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COMMITTEE OF EXPERTS ON THE TRANSPORT
OF DANGEROUS GOODS

REPORT OF THE COMMITTEE OF EXPERTS ON ITS EIGHTEENTH SESSION
(28 November - 7 December 1994)

Addendum 4

Annex 4 : Report of the Working Group on the Rationalization of the Manual of Tests and Criteria.

1. The report of the Working Group on the Rationalization of the Manual of Tests and Criteria as submitted to the Committee during the eighteenth session, is reproduced hereafter (in english only).

2. The decisions taken by the Committee are recorded in its report, ST/SG/AC.10/21, paragraphs 25 to 37.

**REPORT OF THE WORKING GROUP ON
RATIONALIZATION OF THE MANUAL OF TESTS AND CRITERIA**

Introduction

1. A Working Group was established to develop further the draft rationalized Manual of Tests and Criteria proposed by the expert from the United Kingdom, and listing and classification of organic peroxides and self-reactive substances. The terms of reference of the Group were limited by the Committee to editorial review and rationalization of the Manual of Tests and Criteria and consequential amendments to the Recommendations. The Working Group was also requested to consider documents concerning organic peroxides and self-reactive substances in line with the decisions of the Committee. It was chaired by Ing Groothuizen and included representatives from: China, France, Germany, Netherlands, Norway, Spain, Sweden, Switzerland, United Kingdom, United States of America and from the European Chemical Industry Council (CEFIC).

Documents

2. The discussions on rationalization of the Manual were based on the following documents:

- Document ST/SG/AC.10/C.3/R.474 (United Kingdom) giving the base text for the Introduction and Part I;

- Document ST/SG/AC.10/C.3/R.475 (United Kingdom) giving the base text for Parts II and III, and the appendices;

- Document ST/SG/AC.10/C.3/R.572 (CEFIC) proposing a method of vent sizing tank containers for the transport of organic peroxides;

- Addenda 2 and 3 to the report of the ninth session of the Sub-Committee (documents ST/SG/AC.10/C.3/18/Add.2 and Add.3);

- Document ST/SG/AC.10/R.441 (United Kingdom) giving amendments received by the United Kingdom before the submission date for documents to this meeting;

- Document ST/SG/AC.10/R.482 (CEFIC) giving new text for the test for self-heating substances of Division 4.2;

- Document ST/SG/AC.10/C.3/R.489 (Norway) proposing general classification criteria for aqueous solutions of inorganic nitrates;

- Information paper INF. 3 (United Kingdom) giving the consolidated text for the rationalized manual as of September 1994 (including the proposals in -/R.441);

- Information paper INF. 3/Add.1 (United Kingdom) giving the corrections to INF.3 received by the United Kingdom as of the beginning of November 1994;

- Information paper INF. 27 (Sweden) giving examples of test results for liquid oxidizing substances;

- Information paper INF. 31 (Germany) proposing simplification of the test prescription for self-heating substances of Division 4.2;

- Information paper INF. 34 (Netherlands) comparing results from the Series A tests;

- Information paper INF. 38 (USA) commenting on -/R.489;

- Informal proposals from HMAC regarding figure 14.1, and the principles for classification of organic peroxides and self-reactive substances; and

- Informal proposals from Germany regarding insertion of test results for self-reactive substances.

3. The discussions on listing and classification of organic peroxides and self-reactive substances were based on the following documents:

- Document ST/SG/AC.10/R.480 (CEFIC) proposing amendments to tables 11.3 and 11.4;

- Document ST/SG/AC.10/R.481 (CEFIC) proposing amendments to the requirements for transport of organic peroxides in tank containers and IBCs;

- Document ST/SG/AC.10/R.483 (CEFIC) proposing simplification of the packing methods for organic peroxides and self-reactive substances;

- Information paper INF. 14 (CEFIC) proposing further amendments to tables 11.3, 11.4 and 11.5; and

- Information paper INF. 15 (USA) proposing further amendments to tables 11.3, 11.4 and 11.5.

Procedure

4. In order to avoid duplication of effort for the Secretariat and the Working Group, the following procedure was adopted:

(a) All text proposed in translated official documents (-/C.3/R.474, -/C.3/R.475, -/R.441, -/R.483) was accepted, unless otherwise stated in this report, and is<u>not</u> given in the appendices to this report.

(b) All text proposed in translated documents which has been amended is given in the appendices to this report.

(c) All text proposed in information papers, which has been accepted or amended by the Working Group, is given in the appendices to this report.

Minor editorial amendments are not discussed in the narrative part of this report.

5. This report contains the following appendices:

Appendix A Consequential amendments to Chapter 11 of the Recommendations

Appendix B Consequential amendments to Chapter 14 of the Recommendations

Appendix C Amendments to the General Introduction and Part I of the rationalized Manual of Tests and Criteria (document ST/SG/AC.10/C.3/R.474 as amended by documents ST/SG/AC.10/18/add.2 and, apart from stated acceptions, ST/SG/AC.10/R.441/Annex 1)

Appendix D Amendments to Parts II and III, and the appendices of the rationalized Manual of Tests and Criteria (document ST/SG/AC.10/C.3/R.475 as amended by documents ST/SG/AC.10/18/add.3 and, apart from stated acceptions, ST/SG/AC.10/R.441/Annex 2)

TEST MANUAL

General Introduction

6. The general table of contents, as proposed in document -/R.441, was accepted.

PART I

Introduction to Part I

7. As packaged substances are not subjected to the type 4(a) test, the text in 10.3.3.4 was amended as proposed in document INF.3/Add.1. The other minor editorial amendments were accepted.

Section 11

8. The text of paragraph 11.3.1 was amended to remove the requirement to report the density of liquids tested.

9. New results, provided by the expert from the United States, were inserted for the 1(a) test. The editorial amendments proposed in -/R.441 and INF.3/Add.1 were accepted.

Section 12

10. New results, provided by the expert from the United States, were inserted for the 2(a) test. The editorial amendments proposed in -/R.441 and INF.3/Add.1 were accepted.

Section 13

11. New results, provided by the expert from the Netherlands, were inserted for the 3(a)(ii) and 3(b)(i) tests. The editorial amendments proposed in - /R.441 and INF.3/Add.1 were accepted.

Section 14

12. The amendments proposed in document -/R.441 were accepted.

Section 15

13. Only minor editorial amendments were made.

Section 16

14. As decided by the Committee, none of the changes to Section 16 proposed in document -/R.441 were accepted.

Section 17

15. No changes were made.

PART II

Introduction to Part II

16. Only minor editorial changes were made. However, HMAC had proposed copying the principles for classification of organic peroxides from Chapter 11 and self-reactive substances from Chapter 14 of the Recommendations. The Working Group supported this proposal but had insufficient time to prepare the necessary amendments. The Committee is invited to mandate the expert from the United Kingdom to introduce, in collaboration with the Secretariat, the necessary text in the final version of the manual with the understanding that no changes are to be made to the principles.

Test Series A

17. The expert from the Netherlands presented document INF. 34 indicating that there were discrepancies in the results from the four Series A tests, particularly test A.5, currently given. After extensive discussion, it was agreed that it was not possible to improve the comparability at this stage and the Working Group recommends that the Committee make development of a single Series A UN test a priority in the next biennium as proposed in United Kingdom information paper INF. 13.

18. It was agreed that, by analogy with test type 1(a), if a liquid is being considered for transport in tank-containers or intermediate bulk containers with a capacity exceeding 450 litres, a cavitated version of a Series A test may be used.

19. The text of paragraph 21.3.1 was amended to remove the requirement to report the density of liquids tested.

20. As the current screening procedure for detonability could allow organic peroxides to be transported in tank containers or IBCs without performing a Series A test, the procedure was modified so that a Series A test should be performed unless there is data to indicate that there is no propagation of detonation in the formulation with a higher concentration and the same physical state.

21. Different batches of steel tubes may have varying strength leading to different fragmentation lengths for the same stimulus. A calibration procedure was introduced as a new paragraph 21.3.5 and the Series A test criteria adjusted to allow for this.

22. The current results given for test A.5 (in practice, those from the old version of the United States Gap test) were deleted and replaced by new results given in Netherlands document INF.34. Their new results for test A.6 were also inserted.

Test Series B

23. No changes were made.

Test Series C

24. New results on self-reactive substances, provided by the expert from Germany, were inserted in the Examples of results.

Test Series D

25. No changes were made.

Test Series E

26. New test results, on self-reactive substances, from the experts from Germany and the Netherlands were added to the Examples of results for the Koenen and Dutch Pressure Vessel tests.

Test Series F

27. New test results, on self-reactive substances, from the experts from Germany and the Netherlands were added to the Examples of results for some tests.

Test Series G

28. No changes were made.

Test Series H

29. The editorial amendments, new results and diagrams proposed in document INF.3/Add.1 were accepted with minor alterations and improvements were made to the procedures.

PART III

Sections 30 and 32

30. No changes were made.

Section 33

31. Figure 14.1 was copied from the Recommendations as proposed by HMAC. Consequential amendments are proposed in appendix B to harmonise the test prescriptions in Chapter 14 with those agreed for the Manual. The United Kingdom and CEFIC proposals for test N.4 were combined to give an agreed consolidated text. The German proposal in INF. 31 was not accepted as it was considered that it could mean reassignment of some products from Packing Group III to Packing Group II. Experts from Germany and CEFIC promised to check the consequences.

Section 34

32. Only minor editorial amendments were made. The Norwegian and United States proposals for making non-saturated solutions not subject to the Recommendations were discussed. The Working Group considered that there should be a concentration below which it was not necessary to test aqueous solutions of solid oxidizers. The majority was of the opinion that it would be best to set a general exemption level once more test results were available from liquid oxidizer tests. However, it was considered that it may be possible to set a level, e.g. 80% of the saturation concentration, for aqueous solutions of nitrates (weak oxidizers) below which they would not be subject to the Recommendations. No decision was made. The Swedish results on liquid oxidizers were accepted.

Section 38

33. The editorial amendments proposed in INF.3/Add.1 were accepted.

APPENDICES

34. The expert from the United States promised to provide a new specification for the appendix 1 version of the No. 8 (USA) detonator by the end of this week. No changes were made to appendix 2 and only one minor correction was made to appendix 3.

35. The Working Group considered that the Committee needs to address the problem raised in paragraph 21 of United Kingdom document -/R.441 relating to obtaining technical details of UN tests.

36. Some new national contacts were added to appendix 4.

37. As decided by the Committee, the Working Group reviewed CEFIC document-/C.3/R.572 with the aim of incorporating the example test procedure for vent sizing as a new appendix 5. Changes were agreed in principle but it was left to the expert from the United Kingdom to incorporate the changes and

edit the text. The Committee is invited to mandate the expert from the United Kingdom to introduce, in collaboration with the Secretariat and the CEFIC expert, the necessary text in the final version of the manual.

ORGANIC PEROXIDES AND SELF-REACTIVE SUBSTANCES

38. CEFIC document -/R.481 proposed amendments to the requirements for the transport of organic peroxides in IBCs and tank-containers. These were discussed but as they would result in a considerable number of consequential amendments, the Working Group decided that the subject should be considered in the next biennium.

39. CEFIC document -/R.483 was accepted and the Committee is invited to incorporate the proposed changes in the ninth revision of the Recommendations.

40. The CEFIC and USA documents on insertion of new formulations in Tables 11.3, 11.4 and 11.5 were discussed and the supporting data reviewed. The agreed amendments are given in appendix A to this report.

ACTIONS REQUESTED BY THE COMMITTEE

41. The Committee is invited to mandate the expert from the United Kingdom and the Secretariat:

(a) to copy the principles for classification of organic peroxides and self-reactive substances to the manual (see paragraph 16 of this report);

(b) to produce a new appendix 5, in collaboration with the expert from CEFIC, giving the example method for vent sizing (see paragraph 37 of this report).

42. The Committee is invited to adopt the rationalized Manual of Tests and Criteria as proposed by the United Kingdom and as amended by the Working Group.

43. The Committee is invited to give priority to the following work in the next biennium:

(a) Review test 6(c) which is the key test in assignment to a Class 1 hazard division and to the exemption of energetic industrial chemicals from Class 1;

(b) Simplify Test Series A as there is still a mixture of old and new tests;

(c) Development of a UN test to replace the existing pressure vessel tests in Series E;

(d) Harmonisation of the temperature control requirements and exemption requirements for organic peroxides and self-reactive substances; and

(e) Exemption of unsaturated solutions of solid oxidizers from the Recommendations.

(f) Simplification of the classification procedure for self-heating substances of Division 4.2.

Appendix A

AMENDMENTS TO CHAPTER 11 OF THE RECOMMENDATIONS

11.2 Replace the text in sub-section 11.2 with the following:

11.2.1 *Assignment of substances to Division 5.1*

11.2.1.1 Oxidising substances are classified in Division 5.1 in accordance with the test method, procedure and criteria in 11.2.2 and 11.2.3 (see also: Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Part III, section 34). In the event of divergence between test results and known experience, judgement based on known experience should take precedence over test results.

11.2.1.2 Reclassification of existing entries should only be done for single substances and only where necessary for safety.

11.2.2 *Oxidizing solids*

11.2.2.1 Introduction

This test method is designed to measure the potential for a solid substance to increase the burning rate or burning intensity of a combustible substance when the two are thoroughly mixed. Tests are conducted on the substance to be evaluated mixed with dry fibrous cellulose in mixing ratios of 1:1 and 4:1, by mass, of sample to cellulose. The burning characteristics of the mixtures are compared with the standard 3:7 mixture, by mass, of potassium bromate to cellulose. If the burning time is equal to or less than this standard mixture, the burning times should be compared with those from the Packing Group I or II reference standards, 3:2 and 2:3 ratios, by mass, of potassium bromate to cellulose respectively.

11.2.2.2 Procedure

11.2.2.2.1 Technically pure potassium bromate is required as a reference substance. It should be sieved, but not ground, and the fraction with nominal particle sizes in the range 0.15 to 0.30 mm used as the reference substance. The reference substance is dried at 65°C to constant mass (for a minimum of 12 hours) and kept in a desiccator (with desiccant) until cool and required for use.

11.2.2.2.2 Dried fibrous cellulose*/, with a fibre length between 50 and 250 µm and a mean diameter of 25 µm, is used as the combustible material. It is dried in a layer no more than 25 mm thick at 105°C to constant mass (for a minimum of 4 hours) and kept in a desiccator (with desiccant) until cool and required for use. The water content should be less than 0.5% by dry mass. If necessary, the drying time should be prolonged to achieve this.

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*/ Source reference available from the national contact for test details in France (see appendix 4 of the Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria).

11.2.2.2.3 An ignition source is required comprising an inert metal wire (e.g. nickel/chromium) connected to an electrical power source and with the following characteristics:

(a)	Length	=	30 ± 1 cm
(b)	Diameter	=	0.6 ± 0.05 mm
(c)	Electrical resistance	=	6.0 ± 0.5 Ω/m
(d)	Electrical power dissipated in the wire	=	150 ± 7 W

The wire should be shaped as in figure 34.4.1.1.

11.2.2.2.4 A 60° glass funnel, sealed at the narrow end, with an internal diameter of 70 mm is required to form the mixtures into a truncated conical pile with base diameter of 70 mm on a cool, impervious, low heat conducting plate. A 150 mm by 150 mm plate with a thickness of 6 mm and a thermal conductivity (at a temperature of 0°C) of 0.23 $W \cdot m^{-1} \cdot K^{-1}$ is suitable. Other plates with a similar conductivity may be used.

11.2.2.2.5 A fume cupboard or other kind of ventilated area is required in which there is some ventilation but with an air stream velocity of 0.5 m/s or less. ***The fume extraction system should be suitable for the capture of toxic fumes.***

11.2.2.2.6 The substance, in the form in which it will be transported, should be inspected for any particles < 500 µm diameter. If that powder constitutes more than 10% (mass) of the total, or if the substance is friable, then the whole of the test sample should be ground to a powder before testing to allow for a reduction in particle size during handling and transport.

11.2.2.2.7 30.0 g ± 0.1 g mixtures of the reference substance and cellulose are prepared in the potassium bromate to cellulose ratios of 3:7, 2:3 and 3:2, by mass. 30.0 g ± 0.1 g mixtures of the substance to be tested, in the particle size in which it will be transported, and cellulose are prepared in the oxidizer to cellulose ratios of 4:1 and 1:1, by mass. Each mixture should be mixed mechanically as thoroughly as possible without excessive stress. Each sample mixture should be made individually, used as soon as possible, and not taken from a batch.

11.2.2.2.8 Using the conical funnel, the mixture should be formed into a truncated conical pile, with a base diameter of 70 mm, covering the looped ignition wire resting on the low heat conducting plate. The plate should be placed in a ventilated area and the test performed at atmospheric pressure with the ambient temperature at 20°C ± 5°C.

11.2.2.2.9 Power is applied to the ignition wire and is maintained for the duration of the test or for three minutes if the mixture does not ignite and burn. The recorded burning time is from when the power is switched on to when the main reaction (e.g. flame, incandescence or glowing combustion) ends. Intermittent reaction, such as sparking or sputtering, after the main reaction should not be taken into account. If the heating wire breaks during the test

then the test should be repeated unless breaking of the wire clearly does not effect the result. The test should be performed five times on the substance. Five tests should be performed with each reference mixture required to make the Packing Group assignment or to determine if the substance should not be classified in Division 5.1.

11.2.2.3 Criteria

11.2.2.3.1 The results are assessed on the basis of:

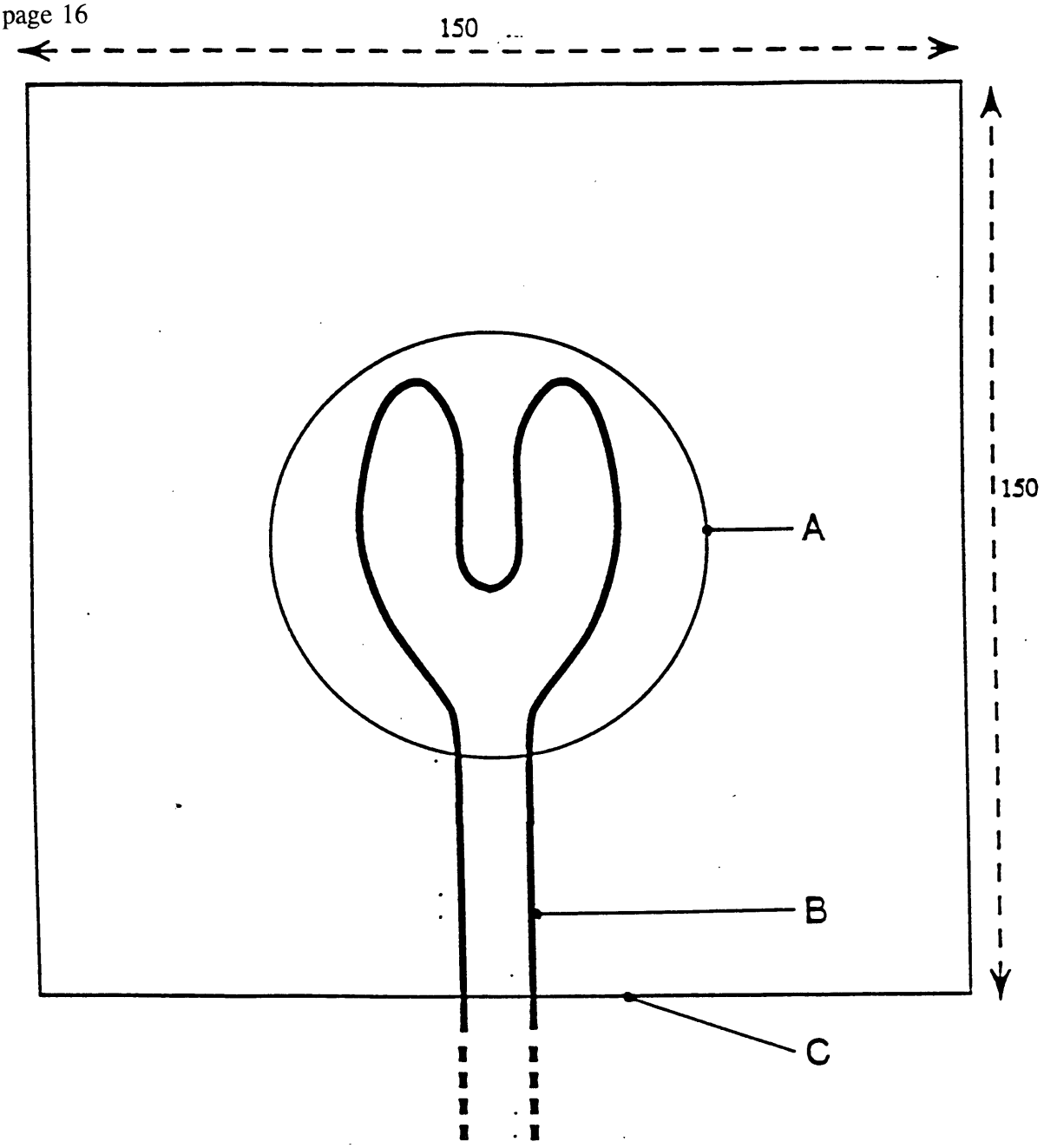
(a) the comparison of the mean burning time with those of the reference mixtures; and

(b) whether the mixture of substance and cellulose ignites and burns.

11.2.2.3.2 The test criteria for determining oxidizing properties of the substance are:

Packing Group I	any substance which, in the 4:1 or 1:1 sample-to-cellulose ratio (by mass) tested, exhibits a mean burning time less than the mean burning time of a 3:2 mixture, by mass, of potassium bromate and cellulose.
Packing Group II	any substance which, in the 4:1 or 1:1 sample-to-cellulose ratio (by mass) tested, exhibits a mean burning time equal to or less than the mean burning time of a 2:3 mixture (by mass) of potassium bromate and cellulose and the criteria for Packing Group I are not met.
Packing Group III	any substance which, in the 4:1 or 1:1 sample-to-cellulose ratio (by mass) tested, exhibits a mean burning time equal to are less than the mean burning time of a 3:7 mixture (by mass) of potassium bromate and cellulose and the criteria for Packing Groups I and II are not met.
Not Division 5.1	any substance which, in both the 4:1 and 1:1 sample-to-cellulose ratio (by mass) tested, does not ignite and burn, or exhibits mean burning times greater than that of a 3:7 mixture (by mass) of potassium bromate and cellulose.

For substances having other risks, e.g. toxicity or corrosivity, the requirements of paragraph 1.44 should be met.



(A) Base of sample cone (70 mm diameter)
(B) Heating wire
(C) Low heat conducting plate

Figure 11.1: TEST PLATE AND IGNITION WIRE

11.2.3 *Oxidizing liquids*

11.2.3.1 Introduction

A test is performed to determine the potential for a liquid substance to increase the burning rate or burning intensity of a combustible substance or for spontaneous ignition to occur when the two are thoroughly mixed. The procedure is given in section 34 of the Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria. It measures the pressure rise time during combustion. Whether a liquid is an oxidizing substance of Division 5.1 and, if so, whether Packing Group I, II or III should be assigned, is decided on the basis of the test result (see also **Precedence of hazards characteristics** in Chapter 1).

11.2.3.2 Assignment of packing group

11.2.3.2.1 The test results are assessed on the basis of:

(a) whether the mixture of substance and cellulose spontaneously ignites.

(b) the comparison of the mean time taken for the pressure to rise from 690 kPa to 2070 kPa gauge with those of the reference substances.

11.2.3.2.2 The test criteria for determining the oxidizing properties of the substance are:

Packing Group I: any substance which, in the 1:1 mixture, by mass, of substance and cellulose tested, spontaneously ignites; or

the mean pressure rise time of a 1:1 mixture, by mass, of substance and cellulose is less than that of a 1:1 mixture, by mass, of 50% perchloric acid and cellulose.

Packing Group II: any substance which, in the 1:1 mixture, by mass, of substance and cellulose tested, exhibits a mean pressure rise time less than or equal to the mean pressure rise time of a 1:1 mixture, by mass, of 40% aqueous sodium chlorate solution and cellulose; and

the criteria for Packing Group I are not met.

Packing Group III: any substance which, in the 1:1 mixture, by mass, of substance and cellulose tested, exhibits a mean pressure rise time less than or equal to the mean pressure rise time of a 1:1 mixture, by mass, of 65% aqueous nitric acid and cellulose; and the criteria for Packing Groups I and II are not met.

Not Division 5.1: any substance which, in the 1:1 mixture, by mass, of substance and cellulose tested, exhibits a pressure rise of less than 2070 kPa gauge; or

exhibits a mean pressure rise time greater than the mean pressure rise time of a 1:1 mixture, by mass, of 65% aqueous nitric acid and cellulose.

For substances having other risks, e.g. toxicity or corrosivity, the requirements of paragraph 1.44 of should be met.

Figure 11.1 Renumber figure 11.1 to figure 11.2 and replace it with figure given in the annex to United Kingdom document -/C.3/R.437.

Table 11.3: LIST OF CURRENTLY ASSIGNED ORGANIC PEROXIDES (to be added to)

ORGANIC PEROXIDE	Concen-tration (%)	Diluent type A (%)	Diluent type B (%) 1)	Inert solid (%)	Water (%)	Packing Method	Control Tempera-ture (°C)	Emergency Tempera-ture (°C)	Number (Generic entry)	Subsidiary risks and remarks
CUMYL PEROXYNEODECANOATE	≤ 52 as a stable dispersion in water					OP8A	- 10	0	3119	
DIBENZOYL PEROXIDE	≤ 42 as a stable dispersion in water					OP8A, N			3109	
DI-n-BUTYL PEROXYDICARBONATE	≤ 42 as a stable dispersion in water(frozen)					OP8B	- 15	- 5	3118	
1,1-DI-(tert-BUTYLPEROXY) CYCLOHEXANE	≤ 42	≥ 58				OP8A, N			3109	
2,4,4-TRIMETHYLPENTYL-2-PEROXY-NEODECANOATE	≤ 52 as a stable dispersion in water					OP8A	- 5	+ 5	3119	
ISOPROPYL sec-BUTYL PEROXYDICARBONATE + DI-sec-BUTYL PEROXYDICARBONATE + DI-ISOPROPYL PEROXYDICARBONATE	≤52 + ≤28 + ≤22					OP5A	- 20	- 10	3111	
tert AMYL PEROXY-ACETATE	≤ 62	≥ 38				OP8A			3107	
tert-AMYL PEROXY-2-ETHYL-HEXYL CARBONATE	≤ 100					OP7A			3105	
n-BUTYL-4,4-DI-(TERT-BUTYL PEROXY) VALERATE	≤ 42			≥ 58		OP8B			3108	
tert-BUTYL PEROXYACETATE	≤ 22		≥ 78			OP8A			3109	25)
tert-BUTYL PEROXY-NEOHEPTANOATE	≤ 77	≥ 23				OP7A	+ 5	+ 10	3115	
CUMYL PEROXY-NEOHEPTANOATE	≤ 77	≥ 23				OP7A	- 10	+ 0	3115	
1,1-DI-(TERT-AMYLPEROXY) CYCLOHEXANE	≤ 82	≥ 18				OP6A			3103	
DIBENZOYL PEROXIDE (as a paste)	≤ 56.5				≥ 15	OP8B			3108	

ORGANIC PEROXIDE	Concen-tration (%)	Diluent type A (%)	Diluent type B (%) 1)	Inert solid (%)	Water (%)	Packing Method	Control Tempera-ture (°C)	Emergency Tempera-ture (°C)	Number (Generic entry)	Subsidiary risks and remarks
1,1-DI-(tert-BUTYLPEROXY) CYCLOHEXANE	≤ 13	≥ 13	≥ 74			OP8A			3109	
1,1-DI-(tert-BUTYL-PEROXY)- 3,3,5-TRIMETHYL -CYCLOHEXANE	≤ 32	≥ 26	≥ 42			OP8A			3107	
DICUMYL PEROXIDE	≤ 52	≥ 48							EXEMPT	
1,1-DIMETHYL-3-HYDROXY-BUTYL PEROXYNEOHEPTANOATE	≤ 52	≥ 48				OP8A	0	+ 10	3117	
Consequential change:										
1,1-DI-(tert-BUTYLPEROXY) CYCLOHEXANE	≤ 52	≥ 48				OP7A			3105	
to be changed to										
1,1-DI-(tert-BUTYLPEROXY) CYCLOHEXANE	> 42 - 52	≥ 48				OP7A			3105	

Table 11.3: LIST OF CURRENTLY ASSIGNED ORGANIC PEROXIDES (to be change to)

ORGANIC PEROXIDE	Concen-tration (%)	Diluent type A (%)	Diluent type B (%) 1)	Inert solid (%)	Water (%)	Packing Method	Control Tempera-ture (°C)	Emergency Tempera-ture (°C)	Number (Generic entry)	Subsidiary risks and remarks
PEROXYACETIC ACID, TYPE F, stabilized	≤ 43					OP8A			3109	13) 16) 19)
to be changed to:										
PEROXYACETIC ACID, TYPE F, stabilized	≤ 43					OP8A, N			3109	13) 16) 19)

ORGANIC PEROXIDE	Concen-tration (%)	Diluent type A (%)	Diluent type B (%) 1)	Inert solid (%)	Water (%)	Packing Method	Control Tempera-ture (°C)	Emergency Tempera-ture (°C)	Number (Generic entry)	Subsidiary risks and remarks
3-CHLOROPEROXYBENZOIC ACID	≤ 72			≥ 10	≥ 18	OP7B			3106	
to be changed to:										
3-CHLOROPEROXYBENZOIC ACID	≤ 77			≥ 6	≥ 17	OP7B			3106	
DI-tert-BUTYL PEROXIDE	≤ 32	≥ 68				OP8A, N, M		3109		
to be changed to:										
DI-tert-BUTYL PEROXIDE	≤ 52		≥ 48			OP8A, N, M		3109	25)	
DI-(2-ETHYLHEXYL) PEROXYDICARBONATE	≤ 42 as a stable dispersion in water						OP8A	- 15	- 5	3117
to be changed to:										
DI-(2-ETHYLHEXYL) PEROXYDICARBONATE	≤ 52 as a stable dispersion in water						OP8A	- 15	- 5	3119
2,5-DIMETHYL-2,5-DI-(tert-BUTYLPEROXY)HEXYNE-3	> 52 - 100					OP5A			3103	
to be changed to:										
2,5-DIMETHYL-2,5-DI-(tert-BUTYLPEROXY)HEXYNE-3	> 52 - 86	≥ 14				OP5A			3103	26)
p-MENTHYL HYDROPEROXIDE	56 - 100					OP7A			3105	13)
	< 56	> 44				OP8A,M			3109	
to be changed to:										
p-MENTHYL HYDROPEROXIDE	>72 - 100					OP7A			3105	13)
	≤ 72	≥ 28				OP8A,M			3109	27)

Notes on Table 11.3: (to be changed to)

25) diluent type B with boiling point > 110 °C

26) with < 0.5% hydroperoxides content.

27) for concentrations more than 56% "CORROSIVE" subsidiary risk label required (Model No 08, see 13.5)

Table 11.4: CURRENTLY ASSIGNED ORGANIC PEROXIDES SUITABLE FOR TRANSPORT IN IBCS (to be added to)

UN No.	Organic peroxide	Type of IBC 1/	Maximum quantity (litres)	Control Temperature	Emergency Temperature
3109	ORGANIC PEROXIDES, TYPE F, LIQUID				
	Peroxyacetic acid, stabilized, not more than 17%	31H1	1000		
	Dibenzoyl peroxide, not more than 42% as a stable dispersion	31H1	1000		
	1,1-Di-(tert-butylperoxy) cyclohexane, not more than 42% in diluent type A	31H1	1000		
	tert-Butyl peroxyacetate, not more than 32% in diluent type A	31A	1250		
	tert-Butyl peroxy-3,5,5-trimethylhexanoate, not more than 32% in diluent type A	31A	1250		
	Di-tert-butyl peroxide, not more than 32% in diluent type A	31A	1250		
	Cumyl hydroperoxide, not more than 90% in diluent type A	31HA1	1250		
	Isopropyl cumyl hydroperoxide, not more than 72% in diluent type A	31HA1	1250		
	p-Menthyl hydroperoxide, not more than 72% in diluent type A	31HA1	1250		
3119	ORGANIC PEROXIDES, TYPE F, LIQUID, TEMPERATURE CONTROLLED				
	tert-Butyl peroxy-2-ethylhexanoate, not more than 32% in diluent type B	31A	1250	+ 30 °C	+ 35 °C
	tert-Butyl peroxypivalate, not more than 27% in diluent type B	31A	1250	+ 10 °C	+ 15 °C
	Di-(3,5,5-trimethylhexanoyl) peroxide, not more than 38% in diluent type A	31A	1250	+ 10 °C	+ 15 °C

1/ See 16.5, bottom openings allowed.

Table 11.5: CURRENTLY ASSIGNED ORGANIC PEROXIDES SUITABLE FOR TRANSPORT IN TANK-CONTAINERS (to be changed to)

UN NO.	ORGANIC PEROXIDE	Control Temperature	Emergency Temperature
3109	ORGANIC PEROXIDES, TYPE F, LIQUID p-Menthyl hydroperoxide, less than 56% in diluent type A **to be changed to** p-Menthyl hydroperoxide, not more than 72% in diluent type A		

11.3.13.1 After the existing text insert: "An example of a method to determine the size of emergency relief-devices for tank-containers allowed for organic peroxides, as required in 12.550, is given in appendix 5 of the Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria.

Appendix B

AMENDMENTS TO CHAPTER 14 OF THE RECOMMENDATIONS

14.1.2 Append "and also in the Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, section 33."

14.2.1.2.1 Insert after 14.5.2: "and in the Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, section 33"

14.3.2.1 Append "and also in the Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, section 33."

14.3.2.2 Append "and also in the Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, section 33."

14.3.3.2 and 14.3.3.3 Delete and replace with:

"14.3.3.2 Packing Group II should be assigned to self-heating substances which give a positive result in a test using a 25 mm sample cube at 140°C.

14.3.3.3 Packing Group III should be assigned to self-heating substances if:

(a) A positive result is obtained in a test using a 100 mm sample cube at 140°C and a negative result is obtained in a test using a 25 mm cube sample at 140°C and the substance is to be transported in packagings with a volume of more than 3 m^3.

(b) A positive result is obtained in a test using a 100 mm sample cube at 140°C and a negative result is obtained in a test using a 25 mm cube sample at 140°C, a positive result is obtained in a test using a 100 mm cube sample at 120°C and the substance is to be transported in packagings with a volume of more than 450 litres.

(c) A positive result is obtained in a test using a 100 mm sample cube at 140°C and a negative result is obtained in a test using a 25 mm cube sample at 140°C and a positive result is obtained in a test using a 100 mm cube sample at 100°C.

14.3.3.4 A substance should not be classified in Division 4.2 if:

(a) A negative is obtained in a test using a 100 mm cube sample at 140°C.

(b) A positive result is obtained in a test using a 100 mm sample cube at 140°C and a negative result is obtained in a test using a 25 mm cube sample at 140°C, a negative result is obtained in a test using a 100 mm cube sample at 120°C and the substance is to be transported in packagings with a volume not more than 3 m^3.

(c) A positive result is obtained in a test using a 100 mm sample cube at 140°C and a negative result is obtained in a test using a 25 mm cube sample at 140°C, a negative result is obtained in a test using a 100 mm

cube sample at 100°C and the substance is to be transported in packagings with a volume not more than 450 litres."

14.4.2.1 Append "and also in the Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, section 33."

14.5.1.2 Amend the text to read:

"The test methods and criteria for Class 4 are also given, with advice on application of the tests, in Section 33 of the Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria. Test methods and criteria for self-reactive substances are given in Part II of the Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria."

14.5.2 Replace the text of sub-section 14.5.2 with the following:

"14.5.2.1 Preliminary screening test

The substance in its commercial form, should be formed into an unbroken strip or powder train about 250 mm long by 20 mm wide by 10 mm high on a cool, impervious, low heat-conducting base plate. A hot flame (minimum temperature 1000°C) from a gas burner (minimum diameter 5 mm) should be applied to one end of the powder train until the powder ignites or for a maximum of 2 minutes (5 minutes for powders of metals or metal-alloys). It should be noted whether combustion propagates along 200 mm of the train within the 2 minute test period (or 20 minutes for metal powders). If the substance does not ignite and propagate combustion either by burning with flame or smouldering along 200 mm of the powder train within the 2 minute (or 20 minute) test period, then the substance should not be classified as a flammable solid and no further testing is required. If the substance propagates burning of a 200 mm length of the powder train in less than 2 minutes or less than 20 minutes for metal powders, the full test programme in 14.5.2.2 should be carried out.

14.5.2.2 Burning rate test

14.5.2.2.1 Procedure

14.5.2.2.1.1 A mould 250 mm long with a triangular cross-section of inner height 10 mm and width 20 mm is used to form the train for the burning rate test. On both sides of the mould, in the longitudinal direction, two metal sheets are mounted as lateral limitations which extend 2 mm beyond the upper edge of the triangular cross-section (figure 14.3). An impervious, non-combustible, low heat-conducting plate is used to support the sample train.

14.5.2.2.1.2 The powdered or granular substance, in its commercial form, should be loosely filled into the mould. The mould is then dropped three times from a height of 20 mm onto a solid surface. The lateral limitations are then removed and the impervious, non-combustible, low heat-conducting plate is placed on top of the mould, the apparatus inverted and the mould removed. Pasty substances are spread on a non-combustible surface in the form

of a rope 250 mm in length with a cross-section of about 100 mm^2. In the case of a moisture sensitive substance, the test should be carried out as quickly as possible after its removal from the container. The pile should be arranged across the draught in a fume cupboard. The air speed should be sufficient to prevent fumes escaping into the laboratory and should not be varied during the test. A draught screen may be erected around the apparatus.

14.5.2.2.1.3 For substances other than metal powders, 1 ml of a wetting solution should be added to the pile 30 - 40 mm beyond the 100 mm timing zone. Apply the wetting solution to the ridge drop by drop, ensuring the whole cross-section of the pile is wetted without loss of liquid from the sides. The liquid should be applied over the shortest possible length of the pile consistent with avoiding loss from the sides. With many substances, water rolls off the sides of the pile, so the addition of wetting agents may be necessary. Wetting agents used should be free from combustible diluents and the total active matter in the wetting solution should not exceed 1%. This liquid may be added to a hollow up to 3 mm deep and 5 mm in diameter in the top of the pile.

14.5.2.2.1.4 Any suitable ignition source such as a small flame or a hot wire of minimum temperature 1000°C is used to ignite the pile at one end. When the pile has burned a distance of 80 mm, measure the rate of burning over the next 100 mm. For substances other than metal powders, note whether or not the wetted zone stops propagation of the flame for at least 4 minutes. The test should be performed six times using a clean cool plate each time, unless a positive result is observed earlier.

14.5.2.2.2 Criteria for classification

14.5.2.2.2.1 Powdered, granular or pasty substances should be classified in Division 4.1 when the time of burning of one or more of the test runs, in accordance with the test method described in 14.5.2.2, is less than 45 s or the rate of burning is more than 2.2 mm/s. Powders of metals or metal alloys should be classified when they can be ignited and the reaction spreads over the whole length of the sample in 10 minutes or less.

14.5.2.2.2.2 For readily combustible solids (other than metal powders), Packing Group II should be assigned if the burning time is less than 45 s and the flame passes the wetted zone. Packing Group II should be assigned to powders of metal or metal alloys if the zone of reaction spreads over the whole length of the sample in five minutes or less.

14.5.2.2.2.3 For readily combustible solids (other than metal powders), Packing Group III should be assigned if the burning time is less than 45 s and the wetted zone stops the flame propagation for at least four minutes. Packing Group III should be assigned to metal powders if the reaction spreads over the whole length of the sample in more than five minutes but not more than ten minutes."

14.5.3 Replace the text of sub-section 14.5.3 with the following:

"14.5.3.1 Principle of the method and procedure

A test is performed to determine if a solid ignites within five minutes of coming in contact with air. Whether a substance is a pyrophoric solid of Division 4.2 is decided on the basis of the test result. Packing Group I is assigned to all pyrophoric solids.

One to two ml of the powdery substance to be tested should be poured from about 1 m height onto a non-combustible surface and it is observed whether the substance ignites during dropping or within 5 minutes of settling. This procedure should be performed six times unless a positive result is obtained earlier.

14.5.3.2 Criteria for classification

If the sample ignites in one of the tests, the substance should be considered pyrophoric and should be classified in Packing Group I of Division 4.2."

14.5.4 Replace the text of sub-section 14.5.4 with the following:

"14.5.4.1 Principle of the method

A test is performed to determine if a liquid ignites when added to an inert carrier and exposed to air for five minutes. If no ignition occurs then the second part of the test is performed to determine if it chars or ignites a filter paper. Whether a substance is a pyrophoric liquid of Division 4.2 is decided on the basis of the test result. Packing Group I is assigned to all pyrophoric liquids.

14.5.4.2 Procedure

14.5.4.2.1 A porcelain cup of about 100 mm diameter and some diatomaceous earth or silica gel is required for the first part of the test, and small pore size filter paper for the second part.

14.5.4.2.2 A porcelain cup of about 100 mm diameter should be filled with diatomaceous earth or silica gel at room temperature to a height of about 5 mm. Approximately 5 ml of the liquid to be tested should be poured into the prepared porcelain cup and it is observed if the substance ignites within 5 minutes. This procedure should be performed six times unless a positive result is obtained earlier. If a negative result is obtained then the procedure in 14.5.4.2.3 should be followed.

14.5.4.2.3 A 0.5 ml test sample should be delivered from a syringe to an indented dry filter paper. The test should be conducted at 25 ± 2°C and a relative humidity of 50 ± 5%. Observations are made to see if ignition or charring occurs on the filter paper within five minutes of addition of the liquid. This procedure should be performed three times using fresh filter paper each time unless a positive result is obtained earlier.

14.5.4.3 Criteria for classification

If the liquid ignites in the first part of the test, or if it ignites or chars the filter paper, it should be considered to be pyrophoric and should be classified in Packing Group I of Division 4.2."

14.5.5 Replace the text of sub-section 14.5.5 with the following:

14.5.5.1 Principle of the method

14.5.5.1.1 Tests are performed to determine if substances in a 25 mm or 100 mm sample cube, at test temperatures of 100°C, 120°C or 140°C, undergo spontaneous ignition or dangerous self-heating which is indicated by a 60°C rise in temperature over the oven temperature within 24 hours. The classification scheme is illustrated in figure 14.4. These criteria are based on the self-ignition temperature of charcoal, which is 50°C for a sample cube of 27 m^3. Substances with a temperature of spontaneous combustion higher than 50°C for a volume of 27 m^3 should not be assigned to Division 4.2. Substances with a spontaneous ignition temperature higher than 50°C for a volume of 450 litres should not be assigned to Packing Group II of Division 4.2.

14.5.5.1.2 If dangerous self-heating does not occur with the substance in a 100 mm sample cube at 140°C then the substance is not a self-heating substance of Division 4.2.

14.5.5.1.3 If dangerous self-heating occurs with the substance in a 100 mm sample cube at 140°C then a test with the substance in a 25 mm sample cube should be performed at 140°C to determine if it should be assigned to Packing Group II.

14.5.5.1.4 If dangerous self-heating occurs at 140°C with the substance in a 100 mm sample cube, but not a 25 mm sample cube, then a test with the substance in a 100 mm sample cube should be performed:

at 120°C if it is to be transported in packagings of not more than 3 m^3 volume; or

at 100°C if the substance is to be transported in packagings of not more than 450 litres volume.

Whether Packing Group III of Division 4.2 is assigned or the substance is not a self-heating substance of Division 4.2, in the packaging to be used, is decided on the basis of the test results.

14.5.5.2 Procedure

14.5.5.2.1 The following apparatus is required:

a hot-air circulating type of oven with an inner volume of more than 9 litres and capable of controlling the internal temperature at 100°C, 120° or 140°C ± 2°C;

cubic sample containers of 25 mm and 100 mm side, made of stainless steel net with a mesh opening of 0.05 mm, with their top surface open; and

Chromel-Alumel thermocouples of 0.3 mm diameter; one placed in the centre of the sample and another between the sample container and

the oven wall.

Each sample container should be housed in a cubic container cover made from a stainless steel net with a mesh opening of 0.60 mm, and slightly larger than the sample container. In order to avoid the effect of air circulation, this cover is installed in a second stainless steel cage, made from a net with a mesh size of 0.60 mm and 150 x 150 x 250 mm in size.

14.5.5.2.2 The sample, powder or granular, in its commercial form, should be filled to the brim of the sample container and the container tapped several times. If the sample settles, more is added. If the sample is heaped it should be levelled to the brim. The container is housed in the cover and hung at the centre of the oven. The oven temperature should be raised to 140°C and kept there for 24 hours. The temperature of the sample and of the oven should be recorded continuously. The first test */ should be conducted with a 100 mm cube sample. A positive result is obtained if spontaneous ignition occurs or if the temperature of the sample exceeds the oven temperature by 60°C. If a negative result is obtained, no further test is necessary. If a positive result is obtained, a second test should be conducted at 140°C with a 25 mm cube sample to determine whether or not Packing Group II should be assigned. If a positive result is obtained at 140°C with the substance in a 100 mm sample cube, but not a 25 mm sample cube, then an additional test with the substance in a 100 mm sample cube should be performed:

at 120°C if the substance is to be transported in packagings of not more than 3 m^3 volume; or

at 100°C if the substance is to be transported in packagings of not more than 450 litres volume.

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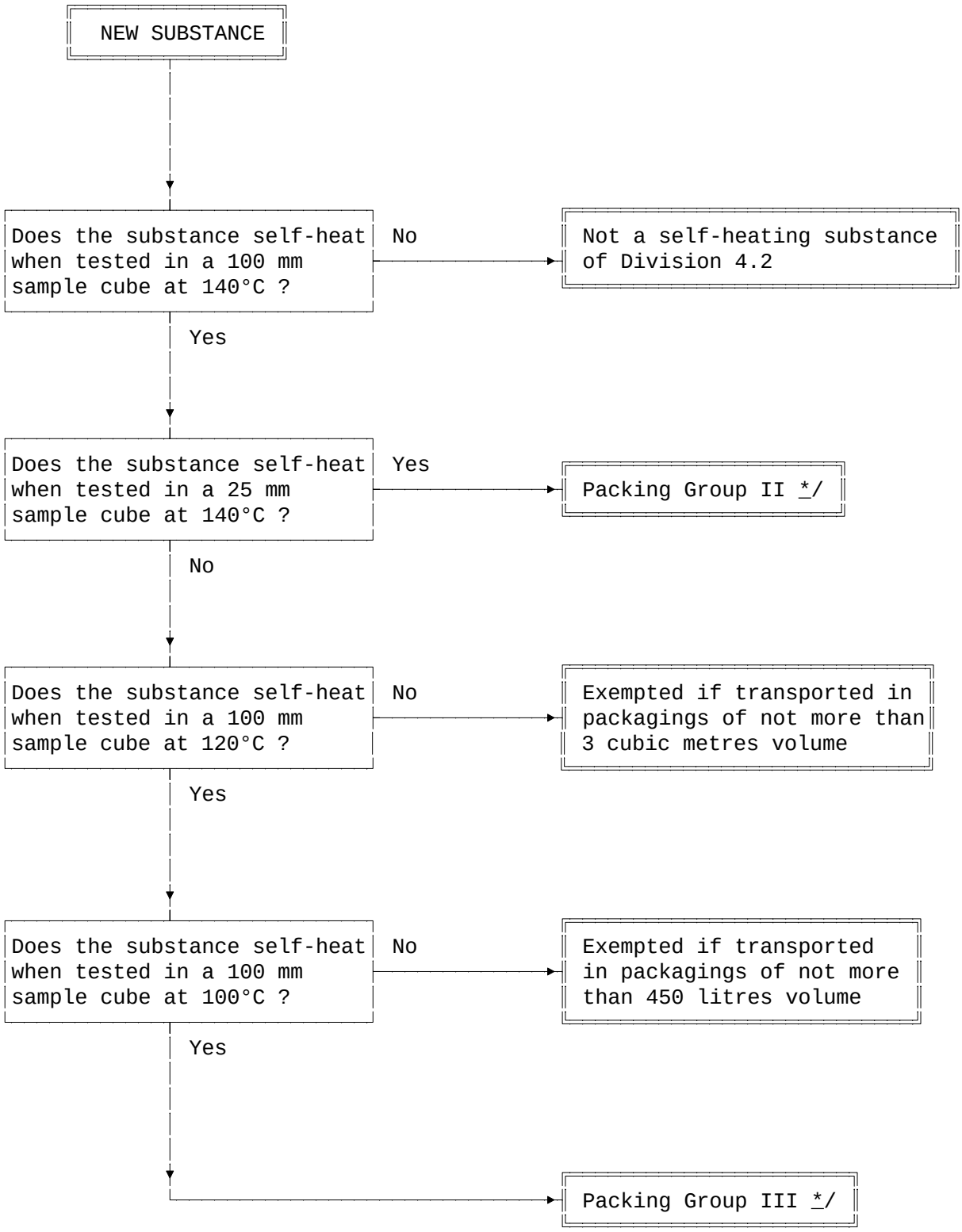
*/ The test may be performed in any order. For example, if it is expected that a positive result will be obtained using a 25 mm cube sample then, for safety and environmental protection, the first test may be performed with a 25 mm cube sample. If a positive result is obtained then a test with a 100 mm cube sample is not necessary.

Figure 14.4: CLASSIFICATION OF SELF-HEATING SUBSTANCES



*/ Substances with a temperature for spontaneous combustion higher than 50°C for 27 m^3 should not be classified in Division 4.2.

14.5.5.3 Criteria for classification

14.5.5.3.1 A positive result is obtained if spontaneous ignition occurs or if the temperature of the sample exceeds the oven temperature by 60°C during the 24 hour testing time. Otherwise, the result is considered negative.

14.5.5.3.2 A substance should be classified in Division 4.2 if:

(a) A positive result is obtained in a test using a 25 mm cube sample at 140°C.

(b) A positive result is obtained in a test using a 100 mm sample cube at 140°C and a negative result is obtained in a test using a 100 mm cube sample at 120°C and the substance is to be transported in packages with a volume of more than 3 m^3.

(c) A positive result is obtained in a test using a 100 mm sample cube at 140°C and a negative result is obtained in a test using a 100 mm cube sample at 100°C and the substance is to be transported in packages with a volume of more than 450 litres.

(d) A positive result is obtained in a test using a 100 mm sample cube at 140°C and a positive result is obtained in a test using a 100 mm cube sample at 100°C."

14.5.6 Replace the text of sub-section 14.5.6 with the following:

14.5.6.1 Principle of the method

The test method can be applied to solid and liquid substances. It is not applicable to pyrophoric substances. The substance should be tested in its commercial form at ambient temperate (20°C) by bringing it into contact with water. If during any stage of the test the gas emitted ignites then no further testing is necessary and the substance should be assigned to Division 4.3. If spontaneous ignition of the emitted gas does not occur then the final stage of the test should be performed to determine the rate of emission of flammable gas. Whether a substance is a water-reactive substance of Division 4.3 and, if so, whether Packing Group I, II or III should be assigned is decided on the basis of the test result.

14.5.6.2 Procedure

14.5.6.2.1 The substance should be tested according to the procedures described below; if spontaneous ignition occurs at any stage then no further testing is necessary. If it is known that the substance does not react violently with water then proceed to 14.5.6.2.5.

14.5.6.2.2 A small quantity (approximately 2 mm diameter) of the test substance should be placed in a trough of distilled water at 20°C. It is noted:

(i) whether any gas is evolved; and
(ii) if spontaneous ignition of the gas occurs.

14.5.6.2.3 A small quantity of the test substance (approximately 2 mm

diameter) should be placed on the centre of a filter paper which is floated flat on the surface of distilled water at 20°C in a suitable vessel, e.g. a 100 mm diameter evaporating dish. The filter paper is to keep the substance in one place, under which condition the likelihood of spontaneous ignition of any gas is greatest. It is noted:

(i) whether any gas is evolved; and
(ii) if spontaneous ignition of the gas occurs.

14.5.6.2.4 The test substance should be made into a pile approximately 20 mm high and 30 mm diameter with a hollow in the top. A few drops of water are added to the hollow. It is noted whether:

(i) any gas is evolved; and
(ii) if spontaneous ignition of the gas occurs.

14.5.6.2.5 For solid substances, the package should be inspected for any particles of < 500 µm diameter. If that powder constitutes more than 1% (mass) of the total, or if the substance is friable, then the whole of the sample should be ground to a powder before testing to allow for a reduction in particle size during handling and transport. Otherwise, as for liquids, the substance should be tested in its commercial state. This test should be performed three times at ambient temperature (20°C) and atmospheric pressure. Water is put into the dropping funnel and enough of the substance (up to a maximum mass of 25 g) to produce between 100 ml and 250 ml of gas is weighed and placed in a conical flask. The tap of the dropping funnel is opened to let the water into the conical flask and a stop watch is started. The volume of gas evolved is measured by any suitable means. The time taken for all the gas to be evolved is noted and where possible, intermediate readings are taken. The rate of evolution of gas is calculated over 7 hours at 1 hour intervals. If the rate of evolution is erratic or is increasing after 7 hours, the measuring time should be extended to a maximum time of 5 days. The five day test may be stopped if the rate of evolution becomes steady or continually decreases and sufficient data has been established to assign a packing group to the substance or to determine that the substance should not be classified in Division 4.3. If the chemical identity of the gas is unknown, the gas should be tested for flammability.

14.5.6.3 Criteria for classification

14.5.6.3.1 A substance should be classified in Division 4.3 if:

(a) spontaneous ignition takes place in any step of the test procedure; or

(b) there is an evolution of a flammable gas at a rate greater than 1 litre per kilogram of the substance per hour.

14.5.6.3.2 Packing Group I should be assigned to any substance which reacts vigorously with water at ambient temperatures and generally demonstrates a tendency for the gas produced to ignite spontaneously, or which reacts readily

with water at ambient temperatures such that the rate of evolution of flammable gas is equal to or greater than 10 litres per kilogram of substance over any one minute period.

14.5.6.3.3 Packing Group II should be assigned to any substance which reacts readily with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 20 litres per kilogram of substance per hour, and which does not meet the criteria for Packing Group I.

14.5.6.3.4 Packing Group III should be assigned to any substance which reacts slowly with water at ambient temperatures such that the maximum rate of evolution of flammable gas is greater than 1 litre per kilogram of substance per hour, and which does not meet the criteria for Packing Groups I or II."

Appendix C

AMENDMENTS TO THE GENERAL INTRODUCTION AND PART I OF THE RATIONALIZED MANUAL OF TESTS AND CRITERIA

GENERAL TABLE OF COMMENTS

Delete "(" in entry 14.

Add a new appendix 5 entry to read "Example of a vent sizing method"

10.3.3.4 Amend the second and third sentences to read: "If the article or packaged articles pass test type 4 (a), test type 4 (b) is performed. Packaged substances are subjected to test type 4 (b) only. If the product fails either test type 4 (a) or 4 (b), it should be rejected."

11.3.1 Insert "apparent" before "density" (three times) and delete the sentence "The density of liquids may be determined by other means."

11.4.1.5 Insert a full set of USA Series 1 UN Gap test results:

Substance	**Apparent density (kg/m^3)**	**Fragmentation length (cm)**	**Witness plate**	**Result**
Ammonium nitrate, prills	800	40	Domed	
+				
Ammonium nitrate, 200 µm	540	40	Holed	+
Ammonium nitrate/fuel oil, 94/6	880	40	Holed	
+				
Ammonium perchlorate, 200 µm	1190	40	Holed	+
Nitromethane	1130	40	Holed	+
Nitromethane/methanol, 55/45	970	20	Domed	–
PETN/lactose, 20/80	880	40	Holed	+

PETN/lactose, 10/90	830	17	No damage	–
TNT, cast	1510	40	Holed	+
TNT, flaked	710	40	Holed	+

11.6.1.2.6 Replace "card" by "insulation".

12.3.1 Insert "apparent" before "density" (three times) and delete the sentence "The density of liquids may be determined by other means."

12.4.1.5 Insert full set of USA Series 2 UN Gap test results:

Substance	**Apparent density (kg/m^3)**	**Fragmentation length (cm)**	**Witness plate**	**Result**
Ammonium nitrate, prills	800	25	Domed	–
Ammonium nitrate, 200 µm	540	40	Holed	+
Ammonium nitrate/fuel oil, 94/6	880	40	Holed	+
Ammonium perchlorate, 200 µm	1190	0	No damage	–
Nitromethane	1130	0	No damage	–
PETN/lactose, 20/80	880	40	Holed	+
TNT, cast	1510	20	No damage	–
TNT, flaked	710	40	Holed	+

12.6.1.2.6 Replace "card" by "insulation".

13.4.1.4.2 Replace " at least 5 out of" by "at least 1 out of".

13.4.2.5 Add a new Netherlands result to read:

Substance	**Limiting impact energy (J)**	**Result**
Lead styphnate	5	–

13.5.1.5 Add a new Netherlands result to read:

Substance	**Limiting load (N)**	**Result**
Lead styphnate	2	+

13.6.1.3.3 Amend the text in brackets to read: "(or 100 cm^3 if the density is less than 1000 kg/m^3)".

14.4.1.4 Amend (e) to read:
"(e) Dangerous exudation occurs i.e. explosive is visible outside the article(s)."

15.5.2.2 Amend "An igniter consisting of black powder .." to read: "An igniter consisting of 5.0 g of black powder ..".

Appendix D

AMENDMENTS TO PARTS II AND III, AND THE APPENDICES OF THE RATIONALIZED MANUAL OF TESTS AND CRITERIA

PART II

Figure 20.1 (b) Amend arrow into Exit G.

21.2.1 Amend the last sentence to read: "If a liquid is being considered for transport in tank-containers or IBCs with a capacity exceeding 450 litres, a cavitated version of Series A may be used (see appendix 3).

21.2.2 Replace the last two sentences by: "For transport in packages (excluding IBCs), if the screening procedure indicates that a Series A test is not needed, the question in Box 1 is answered with a "no". However, if the substance is being considered for transport in tank containers or IBCs, or for exemption, then a Series A test is required unless the result of a Series A test on a formulation of the substance with a higher concentration and the same physical state is "No"."

21.3.1 Insert "apparent" before "density" (three times) and delete the sentence "The density of liquids may be determined by other means."

21.3.4 Amend text to read "***The preliminary procedure should be carried out before performing these tests (see section 20.3)***"

21.3.5 Insert a new paragraph 21.3.5 to read:

"21.3.5 When a fresh batch of steel tubes is used, calibration tests using water (for tests on liquids) and an inert, organic solid (for tests on solids) should be performed to determine the average blank fragmentation length. The "No" / "Partial" criteria should be set to 1.5 times the average blank fragmentation length."

21.4.1.2 Delete the last two sentences.

21.4.1.4.2 Replace the first sentence after "partial": by "the tube is not fragmented completely but the average tube fragmentation length (average over the two tests) is greater than 1.5 times the average fragmentation length found with an inert material with the same physical state; and ...."

Replace the first sentence after "No": by : "the fragmentation length is equal to or smaller than 1.5 times the average fragmentation length found with an inert material with the same physical state; and"

21.4.1.5 Change the apparent density for entry N,N'-dinitrosopentamethylene tetramine, 80% with 17% inorganic solid and 3 % mineral oil to "500".

21.4.2.4.2 Replace the sentence after "partial": by "the tube is not fragmented completely but the average tube fragmentation length (average over the two tests) is greater than 1.5 times the average fragmentation length found with an inert material with the same physical state"

Replace the sentence after "No": by : "the fragmentation length is equal to or smaller than 1.5 times the average fragmentation length found with an inert material with the same physical state"

21.4.3.4.2 Replace the sentence after "partial": by "the tube is not fragmented completely but the average tube fragmentation length (average over the two tests) is greater than 1.5 times the average fragmentation length found with an inert material with the same physical state"

Replace the sentence after "No": by : "the fragmentation length is equal to or smaller than 1.5 times the average fragmentation length found with an inert material with the same physical state"

21.4.3.5 Add to the table "*Examples of results*":

Substance	**Apparent density (kg/m³)**	**Fragmented length (cm)**	**Result**
2,5-Dimethyl-2.5-di-(tert-butylperoxy)-hexyne-3		34	Partial
tert-Butylperoxy-2-ethylhexanoate		25	Partial
tert-Butylperoxybenzoate		25	Partial
Dibenzoylperoxide, 75% with water	685	40	Yes
Dilauroylperoxide	564	28	No
2,2'-Azodi(isobutyronitrile)	366	40	Yes

21.4.4.2 Change the sentence "The tube is instrumented ...." to "The tube may be instrumented ..." and delete after .... "as shown in figure 21.4.4.1" the rest of the sentence.

21.4.4.4.1 Amend item (b) to read "if measured, the rate of propagation in the substance" and delete item (c)

21.4.4.4.2 Amend to read after "yes":- "the tube is fragmented completely".
Amend to read after "partial": "the tube is not fragmented completely but the average tube fragmentation length (average over the two tests) is greater than 1.5 times the average fragmentation length found with an inert material with the same physical state"

Amend to read after "No": "the fragmentation length is equal to or smaller than 1.5 times the average fragmentation length found with an inert material with the same physical state"

21.4.4.5 Add to the table "*Examples of results*":

Substance	**Apparent density (kg/m³)**	**Fragmented length (cm)**	**Result**
2,5-Dimethyl-2.5-di-(tert-butylperoxy)-hexyne-3		30	Partial
tert-Butylperoxy-2-ethylhexanoate		23	No
tert-Butylperoxybenzoate		28	Partial
Dibenzoylperoxide, 75% with water	697	22	No
Dilauroylperoxide	580	32	Partial
2,2'-Azodi(isobutyronitrile)	346	50	Yes

22.3 Add existing text to new sub paragraph 22.3.1
Add new sub paragraph 22.3.2 with text "***The preliminary procedure should be carried out before performing this test (see section 20.3)***"

23.3.1 Amend to read "***The preliminary procedure should be carried out before performing these tests (see section 20.3)*** "

23.4.1.2 Remove underline and change heading to italics.

23.4.1.2.6 Change "card" to "insulation".

23.4.1.5 Add the following Netherlands and German results:

Substance	Maximum pressure (kPa)	Time for a pressure rise from 690 to 2070 kPa (ms)	Result
Azodicarbonamide	> 2070	63	Yes, slowly
Azodicarbonamide, 67% with zinc oxide	> 2070	21	Yes, rapidly
2,2'-Azodi(isobutyronitrile)	> 2070	68	Yes, slowly
2,2'-Azodi(2-methylbutyronitrile)	> 2070	384	Yes, slowly
2-Diazo-1-naphthol-5-sulphohydrazide	> 2070	14	Yes, rapidly
2,5-Diethoxy-4-morpholinobenzene-diazonium tetrafluoroborate, 97%	> 2070	308	Yes, slowly
4-Nitrosophenol	> 2070	498	Yes, slowly

23.4.2.3.2 Add to the last sentence "and there are no lumps."

23.4.2.3.3 Amend the fifth sentence to read: "..., or alternatively, if no ignition occurs within five minutes the gas burner is removed and extinguished."

23.4.2.5 Add the following Netherlands and German results:

Substance	Sample mass (g)	Temperature (°C)	Propagation rate (mm/s)	Result
Azodicarbonamide	174	50	0.35	Yes, slowly
2,2'-Azodi(isobutyronitrile)	101	45	b/	No
4-Nitrosophenol	130	35	0.90	Yes, slowly

b/ Pulsating flame, extinguishing of flame; no stable propagation under test conditions.

24.3 Add existing text to new sub paragraph 24.3.1
Add new sub paragraph 24.3.2 with text "***The preliminary procedure should be carried out before performing this test (section 20.3).***"

Table 25.1 Append to both footnotes: "in combination with one of the other tests"

25.3.1 Amend to read "***The preliminary procedure should be carried out before performing these tests (see section 20.3).***"

25.4.1.5 Add the following results:

Substance	Sample mass (g)	Limiting diameter (mm)	Type of fragmentation a/	Result
Azodicarbonamide	20	1.5	"F"	Medium
Azodicarbonamide, 67% with zinc oxide	24	1.5	"F"	Medium
2.2'-Azodi(2,4-dimethylvaleronitrile)	17.5	< 1.0	"O"	No
2,2'-Azodi(isobutyronitrile)	15	3.0	"F"	Violent
Benzene-1,3-disulphohydrazide		12.0	"F"	Violent
Benzene-1,3-disulphohydrazide, 70% with mineral oil		2.0	"F"	Violent
Benzene sulphohydrazide	18.5	1.0	"F"	Low

2-Diazo-1-naphtol-5-sulphochloride	19.0	2.5	"F"	Violent
N,N'-Dinitroso-N,N'-dimethyl-terephthalamide 70%, with mineral oil	18.0	4.0	"F"	Violent
4-Nitrosophenol	17.0	< 1.0	"A"	Low

Delete the following results:

Dimyristyl peroxydicarbonate, 42% stable, dispersion, in water
Diperoxy dodecane diacid, with 87% sodium sulphate and magnesium sulphate

In footnote b/, amend " < 1.0 m" to read "< 1.0 mm".

25.4.2.5 Add the following Netherlands and German results:

Substance	**Limiting diameter (mm)**	**Result**
Azodicarbonamide	1.5	Low
2,2'-Azodi-(2,4-dimethylvaleronitrile)	6.0	Medium
2,2'-Azodi(isobutyronitrile)	5.5	Medium
2,2'-Azodi(2-methylbutyronitrile)	6.0	Medium
2,5-Diethoxy-4-morpholinobenzene-diazonium tetrafluoroborate, 97%	< 1.0	No
4-Nitrosophenol	1.0*/	Low

*/ test carried out with a 50 g sample

25.4.3.4.1 Change in first sentence "largest" to "smallest"

Figure 26.4.2.2 Amend figure to show 20 mm dimension as in Fig. 7.3.2 of current manual (ST/SG/AC.10/11/Rev.1).

Figure 26.4.2.3 Amend (twice) figures to show 20 mm dimensions as in Fig. 7.3.3 of current manual (ST/SG/AC.10/11/Rev.1).

26.4.3.5 Add new German results:

Substance	**Sample mass (g)**	**Expansion (cm^3/10 g)**	**Result**
Azodicarbonamide		9	No
2,2'-Azodi(isobutyronitrile)		26 a/	Not low
Benzene-1,3-disulphohydrazide		50 a/	Not low
Benzene-1,3-disulphohydrazide, 70% with mineral oil		11 a/	Low
Benzene sulphohydrazide		8.4 8	No
N,N`-Dinitrosopentamethylene tetramine		147 a/	Not low
N,N`-Dinitrosopentamethylene tetramine 80%, with 17% inorganic solid and 3% mineral oil	10.2	7 b/	No
4-Nitrosophenol	7.3	11	Low

b/ Initiation with 3 detonators gives 123 cm^3/10 g, Not low

26.4.4.5 Add new Netherlands results

Substance	**Average net expansion (cm^3)**	**Result**
2,2'-Azodi(isobutyronitrile)	18	Not low
2,2'-Azodi(2-methylbutyronitrile)	14	Not

low

26.4.5.5 Add new Netherlands result:

Substance	**F-value (J/g)**	**Result**
2,2'-Azodi(isobutyronitrile)	101	Not low

28.3.2 Append to the last sentence: "i.e. representative of both the metal(s) and the area of contact."

28.3.4 Append to the first sentence: "provided extra care is taken."

28.3.5 Change "Ln" to "ln".

28.3.6 Change "Ln" to "ln" (twice)

28.4.1.3.1 Add, as a new first sentence: "The package should be weighed."

28.4.1.3.2 Amend the text to read:
"28.4.1.3.2 The sample is heated and the temperature of the sample and test chamber continuously monitored. The time is noted at which the sample temperature reaches a temperature 2°C below the test chamber temperature. The test is then continued for a further seven days or until the sample temperature rises to 6°C or more above the test chamber temperature if this occurs sooner. Note the time taken for the sample to rise from the 2°C below the test chamber temperature to its maximum temperature."

28.4.1.3.4 In the second sentence, delete "In this test".

28.4.1.4.1 Delete "undergoes self-accelerating decomposition and"

28.4.1.5 Change "litre" to "litres" for the last entry.

Figure 28.4.1.1 Change "litre" to "litres" in (B)

28.4.2.2.1 Change "A stainless steel" to "An inert".

28.4.2.3.1 Amend (b) to read:
"(b) Heat the sample in 20°C steps using the internal heating system at a known power rating, e.g. 0.333 or 1.000 W, and determine the heat losses at 40°C, 60°C, 80°C and 100°C."
Delete (c) and reletter "(d)" to "(c)".

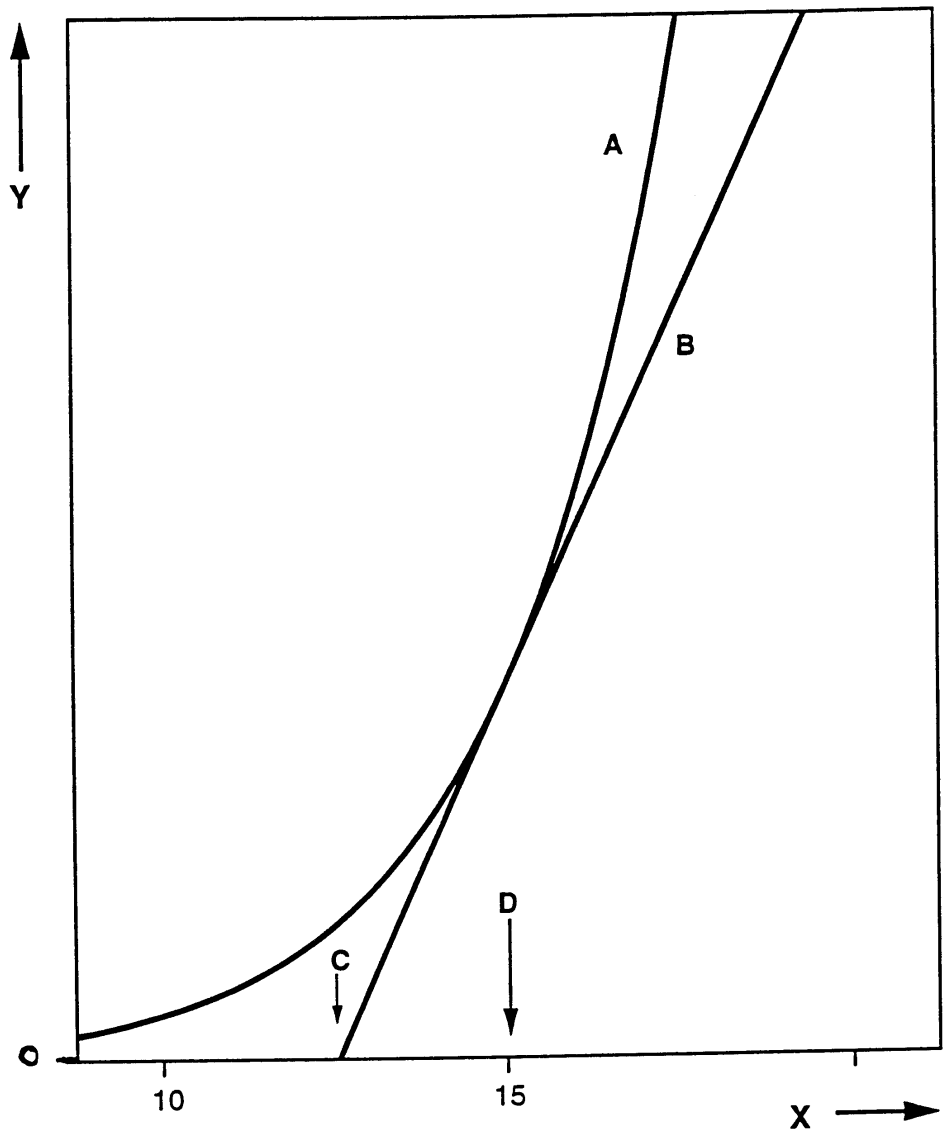
28.4.2.4.6 In the second last sentence, change "nearest" to "next higher".

28.4.2.5 Amend the headings and add Netherlands results to read:

Substance	**Mass (kg)**	**Packaging**	**Heat losses per unit mass (mW/kg.K)**	**SADT (°C)**
Azodicarbonamide	30	1G	100	> 75
tert-Butyl peroxybenzoate	25	6HG2	70	55
tert-Butyl peroxy-2-ethylhexanoate	25	6HG2	70	40
tert-Butyl peroxypivalate	25	6HG2	70	25

Figure 28.4.2.2 and **Figure 28.4.3.2** replace with following new figure.

28.4.3.1.2 Change "heat sink" to "aluminium block".



(A) Heat generation curve

(B) Line with gradient equal to the rate of heat loss and tangential to the heat generation curve

(C) Critical ambient temperature (intercept of heat loss line with the abscissa)

(D) Self-accelerating decomposition temperature (SADT) - critical ambient temperature rounded up to next higher multiple of 5°C

(X) Temperature

(Y) Heat flow (generation or loss) per unit mass

Figure 28.4.2.2 & 28.4.3.2: EXAMPLE OF DETERMINATION OF SADT

28.4.3.5 Amend the headings and add Netherlands results to read:

Substance	**Mass (kg)**	**Packaging**	**Heat losses per unit mass (mW/kg.K)**	**SADT (°C)**
Azodicarbonamide	30	1G	100	> 75
tert-Butyl peroxybenzoate		25	6HG2	70 55
tert-Butyl peroxy-2-ethylhexanoate		25	6HG2	70 40
tert-Butyl peroxypivalate		25	6HG2	70 25

Multiply the current numbers in the heat losses column by 1000 to convert them to mW/kg.K and add "(95%)" to the last substance entry.

28.4.4.3.1 Amend the start of the second sentence to read: "Fill the Dewar vessel 80% of its volume with ...".

28.4.4.3.2 Amend the text to read:
"28.4.4.3.2 The sample is heated and the temperature of the sample and test chamber continuously monitored. The time is noted at which the sample temperature reaches a temperature 2°C below the test chamber temperature. The test is then continued for a further seven days or until the sample temperature rises to 6°C or more above the test chamber temperature if this occurs sooner. Note the time taken for the sample to rise from the 2°C below the test chamber temperature to its maximum temperature."

28.4.4.4.1 Delete "undergoes self-accelerating decomposition and"

28.4.4.5 Delete the heading "Packaging". For the third last entry, append "(66%)" to the substance name. Amend the second last entry to read "Diisotridecyl ...". In footnote a/, amend to read "litres".

PART III

33.2.1.1.1 Change the references "33.1.1" to "33.2.1.3", "14.1 of the Recommendations" to "33.2.1.1.1" and "33.1.1.4" to "33.2.1.4".

Figure 33.2.1.1.1 Copy figure 14.1 from the Recommendations.

33.3.1.1.1 Change the references "33.2.1.4 to 33.2.1.6" to "33.3.1.4 to 33.3.1.6".

33.3.1.3.1 Change the reference "33.2.1.4" to "33.3.1.4".

33.3.1.3.2 Change the reference "33.2.1.5" to "33.3.1.5".

33.3.1.3.3.1 In the first sentence, insert after "or": "dangerous self-heating, which is indicated by".
Insert the following sentence before the last sentence: "Substances with a spontaneous ignition temperature higher than 50°C for a volume of 450 litres should not be assigned to Packing Group II of Division 4.2."

33.3.1.3.3.2 Insert "dangerous" before "self-heating".

33.3.1.3.3.3 Insert "dangerous" before "self-heating".

33.3.1.3.3.4 Insert "dangerous" before "self-heating".
Delete "more than 450 litre volume but" from the first indent.

Figure 33.3.1.3.3.1 Amend "Should be considered for exemption" to read "Exempted" (twice)

33.3.1.6.3 */ Amend the beginning of the footnote to read: "The tests may be performed in any order. For example, if it is expected ..."

33.3.1.6.4.4 Insert a new (a) to read:
"(a) A positive result is obtained in a test using a 100 mm sample cube at 140°C and a negative result is obtained in a test using a 25 mm cube sample at 140°C and the substance is to be transported in packages with a volume of more than 3 m^3."
Reletter (a) and (b) to (b) and (c) respectively.

33.3.1.6.5 For entry "Nickel catalyst granules with 50% white oil", re-align and insert cube sizes of "100" and "25".

34.3.1 The second sentence should be interchanged with the second sentence of **34.3.2**.
Delete "and any toxic or corrosive subsidiary risks" and insert: "also" between "see" and "**Precendence**"

34.3.2 The second sentence should be interchanged with the second sentence of **34.3.1** and the reference should be to section "11.2.2" of the Recommendations.
Delete "and any toxic or corrosive subsidiary risks" and insert: "also" between "see" and "**Precendence**"

34.4.1.2.1 Replace "seived" by "sieved" and change "ground" to "not ground" .

34.4.1.2.2 */ Insert at the beginning of the footnote "Source reference ..".

34.4.1.2.5 Amend the second sentence to read: "***The fume extraction system...***"

34.4.1.4.2 In the last sentence, change "additional" to "other".

34.4.1.5 Delete the heading "Particle size", amend "Mixtures of reference substance to fuel" to read "Burning time (s) for mixtures of reference substance to cellulose". Change "d/" to "a/" and delete footnote "d/". In footnote c/, change to "currently"

Figure 34.4.1.1 Delete "mm" (twice)

34.4.2.1 Amend "form a deflagrating mixture with a fuel" to read "increase the burning rate or burning intensity of a combustible substance".

34.4.2.2.5 */ Insert at the beginning of the footnote "Source reference ..".

34.4.2.2.7 Insert a new paragraph to read:
"34.4.2.2.7 The concentration of the substance tested should be specified in the report. If saturated solutions are tested, they should be prepared at 20°C."

34.4.2.5 Insert new Swedish results to read:

"34.4.2.5 *Examples of results*

Substance	Mean pressure rise time for a 1:1 mixture with cellulose (ms)	Result
Ammonium dichromate, saturated aqueous solution Not Div. 5.1	20800	
Calcium nitrate, saturated aqueous solution Not Div. 5.1	6700	
Ferric nitrate, saturated aqueous solution P.G. III	4133	
Lithium perchlorate, saturated aqueous solution P.G. II	1686	
Magnesium perchlorate, saturated aqueous solution P.G. II	777	
Nickel nitrate, saturated aqueous solution Not Div. 5.1	6250	
Nitric acid, 65% P.G. III b/	4767 a/	
Perchloric acid, 50% P.G. II	121 a/	
Perchloric acid, 55%	59	P.G. I
Potassium nitrate, 30% aqueous solution Not Div. 5.1	26690	
Silver nitrate, saturated aqueous solution Not Div. 5.1	c/	

Sodium chlorate, 40% aqueous solution P.G. II	2555 a/
Sodium nitrate, 45% aqueous solution P.G. III	4133
Inert substance	
Water:cellulose	c/

a/ Mean value from inter-laboratory comparative trials
b/ Packing Group III by the test but Class 8 by the Precedence of Hazards table
c/ Maximum pressure of 2070 kPa not reached"

Figure 33.4.2.3 Amend the legend to read:

(A) Ignition coil
(B) Insulation
(C) Electrodes
(D) Firing plug

38.3.2.2 Change the reference from "38.2.3" to "38.3.4".

38.3.3.1 Change the reference from "38.2.4" to "38.3.4".

38.3.4.3.1 Change the references from "38.3.4.3.2.2 and 38.3.4.3.2.3" to "38.3.4.3.2.2.2 and 38.3.4.3.2.2.3"

38.3.4.7.1 Insert at the beginning of (a), "in the case of tests T.1 to T.6". In the first line of (b) and (c), delete "unless" and append "; or"

38.3.4.7.2 Insert at the beginning of (a), "in the case of tests T.1 to T.6"

CONTENTS OF APPENDICES

Insert a new heading to read:
"5 EXAMPLE OF A TEST METHOD FOR VENT SIZING"

Figure A1.2 Insert a revised specification for USA detonator to be supplied by the USA.

Appendix 3 In 1, change "23" to "28".

Appendix 4 For Germany, change "Fachgruppe 4.3" to "Abteilung 4"
For Sweden, insert a new entry to be supplied.
For Switzerland, insert the code "CH".

Insert a new entry for Spain to read:

SPAIN E Laboratorio Oficial Madariaga (LOM)
Alenza 1y2
Madrid 28002
Spain

Insert a new appendix 5, (to be edited).