



Secretariat

Distr.
GENERAL

ST/SG/AC.10/C.3/2008/40
11 April 2008

Original: ENGLISH

**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

Thirty-third session
Geneva, 30 June-9 July (a.m) 2008
Item 2 of the provisional agenda

EXPLOSIVES AND RELATED MATTERS

Screening test for substances which may have explosive properties and consequential changes
Introduction of additional criteria

Transmitted by the International Council of Chemical Associations (ICCA)*

Background

1. At the thirty-first session of the Sub-Committee (TDG Sub-Committee), the expert from Germany submitted document ST/SG/AC.10/C.3/2007/10 which identified some open issues in the GHS for substances having explosive properties.
2. In response to this paper, the Working Group on Explosives suggested making Test Series 1 mandatory in the classification procedure of the Globally Harmonized System of Classification and Labelling (GHS) for Explosives (informal document UN/SCETDG/31/INF.45).
3. Based on the recommendations of the Working Group on Explosives and of the TDG Sub-Committee, the Secretariat submitted proposal ST/SG/AC.10/C.4/2007/6 to the GHS Sub-Committee at its fourteenth session. Among others, the subject of this proposal was to delete

* In accordance with the programme of work of the Sub-Committee for 2007-2008 approved by the Committee at its third session (refer to ST/SG/AC.10/C.3/60 para. 100 and ST/SG/AC.10/C.3/34, para. 14).

the asterisk from the box “Test series 1” and its related footnote and to introduce a new paragraph 2.1.2.2 reading “*For some regulatory purposes (e.g. transport) substances having explosive properties according to Test Series 1 can be excluded from Division 1.1 to 1.6 when Test Series 2 demonstrates that the substance is too insensitive. The fact that a substance has explosive properties is important for other regulatory purposes and for the hazard communication. It is therefore important that Test Series 1 is performed in the classification procedure.*”

4. In informal document UN/SCETDG/32/INF.35, industry pointed out several practical difficulties and inconsistencies that would arise from the adoption of this proposal and which would make its implementation hardly achievable.

5. The TDG Sub-Committee agreed that the decisions, taken at the previous session and forwarded to the GHS Sub-Committee by document ST/SG/AC.10/C.4/2007/6, needed further consideration, preferably by the Working Group on Explosives which would meet at the next July 2008 session.

6. ICCA therefore proposes to review this paper first in the Working Group on Explosives. Although a number of proposals have been given in this paper, they need indeed further consideration and discussion by this group.

Discussion regarding the proposals

7. For the reasons given in informal document UN/SCETDG/32/INF.35, industry has been looking for a possible way forward. A possible solution would be to amend the screening procedures of Appendix 6 of the UN Manual of Tests and Criteria.

8. The intention of the screening procedures is to identify the presence of reactive groups and the potential for rapid energy release for new substances suspected of having explosive properties, but they should not be used for substances manufactured with the intention of producing a practical explosive or a pyrotechnic effect.

9. According to the NOTE in section 3 of the screening procedures, tests 1 (a) and 2 (a) (“UN gap test”) are not required if the exothermic decomposition energy of organic materials is less than 800 J/g. However, the presence of a single energetic group in a molecule will often bring the decomposition energy to values \gg 800 J/g, and in many cases the oxygen balance criterion is not helpful.

10. As a possible alternative to the UN gap tests, industry has checked the BAM Trauzl test (test F.3 as described in the UN Manual of Tests and Criteria). The results are given in Table 1.

11. Even very insensitive substances such as Ammonium nitrate give a clearly positive result in this test, especially when a stronger initiation is used.

Table 1: Lead block expansion and steel tube tests^{1, 2, 3} (For reference purposes, also self reactives and organic peroxides are included in the table although they have their own classification flowchart.)			
Substance	Lead block expansion (ml/10 g)	2" steel tube test (UN A1)	Comment
Azodicarbonamide	9	no	
Benzene-1,3-disulfohydrazide	50	yes	
Benzene-sulfohydrazide	11	no	
tert-Butylperoxybenzoate	32	partial	
tert-Butylperoxy-2-ethylhexanoate	28	no	
3-Chloroperoxybenzoic acid, not more than 86 %, with 3-chlorobenzoic acid	42	yes	
Cumylhydroperoxide, 84 % in cumene	10	no	
Cyclohexanone peroxide(s)	50	yes	
Dibenzoylperoxide	31	yes	slightly stronger initiation in Trauzl test
Dibenzoylperoxide, 75 %, with water	21	no	slightly stronger initiation in Trauzl test
Di-tert-butylperoxide	28	no	
Dicetylperoxydicarbonate	5	no	
Dicumylperoxide	12	no	
Diisopropylperoxydicarbonate	78	yes	
Dilauroylperoxide	11	partial	Fragmented length in UN A1 test: 25 cm
Dimyristylperoxydicarbonate	11	no	
Nitromethane	430	yes	
Hydroxybenzotriazol, dry	94	yes	
Thioureadioxide	11	no	Decomposition energy: 1050 J/g
N,N'-Dinitrosopentamethylenetetramine, 80 %, with 17 % inorganic solid and 3 % mineral oil	123	yes	with stronger initiation in Trauzl test
Ammonium nitrate, small crystals (0,15 to 0,4 mm)	200		with stronger initiation in Trauzl test
Ammonium nitrate, long rhombic crystals (3 cm long)	135		with stronger initiation in Trauzl test
Ammonium nitrate, large pieces produced by breaking after melting and solidification	15		with stronger initiation in Trauzl test

¹ UN Manual of Tests and Criteria, 4th rev. ed.

² L. A. Medard, Accidental Explosions, Vol. 1, English Edition, Chichester, Ellis Hornwood Limited, 1989.

³ R. Aufschläger, Z. Ges. Schiess Sprengst. **19**, 121 (1924).

12. Most important, there is no substance that would give a propagation of detonation in the 2" steel tube test and a negative response in the Trauzl test. Therefore, the BAM Trauzl test seems to be appropriate to assess the ability of a substance to propagate a detonation. Moreover, the lead block expansion allows assessing the explosive power as well.

13. The 800 J/g criterion as a threshold to perform the UN gap tests appears too conservative. A more appropriate value seems to be 1200 J/g for organic materials. Even for mixtures of high explosives with inert substances (i.e. PETN / lactose), a propagation of detonation is not observed for decomposition energies below 1300 J/g.

Proposals

14. Modify the NOTE in Appendix 6, chapter 3, of the UN Manual of Tests and Criteria to read:

NOTE: Neither a Series 1 type (a) propagation of detonation test nor a Series 2 type (a) test of sensitivity to detonative shock is required if the exothermic decomposition energy of organic materials is less than ~~800 J/g~~ [1200 J/g]. For organic substances and mixtures with a decomposition energy of [1200 J/g] or more, tests 1 (a) or 2 (a) do not have to be performed if the outcome of the BAM Trauzl test (test F.3) with initiation by (... specify initiation) is "no". In this case, the results of test 1(a) and 2(a) are deemed to be "-".

15. Insert a new paragraph 11.3.5 in the UN Manual of Tests and Criteria to read:

For organic substances and mixtures with a decomposition energy of [1200 J/g] or more, test 1 (a) does not have to be performed if the outcome of the BAM Trauzl test (test F.3) with initiation by [... specify initiation] is "no". In this case, the result of test 1(a) is deemed to be "-". If the outcome of the Trauzl test is "not low", the result of test 1(a) shall be deemed to be "+". In this case, a "-" can only be obtained by performing test 1(a).

16. Insert a new paragraph 2.1.1.3 in the GHS to read:

Explosive properties of self-reactive substances and of organic peroxides shall be tested according to the procedures of chapters 2.8 and 2.15, respectively.

17. Modify paragraph 21.2.2 in the UN Manual of Tests and Criteria to read:

For organic peroxides and self-reactive substances, a combination of a test for explosive power (any test of series F except F.5 for organic peroxides and any test of series F except F.4 and F.5 for self-reactive substances) with two tests for the effects of heating under confinement may be used as a screening procedure for assessing the ability to propagate a detonation. A test of series A need not be performed if:

- (a) A "No" result is obtained from the explosive power test; and
 - (b) A "No" or "Low" result is obtained from test E.2 and either test E.1 or E.3.
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