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**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-second session**

Geneva, 3 – 12 December 2012

Item 2 (b) of the provisional agenda

**Recommendations made by the Sub-Committee on its thirty-ninth,  
fortieth and forty-first sessions and pending issues:****Listing, classification and packing****Classification of polymerizing substances****Transmitted by the Dangerous Goods Advisory Council (DGAC)<sup>1</sup>****Introduction**

1. As noted in ST/SG/AC.10/C.3/2012/50 and from discussions at the forty-first session, there is uncertainty as to how substances that polymerize, but which pose no other hazard, should be classified. It was noted:

- There are approximately 45 named substances in the dangerous goods list, that polymerize. Examples include UN 1086 vinyl chloride, UN 1301 vinyl acetate, UN 1303 vinylidene chlorine 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 additional classification testing. Paragraphs 3.1.2.6 and 5.4.1.5.4 cover applicable transport requirements if these polymerizing substances self react

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<sup>1</sup> In accordance with the programme of work of the Sub-Committee for 2011-2012 approved by the Committee at its fifth session (refer to ST/SG/AC.10/C.3/76, para. 116 and ST/SG/AC.10/38, para. 16).

below 55C. The text explicitly indicates that these substances are exclusive of self reactive substances or organic peroxides;

- Provisions for self reactive substances are not relevant because these provisions deal with substances that undergo decomposition reactions whereas polymerizing substances do the opposite;
- Some competent authorities require testing of polymerizing substances as self reactive substances but the 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;
- Less stringent testing requirements could be considered.

2. In DGAC's experience substances that polymerize with a reaction energy between 300 J/g and 500 J/g are either determined by SRS testing for transport in IBCs or portable tanks as either Type F or Type G. To clarify how polymerizing substances should be transported, as well as, defining a simplified test procedure for these substances, DGAC proposes that polymerizing substances with a reaction energy of 300 J/g or more but less than or equal to 500 J/g may be treated as self reactive substance type F without undergoing complete SRS testing. This would provide a conservative classification while eliminating costly testing that provides no additional benefit. This approach is only proposed for new substances that are not stabilized through an inhibitor.

## Proposal

3. 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 500 J/g; and
- the substance, as provided for transport, undergoes a self accelerating polymerization reaction at a temperature of less than or equal to 75C

may be transported as Type F self reactive substances (with or without temperature control) without testing as described in 2.4.2.3.2.4.

4. 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.”

5. 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.”