# PART 2 PHYSICAL HAZARDS

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# **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 predominantly contain extremely insensitive 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
Unstable <sup>a</sup> explosives or explosives of Division	For explosives o be performed:	of Divisions 1.1 to 1.6, the following are the core set of tests that need to
1.1 to 1.6	Explosibility:	according to UN Test Series 2 (Section 12 of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria). Intentional explosives <sup>b</sup> are not subject to UN Test Series 2.
	Sensitiveness:	according to UN Test Series 3 (Section 13 of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria).
	Thermal stability:	according to UN Test 3(c) (Sub-section 13.6.1 of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria).
	Further tests are necessary to allocate the correct Division.	

<sup>&</sup>lt;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.

- **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, diluted with other substances or dissolved or suspended in water or other liquid substances to suppress or reduce their explosives properties. They may be a candidate for classification as desensitized explosives (see Chapter 2.17) or 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.

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

#### 2.1.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 1 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.

	Unstable Explosive	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	Exploding bomb	Exploding bomb; or 1.4 on orange background <sup>a</sup>	1.5 on orange background <sup>a</sup>	1.6 on orange background <sup>a</sup>
Signal word	Danger	Danger	Danger	Danger	Warning	Danger	No signal word
Hazard statement	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	No hazard statement

Table 2.1.2: Label elements for explosives

**NOTE 1:** Unpackaged explosives or explosives repacked in packagings other than the original or similar packaging shall have the following label elements:

- (a) <u>Symbol</u>: exploding bomb;
- (b) <u>Signal word</u>: "Danger"; and
- (c) <u>Hazard statement</u>: "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.

**NOTE 2:** Substances and mixtures, as supplied, with a positive result in Test Series 2 in Part I, Section 12, of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, which are exempted from classification as explosives (based on a negative result in Test Series 6 in Part I, Section 16 of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria,) still have explosive properties. The user should be informed of these intrinsic explosive properties because they have to be considered for handling – especially if the substance or mixture is removed from its packaging or is repackaged – and for storage. For this reason, the explosive properties of the substance or mixture should be communicated in Section 2 (Hazard identification) and Section 9 (Physical and chemical properties) of the Safety Data Sheet in accordance with Table 1.5.2, and other sections of the Safety Data Sheet, as appropriate.

## 2.1.4 Decision logic and guidance

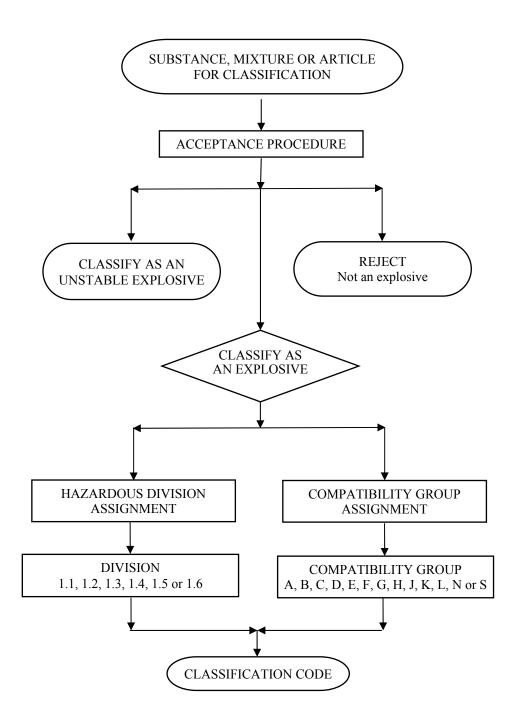
The decision logic and guidance, which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

# 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).

Applies to substances, mixtures and articles subject to some regulatory purposes (e.g. transport).

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)



SUBSTANCE/MIXTURE ARTICLE FOR FOR CLASSIFICATION CLASSIFICATION the substance mixture manufactured with Yes Substance/mixture to be the view to producing considered for this Class a practical explosive or pyrotechnic effect? **TEST SERIES 3** No the substance Is the /mixture a candidate for substance/mixture ammonium nitrate emulsions thermally stable suspension or gel, intermediate for blasting explosive. ANE? Yes No the substance /mixture too dangerous TEST SERIES 8 in the form in which Go to Figure 2.1.4 No it was tested? **TEST SERIES 1** Yes Encapsulate and/or package Is it the substance/mixture an explosive substance/mixture No Yes **TEST SERIES 4 TEST SERIES 2** Is the Is the substance/mixture article, packed too insensitive for article or packaged acceptance into substance/mixture too Yes this Class? dangerous?

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

CLASSIFY as an

unstable explosive

NOT AN

**EXPLOSIVE** 

Yes

CLASSIFY as an

unstable explosive

PROVISIONALLY

ACCEPT INTO

THIS CLASS (go to Figure 2.1.3)

<sup>\*</sup> For classification purposes start with test series 2.

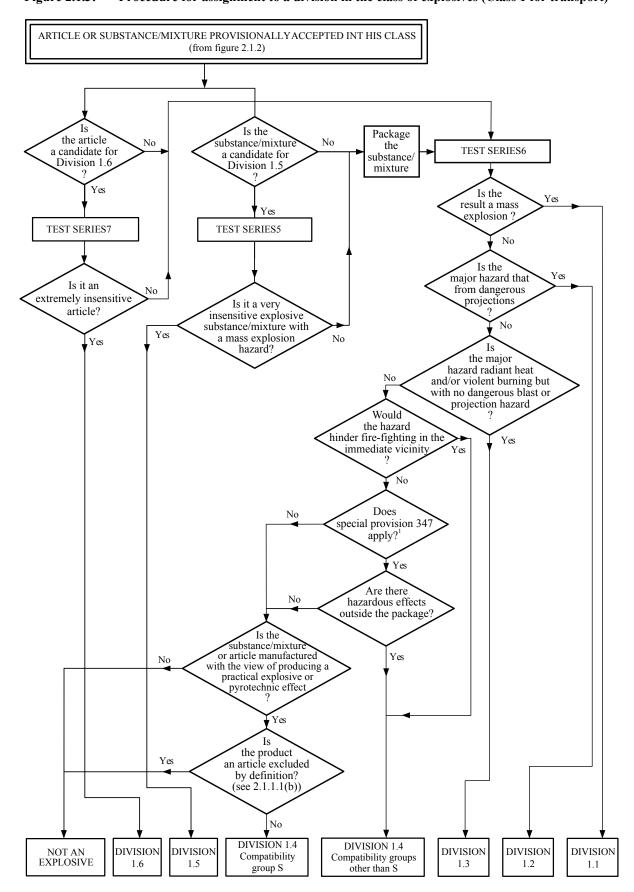


Figure 2.1.3: Procedure for assignment to a division in the class of explosives (Class 1 for transport)

<sup>&</sup>lt;sup>1</sup> See Chapter 3.3 of the UN Model Regulations on the Transport of Dangerous Goods, Model Regulations for details.

TEST SERIES 8 TEST 8(a) No Thermal stability test Classify as unstable explosive Is the substance/mixture thermally stable? Yes Substance/mixture to be considered for TEST 8 (b) classification as an explosive other than as an ANE Large scale gap test unstable explosive; Yes Is the substance/mixture too sensitive If the answer to the question "is it a very to shock to be accepted as an insensitive explosive substance/mixture with oxidizing liquid or an a mass explosion hazard?" in figure 2.1.3 is oxidizing "no", the substance/mixture shall be solid? classified in Division 1.1 No Substance/mixture to be considered for classification as an explosive of Division 1.5, TEST 8 (c) proceed with Test Series 5. If the answer to the question "is it a very Koenen test Yes Is the substance/mixture insensitive explosive substance/mixture with a too sensitive to the effect of mass explosion hazard?" in figure 2.1.3 is intensive heat under "yes", the substance/mixture shall be classified confinement? in Division 1.5; if the answer is "no" the substance/mixture shall be classified in Division 1.1 No ANE substance/mixture shall be classified as a Category 2 oxidizing liquid or a Category 2 oxidizing solid (Chapters 2.13 and 2.14)

Figure 2.1.4: Procedure for the classification of ammonium nitrate emulsion, suspension or gel (ANE)

# 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. For organic substances and mixtures of organic substances with a decomposition energy of 800 J/g or more, tests 1 (a) and 2 (a) need not be performed if the outcome of the ballistic mortar Mk.IIId test (F.1), or the ballistic mortar test (F.2) or the BAM Trauzl test (F.3) with initiation by a standard No.8 detonator (see Appendix 1 to the Manual of Tests and Criteria) is "no". In this case, the results of test 1 (a) and 2 (a) are deemed to be "-".

- 2.1.4.2.2 The acceptance procedure for the hazard class "explosives" need not be applied 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:

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

using the formula:

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

- (c) For an organic substance, or a homogenous mixture of organic substances, containing a chemical group (or groups) associated with explosive properties:
  - the exothermic decomposition energy is less than 500 J/g, or
  - the onset of exothermic decomposition is 500 °C or above

as indicated by Table 2.1.3.

Table 2.1.3: Decision to apply the acceptance procedure for the hazard class "Explosives" for an organic substance or a homogenous mixture of organic substances

Decomposition energy (J/g)	Decomposition onset temperature (°C)	Apply acceptance procedure? (Yes/No)
< 500	< 500	No
< 500	≥ 500	No
≥ 500	< 500	Yes
≥ 500	≥ 500	No

The exothermic decomposition energy may be determined using a suitable calorimetric technique (see section 20.3.3.3 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*); 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.

# FLAMMABLE GASES

## 2.2.1 Definitions

- 2.2.1.1 A *flammable gas* is a gas having a flammable range with air at 20 °C and a standard pressure of 101.3 kPa.
- 2.2.1.2 A *pyrophoric gas* is a flammable gas that is liable to ignite spontaneously in air at a temperature of 54 °C or below.
- 2.2.1.3 A *chemically unstable gas* is a flammable gas that is able to react explosively even in the absence of air or oxygen.

#### 2.2.2 Classification criteria

2.2.2.1 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
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:** Aerosols should not be classified as flammable gases. See Chapter 2.3.
- 2.2.2.2 A flammable gas is additionally classified as pyrophoric if it meets the criteria in the following table:

Table 2.2.2: Criteria for pyrophoric gases

Category	Criteria
Pyrophoric gas	Flammable gas that ignite spontaneously in air at a temperature of 54 °C or below.

- **NOTE 1:** Spontaneous ignition for pyrophoric gases is not always immediate, and there may be a delay.
- **NOTE 2:** In the absence of data on its pyrophoricity, a flammable gas mixture should be classified as a pyrophoric gas if it contains more than 1% (by volume) of pyrophoric component(s).
- 2.2.2.3 A flammable gas that is also chemically unstable is additionally classified in one of the two categories for chemically unstable gases using the methods described in Part III of the Manual of Tests and Criteria according to the following table:

Table 2.2.3: Criteria for chemically unstable gases

Category	Criteria
A	Flammable gases which are chemically unstable at 20°C and a standard pressure of 101.3 kPa
В	Flammable gases which are chemically unstable at a temperature greater than 20°C and/or a pressure greater than 101.3 kPa

#### 2.2.3 Hazard communication

2.2.3.1 General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 1 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.

Flammable gas Additional sub-categories Pyrophoric gas Chemically unstable gas Category 1 Category 2 Pyrophoric gas Category A Category B **Symbol** Flame No symbol Flame No additional No additional symbol symbol No additional signal No additional signal Signal word Danger Warning Danger word word Hazard Extremely Flammable gas May ignite May react May react explosively flammable gas spontaneously if explosively even in even in the absence of statement exposed to air the absence of air air at elevated pressure and/or temperature

Table 2.2.4: Label elements for flammable gases

2.2.3.2 If a flammable gas or gas mixture is additionally classified in one or more sub-categories, then all relevant classification(s) should be communicated on the safety data sheet as specified in Annex 4, and the relevant hazard communication elements included on the label.

## 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 for flammable gases

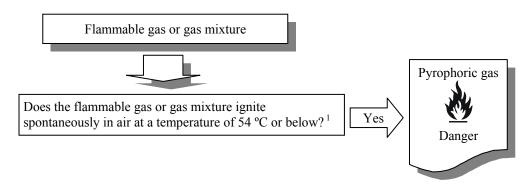
To classify a flammable gas, data on its flammability are required. The classification is according to decision logic 2.2 (a).

# Decision logic 2.2 (a) Gaseous substance or mixture of gases Does it have a flammable range with air at 20 °C and Not classified a standard pressure of 101.3 kPa? Yes At 20 °C and a standard pressure of 101.3 kPa, does it: Go to decision Category 1 ignite when in a mixture of 13% or less by volume in logics 2.2 (b) and 2.2 (c) Yes (b) have a flammable range with air of at least 12 percentage points regardless of the lower flammable Danger limit? Go to decision Category 2 No logics 2.2 (b) No symbol and 2.2 (c) Warning

# 2.2.4.2 Decision logic for pyrophoric gases

To classify a flammable gas as a pyrophoric gas, data on its ability to ignite in air are required. The classification is according to decision logic 2.2 (b).

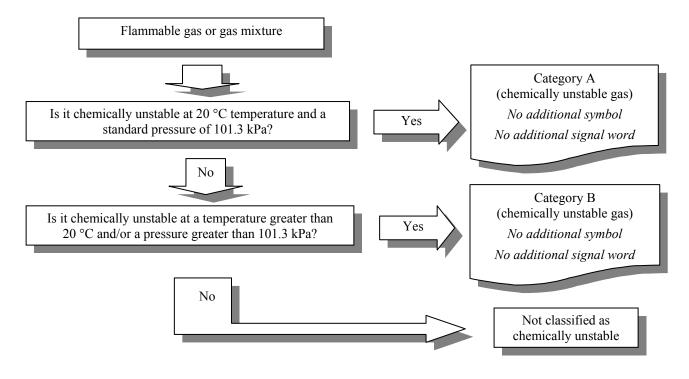
## Decision logic 2.2 (b)



# 2.2.4.3 Decision logic for chemically unstable gases

To classify a flammable gas as chemically unstable, data on its chemical instability are required. The classification is according to decision logic 2.2 (c).

# Decision logic 2.2 (c)



<sup>&</sup>lt;sup>1</sup> In the absence of data on its pyrophoricity, a flammable gas mixture should be classified as a pyrophoric gas if it contains more than 1% (by volume) of pyrophoric component(s).

#### **2.2.4.4** *Guidance*

- 2.2.4.4.1 Flammability should be determined by tests or by calculation in accordance with methods adopted by ISO (see ISO 10156:2010 "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.
- 2.2.4.4.2 Pyrophoricity should be determined at 54°C in accordance with either IEC 60079-20-1 ed1.0 (2010-01) "Explosive atmospheres Part 20-1: Material characteristics for gas and vapour classification Test methods and data" or DIN 51794 "Determining the ignition temperature of petroleum products".
- 2.2.4.4.3 The classification procedure for pyrophoric gases 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 a temperature of 54 °C or below. Flammable gas mixtures, which have not been tested for pyrophoricity and contain more than one percent pyrophoric components, should be classified as a pyrophoric gas. Expert judgement on the properties and physical hazards of pyrophoric gases and their mixtures should be used in assessing the need for classification of flammable gas mixtures containing one percent or less pyrophoric components. In this case, testing need only be considered if expert judgement indicates a need for additional data to support the classification process.
- 2.2.4.4.4 Chemical instability should be determined in accordance with the method described in Part III of the Manual of Tests and Criteria. If the calculations in accordance with ISO 10156:2010 show that a gas mixture is not flammable it is not necessary to carry out the tests for determining chemical instability for classification purposes.

## 2.2.5 Example: Classification of a flammable gas mixture by calculation according to ISO 10156:2010

#### <u>Formula</u>

$$\sum_{i}^{n} \frac{V_{i}\%}{T_{ci}}$$

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<sup>th</sup> 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:

$$\sum_{i}^{n} \frac{V_{i} \%}{T_{ci}} > 1$$

## 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:

$$2\%(H_2) + 6\%(CH_4) + [27\% \times 0.5 + 65\% \times 0.5](N_2) = 2\%(H_2) + 6\%(CH_4) + 46\%(N_2) = 54\%$$

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

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

4. Ascertain the Tci coefficients for the flammable gases:

Tei 
$$H_2 = 5.7\%$$
  
Tei  $CH_4 = 14.3\%$ 

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

$$\sum_{i}^{n} \frac{V_{i}\%}{T_{ci}} = \frac{3.7}{5.7} + \frac{11.1}{14.3} = 1.42$$

Therefore the mixture is <u>flammable</u> in air.

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# **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 are classified in one of the three categories of this hazard class, depending on their flammable properties and their heat of combustion. They should be considered for classification in Category 1 or 2 if they contain more than 1% components (by mass) which are classified as flammable according to the GHS criteria, i.e.:
  - Flammable gases (see Chapter 2.2);
  - Flammable liquids (see Chapter 2.6);
  - Flammable solids (see Chapter 2.7);

or if their heat of combustion is at least 20 kJ/g.

- **NOTE 1**: Flammable components do not cover pyrophoric, self-heating or water-reactive substances and mixtures because such components are never used as aerosol contents.
- **NOTE 2:** Aerosols do not fall additionally within the scope of chapters 2.2 (flammable gases), 2.5 (gases under pressure), 2.6 (flammable liquids) and 2.7 (flammable solids). Depending on their contents, aerosols may however fall within the scope of other hazard classes, including their labelling elements.
- 2.3.2.2 An aerosol is classified in one of the three 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. Aerosols which do not meet the criteria for inclusion in Category 1 or Category 2 (extremely flammable or flammable aerosols) should be classified in Category 3 (non-flammable aerosols).
- **NOTE:** Aerosols containing more than 1% flammable components or with a heat of combustion of at least 20 kJ/g, which are not submitted to the flammability classification procedures in this chapter should be classified as aerosols, Category 1.

## 2.3.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 1 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 aerosols

	Category 1	Category 2	Category 3
Symbol	Flame	Flame	No symbol
Signal word	Danger	Warning	Warning
Hazard statement	Extremely flammable aerosol Pressurized container: May burst if heated	Flammable aerosol Pressurized container: May burst if heated	Pressurized container: May burst if heated

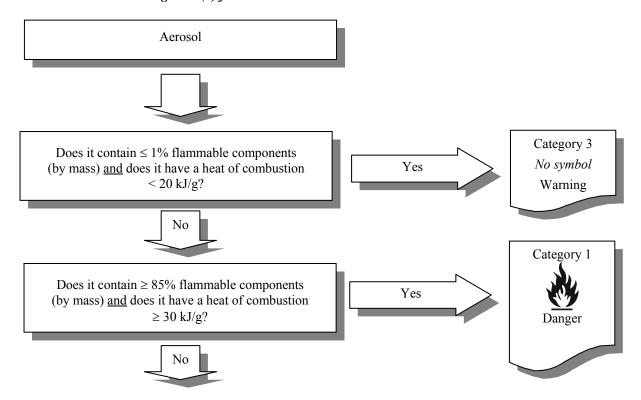
# 2.3.4 Decision logic and guidance

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

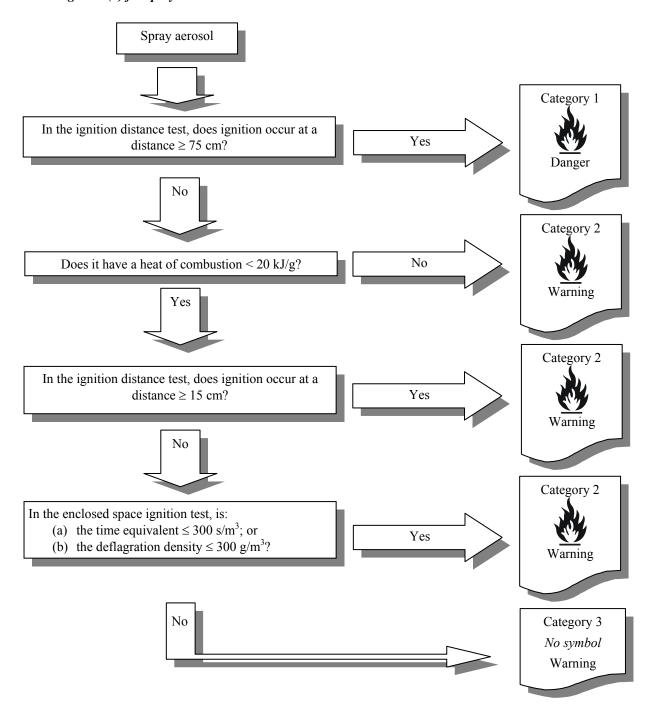
To classify an aerosol data on its flammable components, on its chemical heat of combustion and, if applicable, the results of the foam test (for foam aerosols) and of the ignition distance test and enclosed space test (for spray aerosols) are required. Classification should be made according to decision logics 2.3 (a) to 2.3 (c).

Decision logic 2.3 (a) for aerosols

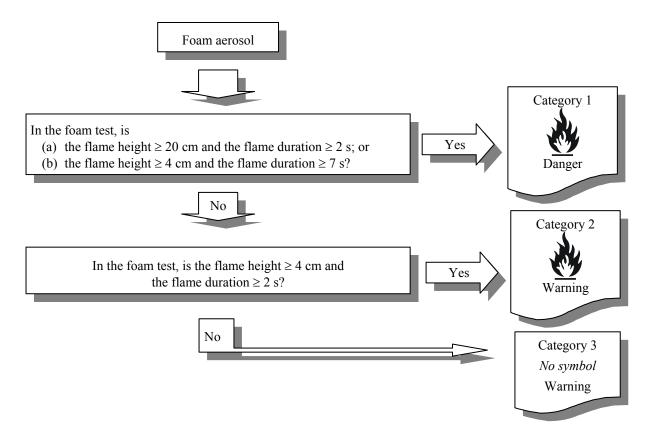


For spray aerosols, go to decision logic 2.3 (b); For foam aerosols, go to decision logic 2.3 (c);

# 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 ( $\Delta$ Hc), 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:

$$\Delta Hc \text{ (product)} = \sum_{i}^{n} [wi\% \times \Delta Hc(i)]$$

where:

 $\Delta$ Hc = chemical heat of combustion (kJ/g);

wi% = mass fraction of component i in the product;

 $\Delta$ Hc(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 *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.

# **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.

**NOTE:** "Gases which cause or contribute to the combustion of other material more than air does" means pure gases or gas mixtures with an oxidizing power greater than 23.5% as determined by a method specified in ISO 10156:2010.

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

#### 2.4.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 1 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	
Symbol	Flame over circle	
Signal word	Danger	
Hazard statement	May cause or intensify fire; oxidizer	

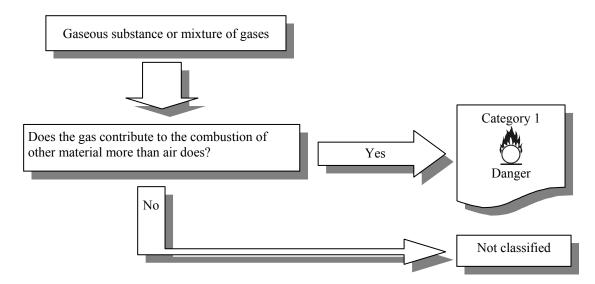
## 2.4.4 Decision logic and guidance

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 10156:2010 "Gases and gas mixtures – Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets" 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 10156:2010.

The classification method described in ISO 10156 uses the criterion that a gas mixture should be considered as more oxidising than air if the oxidising power of the gas mixture is higher than 0.235 (23.5%).

The oxidizing power (OP) is calculated as follows:

$$OP = \frac{\sum_{i=1}^{n} x_{i}C_{i}}{\sum_{i=1}^{n} x_{i} + \sum_{k=1}^{p} K_{k}B_{k}}$$

Where:

 $x_i$  = molar fraction of the i:th oxidising gas in the mixture;

C<sub>i</sub> = coefficient of oxygen equivalency of the i:th oxidising gas in the mixture;

 $K_k$  = coefficient of equivalency of the inert gas k compared to nitrogen;

 $B_k$  = molar fraction of the k:th inert gas in the mixture;

n = total number of oxidising gases in the mixture;

p = total number of inert gases in the mixture;

Example mixture:  $9\% (O_2) + 16\% (N_2O) + 75\% (He)$ 

# Calculation steps

## Step 1:

Ascertain the coefficient of oxygen equivalency (Ci) for the oxidising gases in the mixture and the nitrogen equivalency factors (Kk) for the non-flammable, non-oxidising gases.

 $C_i(N_2O) = 0.6$  (nitrous oxide)

 $C_i(O_2) = 1 \text{ (oxygen)}$ 

 $K_k$  (He) = 0.9 (helium)

# Step 2:

Calculate the oxidising power of the gas mixture

$$OP = \frac{\sum_{i=1}^{n} x_{i} C_{i}}{\sum_{i=1}^{n} x_{i} + \sum_{k=1}^{p} K_{k} B_{k}} = \frac{0.09 \times 1 + 0.16 \times 0.6}{0.09 + 0.16 + 0.75 \times 0.9} = 0.201$$
**20.1 < 23.5**

Therefore the mixture is <u>not</u> considered as <u>an oxidising gas.</u>

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# **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 at 20 °C, 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

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

NOTE: Aerosols should not be classified as gases under pressure. See Chapter 2.3.

#### 2.5.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 1 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
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

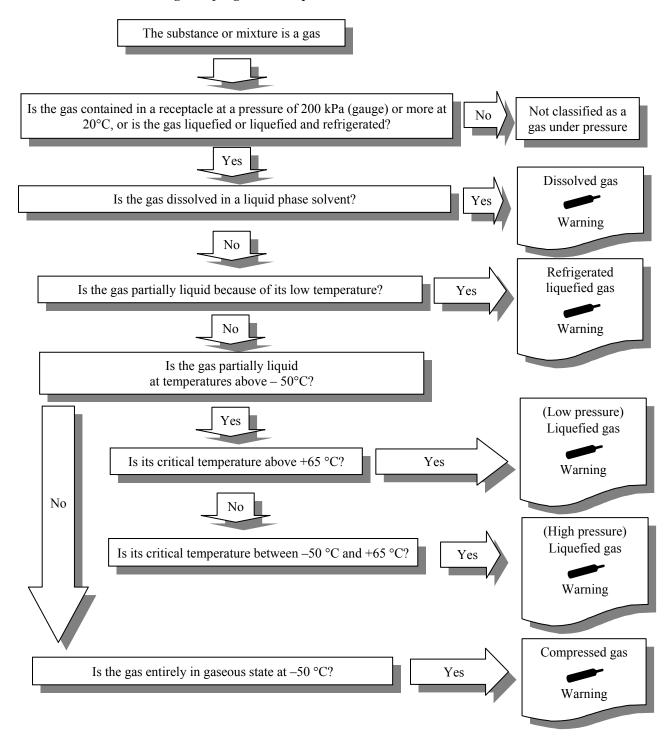
# 2.5.4 Decision logic and guidance

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.

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# FLAMMABLE LIQUIDS

## 2.6.1 Definition

table:

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 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 and not more than 60 °C may be regarded as non-flammable liquids for some regulatory purposes (e.g. transport) if negative results have been obtained in the sustained combustibility test L.2 of Part III, section 32 of the 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.

**NOTE 4:** Aerosols should not be classified as flammable liquids. See Chapter 2.3.

#### 2.6.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 1 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
Symbol	Flame Flame Fla		Flame	No symbol
Signal word	Danger	Danger	Warning	Warning
Hazard statement	ş ş		Flammable liquid and vapour	Combustible liquid

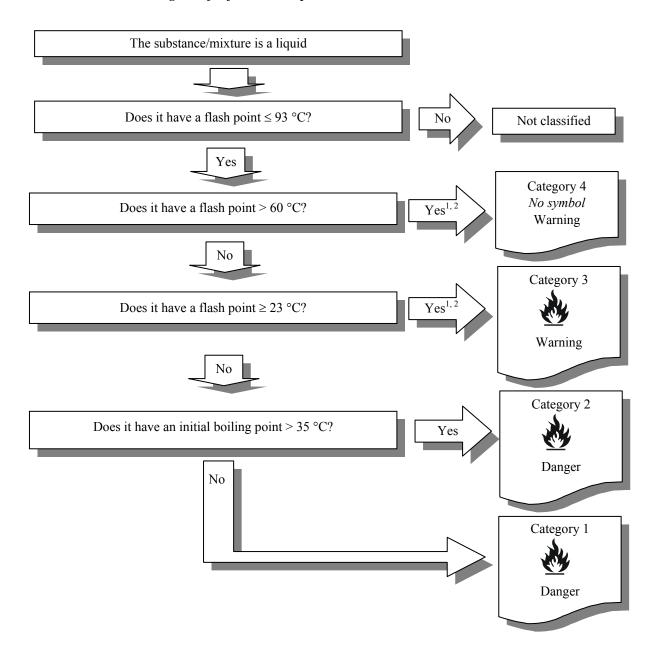
## 2.6.4 Decision logic and guidance

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



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>&</sup>lt;sup>2</sup> Liquids with a flash point of more than 35 °C and not more than 60 °C may be regarded as non-flammable liquids for some regulatory purposes (e.g. transport) if negative results have been obtained in the sustained combustibility test L.2 of Part III, section 32 of the 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<sup>4</sup> greater than the relevant classification criterion (23 °C and 60 °C, respectively) 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 lower explosion limit of each ingredient is known (an appropriate correlation has to be applied when these data are extrapolated to other temperatures than test conditions) as well as a method for calculating the lower explosion limit of the mixture;
  - (c) The temperature dependence of the saturated vapour pressure and of the activity coefficient is known for each ingredient as present in the mixture;
  - (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 methods for determining the flash point of flammable liquids should be used:

### International standards:

ISO 1516

ISO 1523

ISO 2719

ISO 13736

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 D3828-07a, "Standard Test Methods for Flash Point by Small Scale Closed Cup Tester"

ASTM D56-05, "Standard Test Method for Flash Point by Tag Closed Cup Tester"

ASTM D3278-96(2004)e1, "Standard Test Methods for Flash Point of Liquids by Small Scale Closed Cup Apparatus"

ASTM D93-08, "Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester"

<sup>&</sup>lt;sup>3</sup> Up to now, the calculation method is validated for mixtures containing up to six volatile components. These components may be flammable liquids like hydrocarbons, ethers, alcohols, esters (except acrylates), and water. It is however not yet validated for mixtures containing halogenated, sulphurous, and/or phosphoric compounds as well as reactive acrylates.

<sup>&</sup>lt;sup>4</sup> If the calculated flash point is less than 5°C greater than the relevant classification criterion, the calculation method may not be used and the flash point should be determined experimentally.

Association française de normalisation, AFNOR, 11, rue de Pressensé. 93571 La Plaine Saint-Denis Cedex":

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

Deutsches Institut für Normung, Burggrafenstr. 6, D-10787 Berlin:

Standard DIN 51755 (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

2.6.4.2.6 The following methods for determining the initial boiling point of flammable liquids should be used:

## International standards:

ISO 3924

ISO 4626

ISO 3405

#### National standards:

American Society for Testing Materials International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, Pennsylvania, USA 19428-2959:

ASTM D86-07a, "Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure" ASTM D1078-05, "Standard Test Method for Distillation Range of Volatile Organic Liquids"

## Further acceptable methods:

Method A.2 as described in Part A of the Annex to Commission Regulation (EC) No.440/2008<sup>5</sup>.

<sup>&</sup>lt;sup>5</sup> Commission Regulation (EC) No 440/2008 of 30 May 2008 laying down test methods pursuant to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) (Official Journal of the European Union, No. L142 of 31.05.2008, p1-739 and No. L143 of 03.06.2008, p.55).

# 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				
1	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				
2	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 $\le 10$ min				

**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 must also be tested in the new form.

**NOTE 2:** Aerosols should not be classified as flammable solids. See Chapter 2.3.

#### 2.7.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 1 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.

Category 1Category 2SymbolFlameFlameSignal wordDangerWarningHazard statementFlammable solidFlammable solid

Table 2.7.2: Label elements for flammable solids

# 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 The substance/mixture is a solid Not classified Screening test Negative Positive Burning rate test: (a) For substances or mixtures other than metal powders: Burning time < 45 s or burning rate > 2.2 mm/s? Not classified (b) Metal powders: Burning time ≤10 min? Yes Category 1 (a) For substances or mixtures other than metal powders: Danger Does the wetted zone stop propagation of the flame? (b) Metal powders: Burning time > 5 min? Yes Category 2 Warning

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# 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 1 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

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

<sup>&</sup>lt;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

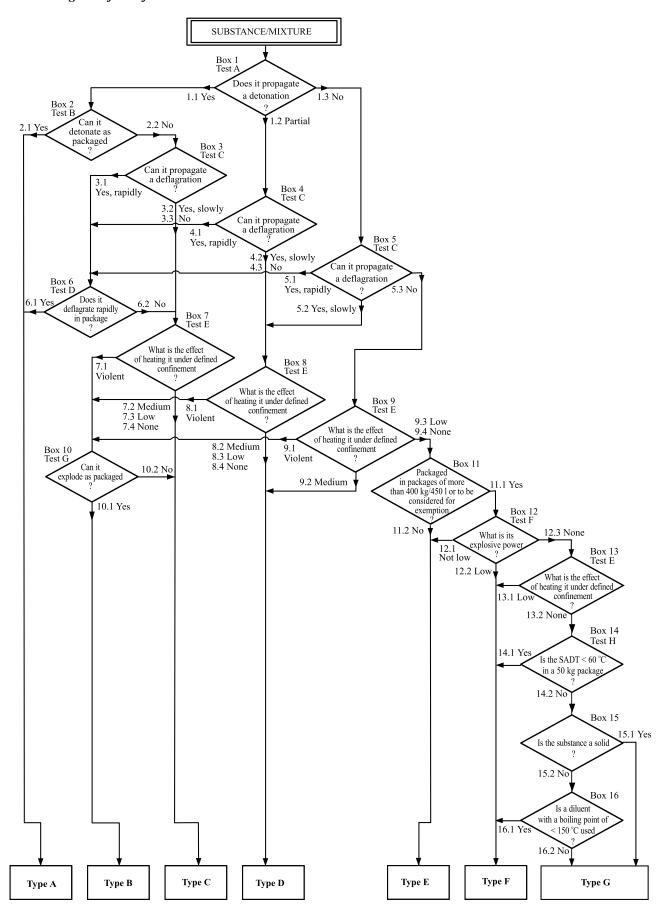
The decision logic and guidance which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

# 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*).

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# **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, subsection 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
	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 1 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		
Symbol	Flame		
Signal word	Danger		
Hazard statement Catches fire spontaneously if exposed to a			

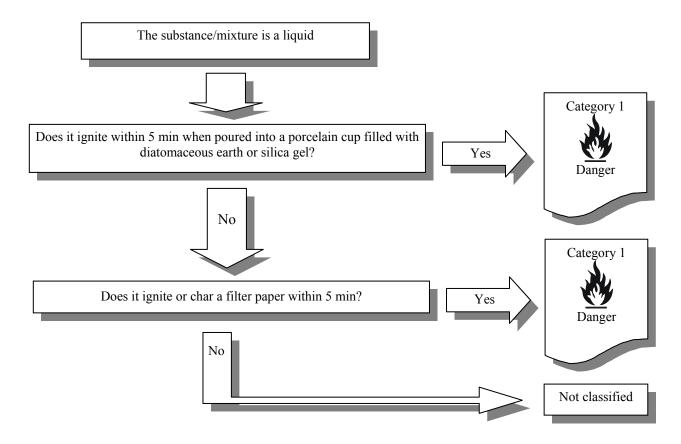
## 2.9.4 Decision logic and guidance

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)).

# 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 1 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		

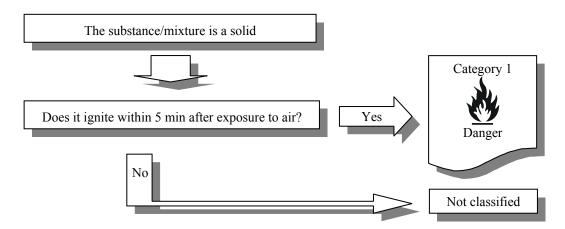
# 2.10.4 Decision logic and guidance

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, sub-section 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)).

# 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 a substance or mixtures is a process where the gradual reaction of that substance or mixture with oxygen (in air) generates heat. If the rate of heat production exceeds the rate of heat loss, then the temperature of the substance or mixture will rise which, after an induction time, may lead to self-ignition and combustion.

#### 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 and 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 and 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 and 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  $50 \,^{\circ}\text{C}$  for a sample cube of  $27 \, \text{m}^3$ . Substances and mixtures with a temperature of spontaneous combustion higher than  $50 \,^{\circ}\text{C}$  for a volume of  $27 \,^{\circ}\text{m}^3$  should not be assigned to this hazard class. Substances and mixtures with a self-ignition temperature higher than  $50 \,^{\circ}\text{C}$  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 1 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	

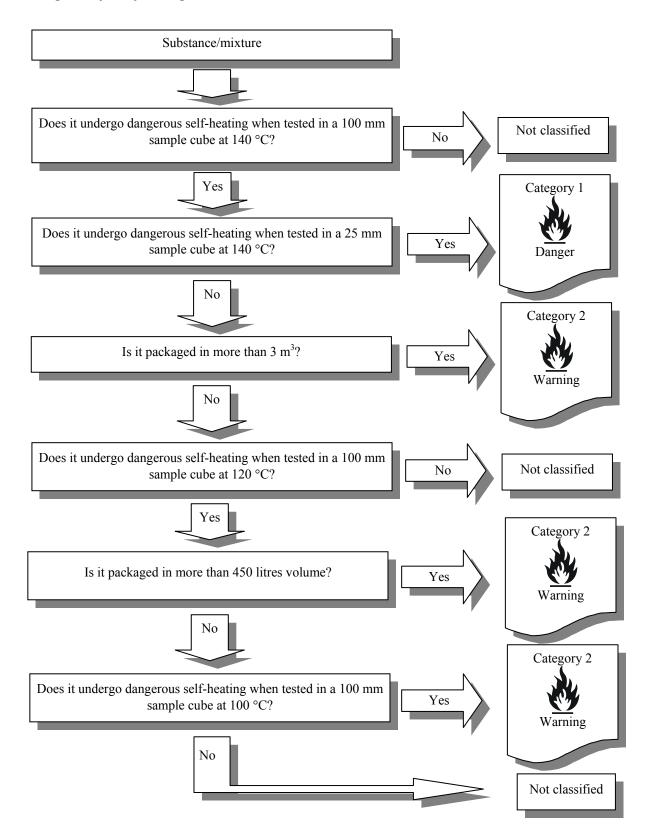
# 2.11.4 Decision logic and guidance

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, sub-section 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*.

# 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 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 1 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

	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	

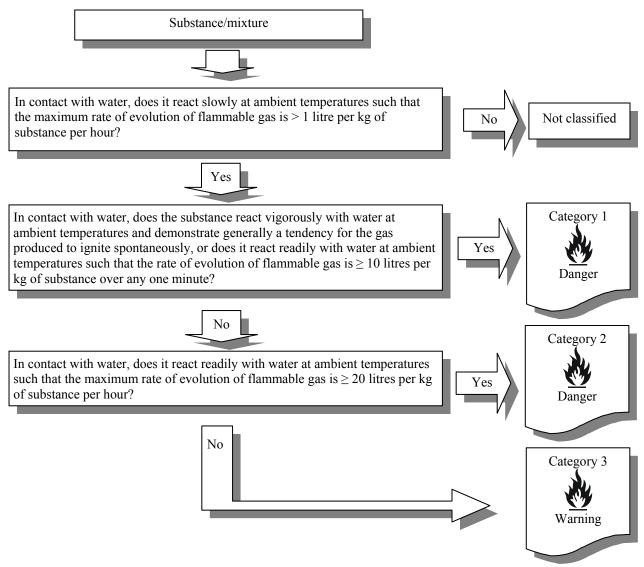
## 2.12.4 Decision logic and guidance

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.

# **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
1	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;
2	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;
3	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 1 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	
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	

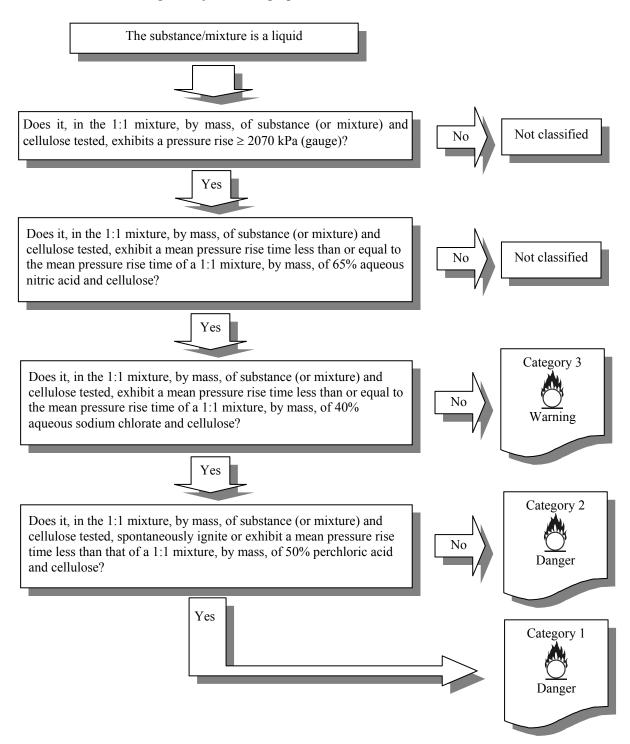
# 2.13.4 Decision logic and guidance

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.

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# **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 or test O.3 in Part III, sub-section 34.4.3, of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, according to the following table:

Criteria using test 0.3 Category Criteria using test O.1 Any substance or mixture which, in the 4:1 Any substance or mixture which, in the 4:1 or 1 or 1:1 sample-to-cellulose ratio (by mass) 1:1 sample-to-cellulose ratio (by mass) tested, tested, exhibits a mean burning time less exhibits a mean burning rate greater than the than the mean burning time of a 3:2 mixture, mean burning rate of a 3:1 mixture (by mass) of (by mass), of potassium bromate and calcium peroxide and cellulose. cellulose. 2 Any substance or mixture which, in the 4:1 Any substance or mixture which, in the 4:1 or or 1:1 sample-to-cellulose ratio (by mass) 1:1 sample-to-cellulose ratio (by mass) tested, tested, exhibits a mean burning time equal to exhibits a mean burning rate equal to or greater or less than the mean burning time of a 2:3 than the mean burning rate of a 1:1 mixture (by mixture (by mass) of potassium bromate and mass) of calcium peroxide and cellulose and the cellulose and the criteria for Category 1 are criteria for Category 1 are not met. not met. 3 Any substance or mixture which, in the 4:1 Any substance or mixture which, in the 4:1 or or 1:1 sample-to-cellulose ratio (by mass) 1:1 sample-to-cellulose ratio (by mass) tested, tested, exhibits a mean burning time equal to exhibits a mean burning rate equal to or greater or less than the mean burning time of a 3:7 than the mean burning rate of a 1:2 mixture (by mass) of calcium peroxide and cellulose and the mixture (by mass) of potassium bromate and cellulose and the criteria for Categories 1 criteria for Categories 1 and 2 are not met. and 2 are not met.

Table 2.14.1: Criteria for oxidizing solids

**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" (IMSBC Code<sup>1</sup>, Appendix 2, Section 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 1 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.

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International Maritime Solid Bulk Cargoes Code, IMO.

Table 2.14.2: 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

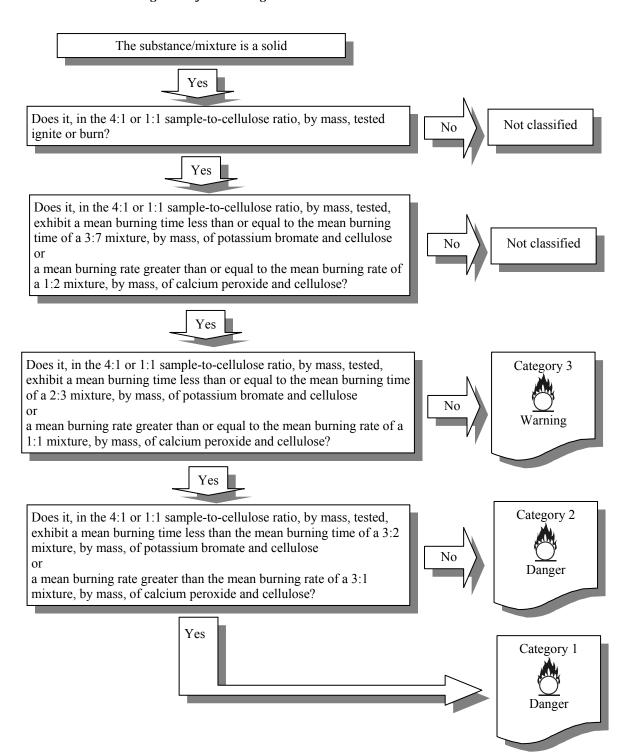
# 2.14.4 Decision logic and guidance

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 or test method O.3 as described in Part III, sub-section 34.4.3 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.

# **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 = number of peroxygen groups per molecule of organic peroxide i;

c = concentration (mass %) of organic peroxide i;

m = 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 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.

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 1 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

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

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

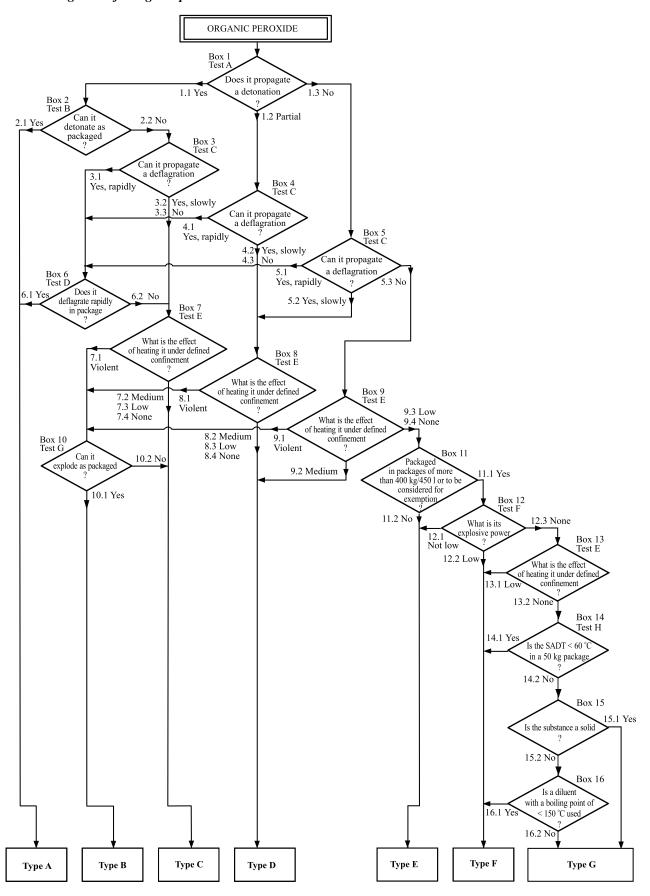
## 2.15.4 Decision logic and guidance

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.

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# **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 1 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	

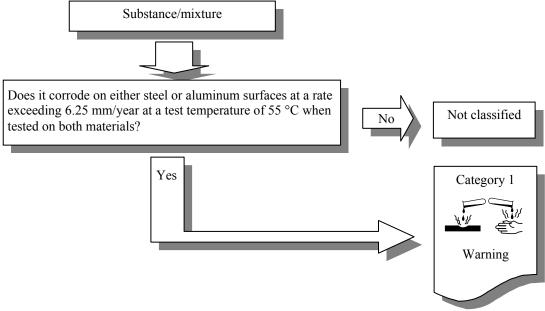
**NOTE:** Where a substance or mixture is classified as corrosive to metals but not corrosive to skin and/or eyes, some competent authorities may allow the labelling provisions described in 1.4.10.5.5.

## 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.

# **DESENSITIZED EXPLOSIVES**

## 2.17.1 Definitions and general considerations

2.17.1.1 Desensitized explosives are solid or liquid explosive substances or mixtures which are phlegmatized to suppress their explosive properties in such a manner that they do not mass explode and do not burn too rapidly and therefore may be exempted from the hazard class "Explosives" (Chapter 2.1; see also Note 2 of paragraph 2.1.2.2).

## 2.17.1.2 The class of desensitized explosives comprises:

(a) Solid desensitized explosives: explosive substances or mixtures which are wetted with water or alcohols or are diluted with other substances, to form a homogeneous solid mixture to suppress their explosive properties.

**NOTE:** This includes desensitization achieved by formation of hydrates of the substances.

(b) Liquid desensitized explosives: explosive substances or mixtures which are dissolved or suspended in water or other liquid substances, to form a homogeneous liquid mixture to suppress their explosive properties.

#### 2.17.2 Classification criteria

2.17.2.1 Any explosive which is desensitized shall be considered in this class, unless:

- (a) It is manufactured with the view to producing a practical, explosive or pyrotechnic effect; or
- (b) It has a mass explosion hazard according to test series 6 (a) or 6 (b) or their corrected burning rate according to the burning rate test described in part V, subsection 51.4 of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria is greater than 1200 kg/min; or
- (c) Their exothermic decomposition energy is less than 300 J/g.

**NOTE 1:** Substances or mixtures which meet the criterion (a) or (b) shall be classified as explosives (see Chapter 2.1). Substances or mixtures which meet the criterion (c) may fall within the scope of other physical hazard classes.

**NOTE 2:** The exothermic decomposition energy may be estimated using a suitable calorimetric technique (see section 20, sub-section 20.3.3.3 in Part II of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria).

2.17.2.2 Desensitized explosives shall be classified as packaged for supply and use in one of the four categories of this class depending on the corrected burning rate (Ac) using the test "burning rate test (external fire)" described in Part V, sub-section 51.4 of the *UN Recommendations of the Transport of Dangerous Goods, Manual of Tests and Criteria*, according to Table 2.17.1:

Unstable explosives as defined in Chapter 2.1 can also be stabilized by desensitization and consequently may be classified as desensitized explosives, provided all criteria of Chapter 2.17 are met. In this case the desensitized explosive should be tested according to test series 3 (Part I of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria) because information about its sensitiveness to mechanical stimuli is likely to be important for determining conditions for safe handling and use. The results should be communicated in the safety data sheet.

Table 2.17.1: Criteria for desensitized explosives

Category	Criteria						
1	Desensitized explosives with a corrected burning rate $(A_C)$ equal to or greater than 300 kg/min but not more than 1200 kg/min						
2	Desensitized explosives with a corrected burning rate $(A_C)$ equal to or greater than $140 \text{ kg/min}$ but less than $300 \text{ kg/min}$						
3	Desensitized explosives with a corrected burning rate (A <sub>C</sub> ) equal to or greater than 60 kg/min but less than 140 kg/min						
4	Desensitized explosives with a corrected burning rate (A <sub>C</sub> ) less than 60 kg/min						

**NOTE 1:** Desensitized explosives should be prepared so that they remain homogeneous and do not separate during normal storage and handling, particularly if desensitized by wetting. The manufacturer/supplier should give information in the safety data sheet about the shelf-life and instructions on verifying desensitization. Under certain conditions the content of desensitizing agent (e.g. phlegmatizer, wetting agent or treatment) may decrease during supply and use, and thus, the hazard potential of desensitized explosive may increase. In addition, the safety data sheet should include advice on avoiding increased fire, blast or protection hazards when the substance or mixture is not sufficiently desensitized.

**NOTE 2:** Desensitized explosives may be treated differently for some regulatory purposes (e.g. transport). Classification of solid desensitized explosives for transport purposes is addressed in Chapter 2.4, section 2.4.2.4 of the UN Recommendations on the Transport of Dangerous Goods, Model Regulations. Classification of liquid desensitized explosives is addressed in Chapter 2.3, section 2.3.1.4 of the Model Regulations.

**NOTE 3:** Explosive properties of desensitized explosives should be determined by test series 2 of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, and should be communicated in the safety data sheet. For testing of liquid desensitized explosives for transport purposes, refer to section 32, sub-section 32.3.2 of the Manual of Tests and Criteria. Testing of solid desensitized explosives for transport purposes is addressed in section 33, sub-section 33.2.3 of the Manual of Tests and Criteria.

**NOTE 4:** For the purposes of storage, supply and use, desensitized explosives do not fall additionally within the scope of chapters 2.1 (explosives), 2.6 (flammable liquids) and 2.7 (flammable solids).

#### 2.17.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 1 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 2.17.2: Label elements for desensitized explosives

	Category 1	Category 2	Category 3	Category 4	
Symbol	Flame	Flame	Flame	Flame	
Signal word	Danger	Danger	Warning	Warning	
Hazard statement	Fire, blast or projection hazard; increased risk of explosion if desensitizing agent is reduced	Fire or projection hazard; increased risk of explosion if desensitizing agent is reduced	Fire or projection hazard; increased risk of explosion if desensitizing agent is reduced	Fire hazard; increased risk of explosion if desensitizing agent is reduced	

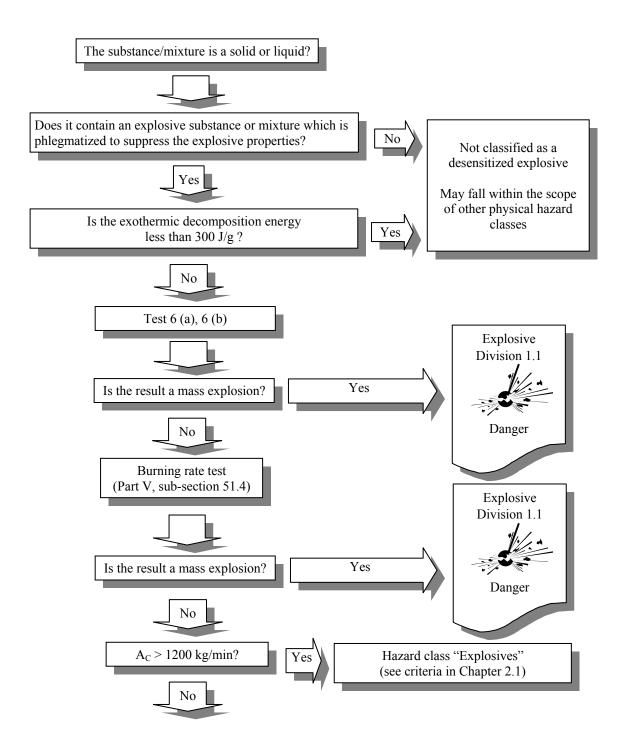
## 2.17.4 Decision logic and guidance

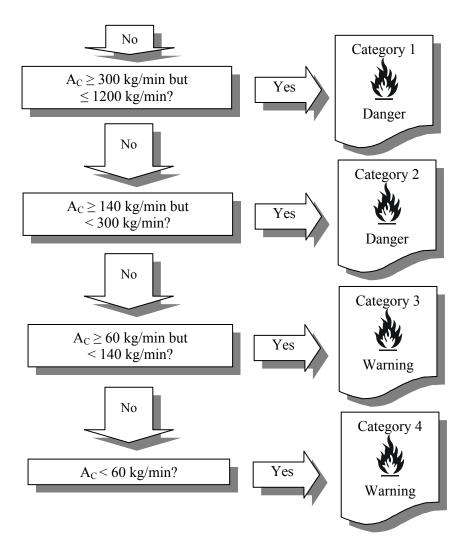
The decision logic and guidance which follow are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

# 2.17.4.1 Decision logic

To classify desensitized explosives, data for the explosive potential and the corrected burning rate should be determined as described in Part V of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*. Classification is according to decision logic 2.17.1.

Decision logic 2.17.1 for desensitized explosives





## **2.17.4.2** Guidance

- 2.17.4.2.1 The classification procedure for desensitized explosives does not apply if:
  - (a) The substances or mixtures contain no explosives according to the criteria in Chapter 2.1; or
  - (b) The exothermic decomposition energy is less than 300 J/g.
- 2.17.4.2.2 The exothermic decomposition energy should be determined using the explosive already desensitized (i.e.: the homogenous solid or liquids mixture formed by the explosive and the substance(s) used to suppress its explosive properties). The exothermic decomposition energy may be estimated using a suitable calorimetric technique (see Section 20, sub-section 20.3.3.3 in Part II of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*).