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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**  
(Twentieth session, 3-12 December 2001,  
agenda item 8 (d))

**EXPLOSIVES, SELF-REACTIVE SUBSTANCES  
AND ORGANIC PEROXIDES**

**Miscellaneous proposals**

**Self-reactive substances, Type G**

**Transmitted by the expert from Germany**

**Background**

Note 1, Chapter 2.4.3.2.3.1 of the UN Model Regulations requires that self-reactive substances, except for Type G, giving also a positive result with the test method for Class 4.2 (see Manual of Test and Criteria, Part III, sub-section 33.3.1.6), shall not be classified in Division 4.2 but in Division 4.1 (see 2.4.2.3.1.1). The competent authority of Germany is of the opinion that self-reactive substances, Type G are not candidates for Class 4.2.

**Characteristics for self-reactives, Type G**

- No propagation of detonation
- No deflagration
- No effect during heating under confinement
- $75\text{ °C} \geq \text{SADT} > 60\text{ °C}$
- explosive power: none

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**but all substances of this type and even substances with an SADT > 75 °C will give a positive result (DT > 60 K) in the 1 l Bowes-Cameron-test (UN test N.4).**

**Definitions, Criteria and Models**

**Definitions and Criteria**

	Self-reactive (class 4.1)	Self heating (class 4.2)
Application to Characteristics	SADT ≤ 75 °C, models 50-200 l package  ΔH <sub>decomp</sub> > 300 J/g  Solids + liquids  Thermally unstable substances liable to undergo a strongly exothermic decomposition even without the participation of oxygen (air)	1 l Bowes-Cameron / 140 °C models 27 m <sup>3</sup> volume  Solids only  Substances, which in contact with air without energy supply are liable to self-heating. The substances will ignite only when in large amounts (kg) and after long periods of time (hours or days)
Initiation	Heat, contact with catalytic impurities, friction of impact	Self-heating of solids, leading to spontaneous combustion, is caused by reaction of the substance with oxygen (in the air) and the heat being developed not being conducted away rapidly enough to the surroundings

**Models for Testing**

Class 4.1	Class 4.2
SADT models behavior of 50 – 200 kg packages	1 l Bowes-Cameron-Test models 27 m <sup>3</sup> bulk; reference: charcoal

**Testing**

- Under Bowes-Cameron conditions, such substances will give the same temperature rise in the presence of air as well as under nitrogen atmosphere
- In a plot of critical temperature vs. volume, the slope for such substances will be considerably flatter than for the self-heating reference system (charcoal)
- The behavior of self-reactive substances is to be described in terms of thermal properties due to decomposition rather than reaction with oxygen (air). Therefore, the SADT is the appropriate criterion rather than the autoignition temperature.

**The graph of the auto-ignition temperature of self-heating substances (coal)/critical temperature (SADT) of self-reactive substances (type G) vs. volume of packagings is attached as an annex to this document.**

**Conclusion**

- Self-heating substances exhibit a totally different behavior with respect to oxidation than self-reactive substances, type G
- Thus, self-reactive substances, type G should not be considered for classification under Class 4.2.

**Proposal**

- Delete Note 1, Chapter 2.4.3.2.3.1 in the Model Regulations and Chapters 20.2.6 and 33.3.1.3.3.5 in the Manual of Tests and Criteria.

### Annex

Auto-ignition temperature of self-heating substances (coal)/critical temperature (SADT) of self-reactive substances (type G) vs. volume of packagings

