



**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****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 (stabilized) substances****Transmitted by the expert from Germany and by the Dangerous Goods
Advisory Council (DGAC)¹****Introduction**

1. At its prior sessions within the current biennium the Sub-Committee considered the question of the classification of polymerizing substances not meeting the criteria for any hazard class on the basis of documents submitted by DGAC, most recently, at the forty-fifth session, document ST/SG/AC.10/C.3/2014/31. At the forty-fifth session, the expert from Germany submitted informal document INF.31 which supported the approach proposed by DGAC in relation to classification in Class 9 of, as well as four new dangerous goods list entries and related provisions for, polymerizing substances not meeting the definition of any other hazard class, and offered certain modifications to the DGAC proposals. Germany also proposed certain amendments relating to polymerizing substances that are already classified in a class other than Class 9. General support was expressed within the Sub-Committee for the proposals in both documents, and a number of comments offered. The main issue addressed was the class or division to which polymerizing substances not meeting the criteria for any existing hazard class or division should be assigned. While many delegations expressed support for classification in Class 9 as proposed by DGAC and Germany, about an equal number expressed a preference for classification in Division 4.1. No final conclusion was reached in this connection, and Germany and DGAC offered to prepare a new, consolidated proposal for consideration by

¹ In accordance with the programme of work of the Sub-Committee for 2013–2014 approved by the Committee at its sixth session (see ST/SG/AC.10/C.3/84, para. 86 and ST/SG/AC.10/40, para. 14).

the Sub-Committee at the next session, and which would maintain the principle of classification of polymerizing substances in Class 9.

2. The proposals offered in this document are essentially a consolidation of the proposals offered by DGAC and Germany in the documents submitted to the prior session. The underlying rationale for the proposed amendments as outlined in documents ST/SG/AC.10/C.3/2014/31 (DGAC) and informal document INF.31 (Germany) continues to apply and will not be repeated here. The Sub-Committee is invited to refer to those documents for that background information.

3. As noted previously, the main issue raised by Sub-Committee members in relation to the prior documents was the class or division to which polymerizing substances not meeting the criteria for any existing hazard class or division should be assigned. Germany and DGAC continue to believe that Class 9 is the most appropriate classification, and the proposals in this document maintain that classification. While some Sub-Committee members expressed the view that it would be a simple matter to revise the current proposals to instead classify these substances in Division 4.1, Germany and DGAC disagree and continue to believe that Class 9 is most appropriate. Some of the reasons for this belief include:

- (a) Dangerous polymerization in and of itself is a “miscellaneous” hazard not specifically included in the definitions of any other hazard class;
- (b) Classification in Class 9 does not necessarily imply a low level of hazard (see last sentence in 2.0.1.1), but rather only a hazard not specifically addressed by any other hazard class;
- (c) The main purpose of regulating polymerizing substances not meeting the definition of any existing hazard class is to provide for their identification in transport so that appropriate operational controls can be applied to ensure they are transported in such a manner as to prevent occurrence of a dangerous polymerization, and classification in Class 9 effectively achieves this objective;
- (d) Classification of polymerizing substances not meeting the criteria for classification in any other hazard class in Division 4.1 will create confusion in relation to the numerous polymerizing substances that have for many years been classified in Classes 2, 3 or 8 or Division 6.1 – particularly in relation to the scheme for precedence of hazards – and could lead to a situation where, for example, packages, IBCs and/or tanks containing polymerizing substances of Class 2 or Class 3 could be required to bear subsidiary risk Division 4.1 labels/placards.

4. One difference between the proposals in this document and in the prior German and DGAC documents relates to the SAPT temperature at which temperature control would be required for polymerizing substances transported in portable tanks. Both prior documents proposed a 50°C threshold for temperature control regardless of the size of the packaging, IBC or tank. The tests used to determine the SAPT envisage maintaining the bulk mean temperature of the substance in the package or tank for a period of 7 days. Germany and DGAC believe that in practice it is highly unlikely (given the effects of wind, night time cooling, etc.) that under normal conditions of transport, even in very warm regions, the bulk mean temperature of a substance in a large portable tank would ever achieve 50°C and remain at that temperature for a period of seven days. Therefore, upon further consideration, the 50°C SAPT threshold seems somewhat unrealistic and overly conservative for large portable tanks under normal conditions of transport. Indeed, it is noted that for organic peroxides allowed to be transported in portable tanks (i.e., type F organic peroxides), temperature control is required only when the SADT is less than or equal to 45°C (see 2.5.3.4.1(c)). Moreover, 7.1.6.5 already addresses the possible need for temperature control under extreme conditions at which the sustained ambient temperature may exceed the

maximum 55°C normally contemplated in transport. Consequently, on this basis, and by analogy to the provisions for organic peroxides transported in portable tanks, it is proposed that in the case of portable tanks with capacities of greater than 3,000 litres, temperature control be required only when the SAPT of the substance in the portable tank as offered for transport is less than or equal to 45°C.

Proposal

5. In consideration of the foregoing, the expert from Germany and DGAC proposes the following amendments to the Model Regulations:

- (a) Insert the following new definitions in 1.2.1:

“Polymerization is the transformation of low-molecular compounds (monomers, oligomers) into high-molecular compounds (polymers). The increase of pressure and the heat of reaction released in the course of polymerization may pose a danger during transport.”

“Self-accelerating polymerization temperature (SAPT) means the lowest ambient temperature at which polymerization may be initiated for a substance in the packaging as used for transport. The SAPT shall be determined in accordance with the test procedures established for the self-accelerating decomposition temperature for self-reactive substances in accordance with the Manual of Tests and Criteria (preferably Section 28, Tests H.1 and H.4).”

- (b) Insert a new 2.2.4 to read:

“Gases not accepted for transport

Chemically unstable substances of Class 2 shall not be accepted for transport unless the necessary precautions have been taken to prevent the possibility of a dangerous decomposition or polymerization under normal conditions of transport or unless transported in accordance with P 200 (r), as applicable. For the precautions necessary to prevent polymerization, see special provision XXX. To this end particular care shall be taken to ensure that receptacles and tanks do not contain any substances liable to promote these reactions.”

- (c) Insert a new 2.3.5 to read:

“Substances not accepted for transport

Chemically unstable substances of Class 3 shall not be accepted for transport unless the necessary precautions have been taken to prevent the possibility of a dangerous decomposition or polymerization under normal conditions of transport. For the precautions necessary to prevent polymerization, see special provision XXX. To this end particular care shall be taken to ensure that receptacles and tanks do not contain any substances liable to promote these reactions.”

- (d) Insert a new 2.6.2.5 to read:

“Substances not accepted for transport

Chemically unstable substances of Division 6.1 shall not be accepted for transport unless the necessary precautions have been taken to prevent the possibility of a dangerous decomposition or polymerization under normal conditions of transport. For the precautions necessary to prevent

polymerization, see special provision XXX. To this end particular care shall be taken to ensure that receptacles and tanks do not contain any substances liable to promote these reactions.”

- (e) Insert a new 2.8.3 to read:

“Substances not accepted for transport

Chemically unstable substances of Class 8 shall not be accepted for transport unless the necessary precautions have been taken to prevent the possibility of a dangerous decomposition or polymerization under normal conditions of transport. For the precautions necessary to prevent polymerization, see special provision XXX. To this end particular care shall be taken to ensure that receptacles and tanks do not contain any substances liable to promote these reactions.”

- (f) Add at the end of 2.9.2:

“Polymerizing substances and mixtures (stabilized)

AAAA	POLYMERIZING SUBSTANCE SOLID, STABILIZED, N.O.S.
BBBB	POLYMERIZING SUBSTANCE LIQUID, STABILIZED, N.O.S.
CCCC	POLYMERIZING SUBSTANCE SOLID, TEMPERATURE CONTROLLED, N.O.S.
DDDD	POLYMERIZING SUBSTANCE LIQUID, TEMPERATURE CONTROLLED, N.O.S.

These designations are used for substances and mixtures not meeting the criteria for classification in any other class but which, without stabilization or temperature control, would be forbidden from transport in accordance with 1.1.2 due to being liable to dangerously react under conditions normally encountered in transport. For substances meeting the criteria of 2.9.5.1 and not meeting the criteria of 2.9.5.2, AAAA or BBBB applies. For substances meeting the criteria of 2.9.5.2, CCCC or DDDD applies.

NOTE: See 2.9.5.”

- (g) Insert a new subsection 2.9.5 into Chapter 2.9 to read:

“2.9.5 Polymerizing (stabilized) substances and mixtures

2.9.5.1 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 Class 9 when:

- (a) Their self-accelerating polymerization temperature (SAPT) is 75⁰C 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 the criteria for classification in any other class.

2.9.5.2 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.

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

- (h) Revise the last sentence in 3.1.2.6 to read:

“When temperature control is used to stabilize such substance to prevent the development of any dangerous excess pressure or the evolution of excessive heat, or when chemical stabilization is used in combination with temperature control, then:

(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, special provision XXX and the provisions of 7.1.6 apply.

(b) For gases: the conditions of transport shall be approved by the competent authority.”

- (i) Insert the following four new entries into the Dangerous Goods List in Chapter 3.2:

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

- (j) In the Dangerous Goods List in Chapter 3.2:

i. Insert special provision “XXX” in column (6) for the following entries:

UN1010, UN 1051, UN 1060, UN 1081, UN 1082, UN 1085, UN 1086, UN 1087, UN 1092, UN 1093, UN 1143, UN 1163, UN 1185, UN 1218, UN 1246, UN 1247, UN 1351, UN 1301, UN 1302, UN 1303, UN 1304, UN 1541, UN 1545, UN 1589, UN 1614, UN 1695, UN 1724, UN 1829, UN 1860, UN 1917, UN 1919, UN 1921, UN 1991, UN 2014, UN 2015, UN 2055, UN 2075, UN 2200, UN 2209, UN 2218, UN 2227, UN 2251, UN 2277, UN 2283, UN 2383, UN 2348, UN 2352, UN 2396, UN 2452, UN

2521, UN 2527, UN 2531, UN 2607, UN 2618, 2838, UN 3022, UN 3073, UN 3079 and UN 3302 ;

ii. For UN2209, revise the proper shipping name to read “FORMALDEHYDE SOLUTION, STABILIZED, with not less than 25% formaldehyde”; and

iii. For UN 3302, revise the proper shipping name to read “2-DIMETHYLAMINOETHYL ACRYLATE, STABILIZED”

(k) In Chapter 3.3, insert new special provisions “XXX” and “YYY” to read:

“XXX When these substances are stabilized by temperature control, the provisions of 7.1.6 apply. When chemical stabilization is employed, the person offering the package, IBC or tank for transport shall ensure that the level of stabilization is sufficient to prevent the substance in the package, IBC or tank from dangerous polymerization at a bulk mean temperature of 50°C, or, in the case of a portable tank with a capacity of greater than 3,000 litres, 45°C. Where chemical stabilization becomes ineffective at lower temperatures within the anticipated duration of transport, temperature control is required. In making this determination factors to be taken into consideration include, but are not limited to, the capacity and geometry of the package, IBC or tank and the effect of any insulation present, the temperature of the substance when offered for transport, the duration of the journey and the ambient temperature conditions typically encountered in the journey (considering also the season of year), the effectiveness and other properties of the stabilizer employed, applicable operational controls imposed by regulation (e.g. requirements to protect from sources of heat, including other cargo carried at a temperature above ambient) and any other relevant factors.

“YYY This entry applies to substances and mixtures that also meet the criteria of 2.9.3 as environmentally hazardous substances. In such case, the word “ENVIRONMENTALLY HAZARDOUS” shall be added as part of the proper shipping name and an additional mark as specified in 5.2.1.6 and 5.3.2.3 shall be applied.”

(l) In the packing instructions in 4.1.4.1 –

i. For packing instruction P001, add a new Special Packing Provision “Pbb” to read:

“Pbb For UN Nos. BBBB and DDDD, packagings shall be designed and constructed to permit the release of gas or vapour to prevent a build-up of pressure that could rupture the packagings in the event of loss of stabilization.”

ii. For packing instruction P002, add a new Special Packing Provision “Paa” to read:

“Paa For UN Nos. AAAA and CCCC, packagings shall be designed and constructed to permit the release of gas or vapour to prevent a build-up of pressure that could rupture the packagings in the event of loss of stabilization.”

(m) In the IBC packing instructions in 4.1.4.2 -

i. For packing instruction IBC03, add a new Special Packing Provision “Bd” to read:

“Bd For UN Nos. BBBB and DDDD, IBCs shall be designed and constructed to permit the release of gas or vapour to prevent a build-up of pressure that could rupture the IBCs in the event of loss of stabilization.”

- ii. For packing instruction IBC07, add a new Special Packing Provision “Bc” to read:

“Bc For UN Nos. AAAA and CCCC, IBCs shall be designed and constructed to permit the release of gas or vapour to prevent a build-up of pressure that could rupture the IBCs in the event of loss of stabilization.”

- (n) In 4.2.5.3, add a new Portable Tank Special Provision “TPee” to read:

“TPee To prevent the tank bursting in any event, including fire engulfment, it shall be provided with a pressure relief device(s) which are adequate in relation to the capacity of the tank and to the nature of the substance transported.”

- (o) Revise 7.1.6.1 to read:

“These provisions apply to the transport of substances for which:

(a) The proper shipping name as indicated in column 2 of the dangerous goods list or according to 3.1.2.6 contains the word “STABILIZED” and

(b) The SADT or the SAPT* determined for the substance (with or without chemical stabilization) in the package, IBC or portable tank in which offered for transport is:

- i. Except as provided in ii) below, 50 °C or less; or
- ii. 45°C or less for portable tanks with a capacity greater than 3,000 litres.

These provisions do not apply to substances for which the SAPT is greater than 50°C, or, in portable tanks with a capacity greater than 3,000 litres, 45°C.

* Footnote: The self-accelerating polymerization temperature (SAPT) shall be determined in accordance with the Manual of Tests and Criteria. The SADT tests in section 28 (preferably Tests H.1 and H.4) may be equally applied to determine a self-accelerating polymerization reaction.”

- (p) Revise 7.1.6.2 to read:

“The provisions of 7.1.5.3.1.1 to 7.1.5.3.1.3 and 7.1.5.3.2 apply to substances meeting the criteria (a) and (b) in 7.1.6.1., with the proviso that the term ‘SADT’ as used in these paragraphs is understood to include also “SAPT” when the substance concerned reacts by polymerization.”

- (q) Delete 7.1.6.4, and renumber existing 7.1.6.5 accordingly.