

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-fourth session
Geneva, 3-10 December 2003
Item 3 (c) of the provisional agenda

EXPLOSIVES, SELF REACTIVE SUBSTANCES AND ORGANIC PEROXIDES

Miscellaneous proposals

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

Transmitted by the expert from FRANCE

Background

In paper **ST/SG/AC.10/C.3/2003/19** *Modification des critères d'exclusion de la division 4.1 matières autoréactives*, France proposes the criterion in part b) to be removed from paragraph 2.4.2.3.1.1., in order to deal with substances having both dangers.

An informal Ad Hoc TDG expert meeting was held in Paris (France), on the 23rd September 2003 to discuss this matter further (Para. 67–72, ST/SG/AC.10/C.3/30, REPORT OF THE SUB-COMMITTEE OF EXPERTS ON ITS FIFTEENTH SESSION, Geneva, 30 June-4 July 2003). Experts from the following countries and Organizations took part in this work : United Kingdom, Germany, Netherlands, France, ICCA.

Finally this group agreed that the problem was related to mixtures containing both organic (combustible) substances and oxidizing substances, and that it would be solved by adding a Note 3 to 2.4.2.3.1.

The following proposal replaces the proposals in ST/SG/AC.10/C.3/2003/19

Points where a decision between two options could not be made are in square brackets.

Proposal

Add the text of NOTE 3.

2.4.2.3 *Division 4.1 Self-reactive substances*

2.4.2.3.1 *Definitions and properties*

2.4.2.3.1.1 Definitions

For the purposes of these Regulations:

Self-reactive substances are thermally unstable substances liable to undergo a strongly exothermic decomposition even without participation of oxygen (air). Substances are not considered to be self-reactive substances of Division 4.1, if:

- (a) They are explosives according to the criteria of Class 1;
- (b) They are oxidizing substances according to the assignment procedure of Division 5.1 (see 2.5.2.1.1);
- (c) They are organic peroxides according to the criteria of Division 5.2;
- (d) Their heat of decomposition is less than 300 J/g; or
- (e) Their self-accelerating decomposition temperature (SADT) (see 2.4.2.3.4) is greater than 75 °C for a 50 kg package.

NOTE 1: *The heat of decomposition can be determined using any internationally recognised method e.g. differential scanning calorimetry and adiabatic calorimetry.*

NOTE 2: *Any substance which shows the properties of a self-reactive substance shall be classified as such, even if this substance gives a positive test result according to 2.4.3.2 for inclusion in Division 4.2.*

NOTE 3: *Formulations [mixtures] containing oxidising substances meeting the criteria of division 5.1 and organic substances, and that are not meeting the criteria mentioned above in (d) or (e), shall be subjected to the self-reactive substances classification procedure.*

A mixture showing the properties of a self-reactive substance type B to E [F] shall be classified as a self-reactive substance of division 4.1.

A mixture showing the properties of a self-reactive type [F and] G shall be considered for classification as substance of division 5.1 (see 2.5.2.1.1).

Justification

Mixtures containing beside oxidising substances according to the criteria of Division 5.1 also organic substances (combustible substances) and mostly other substances may be thermally unstable (heat of decomposition is higher or equal to 300 J/g, SADT is lower or equal to 75 °C for a 50 kg package).

As a rule such mixture containing such a amount of organic substances that the test method of division 5.1 (Manual of Tests and Criteria, Part III, sub-section 34.4.1) is not applicable and leading to false-positive results because combustible substances are always present. The additional mixing with fibrous cellulose leads in such cases only to a dilution of the test item.

During the last years, a lot of different mixtures containing the above-mentioned substances (e. g. cleaner, detergent tablets, hair cosmetics) placed on the market and transported in larger quantities. Some of them are unstable under normal conditions of transport and need temperature control.

According to the criteria of self-reactive substances of division 4.1, these mixtures may be classified as self-reactive substances, solids, type B to type F.

A mixture, classified as self-reactive substances, solids, type G (not subject to the provisions for self-reactive substances of division 4.1) may be considered for classification as a substance of division 5.1 according to the assignment procedure of division 5.1.

It is not intended to classify pure oxidizing substances which fulfill the assignment criteria of Division 5.1 as self-reactive substances of Division 4.1.
