Amendments to the classification flow chart/decision logic for self-reactive substances and organic peroxides

Transmitted by the International Council of Chemical Associations (ICCA)³

I. Introduction

1. Over the last years the classification flow chart/decision logic for self-reactive substances and organic substances was discussed in the International Group of experts on explosion risks of Unstable Substances, working group of Energetic and Oxidising Substances (IGUS-EOS) for several times.

2. Apart from a minor change that was introduced in the second part of both flowcharts in the ninth edition of the Recommendations (1995), these flow charts have remained unchanged since their first introduction more than 25 years ago. At the time of introduction of the flow chart, nearly all substances were transported and handled in packagings. However, over time the transport and handling in intermediate bulk containers (IBCs) and tanks became more and more common practise. It was felt in the discussion in IGUS-EOS that this should have some consequences for the classification flow chart.

³ 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).
3. Further, it was observed that various issues that determine the classification of substances or mixtures are addressed in the text of the Model Regulations and the Globally Harmonized System of Classification and Labelling of Chemicals (GHS), however are not incorporated in the flow chart. These aspects can easily be overlooked by users not so familiar with the detailed text. As they are part of the classification procedure, it is more appropriate to include them in the classification flow charts for both self-reactive substances and organic peroxides. These flow charts are identical.

4. It was agreed during the last IGUS-EOS meeting that ICCA would prepare a proposal to both subcommittees on TDG and GHS.

II. Background to the proposal

A. Aspects not changing the classification principles

5. The following aspects are addressed in the text of the Model Regulations and GHS but are not incorporated in the classification flow charts:

(a) No type G classification possible if the Self-Accelerating Decomposition Temperature (SADT) of the substance is < 60 °C in a 50 kg packaging (see Model Regulations 2.4.2.3.3.2 (g), 2.5.3.3.2 (g) and GHS 2.8.2.2 (g), 2.15.2.2 (g));

(b) No type G classification possible when a diluent is used with a boiling point < 150 °C (see Model Regulations 2.4.2.3.3.2 (g), 2.5.3.3.2 (g) and GHS 2.8.2.2 (g), 2.15.2.2 (g)).

6. In the proposed amended flow chart these two aspects are addressed in the new boxes 14 and 17 respectively. The introduction of these boxes will not lead to a change in the existing classification principles.

B. Aspects changing the classification principles for Type G substances and mixtures

7. In addition, in IGUS-EOS there was a discussion on the requirements for exemption (i.e. Type G in the flow charts). It was felt that for solid materials the existing requirements need not to be changed (there are to our knowledge no type G solids transported in IBCs or tanks). For liquids however, when transported or handled in IBCs or tanks, Type F classification seems to be the most appropriate solution for the following two reasons:

(a) Despite the type G properties, for liquids adequate pressure relief requirements may be needed when transported and handled in IBCs or tanks (for Type G there are no requirements at all);

(b) The requirement for type G substances or mixture is an SADT < 60 °C in a 50 kg packaging. However, the substance or mixture in an IBC or tank will have a lower SADT compared to the SADT in a 50 kg packaging. When classified as Type F, the actual SADT of the substance in IBC or tank has to be chosen for the determination of control- and emergency temperatures, when required according to the criterion for temperature control.

8. In the proposed amended flow chart these two aspects are addressed in the new boxes 15 and 16 and the wording in exit F (in flow chart Model Regulations).
III. Proposals

A. Proposal alternative 1

9. Based on the background given in sub-sections 2.1 (no change in classification principles) and 2.2 (change in classification principles for Type G substances) the following is proposed (changes in grey shading):
(a) In the Model Regulations replace Figures 2.4.1 and 2.5.1 by the following new scheme:

**Figure 2.4.1: Flow chart scheme for self-reactive substances**

**Figure 2.5.1: Flow chart scheme for organic peroxides**
Figure 2.4.1: Flow chart scheme for self-reactive substances (cont’d)

Figure 2.5.1: Flow chart scheme for organic peroxides (cont’d)

Box 11

Is the organic peroxide/self-reactive substance to be considered for transport in IBCs or tanks, or for exemption?

11.1 Yes

11.2 No

12.1 Not low

12.2 Low

12.3 None

Box 12

What is its explosive power?

Box 13

What is the effect of heating it under defined confinement?

13.1 Low

13.2 None

Box 14

Is the SADT < 60 ºC in a 50 kg package?

14.1 Yes

14.2 No

Box 15

Is it a solid?

15.1 Yes

15.2 No

Box 16

Is it to be considered for transport in IBCs or tanks?

16.1 Yes

16.2 No

Box 17

Is a diluent with a boiling point of < 150 ºC used?

17.1 Yes

17.2 No

Exit E

Exit F

Exit G

ACCEPTED FOR TRANSPORT IN PACKAGES OF NOT MORE THAN 400KG/450 LITRES

MAY BE CONSIDERED FOR TRANSPORT IN IBCS OR TANKS IF ADEQUATE PRESSURE RELIEF CAN BE PROVIDED UNDER THE CONDITIONS SPECIFIED BY THE COMPETENT AUTHORITY. OTHERWISE: ACCEPTED FOR TRANSPORT IN PACKAGES OF NOT MORE THAN 400KG/450 LITRES

SHALL BE CONSIDERED FOR EXEMPTION
(b) In GHS replace Figures 2.8 and 2.15 by the following new decision logic:

**Decision logic 2.8 for self-reactive substances and mixtures**

**Decision logic 2.15 for organic peroxides**

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**Diagram:**

- **SUBSTANCE/MIXTURE**
  - 1.1 Yes
  - 1.3 No
  - 1.2 Partial

**Box 1**
- Test A
- Does it propagate a detonation?

**Box 2**
- Test B
- Can it detonate as packaged?
  - 2.1 Yes
  - 2.2 No

**Box 3**
- Test C
- Can it propagate a deflagration?
  - 3.1 Yes, rapidly
  - 3.2 Yes, slowly
  - 3.3 No

**Box 4**
- Test C
- Can it propagate a deflagration?
  - 4.1 Yes, rapidly
  - 4.2 Yes, slowly
  - 4.3 No

**Box 5**
- Test C
- Can it propagate a deflagration?
  - 5.1 Yes, rapidly
  - 5.2 Yes, slowly
  - 5.3 No

**Box 6**
- Test D
- Does it deflagrate rapidly in package?
  - 6.1 Yes
  - 6.2 No

**Box 7**
- Test E
- What is the effect of heating it under defined confinement?
  - 7.1 Violent
  - 7.2 Medium
  - 7.3 Low
  - 7.4 None

**Box 8**
- Test E
- What is the effect of heating it under defined confinement?
  - 8.1 Violent
  - 8.2 Medium
  - 8.3 Low
  - 8.4 None

**Box 9**
- Test E
- What is the effect of heating it under defined confinement?
  - 9.1 Violent
  - 9.2 Medium
  - 9.3 Low
  - 9.4 None

**Box 10**
- Test G
- Can it explode as packaged?
  - 10.1 Yes
  - 10.2 No

**Type A**

**Type B**

**Type C**

**Type D**

*go to box 11*
Decision logic 2.8 for self-reactive substances and mixtures (cont’d)
Decision logic 2.15 for organic peroxides (cont’d)

from box 9

Box 11
Packaged in packages of more than 400 kg/450 l or to be considered for exemption?

11.1 Yes
11.2 No

12.1 Not low
12.2 Low
12.3 None

What is its explosive power?

Box 12
Test F

13.1 Low
13.2 None

What is the effect of heating it under defined confinement?

Box 13
Test E

14.1 Yes
14.2 No

Is the SADT < 60 ºC in a 50 kg package?

Box 14
Test H

15.1 Yes
15.2 No

Is it a solid?

Box 15

16.1 Yes
16.2 No

Packaged in packages of more than 400 kg/450 l?

Box 16

17.1 Yes
17.2 No

Is a diluent with a boiling point of < 150 ºC used?

Box 17

Type E
Type F
Type G

(Note: the grey shaded wording in boxes 10 and 13 are just corrections.)
B. Proposal alternative 2

10. Based on the background given in sub-section 2.1 (no change in classification principles), it is proposed to take proposal alternative 1 with the deletion of boxes 15 and 16 and deleting the grey shaded wording in exit F of the proposed flow chart scheme in paragraph 9 (a) (i.e. proposal for the Model Regulations).

IV. Consequential amendments

11. If alternative 1 or alternative 2 proposal is adopted, the following flow chart is to be amended accordingly:
   – In the Manual of Tests and Criteria the flow chart given in Figure 20.1 (a)

12. If alternative 1 proposal is adopted:
   (a) In the Model Regulations add to 2.4.2.3.3.2 (g), 2.5.3.3.2 (g) the following sentence: when the formulation is a liquid to be transported in IBCs or tanks it should be defined as self-reactive substance type F;
   (b) In the Model Regulations add to 2.5.3.3.2 (g) the following sentence: when the formulation is a liquid to be transported in IBCs or tanks it should be defined as organic peroxide type F;
   (c) In GHS add to 2.8.2.2 (g) the following sentence: when the substance or mixture is a liquid to be handled in IBCs or tanks it should be defined as self-reactive substance type F;
   (d) In GHS add to 2.15.2.2 (g) the following sentence: when the substance or mixture is a liquid to be handled in IBCs or tanks it should be defined as organic peroxide type F.