

**Committee of Experts on the Transport of Dangerous Goods
and on the Globally Harmonized System of Classification
and Labelling of Chemicals**

3 June 2013

**Sub-Committee of Experts on the
Transport of Dangerous Goods**

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Geneva, 24 – 28 June 2013

Item 2 (e) of the provisional agenda

**Explosives and related matters: desensitized
explosives**

**Sub-Committee of Experts on the Globally Harmonized
System of Classification and Labelling of Chemicals**

Twenty-fifth session

Geneva, 1 – 3 July 2013

Item 2 (a) of the provisional agenda

**Classification criteria and hazard communication :
Work of the Sub-Committee of Experts on the
Transport of Dangerous Goods on physical hazards**

**Implementation of a new Chapter 2.17 “Desensitized
Explosives” in the GHS and implementation of
“Classification procedures, test methods and criteria relating
to the class of desensitized explosives” in a new Part V of the
UN Manual of Tests and Criteria**

Transmitted by the expert from Germany

Introduction

1. At its 41st session (June 2012), the Sub-Committee of experts on the transport of dangerous goods (TDG Sub-Committee) endorsed the conclusions of the Working Group on Desensitized Explosives concerning desensitized explosives (see ST/SG/AC.10/C.3/82, paras. 3 and 45) as follows:

- (a) The conclusions of the Working Group on Explosives as reflected in informal document INF.67 (TDG Sub-Committee, 41st session), para. 6 were confirmed;
- (b) A new chapter on desensitized explosives in the GHS is needed;
- (c) The German methodology is a good starting point to develop a comprehensive approach;
- (d) The properties of the mixtures, when the diluent has fallen below the specified level need not be included in the classification method since they would then be considered as explosives;
- (e) Since a number of experts are considering preparing a formal proposal to deal with the details of implementation within the GHS system in the next biennium, this issue should be included in the programme of work for the next biennium.

2. The Sub-Committee of experts on the GHS (GHS Sub-Committee) concurred ST/SG/AC.10/C.4/46 with the TDG Sub-Committee – on its decision to endorse the conclusions of the Working Group on desensitized explosives as recommended by the Working Group on Explosives (see ST/SG/AC.10/C.4/46) as follows:

- (a) A new chapter on desensitized explosives is needed in the GHS;

- (b) The German classification system for storage groups constitutes a good basis for the development of a classification system for desensitized explosives in the GHS, as supported by ICCA;
 - (c) In case a new test is proposed as part of the classification system for desensitized explosives, it should be included in a separate appendix of the Manual of Tests and Criteria, on the understanding that it would not be applicable for transport classification;
 - (d) The properties of mixtures of desensitized explosives when the diluent has fallen below the specified level need not be included in the classification method since they would then be considered as explosives;
 - (e) A number of experts are considering preparing a formal proposal to deal with the details of implementation within the GHS for the next biennium and requested that an item on desensitized explosives be included in the programme of work for 2013–2014.
3. The TDG Sub-Committee included the item of desensitized explosives in its programme of work for 2013-2014 (ST/SG/AC.10/C.3/84) as follows:
- Explosives and related matters (including amendments to the list of dangerous goods; desensitized explosives; tests and criteria for flash compositions; review of test series 6; review of tests in parts I and II of the Manual of Tests and Criteria; review of packing instructions for explosives).
4. The GHS Sub-Committee also included the item of desensitized explosives in its programme of work for 2013-2014 (ST/SG/AC.10/C.4/48) as follows:
- (a) Explosives and related matters (including classification of desensitized explosives)
- Focal point: TDG Sub-Committee
- For classification of desensitized explosives:
- Lead country: Germany
 - Mandate/Terms of reference: ST/SG/AC.10/C.4/46 (paragraph 8) and paragraph 14 of the report (ST/SG/AC.10/C.4/48).

Current status

5. Experts from Germany, France, Sweden, Netherlands, SAAMI and ICCA met twice in Berlin and worked together on the above-mentioned development of a new chapter for inclusion in the GHS and of a new test method for inclusion in the UN Manual of Tests and Criteria. The outcome of this work are drafts for a new Chapter 2.17 (GHS) and a new test method to be included in a new Part V of the UN Manual of Tests and Criteria as attached in Annex 1 and 2, to this document. The draft papers were also discussed at the 2013 meetings of the EOS and of the EPP group of IGUS where a number of further experts have participated. Some proposed improvements have been taken up and are included in the attached documents.
6. The experts of both sub-committees are invited to discuss the attached documents. Suggestions for improvements are most welcome.
7. The attached proposal for a new Chapter in the GHS currently does not include a Table A1.17 for the new hazard class “Desensitized explosives” to be inserted in Annex I (new style for GHS Rev.5 according to ST/SG/AC.10/C.4/2012/22) and also no proposals

for the assignment of precautionary statements to desensitized explosives because some further discussions are needed. The experts of both sub-committees are invited to make suggestions and express their views concerning these matters.

8. It is planned to submit a complete working paper to the next session of both sub-committees.

Annex 1

“Chapter 2.17

Desensitized explosives

2.17.1 Definitions and general considerations

2.17.1.1 *Desensitized explosives* are solid or liquid explosive substances or mixtures which are desensitized to suppress their explosive properties in such a manner that they may be excluded from the hazard class “Explosives” (Chapter 2.1, see also Note 2 of Chapter 2.1.2.2).*

2.17.1.2 The class of desensitized explosives comprises:

- (a) Solid desensitized explosives are explosive substances or mixtures which are wetted with water or alcohols or are diluted with other substances, to form a homogeneous solid mixture to suppress their explosive properties.

NOTE: This includes desensitization achieved by formation of hydrates of the substances.

- (b) Liquid desensitized explosives are explosive substances or mixtures which are dissolved or suspended in water or other liquid substances, to form a homogeneous liquid mixture to suppress their explosive properties.

2.17.2 Classification criteria

2.17.2.1 Any desensitized explosive shall be considered in this class, unless

- (a) They are explosives according to the GHS criteria of chapter 2.1 and are manufactured with the view to producing a practical, explosive or pyrotechnic effect;
- (b) They have a mass explosion hazard according to Test Series 6 or their corrected burning rate according to the burning rate test X is higher than 1200 kg/min;
- (c) Their heat of decomposition is less than 300 J/g.

NOTE 1: Substances or mixtures which meet the criterion (c) may fall within the scope of other hazard classes, including their labeling elements.

NOTE 2: The heat of decomposition should be determined using the homogenous part of the desensitized explosives; (see 20.3.3.3 in Part

* An unstable explosive according to chapter 2.1 can be stabilized by desensitization. In this case the desensitized explosive should be tested according to test series 3 (Part I of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria) and the results should be communicated in the safety data sheet.

II of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria).

2.17.2.2 Desensitized explosives shall be classified as packaged for supply and use in one of four categories depending on the corrected burning rate (A_C) using Method X described in Part V, sub-section XX.X.Z of the UN Recommendations of the Transport of Dangerous Goods, Manual of Tests and Criteria, according to Table 2.17.1:

Table 2.17.1: Criteria for desensitized explosives

Category	Criteria
1	Desensitized explosives of which the corrected burning rate (A_C) is equal to or more than 300 kg/min but not more than 1200 kg/min.
2	Desensitized explosives of which the corrected burning rate (A_C) is equal to or more than 140 kg/min but less than 300 kg/min.
3	Desensitized explosives of which the corrected burning rate (A_C) is equal to or more than 60 kg/min but less than 140 kg/min.
4	Desensitized explosives of which the corrected burning rate (A_C) is less than 60 kg/min.

NOTE 1: The desensitized explosives shall be prepared so that they remain homogeneous and will not separate during storage and handling.

NOTE 2: Desensitized explosives may be treated differently for some regulatory purposes (e.g. transport).

NOTE 3: Explosive properties of desensitized explosives have to be determined by test series 2 of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, and shall be communicated in the SD safety data sheet.

NOTE 4: Desensitized explosives do not fall additionally within the scope of chapters 2.1 (explosives), 2.6 (flammable liquids) and 2.7 (flammable solids).

2.17.3 Hazard communication

General and specific considerations concerning labeling requirements are provided in *Hazard communication: Labeling* (Chapter 1.4). Annex 2 contains summary tables about classification and labeling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

Table 2.17.2: Label elements for desensitized explosives

	Category 1	Category 2	Category 3	Category 4
Symbol	Flame	Flame	Flame	Flame
Signal word	Danger	Danger	Warning	Warning
Hazard statement	Desensitized explosive; Fire, blast or projection hazard	Desensitized explosive; Fire or projection hazard	Desensitized explosive; Fire or projection hazard	Desensitized explosive; Fire hazard

2.17.4 Decision logic and guidance

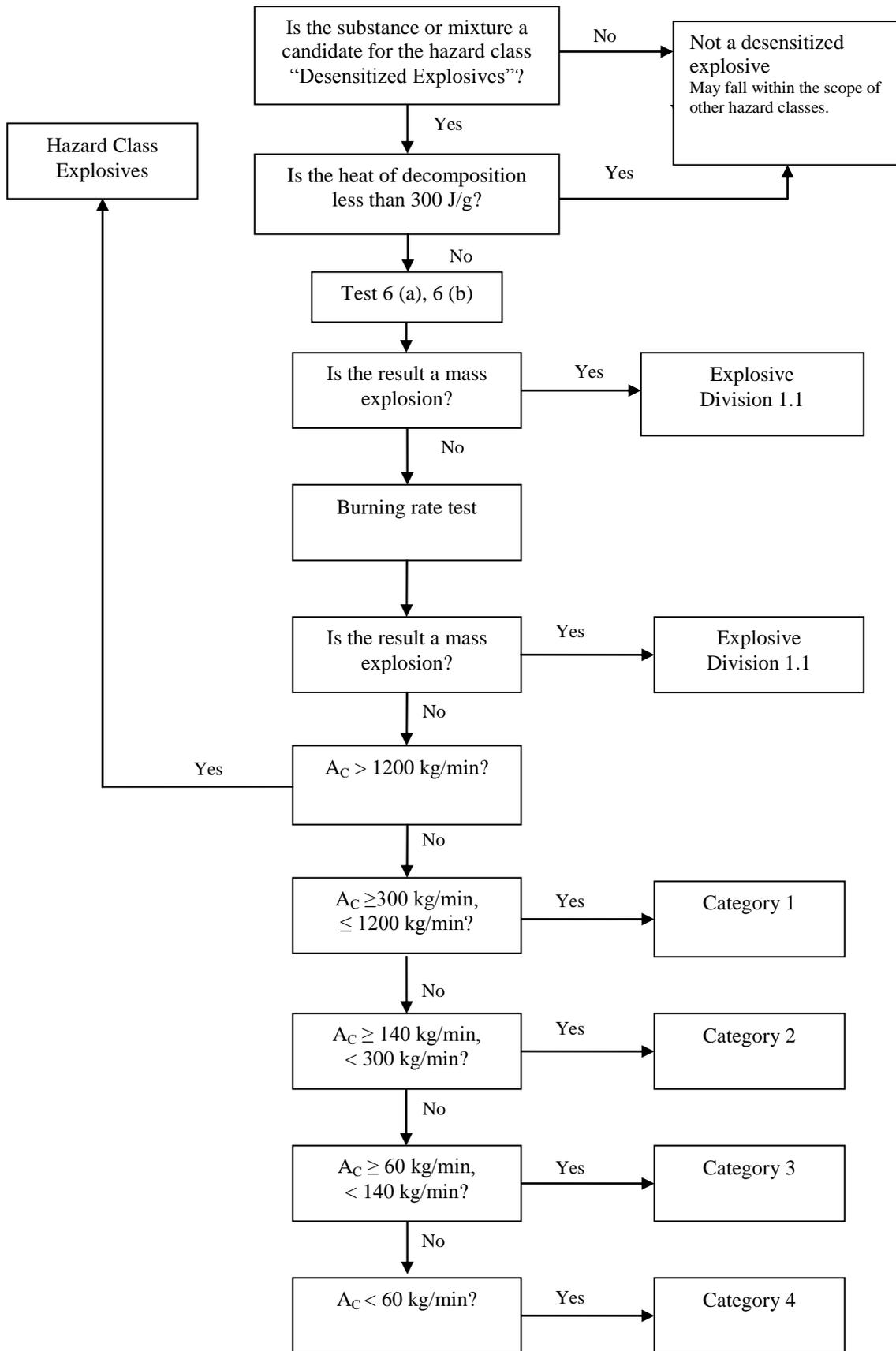
The decision logic and guidance, which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

2.17.4.1 Decision logic

To classify desensitized explosives data for the explosion behavior and the corrected burning rate has to be determined. Reference to Part Y *of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, is necessary.

The classification procedure is according to the following decision logics.

Figure 2.17.1: Decision logic for desensitized explosives



2.17.4.2 Guidance

2.17.4.2.1 The classification procedure for desensitized explosives does not apply if:

- (a) There are no explosives according to the GHS criteria of Chapter 2.1 present;
- (b) The exothermic decomposition energy is less than 300 J/g.

2.17.4.2.2 The heat of decomposition should be determined using the homogenous part of the desensitized explosives; see 20.3.3.3 in Part II of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria.

Annex 2

PART V

**CLASSIFICATION PROCEDURES, TEST METHODS
AND CRITERIA RELATING TO THE GLOBALLY HARMONIZED
SYSTEM OF CLASSIFICATION AND LABELLING OF
CHEMICALS**

CONTENTS OF PART V

NOTE 1: The country or organization of origin of each test method is indicated in brackets after each test name.

NOTE 2: All test methods given in Part V of the Manual are recommended tests as only one test is given for each property.

<u>Section</u>	Page
42. INTRODUCTION TO PART V	4XX
42.1 PURPOSE	4XX
42.2 SCOPE	4XX
43. CLASSIFICATION PROCEDURES, TEST METHODS AND CRITERIA RELATING TO THE CLASS OF DESENSITIZED EXPLOSIVES	4XX
43.1 GENERAL	4XX
43.2 DETERMINATION OF THE 10 000 KG SCALE BURNING RATE (D)	4XX

Section 42

Introduction to Part V

42.1 Purpose

Part V of the Manual presents the United Nations schemes for the classification of substances for supply and use according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

42.2 Scope

The test methods of this Part should be applied when required by the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Section 43

Classification procedures, test methods and criteria relating to the class of desensitized explosives

43.1 General

43.1.1 Desensitized explosives are solid or liquid explosive substances or mixtures which are desensitized to suppress their explosive properties in such a manner that they may be excluded from the hazard class “Explosives” (chapter 2.1 of GHS). Desensitized explosives, should be first tested according to the tests series 1 (type 1(a)), 2 and 6 (type (a) and (b), respectively) of this Manual¹.

43.1.2 The appropriate classification procedures for desensitized explosives should be undertaken before they are offered for supply and use unless:

- (a) They are explosives according to the GHS criteria of chapter 2.1;
- (b) Their heat of decomposition is less than 300 J/g².

43.2 Determination of the 10 000 kg scale burning rate

43.2.1 Purpose

The test method for determination of the 10 000 kg scale burning rate is to be used to determine the behaviour of substances or mixtures as packaged for storage and use if involved in an external fire. The 10 000 kg scale burning rate is to be used for classification into different categories.

43.2.2 Scope

43.2.2.1 Before packaged substances or mixtures are subjected to this burning rate test, the test series 6 types 6 (a) and 6 (b) shall be performed in alphabetical order. The substances or mixtures should be tested first with a standard detonator (Appendix 1 of the Manual) and, if no explosion occurs, with an igniter just sufficient (but not more than 30 g of black powder) to ensure ignition of the substances or mixtures in the packagings. Initiation system which gives a positive result in the 6 (a) test should be used for the 6 (b) test.

43.2.2.2 However, it is not always necessary to conduct tests of all types. Test type 6 (b) may be waived if in each type 6 (a) test:

- (a) The exterior of the package is undamaged by internal detonation and/or ignition; or

¹ An unstable explosive according to chapter 2.1 can be stabilized by desensitization. In this case the desensitized explosive should be tested according to test series 3 (Part I of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria) and the results should be communicated in the safety data sheet.

² The heat of decomposition should be determined using the homogenous part of the desensitized explosives; (see 20.3.3.3 in Part II of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria).

- (b) The contents of the package fail to explode, or explode so feebly as would exclude propagation of the explosive effect from one package to another in test type 6(b).

43.2.2.3 If a substance or mixture gives a negative result (no propagation of detonation) in the Series 1 type 1(a) test, the 6(a) test with a detonator may be waived³). If a substance or mixture gives a negative result (no or slow deflagration) in a Series 2 type 2(c) test, the 6 (a) test with an igniter may be waived.

43.2.2.4 The test for determination of the burning rate by large-scale test need not be performed if, in a test type 6 (b), there is practically instantaneous explosion of virtually the total contents of the stack. In such cases the product is assigned to Division 1.1.

43.2.2.5 The burning rate is defined as the extrapolated burning rate for a mass of 10 000 kg packaged material. In practice, this burning rate is determined using both a single package and stacks of packages, following by an extrapolation procedure. The tests are performed with the substances or mixtures in the packages as provided for storage and use. All types of packages are subjected to the tests unless:

- (a) A substance or mixture, as packed for supply and use, may be unambiguously assigned to a burning rate and category by a competent authority on the basis of results from other tests or of available information; or
- (b) The substance or mixture, as packed for supply and use, is assigned to the hazard class "Explosives", Division 1.1.

43.2.3 Apparatus and materials

43.2.3.1 The test should be applied to packages of substances or mixtures in the condition and form in which they are offered for supply and use (including storage). The test setup is arranged in such a way that the most severe results are anticipated.

43.2.3.2 Tests are performed with:

- (a) 1, 6 and 10 packages, with packages up to a net weight of 25 kg;
- (b) 1, 3 and 6 packages, with packages with a net weight between 25 kg and 50 kg;
- (c) 1 and up to six packages, up to a maximum total net weight of 500 kg, with packages with a net weight of more than 50 kg;

The following items are needed:

- (d) One or two trays with an adequate size and height to contain the wooden pallets and the packages and to protect the ground;
- (e) Wooden pallets (e.g. according to DIN 15146), wood-wool distributed between, under and above the packages;
- (f) A suitable ignition; means that the ignition of the wooden pallets/wood-wool and consequently the tested packages is guaranteed (a mixture of gasoline and light fuel oil 10/90 evenly distributed over the packages and the wood-wool is recommended);
- (g) Cine and/or video cameras and suitable equipment to measure the heat of radiation, e.g. infrared sensors and/or thermo cameras.

³ If the type 1 (a) test is not carried out the Series 6 type 6(a) test cannot be waived.

The number of tests and/or the total mass (whereas necessary) should be increased if the test results are ambiguous and the corresponding hazards is cannot clearly be defined.

43.2.4 Procedure

43.2.4.1 The packages are placed on wooden and leveled pallets. The pallets are placed in one (or two, if necessary) trays. A tray must comprise at least one complete pallet including 10 cm open space all around the pallet. Flammable material (wood-wool, paper, etc.) is placed under and around the packages in such a way that an optimum ignition is guaranteed (see 42.3.2 (f)).

NOTE: A quantity of about 10 kg dry wood-wool is usually sufficient. The wooden pallets and the dry wood-wool shall be soaked with a liquid mixture of fuel (about 10 liter, see 42.3.2 (f)).

43.2.4.2 The heat of radiation is measured during the test by suitable equipment, at least at three locations with three different distances from the seat of fire (the distances depend on the sensitivity of the equipment (sensors, thermo camera, etc.) and should be calculated before the test.

43.2.4.3 The signals are continuously recorded. The starting-point of the fire outbreak is defined as the moment when a reaction of the substance is detected. The end of the fire is determined from registered radiation curves.

43.2.4.4 If a mass explosion or individual explosions or metallic projections (fragments) are observed this should be noted in the test report.

43.2.5 Calculation of the corrected burning rate (A_C)

43.2.5.1 The burning rates A and A_{10t} are determined as follows:

- (a) The starting point of the fire is defined as the moment at which the substance or mixture reacts detectably. The end of the fire is characterized by a decrease in radiation level I (as caused by the fire) to less than 5 % of the maximum level (I_{max}) (see Figure 43.2.1);
- (b) The effect of either remainder or burning materials, if present, shall be taken into account in the evaluation;
- (c) The burning time t is the time span between the starting point and the end of the fire;
- (d) The burning rate A [kg/min] can be calculated for each tested quantity m [kg] and its corresponding burning time t [min] from the equation:

$$A = \frac{m}{t}$$

- (e) Log A is plotted against log m , where A is the determined burning rate, and m is the mass of substance or mixture used for the test. The observed test results are extrapolated by means of this graph to an uncorrected burning rate A_{10t} for a mass of 10 000 kg by applying of the formula:

$$A_{10t} = \left(\frac{10000 \text{ kg}}{m} \right)^{\frac{2}{3}} \cdot A$$

43.2.5.2 The corrected burning rate A_C is determined as follows:

- (a) The energy included in the substance is partially converted into radiation. The percent average radiation efficiency η at a distance from

the fire is determined from the measured radiation level ($dose_{measured}$) and the theoretical maximum energy ($dose_{calculated}$);

$$\eta = \frac{dose_{measured}}{dose_{calculated}}$$

- (b) The theoretical maximum energy is calculated by multiplying the individual mass of tested substance m [kg] with the heat of combustion H_v [kJ/kg].

$$dose_{calculated} = H_v \cdot m$$

- (c) The amount of energy that in practice appears to be transferred by radiation is determined by integrating the area below the measured radiation curve;

$$dose_{measured} = f(t) = \left[\sum_{t=start}^{end} \frac{(I_{(t+\Delta t)} + I_t)}{2} \cdot \Delta t \right] \cdot 4 \pi \cdot r^2$$

The numerical integration of the radiation intensities I_t [W/m²] over the total burning time delivers $dose_{measured}$ [kJ] at the distance r [m].

- (d) To this end a graph is made showing the radiation level I [kW/m²] as a function of time. The complete radiation dose is calculated by integration of the smoothed and corrected curve down to 1 % to 5 % of I_{max} ;
- (e) $I_{relevant}$ is obtained from the maximum of the curve of heat radiation calculated as average value of the radiation by converting the integrated area in a rectangle of equal size during the same time span;
- (f) The form factor f that must be taken into account during the maximum fire intensity can be averaged from the formula:

$$f = \frac{I_{relevant}}{I_{calculated}}$$

where H_v is the heat of combustion ⁴ of the substance [kJ/kg] (i.e. reaction enthalpy of the burning reaction). A_C is the corrected burning rate [kg/min] for a quantity of 10 000 kg.

43.2.6 Test criteria and method of assessing results

43.2.6.1 If a mass explosion or individual explosions or metallic projections (fragments) occur the substance or mixture is classified in the class explosives.

43.2.6.2 The test results are assessed on the basis of the burning rate A_C for a quantity of 10 000 kg of the packaged substance or mixture.

43.2.6.3 The test criteria for determining the burning behavior of substances or mixtures are:

Category 1: Any substance or mixture with a corrected burning rate A_C equal or more than 300 kg/min but not higher than 1200 kg/min;

⁴ Should be determined by a suitable technique e.g. combustion calorimeter.

Category 2: Any substance or mixture with a corrected burning rate A_C equal or more than 140 kg/min but less than 300 kg/min;

Category 3: Any substance or mixture with a corrected burning rate A_C equal or more than 60 kg/min but less than 140 kg/min;

Category 4: Any substance or mixture with a corrected burning rate A_C less than 60 kg/min.

Any substance or mixture with a corrected burning rate higher than 1200 kg/min is classified as an explosive of chapter 2.1.

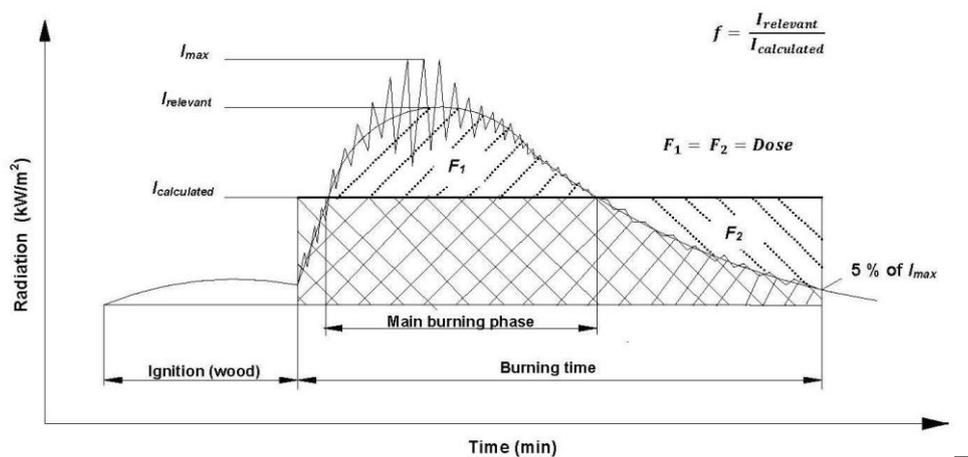


Figure 43.2.1: Measurement of radiation as a function of time

42.2.7 Examples of results

The nitrocellulose formulations are packed in fiber drums (1G) with maximum mass of 140 kg and fiber board boxes (4G) with maximum mass of 25 kg, assigned to categories as follows:

Ester soluble (E-grades) nitrocellulose formulations with different phlegmatizers and a nitrogen content of 11.8 % to 12.3 %

NC-type	IPA 35 %	IPA 30 %	ETH 35 %	ETH 30 %	BUT 35 %	BUT 30 %	Water	Chips ^{a)}
12E	3	2	4	3	2	1 (330 kg/min)	4	1 (1115 kg/min)
22E	3	3	4	3	3	3	4	1 (1115 kg/min)
25E	3	3	4	3	3	3	3	1 (1115 kg/min)

IPA (Isopropanol), ETH (Ethanol), BUT (Butanol), ^{a)} NC-Chips with 20 % plasticizer

Medium soluble (M-grades) nitrocellulose formulations with different phlegmatizers and a nitrogen content of 11.3 % to 11.8 %

NC-type	IPA 35 %	IPA 30 %	ETH 35 %	ETH 30 %	BUT 35 %	BUT 30 %	Water	Chips ^{a)}
15M	-	-	-	-	3	2	-	
27M	3	3	4	4	3	3	4	1 (1115 kg/min)
34M	3	3	4	4	4	-	-	1 (1115 kg/min)

IPA (Isopropanol), ETH (Ethanol), BUT (Butanol), ^{a)} NC-Chips with 20 % plasticizer

Alcohol soluble (A-grades) nitrocellulose formulations with different phlegmatizers and a nitrogen content of 10.7 % to 11.3 %

NC-type	IPA 35 %	IPA 30 %	ETH 35 %	ETH 30 %	BUT 35 %	BUT 30 %	Water	Chips ^{a)}
15A	4	3	4	3	3	2	-	1 (1115 kg/min)
30A	4	3	4	4	3	3	4	1 (1115 kg/min)
32 A	4	3	4	4	4	3	-	-

43.2.8 Example of a calculation:

NC-formulation (nitrogen content 10.7 % to 11.2 %) wetted with 30 % isopropanol:

Mass of the tested NC formulation: $m = 285 \text{ kg}$
 Burning time: $t = 9.7 \text{ min}$
 Efficiency factor: $f = 3.73$
 Shape factor: $\eta = 0.24$
 Enthalpy of combustion: $H_v = 15626 \text{ kJ/kg}$

Calculation of the burning rate A :

$$A = \frac{m}{t} = \frac{285 \text{ kg}}{9.7 \text{ min}} = 29.4 \frac{\text{kg}}{\text{min}}$$

Calculation of the burning rate A_{10t} :

$$A_{10t} = \left(\frac{10000 \text{ kg}}{m} \right)^{\frac{2}{3}} \cdot A = \left(\frac{10000 \text{ kg}}{285 \text{ kg}} \right)^{\frac{2}{3}} \cdot 29.4 \frac{\text{kg}}{\text{min}} = 315 \frac{\text{kg}}{\text{min}}$$

Calculation of the corrected burning rate A_c :

$$A_c = A_{10t} \cdot \frac{H_v}{33500} \cdot \frac{\eta}{0.25} \cdot \frac{f}{2.78} = 315 \frac{\text{kg}}{\text{min}} \cdot \frac{15626 \frac{\text{kJ}}{\text{kg}}}{33500 \frac{\text{kJ}}{\text{kg}}} \cdot \frac{0.24}{0.25} \cdot \frac{3.73}{2.78} = 189 \frac{\text{kg}}{\text{min}}$$

The desensitized explosive is classified in category 2.

References

- [1] German “Guideline for the assignment of substances which may show explosive properties to Storage Groups (SprengLR011)”
- [2] Thermal radiation hazards from organic peroxides, Roberts, T.A. and Merrifield, R., *J. Loss. Prev. Process Ind.* 1990, 3, 244.
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- [4] Storage of Organic Peroxides, Publication Series on Dangerous Substances 8 (PGS 8), Ministries of Social Affairs and of the Interior, The State Secretary of Housing, Spatial Planning and Environment (VROM), The Netherlands 2006.
- [5] The storage and handling of organic peroxides, Guidance Note CS21, Health and Safety Executive, 1998, United Kingdom
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