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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

Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals
(Second session, 12 -14 December 2001,
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GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION AND LABELLING OF CHEMICALS (GHS)

Part 2: Physical hazards

Transmitted by the expert from the United States of America on behalf of the Inter-Organization Programme for the Sound Management of Chemicals (IOMC) Coordinating Group and for the Harmonization of Chemical Classification Systems (CG/HCCS)

NOTE*: In order to meet the deadlines for submission of documents, this document is submitted prior to its formal adoption by IOMC.*

2. PHYSICAL HAZARDS

Chapter 2.1: Explosives

DEFINITIONS AND GENERAL CONSIDERATIONS

1. An explosive substance is a solid or liquid substance (or mixture of substances) which is in itself capable by chemical reaction of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings. Pyrotechnic substances are included even when they do not evolve gases.

2. A pyrotechnic substance is a substance or mixture of substances designed to produce an effect by heat, light, sound, gas or smoke or a combination of these as the result of non-detonative self-sustaining exothermic chemical reactions.

3. An explosive article is an article containing one or more explosive substances.

4. A pyrotechnic article is an article containing one or more pyrotechnic substances.

5. The class of explosives comprises:

   (a) Explosive substances;

   (b) Explosive articles, except devices containing explosive substances in such quantity or of such a character that their inadvertent or accidental ignition or initiation shall not cause any effect external to the device either by projection, fire, smoke, heat or loud noise; and

   (c) Substance and articles not mentioned under (a) and (b) above which are manufactured with the view to producing a practical, explosive or pyrotechnic effect.

CLASSIFICATION CRITERIA FOR SUBSTANCES

6. Substances and articles of this class are assigned to one of the following six divisions depending on the type of hazard they present:

   (a) Division 1.1 Substances and articles which have a mass explosion hazard (a mass explosion is one which affects almost the entire load virtually instantaneously);

   (b) Division 1.2 Substances and articles which have a projection hazard but not a mass explosion hazard;

(c) Division 1.3 Substances and articles which have a fire hazard and either a minor blast hazard or a minor projection hazard or both, but not a mass explosion hazard:

(i) combustion of which gives rise to considerable radiant heat; or

(ii) which burn one after another, producing minor blast or projection effects or both;

(d) Division 1.4 Substances and articles which present no significant hazard: substances and articles which present only a small hazard in the event of ignition or initiation. The effects are largely confined to the package and no projection of fragments of appreciable size or range is to be expected. An external fire shall not cause virtually instantaneous explosion of almost the entire contents of the package;

(e) Division 1.5 Very insensitive substances which have a mass explosion hazard: substances which have a mass explosion hazard but are so insensitive that there is very little probability of initiation or of transition from burning to detonation under normal conditions;

(f) Division 1.6 Extremely insensitive articles which do not have a mass explosion hazard: articles which contain only extremely insensitive detonating substances and which demonstrate a negligible probability of accidental initiation or propagation.

7. Explosives are classified in one of the six divisions above based on Test Series 2 to 7 in Part I of the Manual of Tests and Criteria according to the following table:

Table 1: Criteria for explosives

Category	**Criteria**
Unstable[1] explosives or explosives of Division 1.1 to 1.6	For explosives of Divisions 1.1 to 1.6, the following are the core set of tests that need to be performed: Explosibility: according to UN Test series 2 (Section 12 of the Manual of Tests and Criteria). Intentional explosives[2] are not subject to UN Test series 2 Sensitiveness: according to UN Test series 3 (Section 13 of the Manual of Tests and Criteria) Thermal stability: according to UN Test 3(c) (Sub-section 13.6.1 of the Manual of Tests and Criteria) Further tests are necessary to allocate the correct Division

[1] Unstable explosives are those which are thermally unstable and/or too sensitive for normal handling and use. Special precautions are necessary.

[2] This comprises substances and articles which are manufactured with a view to producing a practical, explosive or pyrotechnic effect.

NOTE 1: Explosive substances in packaged form and articles may be classified under divisions 1.1 to 1.6 and, for some regulatory purposes, are further subdivided into compatibility groups A to S to distinguish technical requirements (see UN Model Regulations, chapter 2.1).

NOTE 2: Some explosive substances are wetted with water or alcohols or diluted with other substances to suppress their explosives properties. They may be treated differently from explosive substances (as desensitised explosives) for some regulatory purposes (e.g. transport).

NOTE 3: For classification tests on solid substances, the tests should be performed on the substance as presented. If for example, for the purposes of supply or transport, the same chemical is to be presented in a physical form different from that which was tested and which is considered likely to materially alter its performance in a classification test, the substance must also be tested in the new form.

CLASSIFICATION CRITERIA FOR MIXTURES

8. The same criteria as for substances apply.

HAZARD COMMUNICATION

Allocation of label elements

9. General and specific considerations concerning labelling requirements are provided in *Hazard Communication : Labelling* (Chapter 1.3). Annex 4 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

Table 2: Label elements for explosives

	Division 1.1	**Division 1.2**	**Division 1.3**	**Division 1.4**	**Division 1.5**	**Division 1.6**
Symbol	Exploding bomb	Exploding bomb	Exploding bomb	1.4 on orange background[1]	1.5 on orange background[1]	1.6 on orange background[1]
Signal word	Danger	Danger	Danger	Warning	Warning	No signal word
Hazard statement	Explosive; mass explosion hazard	Explosive; severe projection hazard	Explosive; fire, blast or projection hazard.	Fire or projection hazard	May explode in fire	No hazard statement

[1] Applies to substances and articles subject to some regulatory purposes (e.g. transport).

DECISION LOGIC AND GUIDANCE[2]

Decision logic

10. The classification of substances, mixtures and articles in the class of explosives and further allocation to a division is a very complex, three step procedure. Reference to Part I of Manual of Tests and Criteria is necessary. The first step is to ascertain whether the substance has explosive effects (Test Series 1). The second step is the acceptance procedure (Test Series 2 to 4) and the third step is the assignment to a hazard division (Test Series 5 to 7). The classification procedure is according to the following decision logic (see Figures 1 to 3).

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[2] Paragraphs 10-13 and the associated decision logic are not part of the agreed text on the harmonised classification for explosives developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of substances and mixtures for explosivity.

Figure 1: OVERALL SCHEME OF THE PROCEDURE FOR CLASSIFYING A SUBSTANCE OR ARTICLE

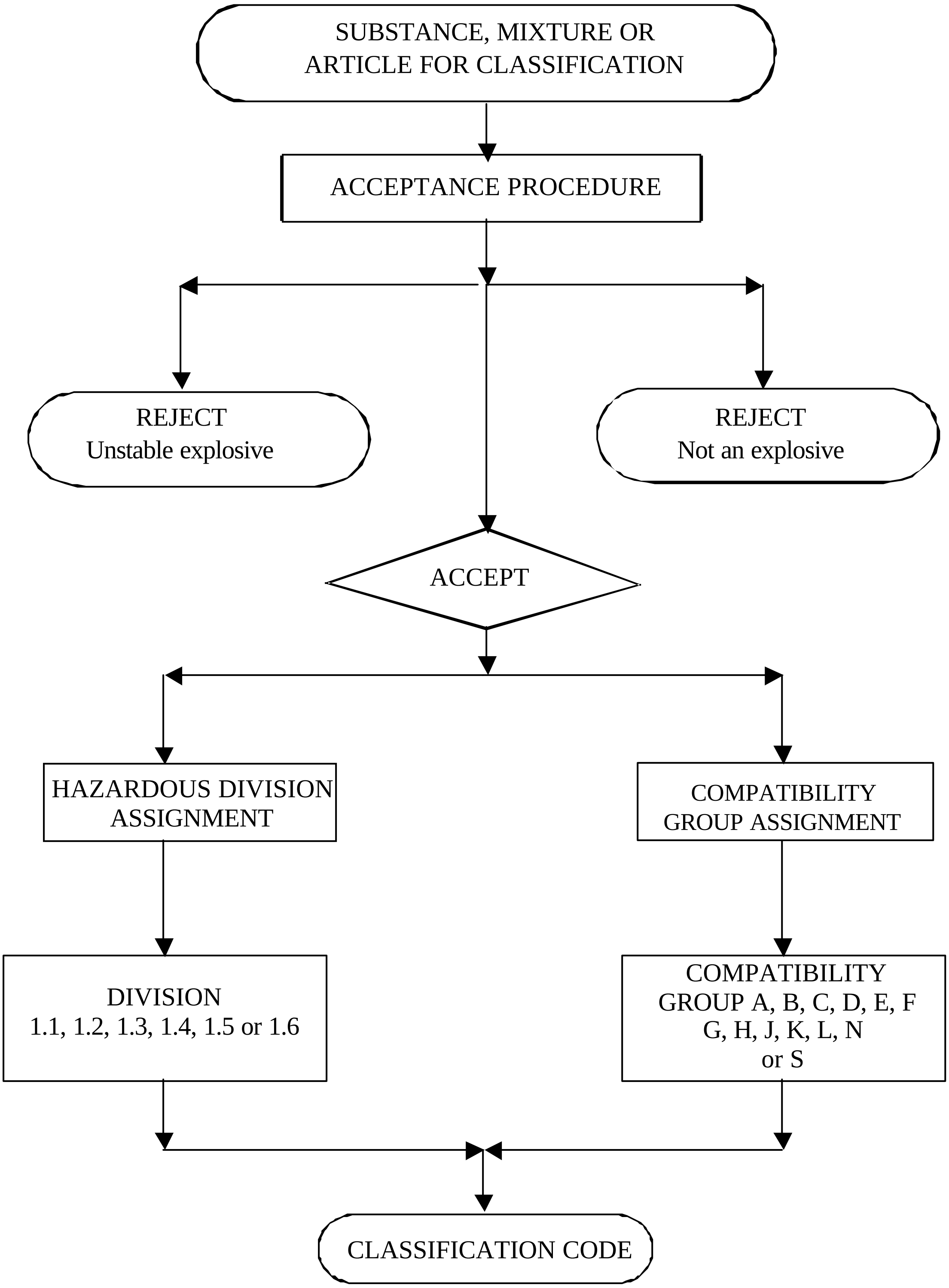
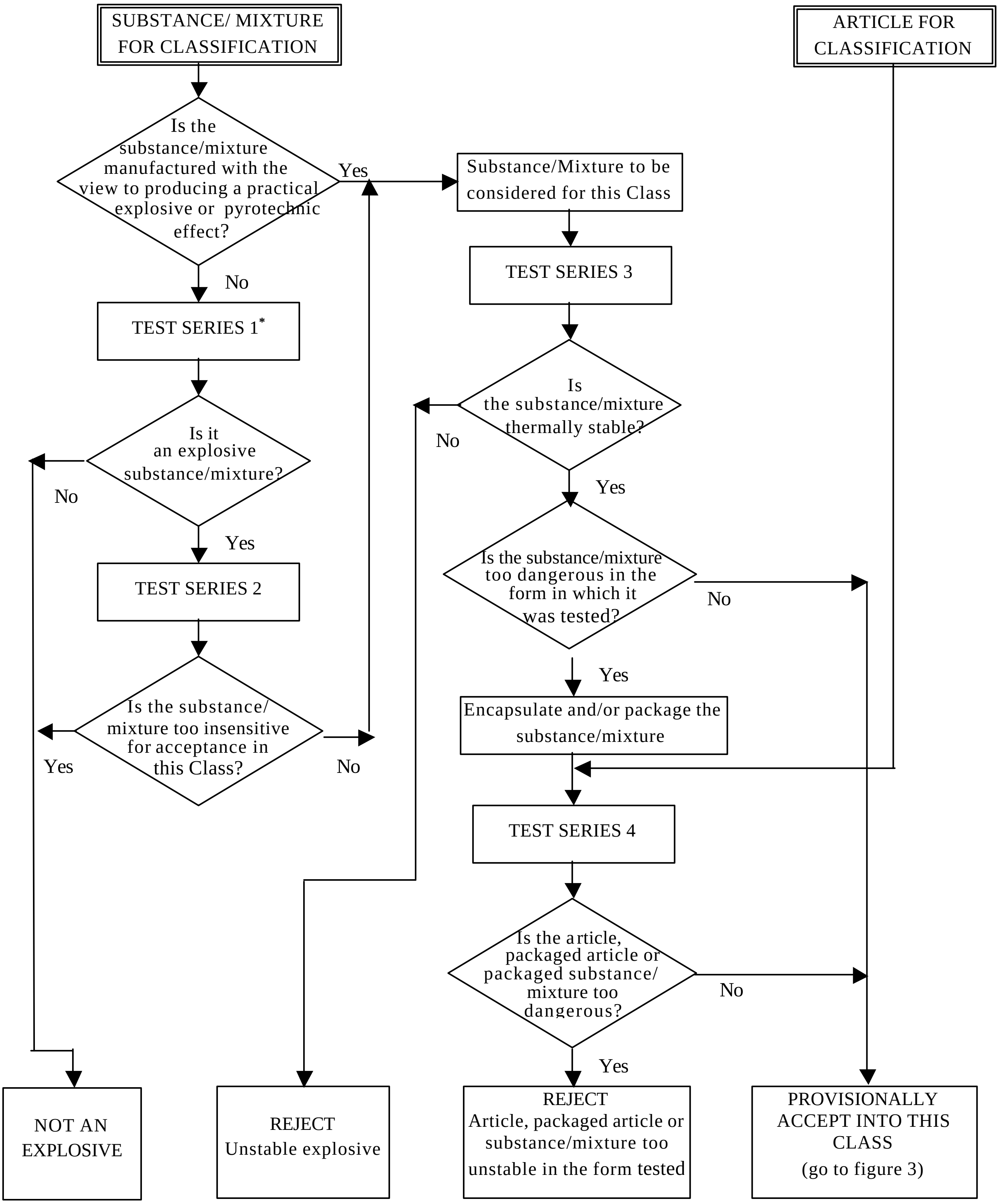


Figure 2: PROCEDURE FOR PROVISIONAL ACCEPTANCE OF A SUBSTANCE/MIXTURE OR ARTICLE IN THE CLASS OF EXPLOSIVES



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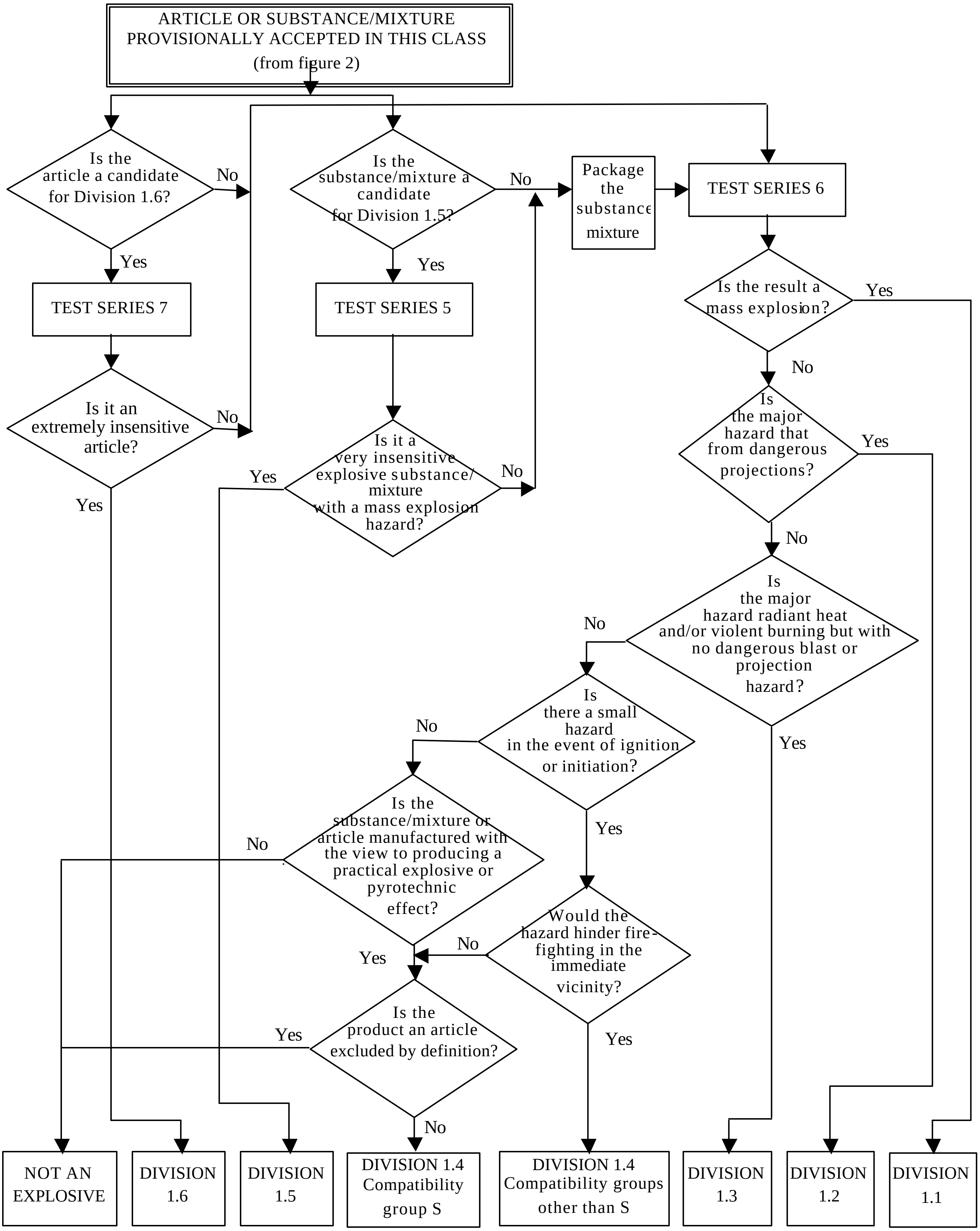
[*] For classification purposes, start with series 2.

Figure 3: PROCEDURE FOR ASSIGNMENT TO A DIVISION



Guidance[3]

11. Explosive properties are associated with the presence of certain chemical groups in a molecule which can react to produce very rapid increases in temperature or pressure. The screening procedure is aimed at identifying the presence of such reactive groups and the potential for rapid energy release. If the screening procedure identifies the substance or mixture to be a potential explosive, the acceptance procedure (see 10.3 of the Manual of Tests and Criteria) has to be performed.

NOTE: Neither a Series 1 type (a) propagation of detonation test nor a Series 2 type (a) test of sensitivity to detonative shock is required if the exothermic decomposition energy of organic materials is less than 800 J/g.

12. A substance or mixture is not classified as explosive if:

(a) There are no chemical groups associated with explosive properties present in the molecule. Examples of groups which may indicate explosive properties are given in Table A6.1 in Appendix 6 of the Manual of Tests and Criteria; or

(b) The substance contains chemical groups associated with explosive properties which include oxygen and the calculated oxygen balance is less than -200.

The oxygen balance is calculated for the chemical reaction:

$C_xH_yO_z + [x + (y/4)-(z/2)].\ O_2 \rightarrow x.\ CO_2 + (y/2).\ H_2O$

using the formula:

oxygen balance = $-1600.[2.x + (y/2) - z]$/molecular weight;

(c) When the organic substance or a homogenous mixture of organic substances contain chemical groups associated with explosive properties but the exothermic decomposition energy is less than 500 J/g and the onset of exothermic decomposition is below 500 °C. (The temperature limit is to prevent the procedure being applied to a large number of organic materials which are not explosive but which will decompose slowly above 500 °C to release more than 500 J/g.) The exothermic decomposition energy may be determined using a suitable calorimetric technique; or

(d) For mixtures of inorganic oxidizing substances with organic material(s), the concentration of the inorganic oxidizing substance is:

less than 15 %, by mass, if the oxidizing substance is assigned to category 1 or 2;
less than 30 %, by mass, if the oxidizing substance is assigned to category 3.

13. In the case of mixtures containing any known explosives, the acceptance procedure has to be performed.

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[3] Paragraphs 10-13 and the associated decision logic are not part of the agreed text on the harmonized classification for explosives developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of substances and mixtures for explosivity.

Chapter 2.2: Flammable gases

DEFINITIONS AND GENERAL CONSIDERATIONS

1. A flammable gas is a gas having a flammable range with air at 20 °C and a standard pressure of 101.3 kPa.

2. There are no general considerations.

CLASSIFICATION CRITERIA FOR SUBSTANCES

3. A flammable gas is classified in one of the two categories for this class according to the following table:

Table 1: Criteria for flammable gases

Category	Criteria
1	Gases, which at 20 °C and a standard pressure of 101.3 kPa: (a) are ignitable when in a mixture of 13% or less by volume in air; or (b) have a flammable range with air of at least 12 percentage points regardless of the lower flammable limit.
2	Gases, other than those of category 1, which, at 20 °C and a standard pressure of 101.3 kPa, have a flammable range while mixed in air.

NOTE 1: Ammonia and methyl bromide may be regarded as special cases for some regulatory purposes.

NOTE 2: For the classification of aerosols, see Chapter 2.3.

CLASSIFICATION CRITERIA FOR MIXTURES

4. The same criteria as for substances apply.

HAZARD COMMUNICATION

Allocation of label elements

5. General and specific considerations concerning labelling requirements are provided in *Hazard Communication : Labelling* (Chapter 1.3). Annex 4 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

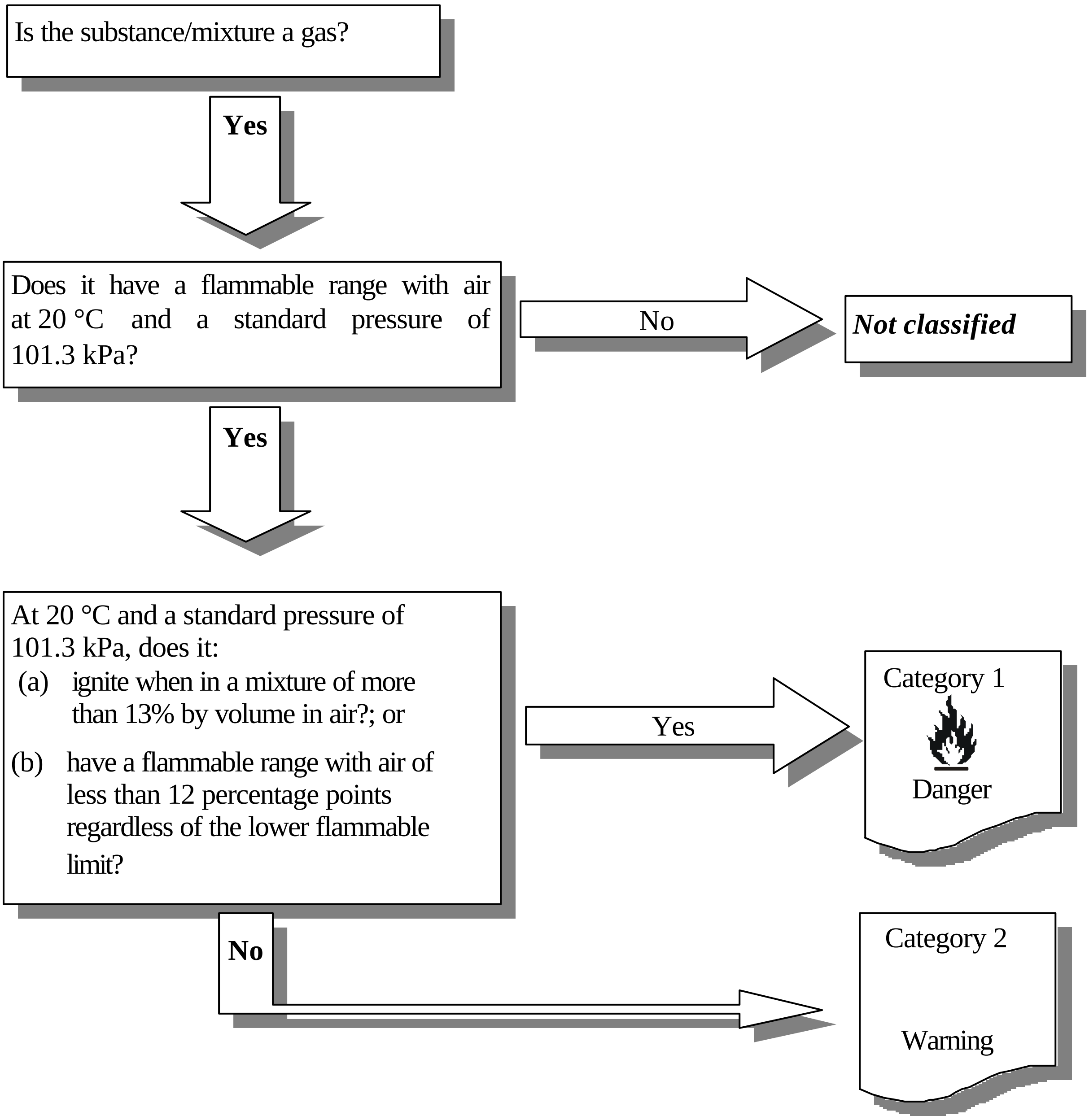
Table 2: Label elements for flammable gases

	Category 1	**Category 2**
Symbol	Flame	*No symbol used*
Signal word	Danger	Warning
Hazard statement	Extremely flammable gas	Flammable gas

DECISION LOGIC AND GUIDANCE[1]

Decision logic

6. To classify a flammable gas, data on its flammability are required. The classification is according to the following decision logic.



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[1] Paragraphs 6-7 and the associated decision logic are not part of the agreed text on the harmonised classification for flammable gases developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of gaseous substances and mixtures for flammability.

Guidance[2]

7. Flammability should be determined by tests or by calculation in accordance with methods adopted by ISO (see ISO 10156:1996). Where insufficient data are available to use these methods, tests by a comparable method recognized by the competent authority may be used.

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[2] Paragraphs 6-7 and the associated decision logic are not part of the agreed text on the harmonised classification for flammable gases developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of gaseous substances and mixtures for flammability.

EXAMPLE: Classification of a flammable gas mixture by calculation according to ISO 10156[3]

Formula

$$\sum_{i}^{n} \frac{V\%}{Tci}$$

Where:

V%	is the equivalent flammable gas content
Tci	is the maximum concentration of a flammable gas in N_2 at which the mixture is still not flammable in air
i	is the first gas in the mixture
n	is the n^{th} gas in the mixture
Ki	is the equivalency factor for an inert gas versus nitrogen

Criterion:

$$\sum_{i}^{n} \frac{V\%}{Tci} \geq 1$$

Gas Mixture

For the purpose of this example the following is the gas mixture to be used

$$2\%(H_2) + 6\%(CH_4) + 27\%(Ar) + 65\%(He)$$

Calculation

1 Ascertain the equivalency factors (Ki) for the inert gases versus nitrogen

Ki (Ar) = 0.5
Ki (He) = 0.5

2 Calculate the equivalent mixture with nitrogen as balance gas using the Ki figures for the inert gases.

$$2\%(H_2) + 6\%(CH_4) + [27\%x0.5 + 65\%x0.5](N_2) = 2\%(H_2) + 6\%(CH_4) + 46\%(N_2) = 54\%$$

3 Adjust the sum of the contents to 100%

$$\frac{100}{54} \text{ x } [2\%(H_2) + 6\%(CH_4) + 46\%(N_2)] = 3.7\%(H_2) + 11.1\%(CH_4) + 85.2\%(N_2)$$

4 Ascertain the Tci coefficients for the flammable gases

Tci H_2 = 5.7%
Tci CH_4 = 14.3%

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[3] This example is not part of the agreed text on the harmonised classification for flammable gases developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of gaseous mixtures for flammability.

5 Calculate the flammability of the equivalent mixture using the formula.

$$\sum_{i}^{n} \frac{V\%}{Tci} = \frac{3.7}{5.7} + \frac{11.1}{14.3} = 1.42$$

1.42 > 1, ***therefore the mixture is flammable in air***

Chapter 2.3: Flammable aerosols

DEFINITIONS AND GENERAL CONSIDERATIONS

1. 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.

2. There are no general considerations.

CLASSIFICATION CRITERIA

3. Aerosols should be considered for classification as flammable if they contain any component which is classified as flammable according to the GHS criteria, i.e.:

   flammable liquids (see Chapter 2.6);

   flammable gases (see Chapter 2.2).

   flammable solids (see Chapter 2.7);

   NOTE: Flammable components do not cover pyrophoric, self-heating or water-reactive substances because such components are never used as aerosol contents.

4. A flammable aerosol is classified in one of the two categories for this Class on the basis of its components, of its chemical heat of combustion and, if applicable, of the results of the foam test (for foam aerosols) and of the ignition distance test and enclosed space test (for spray aerosols). See decision logic in par. 6 below.

HAZARD COMMUNICATION

Allocation of label elements

General and specific considerations concerning labelling requirements are provided in *Hazard Communication : Labelling* (Chapter 1.3). Annex 4 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

Table 1: Label elements for flammable aerosols

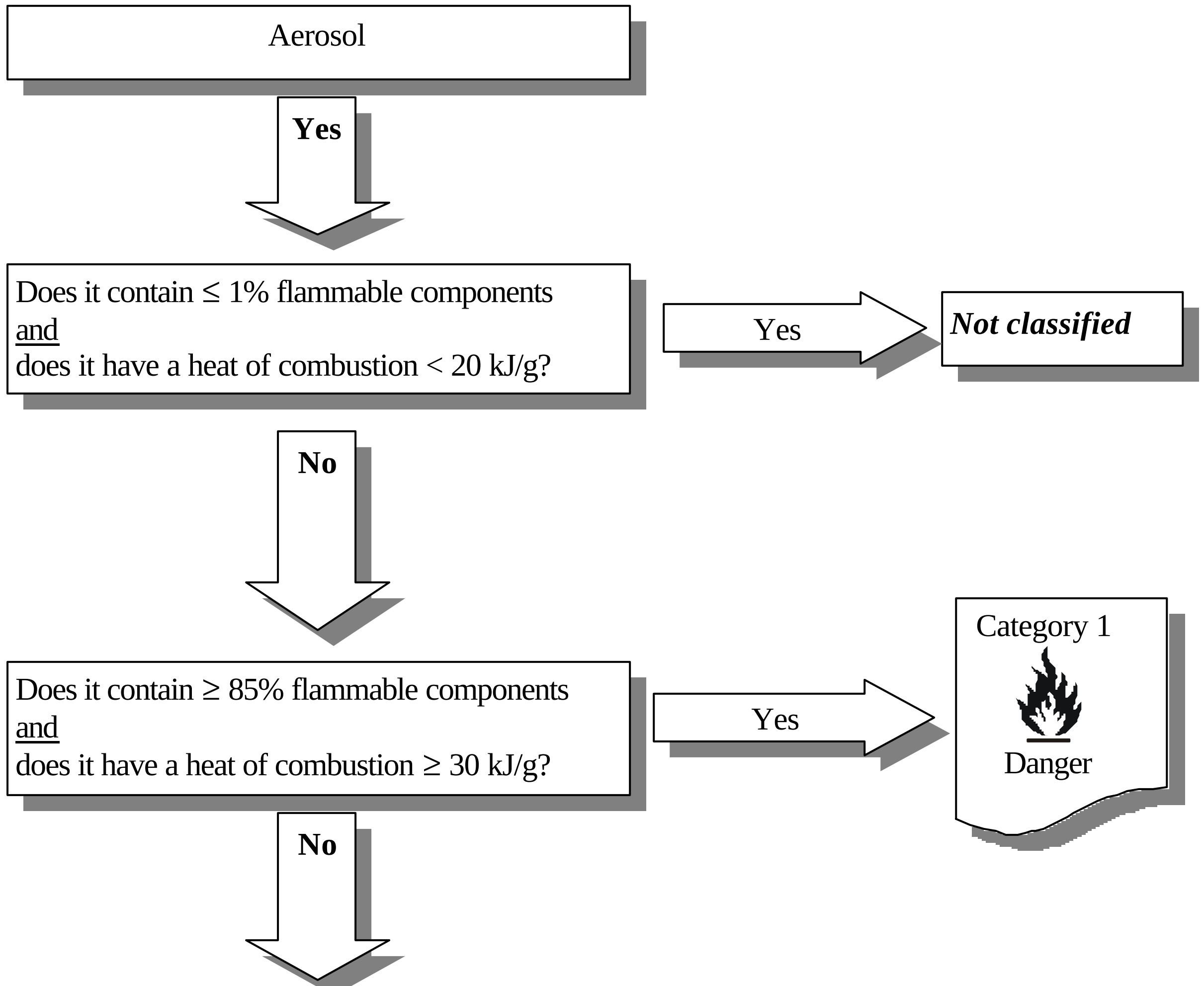
	Category 1	**Category 2**
Symbol	Flame	Flame
Signal word	Danger	Warning
Hazard statement	Extremely flammable aerosol	Flammable aerosol

DECISION LOGIC AND GUIDANCE[1]

Decision logic

6. To classify a flammable aerosol, data on its flammable components, on its chemical heat of combustion and, if applicable, the results of the foam test (for foam aerosols) and of the ignition distance test and enclosed space test (for spray aerosols) are required. Classification should be made according to the following decision logics.

Decision logic 1



For spray aerosols, go to decision logic 2
For foam aerosols, go to decision logic 3

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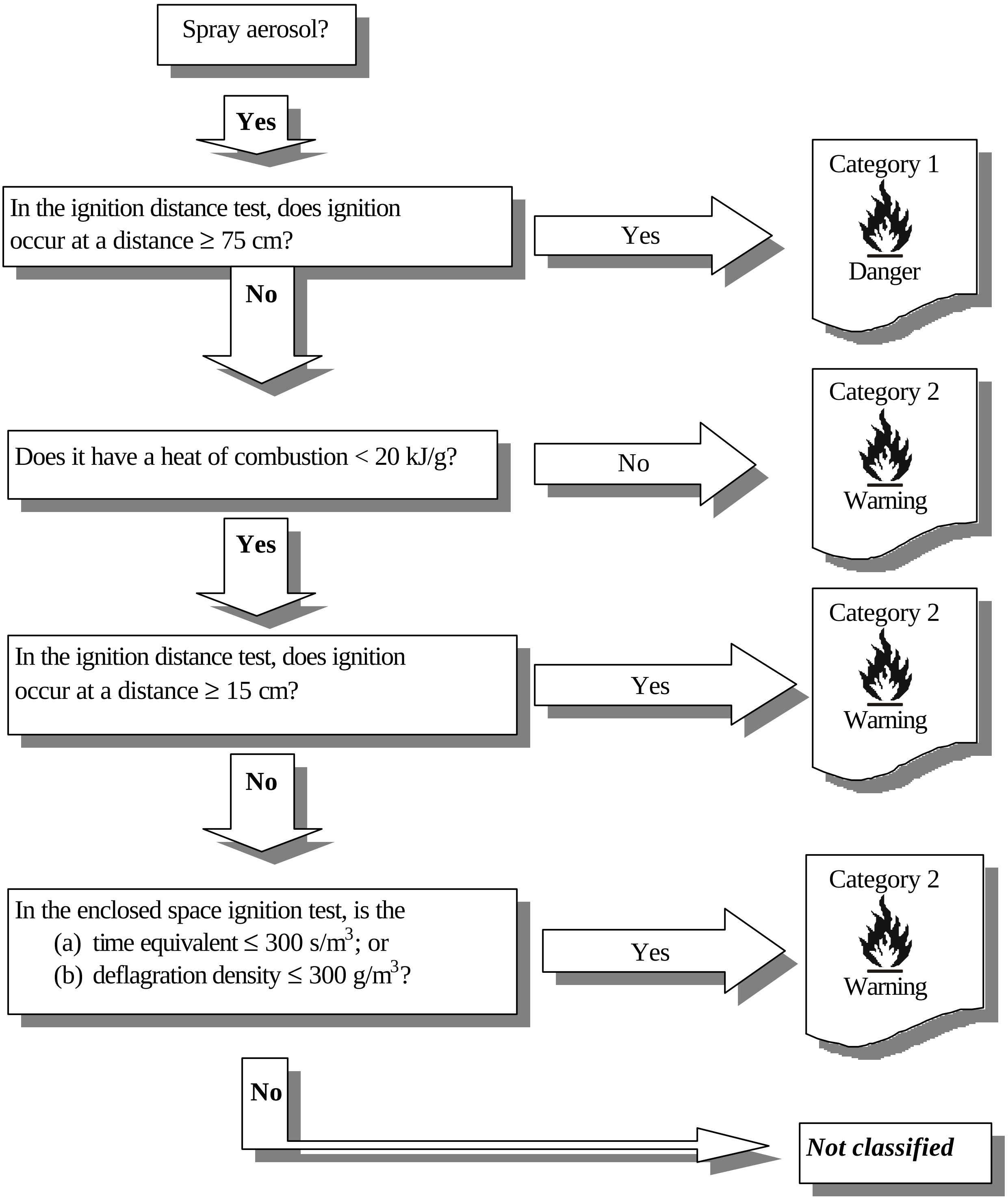
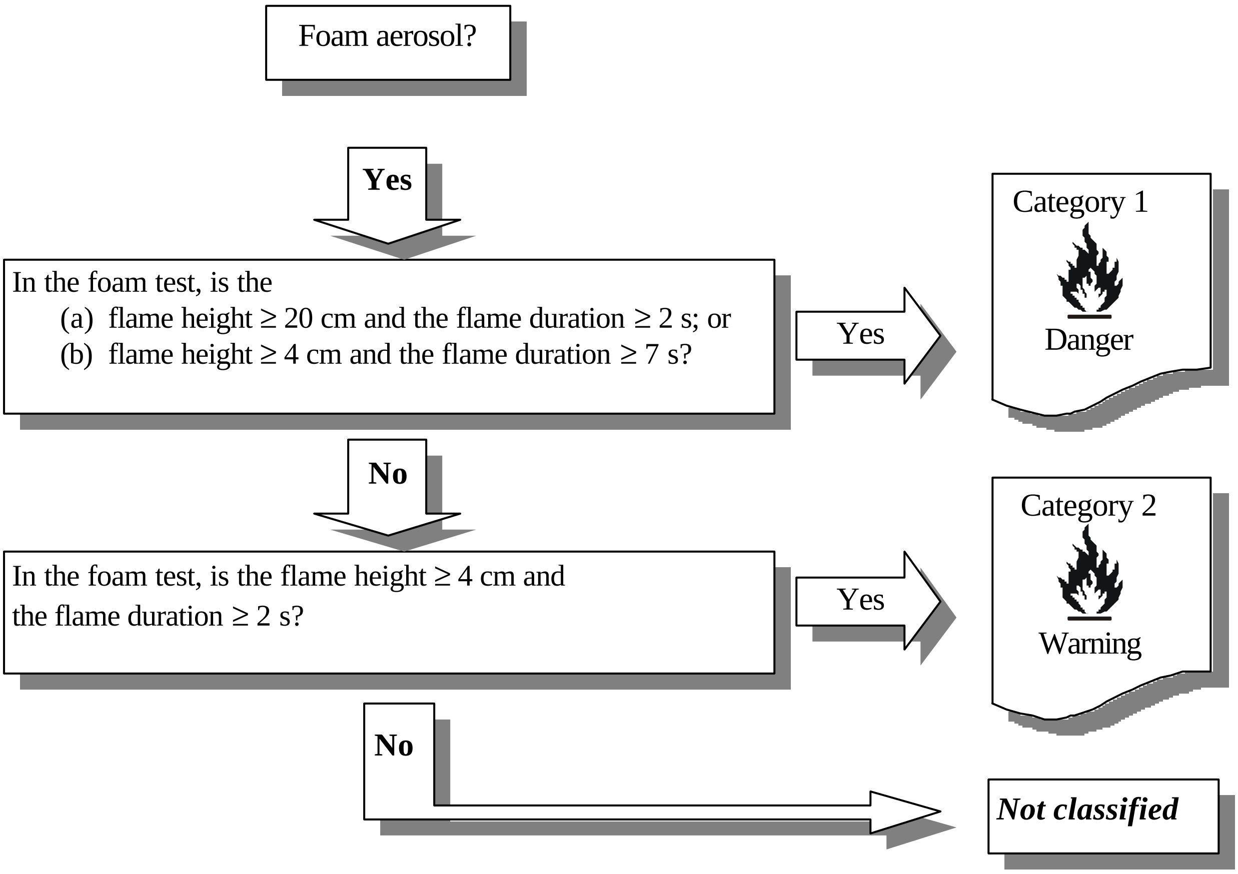
[1] Paragraphs 6-8 and the associated decision logic are not part of the agreed text on the harmonised classification for flammable aerosols developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of aerosols for flammability

Decision logic 2



Decision logic 3



Guidance[2]

7. The chemical heat of combustion (ΔHc), in kilojoules per gram (kJ/g), is the product of the theoretical heat of combustion ($\Delta Hcomb$), and a combustion efficiency, usually less than 1.0 (a typical combustion efficiency is 0.95 or 95%.).

For a composite aerosol formulation, the chemical heat of combustion is the summation of the weighted heats of combustion for the individual components, as follows:

$$\Delta H_c \text{ (product)} = \Sigma \text{ [I\% x } \Delta H_{c(I)}]$$

where:
ΔH_c = chemical heat of combustion (kJ/g)
I% = weight fraction of component I in the product
$\Delta H_{c(I)}$ = chemical heat of combustion of component I (kJ/g).

The chemical heats of combustion can be found in literature, calculated or determined by tests (see ASTM D 240, ISO/FDIS 13943:1999 (E/F) 86.l to 86.3 and NFPA 30B).

8. See Annex 11 for Ignition Distance Test, Enclosed Space Ignition Test and Aerosol Foam Flammability Test.

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[2] Paragraphs 6-8 and the associated decision logic are not part of the agreed text on the harmonised classification for flammable aerosols developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of aerosols for flammability.

Chapter 2.4: Oxidizing gases

DEFINITIONS AND GENERAL CONSIDERATIONS

1. An oxidizing gas is any gas which may, generally by providing oxygen, cause or contribute to the combustion of other material more than air does.

2. There are no general considerations.

CLASSIFICATION CRITERIA FOR SUBSTANCES

3. An oxidizing gas is classified in a single category for this class according to the following table:

Table 1: Criteria for oxidizing gases

Category	Criteria
1	Any gas which may, generally by providing oxygen, cause or contribute to the combustion of other material more than air does.

CLASSIFICATION CRITERIA FOR MIXTURES

4. The same criteria as for substances apply.

HAZARD COMMUNICATION

Allocation of label elements

General and specific considerations concerning labelling requirements are provided in *Hazard Communication : Labelling* (Chapter 1.3). Annex 4 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

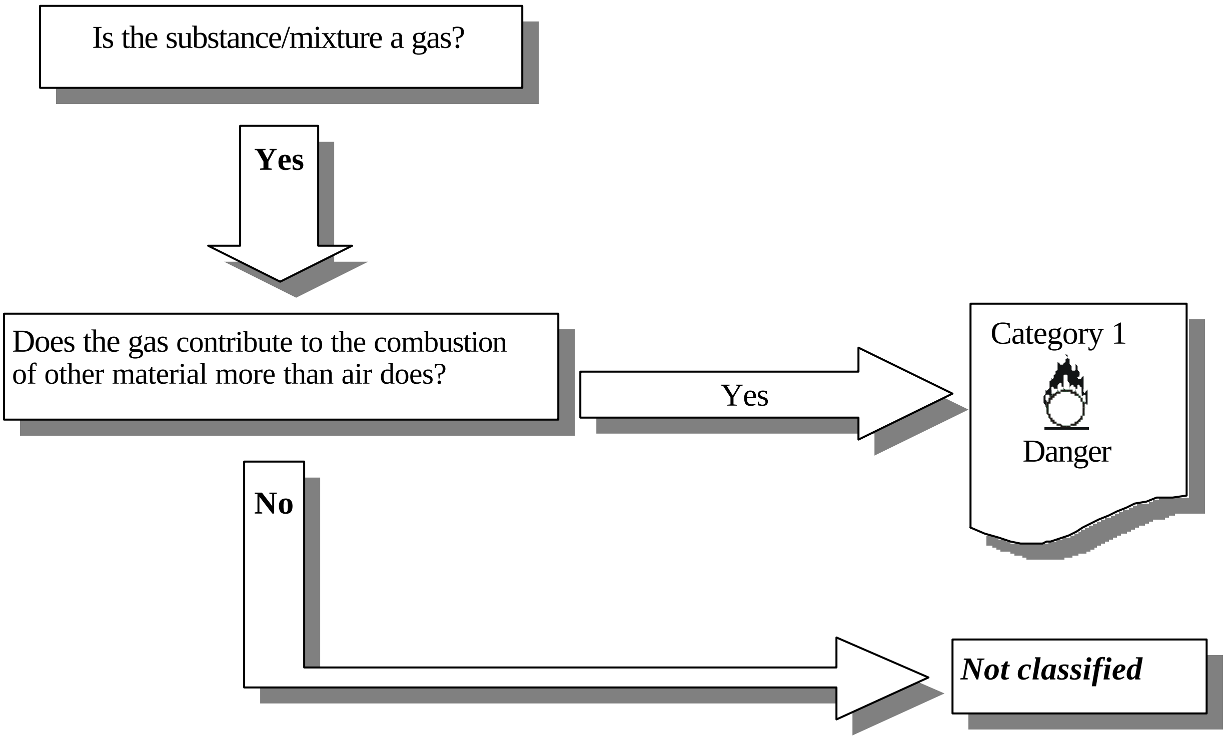
Table 2: Label elements for oxidizing gases

	Category 1
Symbol	Flame over circle
Signal word	Danger
Hazard statement	May cause or intensify fire; oxidizer

DECISION LOGIC AND GUIDANCE[1]

Decision logic

5. To classify an oxidizing gas tests or calculation methods as described in ISO 10156:1996 should be performed.



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[1] Paragraph 6 and the associated decision logic are not part of the agreed text on the harmonised classification for oxidizing gases developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of gases for oxidizing properties.

Example of the classification of an oxidizing gas mixture by calculation according to ISO 10156[2]

Formula

$$\sum_{i}^{n} V\% x Ci$$

Where:

V% is the volume percentage of a gas
Ci is the coefficient of oxygen equivalency
i is the first gas in the mixture
n is the nth gas in the mixture

NOTE: - Balance gas is not taken into consideration

Criterion:

$$\sum_{i}^{n} V\% \times Ci \geq 21$$

Gas Mixture

For the purpose of this example the following is the gas mixture to be used

$9\%(O_2) + 16\%(N_2O) + 75\%(N_2)$

Calculation

1 Ascertain the coefficient of oxygen equivalency (Ci) for the oxidizing gases in the mixture

Ci (N_2O) = 0.6 (nitrous oxide)
Ci (O) = 1 (oxygen)
Ci (all other oxidizing gases) = 40

2 Calculate if the gas mixture is oxidizing using the coefficient of oxygen equivalency figures for the oxidizing gases

$9\%(O_2) + 16\%(N_2O) + 75\%(N_2) = (9 \text{ x } 1) + (16 \text{ x } 0.6)$

$18.6 < 21$

Therefore the mixture is considered less oxidizing than air

If the gas mixture had been 0.6 % F_2 in Nitrogen, the equivalent calculation would have been

$0.6\%(F_2) + 99.4\%(N_2)$

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[2] This example is not part of the agreed text on the harmonised classification for oxidizing gases developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of gaseous mixtures for oxidizing properties.

The coefficient of oxygen equivalency (Ci) for F_2 = 40

$40 \times 0.6 = 24 > 21$

Therefore the mixture is considered more oxidizing than air

Chapter 2.5: Gases under pressure

DEFINITIONS AND GENERAL CONSIDERATIONS

1. Gases under pressure are gases which are contained in a receptacle at a pressure not less than 280 kPa at 20 °C or as a refrigerated liquid.

   They comprise compressed gases; liquefied gases; dissolved gases; refrigerated liquefied gases.

2. There are no general considerations.

CLASSIFICATION CRITERIA FOR SUBSTANCES

3. Gases are classified, according to their physical state when packaged, in one of four groups in the following table:

Table 1: Criteria for gases under pressure

Group	Criteria
Compressed gas	A gas which when packaged under pressure is entirely gaseous at -50 °C; including all gases with a critical temperature ≤ -50 °C.
Liquefied gas	A gas which when packaged under pressure, is partially liquid at temperatures above -50 °C. A distinction is made between: *i)* High pressure liquefied gas: a gas with a critical temperature between -50°C and +65°C; and *ii)* Low pressure liquefied gas: a gas with a critical temperature above +65°C.
Refrigerated liquefied gas	A gas which when packaged is made partially liquid because of its low temperature.
Dissolved gas	A gas which when packaged under pressure is dissolved in a liquid phase solvent.

The critical temperature is the temperature above which a pure gas cannot be liquefied, regardless of the degree of compression.

CLASSIFICATION CRITERIA FOR MIXTURES

4. The same criteria as for substances apply.

HAZARD COMMUNICATION

Allocation of label elements

5. General and specific considerations concerning labelling requirements are provided in *Hazard Communication : Labelling* (Chapter 1.3). Annex 4 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority

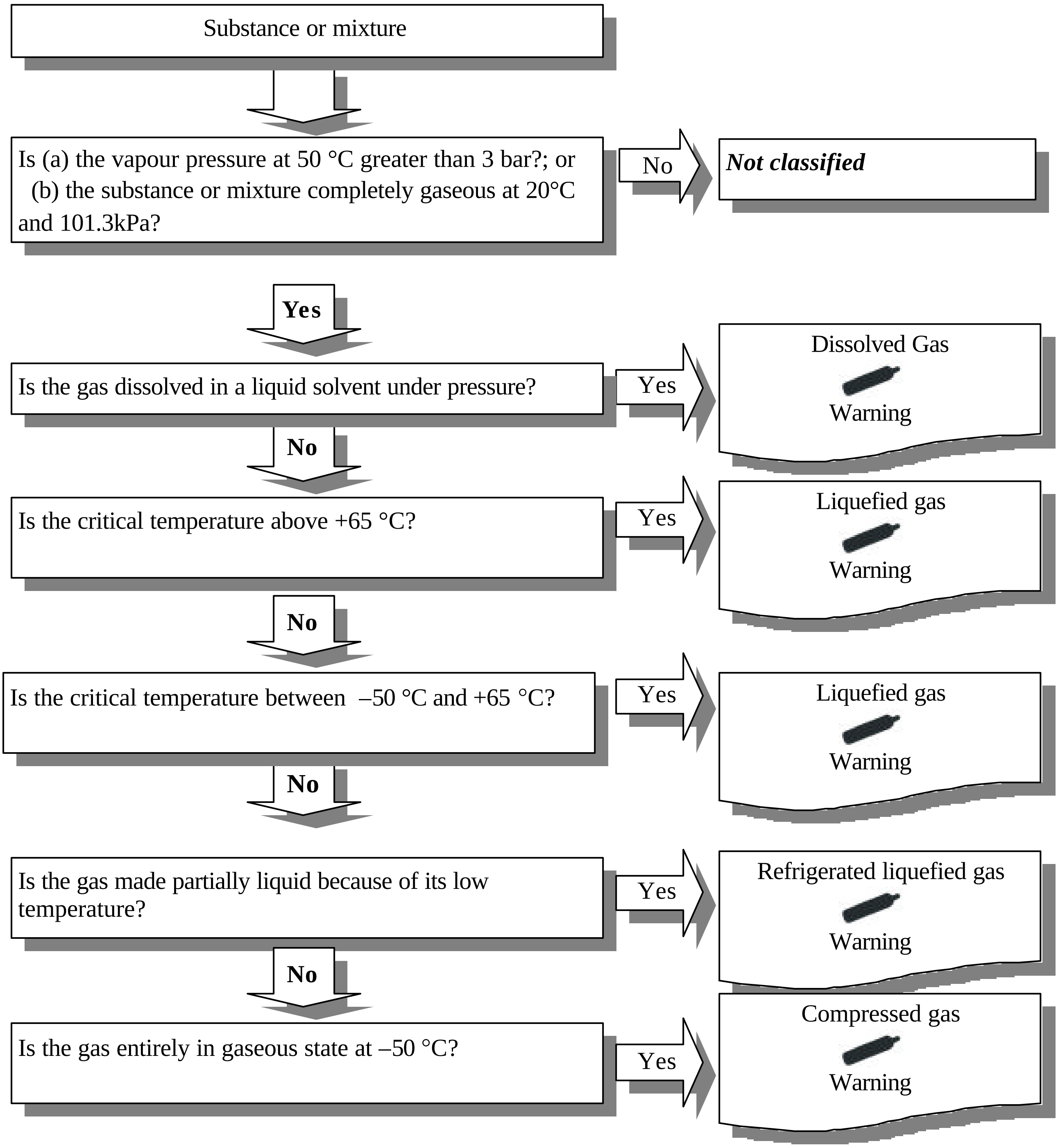
Table 2: Label elements for gases under pressure

	Compressed gas	Liquefied gas	Refrigerated liquefied gas	Dissolved gas
Symbol	Gas cylinder	Gas cylinder	Gas cylinder	Gas cylinder
Signal word	Warning	Warning	Warning	Warning
Hazard statement	Contains gas under pressure; may explode if heated	Contains gas under pressure; may explode if heated	Contains refrigerated gas; may cause cryogenic burns or injury	Contains gas under pressure; may explode if heated

DECISION LOGIC AND GUIDANCE[1]

Decision logic

6. Classification can be made according to the following decision logic.



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[1] Paragraphs 6 - 7 and the associated decision logic are not part of the agreed text on the harmonised classification for gases under pressure developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of gases under pressure

Guidance

7. For this group of gases, the following information is required to be known:
    - The vapour pressure at 50 °C
    - The physical state at 20 °C at standard ambient pressure
    - The critical temperature.

In order to classify a gas, the above data are needed. Data can be found in literature, calculated or determined by testing. Most pure gases are already classified in the UN Model Regulations. Most one off mixtures require additional calculations that can be very complex.

Chapter 2.6: Flammable liquids

DEFINITIONS AND GENERAL CONSIDERATIONS

1. A flammable liquid means a liquid having a flash point of not more than 93 °C.

2. There are no general considerations.

CLASSIFICATION CRITERIA FOR SUBSTANCES

3. A flammable liquid is classified in one of the four categories for this class according to the following table:

Table 1: Criteria for flammable liquids

Category	Criteria
1	Flash point < 23 °C and initial boiling point 35 °C
2	Flash point < 23 °C and initial boiling point > 35 °C
3	Flash point 23 °C and 60 °C
4	Flash point > 60 °C and 93 °C

NOTE 1: Gas oils, diesel and light heating oils in the flash point range of 55 °C to 75 °C may be regarded as a special group for some regulatory purposes.

NOTE 2: Liquids with a flash point of more than 35 °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 the Manual of Tests and Criteria.

NOTE 3: Viscous flammable liquids such as paints, enamels, lacquers, varnishes, adhesives and polishes may be regarded as a special group for some regulatory purposes (e.g. transport). The classification or the decision to consider these liquids as non-flammable may be determined by the pertinent regulation or competent authority.

CLASSIFICATION CRITERIA FOR MIXTURES

4. The same criteria as for substances apply.

HAZARD COMMUNICATION

Allocation of label elements

5. General and specific considerations concerning labelling requirements are provided in *Hazard Communication : Labelling* (Chapter 1.3). Annex 4 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority

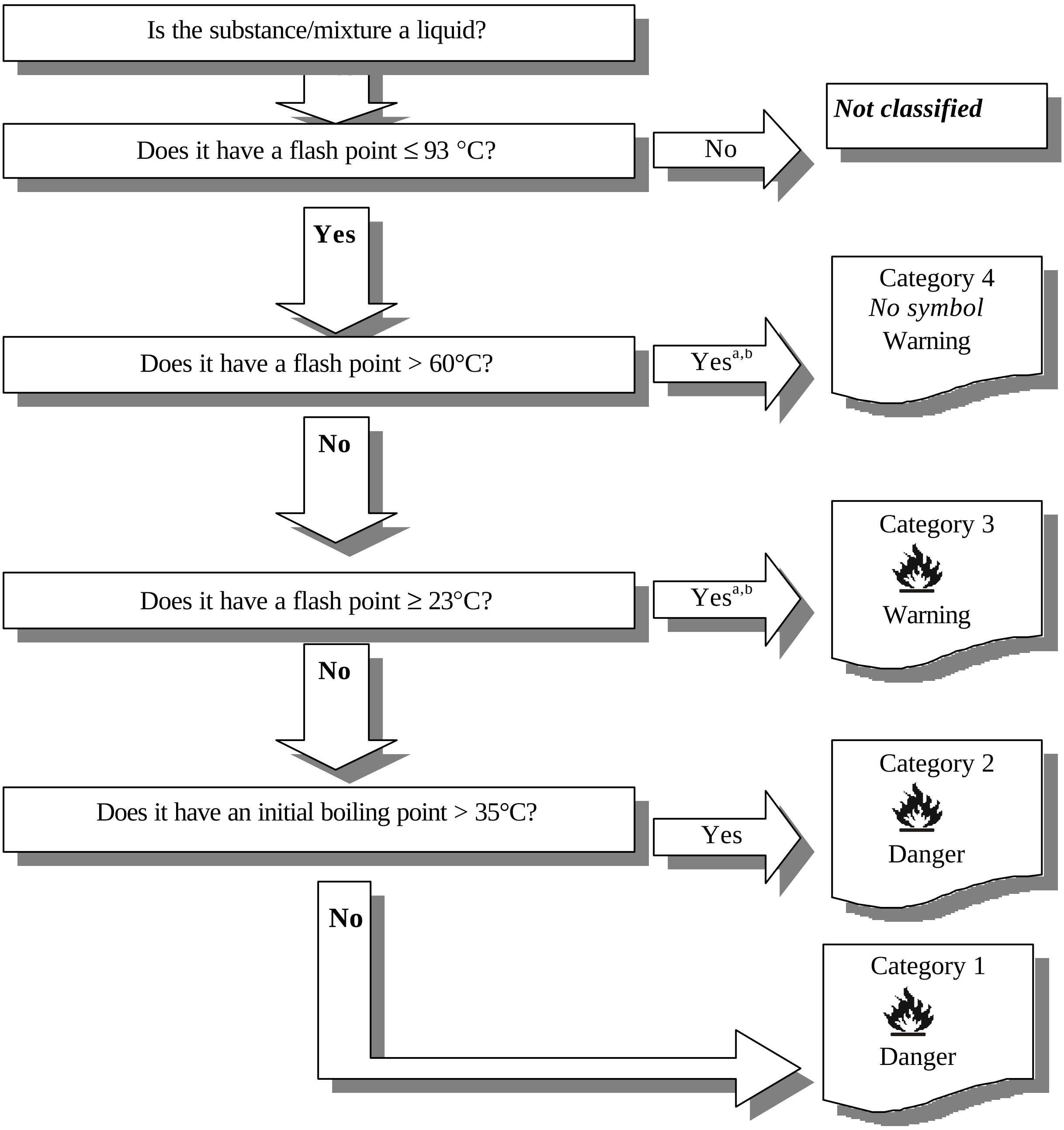
Table 2: Label elements for flammable liquids

	Category 1	**Category 2**	**Category 3**	**Category 4**
Symbol	Flame	Flame	Flame	*No symbol used*
Signal word	Danger	Danger	Warning	Warning
Hazard statement	Extremely flammable liquid and vapour	Highly flammable liquid and vapour	Flammable liquid and vapour	Combustible liquid

DECISION LOGIC AND GUIDANCE[1]

Decision logic

6. Once flash point and initial boiling point are known, the classification of the substance or mixture and the relevant harmonized label information can be obtained with the following decision tree:



[a] Gas oils, diesel and light heating oils in the flash point range of 55 °C to 75 °C may be regarded as a special group for some regulatory purposes as these hydrocarbons mixtures have varying flash point in that range. Thus classification in category 3 or 4 of these products may be determined by the pertinent regulation or competent authority.

[b] Liquids with a flash point of more than 35 °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 the Manual of Tests and Criteria.

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[1] Paragraphs 6 and the associated decision logic are not part of the agreed text on the harmonised classification for flammable liquids developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of liquids for flammability.

Guidance [2]

7. In order to classify a flammable liquid, data on its flash point and initial boiling point are needed. Data can be determined by testing, found in literature or calculated.

8. In the case of mixtures[3] containing known flammable liquids in defined concentrations, although they may contain non-volatile components e.g. polymers, additives, the flash point need not be determined experimentally if the calculated flash point of the mixture, using the method given in paragraph 9 below, is at least 5 °C greater than the relevant classification criterion and provided that

   (a) The composition of the mixture is accurately known (if the material has a specified range of composition, the composition with the lowest calculated flash point should be selected for assessment);

   (b) The flash point (closed cup as given in point 11 below) of each component is known (an appropriate correlation has to be applied when these data are extrapolated to other temperatures than test conditions);

   (c) The activity coefficient is known for each component as present in the mixture including the temperature dependence;

   (d) The liquid phase is homogeneous.

9. A suitable method is described in Gmehling and Rasmussen (Ind. Eng. Chem. Fundament, 21, 186, (1982)). For a mixture containing non-volatile components, e.g. polymers or additives, the flash point is calculated from the volatile components. It is considered that a non-volatile component only slightly decreases the partial pressure of the solvents and the calculated flash point is only slightly below the measured value.

10. If data are not available, the flash point and the initial boiling point shall be determined through testing. The flash point shall be determined by closed-cup test method. Open-cup tests are acceptable only in special cases.

11. The following is a list of documents describing methods for determining the flash point of flammable liquids.

    Association française de normalisation, AFNOR, Tour Europe, 92049 Paris La Défense:
    French Standard NF M 07 - 019
    French Standards NF M 07 - 011 / NF T 30 - 050 / NF T 66 - 009
    French Standard NF M 07 - 036

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[2] Paragraphs 7-11 are not part of the agreed text on the harmonised classification for flammable liquids developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of liquids for flammability.

[3] Screening procedures are well established for ideal mixtures of solvents, i.e. mainly hydrocarbons.

Deutscher Normenausschuss:
Standard DIN 51755 (flash points below 65 °C)
Standard DIN 51758 (flash points 65 °C to 165 °C)
Standard DIN 53213 (for varnishes, lacquers and similar viscous liquids with flash points below 65 °C)

International standards:
ISO 1516
ISO 1523
ISO 3679
ISO 3680

State Committee of the Council of Ministers for Standardization, 113813, GSP, Moscow, M-49 Leninsky Prospect, 9:
GOST 12.1.044-84

British Standards Institution, Linford Wood, Milton Keynes, MK14 6LE:
British Standard BS EN 22719
British Standard BS 2000 Part 170

American Society for Testing Materials, 1916 Race Street, Philadelphia, Penna 19103:
ASTM D 3828-93, Standard Test Methods for Flash Point by Small Scale Closed Tester
ASTM D 56-93, Standard Test Method for Flash Point by Tag Closed Tester
ASTM D 3278-96, Standard Test Methods for Flash Point of Liquids by Setaflash Closed-Cup Apparatus
ASTM D 0093-96, Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester

Chapter 2.7: Flammable solids

DEFINITIONS AND GENERAL CONSIDERATIONS

1. 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.

2. There are no general considerations.

CLASSIFICATION CRITERIA FOR SUBSTANCES

3. Powdered, granular or pasty substances shall be classified as readily combustible solids when the time of burning of one or more of the test runs, performed in accordance with the test method described in the Manual of Tests and Criteria, Part III, sub-section 33.2.1, is less than 45 s or the rate of burning is more than 2.2 mm/s.

4. Powders of metals or metal alloys shall be classified as flammable solids when they can be ignited and the reaction spreads over the whole length of the sample in 10 minutes or less.

5. Solids which may cause fire through friction shall be classified in this class by analogy with existing entries (e.g. matches) until definitive criteria are established.

6. A flammable solid is classified in one of the two categories for this class using Method N.1 as described in 33.2.1 of the Manual of Tests and Criteria according to the following table:

Table 1: Criteria for flammable solids

Category	Criteria
1	Burning rate test: Substances other than metal powders: - wetted zone does not stop fire and - burning time < 45 seconds or burning rate > 2.2 mm/second Metal powders: - burning time ≤ 5 minutes
2	Burning rate test: Substances other than metal powders: - wetted zone stops the fire for at least 4 minutes and - burning time < 45 seconds or burning rate > 2.2 mm/second Metal powders: - burning time > 5 minutes and ≤ 10 minutes

NOTE 1: For classification tests on solid substances, the tests should be performed on the substance as presented. If for example, for the purposes of supply or transport, the same chemical is to be presented in a physical form different from that which was tested and which is considered likely to materially alter its performance in a classification test, the substance must also be tested in the new form.

CLASSIFICATION CRITERIA FOR MIXTURES

7. The same criteria as for substances apply.

HAZARD COMMUNICATION

Allocation of label elements

8. General and specific considerations concerning labelling requirements are provided in *Hazard Communication : Labelling* (Chapter 1.3). Annex 4 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

Table 2: Label elements for flammable solids

	Category 1	**Category 2**
Symbol	Flame	Flame
Signal word	Danger	Warning
Hazard statement	Flammable solid	Flammable solid

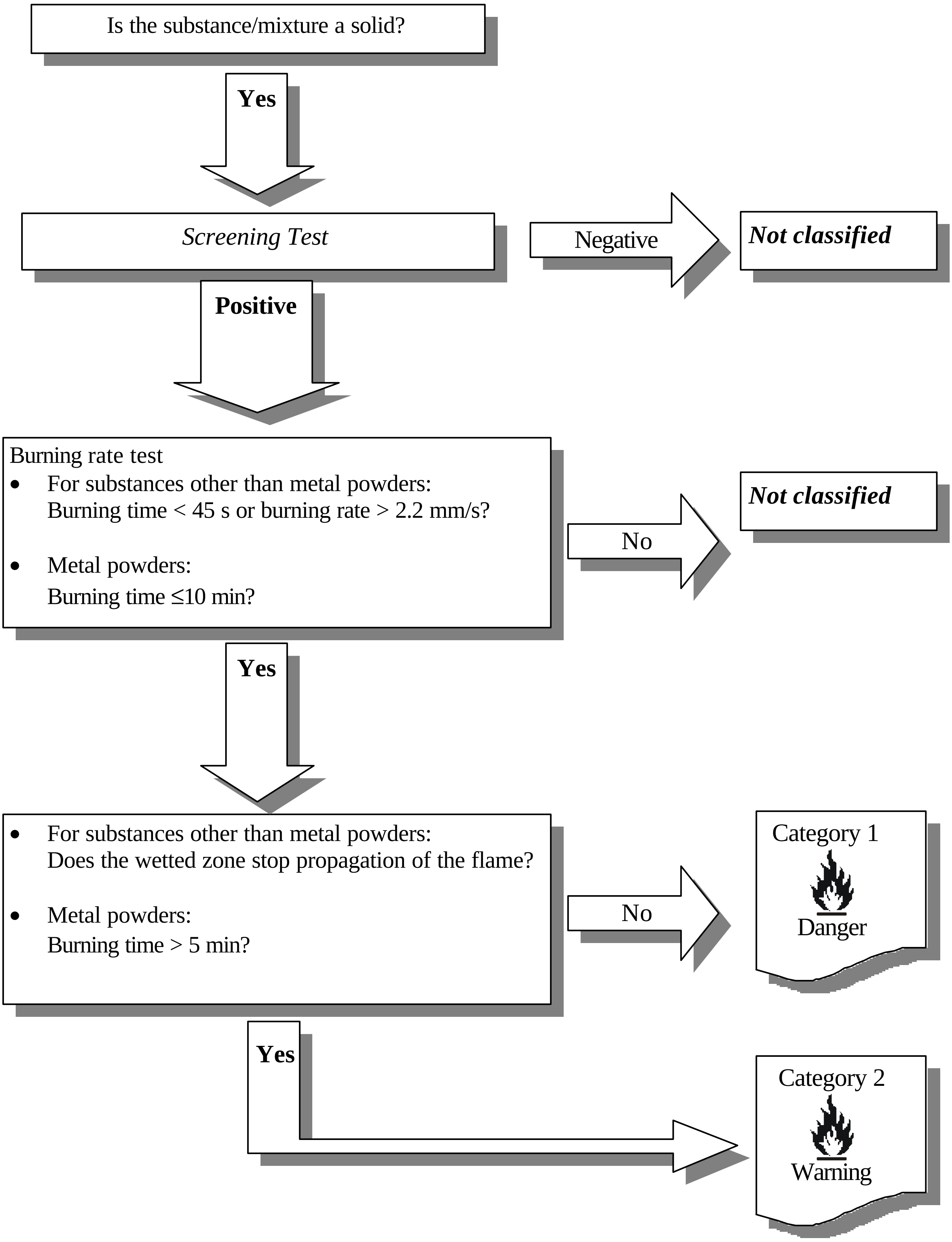
DECISION LOGIC AND GUIDANCE[1]

Decision logic

9. To classify a flammable solid, the test method N.1 as described in 33.2.1 of the Manual of Tests and Criteria should be performed. The procedure consists of two tests: a preliminary screening test and a burning rate test. Classification is according to the following decision tree.

---

[1] Paragraph 9 and the associated decision logic are not part of the agreed text on the harmonised classification for flammable solids developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of solids for flammability.


Is the substance/mixture a solid?
Yes
Screening Test
Negative
Not classified
Positive
Burning rate test
• For substances other than metal powders: Burning time < 45 s or burning rate > 2.2 mm/s?
• Metal powders: Burning time ≤10 min?
No
Not classified
Yes
• For substances other than metal powders: Does the wetted zone stop propagation of the flame?
• Metal powders: Burning time > 5 min?
No
Category 1
Danger
Yes
Category 2
Warning

Chapter 2.8: Self-reactive substances

DEFINITIONS AND GENERAL CONSIDERATIONS

1. Self-reactive substances are thermally unstable liquid or solid substances liable to undergo a strongly exothermic decomposition even without participation of oxygen (air). This definition excludes substances or mixtures classified under the GHS as explosive, organic peroxides or as oxidizing.

2. There are no general considerations.

CLASSIFICATION CRITERIA FOR SUBSTANCES AND MIXTURES

3. Any self-reactive substance should be considered for classification in this class unless:

   (a) They are explosives, according to the GHS criteria of Chapter 2.1;

   (b) They are oxidizing substances, according to the GHS criteria of Chapters 2.13 or 2.14;

   (c) They are organic peroxides, according to the GHS criteria of Chapter 2.15;

   (d) Their heat of decomposition is less than 300 J/g; or

   (e) Their self-accelerating decomposition temperature (SADT) is greater than 75 °C for a 50 kg package.

4. Self-reactive substances 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 which can detonate or deflagrate rapidly, as packaged, will be defined as self-reactive substance **TYPE A**;

   (b) Any self-reactive substance 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 possessing explosive properties when the substance 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 which in laboratory testing:

      (i) detonates partially, does not deflagrate rapidly and shows no violent effect when heated under confinement; or

(ii) does not detonate at all, deflagrates slowly and shows no violent effect when heated under confinement; or

(iii) 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 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 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 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 not less than 150 °C is used for desensitisation 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 desensitisation, the mixture shall be defined as self-reactive substance **TYPE F**.

NOTE 1: Type G has no hazard communication elements assigned but should be considered for properties belonging to other hazard classes.

NOTE 2: Types A to G may not be necessary for all systems.

HAZARD COMMUNICATION

Allocation of label elements

5. General and specific considerations concerning labelling requirements are provided in *Hazard Communication : Labelling* (Chapter 1.3). Annex 4 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

Table 1: Label elements for self-reactive substances

	Type A	**Type B**	**Type C and D**	**Type E and F**	**Type G**[1]
Symbol	Exploding bomb	Exploding bomb and flame	Flame	Flame	*There are no label elements allocated to this hazard category*
Signal word	Danger	Danger	Danger	Warning	
Hazard statement	Heating may cause an explosion	Heating may cause a fire or explosion	Heating may cause a fire	Heating may cause a fire	

[1] Type G has no hazard communication elements assigned but should be considered for properties belonging to other hazard classes.

DECISION LOGIC AND GUIDANCE[1]

Decision logic

5. To classify a self-reactive substance test series A to H as described in Part II of the Manual of Tests and Criteria should be performed. Classification is according to the decision logic following paragraph 7.

6. The properties of self-reactive substances 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).

Guidance

7. The classification procedures for self-reactive substances need not be applied if:

   (a) There are no chemical groups present in the molecule associated with explosive or self-reactive properties; examples of such groups are given in Tables A6.1 and A6.2 in the Manual of Tests and Criteria, Appendix 6; or

   (b) For a single organic substance or a homogeneous mixture of organic substances, the estimated SADT is greater than 75 °C or the exothermic decomposition energy is less than 300J/g. The onset temperature and decomposition energy may be estimated using a suitable calorimetric technique (see 20.3.3.3 of the Manual of Tests and Criteria).

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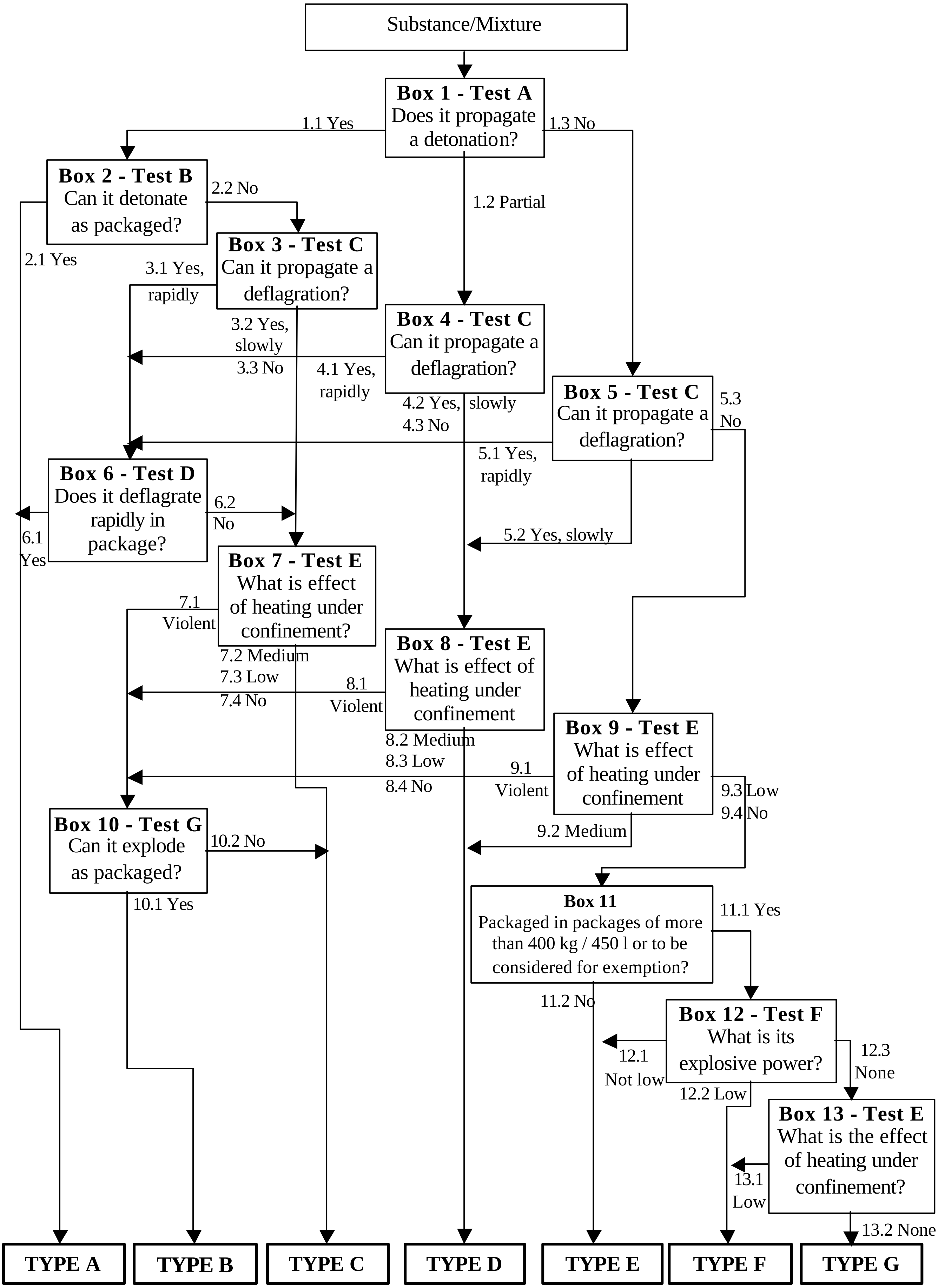
[1] Paragraphs 5-7 and the associated decision logic are not part of the agreed text on the harmonised classification for self-reactive substances developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of self-reactive substances.


Substance/Mixture
Box 1 - Test A
Does it propagate a detonation?
1.1 Yes
1.2 Partial
1.3 No
Box 2 - Test B
Can it detonate as packaged?
2.1 Yes
2.2 No
Box 3 - Test C
Can it propagate a deflagration?
3.1 Yes, rapidly
3.2 Yes, slowly
3.3 No
Box 4 - Test C
Can it propagate a deflagration?
4.1 Yes, rapidly
4.2 Yes, slowly
4.3 No
Box 5 - Test C
Can it propagate a deflagration?
5.1 Yes, rapidly
5.2 Yes, slowly
5.3 No
Box 6 - Test D
Does it deflagrate rapidly in package?
6.1 Yes
6.2 No
Box 7 - Test E
What is effect of heating under confinement?
7.1 Violent
7.2 Medium
7.3 Low
7.4 No
Box 8 - Test E
What is effect of heating under confinement
8.1 Violent
8.2 Medium
8.3 Low
8.4 No
Box 9 - Test E
What is effect of heating under confinement
9.1 Violent
9.2 Medium
9.3 Low
9.4 No
Box 10 - Test G
Can it explode as packaged?
10.1 Yes
10.2 No
Box 11
Packaged in packages of more than 400 kg / 450 l or to be considered for exemption?
11.1 Yes
11.2 No
Box 12 - Test F
What is its explosive power?
12.1 Not low
12.2 Low
12.3 None
Box 13 - Test E
What is the effect of heating under confinement?
13.1 Low
13.2 None
TYPE A
TYPE B
TYPE C
TYPE D
TYPE E
TYPE F
TYPE G

Chapter 2.9: Pyrophoric liquids

DEFINITIONS AND GENERAL CONSIDERATIONS

1. A pyrophoric liquid is a liquid which, even in small quantities, is liable to ignite within five minutes after coming into contact with air.

2. There are no general considerations.

CLASSIFICATION CRITERIA FOR SUBSTANCES

3. A pyrophoric liquid is classified in a single category for this class using test N.3 in 33.3.1.5 of the Manual of Tests and Criteria according to the following table:

Table 1: Criteria for pyrophoric liquids

Category	**Criteria**
1	The liquid ignites within 5 min when added to an inert carrier and exposed to air, or it ignites or chars a filter paper on contact with air within 5 min.

CLASSIFICATION CRITERIA FOR MIXTURES

4. The same criteria as for substances apply.

HAZARD COMMUNICATION

Allocation of label elements

5. General and specific considerations concerning labelling requirements are provided in *Hazard Communication : Labelling* (Chapter 1.3). Annex 4 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

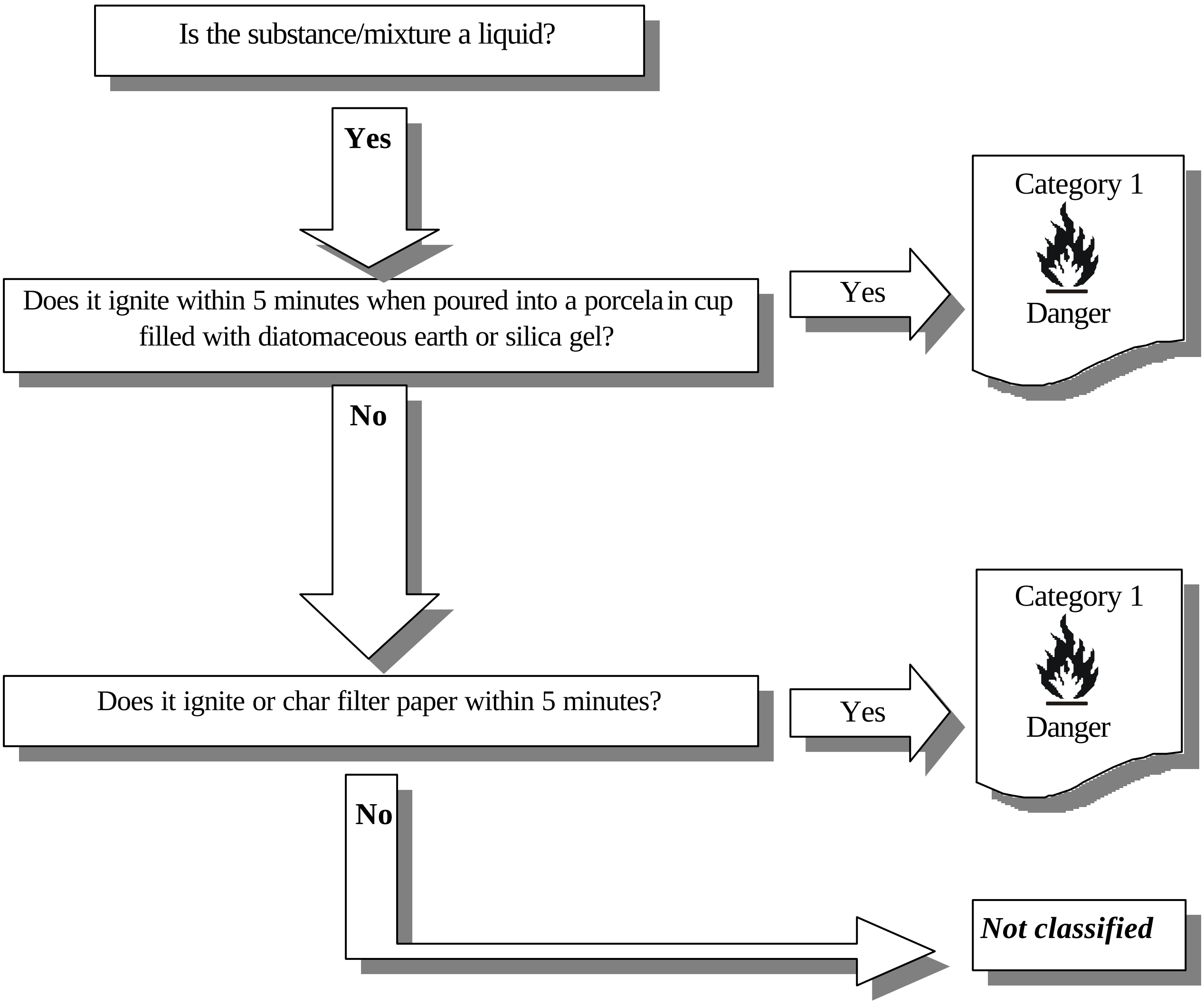
Table 2: Label elements for pyrophoric liquids

	Category 1
Symbol	Flame
Signal word	Danger
Hazard statement	Catches fire spontaneously if exposed to air

DECISION LOGIC AND GUIDANCE[1]

Decision logic

5. To classify a pyrophoric liquid, the test method N.3 as described in 33.3.1.5 of the Manual of Tests and Criteria should be performed. The procedure consists of two steps. Classification is according to the following decision logic.



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[1] Paragraphs 6-7 and the associated decision logic are not part of the agreed text on the harmonised classification for pyrophoric liquids developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of pyrophoric liquids.

Guidance

6. The classification procedure for pyrophoric liquids need not be applied when experience in production or handling shows that the substance does not ignite spontaneously on coming into contact with air at normal temperatures (i.e. the substance is known to be stable at room temperature for prolonged periods of time (days)).

Chapter 2.10: Pyrophoric solids

DEFINITIONS AND GENERAL CONSIDERATIONS

1. A pyrophoric solid is a solid which, even in small quantities, is liable to ignite within five minutes after coming into contact with air.

2. There are no general considerations.

CLASSIFICATION CRITERIA FOR SUBSTANCES

3. A pyrophoric solid is classified in a single category for this class using test N.2 in 33.3.1.4 of the Manual of Tests and Criteria according to the following table:

Table 1: Criteria for pyrophoric solids

Category	Criteria
1	The solid ignites within 5 minutes of coming into contact with air.

NOTE: For classification tests on solid substances, the tests should be performed on the substance as presented. If for example, for the purposes of supply or transport, the same chemical is to be presented in a physical form different from that which was tested and which is considered likely to materially alter its performance in a classification test, the substance must also be tested in the new form.

CLASSIFICATION CRITERIA FOR MIXTURES

4. The same criteria as for substances apply.

HAZARD COMMUNICATION

Allocation of label elements

5. General and specific considerations concerning labelling requirements are provided in *Hazard Communication : Labelling* (Chapter 1.3). Annex 4 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

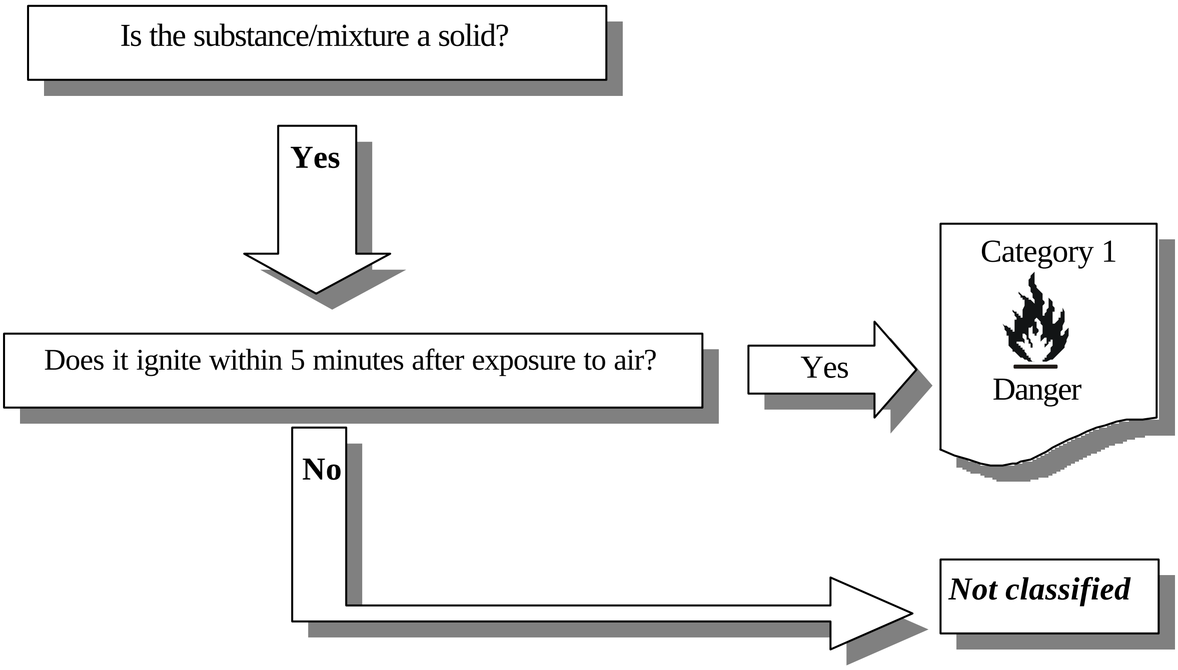
Table 2: Label elements for pyrophoric solids

	Category 1
Symbol	Flame
Signal word	Danger
Hazard statement	Catches fire spontaneously if exposed to air

DECISION LOGIC AND GUIDANCE[1]

Decision logic

6. To classify a pyrophoric solid, the test method N.2 as described in 33.3.1.4 of the Manual of Tests and Criteria should be performed. Classification is according to the following decision logic.



Guidance

7. The classification procedure for pyrophoric solids need not be applied when experience in production or handling shows that the substance does not ignite spontaneously on coming into contact with air at normal temperatures (i.e. the substance is known to be stable at room temperature for prolonged periods of time (days)).

---

[1] Paragraphs 6-7 and the associated decision logic are not part of the agreed text on the harmonised classification for pyrophoric solids developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of pyrophoric solids. `

Chapter 2.11: Self-heating substances

DEFINITIONS AND GENERAL CONSIDERATIONS

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

NOTE: Self-heating of substances, leading to spontaneous combustion, is caused by reaction of the substance with oxygen (in the air) and the heat developed not being conducted away rapidly enough to the surroundings. Spontaneous combustion occurs when the rate of heat production exceeds the rate of heat loss and the auto-ignition temperature is reached.

CLASSIFICATION CRITERIA FOR SUBSTANCES

2. A substance shall be classified as a self-heating substance of this class, if in tests performed in accordance with the test method given in the Manual of Tests and Criteria, Part III, sub-section 33.3.1.6:

   (a) A positive result is obtained using a 25 mm cube sample at 140 °C;

   (b) 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 100 mm cube sample at 120 °C and the substance is to be packed in packages with a volume of more than 3 m^3;

   (c) 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 100 mm cube sample at 100 °C and the substance is to be packed in packages with a volume of more than 450 litres;

   (d) A positive result is obtained in a test using a 100 mm sample cube at 140 °C and a positive result is obtained using a 100 mm cube sample at 100 °C.

3. A self-heating substance is classified in one of the two categories for this class if, in test performed in accordance with test method N. 4 in 33.3.1.6 of the Manual of Tests and Criteria, the result meets the following criteria:

Table 1: Criteria for self-heating substances

Category	**Criteria**
1	A positive result is obtained in a test using a 25 mm sample cube at 140 °C
2	(a) 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 is to be packed in packages with a volume of more than 3 m^3; or (b) 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 is to be packed in packages with a volume of more than 450 litres; or (c) 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.

NOTE: For classification tests on solid substances, the tests should be performed on the substance as presented. If for example, for the purposes of supply or transport, the same chemical is to be presented in a physical form different from that which was tested and which is considered likely to materially alter its performance in a classification test, the substance must also be tested in the new form.

CLASSIFICATION CRITERIA FOR MIXTURES

4. The same criteria as for substances apply.

HAZARD COMMUNICATION

Allocation of label elements

5. General and specific considerations concerning labelling requirements are provided in *Hazard Communication : Labelling* (Chapter 1.3). Annex 4 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

Table 2: Label elements for self-heating substances

	Category 1	**Category 2**
Symbol	Flame	Flame
Signal word	Danger	Warning
Hazard statement	Self-heating; may catch fire	Self-heating in large quantities; may catch fire

DECISION LOGIC AND GUIDANCE[1]

Decision logic

6. To classify a self-heating substance/mixture, test method N.4, as described in 33.3.1.6 of the Manual of Tests and Criteria, should be performed. Classification is according to the decision logic following paragraph 7.

Guidance

7. The classification procedure for self-heating substances need not be applied if the results of a screening test can be adequately correlated with the classification test and an appropriate safety margin is applied. Examples of screening tests are:

    (a) The Grewer Oven test (VDI guideline 2263, part 1, 1990, Test methods for the Determination of the Safety Characteristics of Dusts) with an onset temperature 80 K above the reference temperature for a volume of 1 l;

    (b) The Bulk Powder Screening Test (Gibson, N. Harper, D. J. Rogers, R. Evaluation of the fire and explosion risks in drying powders, Plant Operations Progress, **4** (3), 181 - 189, 1985) with an onset temperature 60 K above the reference temperature for a volume of 1 l.

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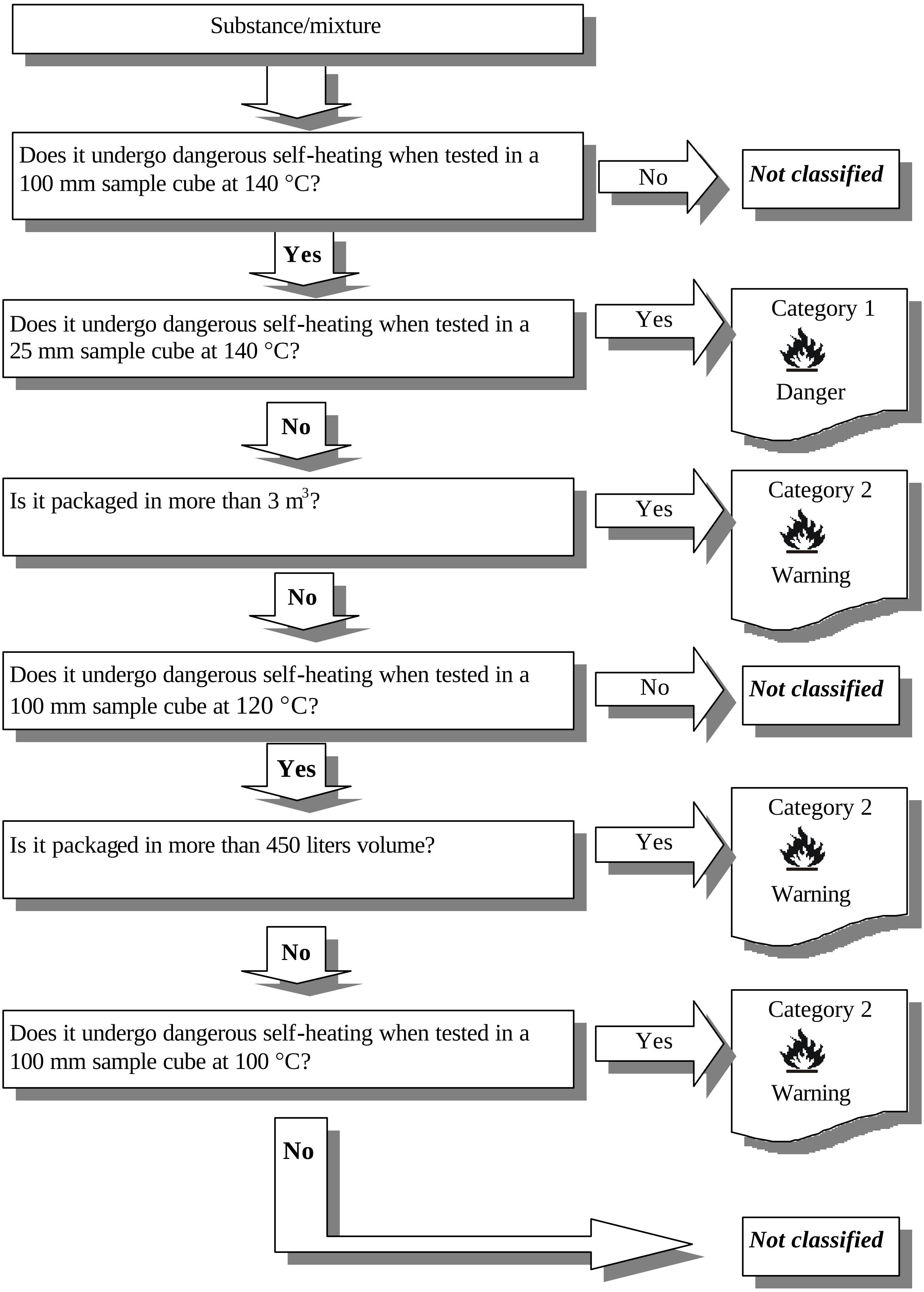
[1] Paragraphs 6-7 and the associated decision logic are not part of the agreed text on the harmonised classification for self-heating substances developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of self-heating substances.


Substance/mixture
Does it undergo dangerous self-heating when tested in a 100 mm sample cube at 140 °C?
No
Not classified
Yes
Does it undergo dangerous self-heating when tested in a 25 mm sample cube at 140 °C?
Yes
Category 1
Danger
No
Is it packaged in more than 3 m^3?
Yes
Category 2
Warning
No
Does it undergo dangerous self-heating when tested in a 100 mm sample cube at 120 °C?
No
Not classified
Yes
Is it packaged in more than 450 liters volume?
Yes
Category 2
Warning
No
Does it undergo dangerous self-heating when tested in a 100 mm sample cube at 100 °C?
Yes
Category 2
Warning
No
Not classified

Chapter 2.12: Substances which, in contact with water, emit flammable gases

DEFINITIONS AND GENERAL CONSIDERATIONS

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

2. There are no general considerations.

CLASSIFICATION CRITERIA FOR SUBSTANCES

3. A substance which, in contact with water, emit flammable gases is classified in one of the three categories for this class, using test N.5 in 33.4.1.4 of the Manual of Tests and Criteria, according to the following table:

Table 1: Criteria for substances which in contact with water emit flammable gases

Category	**Criteria**
1	Any substance 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	Any substance 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	Any substance which reacts slowly with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 1 litre per kilogram of substance per hour, and which does not meet the criteria for categories 1 and 2.

NOTE 1: A substance is classified as a substance which in contact with water emits flammable gases if spontaneous ignition takes place in any step of the test procedure.

NOTE 2: For classification tests on solid substances, the tests should be performed on the substance as presented. If for example, for the purposes of supply or transport, the same chemical is to be presented in a physical form different from that which was tested and which is considered likely to materially alter its performance in a classification test, the substance must also be tested in the new form.

CLASSIFICATION CRITERIA FOR MIXTURES

4. The same criteria as for substances apply.

HAZARD COMMUNICATION

Allocation of label elements

5. General and specific considerations concerning labelling requirements are provided in *Hazard Communication : Labelling* (Chapter 1.3). Annex 4 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

Table 2: Label elements for substances which in contact with water emit flammable gases

	Category 1	**Category 2**	**Category 3**
Symbol	Flame	Flame	Flame
Signal word	Danger	Danger	Warning
Hazard statement	In contact with water releases flammable gases which may ignite spontaneously	In contact with water releases flammable gases	In contact with water releases flammable gases

DECISION LOGIC AND GUIDANCE[1]

Decision logic

6. To classify a substance which, in contact with water emits flammable gases, test N.5 as described in 33.4.1.4 of the Manual of Tests and Criteria should be performed. Classification is according to the following decision logic.

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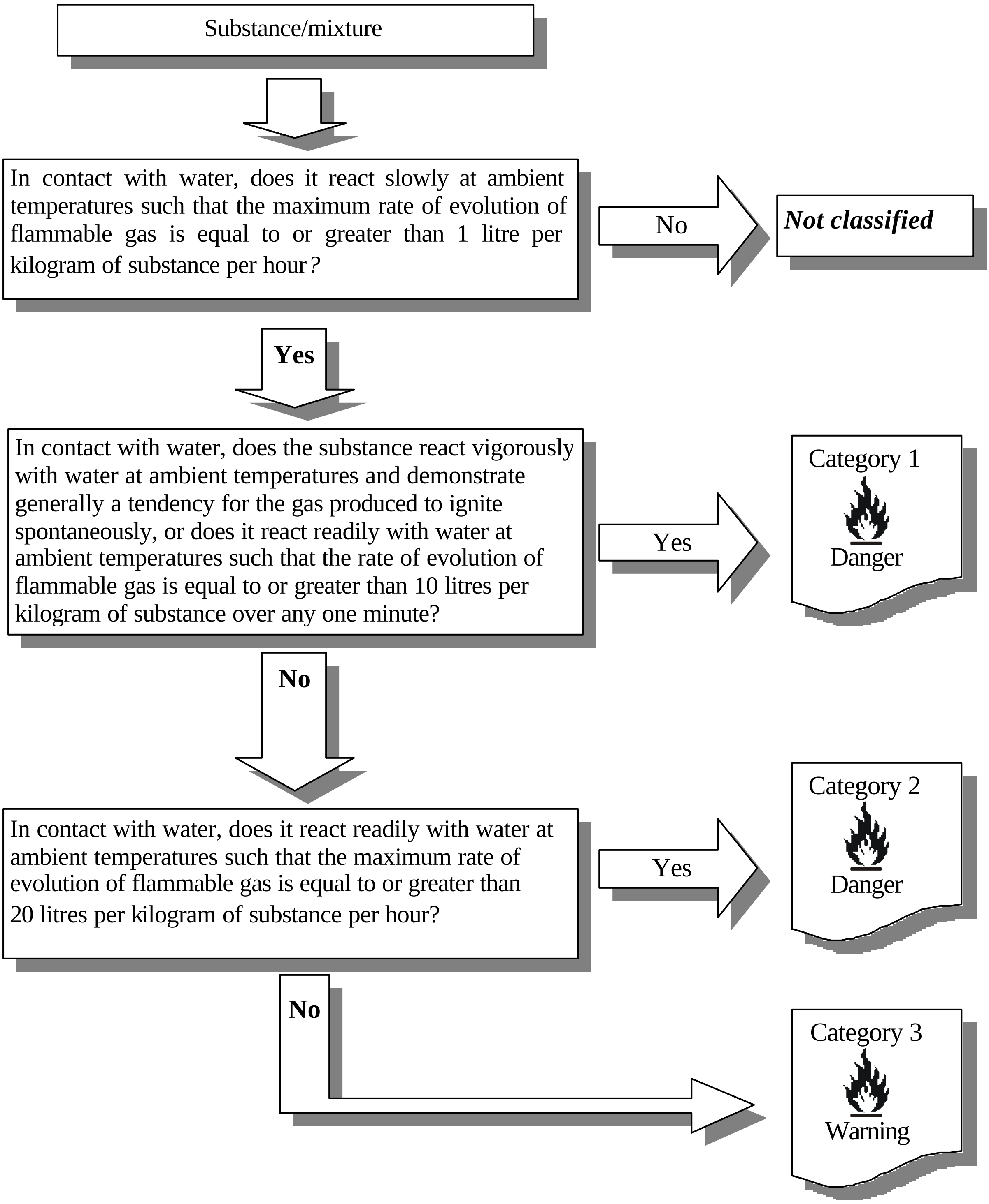
[1] Paragraphs 6-7 and the associated decision logic are not part of the agreed text on the harmonised classification for a substance which in contact with water emits flammable gases developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of such substances.


Substance/mixture
In contact with water, does it react slowly at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 1 litre per kilogram of substance per hour?
No
Not classified
Yes
In contact with water, does the substance react vigorously with water at ambient temperatures and demonstrate generally a tendency for the gas produced to ignite spontaneously, or does it react 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?
Yes
Category 1
Danger
No
In contact with water, does it react 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?
Yes
Category 2
Danger
No
Category 3
Warning

Guidance

7. The classification procedure for this class need not be applied if:

a) The chemical structure of the substance or mixture does not contain metals or metalloids;

b) Experience in production or handling shows that the substance or mixture does not react with water, e.g. the substance is manufactured with water or washed with water; or

c) The substance is known to be soluble in water to form a stable mixture.

Chapter 2.13: Oxidizing liquids

DEFINITIONS AND GENERAL CONSIDERATIONS

1. An oxidizing liquid is a liquid which, while in itself not necessarily combustible, may, generally by yielding oxygen, cause, or contribute to, the combustion of other material.

2. There are no general considerations.

CLASSIFICATION CRITERIA FOR SUBSTANCES

3. An oxidizing liquid is classified in one of the three categories for this class using test O.2 in 34.4.2 of the Manual of Tests and Criteria according to the following table:

Table 1: Criteria for oxidizing liquids

Category	Criteria
1	Any substance which, in the 1:1 mixture, by mass, of substance and cellulose tested, spontaneously ignites; or the mean pressure rise time of a 1:1 mixture, by mass, of substance and cellulose is less than that of a 1:1 mixture, by mass, of 50% perchloric acid and cellulose
2	Any substance which, in the 1:1 mixture, by mass, of substance and cellulose tested, exhibits a mean pressure rise time less than or equal to the mean pressure rise time of a 1:1 mixture, by mass, of 40% aqueous sodium chlorate solution and cellulose; and the criteria for category 1 are not met
3	Any substance which, in the 1:1 mixture, by mass, of substance and cellulose tested, exhibits a mean pressure rise time less than or equal to the mean pressure rise time of a 1:1 mixture, by mass, of 65% aqueous nitric acid and cellulose; and the criteria for category 1 and 2 are not met

CLASSIFICATION CRITERIA FOR MIXTURES

4. The same criteria as for substances apply.

HAZARD COMMUNICATION

Allocation of Label Elements

5. General and specific considerations concerning labelling requirements are provided in *Hazard Communication : Labelling* (Chapter 1.3). Annex 4 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

Table 2: Label elements for oxidizing liquids

	Category 1	**Category 2**	**Category 3**
Symbol	Flame over circle	Flame over circle	Flame over circle
Signal word	Danger	Danger	Warning
Hazard statement	May cause fire or explosion; strong oxidizer	May intensify fire; oxidizer	May intensify fire; oxidizer

DECISION LOGIC AND GUIDANCE[1]

Decision Logic

6. To classify an oxidizing liquid test method O.2 as described in 34.4.2 of the Manual of Tests and Criteria should be performed. Classification is according to the decision logic following paragraph 7.

Guidance

7. Experience in the handling and use of substances which shows them to be oxidizing is an important additional factor in considering classification in this class. In the event of divergence between tests results and known experience, judgement based on known experience should take precedence over test results.

8. In some cases, substances may generate a pressure rise (too high or too low), caused by chemical reactions not characterising the oxidizing properties of the substance. In these cases, it may be necessary to repeat the test described in 34.4.2 of the Manual of Tests and Criteria with an inert substance, e.g. diatomite (kieselguhr), in place of the cellulose in order to clarify the nature of the reaction.

9. For organic substances or mixtures the classification procedure for this class need not be applied if:

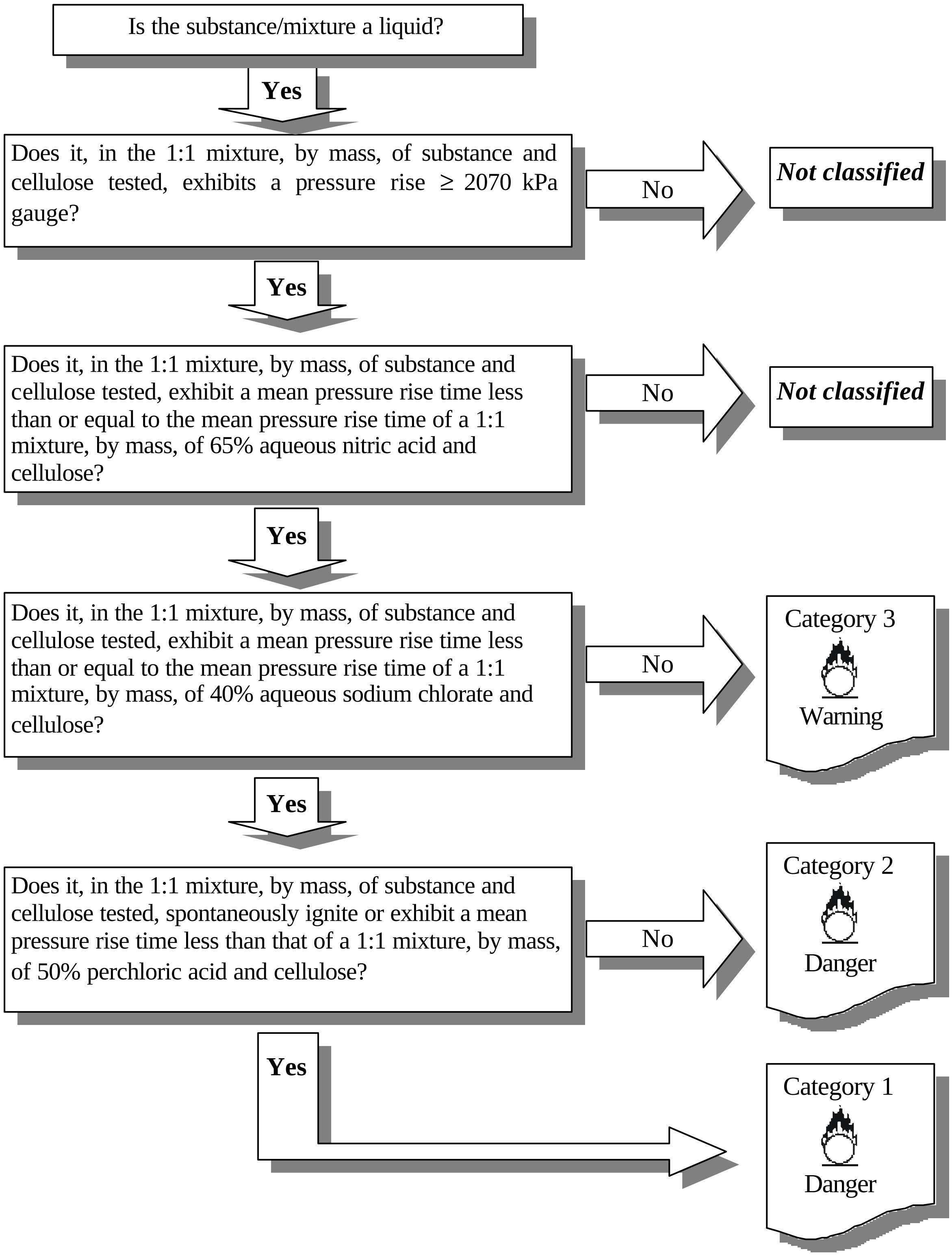
   a) The substance or mixture does not contain oxygen, fluorine or chlorine; or

---

[1] Paragraphs 6-10 and the associated decision logic are not part of the agreed text on the harmonised classification for an oxidizing liquid developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of liquids for oxidizing properties

b) The substance or mixture contains oxygen, fluorine or chlorine and these elements are chemically bonded only to carbon or hydrogen.

10. For inorganic substances or mixtures, the classification procedure for this class need not be applied if they do not contain oxygen or halogen atoms.


Is the substance/mixture a liquid?
Yes
Does it, in the 1:1 mixture, by mass, of substance and cellulose tested, exhibits a pressure rise ≥ 2070 kPa gauge?
No
Not classified
Yes
Does it, in the 1:1 mixture, by mass, of substance and cellulose tested, exhibit a mean pressure rise time less than or equal to the mean pressure rise time of a 1:1 mixture, by mass, of 65% aqueous nitric acid and cellulose?
No
Not classified
Yes
Does it, in the 1:1 mixture, by mass, of substance and cellulose tested, exhibit a mean pressure rise time less than or equal to the mean pressure rise time of a 1:1 mixture, by mass, of 40% aqueous sodium chlorate and cellulose?
No
Category 3
Warning
Yes
Does it, in the 1:1 mixture, by mass, of substance and cellulose tested, spontaneously ignite or exhibit a mean pressure rise time less than that of a 1:1 mixture, by mass, of 50% perchloric acid and cellulose?
No
Category 2
Danger
Yes
Category 1
Danger

Chapter 2.14: Oxidizing solids

DEFINITIONS AND GENERAL CONSIDERATIONS

1. An oxidizing solid is a solid which, while in itself is not necessarily combustible, may, generally by yielding oxygen, cause, or contribute to, the combustion of other material.

2. There are no general considerations.

CLASSIFICATION CRITERIA FOR SUBSTANCES

3. An oxidizing solid is classified in one of the three categories for this class using test O.1 in 34.4.1 of the Manual of Tests and Criteria according to the following table:

Table 1: Criteria for oxidizing solids

Category	Criteria
1	Any substance which, in the 4:1 or 1:1 sample-to-cellulose ratio (by mass) tested, exhibits a mean burning time less than the mean burning time of a 3:2 mixture, by mass, of potassium bromate and cellulose.
2	Any substance which, in the 4:1 or 1:1 sample-to-cellulose ratio (by mass) tested, exhibits a mean burning time equal to or less than the mean burning time of a 2:3 mixture (by mass) of potassium bromate and cellulose and the criteria for category 1 are not met.
3	Any substance which, in the 4:1 or 1:1 sample-to-cellulose ratio (by mass) tested, exhibits a mean burning time equal to or less than the mean burning time of a 3:7 mixture (by mass) of potassium bromate and cellulose and the criteria for categories 1 and 2 are not met.

NOTE: For classification tests on solid substances, the tests should be performed on the substance as presented. If for example, for the purposes of supply or transport, the same chemical is to be presented in a physical form different from that which was tested and which is considered likely to materially alter its performance in a classification test, the substance must also be tested in the new form.

CLASSIFICATION CRITERIA FOR MIXTURES

4. The same criteria as for substances apply.

HAZARD COMMUNICATION

Allocation of label elements

5. General and specific considerations concerning labelling requirements are provided in *Hazard Communication : Labelling* (Chapter 1.3). Annex 4 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

Table 2: Label elements for oxidizing solids

	Category 1	**Category 2**	**Category 3**
Symbol	Flame over circle	Flame over circle	Flame over circle
Signal word	Danger	Danger	Warning
Hazard statement	May cause fire or explosion; strong oxidizer	May intensify fire; oxidizer	May intensify fire; oxidizer

DECISION LOGIC AND GUIDANCE[1]

Decision logic

6. To classify an oxidizing solid test method O.1 as described in 34.4.1 of the Manual of Tests and Criteria should be performed. Classification is according to the decision logic following paragraph 8.

Guidance

7. Experience in the handling and use of substances which shows them to be oxidizing is an important additional factor in considering classification in this class. In the event of divergence between tests results and known experience, judgement based on known experience should take precedence over test results.

8. The classification procedure for this class need not be applied to organic substances or mixtures if:

   a) The substance or mixture does not contain oxygen, fluorine or chlorine; or

   b) The substance or mixture contains oxygen, fluorine or chlorine and these elements are chemically bonded only to carbon or hydrogen.

9. The classification procedure for this class need not be applied to inorganic substances or mixtures if they do not contain oxygen or halogen atoms

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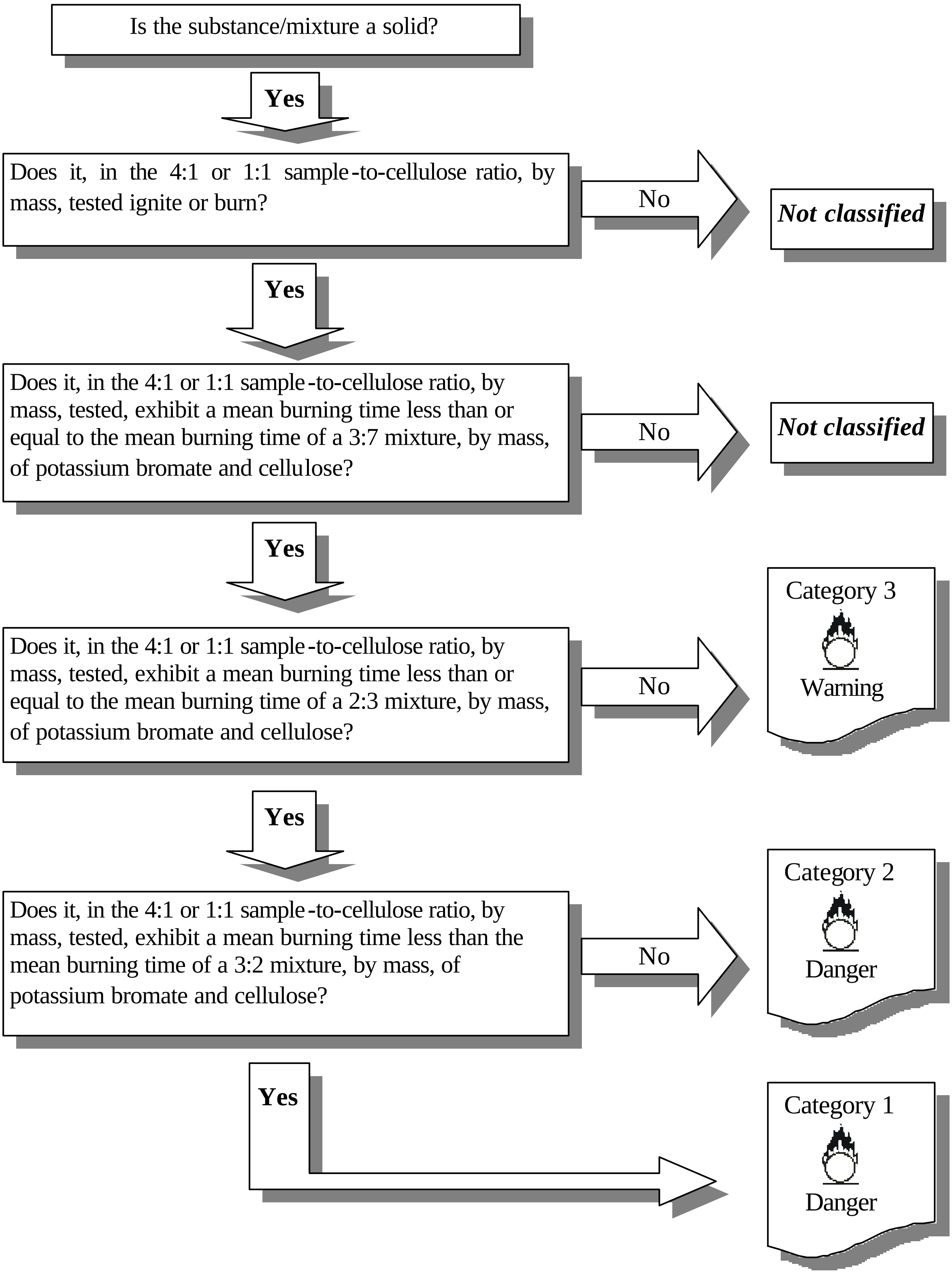
[1] Paragraphs 6-8 and the associated decision logic are not part of the agreed text on the harmonised classification for an oxidizing solid developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of solids for oxidizing properties.



Is the substance/mixture a solid?

Does it, in the 4:1 or 1:1 sample-to-cellulose ratio, by mass, tested ignite or burn?

Does it, in the 4:1 or 1:1 sample-to-cellulose ratio, by mass, tested, exhibit a mean burning time less than or equal to the mean burning time of a 3:7 mixture, by mass, of potassium bromate and cellulose?

Does it, in the 4:1 or 1:1 sample-to-cellulose ratio, by mass, tested, exhibit a mean burning time less than or equal to the mean burning time of a 2:3 mixture, by mass, of potassium bromate and cellulose?

Does it, in the 4:1 or 1:1 sample-to-cellulose ratio, by mass, tested, exhibit a mean burning time less than the mean burning time of a 3:2 mixture, by mass, of potassium bromate and cellulose?

Chapter 2.15: Organic peroxides

DEFINITIONS AND GENERAL CONSIDERATIONS

1. Organic peroxides are liquid or solid organic substances which contain the bivalent -0-0- structure and may be considered derivatives of hydrogen peroxide, where one or both of the hydrogen atoms have been replaced by organic radicals. Organic peroxides are thermally unstable substances, which may undergo exothermic self-accelerating decomposition. In addition, they may have one or more of the following properties:

   (i) be liable to explosive decomposition;
   (ii) burn rapidly;
   (iii) be sensitive to impact or friction;
   (iv) react dangerously with other substances.

CLASSIFICATION CRITERIA FOR SUBSTANCES AND MIXTURES

2. Any organic peroxide shall be considered for classification in this class, unless it contains:

   (a) Not more than 1.0% available oxygen from the organic peroxides when containing not more than 1.0% hydrogen peroxide; or

   (b) Not more than 0.5% available oxygen from the organic peroxides when containing more than 1.0% but not more than 7.0% hydrogen peroxide

NOTE: The available oxygen content (%) of an organic peroxide mixture is given by the formula:

$$16 \times \Sigma (n_i \times c_i / m_i)$$

where: n_i = number of peroxygen groups per molecule of organic peroxide i;
c_i = concentration (mass %) of organic peroxide i;
m_i = molecular mass of organic peroxide i.

3. 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 mixture which can detonate or deflagrate rapidly, as packaged, will be defined as organic peroxide **TYPE A**;

   (b) Any organic peroxide 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 organic peroxide **TYPE B**;

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

(d) Any organic peroxide mixture which in laboratory testing:

  (i) detonates partially, does not deflagrate rapidly and shows no violent effect when heated under confinement; or

  (ii) does not detonate at all, deflagrates slowly and shows no violent effect when heated under confinement; or

  (iii) 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 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 organic peroxide **TYPE E**;

(f) Any organic peroxide 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 organic peroxide **TYPE F**;

(g) Any organic peroxide 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 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 desensitisation, will be defined as organic peroxide **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 organic peroxide **TYPE F**.

NOTE 1: Type G has no hazard communication elements assigned but should be considered for properties belonging to other hazard classes.

NOTE 2: Types A to G may not be necessary for all systems.

HAZARD COMMUNICATION

Allocation of label elements

4. General and specific considerations concerning labelling requirements are provided in *Hazard Communication : Labelling* (Chapter 1.3). Annex 4 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

Table 1: Label elements for organic peroxides

	Type A	**Type B**	**Type C and D**	**Type E and F**	**Type G**[1]
Symbol	Exploding bomb	Exploding bomb and flame over circle	Flame over circle	Flame over circle	*There are no label elements allocated to this hazard category.*
Signal word	Danger	Danger	Danger	Warning	
Hazard statement	Heating may cause an explosion	Heating may cause a fire or explosion	Heating may cause a fire	Heating may cause a fire	

[1] Type G has no hazard communication elements assigned but should be considered for properties belonging to other hazard classes.

DECISION LOGIC AND GUIDANCE[1]

Decision logic

5. 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. Classification is according to the following decision logic:

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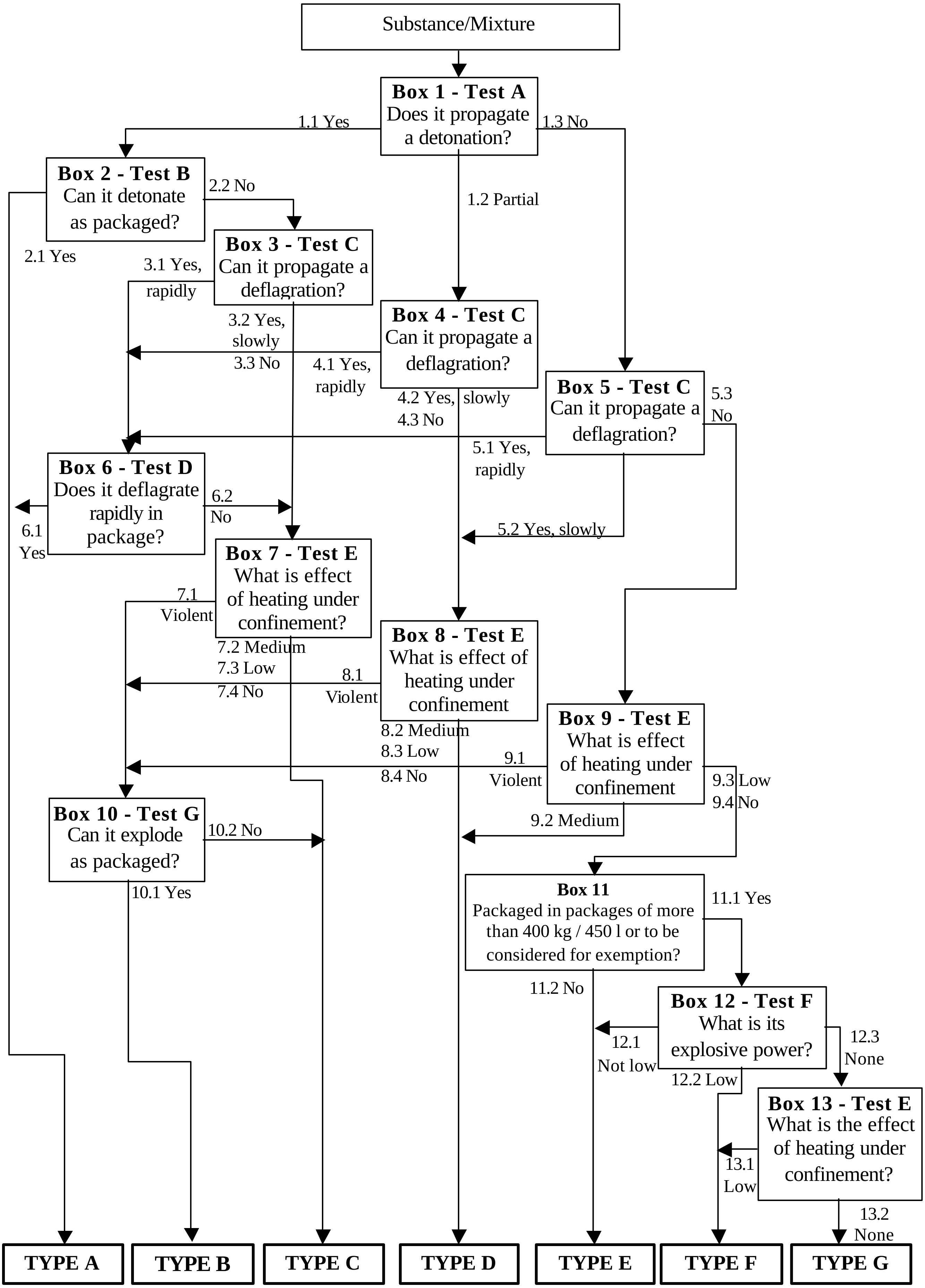
[1] Paragraphs 5 and the associated decision logic are not part of the agreed text on the harmonised classification for organic peroxides developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of such peroxides.


Substance/Mixture
Box 1 - Test A
Does it propagate a detonation?
1.1 Yes
1.2 Partial
1.3 No
Box 2 - Test B
Can it detonate as packaged?
2.1 Yes
2.2 No
Box 3 - Test C
Can it propagate a deflagration?
3.1 Yes, rapidly
3.2 Yes, slowly
3.3 No
Box 4 - Test C
Can it propagate a deflagration?
4.1 Yes, rapidly
4.2 Yes, slowly
4.3 No
Box 5 - Test C
Can it propagate a deflagration?
5.1 Yes, rapidly
5.2 Yes, slowly
5.3 No
Box 6 - Test D
Does it deflagrate rapidly in package?
6.1 Yes
6.2 No
Box 7 - Test E
What is effect of heating under confinement?
7.1 Violent
7.2 Medium
7.3 Low
7.4 No
Box 8 - Test E
What is effect of heating under confinement
8.1 Violent
8.2 Medium
8.3 Low
8.4 No
Box 9 - Test E
What is effect of heating under confinement
9.1 Violent
9.2 Medium
9.3 Low
9.4 No
Box 10 - Test G
Can it explode as packaged?
10.1 Yes
10.2 No
Box 11
Packaged in packages of more than 400 kg / 450 l or to be considered for exemption?
11.1 Yes
11.2 No
Box 12 - Test F
What is its explosive power?
12.1 Not low
12.2 Low
12.3 None
Box 13 - Test E
What is the effect of heating under confinement?
13.1 Low
13.2 None
TYPE A
TYPE B
TYPE C
TYPE D
TYPE E
TYPE F
TYPE G

Guidance[2]

6. Organic peroxides are classified by definition based on their chemical structure and on the available oxygen and hydrogen peroxide content of the mixture (see paragraph 2 above).

7. The properties of organic peroxide 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).

8. Mixtures of organic peroxides may be classified as the same type of organic peroxide as that of the most dangerous component. However, as two stable components can form a thermally less stable mixture, the self-accelerating decomposition temperature (SADT) of the mixture shall be determined.

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[2] Paragraphs 6-8 are not part of the agreed text on the harmonised classification for organic peroxides developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of such peroxides.

Chapter 2.16: Corrosive to metals

DEFINITIONS AND GENERAL CONSIDERATIONS

1. A substance or a mixture that is corrosive to metal is a substance or a mixture which by chemical action will materially damage, or even destroy, metals.

2. There are no general considerations.

CLASSIFICATION CRITERIA FOR SUBSTANCES

3. A substance that is corrosive to metal is classified in a single category for this class according to the following table

Table 1: Criteria for substances corrosive to metal

Category	Criteria
1	Corrosion rate on steel or aluminium surfaces exceeding 6.25 mm per year at a test temperature of 55 °C.

CLASSIFICATION CRITERIA FOR MIXTURES

4. The same criteria as for substances apply.

HAZARD COMMUNICATION

Allocation of label elements

5. General and specific considerations concerning labelling requirements are provided in *Hazard Communication : Labelling* (Chapter 1.3). Annex 4 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

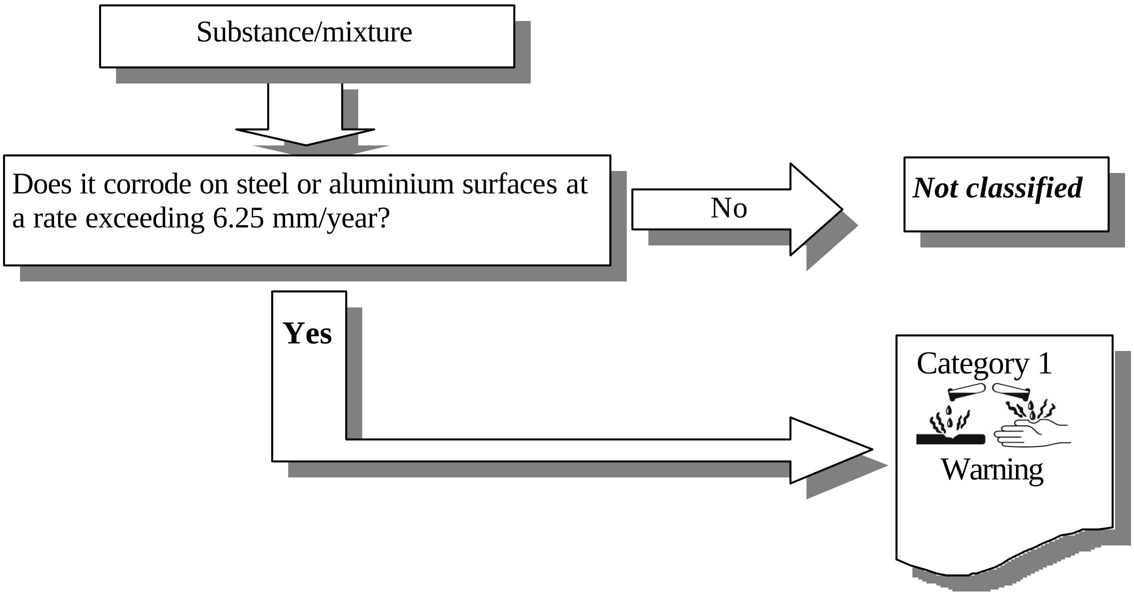
Table 2: Label elements for substances corrosive to metals

	Category 1
Symbol	Corrosive
Signal word	Warning
Hazard statement	May be corrosive to metals

DECISION LOGIC AND GUIDANCE[1]

Decision Logic

6.



Guidance

7. The corrosion rate can be measured with the following tests methods:

- for the purposes of testing steel, type P235 (ISO 9328 (II):1991) or a similar type shall be used;
- for testing aluminium, non-clad types 7075-T6 or AZ5GU-T6 shall be used.

An acceptable test is prescribed in ASTM G31-72 (Reapproved 1990).

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[1] The decision logic in paragraph 6 and the guidance in paragraph 7 are not part of the agreed text on the harmonised classification for corrosive to metals developed by the UNCETDG-ILO Working Group, but have been provided in this chapter as additional guidance on the classification of such substances or mixtures.