

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

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Listing, classification and packing: polymerizing substances

Classification of polymerizing substances

Transmitted by the Dangerous Goods Advisory Council (DGAC)

Introduction

1. DGAC's paper ST/SG/AC.10/C.3/2013/33 was discussed by the International Group of experts on the explosion risks of Unstable Substances (IGUS) Energetic and Oxidising Substances (EOS) in a meeting held in April 2013. While DGAC did not participate directly in the meeting, there appear to have been a number of points made by technical experts that have relevance to the Subcommittee's discussion on the paper. Considering that a report of the IGUS EOS meeting will not be available for some time, DGAC provides its understanding of the outcome below. In doing so, DGAC has taken steps to ensure IGUS EOS participants agree that the information below is correct.

2. In addition, DGAC takes the opportunity of this paper to clarify its intention that the term "polymerizing substances" in this paper and for purposes of ST/SG/AC.10/C.3/2013/33 should be taken to include mixtures of substances which react in a polymerization reaction (e.g., mixtures consisting of an epoxy resin and hardener).

IGUS EOS Comments/Observations

3. In document ST/SG/AC.10/C.3/2013/33, polymerizing substances addressed included:

- Substances that polymerize with an SADT of 75°C or less;
- Have a polymerizing reaction energy of more than 300 J/g but not more than 800 J/g.

With respect to these polymerizing substances, the IGUS EOS indicated:

- These substances do not pose a detonation hazard or deflagration hazard; and
- For these substances a pressure effect risk should be considered owing to the potential for increased temperature due to thermal reactivity.

"Many experts stated that these substances do not meet the definition of self-reactive substances, as they behave differently: chemically seen a polymerization reaction is not a type of self-reactivity. It was also noted that in relation to the current classification criteria, classification as a self-reactive could be the least bad option, but other solutions could be preferred."

As for the use of test series E, some remarked that a test series E test is not appropriate because the orifice may become blocked. In addition, after testing a polymerizing substance, it could be difficult to clean the test equipment because the test substance will have solidified as opposed to dissipating through an exothermic decomposition reaction as in the case of SRS and organic peroxides.

DGAC Reaction to IGUS EOS Comments

4. DGAC's reaction to the IGUS EOS comments concerning transport risks are as follows:

- DGAC agrees that these substances do not pose a detonation/deflagration risk. On that basis DGAC had proposed in ST/SG/AC.10/C.3/2013/33 simplified testing based on that assumption.
- DGAC agrees that these substances may pose a pressure risk. For example, if the substance contains water, the heat given off in a polymerization reaction could heat the contained water above its boiling point causing a buildup of pressure within a package. Whether a pressure buildup can occur will depend on the volatility of components making up the substance. If no volatile materials are present, no pressure rise would normally result from a polymerization reaction. As with other substances posing similar risks, pressure buildup may be controlled through temperature control and venting of packages such as tanks.

5. With respect to the IGUS EOS comments concerning the appropriateness of self reactive substance classification:

- DGAC also agrees that these substances should not be treated as self-reactive substances, and has noted that substances of other classes that pose a polymerizing hazard are currently authorized without consideration of SRS classification. Classification as self reactive substances is inconsistent with the approach for other polymerizing substances in other classes.
- Due to differing opinions among competent authorities on how such substances should be treated and based on previous Subcommittee discussions, DGAC had nevertheless proposed a simplified scheme for classifying these substances as self reactive substances while allowing self classification consistent with classification of other polymerizing substances in other classes.

Proposed Next Step

6. How these substances should be classified is key to resolving the current confusion on how these substances should be regulated under the UN Model Regulations. DGAC recommends that the Subcommittee resolve this issue first. Two options present themselves at this point:

Option 1

Consider these polymerizing substances and mixtures to be self-reactive substances of Division 4.1 and adopt the text proposed in ST/SG/AC.10/C.3/2013/33. As discussed above, the following note should be added at the end of the proposed new 2.4.2.3.2.5 in ST/SG/AC.10/C.3/2013/33:

“NOTE: In this context, the word ‘substances’ is intended to include mixtures of substances which self-react in a polymerization reaction (e.g., mixtures consisting of an epoxy resin and hardener).”

Option 2

Taking into account the comments by IGUS EOS that these substances and mixtures should not be considered self-reactive substances, add a new note to the definition of self-reactive substances in 2.4.2.3.1.1 to read as follows:

“NOTE 4: Polymerizing substances are not self-reactive substances of Division 4.1. In this context, the word “substances” is intended to include mixtures of substances which self-react in a polymerization reaction (e.g., mixtures consisting of an epoxy resin and hardener). Polymerizing substances and mixtures should be classified according to their primary hazard and transported under the appropriate UN number. When the substance or mixture exhibits an SADT of less than 50oC and it is stabilized for transport by temperature control, the applicable requirements in 7.1.6 will apply. If the polymerizing substance meets no other hazard class but has an SADT of less than 50oC, as presented for transport, and reaction energy of more than 300 J/g, it shall be assigned to UNXXXX.”
