusions on the correlation between both tests.

37. Spain asked for a discussion on INF.85, in particular on four questions:
- should the MVPT be an alternative to the current 8(d) test or become the only type (d) test?
  - is the vent size of 75 mm acceptable?
  - does the WG agree that the test should be performed (at least) twice?
  - are the proposed criteria acceptable?

38. Several experts considered that it is not the right time to answer the questions, partly because of lack of experience with the modified test. Some views on the 4 questions were given but no firm conclusions could be drawn at this moment. With regards to the specification of the materials (e.g. steel for the vessel, formulations) the group agreed that the proposed specifications should be readily available all over the world.

39. The expert from Australia presented some background information on the changes made in Australia to the current 8(d) test. Aspects like heat input, heated surface, absorbed heat flux of 8(d) test and MVPT, Koenen tests and tank containers were compared. The Australian modification was chosen to best resemble the transport conditions in ISO containers and 1.3 ton hoppers. The Scandinavian results obtained some years ago were compared with these parameters and, when plotted in this way the provided heat input was about  $\frac{2}{3}$  of that needed to reach the boiling point of the test substance. When calculating backwards from a 20 m<sup>3</sup> IMDG tanks with a 250 mm burst disk the vent size on a VPT test should be 9 mm and the test vehicle should be fitted with a 1.7 mm thick bursting disk (of 180 mm diameter) to have a similar strength.

40. The expert from Australia has identified an inconsistency in the description of the 8(b) test. In the general introduction to Test Series 8, paragraph 18.3.1 reads: “The substance should be tested as offered for transport, at the highest transport temperature (see 1.5.4 of this Manual).” But in paragraph 18.5.1.3.1 it is stated: “The test sample and booster should be at ambient temperature for the test.” This item should be resolved when a possible review of Test Series 8 is agreed upon.

41. The WG agreed that the recent research activities demonstrated the shortcomings of the current tests in Test Series 8 and recommends to the Sub-Committee to include the revision and improvement of Test Series 8 in the work programme of the next biennium.

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