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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 Globally Harmonized System of Classification and Labelling of Chemicals

(Fifth session, 7-9 July 2003,
agenda item 4)

PROPOSALS FOR AN AMENDMENT TO THE GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION AND LABELLING OF THE CHEMICALS (GHS)

Comments on ST/SG/AC.10/C.4/2003/5

Transmitted by the Expert from the United Kingdom

Background

1 In paper **ST/SG/AC.10/C.4/2003/5** *PROPOSITIONS D'AMENDEMENTS AU SYSTÈME GÉNÉRAL HARMONISÉ DE CLASSIFICATION ET D'ÉTIQUETAGE DES PRODUITS CHIMIQUES (SGH): Matières Autoréactives*, the Expert from France proposes that the criterion in part b) is removed from paragraph 2.8.2.1 of Chapter 2.8 of the Globally Harmonized System of Classification and Labelling of Chemicals.

2 An identical proposal has been made to the Sub-Committee of Experts on the Transport of Dangerous Goods, in paper **ST/SG/AC.10/C.3/2003/19** *Modification des Critères d'Exclusion de la Division 4.1: Matières Autoréactives*. Similar proposals have been made to the transport Sub-Committee on at least two occasions in the past, most recently in **ST/AG/AC.10/C.3/1998/55**. The proposals were rejected, because the Sub-Committee 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).

Recommendation

3 Part b) of Paragraph 2.8.2.1 in The Globally Harmonized System of Classification and Labelling of Chemicals is retained on safety grounds.

Justification

4 It is bad practice to store or transport oxidisers and fuels together, to do so makes any fire substantially worse.

5 Self-reactive substances or mixtures are defined in paragraph 2.8.1 of The Globally Harmonized System of Classification and Labelling of Chemicals as materials that are:

"thermally unstable liquid or solid substances or mixtures liable to undergo a strongly exothermic decomposition even without participation of oxygen (air)."

This definition excludes substances and mixtures classified under the GHS as explosives, organic peroxides or as oxidising. These substances are labelled with an exploding bomb and / or a flame, which are considered to best reflect the properties of these substances.

6 The definition of an oxidising liquid (Para 2.13.1) and an oxidizing solid (Para 2.14.1), is a substance that:

“while in itself not necessarily combustible, may, generally by yielding oxygen, cause, or contribute to, the combustion of other material.

When an oxidising substance is also relatively thermally unstable, it will very readily undergo decomposition to give oxygen under fire conditions. These substances are labelled with a “flame over ‘O’”.

7 Many self-reactive substances are flammable and burn quickly; in the case of solids, they often meet one or more of the criteria used to classify flammable solids (Table 2.7.1). 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 flammable self-reactive substance.

8 The consequence of removing part b) of Paragraph 2.8.2.1 would be to allow thermally unstable fuels and thermally unstable oxidisers to be stored and transported together. They would carry the same label, and there would be no means by which they can be identified as being chemically incompatible.

9 Evidence that oxidisers of 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, which occurred in the UK in 1992. The incompatible materials, contained in their transport packages, were stored together on shelves in the same (small, enclosed) room in the warehouse complex. 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 to the main storage area of the warehouse.

10 The self-reactive substance was azo-2,2'-di(isobutyronitrile) (AZDN), a temperature controlled solid of “TYPE C” (UN 3234). The oxidisers were potassium nitrate (UN 1486), calcium nitrate (UN1454), sodium persulphate (UN1505) and ammonium persulphate (UN1444), all these compounds are oxidising solids of hazard category 3. Inorganic nitrates are thermally more stable than inorganic persulphates; the persulphate anion can produce oxygen at much lower temperatures, as low as 50 to 80°C. Ammonium persulphate is a borderline oxidising substance, and it also meets the thermal stability and energy of decomposition criteria of a self-reactive solid.

11 The effect of the different oxidisers on the burning rate of AZDN was investigated using a modification of the procedure in 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 an 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.

12 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 measured when it is in contact with the inert solid, approximately 2 mm.s⁻¹. On a layer of sodium persulphate the burning rate increases substantially, to almost 5 times the baseline value (approximately 10 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 mm.s⁻¹.

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

Mixture	Rate of Flame Propagation ⁽¹⁾ (mm.s ⁻¹)				Burning Rate Ratio ⁽²⁾
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
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