



**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 fifth session**

Geneva, 23 June – 2 July 2014

Item 4 (a) of the provisional agenda

Listing, classification and packing: polymerizing substances**Classification of polymerizing (stabilized) substances****Transmitted by the Dangerous Goods Advisory Council (DGAC)¹****Introduction**

1. At its prior two sessions 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-fourth session, document ST/SG/AC.10/C.3/2013/62. While no final conclusions were reached, several fundamental principles were agreed regarding the classification of such substances. Importantly, and based on input from the IGUS Energetic and Oxidising Substances Group (EOS), it was agreed that such substances should not be classified as self-reactive substances of Division 4.1, and need not be evaluated under the associated test regime. Moreover, while DGAC had originally suggested addressing only substances that are stabilized by temperature control, several Sub-Committee members expressed the view that chemically stabilized substances should also be considered. Varying views were offered regarding an appropriate class in which to place these substances, with Divisions 4.1 and 4.2, and Class 9 offered as candidates, as well as the possibility of a new Division 4.4 – although it was questioned whether the number of substances that might be addressed and the risk posed warranted a new division with associated new labels and placards. Based on these prior discussions, DGAC has continued to consider this question, and now offers the proposals in this document for consideration by the Sub-Committee.

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).

2. As DGAC has noted previously, the Model Regulations already contain requirements for polymerizing substances of other classes. Applicable requirements are provided in the Annex. These requirements are relevant to this discussion.

Substances addressed, classification and packaging

3. As noted previously, there are approximately 45 named substances in the dangerous goods list, which are identified as requiring stabilization. These are substances that may have a risk of Class 2, 3, 5.1, 6.1 or 8. Examples include UN 1086 vinyl chloride, UN 1301 vinyl acetate, UN 1303 vinylidene chlorine and UN 3073 vinylpyridenes. While these UN numbers are for pure substances, mixtures (e.g., thermal setting plastics, epoxy/hardner mixtures) may pose a similar risk. Substances that polymerize (require stabilization) typically have at least one double bond that is broken as part of the polymerization reaction. They may contain the word STABILIZED as part of the shipping name in the Dangerous Goods List or it may be required to be added on the basis of 3.1.2.6 (e.g., TOXIC LIQUID, ORGANIC, N.O.S., STABILIZED). In many cases, stabilization (or prevention of polymerization) is provided through the use of a chemical inhibitor. In other instances temperature control is used.

4. As noted in 3.1.2.6, the risk of a substance requiring stabilization is that, “without stabilization, [it] would be forbidden from transport in accordance with 1.1.2 due to it being liable to dangerously react under conditions normally encountered in transport.” For polymerizing substances not meeting the definition of any class the risk to be considered is limited to the overpressure risk associated with the loss of stabilization, and the associated evolution of heat. The uncontrolled build up of heat and pressure can cause a fire or an explosion, or can rupture closed containers in severe cases. Depending on the material, temperature increases from climatic exposure such as sunlight or stowage adjacent to heat sources can deplete the inhibitor and trigger such reactions. To control this risk it is important to ensure the containment system is adequately vented so as to avoid over-pressurization in the event of a loss of stabilization. In terms of modal requirements, which need not necessarily be addressed in the Model Regulations, precautions to ensure the avoidance of exposure to sources of heat, including radiant heat and heat evolved from other cargo carried above ambient temperature, may be appropriate.

5. DGAC believes it is important to establish a lower level in terms of heat of polymerization below which substances would not be subject to regulation. Based on the precedent of self-reactive substances, which by definition are subject to *decomposition* reactions, 300 J/g is considered a suitable value. Further, it is DGAC’s view that any requirements developed should address only substances, including mixtures, not meeting the definition of any other class so as not to affect or create confusion regarding long-standing dangerous goods entries for polymerizing substances already classified (e.g., UN 1086, vinyl chloride). Also, DGAC believes that to the extent practical, existing requirements applicable to listed substances requiring stabilization (other than self-reactive substances and organic peroxides) should be applied. On this basis the substances covered would be those which:

- Exhibit (absent stabilization) an SADT of 50⁰C or less in the packaging, IBC or portable tank in which the substance is to be transported;
- Exhibit a heat of reaction of more than 300 J/g (from 2.4.2.3.1.1(d)); and
- Do not meet the criteria for classification in any other class.

6. In this regard, DGAC notes that while technically “SADT” means a self-accelerating *decomposition* temperature, the same term is commonly applied to polymerization reactions, and the SADT tests in Section 28 of the Manual of Tests and Criteria may equally be applied to determine the onset temperature for a self-accelerating polymerization reaction. Accordingly, rather than introduce new terminology, DGAC believes the term “SADT” and the associated tests may be applied to polymerization reactions in the context of the provisions of the Model Regulations and the Manual of Test and Criteria.

7. In paragraph 9 of document ST/SG/AC.10/C.3/2013/62, DGAC outlined some of the advantages and disadvantages of assigning these polymerizing substances to one of the various classes or divisions that had been suggested. This assessment will not be repeated here, but Sub-Committee members may wish to review the pros and cons identified in that document. Based on further consideration of these, and on comments offered at the previous session, DGAC believes it appropriate for various reasons to classify these polymerizing substances in Class 9. First, as already noted, for polymerizing substances not meeting the definition of any class the risk to be considered is limited to the overpressure risk associated with the loss of stabilization, and the associated evolution of heat. This is certainly a “miscellaneous” hazard not specifically attributed to any other hazard class. Moreover, classification of polymerizing substances in a class or division other than Class 9 could result in confusion and apparent inconsistencies with the classification of many well known and widely transported polymerizing substances already listed by name and classified in other classes (e.g., in Class 3).

8. When chemical stabilization is employed, it is important to ensure that the level of stabilization is sufficient to prevent the onset of a dangerous reaction under conditions normally incident to transportation. The level required to accomplish this will vary depending on a number of factors, including the anticipated length of the journey and the ambient conditions expected to be encountered over the journey. Owing to these variances, DGAC believes it would be difficult to impose a very detailed or prescriptive method for determining the degree of stabilization required, and that a more general “performance-oriented” approach should be taken. In this connection, DGAC proposes that the degree of chemical stabilization present at the time the package, IBC or tank is offered for transport shall be appropriate to ensure that the sustained bulk mean temperature of the substance in the package, IBC or tank will not exceed 50°C under conditions normally incident to transportation. 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, and any other relevant factors. In making this determination the person offering the package, IBC or tank for transport should be entitled to assume that appropriate operational controls, as may be established by the relevant modal authorities and prescribed in modal regulations (e.g., shading packages from radiant heat, stowing packages away from sources of heat, etc.) are adhered to by carriers.

Proposal

9. In consideration of the foregoing, DGAC proposes the following amendments to the Model Regulations:

- a) Insert a new subsection 2.9.5 into Chapter 2.9 to read:
“2.9.5 **Polymerizing (stabilized) substances and mixtures**

Polymerizing (stabilized) substances and mixtures 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 they:

- Exhibit (absent stabilization) an SADT of 50⁰C or less in the packaging, IBC or portable tank in which the substance or mixture is to be transported;
- Exhibit a heat of reaction of more than 300 J/g; and
- Do not meet the criteria for classification in any other class.

NOTE 1: While literally “SADT” means a self-accelerating decomposition temperature, since the same term is commonly applied to polymerization reactions, and the SADT tests in Section 28 of the Manual of Tests and Criteria may equally be applied to determine the onset temperature for a self-accelerating polymerization reaction, the term “SADT” and the associated tests are applied to polymerization reactions in the context of the provisions of the Model Regulations and the Manual of Test and Criteria.”

NOTE 2: The term stabilized refers to the addition of an inhibitor or temperature control.

b) 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 XYZ	0	E0	P002 IBC07	PPaa Bc	T3	TP33 TPee
BBBB	POLYMERIZING SUBSTANCE, LIQUID, STABILIZED, N.O.S.	9		III	274 XYZ	0	E0	P001 IBC03	PPbb Bd	T4	TP1 TPee
CCCC	POLYMERIZING SUBSTANCE, SOLID, TEMPERATURE CONTROLLED, N.O.S.	9		III	274 XYZ	0	E0	P002 IBC07	PPaa Bc	T3	TP33 TPee
DDDD	POLYMERIZING SUBSTANCE, LIQUID, TEMPERATURE CONTROLLED, N.O.S.	9		III	274 XYZ	0	E0	P001 IBC03	PPbb Bd	T4	TP1 TPee

c) In Chapter 3.3, insert a new special provision “XYZ” to read:

“XYZ This entry applies to substances and mixtures classified in Class 9 on the basis of the criteria in 2.9.5 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. 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 sustained bulk mean temperature of the substance in the package, IBC or tank from exceeding 50⁰C such that under conditions normally incident to transportation the substance will not dangerously polymerize. 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.

- d) 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.”
- e) 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.”
- f) 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. ”

Consequential amendments

10. Add at the end of 2.9.2:

“Polymerizing (stabilized) substances and mixtures

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.

11. 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.”

Annex

Existing Model Regulations requirements applicable to stabilized substances requiring temperature control

1. Proper Shipping Name to include the word “STABILIZED”
 - 3.1.2.6 Except for self-reactive substances and organic peroxides and unless it is already included in capital letters in the name indicated in the Dangerous Goods List, the word STABILIZED shall be added as part of the proper shipping name of a substance which, without stabilization, would be forbidden from transport in accordance with 1.1.2 due to it being liable to dangerously react under conditions normally encountered in transport (e.g: “TOXIC LIQUID, ORGANIC, N.O.S., STABILIZED”).
 -
2. Transport document requirements to include control and emergency temperatures
 - 5.4.1.5.4 Substances stabilized by temperature control

If the word “STABILIZED” is part of the proper shipping name (see also 3.1.2.6), when stabilization is by means of temperature control, the control and emergency temperatures (see 7.1.5.3.1) shall be indicated in the transport document, as follows:

“Control temperature: °C Emergency temperature: °C”

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3. Special transport provisions in Part 7
 - 7.1.6 Special provisions applicable to the transport of substances stabilized by temperature control (other than self-reactive substances and organic peroxides)
 - 7.1.6.1 These provisions apply to the transport of substances for which:
 - (a) The proper shipping name contains the word “STABILIZED”; and
 - (b) The SADT (see 7.1.5.3.1.3) as presented for transport in the package, IBC or tank is 50 °C or lower.

When chemical inhibition is not used to stabilize a reactive substance which may generate dangerous amounts of heat and gas, or vapour, under normal transport conditions, these substances need to be transported under temperature control. These provisions do not apply to substances which are stabilized by the addition of chemical inhibitors such that the SADT is greater than 50 °C.

NOTE: Some substances which are transported under temperature control are prohibited from transport by certain modes.
 - 7.1.6.2 The provisions in 7.1.5.3.1.1 to 7.1.5.3.1.3 and 7.1.5.3.2 apply to substances meeting criteria (a) and (b) in 7.1.6.1.

7.1.6.3 The actual transport temperature may be lower than the control temperature (see 7.1.5.3.1.1) but shall be selected so as to avoid dangerous separation of phases.

7.1.6.4 When these substances are transported in IBCs or portable tanks, the provisions for a SELF-REACTIVE LIQUID TYPE F, TEMPERATURE CONTROLLED shall apply. For transport in IBCs, see the special provisions in 4.1.7.2 and the “Additional requirements” in packing instruction IBC520; for transport in portable tanks, see the additional provisions in 4.2.1.13.

7.1.6.5 If a substance the proper shipping name of which contains the word “STABILIZED” and which is not normally required to be transported under temperature control is transported under conditions where the temperature may exceed 55 °C, it may require temperature control.
