



**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 fourth session**

Geneva, 25 November – 4 December 2013

Item 2 (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 the 43rd session, on the basis of ST/SG/AC.10/C.3/2013/33 and informal document INF 17, the Sub-Committee considered the classification of polymerizing substances that did not meet the criteria of any hazard class. In conclusion, DGAC was invited to lead an intersessional working group to evaluate how these substances should be dealt with under the Regulations. This paper is to provide a basis for discussion among Sub-Committee members with an interest in this topic. The objective is to obtain comments in advance of the 44th session and to report the results of those discussions to the 44th session.

2. In summary form, some of the conclusions and issues raised at the 43rd session included:

- Some participants wanted a clearer understanding of what products were considered within the term polymerizing substances;
- There was general agreement, supported by the IGUS Energetic and Oxidising Substances (EOS) group, that these substances did not pose a detonation/deflagration risk represented by self-reactive substances (SRS). In addition some SRS tests are unworkable (e.g., clogging of test orifices) for these substances. The general conclusion was that these substances should not be evaluated under the SRS test regime;

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).

- Many expressed the view that these substances should be classified differently from self-reactive substances; and
 - There was a need for classification criteria.
3. 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.

Terminology

4. While DGAC has referred to polymerizing substances in its previous documents, the Model Regulations refer to these substances, independent of the class to which they are assigned, as “substances stabilized by temperature control (other than self-reactive substances and organic peroxides)” – see 7.1.6. For purposes of this discussion, only substances which do not pose a risk of another hazard class would be addressed. It is recommended that they be referred to as “Stabilized Substances, Temperature Controlled NOS” (abbreviated as SSTC for purposes of this discussion).

Substances addressed

5. 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 chloride and UN 3073 vinylpyridenes. While these UN numbers are for pure substances, mixtures (e.g., thermal setting plastics, epoxy/hardener 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.

6. 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.” As the text goes on to imply, they may be stabilized by temperature control “to prevent the development of any dangerous excess pressure.” Given that SSTC pose no other hazard addressed in the Model Regulations, their risk may be considered as limited to the overpressure risk associated with the loss of stabilization.

7. While among listed substances, the highest known heat of polymerization is considered to be approximately 2500 J/g (low molecular weight gas with two double bonds), a lower heat of polymerization is expected for substances to be addressed as SSTC. The highest energy noted during discussions at the 43rd session was approximately 800 J/g. For these substances, a polymerization reaction inside a containment vessel may lead to heating, vaporization of volatile components and a build-up of pressure as the polymerization reaction progresses. In the case of one such substance with a polymerization energy of approximately 500 J/g, a reaction, under adiabatic conditions, resulted in a pressure of 14 bar through heating of entrained water. For this type of substance, it is important to ensure the containment system is adequately vented in the event of a loss of temperature control.

Proposed terms of reference

8. The following terms of reference are recommended:
- (a) The effort should be limited to substances requiring stabilization by temperature control but which are not already covered by a hazard classification. The effort would not affect:
- Named substances covered by an existing proper shipping name (e.g., UN 1086 vinyl chloride);
 - Substances regulated as self-reactive substances or organic peroxides;
or
 - Substances that are stabilized by means of an inhibitor.
- (b) To the extent practical, existing requirements applicable to listed substances requiring temperature control (other than self-reactive substances and organic peroxides) should be applied. On this basis the effort would include liquids:
- That have an SADT of 50C or less;
 - Have a heat of reaction of more than 300 J/g (from 2.4.2.3.1.1(d)).
- (c) Self-classification should be permitted as other stabilized substances are self classified.
- (d) An appropriate hazard class should be assigned, criteria developed, new proper shipping names proposed, where appropriate test methods should be prescribed, and transport conditions assigned.

Classification

9. Based on discussion at the 43rd session, most speakers agreed that these substances should not be treated as self-reactive substances. Suggested options along with potential issues include:

A subcategory of self-reactive substances (SRS). Issues include:

- The SRS test methods are not relevant, the nature of the reaction is different than that of SRS and the substances are different chemically;
- The precedence of hazard requirements in Chapter 2.0 designate the SRS hazard as taking precedence over other hazards whereas the risk related to stabilization is not addressed in the precedence of hazards.

A new Division 4.4. Issues include:

- It is questioned whether these substances are transported in a sufficient quantity to warrant a separate classification, new labels/placards etc.

Assignment to Division 4.2. Issues include:

- The current criteria for self-heating substances in Division 4.2 is limited to substances that self-heat in the presence of air.

Assignment to Class 9.

Classification criteria

10. Proposed classification criteria would include:
- An SADT of less than 50C;
 - The substance meets no other hazard classification (i.e, classes 3, 4, divisions 5.1 or 6.1 or class 8);
 - The heat of reaction is more than 300 J/g; and
 - The substance is a liquid.

Potential proper shipping name

11. A single shipping name is proposed:
“UNXXX Stabilized substance, temperature controlled, No.”

Testing

12. The only relevant test criteria currently used for polymerizing substances of other classes is the SADT. The test procedures currently in the Manual of Test and Criteria for SADT are relevant.

13. A method of evaluating the venting capacity of an IBC or portable tank could be developed to assess vent capacity. Currently substances that require stabilization are subject to venting requirements prescribed for self-reactive substances and organic peroxides (see 7.1.6.4). Alternatively, the method provided in Appendix 5 (Example of a test method for vent sizing) could be used.

Action requested

14. DGAC recommends that this document be used as a basis for discussion and requests that in the period leading up to the 44th session, Sub-Committee participants comment on the document to Frits Wybenga at fwybenga@dgac.org.

Annex

Existing UN 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”

.....
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.
