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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-first session**

Geneva, 25 June – 4 July 2012

Item 3 (b) of the provisional agenda

**Listing, classification and packing: miscellaneous****Classification of Self- Reactive substances****Transmitted by the Dangerous Goods Advisory Council (DGAC)<sup>1</sup>****Introduction**

1. It has come to DGAC's attention that there may be inconsistencies in classification practices regarding self-reactive substances (SRS) and that some practices appear to deviate from the classification system as described in the Model Regulations. In the interest of greater international uniformity, DGAC offers this paper as a basis for discussion. In particular, it appears some monomers that have the potential to polymerize are being classified as self-reactive substances. Considering the historical classifications of monomers with a potential to polymerize, the definition for SRS, and the current provisions for materials that must be transported in a stabilized condition, DGAC questions whether the practice of classifying monomers with a potential to polymerize as SRS is correct.

2. Historically substances that have a potential to polymerize have been assigned to the hazard class representing the primary hazard (e.g., Division 2.1, Class 3 and Division 6.1). Examples include UN 1086 vinyl chloride, UN 1301 vinyl acetate, UN 1303 vinylidene chloride and UN 3073 vinylpyridenes (a more extensive list of approximately 45 named substances may be found in document ST/SG/AC.10/1998/10. Shipping names for these substances typically include the word "STABILIZED" as described in 3.1.2.6 and 5.4.1.5.4 and the term stabilized is defined in the glossary as:

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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).

“Stabilized in relation to polymeric monomers means that the substance is in a condition that precludes uncontrolled polymerization. This may be achieved by methods such as the addition of an inhibiting chemical, degassing the substance to remove dissolved oxygen and inerting the air space in the package, or **maintaining the substance under temperature control.**”

If stabilization is by temperature control, control and emergency temperatures must be provided on the transport document. While temperature control may be required to safely transport these substances, it is important to note that the 45 named substances were never subjected to SRS classification testing as part of their classification.

3. The UN text for self-reactive substances suggests that polymerizing substances do not fall within this category. The definition of self-reactive substances in 2.4.2.3.1.1 limits self-reactive substances to substances that are “liable to undergo a strongly exothermic **decomposition**”. The minimum criteria for considering a substance for classification as self-reactive in 2.4.2.3.1.1(d) includes a criterion of a heat of **decomposition** of 300 J/g. In 2.4.2.3.1.1(e) a Self-Accelerating **Decomposition** Temperature (SADT) of 75C is referenced. In addition, in paragraph 2.4.2.3.1.2, the properties of self-reactive substances are described. This text also refers to the potential for a decomposition reaction and identifies example chemical structures that are prone to reactive decomposition. Substances in the SRS table all appear to be liable to decomposition.

4. Paragraphs 3.1.2.6 and 5.4.1.5.4 were introduced on the basis of ST/SG/AC.10/C.3/1999/81 by the expert from the United Kingdom. It is clear from this document that these paragraphs were included to take account substances that polymerize. Paragraph 3.1.2.6 requires that for substances, **other than self-reactive substances and organic peroxides**, the word STABILIZED be included in the proper shipping name of substances that are liable to dangerously react. The example shows the word stabilized associated with a toxic liquid. The requirements would seem to imply that a consignor is permitted to self-classify a unnamed polymerizing substance. For unnamed substances, shipping descriptions such as:

“UN 1993 Flammable liquid, N.O.S, stabilized”

“UN 3082 Environmentally hazardous substance, liquid, stabilized”

would seem possible, where the substance meets one of the hazard criteria. But a deficiency of the current text is that it does not provide for a proper shipping name for substances that pose only a polymerization risk and meets none of the criteria of the Model Regulations.

5. Resins are one group of materials which may only pose a polymerization risk. In some cases resins are transported with a hardener already added. During application at the destination they are allowed to exothermically cure. They may be transported under cooled conditions. These and others react at low temperatures and sometimes have a reaction energy slightly above 300 J/g. However, violent reaction is not a characteristic of these types of substances. In fact, considering their use as thermally setting plastics, propensity to deflagrate or detonate are not desirable properties. It may be that the heat of polymerization leads to a heating of the resin to a point where entrained water is vaporized but no other gases are produced. What do the words “dangerously react” mean in the context of such materials where the only hazard is polymerization? What shipping name should be assigned?

6. It is DGAC’s opinion that application of SRS testing is not intended by the current provisions and that such testing is more than what is needed. Considering their degree of risk, it would seem that the consignor should continue to be allowed to self-classify these substances. To provide greater uniformity, criteria should be provided and a shipping name for substances with no hazard other than polymerization should also be provided.

7. Based on the above, we would welcome discussion by the Sub-Committee on the following:

- (a) Should substances that polymerize be classified as SRS?
- (b) Are the test methods for SRS appropriate? For substances that exothermically self-react by polymerization (e.g., an SADT of 50C or less and a heat of reaction of more than 300 J/g) could more limited testing suffice (e.g. a time pressure test (Test Series C))?
- (c) Considering the low degree of risk, is it necessary for polymerizing substances to be classified by the competent authority or should continued classification by the consignor be permitted?
- (d) What proper shipping name should be assigned if such a substance poses no other hazard than polymerization? How should it be classified?

If appropriate, DGAC would prepare a written proposal for the 42<sup>nd</sup> session on the basis of the Sub- Committee's comments.

**Note:** Documents ST/SG/AC.10/1998/10 by the expert from the United States and ST/SG/AC.10/C.3/1999/81 by the expert from the United Kingdom, are both accessible at <http://documents.un.org/>.