

Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

25 November 2014

Sub-Committee of Experts on the Transport of Dangerous Goods

Forty-sixth session

Geneva, 1–9 December 2014

Item 2 (b) of the provisional agenda

Recommendations made by the Sub-Committee on its forty-third, forty-fourth and forty-fifth sessions and pending issues: listing, classification and packing

Classification of polymerizing substances

Transmitted by the expert from the United States of America

Introduction

1. Over the course of the present biennium, the Sub-Committee has considered developing suitable provisions to address polymerizing substances not meeting the criteria for any hazard class but capable of reacting dangerously under certain conditions. The work done by Germany and the Dangerous Goods Advisory Council in preparing document ST/SG/AC.10/C.3/2014/82 for consideration at the present session is appreciated.
2. While there has been general support for introducing appropriate provisions for polymerizing substances, there have been varying views with respect to the most appropriate classification based on their dangerous properties. Some delegations have considered it appropriate to include provisions in Division 4.1 while others have considered Class 9 to be sufficient.
3. The risks inherent in the transportation of polymerizing substances are similar to those of self-reactive substances. Fire or explosion may occur due to build-up of heat and/or pressure. Temperature control may be required in some cases to preclude polymerization in transport. It has been noted that the term “self-accelerating decomposition temperature” (SADT) is often applied to polymerization reactions. Although a new term (SAPT) is proposed to distinguish between self-accelerating “decomposition” and self-accelerating “polymerization”, the potential hazard in transport - exothermic effects and/or the potential for generation of gases – is similar.
4. The Sub-Committee has in recent years been increasingly mindful to reserve the use of Class 9 for cases where an existing Class does not more adequately address the substance’s associated physical hazards. Inclusion in Division 4.1 would ensure appropriate visual hazard communication (the flame pictogram would appear on the label or placard). This corresponds to the proposed criteria that establish a minimum heat generation threshold. Inclusion in Division 4.1 also facilitates application of appropriate existing transport requirements by relevant modal authorities. For example, the stowage and segregation requirements of the International Maritime Dangerous Goods Code stipulate

that Division 4.1 substances be “separated” from materials in Class/Division: 1, 5.2, 6.2, and 7; and “away from” materials in Divisions 2.1, 4.2, 5.1 and Class 8. Based on the similarity of hazard to self-reactive substances, and the appropriate regulatory provisions that would apply, it is proposed that substances capable of dangerous polymerization be included in Division 4.1.

5. If the technical aspects of the proposal in ST/SG/AC.10/C.3/2014/82 are agreed, in order to facilitate consideration by the Sub-Committee, the below amendments are proposed to the text in ST/SG/AC.10/C.3/2014/2014/82 in order accommodate the provisions within Division 4.1.

Proposal

6. Insert a new 2.4.2.5 to read:

2.4.2.5 Division 4.1 Polymerizing substances and mixtures (stabilized)

2.4.2.5.1 Definitions and properties

2.4.2.5.1.1 Definitions

Polymerizing substances and mixtures (stabilized) include substances and mixtures which, without stabilization, would be forbidden from transport in accordance with 1.1.2 due to being liable to dangerously react under conditions normally encountered in transport. Such substances and mixtures are classified in Division 4.1 when:

(a) Their self-accelerating polymerization temperature (SAPT) is 75°C or less under the conditions (with or without chemical stabilization as offered for transport) and in the packaging, IBC or portable tank in which the substance or mixture is to be transported;

(b) They exhibit a heat of reaction of more than 300 J/g; and

(c) They do not meet any other criteria for inclusion in Classes 1-8.

2.4.2.5.2 Polymerizing substances and mixtures are subject to temperature control in transport if as offered for transport (including whether chemically stabilized or not when offered) their self-accelerating polymerization temperature is:

(a) Except as provided in (b) below, 50°C or less in the packaging, IBC or portable tank in which the substance or mixture is to be transported; or

(b) When offered for transport in a portable tank with a capacity exceeding 3,000 litres, 45°C or less.

2.4.2.5.3 Polymerizing substances that also meet the criteria of 2.9.3 shall be consigned under the appropriate polymerizing substance entry.”

7. Consequential amendments to the text proposed in ST/SG/AC.10/C.3/2014/82:

- Delete the proposed amendment to 2.9.2.
- Delete the proposed 2.9.5.

- The reference to 2.9.5.2 in the proposed new last sentence of 3.1.2.6(a) should be corrected as follows:

(a) For liquids: where the SAPT (measured without or with inhibitor, when chemical stabilization is applied) is less than or equal to that prescribed in ~~2.9.5.2~~ 2.4.2.5.2, special provision XXX and the provisions of 7.1.6 apply.

- The newly proposed entries for inclusion within the Dangerous Goods List in Chapter 3.2 would be revised to reflect Division 4.1:

(1)	(2)	(3)	(4)	(5)	(6)	(7a)	(7b)	(8)	(9)	(10)	(11)
AAAA	POLYMERIZING SUBSTANCE, SOLID, STABILIZED, N.O.S.	<u>4.19</u>		III	274 XXX YYY	0	E0	P002 IBC07	PPaa Bc	T3	TP33 TPee
BBBB	POLYMERIZING SUBSTANCE, LIQUID, STABILIZED, N.O.S.	<u>4.19</u>		III	274 XXX YYY	0	E0	P001 IBC03	PPbb Bd	T4	TP1 TPee
CCCC	POLYMERIZING SUBSTANCE, SOLID, TEMPERATURE CONTROLLED, N.O.S.	<u>4.19</u>		III	274 XXX YYY	0	E0	P002 IBC07	PPaa Bc	T3	TP33 TPee
DDDD	POLYMERIZING SUBSTANCE, LIQUID, TEMPERATURE CONTROLLED, N.O.S.	<u>4.19</u>		III	274 XXX YYY	0	E0	P001 IBC03	PPbb Bd	T4	TP1 TPee