

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

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Item 4 (a) of the provisional agenda

Listing, classification and packing: polymerizing substances

Comments on document ST/SG/AC.10/C.3/2014/31

Submitted by the expert from Germany

Introduction

1. The German expert would like to thank DGAC for the new proposal on the classification of polymerizable substances. In the case of an exothermic reaction, such substances may result in serious hazards during transport due to the heat evolution. This is also demonstrated by the accident of the MSC Flaminia; the final investigation report on this accident has been issued by the Federal Bureau of Maritime Casualty Investigation (BSU) and made available on the internet at www.bsu.de. The investigation report is also available to the Sub-Committee at:

http://www.bsu-bund.de/SharedDocs/pdf/EN/Investigation_Report/2014/Investigation_Report_255_12.pdf?__blob=publicationFile

2. According to the accident report on the MSC Flaminia, the exact causes of the fire and the explosion could not be established; however, as a conclusion, it is to be noted that a polymerization of divinylbenzene (DVB) occurred which had an impact on the accident. Due to the effects of temperature, the chemical stabilization by means of 4-*tert*-Butylbenzene-1,2-diol (*tert*-Butylcatechol (TBC)) lost its effect after some time, which led to the release of heat and the evolution of fumes as a consequence of the polymerization. As information about these properties had not been communicated, no appropriate measures with regard to stowage and segregation were taken that could have prevented so negative an effect on the accident.

3. Therefore, it is imperative that all substances with polymerizable properties be identified as such in the dangerous goods regulations. For substances that meet the criteria of another class, this is done by means of the word “STABILIZED” in the proper shipping name, either in accordance with column 2 of the Dangerous Goods List or in accordance with 3.1.2.6. For substances that have not yet been classified as a dangerous good, document ST/SG/AC.10/C.3/2014/31 contains a proposal for 4 new entries in Class 9.

4. Germany explicitly supports the proposed approach but also proposes a few amendments which are explained in the following.

5. In addition to the new section 2.9.5, a definition of polymerization should be inserted in 1.2.1.

6. In the proposal, one of the classification criteria is “Exhibit a heat reaction of more than 300J/g”. Prior to establishing such a criterion, its suitability should be verified by

testing the substances that, according to the Dangerous Goods List, are to be designated as stabilized to establish whether the heat of reaction is actually above 300J/g.

7. The use of the term SADT (self-accelerating decomposition temperature) in connection with polymerizable substances is ambiguous. This is why the term SAPT (self-accelerating polymerization temperature) should be used instead. SAPT is to be defined as follows in 1.2.1: The self-accelerating polymerization temperature is defined as the lowest ambient temperature at which self-accelerating polymerization may occur in a substance in the packaging as used in transport. The SAPT is to be determined by applying the same test methods (preferably H.1 and H.4) as for the SADT; these methods are described in section 28 of part II of the Manual. The SAPT should be determined for the substance in the intended transport packaging and under the intended transport conditions (with or without chemical stabilization) in order to establish whether the substance must be classified as a polymerizable substance. At a value of the SAPT ≤ 75 C, it shall be classified as a polymerizable substance. At an SAPT ≤ 50 C, temperature control is required.

8. The same requirements should apply to all polymerizable substances, regardless of whether they have already been classified as a dangerous good of another class or whether they have been assigned to Class 9 solely on the basis of their liability to polymerize. This is why the proposed special provision should be assigned to all entries of the Dangerous Goods List whose proper shipping name contains the word “stabilized” and which are stabilized to avoid polymerization. In the process of establishing for which substances this is true, it emerged that the word “stabilized” is missing from the proper shipping names of UN 2209 and UN 3302. The proper shipping name of these UN numbers should be amended accordingly.

9. The requirements should also apply to substances to whose proper shipping name the word “stabilized” is to be added in accordance with 3.1.2.6. To this end, appropriate rules should be inserted in part 2 for classes comprising polymerizable substances.

10. In the accident of the MSC Flaminia, the divinylbenzene was carried as an environmentally hazardous substance without reference to the stabilization. If a substance exhibits environmentally hazardous properties and is polymerizable, it is to be determined by means of a special provision which entry must be used. As in case of doubt the potential evolution of heat is more important with regard to the stowage and segregation requirements in sea transport, the entry for the polymerizable substance should have priority.

11. The proposed packing instructions provide for venting devices to prevent a dangerous build-up of pressure. In principle, this requirement is to be supported, but it also has to be ensured that these devices remain effective during transport and do not fail due to jamming. One option is the use of frangible discs. However, this issue does not only arise in connection with the newly proposed entries but for all polymerizable substances. Thus, no amendment to the provisions suggested in ST/SG/AC.10/C.3/2014/31 is proposed.

12. The provisions concerning transport under temperature control have to be amended accordingly. The term SADT and the reference to 7.1.5.3.1.3 are to be replaced by the term SAPT.

13. The above results in the following proposal:

Proposal

Insert the following 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 cause dangerous situations 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- reacting substances in accordance with the Manual of Tests and Criteria (preferably Section 28, Tests H.1 and H.4).”

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 steps have been taken to prevent all possibilities of a dangerous decomposition or polymerization under normal conditions during transport. For necessary steps 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.”

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 steps have been taken to prevent all possibilities of a dangerous decomposition or polymerization under normal conditions during transport. For necessary steps 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.”

Insert a new 2.6.2.5 to read:

“Substances not accepted for transport:

Chemically unstable substances of Class 6.1 shall not be accepted for transport unless the necessary steps have been taken to prevent all possibilities of a dangerous decomposition or polymerization under normal conditions during transport. For necessary steps 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.”

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 steps have been taken to prevent all possibilities of a dangerous decomposition or polymerization under normal conditions during transport. For necessary steps 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.”

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”

Insert a new subsection 2.9.5 into Chapter 2.9 to read:

“2.9.5 Polymerizing substances and mixtures (stabilized)

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 react dangerously under conditions normally encountered during transport. Such substances and mixtures are classified in class 9 when:

- Their self-accelerating polymerization temperature SAPT is 75°C or less under the conditions (with or without chemical stabilization) and in the packaging, IBC or portable tank in which the substance or mixture is to be transported and
- They do not meet the criteria for classification in any other class.

2.9.5.2 Polymerizing substances and mixtures (stabilized) are subject to temperature control in transport if their self-accelerating polymerization temperature is 50°C or less under the conditions (with or without chemical stabilization) and in the packaging, IBC or portable tank in which the substance or mixture is to be transported

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

Amend 3.1.2.6 as follows

The last sentence should 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 SADT or the SAPT (measured with or without inhibitor, when chemical stabilization is applied) is less than or equal to 50°C, 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.”

In Chapter 3.2, dangerous goods list: Insert the following four new entries:

(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

In Chapter 3.2, dangerous goods list: Insert the special provision “XXX” in Column 6 to 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

In Chapter 3.2, dangerous goods list:

UN 2209: Amend the proper shipping name to read as follows:
“FORMALDEHYDE SOLUTION, STABILIZED, with not less than 25%
formaldehyde”

UN 3302: Amend the proper shipping name to read as follows: “2-
DIMETHYLAMINOETHYL ACRYLATE, STABILIZED”

In Chapter 3.3, insert a new special provision “XXX” to read:

“XXX When this substance is 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 polymerization at a bulk mean temperature of up to 50⁰C. 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 or 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.”

In Chapter 3.3, insert a new special provision “YYY” to read:

“This entry applies also to environmentally hazardous substances meeting the criteria of 2.9.3. 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.”

In 4.1.4.1, 4.1.4.2, 4.2.5.3

See d), e) and f) of ST/SG/AC.10/C.3/2014/31

Amend 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 as offered for transport (with or without chemical stabilization) and as presented for transport in the package, IBC or tank is 50°C or lower.

These provisions do not apply to substances for which the SAPT is greater than 50°C.

* Footnote: The self-accelerating polymerization temperature (SAPT) shall be determined in accordance with the latest version of the United Nations 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.”

Amend 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” used in these paragraphs is understood also as “SAPT”.”

Delete 7.1.6.4.

Renumber 7.1.6.5 accordingly.
