

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

20 November 2024

Sixty-fifth session

Geneva, 25 November-3 December 2024

Item 3 of the provisional agenda

Listing, classification and packing

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. As described in earlier informal documents on this topic, background of this activity 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. In earlier informal correspondence group (ICG) meetings it was noted that simple application of the SAPT does not ensure safety and that for stabilized polymerizing substances the so-called Polymerizing Induction Time (PIT) at a given temperature is the parameter for ensuring the safe transport of stabilized monomers. Update on this was given in informal document INF.39 as submitted to the sixty-fourth session by Cefic on behalf of the ICG.
4. In this informal document an update is given on the progress made in the ICG.

II. Informal correspondence group (ICG)

5. The third ICG meeting was held on 5 November 2024 and hosted by BAM, in Berlin, Germany. Attendees (authorities and industries) were from Belgium, China, Germany, The Netherlands, Spain, United States of America, Cefic and DGAC. The aim of the third meeting was to review existing regulatory text to see where changes are needed regarding the classification criteria for polymerizing substances (stabilized and non-stabilized) and to discuss technical aspects in determining SAPT and Polymerizing Induction Times (PIT).
6. Aspects discussed were (see Annex I):
 - Definition of polymerizing substances: non-stabilized and stabilized
 - 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 (see Annex II)
 - Relation to Special Provision SP 386 – stabilization

Determination of PIT by test series H of the manual of tests and criteria or alternative testing was discussed briefly and will be on the agenda for a next ICG meeting.

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 Annexes I and II to this document.

III. Path forward

8. It was agreed to have a next ICG meeting in Spring 2025.

Annex I

Notes:

Text which can be used in the introduction and/or Manual of Tests and Criteria

Introduction

Many monomers are capable of exothermic self-accelerating polymerization, even at low temperatures.

Non stabilized polymerizing substances

Text to be drafted.

It should contain a reference to the ability to show Self-Accelerating Polymerization and a reference to the Self-Accelerating Polymerization Temperature (SAPT).

Stabilized polymerizing substances

When handled at normal shipping including transshipments [and storage] conditions, stabilized polymerizing substances, exhibit a period of induction, ~~or stability~~, during which no polymerization reaction occurs. After this period, a reaction occurs at an increasing rate. This time period is called the Polymerization Induction Time (PIT) and is used to evaluate the stability of monomers during transportation and handling.

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 under the conditions normally encountered in transport.

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

2.4.2.5 (UN) Division 4.1 - Polymerizing substances and mixtures (~~stabilized~~)

1. 2.4.2.5.1 (UN) Definitions and properties

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 is 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 a time period of 7 days at a temperature of 75 °C under the conditions in which the substance or mixture is to be transported.

(Comment ICG: justification of this will be given by the ICG in a formal proposal when the work is completed. It seems that this rule is very 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.

2.4.2.5.2 (UN) 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 °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 °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 SP 386. Text to be drafted. See also “**Process temperature control stabilized polymerizing substances (For further consideration)**” in Annex 2.

2. 7.1.5.3 Temperature control provisions

7.1.5.3.1 These provisions apply to certain self-reactive substances when required by 2.4.2.3.4, and certain organic peroxides when required by 2.5.3.4.1 and certain non stabilized polymerizing substances when required by 2.4.2.5.2 or by 2.4.2.5.3 (new!) or special provision 386 of chapter 3.3 which may only be transported under conditions where the temperature is controlled.

7.1.5.3.2 These provisions also apply to the transport of substances for which:

- (a) The proper shipping name as indicated in column 2 of the Dangerous Goods List of chapter 3.2 or according to 3.1.2.6 contains the word "TEMPERATURE CONTROLLED"; and
- (b) The self-accelerating decomposition temperature (SADT) or the self-accelerating polymerisation temperature (SAPT) determined for the substance (~~with or~~ without chemical stabilization) as offered for transport is:
 - (i) 50 °C or less for single packagings and IBCs; or
 - (ii) 45 °C or less for portable tanks.

When chemical inhibition is not used to stabilize a reactive substance which may generate dangerous amounts of heat and gas, or vapour, under normal transport conditions, these substances need to be transported under temperature control. These provisions do not apply to substances which are stabilized by the addition of chemical inhibitors such that the SADT or the SAPT is greater than that prescribed in (b) (i) or (ii), above.

7.1.5.3.5 Derivation of control and emergency temperatures for self reactive substances, organic peroxides and non-stabilized polymerizing substances

Type of receptacle	SADT ^a /SAPT ^a	Control temperature	Emergency temperature
Single packagings and IBCs	≤ 20 °C	20 °C below SADT/SAPT	10 °C below SADT/SAPT
	> 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

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

Annex II

1. Process temperature control stabilized polymerizing substances (for further consideration)

Process to be incorporated in a flowchart (to be developed):

1. *What is the duration of transport? (Note: Safety margin/ see also text SP386)*
2. *Is this less than the PIT @ 50 °C*
 - a. *Yes – No issues*
3. *No – Calculate / Test PIT at lower temperature until duration is longer than the anticipated duration of transport*
4. *Control temperature = T(PIT = ADT) – 10 °C*

Additional remarks from the ICG:

- Temperatures to be determined in steps of 5 °C
- 50 °C is very conservative approach. This statement to be included in a note
- Suggestion: typical transport times: road 2 weeks / sea transport 3 months (unless transport time deviates significantly) ? (to be incorporated as a note?)

2. Example (include some real substances)

Duration of transport is 90 days

PIT @ 50 °C = 50 days

PIT @ 45 °C = 100 days

Control Temperature = 35 °C

Emergency Temperature = 40 °C

Legislative points

2.4.2.5.2 Polymerizing substances are subject to temperature control in transport if their Polymerizing Induction Time (PIT) is:

- (a) When offered for transport in a packaging or IBC, less than the anticipated duration of transport (ADT) @ 50 °C
- (a) When offered for transport in a portable tank, less than the anticipated duration of transport (ADT) @ 45 °C

Definition

T(PIT = ADT) - Temperature at which the Polymerizing Induction Time (PIT) is equal to the Anticipated Duration of Transport (ADT)

7.1.5.3.5

Type of receptacle	Control Temperature	Emergency Temperature
Single Packaging's and IBC's	10 °C below T(PIT = ADT)	5 °C below T(PIT = ADT)
Portable tanks	10 °C below T(PIT = ADT)	5 °C below T(PIT = ADT)

The control temperature is the 10 °C below the temperature at which the PIT = Anticipated Duration of Transport
The Emergency temperature is 5 °C below the temperature at which the PIT = ADT

Remark: no difference between Tanks/IBCs and packagings. PIT is packaging/volume and time independent.

Whole section 7.1.5.3 to be reviewed/amended as well as the manual of tests and criteria (MTC).