

# **PART 2**

# **PHYSICAL HAZARDS**



## CHAPTER 2.1

### EXPLOSIVES

#### 2.1.1 Definitions and general considerations

2.1.1.1 An *explosive substance (or mixture)* 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.

A *pyrotechnic substance (or mixture)* 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.

An *explosive article* is an article containing one or more explosive substances or mixtures.

A *pyrotechnic article* is an article containing one or more pyrotechnic substances or mixtures.

2.1.1.2 The class of explosives comprises:

- (a) Explosive substances and mixtures;
- (b) Explosive articles, except devices containing explosive substances or mixtures 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) Substances, mixtures and articles not mentioned under (a) and (b) above which are manufactured with the view to producing a practical, explosive or pyrotechnic effect.

#### 2.1.2 Classification criteria

2.1.2.1 Substances, mixtures and articles of this class, which are not classified as an unstable explosive, are assigned to one of the following six divisions depending on the type of hazard they present:

- (a) Division 1.1 Substances, mixtures and articles which have a mass explosion hazard (a mass explosion is one which affects almost the entire quantity present virtually instantaneously);
- (b) Division 1.2 Substances, mixtures and articles which have a projection hazard but not a mass explosion hazard;
- (c) Division 1.3 Substances, mixtures 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, mixtures and articles which present no significant hazard: substances, mixtures 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 or mixtures which have a mass explosion hazard: substances and mixtures 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 or mixtures and which demonstrate a negligible probability of accidental initiation or propagation.

2.1.2.2 Explosives, which are not classified as an unstable explosive, are classified in one of the six divisions above based on Test Series 2 to 8 in Part I of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria* according to the following table:

**Table 2.1.1: Criteria for explosives**

Category	Criteria
<b>Unstable<sup>a</sup> explosives or explosives of Division 1.1 to 1.6</b>	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 <i>UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria</i> ). Intentional explosives <sup>b</sup> are not subject to UN Test series 2. Sensitiveness: according to UN Test Series 3 (Section 13 of the <i>UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria</i> ). Thermal stability: according to UN Test 3(c) (Sub-section 13.6.1 of the <i>UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria</i> ). Further tests are necessary to allocate the correct Division.

<sup>a</sup> *Unstable explosives are those which are thermally unstable and/or too sensitive for normal handling, transport and use. Special precautions are necessary.*

<sup>b</sup> *This comprises substances, mixtures and articles which are manufactured with a view to producing a practical, explosive or pyrotechnic effect.*

**NOTE 1:** *Explosive substances or mixtures 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 Recommendations on the Transport of Dangerous Goods, Model Regulations, Chapter 2.1*).*

**NOTE 2:** *Some explosive substances and mixtures are wetted with water or alcohols or diluted with other substances to suppress their explosives properties. They may be treated differently from explosive substances and mixtures (as desensitized explosives) for some regulatory purposes (e.g. transport), see 1.3.2.4.5.2.*

**NOTE 3:** *For classification tests on solid substances or mixtures, the tests should be performed on the substance or mixture 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 or mixture must also be tested in the new form.*

### 2.1.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 2 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

**Table 2.1.2: Label elements for explosives**

	<b>Unstable Explosive</b>	<b>Division 1.1</b>	<b>Division 1.2</b>	<b>Division 1.3</b>	<b>Division 1.4</b>	<b>Division 1.5</b>	<b>Division 1.6</b>
<b>Symbol</b>	Exploding bomb	Exploding bomb	Exploding bomb	Exploding bomb	Exploding bomb; <i>or</i> 1.4 on orange background <sup>a</sup>	1.5 on orange background <sup>a</sup>	1.6 on orange background <sup>a</sup>
<b>Signal word</b>	Danger	Danger	Danger	Danger	Warning	Danger	<i>No signal word</i>
<b>Hazard statement</b>	Unstable Explosive	Explosive; mass explosion hazard	Explosive; severe projection hazard	Explosive; fire, blast or projection hazard.	Fire or projection hazard	May mass explode in fire	<i>No hazard statement</i>

<sup>a</sup> Applies to substances, mixtures and articles subject to some regulatory purposes (e.g. transport).

**NOTE:** Unpackaged explosives or explosives repacked in packagings other than the original or similar packaging shall have the following label elements:

- (a) Symbol: exploding bomb;
- (b) Signal word: “Danger”; and
- (c) Hazard statement: “explosive; mass explosion hazard”

unless the hazard is shown to correspond to one of the hazard categories in table 2.1.2, in which case the corresponding symbol, signal word and/or the hazard statement shall be assigned.

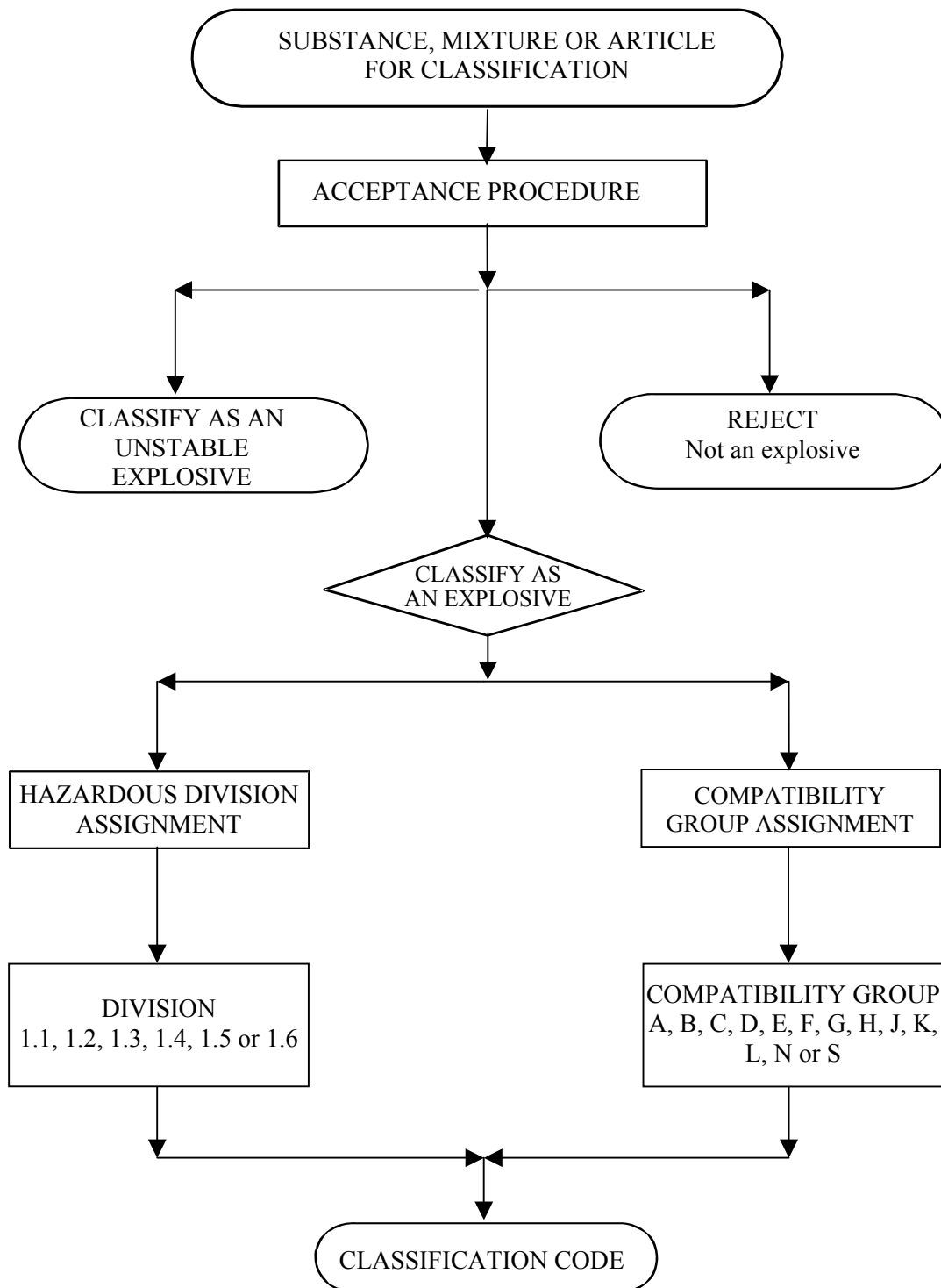
### 2.1.4 Decision logic and guidance

The decision logic and guidance, which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

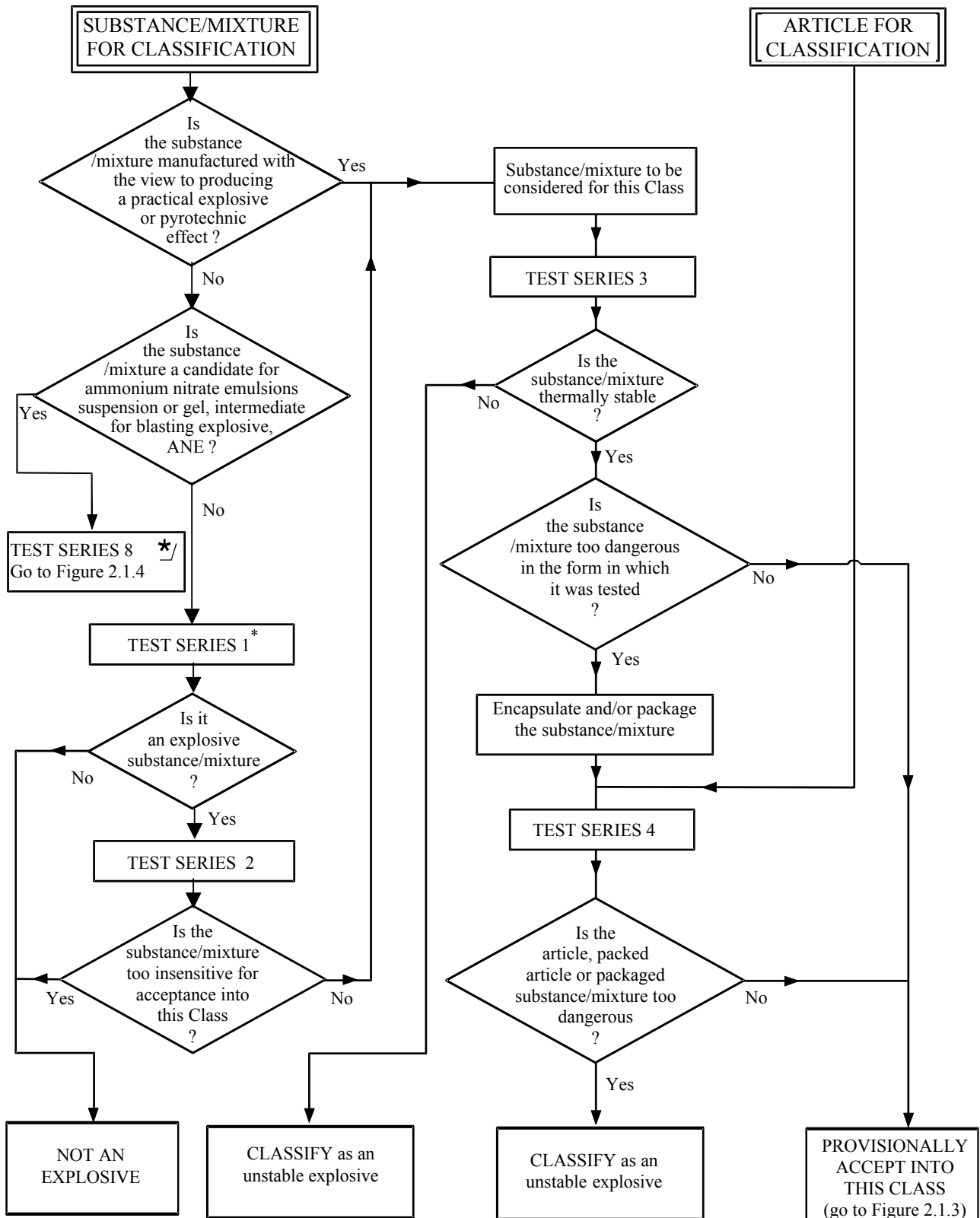
#### 2.1.4.1 Decision logic

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 the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, is necessary. The first step is to ascertain whether the substance or mixture 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 assessment whether a candidate for “ammonium nitrate emulsion or suspension or gel, intermediate for blasting explosives (ANE)” is insensitive enough for inclusion as an oxidizing liquid (Chapter 2.13) or an oxidizing solid (Chapter 2.14) is answered by Test Series 8 tests. The classification procedure is according to the following decision logics (see Figures 2.1.1 to 2.1.4).

**Figure 2.1.1: Overall scheme of the procedure for classifying a substance, mixture or article in the class of explosives (Class 1 for transport)**

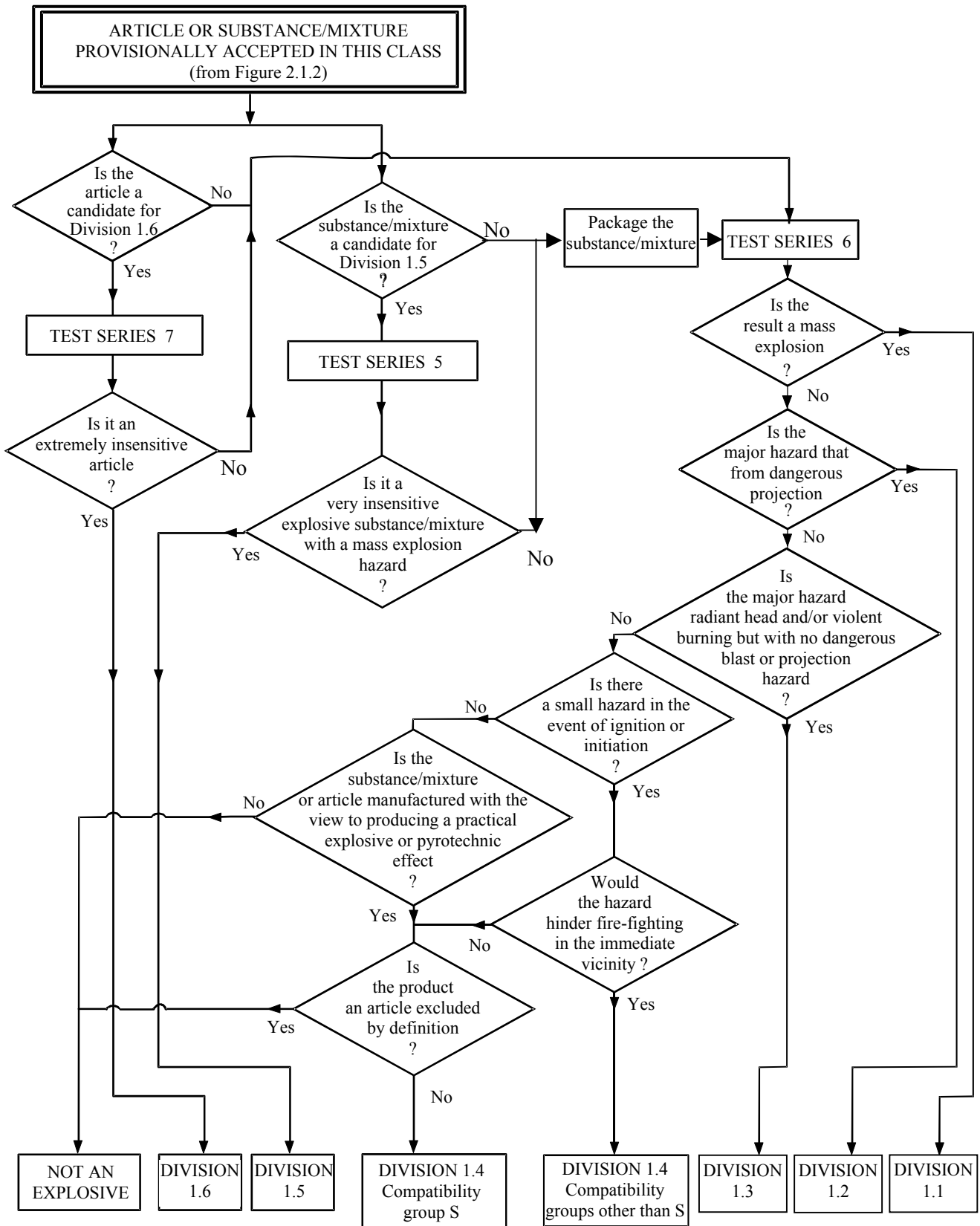


**Figure 2.1.2: Procedure for provisional acceptance of a substance, mixture or article in the class of explosives (Class 1 for transport)**



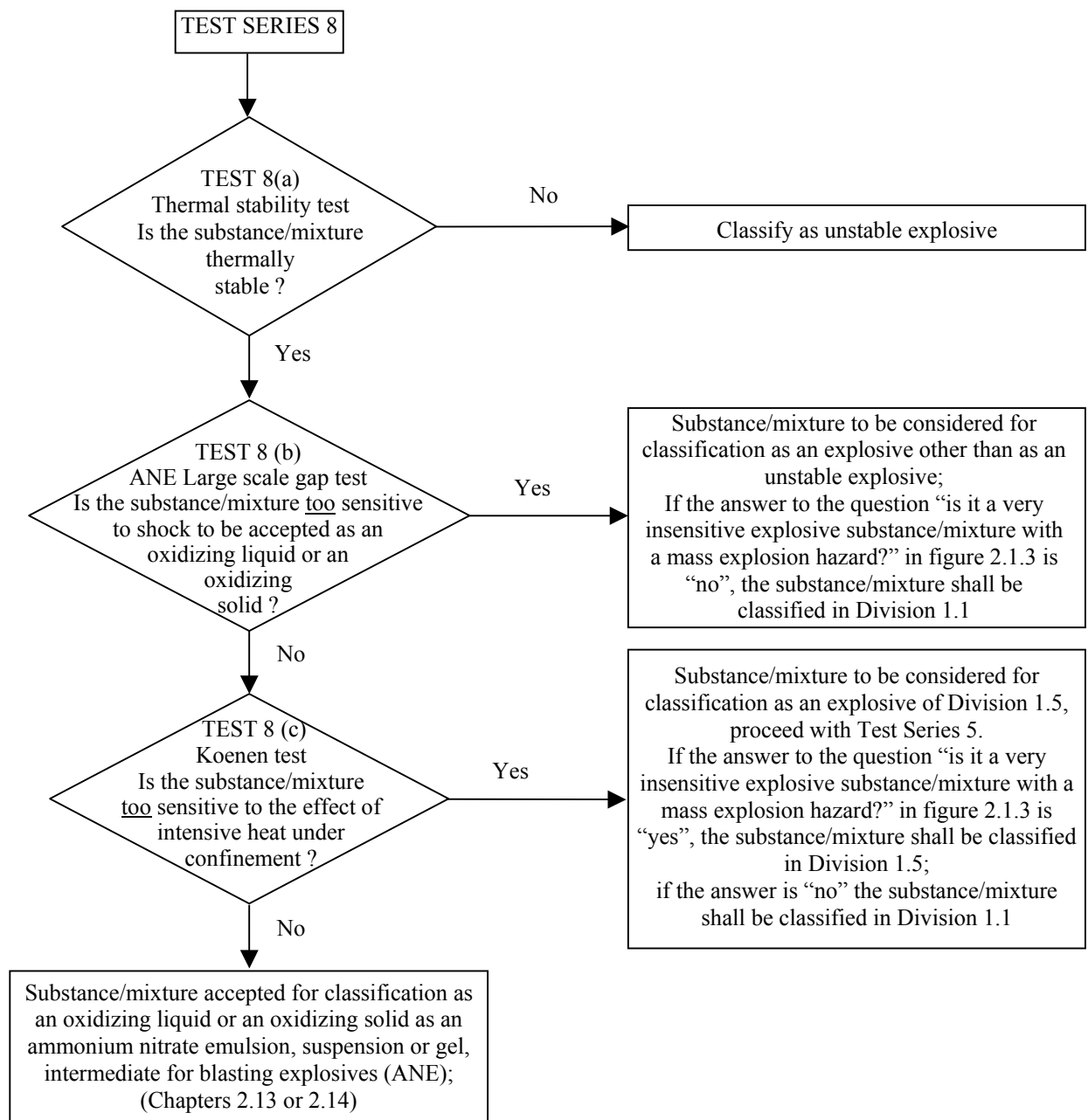
\* For classification purposes, start with Test Series 2.

**Figure 2.1.3: Procedure for assignment to a division in the class of explosives (Class 1 for transport)**





**Figure 2.1.4: Procedure for classification of ammonium nitrate emulsions, suspensions or gels**



#### 2.1.4.2 *Guidance*

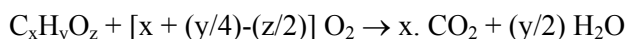
2.1.4.2.1 Explosive properties are associated with the presence of certain chemical groups in a molecule which can react to produce very rapid increases in temperature or pressure. The screening procedure is aimed at identifying the presence of such reactive groups and the potential for rapid energy release. If the screening procedure identifies the substance or mixture to be a potential explosive, the acceptance procedure (see section 10.3 of the *UN Recommendations on the Transport of Dangerous Goods, 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.*

2.1.4.2.2 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 *UN Recommendations on the Transport of Dangerous Goods, 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:



using the formula:

$$\text{oxygen balance} = -1600 [2x + (y/2) - z] / \text{molecular weight};$$

- (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.

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

## CHAPTER 2.2

### FLAMMABLE GASES

#### 2.2.1 Definition

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

#### 2.2.2 Classification criteria

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

**Table 2.2.1: Criteria for flammable gases**

Category	Criteria
<b>1</b>	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.
<b>2</b>	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.

#### 2.2.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 2 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

**Table 2.2.2: Label elements for flammable gases**

	Category 1	Category 2
<b>Symbol</b>	Flame	<i>No symbol</i>
<b>Signal word</b>	Danger	Warning
<b>Hazard statement</b>	Extremely flammable gas	Flammable gas

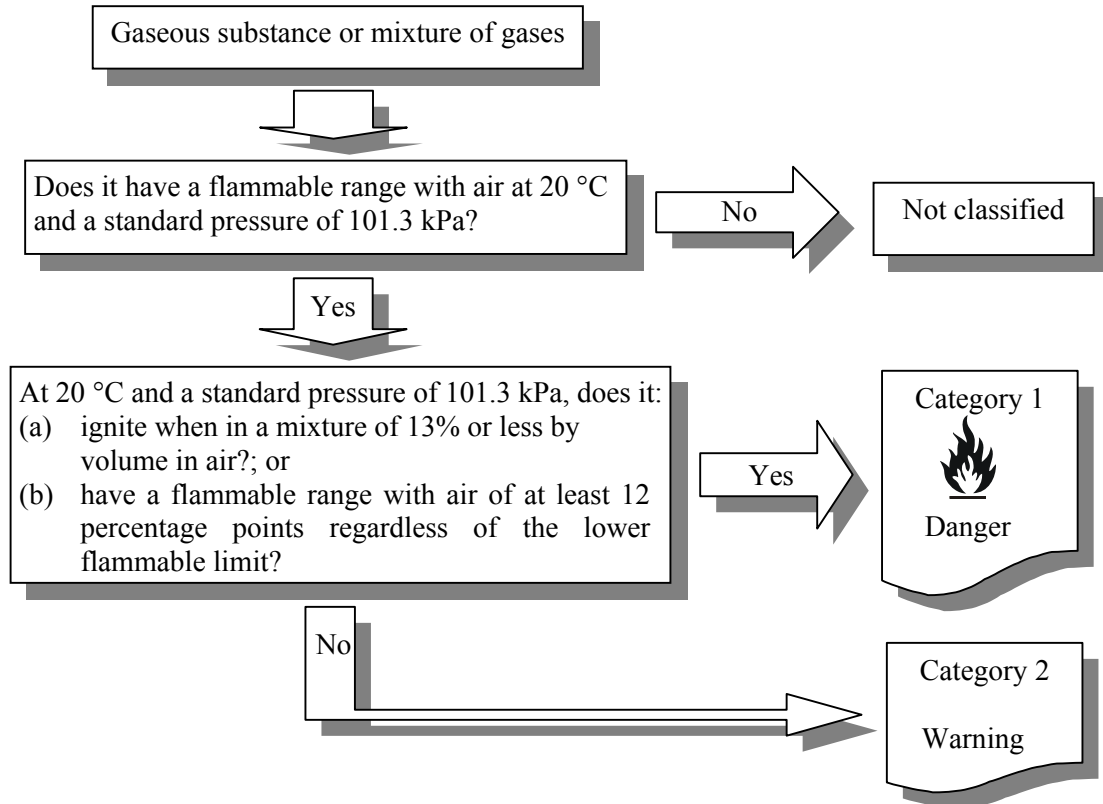
#### 2.2.4 Decision logic and guidance

The decision logic and guidance, which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

**2.2.4.1 Decision logic**

To classify a flammable gas, data on its flammability are required. The classification is according to decision logic 2.2.

**Decision logic 2.2 for flammable gases**



**2.2.4.2 Guidance**

Flammability should be determined by tests or by calculation in accordance with methods adopted by ISO (see ISO 10156:1996 “Gases and gas mixtures – Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets”). Where insufficient data are available to use these methods, tests by a comparable method recognized by the competent authority may be used.

**2.2.5 Example: Classification of a flammable gas mixture by calculation according to ISO 10156:1996**

Formula

$$\sum_i^n \frac{V_i\%}{T_{ci}}$$

where:

- $V_i\%$  = the equivalent flammable gas content;
- $T_{ci}$  = the maximum concentration of a flammable gas in nitrogen at which the mixture is still not flammable in air;
- $i$  = the first gas in the mixture;
- $n$  = the  $n^{\text{th}}$  gas in the mixture;
- $K_i$  = the equivalency factor for an inert gas versus nitrogen;

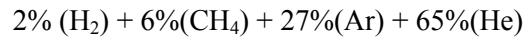
Where a gas mixture contains an inert diluent other than nitrogen, the volume of this diluent is adjusted to the equivalent volume of nitrogen using the equivalency factor for the inert gas ( $K_i$ ).

Criterion:

$$\sum_i^n \frac{V_i\%}{T_{ci}} \geq 1$$

Gas mixture

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



Calculation

1. Ascertain the equivalency factors ( $K_i$ ) for the inert gases versus nitrogen:

$$K_i (\text{Ar}) = 0.5$$

$$K_i (\text{He}) = 0.5$$

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

$$2\%(\text{H}_2) + 6\%(\text{CH}_4) + [27\% \times 0.5 + 65\% \times 0.5](\text{N}_2) = 2\%(\text{H}_2) + 6\%(\text{CH}_4) + 46\%(\text{N}_2) = 54\%$$

3. Adjust the sum of the contents to 100%:

$$\frac{100}{54} \times [2\%(\text{H}_2) + 6\%(\text{CH}_4) + 46\%(\text{N}_2)] = 3.7\%(\text{H}_2) + 11.1\%(\text{CH}_4) + 85.2\%(\text{N}_2)$$

4. Ascertain the  $T_{ci}$  coefficients for the flammable gases:

$$T_{ci} \text{ H}_2 = 5.7\%$$

$$T_{ci} \text{ CH}_4 = 14.3\%$$

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

$$\sum_i^n \frac{V_i\%}{T_{ci}} = \frac{3.7}{5.7} + \frac{11.1}{14.3} = 1.42$$

$$1.42 > 1$$

Therefore the mixture is flammable in air.



## CHAPTER 2.3

### FLAMMABLE AEROSOLS

#### 2.3.1 Definition

*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.

#### 2.3.2 Classification criteria

2.3.2.1 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 and mixtures because such components are never used as aerosol contents.*

2.3.2.2 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 2.3.4.1.

#### 2.3.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 2 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

**Table 2.3.1: Label elements for flammable aerosols**

	<b>Category 1</b>	<b>Category 2</b>
<b>Symbol</b>	Flame	Flame
<b>Signal word</b>	Danger	Warning
<b>Hazard statement</b>	Extremely flammable aerosol	Flammable aerosol

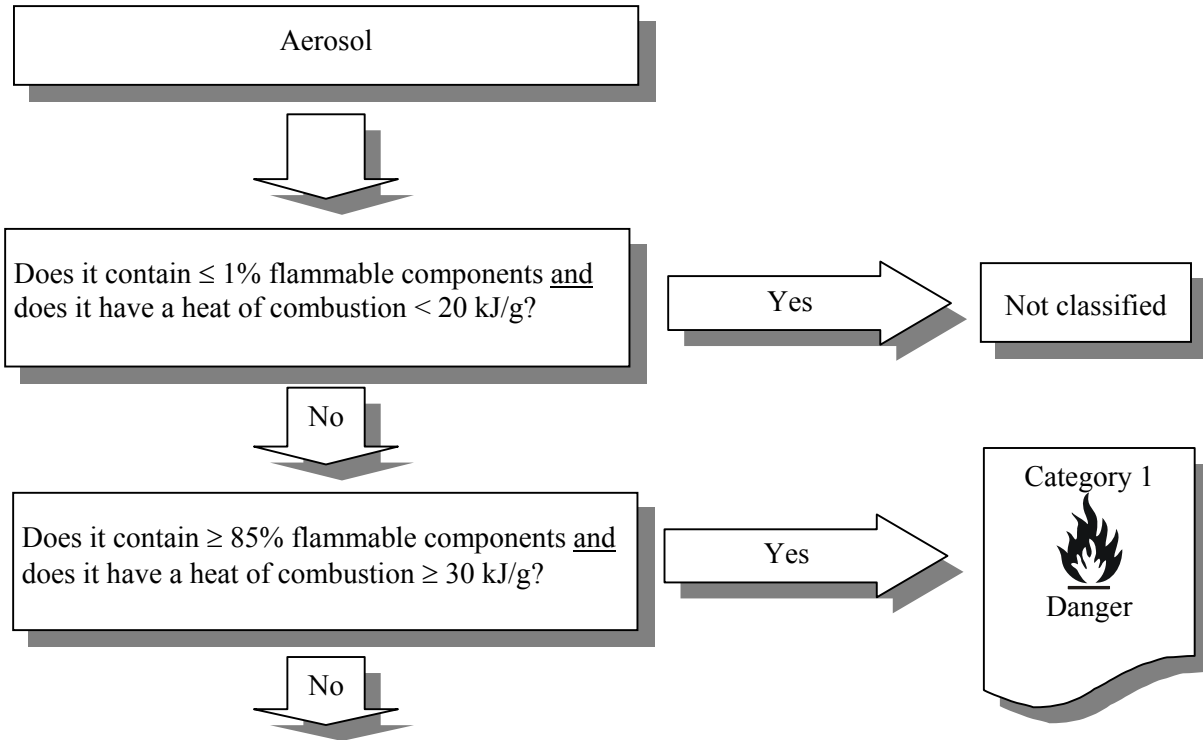
#### 2.3.4 Decision logic and guidance

The decision logic and guidance, which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

### 2.3.4.1 *Decision logic*

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 decision logics 2.3 (a) to 2.3 (c).

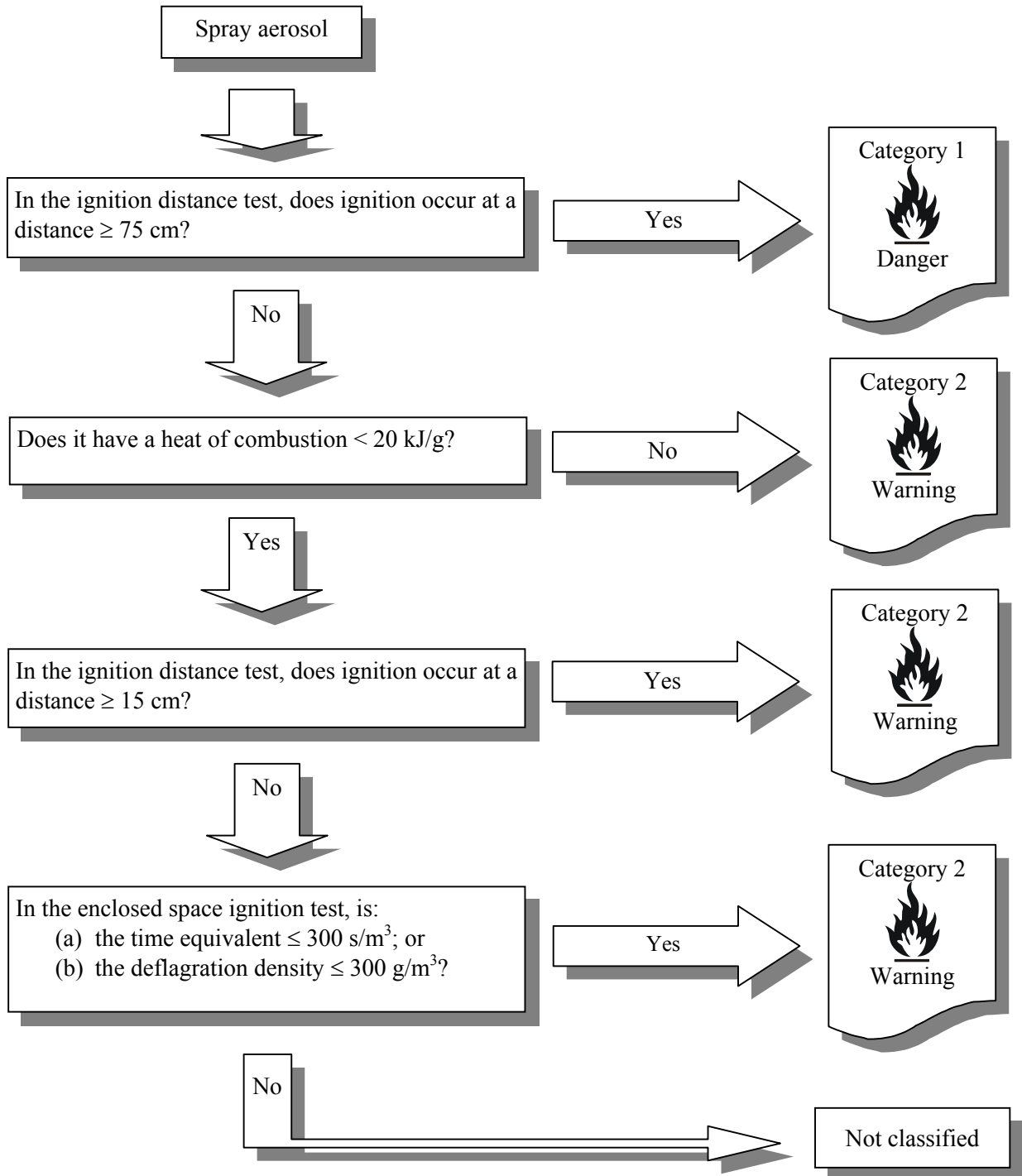
#### *Decision logic 2.3 (a) for flammable aerosols*



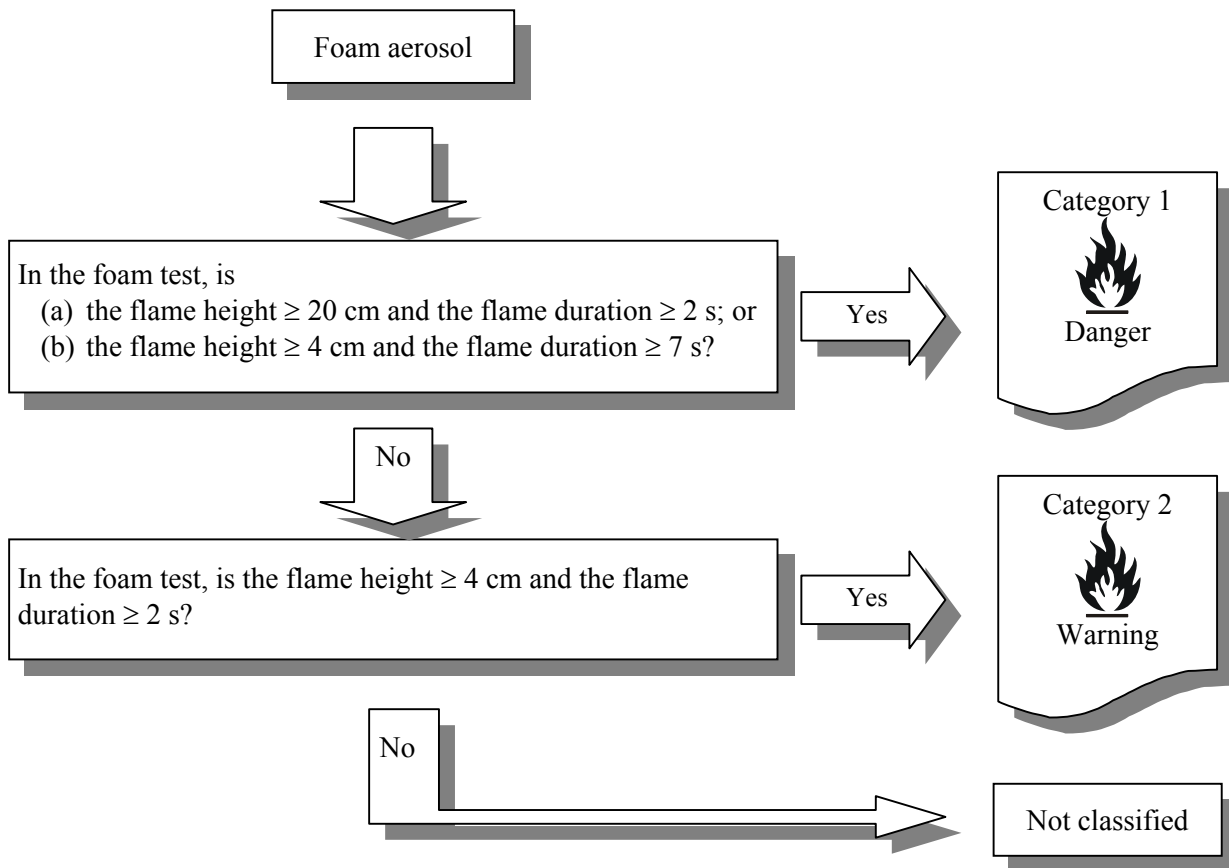
For spray aerosols, go to decision logic 2.3 (b);  
For foam aerosols, go to decision logic 2.3 (c);



**Decision logic 2.3 (b) for spray aerosols**



**Decision logic 2.3 (c) for foam aerosols**



**2.3.4.2 Guidance**

2.3.4.2.1 The chemical heat of combustion ( $\Delta H_c$ ), in kilojoules per gram (kJ/g), is the product of the theoretical heat of combustion ( $\Delta H_{comb}$ ), 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:

$$\Delta H_c (\text{product}) = \sum_i^n [w_i\% \times \Delta H_c(i)]$$

where:

- $\Delta H_c$  = chemical heat of combustion (kJ/g);
- $w_i\%$  = mass fraction of component i in the product;
- $\Delta H_c(i)$  = specific heat of combustion (kJ/g) of component i in the product;

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) 86.1 to 86.3 and NFPA 30B).

2.3.4.2.2 See sub-sections 31.4, 31.5 and 31.6 of the *of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, for Ignition distance test, Enclosed space ignition test and Aerosol foam flammability test.

## CHAPTER 2.4

### OXIDIZING GASES

#### 2.4.1 Definition

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.

#### 2.4.2 Classification criteria

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

**Table 2.4.1: Criteria for oxidizing gases**

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

**NOTE:** Artificial air containing up to 23.5% oxygen by volume may be regarded as not oxidizing for some regulatory purposes (e.g. transport).

#### 2.4.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 2 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

**Table 2.4.2: Label elements for oxidizing gases**

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

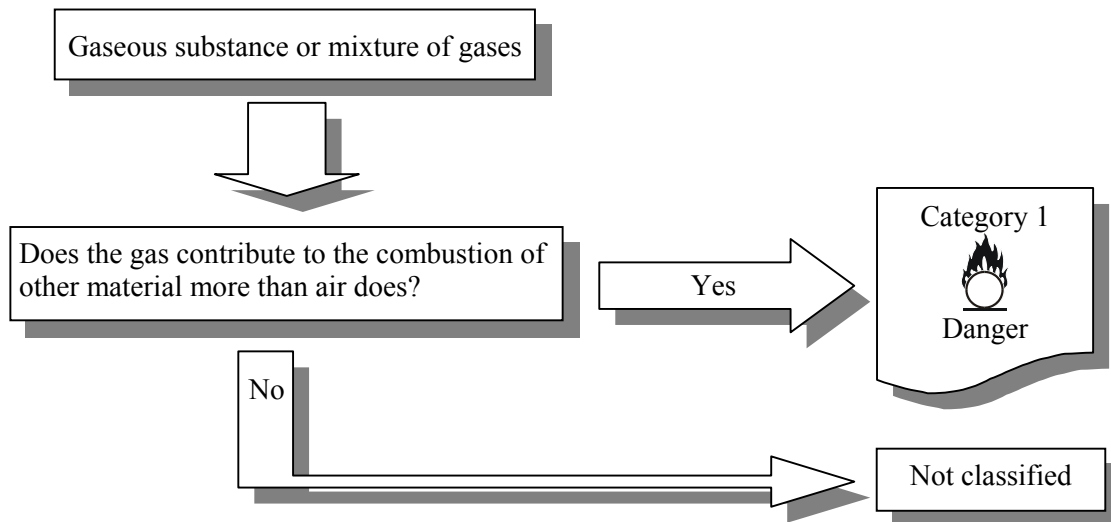
#### 2.4.4 Decision logic and guidance

The decision logic and guidance, which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

##### 2.4.4.1 Decision logic

To classify an oxidizing gas, tests or calculation methods as described in ISO 10156:1996 “Gases and gas mixtures – Determination of fire potential and oxidizing ability for the selection of cylinder valve outlet” and ISO 10156-2:2005 “Gas cylinders, Gases and gas mixtures. Part 2: Determination of oxidizing ability of toxic and corrosive gases and gas mixtures” should be performed.

**Decision logic 2.4 for oxidizing gases**



**2.4.4.2 Guidance**

Example of the classification of an oxidizing gas mixture by calculation according to ISO 10156:1996 and ISO 10156-2:2005

Formula

$$\sum_i^n V_i\% \times C_i$$

Where:

- $V_i\%$  = the volume percentage of a gas
- $C_i$  = the coefficient of oxygen equivalency
- $i$  = the first gas in the mixture
- $n$  = the  $n^{\text{th}}$  gas in the mixture

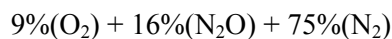
**NOTE:** Balance gas is not taken into consideration.

Criterion:

$$\sum_i^n V_i\% \times C_i \geq 21$$

Gas mixture

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



Calculation

1. Ascertain the coefficient of oxygen equivalency ( $C_i$ ) for the oxidizing gases in the mixture

- $C_i$  ( $N_2O$ ) = 0.6 (nitrous oxide)
- $C_i$  (O) = 1 (oxygen)
- $C_i$  (all other oxidizing gases) = 40

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

$$9\%(O_2) + 16\%(N_2O) + 75\%(N_2) = (9 \times 1) + (16 \times 0.6)$$

$$18.6 < 21$$

Therefore the mixture is considered less oxidizing than air.

If the gas mixture had been 0.6 % F<sub>2</sub> in Nitrogen, the equivalent calculation would have been

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

The coefficient of oxygen equivalency (Ci) for F<sub>2</sub> = 40

$$40 \times 0.6 = 24 > 21$$

Therefore the mixture is considered more oxidizing than air.



## CHAPTER 2.5

### GASES UNDER PRESSURE

#### 2.5.1 Definition

*Gases under pressure* are gases which are contained in a receptacle at a pressure of 200 kPa (gauge) or more, or which are liquefied or liquefied and refrigerated.

They comprise compressed gases, liquefied gases, dissolved gases and refrigerated liquefied gases.

#### 2.5.2 Classification criteria

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

**Table 2.5.1: Criteria for gases under pressure**

Group	Criteria
<b>Compressed gas</b>	A gas which when packaged under pressure is entirely gaseous at -50 °C; including all gases with a critical temperature $\leq$ -50 °C.
<b>Liquefied gas</b>	A gas which when packaged under pressure, is partially liquid at temperatures above -50 °C. A distinction is made between: (a) High pressure liquefied gas: a gas with a critical temperature between -50°C and +65°C; and (b) Low pressure liquefied gas: a gas with a critical temperature above +65°C.
<b>Refrigerated liquefied gas</b>	A gas which when packaged is made partially liquid because of its low temperature.
<b>Dissolved gas</b>	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.

#### 2.5.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 2 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

**Table 2.5.2: Label elements for gases under pressure**

	Compressed gas	Liquefied gas	Refrigerated liquefied gas	Dissolved gas
<b>Symbol</b>	Gas cylinder	Gas cylinder	Gas cylinder	Gas cylinder
<b>Signal word</b>	Warning	Warning	Warning	Warning
<b>Hazard statement</b>	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

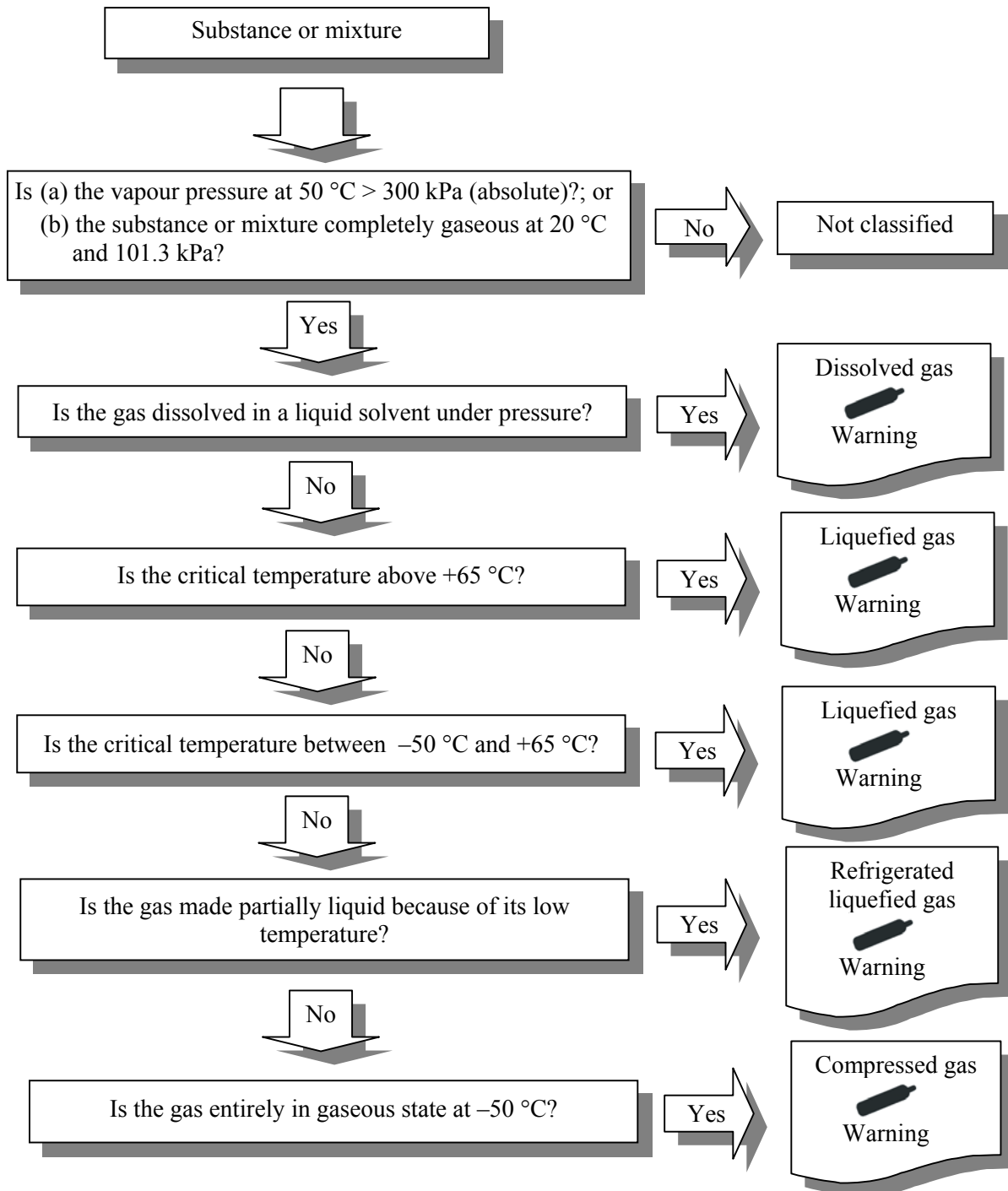
## 2.5.4 Decision logic and guidance

The decision logic and guidance, which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

### 2.5.4.1 Decision logic

Classification can be made according to decision logic 2.5.

#### Decision logic 2.5 for gases under pressure





**2.5.4.2**      ***Guidance***

For this group of gases, the following information is required to be known:

- (a) The vapour pressure at 50 °C;
- (b) The physical state at 20 °C at standard ambient pressure;
- (c) 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 Recommendations on the Transport of Dangerous Goods, Model Regulations*. Most one off mixtures require additional calculations that can be very complex.



## CHAPTER 2.6

### FLAMMABLE LIQUIDS

#### 2.6.1 Definition

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

#### 2.6.2 Classification criteria

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

**Table 2.6.1: 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 Part III, section 32 of the UN Recommendations on the Transport of Dangerous Goods, 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.

#### 2.6.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 2 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

**Table 2.6.2: Label elements for flammable liquids**

	Category 1	Category 2	Category 3	Category 4
<b>Symbol</b>	Flame	Flame	Flame	No symbol
<b>Signal word</b>	Danger	Danger	Warning	Warning
<b>Hazard statement</b>	Extremely flammable liquid and vapour	Highly flammable liquid and vapour	Flammable liquid and vapour	Combustible liquid

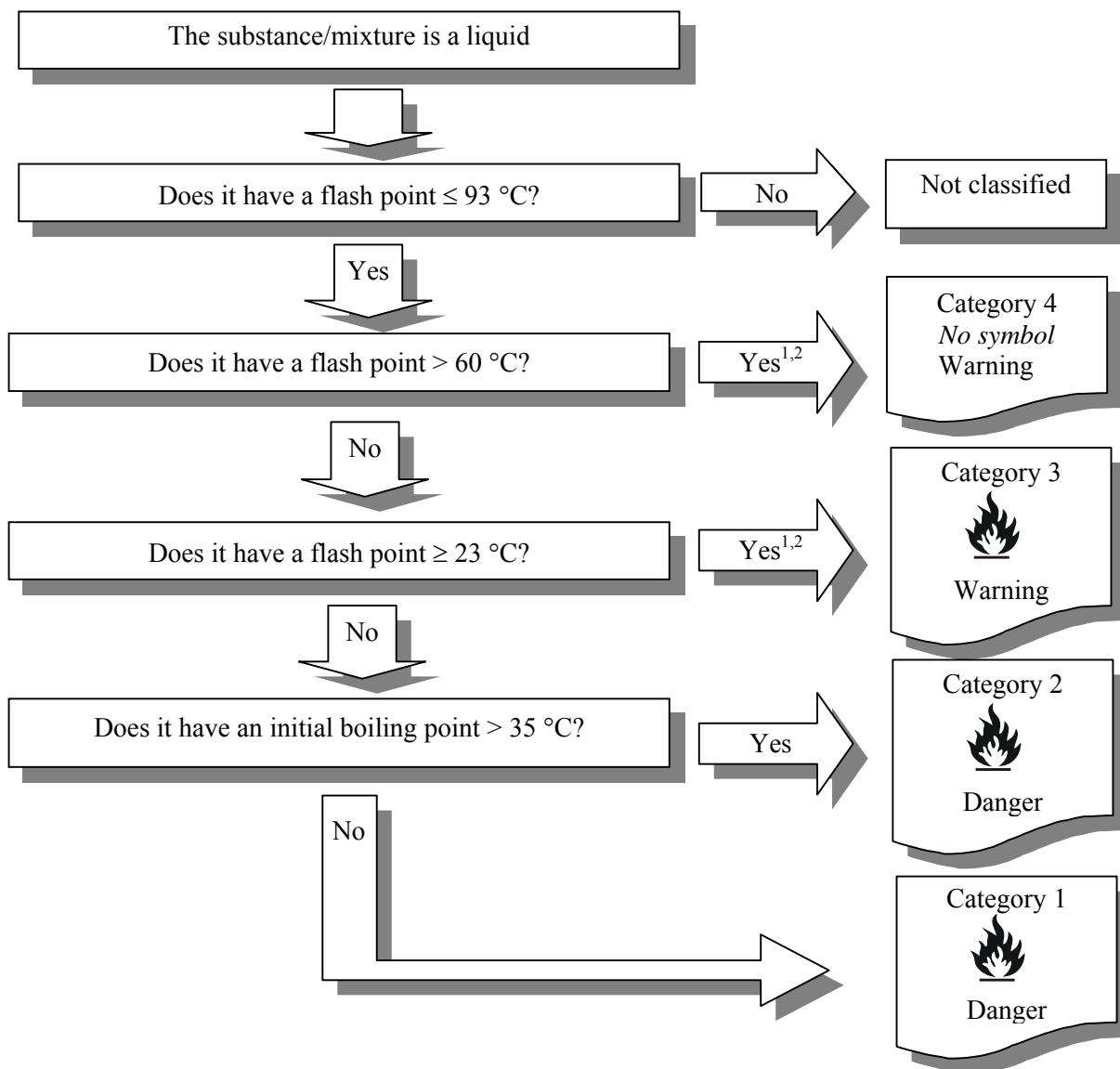
## 2.6.4 Decision logic and guidance

The decision logic and guidance, which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

### 2.6.4.1 Decision logic

Once the flash point and the initial boiling point are known, the classification of the substance or mixture and the relevant harmonized label information can be obtained according to decision logic 2.6.

#### Decision logic 2.6 for flammable liquids



<sup>1</sup> 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 of these products in Category 3 or 4 may be determined by the pertinent regulation or competent authority.

<sup>2</sup> Liquids with a flash point > 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 Part III, section 32 of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria.

#### 2.6.4.2 *Guidance*

2.6.4.2.1 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.

2.6.4.2.2 In the case of mixtures<sup>3</sup> containing known flammable liquids in defined concentrations, although they may contain non-volatile ingredients 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 2.6.4.2.3 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 2.6.4.2.5 below) of each ingredient 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 ingredient as present in the mixture including the temperature dependence;
- (d) The liquid phase is homogeneous.

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

2.6.4.2.4 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.

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

##### International standards:

ISO 1516  
ISO 1523  
ISO 3679  
ISO 3680

##### National standards:

*American Society for Testing Materials International*, 100Barr Harbor Drive, PO Box C 700, West Conshohocken, Pennsylvania, USA 19428-2959:

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

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<sup>3</sup> *Screening procedures are well established for ideal mixture of solvents, i.e. mainly hydrocarbures.*

*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

*British Standards Institute*, Customer Services, 389 Chiswick High Road, London, N7 8LB:

British Standard BS EN 22719

British Standard BS 2000 Part 170

*Deutsches Institut für Normung*, Burggrafenst 6, D-10787 Berlin:

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)

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

GOST 12.1.044-84

## CHAPTER 2.7

### FLAMMABLE SOLIDS

#### 2.7.1 Definitions

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.

#### 2.7.2 Classification criteria

2.7.2.1 Powdered, granular or pasty substances or mixtures 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 *UN Recommendations on the Transport of Dangerous Goods, 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.

2.7.2.2 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 min or less.

2.7.2.3 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.

2.7.2.4 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 33.2.1 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, according to the following table:

**Table 2.7.1: Criteria for flammable solids**

Category	Criteria
<b>1</b>	Burning rate test: Substances or mixtures other than metal powders: (a) wetted zone does not stop fire; and (b) burning time < 45 s or burning rate > 2.2 mm/s Metal powders: burning time ≤ 5 min
<b>2</b>	Burning rate test: Substances or mixtures other than metal powders: (a) wetted zone stops the fire for at least 4 min; and (b) burning time < 45 s or burning rate > 2.2 mm/s Metal powders: burning time > 5 min and ≤ 10 min

**NOTE:** For classification tests on solid substances or mixtures, the tests should be performed on the substance or mixture 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.

### 2.7.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 2 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

**Table 2.7.2: Label elements for flammable solids**

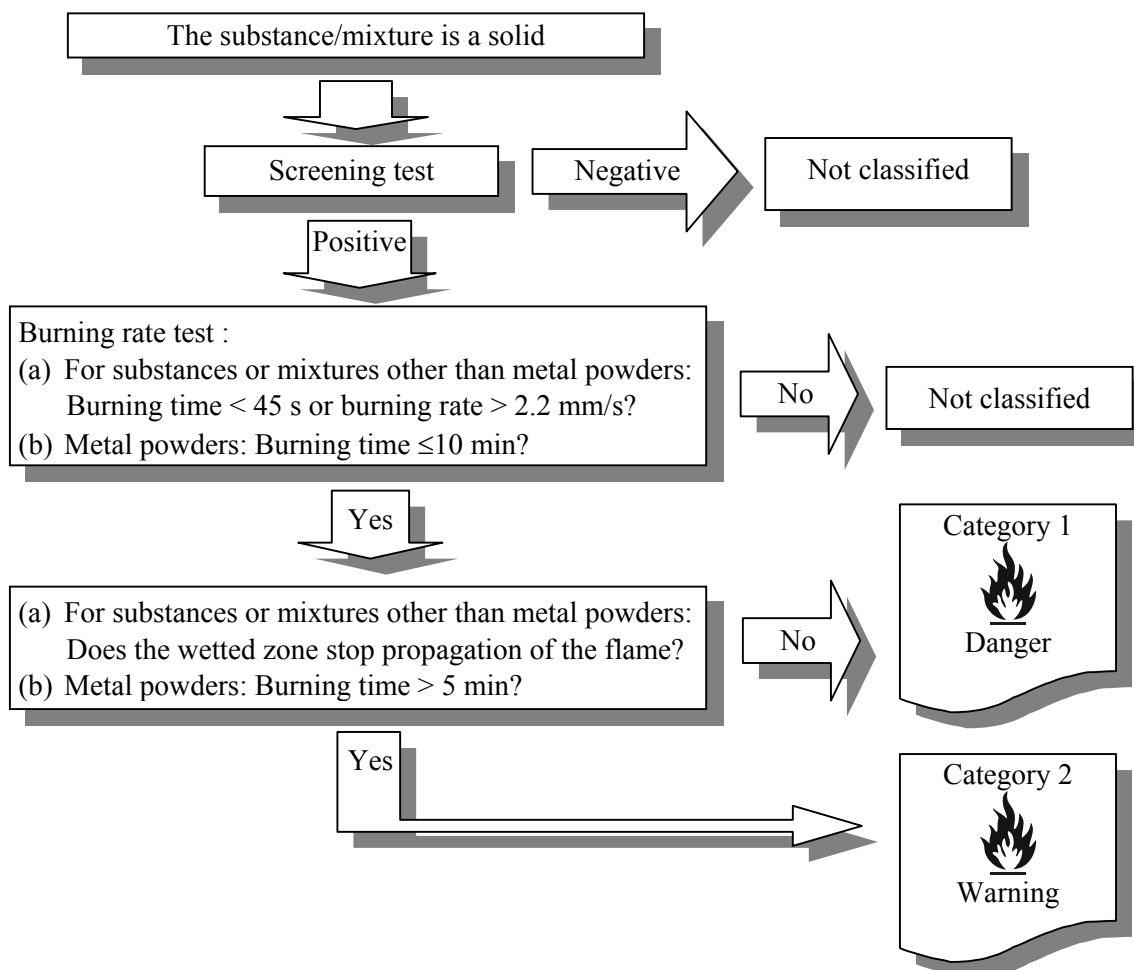
	Category 1	Category 2
<b>Symbol</b>	Flame	Flame
<b>Signal word</b>	Danger	Warning
<b>Hazard statement</b>	Flammable solid	Flammable solid

### 2.7.4 Decision logic

The decision logic which follows, is not part of the harmonized classification system, but has been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

To classify a flammable solid, the test method N.1 as described in Part III, sub-section 33.2.1 of the *UN Recommendations on the Transport of Dangerous Goods, 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 decision logic 2.7.

#### *Decision logic 2.7 for flammable solids*





## CHAPTER 2.8

### SELF-REACTIVE SUBSTANCES AND MIXTURES

#### 2.8.1 Definitions

2.8.1.1 *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.

2.8.1.2 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.

#### 2.8.2 Classification criteria

2.8.2.1 Any self-reactive substance or mixture 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 liquids or solids, according to the criteria of Chapters 2.13 or 2.14, except that mixtures of oxidizing substances which contain 5% or more of combustible organic substances shall be classified as self-reactive substances according to the procedure defined in the note below;
- (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.

**NOTE:** *Mixtures of oxidizing substances, meeting the criteria for classification as oxidizing substances, which contain 5.0% or more of combustible organic substances and which do not meet the criteria mentioned in (a), (c), (d) or (e) above, shall be subjected to the self-reactive substances classification procedure;*

*Such a mixture showing the properties of a self-reactive substance type B to F (see 2.8.2.2) shall be classified as a self-reactive substance.*

2.8.2.2 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:
- (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 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 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.*

### **2.8.2.3** *Criteria for temperature control*

Self-reactive substances need to be subjected to temperature control if their self-accelerating decomposition temperature (SADT) is less than or equal to 55 °C. Test methods for determining the SADT as well as the derivation of control and emergency temperatures are given in the *UN Recommendations for the Transport of Dangerous Goods, Manual of Tests and Criteria*, Part II, section 28. The test selected shall be conducted in a manner which is representative, both in size and material, of the package.

### **2.8.3** **Hazard communication**

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 2 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

**Table 2.8.1: Label elements for self-reactive substances and mixtures**

	<b>Type A</b>	<b>Type B</b>	<b>Type C and D</b>	<b>Type E and F</b>	<b>Type G<sup>a</sup></b>
<b>Symbol</b>	Exploding bomb	Exploding bomb and flame	Flame	Flame	<i>There are no label elements allocated to this hazard category</i>
<b>Signal word</b>	Danger	Danger	Danger	Warning	
<b>Hazard statement</b>	Heating may cause an explosion	Heating may cause a fire or explosion	Heating may cause a fire	Heating may cause a fire	

<sup>a</sup> *Type G has no hazard communication elements assigned but should be considered for properties belonging to other hazard classes.*

## **2.8.4 Decision logic and guidance**

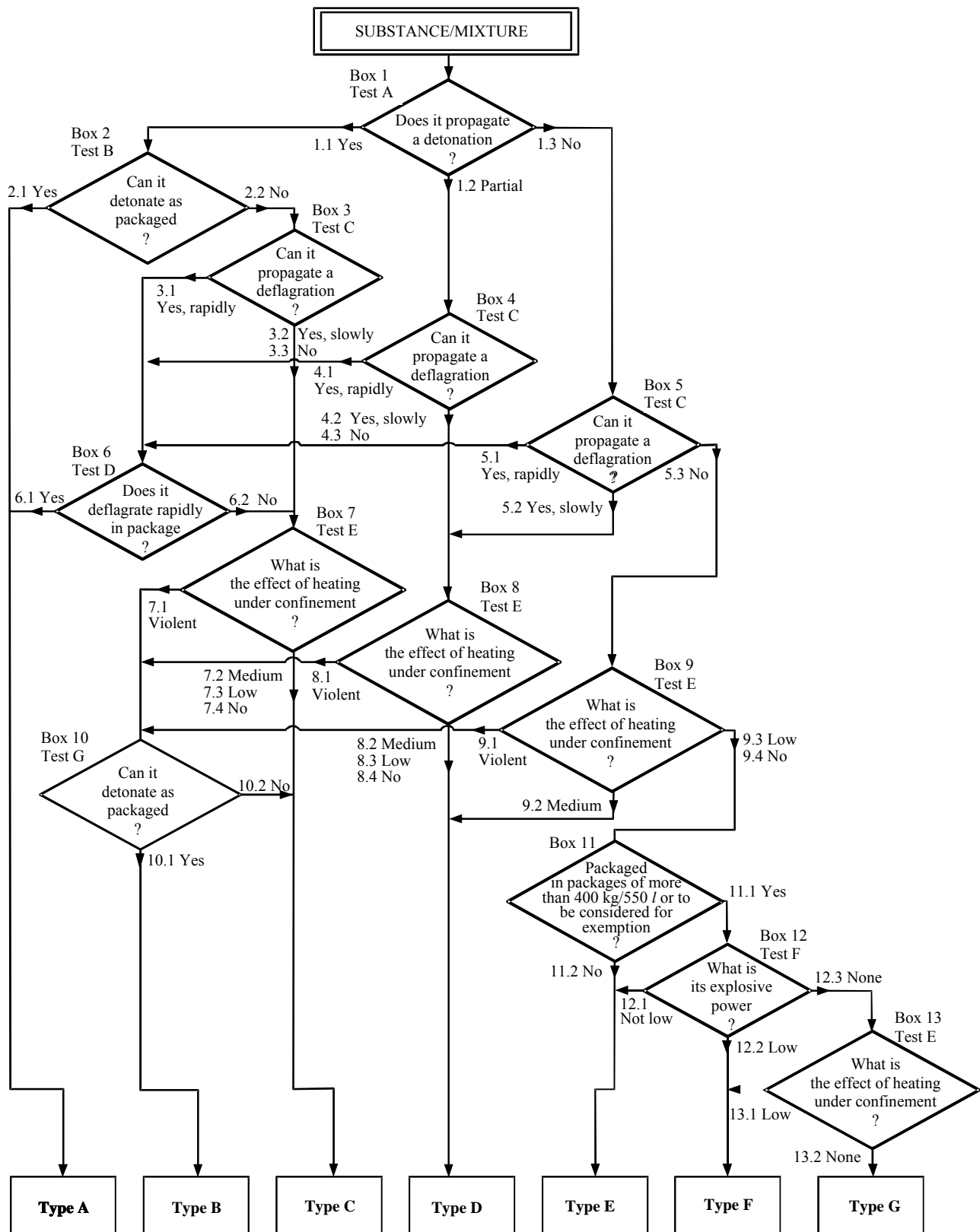
The decision logic and guidance which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

### **2.8.4.1 Decision logic**

To classify a self-reactive substance or mixture test series A to H as described in Part II of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria* should be performed. Classification is according to decision logic 2.8.

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 *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, Part II (test series A to H).

**Decision logic 2.8 for self-reactive substances and mixtures**



#### 2.8.4.2

#### **Guidance**

The classification procedures for self-reactive substances and mixtures 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 Appendix 6 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*; 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 300 J/g. The onset temperature and decomposition energy may be estimated using a suitable calorimetric technique (see 20.3.3.3 in Part II of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*).



## CHAPTER 2.9

### PYROPHORIC LIQUIDS

#### 2.9.1 Definition

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

#### 2.9.2 Classification criteria

A pyrophoric liquid is classified in a single category for this class using test N.3 in Part III, sub-section 33.3.1.5 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, according to the following table:

**Table 2.9.1: 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.

#### 2.9.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 2 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

**Table 2.9.2: Label elements for pyrophoric liquids**

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

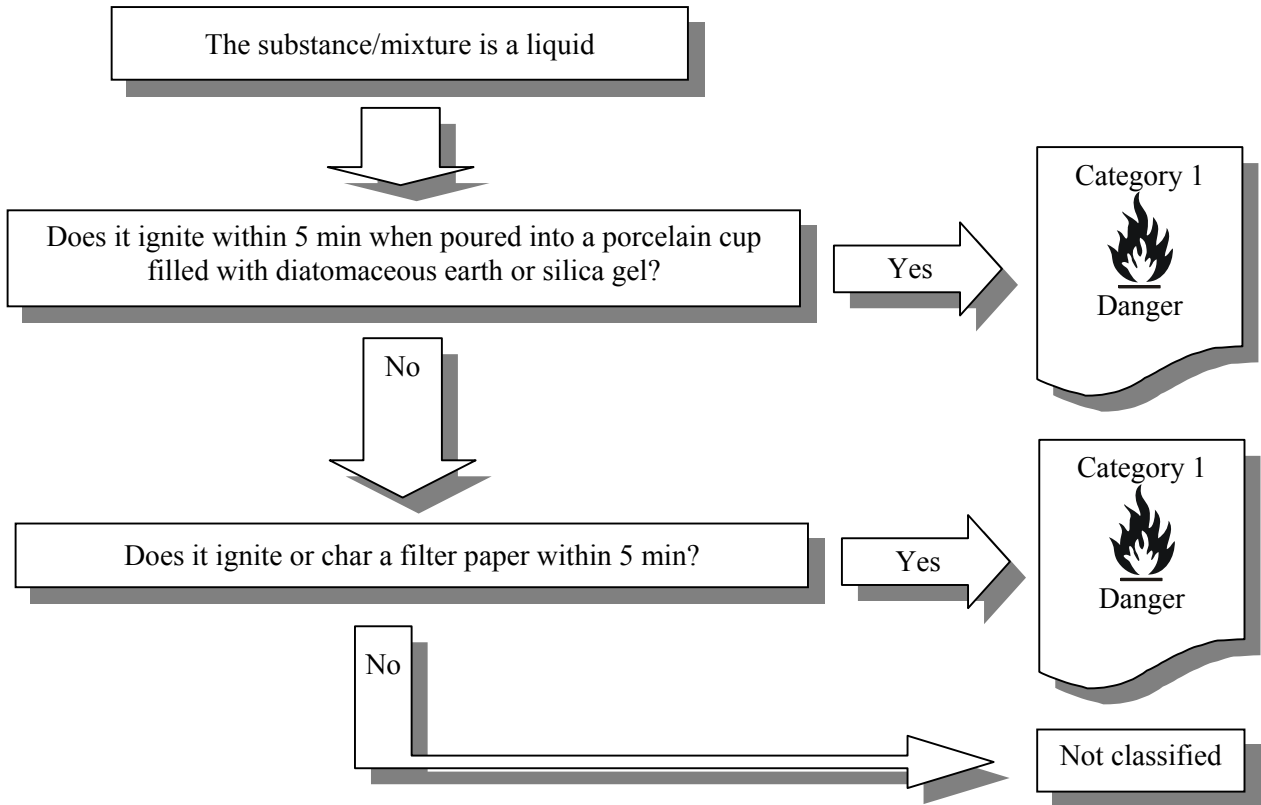
#### 2.9.4 Decision logic and guidance

The decision logic and guidance which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

**2.9.4.1 Decision logic**

To classify a pyrophoric liquid, the test method N.3 as described in Part III, sub-section 33.3.1.5 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria* should be performed. The procedure consists of two steps. Classification is according to decision logic 2.9.

**Decision logic 2.9 for pyrophoric liquids**



**2.9.4.2 Guidance**

The classification procedure for pyrophoric liquids need not be applied when experience in production or handling shows that the substance or mixture 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

#### 2.10.1 Definition

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

#### 2.10.2 Classification criteria

A pyrophoric solid is classified in a single category for this class using test N.2 in Part III, sub-section 33.3.1.4 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria* according to the following table:

**Table 2.10.1: Criteria for pyrophoric solids**

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

**NOTE:** For classification tests on solid substances or mixtures, the tests should be performed on the substance or mixture 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 or mixture must also be tested in the new form.

#### 2.10.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 2 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

**Table 2.10.2: Label elements for pyrophoric solids**

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

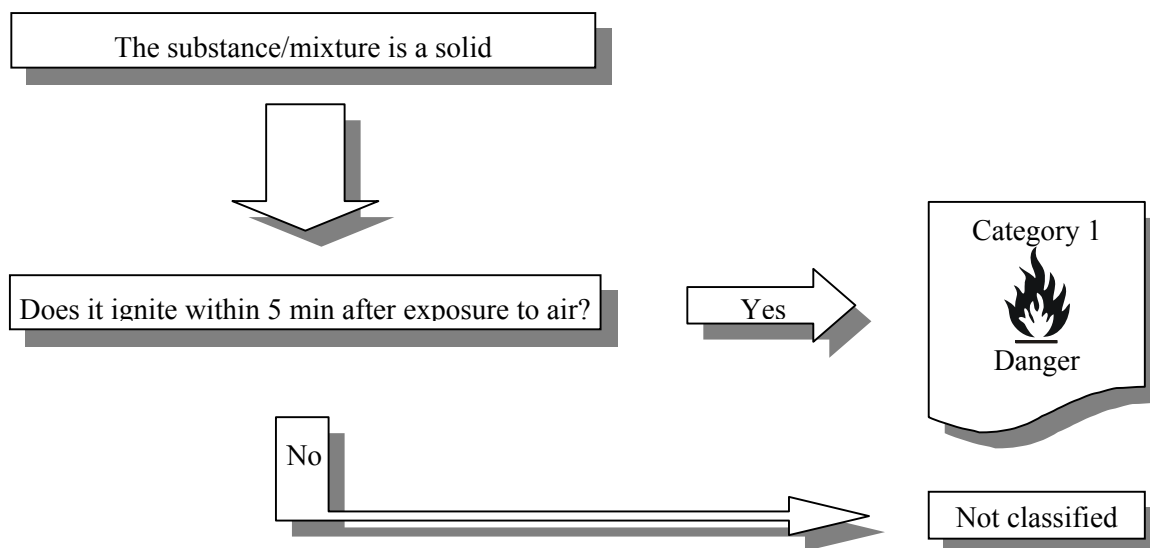
#### 2.10.4 Decision logic and guidance

The decision logic and guidance which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

#### 2.10.4.1 *Decision logic*

To classify a pyrophoric solid, the test method N.2 as described in Part III, subsection 33.3.1.4 of *the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria* should be performed. Classification is according to decision logic 2.10.

#### *Decision logic 2.10 for pyrophoric solids*



#### 2.10.4.2 *Guidance*

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

## CHAPTER 2.11

### SELF-HEATING SUBSTANCES AND MIXTURES

#### 2.11.1 Definition

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).

**NOTE:** *Self-heating of substances or mixtures, leading to spontaneous combustion, is caused by reaction of the substance or mixture 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.*

#### 2.11.2 Classification criteria

2.11.2.1 A substance or mixture shall be classified as a self-heating substance of this class, if in tests performed in accordance with the test method given in the *UN Recommendations on the Transport of Dangerous Goods, 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 or mixture is to be packed in packages with a volume of more than 3 m<sup>3</sup>;
- (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 or mixture 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.

2.11.2.2 A self-heating substance or mixture is classified in one of the two categories for this class if, in test performed in accordance with test method N.4 in Part III, sub-section 33.3.1.6 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, the result meets the criteria shown in Table 2.11.1.

**Table 2.11.1: Criteria for self-heating substances and mixtures**

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 <u>and</u> the substance or mixture is to be packed in packages with a volume of more than 3 m <sup>3</sup> ; 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 <u>and</u> the substance or mixture 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 <u>and</u> a positive result is obtained in a test using a 100 mm cube sample at 100 °C.

**NOTE 1:** For classification tests on solid substances or mixtures, the tests should be performed on the substance or mixture 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 or mixture must also be tested in the new form.

**NOTE 2:** The criteria are based on the self-ignition temperature of charcoal, which is 50 °C for a sample cube of 27 m<sup>3</sup>. Substances and mixtures with a temperature of spontaneous combustion higher than 50 °C for a volume of 27 m<sup>3</sup> should not be assigned to this hazard class. Substances and mixtures with a spontaneous ignition temperature higher than 50 °C for a volume of 450 litres should not be assigned to hazard Category 1 of this hazard class.

### 2.11.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 2 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

**Table 2.11.2: Label elements for self-heating substances and mixtures**

	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

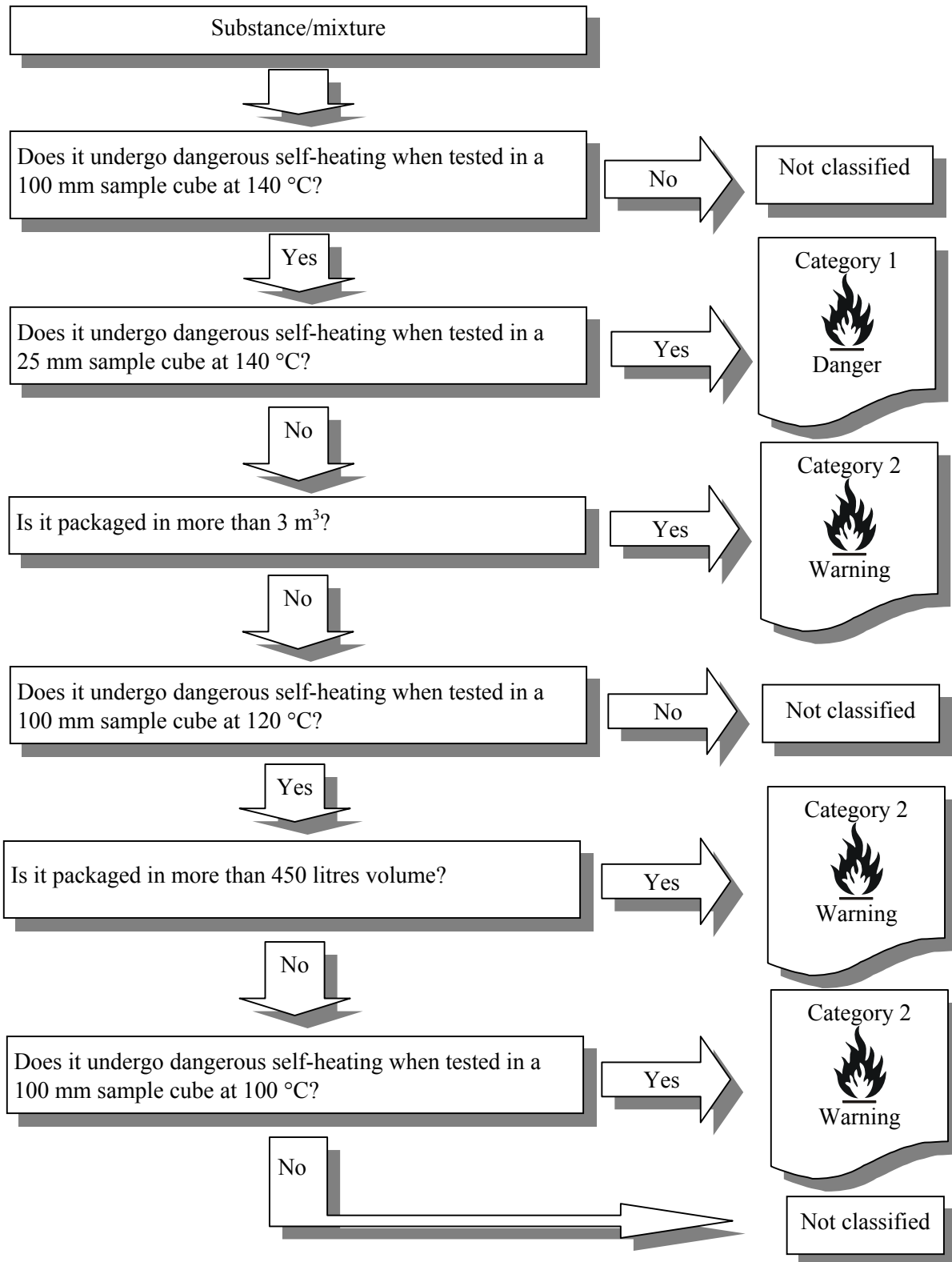
### 2.11.4 Decision logic and guidance

The decision logic and guidance which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

**2.11.4.1 Decision logic**

To classify a self-heating substance or mixture, test method N.4, as described in Part III, subsection 33.3.1.6 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, should be performed. Classification is according to decision logic 2.11.

**Decision logic 2.11 for self-heating substances and mixtures**



**2.11.4.2**      ***Guidance***

The classification procedure for self-heating substances or mixtures 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*.

## CHAPTER 2.12

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

#### 2.12.1 Definition

*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.

#### 2.12.2 Classification criteria

A substance or mixture which, in contact with water, emit flammable gases is classified in one of the three categories for this class, using test N.5 in Part III, sub-section 33.4.1.4 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, according to the following table:

**Table 2.12.1: Criteria for substances and mixtures which, in contact with water, emit flammable gases**

Category	Criteria
1	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	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	Any substance or mixture 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 or mixture 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 or mixtures, the tests should be performed on the substance or mixture 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 or mixture must also be tested in the new form.

#### 2.12.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 2 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

**Table 2.12.2: Label elements for substances and mixtures, which in contact with water, emit flammable gases**

	<b>Category 1</b>	<b>Category 2</b>	<b>Category 3</b>
<b>Symbol</b>	Flame	Flame	Flame
<b>Signal word</b>	Danger	Danger	Warning
<b>Hazard statement</b>	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

#### **2.12.4 Decision logic and guidance**

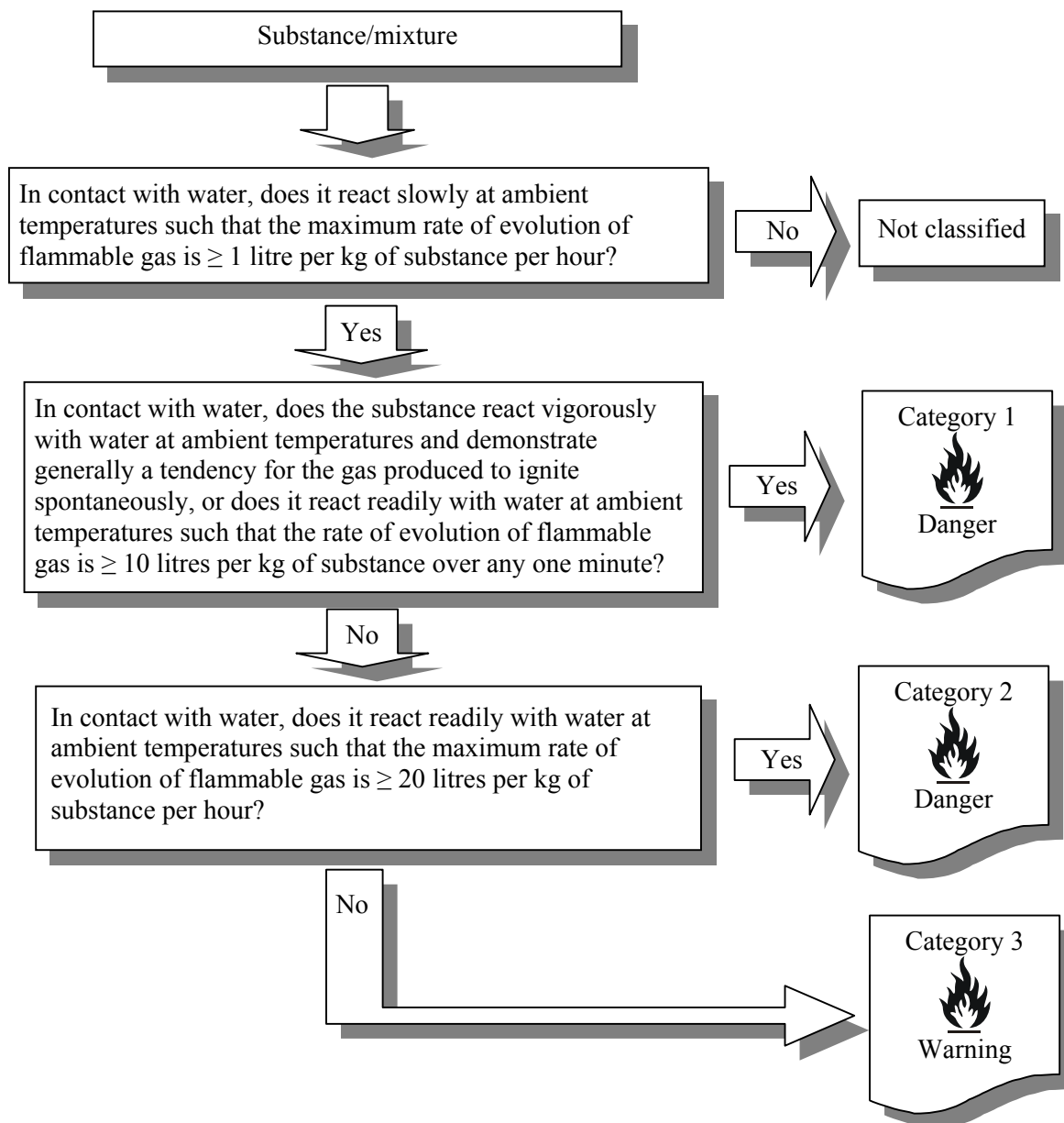
The decision logic and guidance which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

##### **2.12.4.1 Decision logic**

To classify a substance or mixture which, in contact with water emits flammable gases, test N.5 as described in Part III, sub-section 33.4.1.4 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, should be performed. Classification is according to decision logic 2.12.



**Decision logic 2.12 for substances and mixtures which, in contact with water, emit flammable gases**



**2.12.4.2 Guidance**

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 or mixture is known to be soluble in water to form a stable mixture.



## CHAPTER 2.13

### OXIDIZING LIQUIDS

#### 2.13.1 Definition

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.

#### 2.13.2 Classification criteria

An oxidizing liquid is classified in one of the three categories for this class using test O.2 in Part III, sub-section 34.4.2 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, according to the following table:

**Table 2.13.1: Criteria for oxidizing liquids**

Category	Criteria
<b>1</b>	Any substance or mixture which, in the 1:1 mixture, by mass, of substance (or mixture) 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;
<b>2</b>	Any substance or mixture which, in the 1:1 mixture, by mass, of substance (or mixture) 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;
<b>3</b>	Any substance or mixture which, in the 1:1 mixture, by mass, of substance (or mixture) 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 Categories 1 and 2 are not met.

#### 2.13.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 2 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

**Table 2.13.2: Label elements for oxidizing liquids**

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

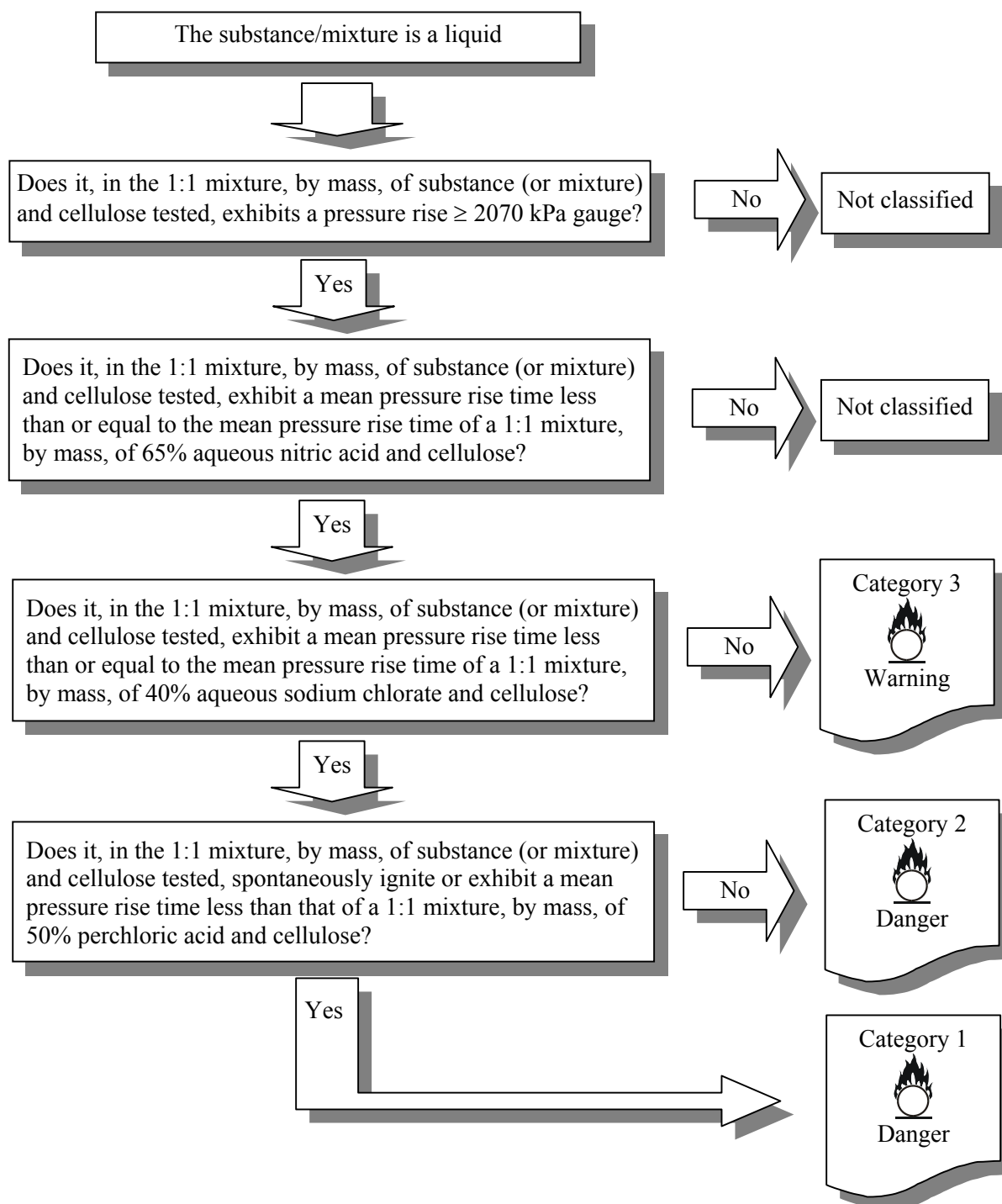
## 2.13.4 Decision logic and guidance

The decision logic and guidance which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

### 2.13.4.1 Decision logic

To classify an oxidizing liquid test method O.2 as described in Part III, sub-section 34.4.2 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria* should be performed. Classification is according to decision logic 2.13.

#### Decision logic 2.13 for oxidizing liquids



#### 2.13.4.2 *Guidance*

2.13.4.2.1 Experience in the handling and use of substances or mixtures 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.

2.13.4.2.2 In some cases, substances or mixtures may generate a pressure rise (too high or too low), caused by chemical reactions not characterising the oxidizing properties of the substance or mixture. In these cases, it may be necessary to repeat the test described in Part III, sub-section 34.4.2 of the *UN Recommendations on the Transport of Dangerous Goods, 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.

2.13.4.2.3 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
- (b) The substance or mixture contains oxygen, fluorine or chlorine and these elements are chemically bonded only to carbon or hydrogen.

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



## CHAPTER 2.14

### OXIDIZING SOLIDS

#### 2.14.1 Definition

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.

#### 2.14.2 Classification criteria

An oxidizing solid is classified in one of the three categories for this class using test O.1 in Part III, sub-section 34.4.1 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, according to the following table:

**Table 2.14.1: Criteria for oxidizing solids**

Category	Criteria
1	Any substance or mixture 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 or mixture 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 or mixture 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 1:** *Some oxidizing solids may also present explosion hazards under certain conditions (e.g. when stored in large quantities). For example, some types of ammonium nitrate may give rise to an explosion hazard under extreme conditions and the “Resistance to detonation test” (BC Code<sup>1</sup>, Annex 3, Test 5) may be used to assess this hazard. Appropriate comments should be made in the Safety Data Sheet.*

**NOTE 2:** *For classification tests on solid substances or mixtures, the tests should be performed on the substance or mixture 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 or mixture must also be tested in the new form.*

#### 2.14.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 2 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

<sup>1</sup> *Code of Safe Practice for Solid Bulk Cargoes, IMO, 2005.*

**Table 2.14.2: Label elements for oxidizing solids**

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

#### **2.14.4 Decision logic and guidance**

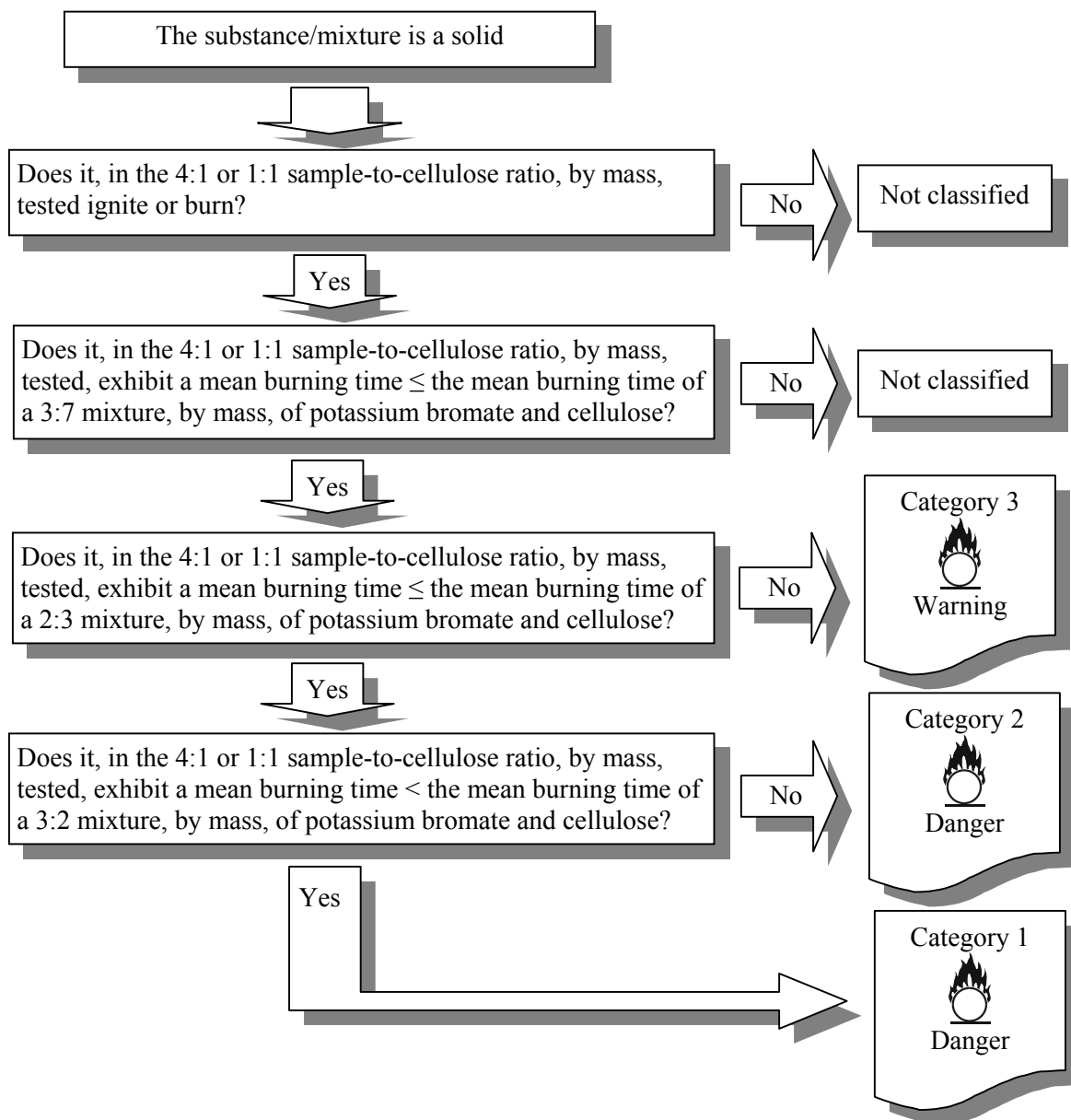
The decision logic and guidance which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

##### **2.14.4.1 Decision logic**

To classify an oxidizing solid test method O.1 as described in Part III, sub-section 34.4.1 of *the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, should be performed. Classification is according to decision logic 2.14.



**Decision logic 2.14 for oxidizing solids**



**2.14.4.2 Guidance**

2.14.4.2.1 Experience in the handling and use of substances or mixtures 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.

2.14.4.2.2 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.

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



## CHAPTER 2.15

### ORGANIC PEROXIDES

#### 2.15.1 Definition

2.15.1.1 *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.

2.15.1.2 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.

#### 2.15.2 Classification criteria

2.15.2.1 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:*

$$16 \times \sum_i^n \left( \frac{n_i \times c_i}{m_i} \right)$$

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  $i$ .

2.15.2.2 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:
  - (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 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 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.*

### **2.15.2.3 Criteria for temperature control**

The following organic peroxides need to be subjected to temperature control:

- (a) Organic peroxide types B and C with an SADT  $\leq 50$  °C;
- (b) Organic peroxide type D showing a medium effect when heated under confinement<sup>1</sup> with an SADT  $\leq 50$  °C or showing a low or no effect when heated under confinement with an SADT  $\leq 45$  °C; and
- (c) Organic peroxide types E and F with an SADT  $\leq 45$  °C.

Test methods for determining the SADT as well as the derivation of control and emergency temperatures are given in the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, Part II, section 28. The test selected shall be conducted in a manner which is representative, both in size and material, of the package.

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<sup>1</sup> *As determined by test series E as prescribed in the Manual of Tests and Criteria, Part II.*

**2.15.3 Hazard communication**

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 2 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

**Table 2.15.1: Label elements for organic peroxides**

	<b>Type A</b>	<b>Type B</b>	<b>Type C and D</b>	<b>Type E and F</b>	<b>Type G <sup>a</sup></b>
<b>Symbol</b>	Exploding bomb	Exploding bomb and flame	Flame	Flame	<i>There are no label elements allocated to this hazard category.</i>
<b>Signal word</b>	Danger	Danger	Danger	Warning	
<b>Hazard statement</b>	Heating may cause an explosion	Heating may cause a fire or explosion	Heating may cause a fire	Heating may cause a fire	

<sup>a</sup> *Type G has no hazard communication elements assigned but should be considered for properties belonging to other hazard classes.*

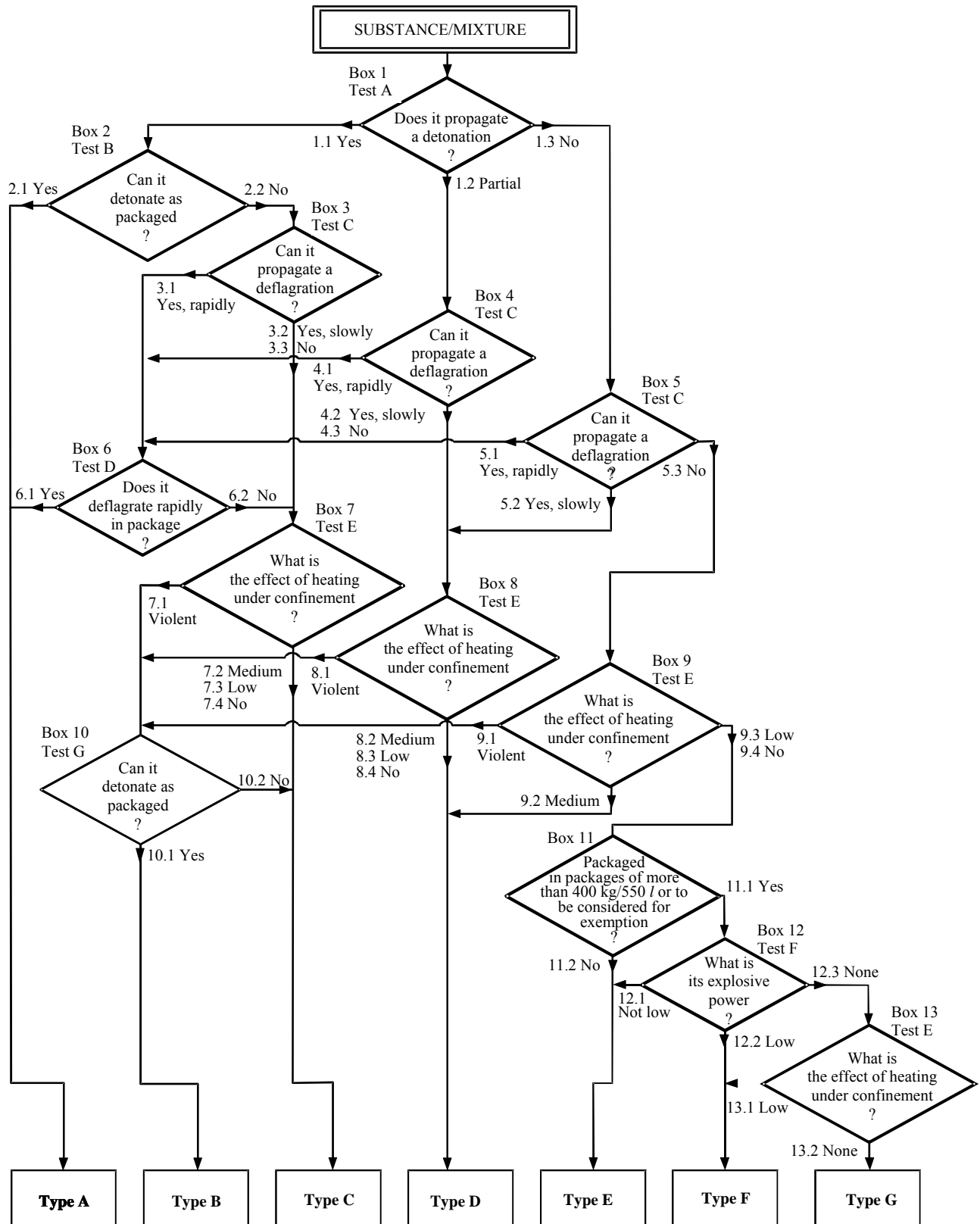
**2.15.4 Decision logic and guidance**

The decision logic and guidance which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

**2.15.4.1 Decision logic**

To classify an organic peroxide test series A to H as described in Part II of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, should be performed. Classification is according to decision logic 2.15.

**Decision logic 2.15 for organic peroxides**



**2.15.4.2**      ***Guidance***

2.15.4.2.1      Organic peroxides are classified by definition based on their chemical structure and on the available oxygen and hydrogen peroxide contents of the mixture (see 2.15.2.1).

2.15.4.2.2      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 *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, Part II (Test Series A to H).

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





## CHAPTER 2.16

### CORROSIVE TO METALS

#### 2.16.1 Definition

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

#### 2.16.2 Classification criteria

A substance or a mixture which is corrosive to metals is classified in a single category for this class, using the test in Part III, sub-section 37.4 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of tests and Criteria*, according to the following table:

**Table 2.16.1: Criteria for substances and mixtures corrosive to metal**

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

**NOTE:** Where an initial test on either steel or aluminium indicates the substance or mixture being tested is corrosive the follow-up test on the other metal is not required.

#### 2.16.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 2 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

**Table 2.16.2: Label elements for substances and mixtures corrosive to metals**

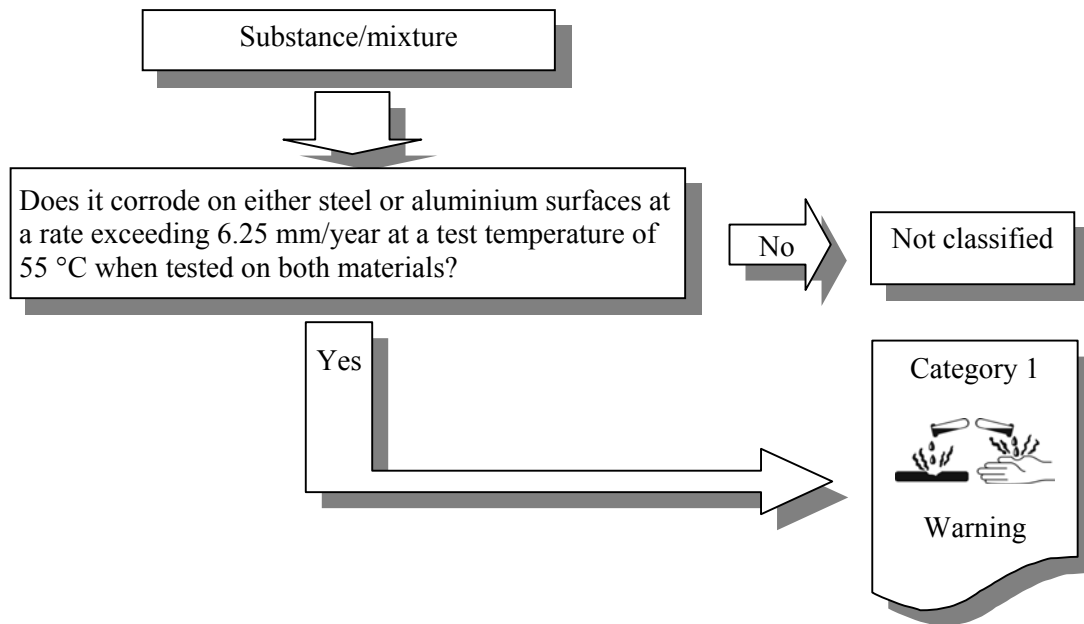
	Category 1
Symbol	Corrosion
Signal word	Warning
Hazard statement	May be corrosive to metals

#### 2.16.4 Decision logic and guidance

The decision logic and guidance which follow, are not part of the harmonized classification system but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

#### 2.16.4.1 *Decision logic*

##### *Decision logic 2.16 for substances and mixtures corrosive to metals*



#### 2.16.4.2 *Guidance*

The corrosion rate can be measured according to the test method of Part III, sub-section 37.4 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*. The specimen to be used for the test should be made of the following materials:

- (a) For the purposes of testing steel, steel types S235JR+CR (1.0037 resp.St 37-2), S275J2G3+CR (1.0144 resp.St 44-3), ISO 3574, Unified Numbering System (UNS) G 10200, or SAE 1020;
- (b) For the purposes of testing aluminium: non-clad types 7075-T6 or AZ5GU-T6.