UNITED NATIONS ST



Secretariat

Distr. GENERAL

ST/SG/AC.10/C.3/38/Add.2 2 August 2001

ORIGINAL: ENGLISH

COMMITTEE OF EXPERTS ON THE TRANSPORT OF DANGEROUS GOODS AND ON THE GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION AND LABELLING OF CHEMICALS

Sub-Committee of Experts on the Transport of Dangerous Goods

REPORT OF THE SUB-COMMITTEE OF EXPERTS ON ITS NINETEENTH SESSION

(Geneva, 2-6 July 2001)

Addendum 2

Annex 3: Report of the United Nations / ILO Working Group on the Harmonization of the Classification Criteria for Physical Hazards

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Informal documents:

1. The UN/ILO Working Group on the Harmonization of Classification Criteria for Physical Hazards met on 5 July 2001 under the chairmanship of Mr. G. Oberreuter (Germany).

Classification criteria for flammability of aerosols

Documents: ST/SG/AC.10/C.3/36, annex 4

ST/SG/AC.10/27, annex 5

ST/SG/AC.10/C.3/2001/22 (Secretariat) ST/SG/AC.10/C.3/2001/8 (CSPA/FEA) ST/SG/AC.10/C.3/2001/9 (CSPA) ST/SG/AC.10/C.3/2000/34 (FEA/CSMA)

INF.34, 35and 48 (FEA)

INF 43 (France)

INF.16 (CSPA)

2. The representative of the European Commission informed the Working Group that an amendment of the European Directive on aerosol dispensers was under preparation and that it would attempt to take account of the final conclusion of the Working Group as far as possible. However, this amendment needs to be finalized as a matter of urgency. The European Commission representative also noted that it is conceivable that a product, the chemical heat of combustion of which is above 20 kJ/g, may pass the flammability test which would indicate that there is no risk of flammability, under reasonably foreseeable conditions of use. In such a case, there should be no mandatory requirement to label the individual dispensers as flammable.

3. On the basis of document ST/SG/AC.10/C.3/2001/22, the Working Group reviewed the decisions already taken and reached the following agreements.

Hazard levels

4. The Working Group agreed that there should be only two hazard levels (FLAMMABLE and EXTREMELY FLAMMABLE).

Flammable components criteria

- 5. It was noted by some delegations that classification of aerosols as non flammable or as extremely flammable could not be based only on the flammable components criterion. The chemical heat of combustion should also be taken into account.
- 6. The following classification criteria for spray and foam aerosols have been adopted:
 - An aerosol product is classified as extremely flammable if the product contains 85% or more flammable components and the chemical heat of combustion exceeds or is equal to 30 kJ/g;
 - An aerosol product is classified as non flammable if the product contains 1% or less flammable components and the chemical heat of combustion is less than 20 kJ/g.
- 7. It was recalled that test methods for the chemical heat of combustion were already available and were given for reference in document ST/SG/AC.10/2000/26 (ASTM D 240*, ISO/FDIS 13943:1999 (E/F) 86.1 to 86.3 and NFPA 30B).

^{*} The Secretariat has been informed by the expert from the United States of America that ASTM E-1354-97 should be replaced by ASTM D 240.

Foam test

- 8. The cut-off value in the foam test for extremely flammable aerosols has been adopted as proposed in document ST/SG/AC.10/C.3/2001/8. The aerosol product should be classified as extremely flammable if:
- (i) The flame height ≥ 20 cm and the flame duration ≥ 2 sec; or
- (ii) The flame duration ≥ 7 sec and the flame height ≥ 4 cm.

Spray aerosol

- 9. After a lengthy discussion the Working Group agreed on all the remaining issues for the classification of spray aerosol:
- (a) If the chemical heat of combustion is less than 20 kJ/g, an ignition distance test shall be performed:
 - (i) The aerosol is classified as flammable if ignition occurs at a distance equal or greater than 15 cm but less than 75 cm;
 - (ii) The aerosol is classified as extremely flammable if ignition occurs at a distance of 75 cm or more;
 - (iii) If no ignition occurs in the ignition distance test, the enclosed space test shall be performed:
 - The aerosol is classified as flammable if the time equivalent is less than or equal to 300 s/m³ or the deflagration density is less than or equal to 300 g/m³;
 - Otherwise the aerosol is classified as non flammable;
- (b) If the chemical heat of combustion is equal to or more than 20 kJ/g, an ignition distance test shall be performed:
 - (i) The aerosol is classified as extremely flammable if ignition occurs at a distance of 75 cm or more:
 - (ii) Otherwise the aerosol is classified as flammable.
- 10. The final classification criteria adopted by the Working Group are summarized in the decision trees 1 to 3 reproduced in Appendix 1 to this document.

Test methods

11. The Working Group endorsed the revised test methods (ignition distance test, enclosed space test and foam test) as described in document INF.34 and reproduced in Appendices 2 to 4. It was also agreed that, only in the case of the ignition distance test, it should be necessary to repeat the test in the position of the dispenser most likely to result in a positive result, when the result of the test in the position in which the dispenser is designed to be used gives a negative result.

Globally Harmonized System of Classification and Labelling

<u>Informal document:</u> INF.21 (Germany, Chairman of Working Group)

12. The Working Group endorsed the hazard communication elements (symbol, signal word and hazard statement) for flammable aerosols as they appear in document INF.21, noting that the proposed elements are consistent with what was adopted by the ILO Working Group for the Harmonization of Chemical Hazard

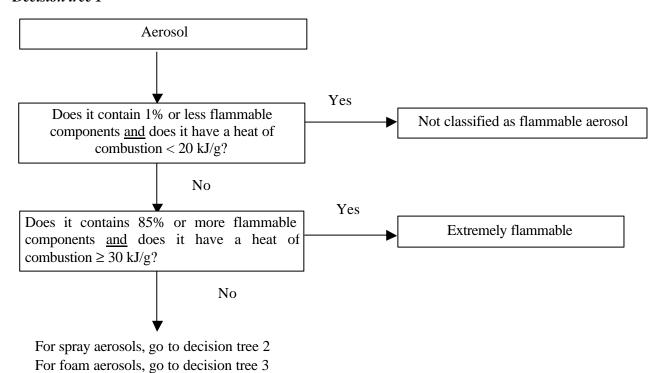
Communication for the other physical hazard classes. The adopted hazard communication elements for flammable aerosols are:

	Extremely flammable	Flammable		
Symbol	Flame	Flame		
Signal word	Danger	Warning		
Hazard statement	Extremely flammable aerosol	Flammable aerosol		

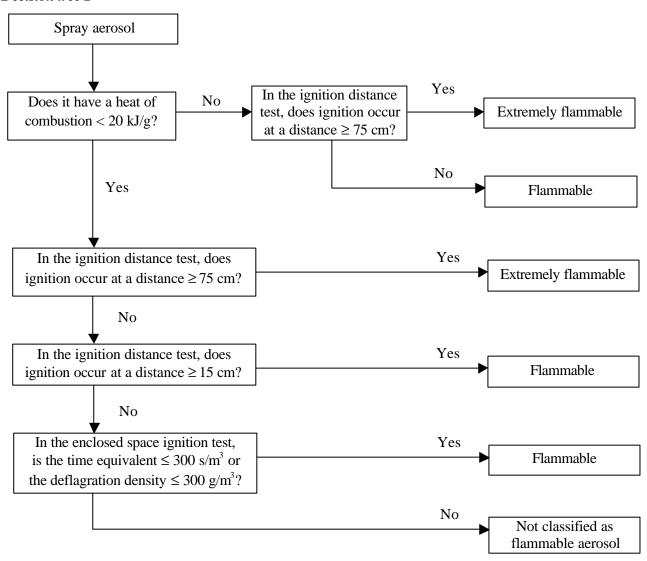
13. The Group was informed that, notwithstanding its previous decision, the definitions and criteria for types A to G for self-reactive substances and organic peroxides and for Divisions 1.1 to 1.6 were deemed necessary by the ILO Working Group for the Harmonization of Chemical Hazard Communication and thus were taken into account in developing and assigning the hazard communication elements. The Group agreed that the definitions and criteria for types A to G and Divisions 1.1 to 1.6 of the 12th revised edition of the UN Recommendations on the Transport of Dangerous Goods should be included in the GHS.

Decision trees for classification of flammable aerosols

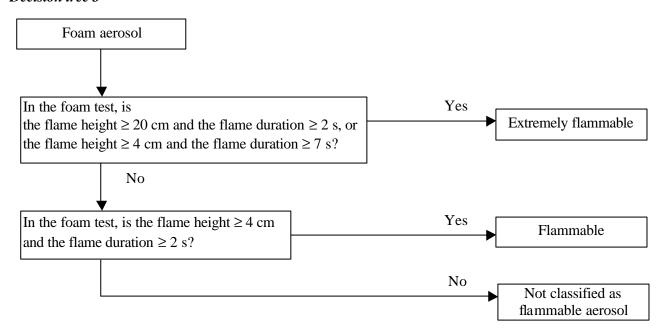
Decision tree 1



Decision tree 2



Decision tree 3



Ignition distance test

OBJECTIVE

This test standard describes the method to determine the ignition distance of an aerosol spray in order to assess the associated flame risk.

PRINCIPLE

An aerosol is sprayed in the direction of an ignition source at intervals of 15 cm to observe if ignition and sustained combustion of the spray takes place.

Ignition and sustained combustion is defined as when a stable flame is maintained for at least 5 seconds.

The ignition source is defined as a gas burner with a blue, non-luminous flame 4-5 cm in height.

SCOPE

This test is applicable to aerosol products with a spray distance of 15 cm or more. Aerosol products with a spray distance of less than 15 cm such as dispensing foams, mousses, gels and pastes or fitted with a metering valve, are excluded from this test. Aerosol products that dispense foams, mousses, gels or pastes are subject to testing under the aerosol foam flammability test.

GENERAL REQUIREMENTS

Before testing, each aerosol dispenser should be conditioned and then primed by discharging for approximately 1 second. The purpose of this action is to remove non-homogeneous material from the diptube.

Follow strictly the instructions of use, including whether the dispenser is intended to be used in the upright or inverted position. When shaking is required, shake immediately before testing.

The tests should be carried out in a draught-free environment capable of ventilation, with the temperature controlled at $20 \, ^{\circ}\text{C} \pm 5 \, ^{\circ}\text{C}$ and relative humidity in the range 30 - 80%.

EQUIPMENT AND APPARATUS

Water bath maintained at 20°C Calibrated laboratory scales (balance) Chronometer (stopwatch)	accurate to \pm 1 °C. accurate to \pm 0.1 g accurate to \pm 0.2 s		
Graduated scale, support and clamp	graduations in cm		
Gas burner with support and clamp			
Thermometer	accurate to ± 1 °C		
Hygrometer	accurate to \pm 5 %		
Pressure gauge	accurate to ± 0.1 bar		

TESTING

Each aerosol dispenser is to be tested:

- when full according to the complete procedure, with the gas burner in the range of 15 – 90 cm distance from the actuator of the aerosol can:

- when 10 - 12% full nominal (% by mass) only one test, either at 15 cm distance from the actuator when the spray from a full can did not ignite at all, or at the flame ignition distance of the spray of a full can plus 15 cm.

Can position during the test to be as per label instructions. The ignition source will be positioned accordingly.

The following procedure requires testing the spray at intervals of 15 cm between the burner flame and the aerosol actuator, in the range of 15 - 90 cm. It is efficient to start at 60 cm distance between burner flame and aerosol actuator. The distance between burner flame and aerosol actuator should be increased by 15 cm in the case of an ignition of the spray at 60 cm distance. The distance should be decreased by 15 cm in the case of no ignition at 60 cm distance between burner flame and aerosol actuator. The aim of the procedure is to determine the maximum distance between aerosol actuator and burner flame that leads to sustained combustion of the spray or to determine that ignition could not be obtained at 15 cm distance between the burner flame and the aerosol's actuator.

TEST PROCEDURE

- (a) A minimum of 3 full aerosol dispensers per product shall be conditioned to $20 \, ^{\circ}\text{C} \pm 1 \, ^{\circ}\text{C}$ with at least 95% of the dispenser immersed in the water for at least 30 minutes before each test (if the aerosol is fully immersed, 30 minute conditioning is sufficient).
- (b) Comply with general requirements. Record the temperature and relative humidity of the environment.
- (c) Weigh an aerosol dispenser and note its mass.
- (d) Determine the internal pressure and initial discharge rate at $20 \,^{\circ}\text{C} \pm 1 \,^{\circ}\text{C}$ (to eliminate faulty or partly filled aerosol dispensers).
- (e) Support the gas burner on a flat horizontal surface or fix the burner to a support by means of a clamp.
- (f) Ignite the gas burner; the flame shall be non-luminous and approximately 4-5 cm high.
- (g) Place the actuator's exit orifice at the required distance from the flame. The aerosol should be tested in the position it is designed to be used, e.g. upright or inverted.
- (h) Level the actuator's orifice and burner flame, ensuring that the orifice is properly directed towards and aligned with the flame (see Figure 1). The spray shall be expelled through the top half of the flame.
- (i) Comply with the general requirements regarding shaking of the dispenser.
- (j) Actuate the valve of the aerosol dispenser, to discharge its contents for 5 seconds, unless ignition occurs. If ignition occurs, continue discharging and time the duration of the flame for 5 seconds, from the start of ignition.
- (k) Note the ignition results for the distance between the gas burner and the aerosol dispenser in the table provided.
- (l) If no ignition occurs during step (j), the aerosol should be tested in alternative orientations, e.g. inverted for upright use products, to check if ignition is obtained.
- (m) Repeat steps (g) to (l) twice more (a total of 3) for the same can at the same distance between the gas burner and the aerosol actuator.

- (n) Repeat the test procedure for another two aerosol cans of the same product at the same distance between gas burner and aerosol actuator.
- (o) Repeat steps (g) to (n) of the test procedure at a distance between 15 and 90 cm between the actuator of the aerosol can and the burner flame depending on the outcome of each test (see also the paragraph on Testing).
- (p) If no ignition occurs at 15 cm, the procedure is finished for initially full cans. The procedure is also finished when ignition and sustained combustion is obtained at a distance of 90 cm. If ignition could not be obtained at 15 cm distance, record that ignition did not occur. The maximum distance between burner flame and the aerosol's actuator for which an ignition and sustained combustion was observed is noted as the "ignition distance", in all other circumstances.
- (q) One test should also be conducted on 3 cans of 10 12% nominal fill level. These cans should be tested at a distance between the aerosol's actuator and the burner flame of "the flame ignition distance of full cans + 15 cm".
- (r) Discharge an aerosol can to a 10 12% nominal fill level (by mass) in bursts of 30 seconds maximum. Observe a 300 seconds minimum time period between bursts. During this interim period dispensers should be placed in the water bath for conditioning.
- (s) Repeat steps (g) to (n) for 10 12% nominal fill aerosol cans, omitting steps (l) and (m). This test should only be performed with the aerosol in one position, e.g. upright or inverted, corresponding with that which produced the ignition (if any) for filled cans.
- (t) Record all results in the Table 1 as shown below.

REMARKS

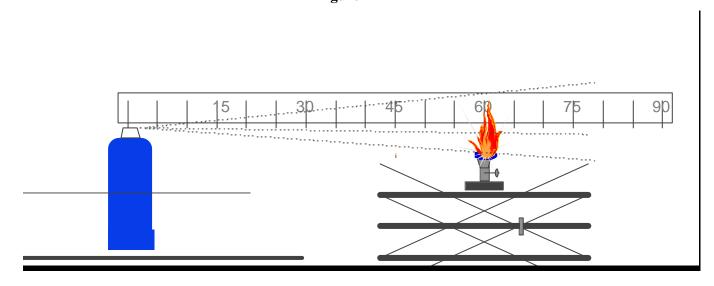
Perform all experiments in a fume hood in a room that may be well ventilated. Ventilation of the fume hood and room can be applied for at least 3 minutes after each test. Take all necessary safety precautions to prevent the inhalation of combustion products.

The cans with a 10 - 12% nominal fill level are tested only once. The result tables needs only one result per can indicated.

Table 1

Date		Temperature Relative humidity		°C %						
Name of product										
Net volume		Can 1		Can 2			Can 3			
Initial level of filling			%			%			%	
Dispenser distance	Test	1	2	3	1	2	3	1	2	3
15 cm	Ignition? Y or N									
30 cm	Ignition? Y or N									
45 cm	Ignition? Y or N									
60 cm	Ignition? Y or N									
75 cm	Ignition? Y or N									
90 cm	Ignition? Y or N									
Observations – including can position										

Figure 1



Enclosed space ignition test

OBJECTIVE AND SCOPE

This test standard describes the method to assess the flammability of products emerging from aerosol dispensers due to their propensity to ignite in an enclosed or confined space.

PRINCIPLE

The contents of an aerosol dispenser are sprayed into a cylindrical test vessel containing a burning candle. If an observable ignition occurs, the elapsed time and amount discharged is noted.

GENERAL REQUIREMENTS

Before testing, each aerosol dispenser should be conditioned and then primed by discharging for approximately 1 second. The purpose of this action is to remove non-homogeneous material from the diptube.

Follow strictly the instructions of use, including whether the dispenser is intended to be used in the upright or inverted position. When shaking is required, shake immediately before testing.

The tests should be carried out in a draught-free environment capable of ventilation, with the temperature controlled at $20 \, ^{\circ}\text{C} \pm 5 \, ^{\circ}\text{C}$ and relative humidity in the range 30 - 80%.

EQUIPMENT AND APPARATUS

 $\begin{array}{lll} \hbox{Chronometer (stopwatch)} & \mbox{accurate to} \pm 0.2 \ s \\ \hbox{Water bath maintained at 20 °C} & \mbox{accurate to} \pm 1 \ ^{\circ} C \\ \hbox{Calibrated laboratory scales (balance)} & \mbox{accurate to} \pm 0.1 \ g \\ \hbox{Thermometer} & \mbox{accurate to} \pm 1 \ ^{\circ} C \\ \hbox{Hygrometer} & \mbox{accurate to} \pm 5\% \\ \hbox{Pressure gauge} & \mbox{accurate to} \pm 0.1 \ bar \\ \hbox{Cylindrical test vessel} & \mbox{as detailed below} \\ \end{array}$

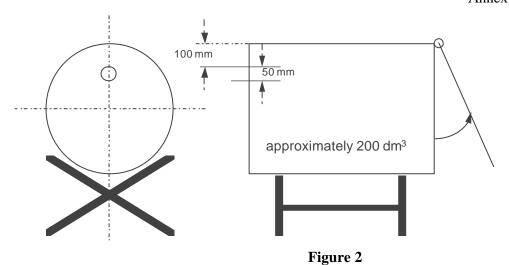
PREPARATION OF TEST APPARATUS

A cylindrical vessel approximately 200 dm³ (55 gallons) volume, approximately 600 mm in diameter and approximately 720 mm long and open at one end should be modified as follows:

- A closure system consisting of a hinged cover should be matched to the open end of the receptacle, or;
- A plastic film 0.01 to 0.02 mm thick may be used as a closure system. If the test is carried out with a plastic film this must be used as described below:

Stretch the film over the open end of the drum and hold it in place with an elastic band. The strength of the band should be such that when placed around the drum resting on its side, it stretches by only 25 mm when a mass of 0.45 kg is attached to its lowest point. Cut a 25 mm slit in the film, starting 50 mm from the edge of the drum. Ensure that the film is taut.

At the other end of the drum drill a 50 mm diameter hole 100 mm from the edge in such a way that the orifice is uppermost when the receptacle is laid down and ready for the test (Figure 2).



On a 200 x 200 mm metal support place a paraffin wax candle 20 to 40 mm in diameter and 100 mm high. The candle shall be replaced when having a height of less than 80 mm. The candle's flame is protected from the action of the spray by a 150 mm wide, 200 mm high deflector. This includes the plane inclined at 45° produced 150 mm from the base of the deflector (Figure 3).

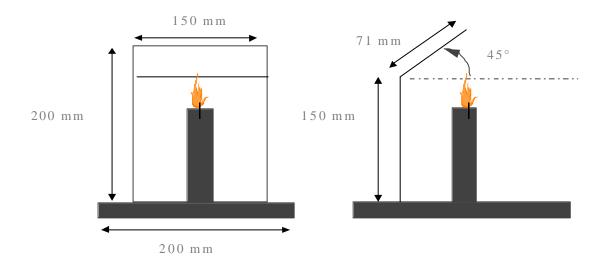


Figure 3

The candle placed on the metal support should be positioned midway between the two ends of the drum (Figure 4).

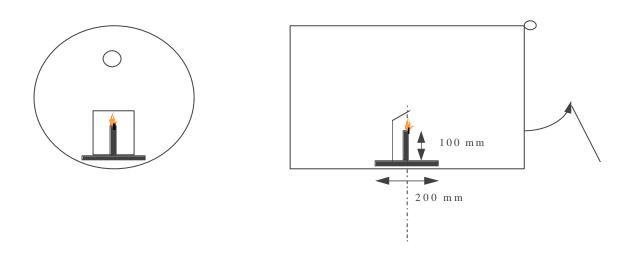


Figure 4

The drum is laid on the ground or on a support at a spot where the temperature is between 15 $^{\circ}$ C and 25 $^{\circ}$ C. The product to be tested will be sprayed within the drum of roughly 200 dm³ in which there will be a source of ignition.

Usually, the product leaves the aerosol can at an angle of 90° relevant to the vertical axis of the can. The layout and procedure described refers to this kind of aerosol product. In the case of unusually operating aerosols (e.g. vertical-spray aerosol dispensers) it will be necessary to record changes to equipment and procedures in accordance with GLP, such as ISO/IEC 17025:1999, General requirements for the competence of testing and calibration laboratories.

TEST PROCEDURE

- (a) A minimum of 3 full aerosol dispensers per product shall be conditioned to $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$ in a water bath with at least 95% of the dispenser immersed in the water for at least 30 minutes (if the aerosol is fully immersed, 30 minute conditioning is sufficient).
- (b) Measure or calculate the actual volume of the drum in dm³.
- (c) Comply with general requirements. Record the temperature and relative humidity of the environment.
- (d) Determine the internal pressure and initial discharge rate at 20 °C \pm 1 °C (to eliminate faulty or partly filled aerosol dispensers).
- (e) Weigh one of the aerosol dispensers and note its mass.

- (f) Light the candle and apply the closure system (cover or plastic film).
- (g) Place the aerosol dispenser actuator orifice 35 mm or closer for a wide spray product, from the centre of the entrance hole in the drum. Start the chronometer (stopwatch) and following the instructions for use of the product; direct the spray towards the centre of the opposite extremity (cover or plastic film). The aerosol should be tested in the position it is designed to be used, e.g. upright or inverted.
- (h) Spray until ignition occurs. Stop the chronometer and note the time elapsed. Re-weigh the aerosol dispenser and note its mass.
- (i) Ventilate and clean the drum removing any residue likely to affect subsequent tests. Allow the drum to cool if necessary.
- (j) Repeat the test procedure steps (d) to (i) for another two aerosol dispensers of the same product (3 in total, note: each dispenser is only tested once).

REMARKS

The test report must include the following information:

- The product tested and its references
- The internal pressure and discharge rate of the aerosol dispenser
- The temperature and relative air humidity of the room
- For each test, the discharge time (seconds) needed to achieve ignition (if the product does not ignite, state this)
- The mass of the product sprayed during each test, expressed in g
- The actual volume of the drum (expressed in dm³).

The time equivalent (t_{eq}) needed to achieve ignition in one cubic metre can be calculated where:

 $t_{eq} = \frac{1000 \text{ x discharge time (s)}}{\text{Actual volume of drum (dm}^3)}$

The deflagration density (D_{def}) needed to achieve ignition during the test may also be calculated where

 $D_{def} = \frac{1000 \text{ x Amount of product dispensed (g)}}{\text{Actual volume of drum (dm}^3)}$

Aerosol foam flammability test

OBJECTIVE

This test standard describes the method to determine the flammability of an aerosol spray emitted in the form of a foam, mousse, gel or paste.

PRINCIPLE

An aerosol, which emits a foam, mousse, gel or paste is sprayed (approx. 5 grams) on a watchglass and an ignition source (candle, wax taper, match or lighter) is placed at the base of the watchglass to observe if ignition and sustained combustion of the foam, mousse, gel or paste occurs.

Ignition is defined as a stable flame maintained for at least 2 seconds and a minimum 4 cm in height.

SCOPE

This method can be used for aerosols that are emitted in the form of a foam, mousse, gel or paste.

GENERAL REQUIREMENTS

Before testing, each aerosol dispenser should be conditioned and then primed by discharging for approximately 1 second. The purpose of this action is to remove non-homogeneous material from the diptube.

Follow strictly the instructions of use, including whether the dispenser is intended to be used in the upright or inverted position. When shaking is required, shake immediately before testing.

The tests must be carried out in a draught-free environment capable of ventilation, with the temperature controlled at 20 °C \pm 5 °C and relative humidity in the range of 30 – 80%.

gradations in cm

EQUIPMENT AND APPARATUS

Graduated scale, support and clamp

Fire-resistant watchglass roughly 150 mm in diameter	-
Chronometer (stopwatch)	accurate to $\pm 0.2 \text{ s}$
Candle, wax taper, match or lighter	
Calibrated laboratory scales (balance)	accurate to ± 0.1 g
Water bath maintained at 20 °C	accurate to ± 1 °C
Thermometer	accurate to ± 1 °C
Hygrometer	accurate to \pm 5%
Pressure gauge	accurate to ± 0.1 bar

The watchglass is placed on a fire-resistant surface within a draught-free area that may be ventilated after each test. The graduated scale is positioned exactly behind the watchglass and held vertically by means of a support and clamp.

The scale is positioned in such a way that its origin is on a level with the watchglass base in a horizontal plane.

TEST PROCEDURE

- (a) A minimum of four full aerosol dispensers per product shall be conditioned to $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$ with at least 95% of the dispenser immersed in the water for at least 30 minutes before each test (if the aerosol is fully immersed, 30 minute conditioning is sufficient).
- (b) Comply with general requirements. Record the temperature and relative humidity of the environment.
- (c) Determine the internal pressure at $20 \,^{\circ}\text{C} \pm 1 \,^{\circ}\text{C}$ (to eliminate faulty or partly filled aerosol dispensers).
- (d) Measure the discharge or flow rate of the aerosol product to be examined, so that the amount of test product dispensed can be more accurately gauged.
- (e) Weigh one of the aerosol dispensers and note its mass.
- (f) On the basis of the measured discharge or flow rate and following the manufacturer's instructions, release approximately 5 g of the product onto the centre of the clean watchglass with the aim of producing a mound no higher than 25 mm.
- (g) Within 5 seconds of completion of discharge, apply the source of ignition to the edge of the sample at its base and at the same time start the chronometer (stopwatch). If necessary, the ignition source should be removed from the edge of the sample after approximately two seconds, in order to clearly observe if ignition has occurred. If no ignition of the sample is apparent, the ignition source should be reapplied to the edge of the sample.
- (h) If ignition occurs note the following points:
 - The maximum height of the flame in cm above the base of the watchglass
 - The flame duration in seconds
 - Dry and re-weigh the aerosol dispenser and calculate the mass of the released product.
- (i) Ventilate the test area immediately after each test.
- (j) If ignition is not obtained and the released product remains in the form of a foam or paste throughout its period of use, steps (e) to (i) should be repeated. Allow the product to stand for 30 sec, 1 min, 2 min or 4 min before applying the ignition source.
- (k) Repeat the test procedure steps (e) to (j) twice more (a total of 3) for the same can.
- (l) Repeat the test procedure steps (e) to (k) for another two aerosol cans (3 cans in total) of the same product.

REMARKS

The test report should include the following information:

- whether the product ignites
- maximum flame height in cm
- duration of flame in seconds
- the mass of the product tested.