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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Informal correspondence group on polymerizing substances and self-accelerating polymerization temperature (SAPT)

Submitted by the representative of European Chemical Industry Council (Cefic) on behalf of the informal correspondence group

I. Introduction

1. Background is a proposal submitted to the International Maritime Organization (IMO), Sub-Committee on Carriage of Cargoes and Containers (CCC) at its eighth session, document CCC 8/6/11, in which it was proposed to require the SAPT to be included in the transport documentation.

2. Cefic and DGAC noted that simple application of the SAPT does not ensure safety and that there are other industry best practices for ensuring the safe transport of monomers, i.e. the presence of stabilizer. These practices work very well, but regulation needs to recognize these practices. Cefic and DGAC requested an informal correspondence group (ICG) to continue this work. The Explosives Working Group (EWG) agreed during the sixty-second session of the Sub-Committee of Experts on the Transport of Dangerous Goods that an ICG could work on evaluating industry best practices for ensuring stabilizer is present and effective to ensure safety in transport.

3. During the sixty-third session of the Sub-Committee of Experts on the Transport of Dangerous Goods, the representative of Cefic on behalf of the ICG submitted informal document INF.41 on the applicability of the Self-Accelerating Polymerization Temperature (SAPT) used for Polymerizing Substances and progress made at the first ICG meeting.

4. In this information paper an update is given regarding the progress made in the ICG.

II. Informal correspondence group (ICG)

5. The second ICG meeting was held on 17 April 2024 and hosted by BAM, in Berlin, Germany. Attendees (authorities and industries) were from Belgium, China, France, Germany, The Netherlands, Spain, United Kingdom, United States, Cefic and DGAC. The aim of the second meeting was to review existing regulatory text to see where changes are needed and to discuss technical aspects in determining SAPT and Polymerizing Induction Times (PIT).

- 6. Aspects discussed were:
 - Definition of polymerizing substances
 - Criteria for classification
 - Non-stabilized and stabilized systems: Applicability of SAPT for non-stabilized polymerizing substances, and introduction of the Polymerizing Induction Time (PIT) for stabilized polymerizing substances.
 - Criteria for temperature control



- Determination of PIT test series H of the manual of tests and criteria
- Special provision SP 386 stabilization

7. The first thoughts regarding amending the text in the *Model Regulations* were discussed and the outcome, including remarks for further consideration, are given in the Annex.

III. Path forward

8. It was agreed to have a next ICG meeting in Fall 2024.

Annex

In 1.2.1 Definitions:

Polymerizing substances are substances which are liable to undergo a strongly exothermic reaction resulting in the formation of larger molecules or resulting in the formation of polymers.

Polymerizing Induction Time (PIT) is the time at a given temperature after which irreversible self-accelerating polymerization starts.

Remarks from the meeting:

- PIT is only relevant for stabilized polymerizing substances
- Influence of impurities, incompatibilities (container) to be considered
- For non-stabilized polymerizing substances, the SAPT is relevant and this is already regulated in the model regulations and modal regulations
- For stabilized polymerizing substances the PIT (see definition above) is relevant

2.4.2.5 Division 4.1 - Polymerizing substances and mixtures (stabilized) ("stabilized" to be removed)

2.4.2.5.1 Definitions and properties (split stabilized / non-stabilized)

Polymerizing substances are substances which, without stabilization, are liable to undergo a strongly exothermic reaction resulting in the formation of larger molecules or resulting in the formation of polymers under conditions normally encountered in transport. [Chemical stabilization] may be used to inhibit this exothermic reaction for a certain period of time until the stabilization is no longer effective.

Such substances are considered to be polymerizing substances of Division 4.1 when:

(a1) For non-stabilized substances, their self-accelerating polymerization temperature (SAPT) is 75 °C or less under the conditions (with or without chemical stabilization as offered for transport) and in the packaging, IBC or portable tank in which the substance or mixture is to be transported; or

(a2) For stabilized substances, their Polymerization induction time (PIT) is less than an XYZ (time period TBD 7 days??) at a temperature of [75 $^{\circ}$ C?] under the conditions in which the substance or mixture is to be transported.

(Note from the meeting: this is only for classification - to be checked in relation to 50 $^{\circ}$ C/ and reasonable and safe induction time - is 6 months reasonable - conservative?)

- (b) They exhibit a heat of reaction of more than 300 J/g; and
- (c) They do not meet any other criteria for inclusion in Classes 1-8

Remarks from the meeting:

• Definition of stabilization, chemical stabilization should be clarified.

2.4.2.5.2 Non-stabilized polymerizing substances are subject to temperature control in transport if their self accelerating polymerization temperature (SAPT) is:

(a) When offered for transport in a packaging or IBC, $50 \,^{\circ}$ C or less in the packaging or IBC in which the substance is to be transported; or

(b) When offered for transport in a portable tank, $45 \,^{\circ}$ C or less in the portable tank in which the substance is to be transported.

2.4.2.5.3 (new) Stabilized polymerizing substances may be subject to temperature control in transport as defined in Special Provision 386

SP 386 reads: When substances are stabilized by temperature control, the provisions of 7.1.5 apply.

When chemical stabilization is employed, the person offering the packaging, IBC or tank for transport shall ensure that the level of stabilization is sufficient to prevent the substance in the packaging, IBC or tank from dangerous polymerization at a bulk mean temperature of 50 °C, or, in the case of a portable tank, 45 °C.

Where chemical stabilization becomes ineffective at lower temperatures within the anticipated duration of transport, temperature control is required. In making this determination factors to be taken into consideration include, but are not limited to, the capacity and geometry of the packaging, IBC or tank and the effect of any insulation present, the temperature of the substance when offered for transport, the duration of the journey and the ambient temperature conditions typically encountered in the journey (considering also the season of year), the effectiveness and other properties of the stabilizer employed, applicable operational controls imposed by regulation (e.g. requirements to protect from sources of heat, including other cargo transported at a temperature above ambient) and any other relevant factors.

Remarks from the meeting

- Is there a need to split SP 386 in two parts? temperature control vs chemical stabilization or both combined?
- Should SP 386 be more detailed, e.g., oxygen content?

Discussion on 7.1.5.3.5

Type of receptacle	SADT ^a /SAPT ^a	Control temperature	Emergency temperature
Single packagings	≤ 20 °C	20 °C below SADT/SAPT	10 °C below SADT/SAPT
and IBCs	> 20 °C and < 35 °C	15 °C below SADT/SAPT	10 °C below SADT/SAPT
	>35 °C	10 °C below SADT/SAPT	5 °C below SADT/SAPT
Portable tanks	≤45 °C	10 °C below SADT/SAPT	5 °C below SADT/SAPT

7.1.5.3.5 Derivation of control and emergency temperatures

i.e. the SADT/SAPT of the substance as packed for transport.

New table based on PIT:

-Temperature at which PIT is long enough for a safe transport given the maximum duration of transport (see also SP 386)

-Control temperature = 10 °C lower

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-Emergency temperature = $5 \,^{\circ}$ C lower

Remarks from the meeting:

- Explanatory text needed regarding PIT/temperatures safe transport times
- Manual of tests and criteria to be reviewed/amended
- Split stabilized / non-stabilized
- Tests for non-stabilized -> no change needed (SAPT is already included)
- Tests for stabilized: check relevance for PIT
- MTC: test methods (existing / alternatives ? (chemical analysis?)