

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-third session, 30 June-4 July 2003)

Agenda item 6(b))

LISTING, CLASSIFICATION AND USE OF PACKAGINGS

Miscellaneous amendment proposals (Parts 2 and 3)

Comments on ST/SG/AC.10/C.3/2003/19

Transmitted by the Expert from the United Kingdom

**Background**

1. In paper **ST/SG/AC.10/C.3/2003/19** *Modification des Critères d'Exclusion de la Division 4.1 Matières Autoréactives* the Expert from France proposes that the criterion in part b) is removed from paragraph 2.4.2.3.1.1.
2. The expert from the United Kingdom notes that this proposal has been made on at least two occasions in the past, most recently in ST/AG/AC.10/C.3/1998/55 when it was again rejected by the Sub-Committee because they agreed that this criterion is a "compromise based on safety considerations" (Para. 101–102, ST/SG/AC.10/C.3/30, REPORT OF THE SUB-COMMITTEE OF EXPERTS ON ITS FIFTEENTH SESSION, Geneva, 29 June-9 July 1998).
3. **Recommendation/Proposal**

Part b) of paragraph 2.4.2.3.1.1 should be retained on safety grounds.

Add a third note to paragraph 2.4.2.3.1.1:

**“NOTE 3** Oxidizing substances and combustible substances are chemically incompatible. Based on safety considerations, any substance which demonstrates the properties of a self-reactive substance and which is an oxidizing substance in accordance with paragraph 2.5.2.1.1, shall not be classified as a self-reactive substance of Division 4.1.

**Justification**

4. It is not good practice to transport or store oxidisers and fuels together, to do so is likely to make any fire substantially worse.
5. It is true that the property “self-reactive” is a primary hazard (Para 2.0.3.1) whilst that of “oxidizing” is not; the latter is dealt with by means of the precedence of hazards (Table 2.0.3.3). At first sight it would seem that part b) of paragraph 2.4.2.3.1.1 is a contradiction, but it was included in the criteria for self-reactive substances to ensure that oxidising substances, in particular thermally unstable oxidising substances, are excluded from a flammables Class because this is incompatible with safety.
6. Self-reactive substances are assigned to a Division in a flammables Class; indeed, many of these substances burn so quickly that they meet the criterion of a flammable solid of Division 4.1. In general, self-reactive substances are organic and contain a high proportion of carbon and hydrogen; the

exothermic decomposition they undergo at relatively low temperatures tends to make them prone to combustion and / or deflagration. The contribution from the energy released during decomposition and the active centres produced, which are susceptible to attack by atmospheric oxygen, tend to enhance their rate of combustion. Conversely, thermally unstable oxidisers are almost invariably inorganic (e.g. percarbonates, perborates, persulphates etc.). These substances do not burn, and they decompose to releases oxygen (or possibly free halogen) which significantly assists combustion of any flammable material in the immediate vicinity, particularly if that material is a self-reactive substance.

7. The consequence of removing part b) of 2.4.2.3.1.1 would be to allow thermally unstable fuels and thermally unstable oxidisers to be transported together and, in the context of the GHS, stored together. They would carry the same label, and there would be no ready means by which they can be identified as being chemically incompatible.
8. Evidence that oxidisers with relatively low thermal stability have an adverse effect on the rate of combustion of a self-reactive substance was shown by tests following the major fire at Allied Colloids (in the UK in 1992). Whilst this was not an incident in transport, the materials were contained in their transport packages. Storing the self-reactive substance immediately above the oxidisers is not believed to have caused the ignition, but it is believed to have been the reason for the extremely rapid spread of the fire.
9. Azo-2,2'-di(isobutyronitrile) (AZDN), a temperature controlled self-reactive solid "TYPE C" (UN 3234), and several oxidisers were stored together in a room adjacent to the main warehouse storage area. The oxidisers were potassium nitrate (UN 1486), calcium nitrate (UN1454), sodium persulphate (UN1505) and ammonium persulphate (UN1444), all substances of UN Division 5.1 (PGIII). Ammonium persulphate is a borderline oxidising substance of UN Division 5.1. Inorganic nitrates are thermally more stable than inorganic persulphates because the persulphate anion can produce oxygen at temperatures as low as 50 to 80°C. Ammonium persulphate meets the thermal stability and energy of decomposition criteria of a self-reactive solid.
10. The effect of different oxidisers on the burning rate of AZDN was investigated using a modification of the procedure in UN Test N.1. The piles comprised an upper layer of AZDN, which formed the apex of the pile, on top of a lower layer of the inert solid, the mineral clay Bentonite, or the solid oxidiser. The solids were **not** mixed, and the AZDN constituted approximately 5 mass% of the pile.

**Table 1 Rate of combustion of a self-reactive solid in contact with various oxidisers**

Mixture	Rate of Flame Propagation <sup>(1)</sup> (mm.s <sup>-1</sup> )				Burning Rate Ratio <sup>(2)</sup>
AZDN/ Bentonite	2.3	2.1	-	-	1.0
AZDN/ Potassium Nitrate	1.9	-	-	-	0.9
AZDN/ Calcium Nitrate	2.4	-	-	-	1.1
AZDN/ Sodium Persulphate	11	9	11	11	4.8
AZDN/ Ammonium Persulphate	17	15	-	-	7.3

*Notes: (1) United Nations Recommendations on the Transport of Dangerous Goods; UN publication ST/SG/AC.10/1/Rev7, Pub. United Nations; New York, Geneva; 1991, p 371, ISBN 92-1-139035-4.*

*(2) AZDN/ Bentonite = 1.0*

11. Table 1 clearly shows the effect that the thermal stability of the oxidiser has on the rate of combustion of a self-reactive solid. The burning rates of AZDN in contact with the relatively stable nitrates are comparable with the rate when it is in contact with the inert solid, approximately  $2 \text{ mm.s}^{-1}$ . On a layer of sodium persulphate the burning rate increases substantially, to almost 5 times the baseline value (approximately  $10 \text{ mm.s}^{-1}$ ). When AZDN is in contact with ammonium persulphate, which itself has self-reactive properties, the burning rate increases by a further 50% to nearly 7.5 times the base value i.e. approximately  $16 \text{ mm.s}^{-1}$ .
  12. Concern is expressed in ST/SG/AC.10/C.3/2003/19 that an oxidiser that is thermally unstable under the conditions likely to be encountered during transport may present a greater risk than one that is thermally stable. Whilst this is justified, the problem should not be addressed by classifying the oxidizing substance as a self-reaction substance, to do so will adversely affect safety. Consideration should be given to resolving this problem without compromising safety. Where a substance is an oxidising substance by the criteria in paragraph 2.5.2.1.1, but is capable of undergoing exothermic decomposition in a transport package at temperatures likely to be encountered during transport, it should be assigned its own individual UN number in the Dangerous Goods List in Chapter 3.2 of the Model Regulations, with a suitable special provision in Chapter 3.3 and, if necessary, a special packing provision under the appropriate Packing Instruction.
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