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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, 5-14 July 2004  
Item 3 (c) of the provisional agenda

Sub-Committee of Experts on the Globally Harmonized  
System of Classification and Labelling of Chemicals

Seventh session, 14-16 July 2004,  
Item 2 (a) of the provisional agenda

EXPLOSIVES, SELF-REACTIVE SUBSTANCES AND ORGANIC PEROXIDES

Miscellaneous proposals

Transmitted by the expert from France

**Background**

France proposed a modification to the criteria for self-reactive substances, in order to deal with substances having both oxidizing and self-reactive properties (see ST/SG/AC.10/C.3/2003/19, UNSCETDG/23/INF.7 and UNSCETDG/23/INF.28 (twenty-third session of the Sub-Committee of Experts on the Transport of Dangerous Goods) and ST/SG/AC.10/C.4/2003/5 (fifth session of the Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals)).

Based on comments made during the Sub-Committee and taking advantage of the presence of some IGUS experts, an ad hoc TDG expert meeting was held in Paris (France), on 23 September 2003 to discuss this matter further (ST/SG/AC.10/C.3/46, paras. 67–72, report of the Sub-Committee of Experts, July 2003). Experts from the following countries and organizations took part in this work: United Kingdom, Germany, Netherlands, Sweden, 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 to the appropriate parts of the Model rules and the GHS.

An informal paper was presented to the twenty-fourth session of the Sub-Committee in December 2003 (INF.35).

This formal proposal is based on the above mentioned document and on the comments that have been made by the experts during the Committee meeting.

It is presented to both Sub-Committees. Therefore, two versions having the same content but formally suitable to each case are provided.

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## **Proposal**

### **1. Text proposed for inclusion in the Model Regulations on Transport of Dangerous Goods**

2.4.2.3 Shall be amended as follows:

#### **“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) **and they are not mixtures of oxidizing substances and organic substances subject to the procedure defined in NOTE 3 ;**
- (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 recognized 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:** **Mixtures of oxidizing substances meeting the criteria of division 5.1 and organic substances, which do not meet the criteria mentioned in (a), (c), (d) or (e) above, shall be subjected to the self-reactive substance classification procedure;**

**A mixture showing the properties of a self-reactive substance type B to E shall be classified as a self-reactive substance of division 4.1;**

**A mixture showing the properties of a self-reactive substance type F shall be considered for classification as substance of division 5.1 (see 2.5.2.1.1). If the criteria for oxidizing substances are not met, the substance shall be classified as self-reactive substance of type F;**

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

## 2. Text proposed for inclusion in the GHS document

“2.8.2.1 Any self-reactive substance or mixture should be considered for classification in this class unless:

- (a) They are explosives, according to the GHS criteria of Chapter 2.1;
- (b) They are oxidizing liquids or solids, according to the GHS criteria of Chapters 2.13 or 2.14. **and they are not mixtures of oxidizing substances and organic substances subject to the procedure defined in NOTE 1;**
- (c) They are organic peroxides, according to the GHS criteria of Chapter 2.15;
- (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 : Mixtures containing oxidizing substances according to the GHS criteria of chapters 2.13 or 2.14, and organic substances, and that are not meeting the criteria mentioned above in (a) (c) (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 shall be classified as a self-reactive substance;**

**A mixture showing the properties of a self-reactive substance type F shall be considered for classification as substance of Division 5.1 (see 2.13 and 2.14). If the criteria for oxidizing substances are not met, the substance shall be considered as a self-reactive substance of type F;**

**A mixture showing the properties of a self-reactive substance type G shall be considered for classification as a substance of Division 5.1 (see 2.13 and 2.14). "**

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### Justification

Mixtures containing beside oxidizing substances according to the criteria of Division 5.1 also organic substances (combustible 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).

These mixtures containing such an amount of organic substances lead to false-positive results in the test method of Division 5.1 (Manual of Tests and Criteria, Part III, sub-section 34.4.1) 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 recent years, many different mixtures containing the above-mentioned substances (e. g. cleaner, detergent tablets, hair cosmetics) have been 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 substance, solid, type B to type F.

A mixture, classified as self-reactive substance, solid, 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 fulfil the assignment criteria of Division 5.1 as self-reactive substances of Division 4.1.

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