



**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-third session**

Geneva, 24–28 June 2013

Item 3 (a) of the provisional agenda

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

1. As noted in previous DGAC papers (ST/SG/AC.10/C.3/2012/50 and ST/SG/AC.10/C.3/2012/82), there is uncertainty as to how substances that polymerize, but which pose no other hazard, should be classified. At its forty-second session, the Sub-Committee recognized the need for comprehensive guidance in this area.

Background

2. As background, DGAC has previously noted:
- There are approximately 45 named substances in the dangerous goods list, which polymerize. Examples include UN 1086 vinyl chloride, UN 1301 vinyl acetate, UN 1303 vinylidene chloride and UN 3073 vinylpyridenes. These substances have not been subjected to classification testing based on their polymerization potential but may be transported under temperature control to provide stabilization;
 - It remains possible to classify new polymerizing substances under generic entries for flammable liquids and toxic substances without subjecting them to

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

additional classification testing. Paragraphs 3.1.2.6 and 5.4.1.5.4 cover applicable transport requirements if these polymerizing substances self-react by way of polymerization below 55C. The text explicitly indicates that these substances are exclusive of self-reactive substances or organic peroxides;

- This would suggest, provisions for self-reactive substances are not relevant because these provisions deal with substances that undergo decomposition reactions whereas polymerizing substances do the opposite;
- Nevertheless, some competent authorities require testing of polymerizing substances as self-reactive substances. But this approach is not universally applied;
- Polymerizing substances such as resins used in thermal setting plastics polymerize but do not pose a high degree of risk;
- If the Subcommittee decides that some level of testing is needed, less stringent testing requirements should be considered;
- Clarification should not affect listed substances where safety has been demonstrated over many years.

3. Guidance provided in Appendix 6 of the Manual of Tests and Criteria is also relevant in relation to these substances. The text in paragraph 3.2 indicates that “explosive properties are associated with the presence of certain chemical groups which may react to produce very rapid increases in temperature and pressure”. A note indicates that tests evaluating explosive properties of organic materials is not generally considered necessary when the decomposition energy is less than 800 J/g. For substances that contain reactive chemicals simplified test procedures are permitted when the **decomposition** energy is less than 500 J/g.

4. In DGAC’s experience, substances that polymerize are not known to contain reactive groups of the type described in Appendix 6 Table A6.1 or those described for organic peroxides or self-reactive substances (see 2.4.2.3.1.2). It would be DGAC’s intent to limit testing relief to only those substances that do not contain reactive chemical groups. It is expected that the test proposed would accomplish this.

5. Preliminary discussions among other Sub-Committee experts indicate that detonation and deflagration testing of these substances does not provide meaningful information. At the same time there is some thought that a Series E test (heating under confinement) may be useful. A test of explosive power as demonstrated by a series F test would also appear to be of limited or no value. DGAC invites additional comment on whether exemption from Test Series F is appropriate.

Proposal

6. As a basis for further discussion, DGAC proposes to add the following new paragraph to read as follows:

2.4.2.3.2.5 Substances which self-react in a polymerization reaction, which are not listed by name in the Dangerous Goods List and meet no other hazard of Classes 1 to 8 where:

- The substance has a heat of reaction of 300 J/g or more but less than or equal to 800 J/g;

- The substance, as provided for transport, undergoes a self-accelerating polymerization reaction at a temperature of less than or equal to 75°C
- A heating under confinement test (Series E test) leads to a result of low or none.

may be transported as a Type E, F or G self-reactive substance, as appropriate based on the results of a Series E test and Series F test when bulk transport is being considered, (with or without temperature control) without testing as described in 2.4.2.3.2.4.

7. It is further proposed that a new note be added to the table in 2.4.2.3.2.3 to read as follows:

“(10) Polymerizing substances may be classified in accordance with 2.4.2.3.2.5 without specifically being listed. Packing method OP8 applies. Where applicable, the control and emergency temperatures shall be determined by the procedure given in 7.1.5.3 to 7.1.5.3.1.3.”

8. It is also proposed that vent sizing of portable tanks be done in accordance with TP6. This may be accomplished by adding the following to the end of 4.2.1.13.1:

“Design of pressure and emergency relief devices for polymerizing substances classified on the basis of 2.4.2.3.2.5 may be determined on the basis of TP 6.”
