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GUIDANCE DOCUMENT FOR FLAMMABILITY TESTING OF PLANT PROTECTION AND BIOCIDAL PRODUCTS

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GUIDANCE DOCUMENT FOR FLAMMABILITY TESTING OF PLANT PROTECTION AND BIOCIDAL PRODUCTS

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Foreword

This Guidance Document provides guidance and practical advice for applicants on the requirements for flammability testing of biocides and agricultural pesticides/plant protection products in various OECD jurisdictions. Though many of the available methods are common they can differ in small but important ways. Thus a summary of parameters can help an applicant ensure their data set is viable in all OECD countries, thereby saving resources for both the applicant and the receiving government.

The document was developed by the Expert Group on Biocide Chemistry (EGBC) of the Working Group on Biocides (WGB) under the leadership of the Netherlands and benefitted from further review by the WGB, the Working Group of National Coordinators of the Test Guidelines Programme (WNT) and the Working Group on Pesticides (WGP) in November 2018.

This Guidance Document was approved by the Working Group on Biocides, the Working Group of National Coordinators of the Test Guidelines Programme and the Working Group on Pesticides on 23 September 2020. The Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology agreed to its declassification on 14 December, 2020.

This document is published under the responsibility of the Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology.

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GUIDANCE DOCUMENT FOR FLAMMABILITY TESTING OF PLANT PROTECTION AND BIOCIDAL PRODUCTS

1. INTRODUCTION

1. This guidance document cites various testing procedures for the determination of flammability of plant protection and biocidal products. These testing procedures do not necessarily generate the same measure or classification of flammability. The data generated by the various procedures is required for determining the correct labelling and appropriate conditions for storage, use and transport of the products. Agencies responsible for regulations related to the transport and storage of flammable products may specify flammability testing procedures and classification beyond the scope of this document. The definitions used throughout this guidance document are as per the Globally Harmonised System (GHS).
2. This guidance document outlines the differences and similarities in flammability testing and reporting requirements among various regulatory jurisdictions and, where appropriate, identifies common characteristics or requirements among those jurisdictions, and harmonizes methodology among guidelines where possible.
3. Procedures for determining flammability are frequently the work product of national and international standardizing bodies and are often cited in statutes by governmental agencies for flammability classification. No attempt to circumvent these statutes is proposed in this document.

Note 1: The terms “active ingredient”, “active substance” and “active constituent” are used in different jurisdictions. These three terms are considered equivalent and valid for purposes of this guidance document.

Note 2: The terms “product”, “mixture”, “preparation” and “formulation” are also used in different jurisdictions. These four terms are considered to be equivalent for the purposes of this guidance document.

4. Tests on physico-chemical properties and safety-relevant substance data should be performed at least according to international standards. Some jurisdictions required the data to be performed according to Good Laboratory Practices. Of particular importance is the reporting of results: Identification of the method or standard used and information on specific test conditions and the test item, such as purity, particle size, water content,

which may have an influence on the test results, should be stated in the study report in order to allow for correct interpretation of the test results.

2. FLAMMABLE GASES

5. A *flammable gas* is a gas having a flammable range with air at 20 °C and a standard pressure of 101.3 kPa. A *pyrophoric gas* is a flammable gas that is liable to ignite spontaneously in air at a temperature of 54 ºC or below. A *chemically unstable gas* is a flammable gas that is able to react explosively even in the absence of air or oxygen. A flammable gas is classified in Category 1A, 1B or 2 according to the following Table 1. Flammable gases that are pyrophoric and/or chemically unstable are always classified in Category 1A.

Table 1. Classification criteria for flammable, pyrophoric and chemically unstable gases according to the Globally Harmonized System in 2019 (GHS, 2019)

Category			Signal word	Hazard statement	Classification Criteria
1A	Flammable gas		Danger	Extremely flammable gas	Gases, which at 20 °C and a standard pressure of 101.3 kPa: are ignitable when in a mixture of 13% or less by volume in air; or have a flammable range with air of at least 12 percentage points regardless of the lower flammability limit. unless data shows them to meet the criteria of category 1B
	Pyrophoric gas		Danger	Extremely flammable gas. May ignite spontaneously if exposed to air	Flammable gases that ignite spontaneously in air at a temperature of 54 ºC or below
	Chemically unstable gas	A	Danger	Extremely flammable gas. May react explosively even in the absence of air	Flammable gases which are chemically unstable at 20 °C and a standard pressure of 101.3 kPa
		B	Danger	Extremely flammable gas. May react explosively even in the absence of air at elevated pressure and/or temperature	Flammable gases which are chemically unstable at a temperature greater than 20 °C and/or a pressure greater than 101.3 kPa
1B	Flammable gas		Danger	Flammable gas	Gases which meet the flammability criteria for Category 1A, but which are not pyrophoric, nor chemically unstable, and which have at least either: A lower flammability limit of more than 6% by volume in air; or A fundamental burning velocity of less than 10 cm/s.
2	Flammable gas		Warning	Flammable gas	Gases, other than those of Category 1A or 1B, which, at 20 °C and a standard pressure of 101.3 kPa, have a flammable range while mixed in air.

6. Procedures to determine the flammability of a gas are described in standardized test guidelines. All procedures involve testing the flammability of a specific gas-air mixture (well mixed but not continuously stirred) using an electric spark. Starting from very low concentrations the gas concentration is incrementally increased until flammability occurs (the lower flammability limit is reached). Starting from very high concentrations

the concentration is incrementally decreased until flammability occurs again (the upper flammability limit is reached). The ISO 10156 flammability method also describes methodology to estimate upper and lower flammability limits of gases.

Table 2. Flammable Gas Testing Guidelines for Plant Protection and Biocidal Products

Jurisdiction/Agency	Classification Criteria	Test Method
FAO/WHO	Guideline on Good Labelling Practice for Pesticides, , WHO/FAO 2015	Not Specified
USEPA	None	None*
EU	CLP Regulation, section 2.2.2 of Annex I	EN 1839, ISO 10156 or ISO 817 as amended Chemical instability of gases: UN-MTC Part III, sub-section 35.4 Pyrophoricity: IEC 60079-20-1 ed1.0** or DIN 51794
APVMA	Australian Dangerous Goods Code, Edition 7.3, National Transportation Commission, Melbourne, Australia, August 2014, Chapter 2.2.	None identified.
PMRA	None	None
Globally Harmonised System	Table 1	ISO 10156 Burning velocity: ISO 817, Annex C Chemical instability of gases: UN-MTC Part III, sub-section 35.4 Pyrophoricity: IEC 60079-20-1 ed1.0** or DIN 51794

* ASTM E681 is cited in the United States Code of Federal Regulations (49CFR173.115) as a test for the classification of a flammable gas related to transportation.

** IEC 60079-20-1 ed1.0 has been replaced by ISO/IEC 80079-20-1:2017.

3. FLAMMABLE LIQUIDS

7. A *flammable liquid* means a liquid having a flash point of not more than 93 °C as follows:

Table 3. Flammable Liquid Classification

Category	Signal word	Hazard statement	Classification criteria*	
			Globally Harmonized System (GHS, 2019)	40 CFR 156.78
1	Danger	Extremely flammable liquid and vapour	Flash point < 23 °C and initial boiling point ≤ 35 °C	Flash point at or below 20 °F(-6.7 °C)
2	Danger	Highly flammable liquid and vapour	Flash point < 23 °C and initial boiling point > 35 °C	Not defined
3	Warning	Flammable liquid and vapour	Flash point ≥ 23 °C and ≤ 60 °C **	Flash point > 20 °F (- 6.7 °C) & ≤ 80 °F (26.7 °C)
4†	Warning	Combustible liquid	Flash point > 60 °C and ≤ 93 °C	Flash point > 80 °F (26.7 °C) & < 150 °F (65.6 °C)

* ASTM D86, ASTM D1078, ISO 3924, ISO 4626, ISO 3405 and A.2 (Part A of the Annex to Regulation (EC) No 440/2008) provide methods for determining the initial boiling point of flammable liquids.

** Liquids with a flash point of more than 35 °C and not more than 60 °C may be regarded as non-flammable liquids for some regulatory purposes (e.g. transport) if negative results have been obtained in the sustained combustibility test L.2 of Part III, section 32 of the *Manual of Tests and Criteria" (ST/SG/AC.10/11/Rev.7)*.

† Category 4 is not part of the CLP regulation.

8. *Flash point* is the lowest temperature of a flammable liquid, corrected to 101.3 kPa, at which – under defined test conditions – the vapour phase of the sample is ignited by the test flame and the flame propagates across the surface of the sample. In general, the liquid test item is heated in a closed cup and the headspace vapour-air mixture thus produced is periodically exposed to a source of ignition to ascertain if it is ignitable.

9. There are a number of closed-cup flash point procedures specified by agencies for classifying combustible liquids. OCSPP 830.6315 and the Globally Harmonized System (GHS, 2019) Chapter 2.6 list standardized procedures to determine the flash point of a liquid based on the physical properties of the liquid under test.

Table 4. Summary of Closed-Cup Flash Point Methods

Method/Apparatus	Flash Point Range*	Notes
Abel Closed Cup (ISO 13736,	-30 °C to 75 °C	For petroleum liquids and mixtures. Some apparatus allow flash point determination up to 100 °C while others limit the determination to a range between -8.5 °C and 70 °C
Abel-Pensky Closed Cup (DIN 51755- Part 1, NF M07-036)	5 °C to 65 °C	
Tag (Tagliabue) Closed Cup (ASTM D56)	Ambient to < 93 °C	Viscosity < 5.5 mm2/s at 40 ºC, or < 9.5 mm2/s at 25 ºC
Setaflash Closed Cup (ASTM D3828, ASTM D3278, ISO 3679, ISO 3680**, ISO 1516, ISO 1523)	0 °C to 300 °C	Viscosity < 150 St at 25 °C
Pensky-Martens Closed Cup (ASTM D93†, ISO 2719).	40 °C to 360 °C	Part A: stirring at 115 RPM Part B: stirring at 250 RPM

* There is variation among manufacturers of flash point apparatus with features such as ancillary cooling and "extended range."

** ISO 3680:2004 was withdrawn and replaced by ISO 3679:2015.

† ASTM D6450 a continuously closed cup method, or D7094, a modified continuously closed cup method, have been allowed to replace ASTM D93 in some jurisdictions.

10. Remark on evaluation of flash point studies: For mutual recognition on test data it is important that the international standard for determining the flash point of flammable liquids is indicated in the test report, such as the apparatus (e.g. Pensky-Martens cup), the procedure applied and the publication date of the standard. For classification purposes, it is recommended to use the mean of at least two test runs. The result of the mean flash point, in degrees Celsius and corrected to a pressure of 101.3 kPa, and the type of sample and all the information necessary for a clear identification of the sample examined, must be included in the test report. When the flash point, determined by a non-equilibrium method is found to be 23 ± 2 °C or 60 ± 2 °C, it shall be confirmed for each temperature range by an equilibrium method to avoid any dispute to the classification of a flammable liquid.

Table 5. Flammable Liquid Testing Guidelines for Plant Protection and Biocidal Products

Jurisdiction/Agency	Classification Criteria	Non-Equilibrium Methods	Equilibrium Methods
FAO/WHO	Guideline on Good Labelling Practice for Pesticides, WHO/FAO 2015	Not Specified	Not Specified
USEPA	Part 40, Code of Federal Regulations, Section 156.78.	OCSPP 830.6315: ASTM D3828, ASTM D56, ASTM D3278, ASTM D93, CIPAC MT-12	Not Specified
EU	CLP Regulation, section 2.6.2 of Annex I	ASTM D3828*, ASTM D56*, ASTM D3278*, ASTM D93*, DIN 51755, ISO 2719, ISO 13736, NF M07-036,	ISO 1516, ISO 1523, ISO 3679, ISO 3680,
APVMA	Australian Dangerous Goods Code, Edition 7.3, National Transportation Commission, Melbourne, Australia, August 2014, Chapter 2.3.	AS 2106, ASTM D3828, ASTM D56, ASTM D3278, ASTM D93, DIN 51755, ISO 2719, ISO 13736, NF M07-011, NF M07- 019, NF M07-036, NF T 30-050	ISO 1516, ISO 1523, ISO 3679, ISO 3680,
PMRA	Harmonized with USEPA	ASTM D3828, ASTM D56, ASTM D3278, ASTM D93, CIPAC MT-12	Not Specified
Globally Harmonised System	Table 3	ISO 2719, ISO 13736, ASTM D3828-07a, ASTM D56-05, ASTM D3278-96(2004)e1, ASTM D93-08, NF M 07 – 019, NF M 07 - 011 / NF T 30 - 050 / NF T 66 – 009, NF M 07 – 036, DIN 51755, GOST 12.1.044-84	ISO 1516, ISO 1523, ISO 3679, ISO 3680

* Standard not cited in the CLP-Regulation, but in EU transport regulations (e.g. ADR)

4. FLAMMABLE SOLIDS

11. A *flammable solid* is a solid which is readily combustible, or may cause or contribute to fire through friction. *Readily combustible solids* are powdered, granular, or pasty substances which are dangerous if they can be easily ignited by brief contact with an ignition source, such as a burning match, and if the flame spreads rapidly.

12. A flammable solid is classified in one of the two categories for this class using Method N.1 as described in Part III, sub-section 33.2.4 of the Manual of Tests and Criteria, according to the following table:

Table 6. Flammable Solid Classification According to the Globally Harmonized System (GHS, 2019)

Category	Signal Word	Hazard statement	Classification criteria
1	Danger	Flammable solid	Burning rate test (100 mm): Substances or mixtures other than metal powders: wetted zone does not stop fire; and burning time < 45 s or burning rate > 2.2 mm/s Metal powders: burning time ≤ 5 min
2	Warning	Flammable solid	Burning rate test (100 mm): Substances or mixtures other than metal powders: wetted zone stops the fire for at least 4 min; and burning time < 45 s or burning rate > 2.2 mm/s Metal powders: burning time > 5 min and ≤ 10 min

Table 7. Flammable Solid Testing Guidelines for Plant Protection and Biocidal Products

Jurisdiction/Agency	Classification Criteria	Test Method
FAO/WHO	Guideline on Good Labelling Practice for Pesticides, , WHO/FAO 2015	Not Specified
USEPA	None	None
EU	CLP Regulation, section 2.7.2 of Annex I	UN Test N.1*
APVMA	Australian Dangerous Goods Code, Edition 7.3, National Transportation Commission, Melbourne, Australia, August 2014, Chapter 2.3.	UN Test N.1*
PMRA	None	None
Globally Harmonised System	Table 6	UN Test N.1*

*Test N.1: “Test method for readily combustible solids” as described in Part III, sub-section 33.2.4 of the *Manual of Tests and Criteria*, 2019.

5. AEROSOLS

13. Aerosols, this means aerosol dispensers, are any non-refillable receptacles made of metal, glass or plastics and containing a gas compressed, liquefied or dissolved under pressure, with or without a liquid, paste or powder, and fitted with a release device allowing the contents to be ejected as solid or liquid particles in suspension in a gas, as a foam, paste or powder or in a liquid state or in a gaseous state.

Table 8. Aerosol Classification

Category	Signal Word	Hazard statement	Classification Criteria	
			Globally Harmonized System	40 CFR 156.78*
1	Danger	Extremely flammable aerosol Pressurized container: May burst if heated	Aerosols whose content of flammable components (by mass) is 85% or more and whose heat of combustion is 30 kJ/g or larger, or Spray aerosols for which ignition occurs at a distance of 75 cm or more in the flame distance (ignition distance) test, or Foam aerosols which have, in the foam test, a flame height of 20 cm or more and a flame duration of 2 seconds or longer or a flame height of 4 cm or more and a flame duration of 7 seconds or longer.	Flash point at or below 20 °F (-7 °C) or if there is a flashback at any valve opening†
2	Warning	Flammable aerosol Pressurized container: May burst if heated	Spray aerosols for which the heat of combustion is 20 kJ/g or larger and either for which ignition occurs at a distance of 15 cm or more in the flame distance (ignition distance) test or for which the time equivalent is 300 s/m^3 or less, or the deflagration density is 300 g/m^3 or less, in the enclosed space ignition test, Foam aerosols which have, in the foam test, a flame height of 4 cm or more and a flame duration of 2 seconds or longer.	Flash point above 20 °F (- 7 °C) to 80 °F (27 °C) or if the flame extension is greater than 18 inches long at a distance of 6 inches from the flame†
3	Warning	Pressurized container: May burst if heated	Aerosols whose content of flammable components is 1% or less and the heat of combustion is less than 20 kJ/g, or Spray aerosols which are not classified in Category 1 or 2 in the enclosed space ignition test Foam aerosols which are not classified in Category 1 or 2 in the foam test.	

* There is another category called “Total Release Fogger Products”. These are defined as a pesticide product in a pressurized container designed to automatically release the total contents in one operation, for the purpose of creating a permeating fog within confined space to deliver the pesticide throughout the space. A separate warning along with graphic symbol is required on the product label for such products.

† OPPTS 830.6315 Flammability, states that the flash point method is inadequate for determining the flammability of aerosols.

14. Procedures to test the flammability of an aerosol are described in standardized test guidelines listed in Table 9. These consist of testing for flammability of an aerosol spray at a distance from a source of ignition (ASTM D-3065 or UN Tests) as described in Part III, sub-sections 31.4 (Ignition distance test for spray aerosols), 31.5 (Enclosed space ignition test) and 31.6 (Aerosol foam flammability test) of the Manual of Tests and Criteria, 2019.

Table 9. Flammable Aerosol Testing Guidelines for Plant Protection and Biocidal Products

Jurisdiction/Agency	Classification Criteria	Test Method
FAO/WHO	Guideline on Good Labelling Practice for Pesticides, WHO/FAO 2015	Not Specified
USEPA	Part 40 of the Code of Federal Regulations, Section 156.78	ASTM D-3065*
EU	CLP Regulation, section 2.3.2 of Annex I	UN-MTC, Part III, sub-sections 31.4, 31.5, 31.6.
APVMA	Australian Dangerous Goods Code, Edition 7.3, National Transportation Commission, Melbourne, Australia, August 2014, Chapter 2.2.	ISO 10156
PMRA	Harmonized with USEPA	ASTM D-3065
Globally Harmonised System	Table 8	Table 10

* 40CFR158 (*i.e.* FIFRA) “Data Requirements for Pesticides” via OCSPP 830.6315 specifies test method ASTM D-3065 however, 6CFR1500.3(c)(6) (i.e. Hazardous Substances Control Act) specifies test method 16CFR1500.45. There are differences between ASTM D-3065 and 16CFR1500.45: (a) ASTM D-3065 specifies that the container should be conditioned to 70 ° F ± 1 ° F and shaken prior to the flame projection test. 16 CFR 1500.45 does not include these parameters. (b) ASTM D-3065 specifies a spray time of 4 seconds while 16 CFR 1500.45 specifies a spray time of 15 to 20 seconds.

15. A harmonized procedure to test the flammability of an aerosol is described in Table 10.

Table 10. Aerosol Flammability Test Parameters

Test Parameter	UN Method: 31.4 Ignition distance test for spray aerosols	EPA Method (D3065 ASTM Method)	New Proposal for a Harmonized Method
Source of Ignition	Gas Flame	Candle	Gas Flame
Spray timing	At least 5 sec	4 sec	5 sec
General requirements	The test shall be carried out in a draught-free environment capable of ventilation, with the temperature controlled at 20 °C ± 5 °C and relative humidity in the range 30 - 80%.		The test shall be carried out in a draught-free environment capable of ventilation, with the temperature controlled at 20 °C ± 5 °C and relative humidity in the range 30 - 80%.
Conditioning Temp	A minimum of 3 full aerosol dispensers per product shall be conditioned to 20 °C ± 1 °C with at least 95% of the dispenser immersed in the water for at least 30 min before each test (if the aerosol is fully immersed, 30 min conditioning is sufficient).	21 ± 0.5 ˚C	A minimum of 3 full aerosol dispensers per product shall be conditioned to 20 °C ± 1 °C with at least 95% of the dispenser immersed in the water for at least 30 min before each test (if the aerosol is fully immersed, 30 min conditioning is sufficient).
Agitation of Contents	The instructions of use shall be strictly followed, including whether the dispenser is intended to be used in the upright or inverted position. When shaking is required, shake immediately before testing.	Shake the dispenser, and hold it upright unless the label states otherwise.	The instructions of use shall be strictly followed, including whether the dispenser is intended to be used in the upright or inverted position. When shaking is required, shake immediately before testing.
Priming of actuator	Before testing, each aerosol dispenser shall be conditioned and then primed by discharging for approximately 1 s. The purpose of this action is to remove non-homogeneous material from the dip tube.	NA	Before testing, each aerosol dispenser shall be conditioned and then primed by discharging for approximately 1 s. The purpose of this action is to remove non-homogeneous material from the dip tube.
Ignition distance (between actuator and flame)	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 shall be increased by 15 cm	15 cm only	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

	in the case of an ignition of the spray at 60 cm distance. The distance shall 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.		aerosol's actuator.15 cm and 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 shall be increased by 15 cm in the case of an ignition of the spray at 60 cm distance. The distance shall be decreased by 15 cm in the case of no ignition at 60 cm distance between burner flame and aerosol actuator.
Repetitions	At distance ignition occurs or at 15 cm, 3 full samples are tested 3 times each for a total of 9 repetitions	1 sample is tested 3 times at 15 cm distance whether flame extension occurs or not	If flame extension occurs at 15 cm, 3 full samples are tested 3 times each; if flame extension occurs at a greater distance, 3 samples/3 reps each will be tested at that distance as well as 1 sample, tested 3 times at 15 cm
Reported Results*	Note the ignition results (Y/N) for the distance between the gas burner and the aerosol dispenser, in a range of 15 cm to 90 cm.*	Distance of flame extension from actuator at 15 cm	Note the ignition results (Y/N) for the distance between the gas burner and the aerosol dispenser, in a range of 15 cm to 90 cm and length of flame extension at 15 cm.
Other	NA	Flashback noted for report	Flashback noted for report

* Table 31.4 in UN Method 31.4 'Ignition distance test for spray aerosols', is a model for a "result table"

6. PYROPHORIC LIQUIDS and SOLIDS

16. A *pyrophoric* liquid or solid is a substance or mixture, which, even in small quantities, is liable to ignite within five minutes after coming into contact with air.

Table 11. Pyrophoric liquids and solids Classification According to the Globally Harmonized System

Category	Signal Word	Hazard statement	Classification Criteria
1	Danger	Catches fire spontaneously if exposed to air	The solid ignites within 5 minutes of coming into contact with air.* The liquid ignites within 5 minutes when added to an inert carrier and exposed to air, or it ignites or chars a filter paper on contact with air within 5 minutes.†

*Test N.2: "Test method for pyrophoric solids," as described in Part III, sub-sections 33.4.4 of the *Manual of Tests and Criteria,* 2019.

† Test N.3: "Test method for pyrophoric liquids," as described in Part III, sub-sections 33.4.5 of the *Manual of Tests and Criteria,* 2019.

Table 12. Pyrophoric Substances Testing Guidelines for Plant Protection and Biocidal Products

Jurisdiction/Agency	Classification Criteria	Test Method
FAO/WHO	None	None
USEPA	None	None
EU	CLP Regulation, section 2.9.2 and 2.10.2 of Annex I	Solids: UN Test N.2* Liquids: UN Test N.3†
APVMA	Australian Dangerous Goods Code, Edition 7.3, National Transportation Commission, Melbourne, Australia, August 2014, Chapter 2.4.3	Solids: UN Test N.2* Liquids: UN Test N.3†
PMRA	None	None
Globally Harmonised System	Table 11	Solids: UN Test N.2* Liquids: UN Test N.3†

*Test N.2: "Test method for pyrophoric solids," as described in Part III, sub-sections 33.4.4 of the *Manual of Tests and Criteria,* 2019.

† Test N.3: "Test method for pyrophoric liquids," as described in Part III, sub-sections 33.4.5 of the *Manual of Tests and Criteria,* 2019.

7. SELF-HEATING SUBSTANCES and MIXTURES

17. A *self-heating substance* or mixture is a solid or liquid substance or mixture, other than a pyrophoric liquid or solid, which, by reaction with air and without energy supply, is liable to self-heat; this substance or mixture differs from a pyrophoric liquid or solid in that it will ignite only when in large amounts (kilograms) and after long periods of time (hours or days).

Table 13. Self-Heating Substances and mixtures Classification According to the Globally Harmonized System.

Category	Signal Word	Hazard statement	Classification Criteria*
1	Danger	Self-heating; may catch fire	A positive result is obtained in a test using a 25 mm sample cube at 140 °C
2	Warning	Self-heating in large quantities; may catch fire.	A positive result is obtained in a test using a 100 mm sample cube at 140 °C and a negative result is obtained in a test using a 25 mm cube sample at 140 °C and the substance or mixture is to be packed in packages with a volume of more than 3 m^3; or A positive result is obtained in a test using a 100 mm sample cube at 140 °C and a negative result is obtained in a test using a 25 mm cube sample at 140 °C, a positive result is obtained in a test using a 100 mm cube sample at 120 °C and the substance or mixture is to be packed in packages with a volume of more than 450 litres; or A positive result is obtained in a test using a 100 mm sample cube at 140 °C and a negative result is obtained in a test using a 25 mm cube sample at 140 °C and a positive result is obtained in a test using a 100 mm cube sample at 100 °C.

*Test N.4: "Test method for self-heating substances" as described in Part III, sub-section 33.4.6 of the *Manual of Tests and Criteria,* 2019.

Table 14. Self-Heating Substances and Mixtures Testing Guidelines for Plant Protection and Biocidal Products

Jurisdiction/Agency	Classification Criteria	Test Method
FAO/WHO	None	None
USEPA	None	None
EU	CLP Regulation, section 2.11.2 of Annex I	UN Test N.4*
APVMA	Australian Dangerous Goods Code, Edition 7.3, National Transportation Commission, Melbourne, Australia, August 2014, Chapter 2.4.3	UN Test N.4*
PMRA	None	None
Globally Harmonised System	Table 13	UN Test N.4*

*Test N.4: "Test method for self-heating substances," as described in Part III, sub-sections 33.4.6 of the *Manual of Tests and Criteria,* 2019.

8. SUBSTANCES AND MIXTURES WHICH, IN CONTACT WITH WATER, EMIT FLAMMABLE GASES

18. Substances or mixtures which, in contact with water, emit flammable gases are solid or liquid substances or mixtures which, by interaction with water, are liable to become spontaneously flammable or to give off flammable gases in dangerous quantities.

Table 15. Substances and mixtures, which, in contact with water, emit flammable gases according to the Globally Harmonized System

Category	Signal Word	Hazard statement	Classification Criteria*
1	Danger	In contact with water releases flammable gases which may ignite spontaneously.	Any substance or mixture which reacts vigorously with water at ambient temperatures and demonstrates generally a tendency for the gas produced to ignite spontaneously, or which reacts readily with water at ambient temperatures such that the rate of evolution of flammable gas is equal to or greater than 10 litres per kilogram of substance over any one minute.
2	Danger	In contact with water releases flammable gases	Any substance or mixture which reacts readily with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 20 litres per kilogram of substance per hour, and which does not meet the criteria for category 1.
3	Warning	In contact with water releases flammable gases.	Any substance or mixture which reacts slowly with water at ambient temperatures such that the maximum rate of evolution of flammable gas is greater than 1 litre per kilogram of substance per hour, and which does not meet the criteria for categories 1 and 2.

*Test N.5: "Test method for substances which in contact with water emit flammable gases," as described in Part III, sub-section 33.5.4 of the *Manual of Tests and Criteria,* 2019.

Table 16. Water-Reactive Substances Testing Guidelines for Plant Protection and Biocidal Products

Jurisdiction/Agency	Classification Criteria	Test Method
FAO/WHO	None	None
USEPA	None	None
EU	CLP Regulation, section 2.12.2 of Annex I	UN Test N.5.*
APVMA	Australian Dangerous Goods Code, Edition 7.3, National Transportation Commission, Melbourne, Australia, August 2014, Chapter 2.4.4	UN Test N.5.*
PMRA	None	None
Globally Harmonised System	Table 15	UN Test N.5.*

*Test N.5: "Test method for substances which in contact with water emit flammable gases," as described in Part III, sub-section 33.5.4 of the *Manual of Tests and Criteria,* 2019.

9. SELF-REACTIVE SUBSTANCES and MIXTURES

19. *Self-reactive substances or mixtures* are thermally unstable liquid or solid substances or mixtures liable to undergo a strongly exothermic decomposition even without participation of oxygen (air). This definition excludes substances and mixtures classified under the GHS as explosives, organic peroxides or as oxidizing. A self-reactive substance or mixture is regarded as possessing explosive properties when in laboratory testing the formulation is liable to detonate, to deflagrate rapidly or to show a violent effect when heated under confinement.

Table 17. Self-Reactive Substances and Mixtures Classification Criteria According to Globally Harmonized System

Self-reactive substances and mixtures are classified in one of the seven categories of “types A to G” for this class, according to the following principles:

a) Any self-reactive substance or mixture which can detonate or deflagrate rapidly, as packaged, will be defined as **self-reactive substance TYPE A**;
b) Any self-reactive substance or mixture possessing explosive properties and which, as packaged, neither detonates nor deflagrates rapidly, but is liable to undergo a thermal explosion in that package will be defined as **self-reactive substance TYPE B**;
c) Any self-reactive substance or mixture possessing explosive properties when the substance or mixture as packaged cannot detonate or deflagrate rapidly or undergo a thermal explosion will be defined as **self-reactive substance TYPE C**;
d) Any self-reactive substance or mixture which in laboratory testing: detonates partially, does not deflagrate rapidly and shows no violent effect when heated under confinement; or does not detonate at all, deflagrates slowly and shows no violent effect when heated under confinement; or does not detonate or deflagrate at all and shows a medium effect when heated under confinement; will be defined as **self-reactive substance TYPE D**
e) Any self-reactive substance or mixture which, in laboratory testing, neither detonates nor deflagrates at all and shows low or no effect when heated under confinement will be defined as **self-reactive substance TYPE E**;
f) Any self-reactive substance or mixture which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows only a low or no effect when heated under confinement as well as low or no explosive power will be defined as **self-reactive substance TYPE F**;
g) Any self-reactive substance or mixture which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows no effect when heated under confinement nor any explosive power, provided that it is thermally stable (self-accelerating decomposition temperature is 60 °C to 75 °C for a 50 kg package), and, for liquid mixtures, a diluent having a boiling point greater than or equal to 150 °C is used for desensitization will be defined as **self-reactive substance TYPE G**.
If the mixture is not thermally stable or a diluent having a boiling point less than 150 °C is used for desensitization, the mixture shall be defined as **self-reactive substance TYPE F**

Note: To classify a self-reactive substance or mixture test series A to H as described in Part II of the *Manual of Tests and Criteria* should be performed and the scheme for classifying these substances is illustrated in Figure 20.1. The properties of self-reactive substances or mixtures which are decisive for their classification should be determined experimentally. Test methods with pertinent evaluation criteria are given in the *Manual of Tests and Criteria*, Part II (test series A to H).

Table 18. Self-reactive Substances and mixtures Testing Guidelines for Plant Protection and Biocidal Products

Jurisdiction/Agency	Classification Criteria	Test Methods
FAO/WHO	None identified	None identified
USEPA	None identified	None identified
EU	CLP Regulation, section 2.8.2 of Annex I	UN Test Series A to H*
APVMA	None identified	None identified
PMRA	None identified	None identified

Globally Harmonised System	Table 17	UN Test Series A to H*

*Test Series A to H: Test methods as described in Part II of the *Manual of Tests and Criteria*, 2019.

10. ORGANIC PEROXIDES

20. *Organic peroxides* are liquid or solid organic substances which contain the bivalent -O-O- structure and may be considered derivatives of hydrogen peroxide, where one or both of the hydrogen atoms have been replaced by organic radicals. The term also includes organic peroxide formulations (mixtures). Organic peroxides are thermally unstable substances or mixtures, which may undergo exothermic self-accelerating decomposition. In addition, they may have one or more of the following properties:

a) be liable to explosive decomposition;

b) burn rapidly;

c) be sensitive to impact or friction;

d) react dangerously with other substances.

An organic peroxide is regarded as possessing explosive properties when in laboratory testing the formulation is liable to detonate, to deflagrate rapidly or to show a violent effect when heated under confinement.

Table 19. ORGANIC PEROXIDES Classification criteria According to the Globally Harmonized System

Organic peroxides are classified in one of the seven categories of “types A to G” for this class, according to the following principles:

a) Any organic peroxide which, as packaged, can detonate or deflagrate rapidly will be defined as **organic peroxide TYPE A**;

b) Any organic peroxide possessing explosive properties and which, as packaged, neither detonates nor deflagrates rapidly, but is liable to undergo a thermal explosion in that package will be defined as **organic peroxide TYPE B**;

c) Any organic peroxide possessing explosive properties when the substance or mixture as packaged cannot detonate or deflagrate rapidly or undergo a thermal explosion will be defined as **organic peroxide TYPE C**;

d) Any organic peroxide which in laboratory testing:

21. detonates partially, does not deflagrate rapidly and shows no violent effect when heated under confinement; or
22. does not detonate at all, deflagrates slowly and shows no violent effect when heated under confinement; or
23. does not detonate or deflagrate at all and shows a medium effect when heated under confinement; will be defined as **organic peroxide TYPE D**

e) Any organic peroxide which, in laboratory testing, neither detonates nor deflagrates at all and shows low or no effect when heated under confinement will be defined as **organic peroxide TYPE E**;

f) Any organic peroxide which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows only a low or no effect when heated under confinement as well as low or no explosive power will be defined as **organic peroxide TYPE F**;

g) Any organic peroxide which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows no effect when heated under confinement nor any explosive power, provided that it is thermally stable (self-accelerating decomposition temperature is 60 °C or higher for a 50 kg package), and, for liquid mixtures, a diluent having a boiling point of not less than 150 °C is used for desensitization, will be defined as **organic peroxide TYPE G**. If the organic peroxide is not thermally stable or a diluent having a boiling point less than 150 °C is used for desensitization, it shall be defined as **organic peroxide TYPE F**.

Note: To classify an organic peroxide test series A to H as described in Part II of the *Manual of Tests and Criteria* should be performed and the scheme for classifying these substances is illustrated in Figure 20.1. The properties of organic peroxides which are decisive for their classification should be determined experimentally. Test methods with pertinent evaluation criteria are given in the *Manual of Tests and Criteria*, Part II (test series A to H).

Table 20. Organic peroxides Test Guidelines for Plant Protection and Biocidal Products

Jurisdiction/Agency	Classification Criteria	Test Methods
FAO/WHO	None identified	None identified
USEPA	None identified	None identified
EU	CLP Regulation, section 2.15.2 of Annex I	UN Test Series A to H*
APVMA	None identified	None identified
PMRA	None identified	None identified
Globally Harmonised System	Table 19	UN Test Series A to H*

*Test Series A to H: Test methods as described in Part II of the *Manual of Tests and Criteria*, 2019.

11. LITERATURE

(1) Manual of Tests and Criteria, Seventh Revised Edition, New York and Geneva: United Nations, 2019, ISBN 978-92-1-130394-0, ST/SG/AC.10/11/Rev.7.

(2) Globally Harmonized System of Classification and Labelling of Chemicals (GHS), Eighth revised edition, New York and Geneva: United Nations, 2019, ISBN 978-92-1-117199-0, ST/SG/AC. 10/30/Rev.8

(3) Annex to COMMISSION REGULATION (EC) No 440/2008 of 30 May 2008 laying down test methods pursuant to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

12. DEFINITIONS AND ABBREVIATIONS

APVMA	Australian Pesticides and Veterinary Medicines Authority
ADR	Accord européen relatif au transport international des marchandises Dangereuses par Route.
CFR	Code of Federal Regulations of the Government of the United States of America
CIPAC-MT	Collaborative International Pesticides Analytical Council- Miscellaneous Technique
CLP	Classification, Labelling and Packaging of substances and mixtures according to Regulation (EC) No 1272/2008
EU	European Union
FAO	Food and Agriculture Organisation of the United Nations
FIFRA	The Federal Insecticide, Fungicide, and Rodenticide Act of the United States
GHS	Globally Harmonized System of Classification and Labelling of Chemicals
ISO	International Organization for Standardization
OCSPP	US EPA's Office of Chemical Safety and Pollution Prevention
PMRA	Pest Management Regulatory Agency, a branch of Health Canada
UN-MTC	UN Manual of Tests and Criteria
US EPA	United States Environmental Protection Agency
WHO	World Health Organization of the United Nations