

**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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**Sub-Committee of Experts on the
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Item 10 (c) of the provisional agenda

**Issues relating to the Globally Harmonized System of
Classification and Labelling of Chemicals:
tests and criteria for oxidizing solids**

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

Twenty-third session

Geneva, 4 – 6 July 2012

Item 2 (a) of the provisional agenda

**Updating of the Globally Harmonized System of
Classification and Labelling of Chemicals (GHS):
physical hazards**

UN Test O.1: Test for oxidizing solids

Transmitted by the expert from Germany

Introduction

1. In informal document UN/SCEGHS/19/INF.12 and UN/SCETDG/37/INF.31 the work of the IGUS working group Energetic and Oxidizing Substances (EOS) concerning the test method O.1 was introduced. The (EOS) working group as a sub-group of IGUS is dealing with test methods, classification and safety aspects relating to organic peroxides, self-reactive substances and other energetic substances, fertilizers, ammonium nitrate and oxidizers.
2. Its status does not allow IGUS to participate in the work of the TDG and GHS sub-committees, nevertheless German experts participate in the work of this group of voluntary experts and the expert from Germany is happy to endorse the outcome of its work on the improvement of UN Test O.1 and to submit the proposal below for further action.
3. Test method O.1 aims at determining the potential of a solid substance to increase the burning rate or burning intensity of a combustible material when the two are thoroughly mixed. Therefore, the substance to be evaluated is mixed with cellulose in different mass ratios. The burning characteristics of these mixtures are compared with reference mixtures of the same mass ratios of potassium bromate and cellulose. The packing group for transport or the hazard category according to the GHS, respectively, are assigned based on the results of the comparison of the measured burning times.
4. Two basic problems are associated with the current test method. The first one is the carcinogenicity and oral acute toxicity of the reference substance potassium bromate. It is therefore advisable to replace this reference substance. Calcium peroxide was suggested by the ad-hoc working group because it is neither carcinogenic nor acutely toxic.
5. The second one is associated with the visual determination of the burning time which is highly subjective. This results in a broad range of results even for the reference mixtures and, hence, influences the classification. Therefore, the ad-hoc working group suggested a gravimetric determination of the burning rate.

6. Details on an interlaboratory test in which the new method was applied by different laboratories world-wide using calcium peroxide as reference substance and the gravimetric determination of the burning rate can be found in the resp. report

www.bam.de/de/service/publikationen/publikationen_medien/fg22_round_robin_solid_oxidizer_test.pdf

Proposed way forward

7. The EOS working group is still working on that topic in order to present a solution within this biennium.

8. The Annex to this document contains the draft proposal for the alternative O.1 test method.

9. The proposal of the EOS working group would be to add the new test method to the UN Manual of Tests and Criteria as an alternative to the current O.1 method. The sub-committees may wish to express their opinion on this proposed way forward.

10. The expert from Germany intends to submit an official proposal as outlined above for discussion at the next sessions of the sub-committees in December 2012.

Annex

34.4 Test methods for oxidizing substances and mixtures

34.4.x *Test O.x: Test for oxidizing solids*

34.4.x.y *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 test substance to be evaluated mixed with dry fibrous cellulose in mixing ratios of 1:1 and 4:1, by mass. The burning rates of these mixtures are compared to the reference mixture of calcium peroxide and cellulose in a mixing ratio of 1:2, by mass. The mass loss of the mixtures during combustion is determined using a balance connected to a [suitable] data recording system, and is recorded as a function of time. If the burning rate (g/s) is equal to or greater than the burning rate of the reference mixture for Packing Group III, it is then compared to the burning rate of the reference mixtures for Packing Group I or II (see table in 34.4.x.y.z).

The UN Globally Harmonized System of classification and labeling of chemicals, GHS, also refers to this test for classification within the hazard class Oxidizing Solids. For the ranking according to oxidizing power, the GHS uses three Categories which correspond exactly to the Packing Groups used within the transport of dangerous goods regime. The GHS Categories 1, 2 and 3 thus correspond directly to Packing Groups I, II and III, respectively.

It is useful to have preliminary information on any potentially explosive properties of the substance before performing the test, screening procedures can be found in Appendix 6. This test is not applicable for substances or mixtures which are explosive or flammable and also not to organic peroxides.

Note that whenever “substance” is used in this text it should be understood to mean “substance or mixture”, since this test is used to classify both substances and mixtures on basis of their oxidizing properties.

34.4.x.y *Materials*

34.4.x.y.z Technically pure, finely powdered calcium peroxide with a concentration of 75 % ± 0.5 % is required as the reference oxidizer. The concentration of impurities such as chlorides or compounds which generate water during combustion should be low, as they may impact on the burning behavior of the reference piles. Calcium peroxide meeting the specification below can be used without further pretreatment.*

CaO ₂ :	75 % ± 0.5 %
Ca(OH) ₂ :	20 % to 25 %
CaCO ₃ :	0 % to 5 %
Chloride:	max 500 ppm
Particle size:	min 99 % < 75 µm, and thereof min 50 % < 20 µm

34.4.x.y.z Dried fibrous cellulose with a fibre length between 50 µm and 250 µm and a mean diameter of 25 µm is used as the combustible material. It is dried to constant mass (for a minimum of 4 hours), in a layer no more than 25 mm thick, at 105 °C and kept in a desiccator (with desiccant) until cool and

* Obtainable from the national contact for test details in Germany (see Appendix 4)

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. The bulk density of the cellulose used for the test should be such (sufficiently high) that the test mixture for Packing Group III (30.0 g ± 0.1 g) can be completely accommodated in the conical funnel.

34.4.x.y.z The test-substance, in the form in which it will be presented, should be inspected for any particles less than 500 µm in diameter. If that powder constitutes more than 10 % (by mass) of the total, or if the substance is friable, then the whole of the test sample should be ground to a powder of less than 500 µm before testing, to allow for a reduction in particle size during handling and transport. Because the particle size influences the oxidizing properties of a substance, a coarse oxidizer may be classified as Packing Group III, while a finer grade of the same material may show a faster burning rate and may result in different GHS-classifications and assigned transport Packing Groups for different forms of the same material. It is therefore important that the test is done on the substance or material as it is actually presented, see NOTE 2 to Section 2.14.2 in Chapter 2.14 of the GHS, 4th revised edition.

34.4.x.y Apparatus[†]

34.4.x.y.z An appropriate balance is required, with a suitable range, accuracy and data transfer capability, equipped with an interface (e.g. USB or RS232) to allow data acquisition. The required data (time, mass) are recorded, preferably with a frequency of at least 5 data per second. Any suitable software capable of recording the output of the balance may be used. It is recommended to check the time frequency of the software and the monitoring of time by a stopwatch maybe useful.

34.4.x.y.z An ignition source is required, comprising an inert metal wire connected to an electrical power source capable of maintaining the power dissipation specified below. The electrical resistance depends on the wire material. It is recommended to use Nickel/Chromium or AluChrom wire as follows:

- (a) Length = 30 cm ± 1 cm;
- (b) Diameter below 1 mm;
- (c) Electrical power dissipated in the wire = 150 W ± 7 W.

The wire should be shaped as shown in figure 34.4.x.y. It is very important that the power connection to the heating wire is flexible enough to avoid any influence on the proper operation of the balance.

34.4. x.y.z A 60° funnel, with an internal diameter of 70 mm and sealed at the narrow end, is required to form the mixtures into a truncated conical pile with a base diameter of 70 mm on a cool, impervious, low heat conducting plate.

34.4. x.y.z An insulating test plate is needed to avoid loss of energy by thermal conduction. A 150 mm by 150 mm test plate with a thickness of at least 6 mm and a thermal conductivity at 0 °C of 0.23 W*m⁻¹*K⁻¹ or less is suitable. Other plates with a similar conductivity may be used. In order to increase the lifetime of the test plate, it may be covered with a thin ceramic sheet with the same low thermal conductivity.

34.4. x.y.z A fume cupboard or other suitably ventilated area is required but the air stream velocity should be 0.5 m/s or less. ***The fume extraction system should be capable of capturing all toxic fumes.***

34.4. x.y.z To construct the support for the burning trial on the balance a base plate of solid material (steel or other suitable material), a positioning plate of fire resistant material (the same material as test-plate is recommended) and guide bars are required.

[†] Technical information about a suitable design and video training are obtainable from the national contact for test details in Germany (Appendix 4)

34.4. x.y.z The air stream of the ventilation must be prevented from affecting the balance and thereby altering the test result. A windshield protecting the complete test equipment against draughts from the ventilation or environment is the preferred means.

34.4. x.y.z It is mandatory that the burning conical pile is always placed at the centre of the balance. It is also important to protect the balance from heat and burning particles during the test. To achieve this, the following general configuration is recommended (the letters in brackets refer to figure 34.4.x.y):

Two plates are used to ensure always the same position on the balance and to protect the balance. The base plate (H) is larger than the balance and made of solid material. It is recommended to use some buffers fixed to the lower side to reduce vibrations from the environment. 2 to 4 metal guide bars (G) are fixed on the bottom plate as shown in figure 34.4.x.y to ensure always the same positioning of the positioning plate (F) and test plate (C) on the balance during testing. The base plate should be rigid enough to keep the guide bars always in a stable position (e.g. 4 mm steel or 16 mm polyamide). The balance has to be placed always at the same central position on the base plate.

The positioning plate (F) is made of fire resistant low conductivity material, similar in properties to the test plate (see 34.4.1.2.6). The holes drilled in the positioning plate for the bars should be about 8 mm larger in diameter than the bars themselves.

The bars always have to be positioned in the center of the holes to prevent any contact between the positioning plate (F) and the bars, in order not to affect the operation of the balance. Some check marks should be fixed on the positioning plate (F) to position the test plate (C) in the correct position in the center of the balance.

The electrical connection between the power supply and the heated wire must be flexible enough to avoid interfering with free movement of the balance pan due to resistance or movement. This can be achieved by using a flexible wire and a support close to the test plate. Coiling of the wire between the support and the test plate will provide additional flexibility.

The windshield (D) can be integral with the bottom plate or placed around the complete test equipment. The windshield should have no gaps at the bottom. The windshield itself should be closed and about 10 cm higher than the equipment to prevent air streams from the top.

34.4.x.y Procedure

The following samples are required:

Sample	Components	Mixing ratio by mass
Test substance mixture 1:1	Test substance and cellulose	1:1
Test substance mixture 4:1	Test substance and cellulose	4:1
Reference mixture for Packing Group I	Reference substance and cellulose	3:1
Reference mixture for Packing Group II	Reference substance and cellulose	1:1
Reference mixture for Packing Group III	Reference substance and cellulose	1:2

34.4.x.y.z 30.0 g ± 0.1 g of each of the reference mixtures and 30.0 g ± 0.1 g of both mixtures of the test substance are prepared. Each mixture should be mixed mechanically as thoroughly as possible for at least 1 minute, but without excessive stress. Each mixture should be prepared individually, used as soon as possible, and not taken from a batch.

34.4. x.y.z Using the conical funnel, the mixture should be formed into a truncated conical pile with a base diameter of 70 mm. Form the pile by tapping the funnel slightly after filling; cover the funnel with the test plate -including the sheet (if any)- and invert both. Tap slightly on the funnel before removing. The pile should now cover the looped ignition wire resting on test plate. The test should be performed at atmospheric pressure with an ambient temperature of 20 °C ± 5 °C and a relative humidity below 60 %, to reduce absorption of moisture by the cellulose during handling.

34.4. x.y.z The balance, placed in the ventilated area as mentioned above, is set to zero. 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. Data collection should start a few seconds before the power supply is switched on, and should proceed until the reaction ends or the mass loss over 1 minute is less than 1 g. If the heating wire breaks, the test should be repeated to ensure that early breakage of the wire does not influence the test result.

34.4.x.y *Test criteria and method of assessing results*

34.4. x.y.z The results are assessed on the basis of:

- (a) The comparison of the mean burning rate with those of the reference mixtures;
- (b) Whether the mixture of the test substance and cellulose ignites and burns.

34.4. x.y.z The combustion of the conical pile can be divided into three periods:

- Start period, between 0 % and 20 % of the total mass loss;
- Main combustion period, between 20 % and 80 % of the total mass loss; and
- End of the reaction, between 80 % mass loss and the end of the reaction.

In the main combustion period the mass loss per unit time is quite constant. For this reason a linear regression (based on the least square approach) can be used to check the quality of the data collected.

34.4.x.y.z The burning rate (BR) depends on the burning intensity and the amount of cellulose in the mixture. It is therefore defined as the quotient of 60 % of the total amount of cellulose in the conical pile and the main combustion time t_{20-80} . The time t_{20-80} is the time between 20 % and 80 % of the total mass loss. The total mass loss is the difference in weight before ignition and at the end of the main reaction, defined as a rate of mass loss rate of less than 1 g per minute.

The burning rate BR_{20-80} is therefore calculated by the following equation:

$$BR_{20-80} = \frac{0.6 \times m_{cellulose}}{t_{20-80}}$$

where:

BR_{20-80} = burning rate between 20 % to 80% in g/s

$m_{cellulose}$ = mass of cellulose in mixture in gram

t_{20-80} = burning time between 20 % to 80 % of total mass loss in seconds

The profile of each burning test has to be examined by plotting the mass loss as a function of time. The graph can also be used for decision making and should be used in case of doubt. The coefficient of correlation (R^2) of the mass curve of each burning test should be at least 0.95 between 20 % to 80% mass loss, otherwise the burning trial has to be repeated. Five valid tests should be performed with each reference and test substance mixture. The standard deviation of the burning rates within these five tests should not exceed 10 % in total.

34.4.x.y.z The test criteria for determining transport Packing Groups on basis of the 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 rate greater than the mean burning rate of a 3:1 mixture, by mass, of calcium peroxide and cellulose.

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- Packing Group II: Any substance which, in the 4:1 or 1:1 sample-to-cellulose ratio (by mass) tested, exhibits a mean burning rate equal to or greater than the mean burning rate of a 1:1 mixture (by mass) of calcium peroxide 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 rate equal to or greater than the mean burning rate of a 1:2 mixture (by mass) of calcium peroxide 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 rates less than that of a 1:2 mixture (by mass) of calcium peroxide and cellulose.

For substances having other risks, e.g. toxicity or corrosivity, section 2.0.3 of the Model Regulations applies.

In GHS-terminology, the test criteria for determining the classification due to the oxidizing properties of a solid substance are analogous to those used in transport:

- Category 1: Any substance which, in the 4:1 or 1:1 sample-to-cellulose ratio (by mass) tested, exhibits a mean burning rate greater than the mean burning rate of a 3:1 mixture, by mass, of calcium peroxide and cellulose.
- Category 2: Any substance which, in the 4:1 or 1:1 sample-to-cellulose ratio (by mass) tested, exhibits a mean burning rate equal to or greater than the mean burning rate of a 1:1 mixture (by mass) of calcium peroxide and cellulose and the criteria for Category 1 are not met.
- Category 3: Any substance which, in the 4:1 or 1:1 sample-to-cellulose ratio (by mass) tested, exhibits a mean burning rate equal to or greater than the mean burning rate of a 1:2 mixture (by mass) of calcium peroxide and cellulose and the criteria for Category 1 and 2 are not met.
- Not an Oxidizing Solid: 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 rates less than that of a 1:2 mixture (by mass) of calcium peroxide and cellulose.

34.4.x.y.z If a false positive result is suspected, the results obtained when testing the substance mixed with an inert material and/or when testing under an inert atmosphere should also be considered when interpreting the results.

34.4.x.y.z If the shape of the mass loss curve indicates the test is invalid, the mixing procedure or test set-up affecting free movement of the balance pan should be examined.

34.4.x.y *Example of results*

NOTE: The results given in this table should be understood as illustrative examples since the results obtained with a particular oxidizer will depend on the particle size etc. The test results of the examples are not intended to form the basis for classifications (see also 2.14.4.2.1 of Chapter 2.14 in Part 2 of the GHS, and 2.5.2.1.1 of Chapter 2.5 in the Model Regulations, respectively).

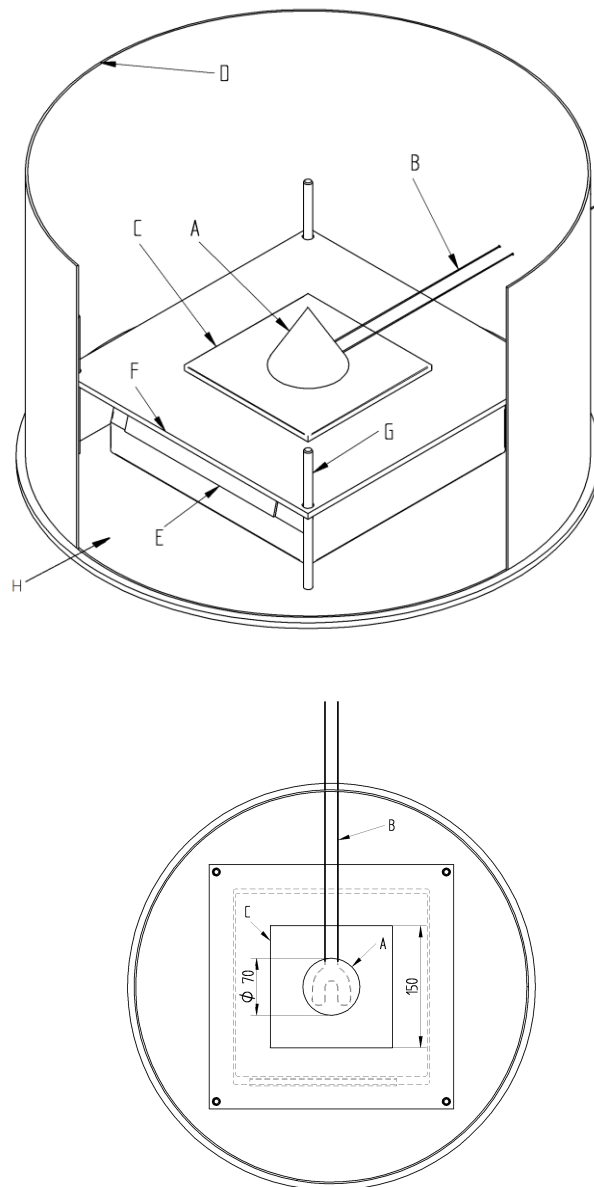
Substance	Particle size, median value (D50 [μm])	Resulting Packing Group
Ammonium dichromate	300	III ¹
Ammonium nitrate (crystalline)	>2500	Not 5.1 ^{1,b}
Ammonium nitrate (crystalline)	250	II ^{1,b}
Calcium nitrate (tetra hydrate)	1050	III ¹
Cobalt nitrate (hexahydrate)	1200	Not 5.1 ¹
Nickel nitrate	1200	Not 5.1 ¹
Potassium nitrate (prills)	2000	Not 5.1 ^{1,b}
Potassium nitrite	200	I ^{2,a}
Potassium perchlorate	220	II ¹
Potassium perchlorate	30	II ²
Potassium permanganate	200	I ^{1,2,a}
Sodium chlorate	220	I ^{2,a}
Sodium nitrite	320	II ^{1,b}
Sodium nitrate	200	II ^{1,b}
Sodium nitrate (prills)	2500	Not 5.1 ^{1,b}
Strontium nitrate (anhydrous)	250	Not 5.1 ¹

^a Currently PG II

^b Currently PG III

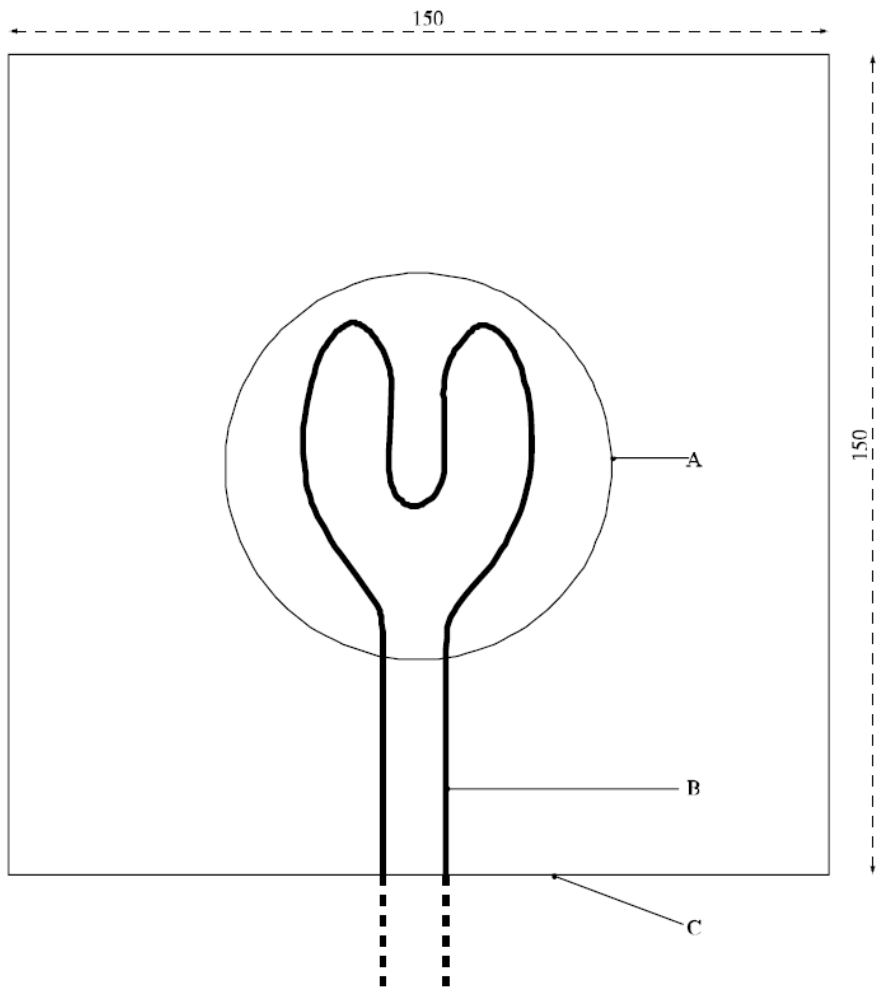
¹Solvay

²BAM



- A) Conical pile
- B) Heating wire
- C) Test plate
- D) Wind shield
- E) Balance with interface
- F) Positioning plate
- G) Bars to fix positioning plate (F) and test plates (C) at defined location on balance
- H) Base plate

Figure 34.4.x.y: Scheme of UN O.1 Test configuration



- (A) Conical pile (base)
- (B) Heating wire
- (C) Test plate

Figure 34.4.x.y: TEST PLATE AND IGNITION WIRE