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

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Recommendations made by the Sub-Committee at its sixty-second, sixty-third and sixty-fourth sessions and pending issues: Explosives and related matters: Miscellaneous

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

Forty-seventh session
Geneva, 4-6 December 2024
Item 2 (a) of the provisional agenda
Work on the Globally Harmonized System of Classification and Labelling of Chemicals: Work of the Sub-Committee of Experts on the Transport of Dangerous Goods on matters of interest to the Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals

Report of the informal correspondence group on burning rate: Amendments to subsection 51.4 of the Manual of Tests and Criteria

Transmitted by the expert from China on behalf of the informal correspondence group

Introduction

1. This document contains the text of section 51 of the Manual of Tests and Criteria with the amendments proposed by the informal correspondence group listed in document ST/SG/AC.10/C.3/2024/94 − ST/SG/AC.10/C.3/2024/15.

2. All changes are indicated: deleted text appears in ~~strikethrough~~ and new text in **bold underlined**.

“Section 51

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

51.1 Purpose

51.1.1 This section presents the United Nations scheme for the classification of liquid and solid desensitized explosives (see chapter 2.17 of the *GHS*). The text should be used in conjunction with the classification principles of chapter 2.17 of the *GHS* and the test series given in sections 12 and 13 and subsections 16.4 and 16.5 of this *Manual.*

For testing of liquid desensitized explosives for transport purposes, refer to section 32, subsection 32.3.2 of this "Manual" and to chapter 2.3, subsection 2.3.1.4 of the "Model Regulations". Testing of solid desensitized explosives for transport purposes is addressed in section 33, subsection 33.3 of this "Manual" and in chapter 2.4, subsection 2.4.2.4 of the "Model Regulations".

51.2 Scope

51.2.1 Desensitized explosives are substances and mixtures in the scope of chapter 2.1 of the *GHS* which are phlegmatized to suppress their explosive properties in such a manner that they meet the criteria as specified in 2.17.2 of the *GHS* and thus may be exempted from the hazard class "Explosives" (Chapter 2.1 of *GHS*).

51.2.2 Desensitized explosives should be tested:

(a) For their exothermic decomposition energy,[1] if attempting to exit the class of desensitized explosives;

(b) In accordance with test 1 (a), test series 2 and 3 and tests 6 (a) and (b), respectively of this *Manual* and in accordance with the classification procedure in section 51.3, to preclude a mass explosion in the corrected burning rate test;

(c) In accordance with the corrected burning rate test; and

(d) Nitrocellulose should be tested in accordance with appendix 10 of this *Manual* in order to be used in nitrocellulose mixtures.

51.3 Classification procedure

51.3.1 Before packaged substances or mixtures are subjected to the burning rate test, tests as specified below should be performed to rule out the possibility of mass explosion. In accordance with test 6 (a), substances and 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 substance or mixture in the packaging. If there is a positive result in test 6 (a), test 6 (b) should be performed with the same initiation system that caused the positive result in test 6 (a).

51.3.2 It is not always necessary to conduct tests of all types:

(a) Test series 3 may be waived if the explosive itself (i.e. before being phlegmatized) is not too sensitive or thermally unstable in accordance with test series 3;

(b) Test series 3 and tests 6 (a) and (b) may be waived if test series 2 has been passed;

[1] *The exothermic decomposition energy should be determined using the explosive already desensitized (i.e.: the homogenous solid or liquids mixture formed by the explosive and the substance(s) used to suppress its explosive properties). The exothermic decomposition energy may be estimated using a suitable calorimetric technique (see section 20, subsection 20.3.3.3 in part II of this "Manual").*

(c) Test series 3 is not applicable to nitrocellulose mixtures containing no explosives other than nitrocellulose, for which the stability of the nitrocellulose has been established in accordance with appendix 10;

(d) Tests 6 (a) and 6 (b) may be modified or waived in accordance with section 51.3.3;

(e) Test 6 (b) may be waived if in each type 6 (a) test:

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

(ii) 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 6(b).

51.3.3 If a substance or mixture gives a negative result (no propagation of detonation) in test 1 (a), test 6 (a) with a detonator may be waived.[2] If a substance or mixture gives a negative result (no or slow deflagration) in test 2 (c), test 6 (a) with an igniter may be waived.

51.3.4 The test for determination of the burning rate by large-scale test need not be performed if, in test 6 (b), there is practically instantaneous explosion of virtually the total contents of the stack. In such cases the product is assigned to the class of explosives (see chapter 2.1 of the *GHS*).

51.4 Burning rate test (external fire)

51.4.1 *Introduction*

51.4.1.1 The test method for determination of the burning rate (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. This test is performed with several packages of the substances or mixtures to determine:

(a) Whether there is a mass explosion hazard, a hazard from dangerous projection or a too violent burning,

(b) A burning rate (10 000 kg scaled), which depends on the total mass.

51.4.1.2 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~~.

51.4.1.3 The corrected burning rate (10 000 kg scaled) is to be used for classification into four different categories.

51.4.2 *Apparatus and materials*

51.4.2.1 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 following elements are needed:

(a) A number of 1, 6 and 10 packages, with a net mass of desensitized explosive of 25 kg in each package;

[2] *If the type l (a) test is not carried out test 6 (a) cannot be waived.*

(b) A number of 1, 3 and 6 packages, with a net mass of desensitized explosive between 25 kg and 50 kg in each package;

(c) A number of 1 and up to six packages, with a net mass of desensitized explosive of more than 50 kg, the total net mass should not be greater than 500 kg;

(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), with wood-wool distributed between, under and above the packages;

(f) A suitable ignition source guaranteeing the ignition of the wooden pallets/wood-wool and consequently the tested packages (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.

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

51.4.3 ***Procedure***

51.4.3.1 The tests start with a single package and then the number of packages are successively increased as mentioned under 51.4.2.1 (a), (b) or (c). Normally the burning rate test should be performed once for each number of packages. The required numbers of packages, in the condition and way in which they are offered for supply and use (including storage), are arranged in such way, that the most severe results are anticipated, 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 51.4.2.1 (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 51.4.2.1 (f)).*

51.4.3.2 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.

51.4.3.3 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.

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

51.4.4 ***Test criteria and method of assessing results***

51.4.4.1 The burning rates A and A10t 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 **point** of the fire is characterized by a decrease in **irradiance** ~~radiation level~~ *I* (as caused by the fire) to less than 5 % of the maximum ~~level~~ **irradiance** (*Imax*)**. The total burning time *t* is the time span between the starting point and the end point of the fire** (see figure 51.4.1);

(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~~**c**) The burning rate *A* [kg/min] can be calculated for each tested quantity *m* [kg] and its corresponding **total** burning time *t* [min] from the equation:

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

(~~e~~**d**) 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 *A10t* for a mass of 10 000 kg corresponding to the following function:

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

51.4.4.2 The corrected burning rate *AC* is determined as follows:

(a) The internal amount of energy of 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~~ **energy** ($dose_{measured}$) 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]:[3]

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

(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~~ **irradiance** *It* [**k**W/m^2] 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~~ **irradiance** *I* [kW/m^2] 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 *Imax*;

(e) *Irelevant* is obtained from the maximum of the **smoothed and corrected** curve of **the measured** heat radiation**.** $I_{calculated}$ ~~calculated~~ **is the** ~~as~~ average value of the radiation **obtained** by converting the integrated area in a rectangle of equal size during the same **total burning** time ~~span~~ **(see figure 51.4.1)**;

(f) The form factor *f* that must be taken into account during the maximum fire intensity can be averaged from the formula:

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

[3] *Should be determined by a suitable technique e.g. combustion calorimeter.*

(g) The corrected burning rate A_c is calculated as follows:

$$A_c = A_{10t} \cdot \frac{H_v}{33\ 500} \cdot \frac{\eta}{0.25} \cdot \frac{f}{2.78}$$

Where H_v is the heat of combustion of the substance [kJ/kg] (i.e. reaction enthalpy of the burning reaction); η is the radiation efficiency and f ***is*** the form factor. AC is the corrected burning rate [kg/min] for a quantity of 10 000 kg.

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

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

51.4.4.5 The test criteria for determining the burning behaviour of substances or mixtures are:

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

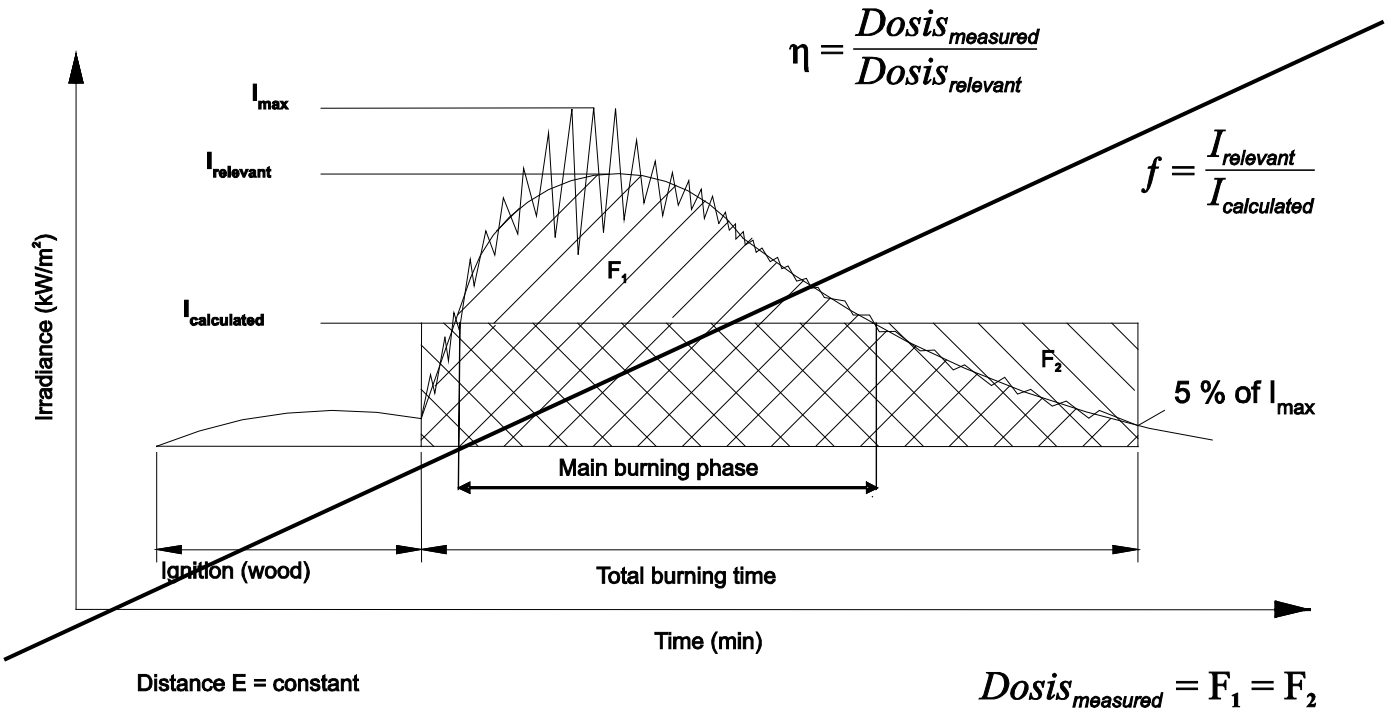
Category 2: Any substance or mixture with a corrected burning rate AC equal to or greater than 140 kg/min but less than 300 kg/min;

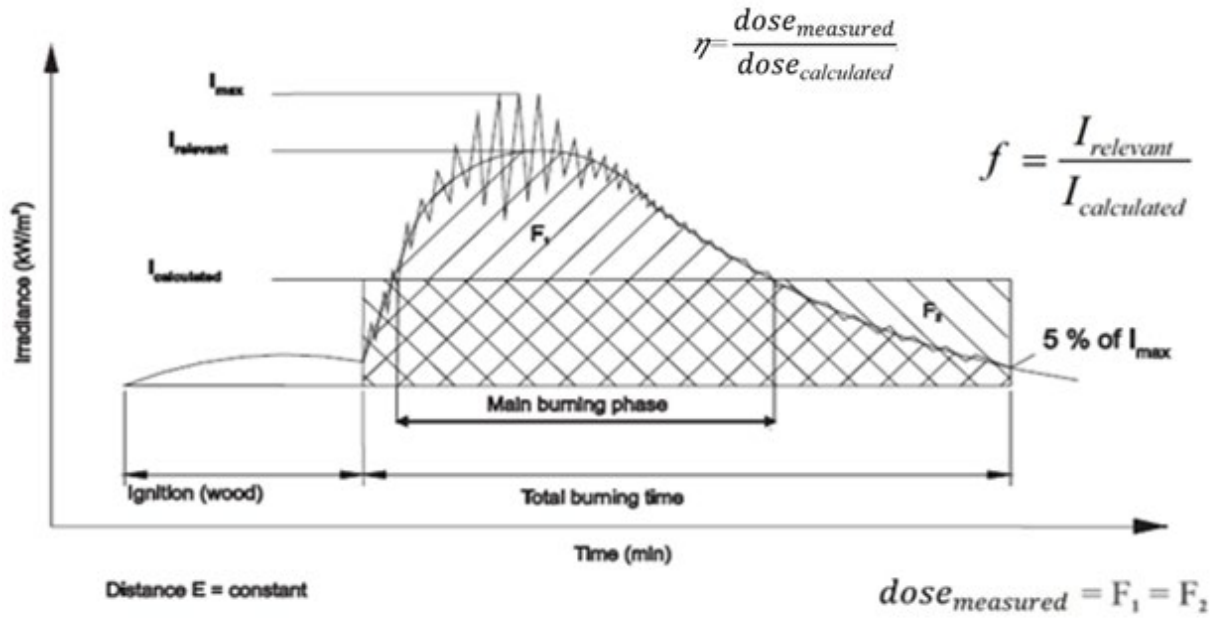
Category 3: Any substance or mixture with a corrected burning rate AC equal to or greater than 60 kg/min but less than 140 kg/min;

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

Any substance or mixture with a corrected burning rate greater than 1200 kg/min is classified as an explosive (See chapter 2.1 of the *GHS*).

Figure 51.4.1: Measurement of radiation as a function of time





51.4.5 ***Examples of results***

A compilation for the test results and classification data for more than 200 industrial nitrocellulose products is given in appendix 11.

51.4.6 ***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 kg
Total burning ~~Burning~~ time:	t = 9.7 min
Form factor:	f = 3.73
Radiation efficiency:	η = 0.24
Heat ~~Enthalpy~~ of combustion:	H_v = 15626 kJ/kg

Calculation of the burning rate A:

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

Calculation of the burning rate A_{10t}:

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

Calculation of the corrected burning rate *Ac*:

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

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.

[3] Thermal radiation hazard and separation distances for industrial cellulose nitrate, Roberts, T.A. and Merrifield, R., J. Loss. Prev. Process Ind. 1992, 5,311.

[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.

[6] Organic Peroxides: Storage (Guideline for the labour-safe, environment-safe and fire-safe storage of organic peroxides), Hazardous Substances Publication Series 8:2011 (PGS 8:2011) version 1.0, December 2011."