# UN/GHS-SC/1/INF.10 [UN/SCETDG/19/INF.46]

Sub-Committee of Experts on the Transport of Dangerous Goods (Nineteenth session, 2-6 July 2001, agenda item 11))

The secretariat reproduces in the annex hereto, for information of the Sub-Committee, the chapters concerning physical hazards of the document on the Globally Harmonized System of Classification and Labelling of Chemicals of the Inter-Organization Programme for the Sound Management of Chemicals (IOMC) Coordinating Group

# Chapter 15: EXPLOSIVES

#### DEFINITIONS

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

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

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

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

**NOTE**: The use of the word "explosive" can have different meanings and interpretations. Reference to "an explosive" or "explosives" is commonly understood to mean substances or articles in Class 1 of the scheme of the UN Recommendations on the Transport of Dangerous Goods, that is those which are intentional explosives or have properties which when assessed under the test procedure of the Manual of Tests and Criteria place them in UN Class 1. The description "explosive" can, however, be used to describe a property and as such it encompasses a wider range of substances than just those in UN Class 1. The Global Harmonized System (GHS) requires that classification is based on intrinsic properties and the word "explosive" in that context can be used to describe the property of a substance i.e. its ability to explode, as well as referring to a substance or article that has been designed to have explosive properties. This can lead to confusion and difficulty but in the above definition "explosive" refers to explosion hazard of substances and articles and is not limited to those which would be placed in Class 1 of the UN scheme.

- 2. The class of explosives comprises:
  - (a) Explosive substances;
  - (b) Explosive articles, except devices containing explosive substances in such quantity or of such a character that their inadvertent or accidental ignition shall not cause any effect external to the device either by projection, fire, smoke, heat or loud noise; and
  - (c) Substance and articles not mentioned under (a) and (b) above which are manufactured with the view to producing a practical explosive or pyrotechnic effect.

#### CLASSIFICATION CRITERIA FOR SUBSTANCES

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

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

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

- (c) Division 1.3 Substances and articles which have a fire hazard and either a minor blast hazard or a minor projection hazard or both, but not a mass explosion hazard:
  - (i) combustion of which gives rise to considerable radiant heat; or
  - (ii) which burn one after another, producing minor blast or projection effects or both;
- (d) Division 1.4 Substances and articles which present no significant hazard: substances and articles which present only a small hazard in the event of ignition or initiation. The effects are largely confined to the package and no projection of fragments of appreciable size or range is to be expected. An external fire shall not cause virtually instantaneous explosion of almost the entire contents of the package;
- (e) Division 1.5 Very insensitive substances which have a mass explosion hazard
- (f) Division 1.6 Extremely insensitive articles which do not have a mass explosion hazard: articles which contain only extremely insensitive detonating substances and which demonstrate a negligible probability of accidental initiation or propagation.

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

#### Table 1: Criteria for explosives

Category		Criteria	
Unstable <sup>1</sup> and	The following are the core set of tests that need to be performed:		
Division	Explosibility:	according to UN Test series 2 (Section 12 of the Manual of	
1.1 to 1.6	Tests and Criteria). Intentional explosives <sup>2</sup> are not su		
	to UN Test series 2.		
	Sensitiveness:	according to UN Test series 3 (Section 13 of the Manual of	
	Tests and Criteria) $^{3}$		
	Thermal stability: according to UN Test 3(c) (Sub-section 13)		
	Manual of Tests and Criteria)		
	Further tests are necessary to allocate the correct Division		

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

<sup>2</sup> This comprises substances and articles which are manufactured with a view to producing a practical explosive or pyrotechnic effect.

<sup>3</sup> Explosive substances which do not meet the criteria for impact and/or friction sensitivity may be classified as explosives for some regulatory purposes.

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

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

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

# CLASSIFICATION CRITERIA FOR MIXTURES

4. The same criteria as for substances apply.

# HAZARD COMMUNICATION

#### **Allocation of Label Elements**

5. The following table contains the harmonized label elements for each Division of this Class (for general provisions on labelling see Chapter 4, for precautionary statements see Annex 3).

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

#### Table 2: Label elements for explosives

<sup>1</sup> Apply to substances and articles subject to the UN Recommendations on the Transport of Dangerous Goods.

# DECISION LOGIC AND GUIDANCE

# **Decision Logic**

6. The classification of substances, mixtures and articles in the class of explosives and further allocation to a division is a very complex procedure. Reference to Part I of Manual of Tests and Criteria is necessary.

# **Guidance**

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

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

- 8. A substance or mixture is not classified as explosive if:
  - (a) There are no chemical groups associated with explosive properties present in the molecule. Examples of groups which may indicate explosive properties are given in Table A6.1 of the Manual of Tests and Criteria; or
  - (b) The substance contains chemical groups associated with explosive properties which include oxygen and the calculated oxygen balance is less than -200.

The oxygen balance is calculated for the chemical reaction:

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

using the formula:

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

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

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

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

Hazard category	Criteria	Hazard communication elements		
Division	According to the results of the test in Part I of Symbol		Exploding bomb	
1.1	the Manual of Tests and Criteria	Signal word	Danger	
		Hazard statement	Explosive; mass explosion hazard	
Division	According to the results of the test in Part I of		Exploding Bomb	
1.2	the Manual of Tests and Criteria	Signal word	Danger	
		Hazard statement	Explosive; severe projection hazard	
Division	According to the results of the test in Part I of	Symbol	Exploding Bomb	
1.3	the Manual of Tests and Criteria	Signal word	Danger	
		Hazard statement	Explosive; fire, blast or projection hazard.	
Division 1.4	According to the results of the test in Part I of the Manual of Tests and Criteria	Symbol	1.4 on orange background	
		Signal word	Warning	
		Hazard statement	Explosive; fire, blast or projection hazard.	
Division 1.5	According to the results of the test in Part I of the Manual of Tests and Criteria	Symbol	1.5 on orange background	
		Signal word	Warning	
		Hazard statement	May explode in fire	
Division 1.6		Symbol	1.6 on orange background	
	Signal word		No signal word	
		Hazard statement	No hazard statement	

# SUMMARY TABLE FOR EXPLOSIVES

# Chapter 16: FLAMMABLE GASES

# DEFINITIONS

1. A flammable gas is a gas having a flammable range with air at 20  $^{\circ}$ C and a standard pressure of 101.3 kPa.

# CLASSIFICATION CRITERIA FOR SUBSTANCES

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

Category	Criteria
1	<ul> <li>Gases, which at 20 °C and a standard pressure of 101.3 kPa:</li> <li>(a) are ignitable when in a mixture of 13% or less by volume in air; or</li> </ul>
	<ul><li>(b) have a flammable range with air of at least 12 percentage points regardless of the lower flammable limit.</li></ul>
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.

#### Table 1: Criteria for flammable gases

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

**NOTE 2**: The classification of aerosols are regulated separately.

# CLASSIFICATION CRITERIA FOR MIXTURES

3. The same criteria as for substances apply.

# HAZARD COMMUNICATION

# **Allocation of Label Elements**

4. The following table contains the harmonized label elements for products classified in this class (for general provisions on labelling see Chapter 4, for precautionary statements see Annex 3).

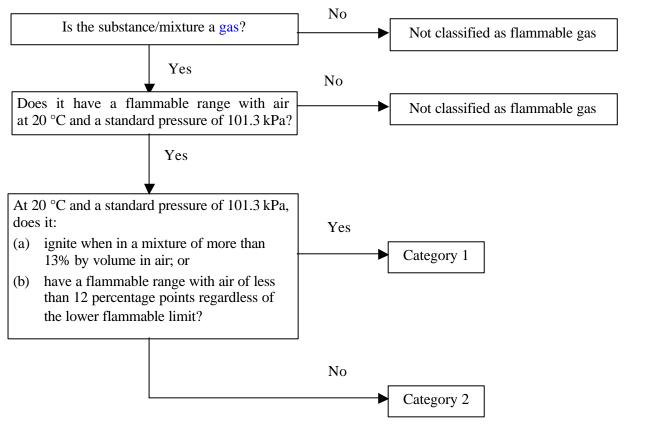
	Category 1	Category 2
Symbol	Flame	No symbol used
Signal word	Danger	Warning
Hazard statement	Extremely flammable gas	Flammable gas

#### Table 2: Label elements for flammable gases

# DECISION LOGIC AND GUIDANCE

# **Decision Logic**

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



# **Guidance**

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

Hazard category	( 'riteria		Hazard communication elements	
	Gases and gas mixtures, which at 20 °C and a standard pressure of 101.3 kPa:	Symbol	Flame	
1	<ul> <li>(a) are ignitable when in a mixture of 13% or less by volume in air; or</li> <li>(b) have a flammable range with air of at least 12 percentage points regardless of the lower flammable limit.</li> </ul>	Signal word	Danger	
		Hazard statement	Extremely flammable gas	
		Symbol	No symbol used	
2	Gases or gas mixtures, other than those of category 1, which, at 20 °C and a standard pressure of 101.3 kPa, have a	Signal word	Warning	
	flammable range while mixed in air.	Hazard statement	Flammable gas	

# SUMMARY TABLE FOR FLAMMABLE GASES

# Chapter 17: OXIDIZING GASES

# DEFINITIONS

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

# CLASSIFICATION CRITERIA FOR SUBSTANCES

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

# Table 1: Criteria for oxidizing gases

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

# CLASSIFICATION CRITERIA FOR MIXTURES

3. The same criteria as for substances apply.

#### HAZARD COMMUNICATION

#### **Allocation of Label Elements**

4. The following table contains the harmonized label elements for products classified in this class (for general provisions on labelling see Chapter 4, for precautionary statements see Annex 3).

#### Table 2: Label elements for oxidizing gases

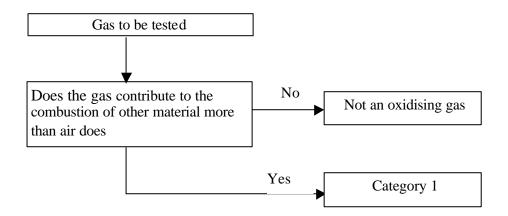
	Category 1
Symbol	Flame over circle
Signal word	Danger
Hazard statement	May cause or intensify fire; oxidizer.

# **DECISION LOGIC AND GUIDANCE**

# **Decision Logic**

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

**NOTE:** Improvement of this standard is under consideration by ISO.



# SUMMARY TABLE FOR OXIDIZING GASES

Hazard category	Criteria	Hazard communication elements	
1	Any gas which may, generally by providing	Symbol	Flame over circle
	oxygen, cause or contribute to the combustion of other material more than air does.	Signal word	Danger
		Hazard statement	May cause or intensify fire; oxidizer

# Chapter 18:

# **FLAMMABLE LIQUIDS**

#### DEFINITIONS

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

# CLASSIFICATION CRITERIA FOR SUBSTANCES

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

Category	Criteria			
1	Initial boiling point 35°C			
2	Initial boiling point $> 35^{\circ}$ C and flash point $< 23^{\circ}$ C			
3	Initial boiling point $> 35^{\circ}$ C and flash point $23^{\circ}$ C and $60^{\circ}$ C			
4	Flash point $> 60^{\circ}$ C and $93^{\circ}$ C			

Table 1: Criteria for flammable liquids

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

**NOTE 2:** Liquids with a flash point of more than 35 °C may be regarded as non-flammable liquids for some regulatory purposes (e.g. transport) if negative results have been obtained in the sustained combustibility test L.2 of the Manual of Tests and Criteria.

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

# CLASSIFICATION CRITERIA FOR MIXTURES

3. The same criteria as for substances apply.

# HAZARD COMMUNICATION

# **Allocation of Label Elements**

4. The following table contains the harmonized label elements for products classified in this class (for general provisions on labelling see Chapter 4, for precautionary statements see Annex 3).

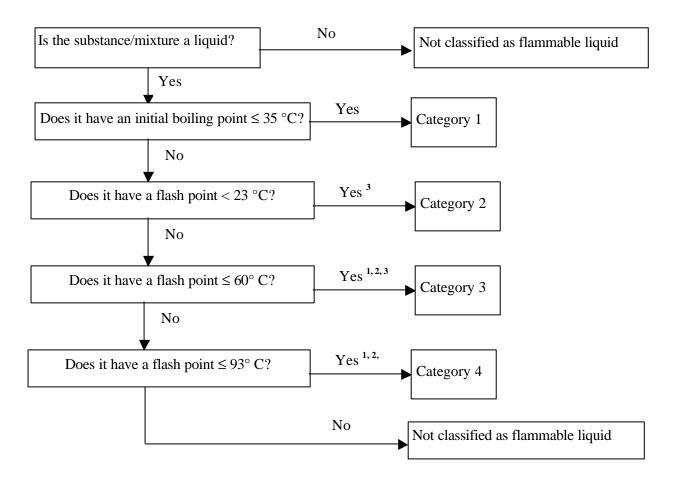
	Category 1	Category 2	Category 3	Category 4
Symbol	Flame	Flame	Flame	No symbol used
Signal word	Danger	Danger	Warning	Warning
Hazard statement	Extremely flammable liquid and vapour	Highly flammable liquid and vapour	Flammable liquid and vapour	Combustible liquid

Table 2: Label elements for flammable liquids

# **DECISION LOGIC AND GUIDANCE**

#### **Decision Logic**

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



<sup>1</sup> Gas oils, diesel and light heating oils in the flash point range of 55 °C to 75 °C may be regarded as a special group for some regulatory purposes as these hydrocarbons mixtures have varying flash point in that range. Thus classification in category 3 or 4 of these products may be determined by the pertinent regulation or competent authority.

<sup>2</sup> Liquids with a flash point of more than 35 °C may be regarded as non-flammable liquids for some regulatory purposes (e.g. transport) if negative results have been obtained in the sustained combustibility test L.2 of the Manual of Tests and Criteria i.e. the liquid doesn't sustain combustion. The classification in category 3 or 4 or the decision of considering these liquids as non-flammable may be determined by the pertinent regulation or competent authority.

<sup>3</sup> Viscous flammable liquids such as paints, enamels, lacquers, varnishes, adhesives and polishes may be regarded as a special group for some regulatory purpose (e.g. transport). The classification or the decision of considering these liquids as non-flammable may be determined by the pertinent regulation or competent authority.

# Guidance

6. 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.

7. In the case of mixtures<sup>1</sup> containing known flammable liquids in defined concentrations, the flash point can be calculated with the method described by Gmehling and Rasmussen (Ind. Eng. Chem. Fundament, 21, 186, (1982)) provided that:

- (a) The composition of the mixture is accurately known (if the material has a specified range of composition, the composition with the lowest calculated flash point should be selected for assessment);
- (b) The flash point (closed cup as given in point 11 below) of each component is known (an appropriate correlation has to be applied when these data are extrapolated to other temperatures than test conditions);
- (c) The activity coefficient is known for each component as present in the mixture including the temperature dependence;
- (d) The liquid phase is homogeneous.

8. The mixture can be classified on the basis of the calculated flash point only if the latter is at least 5  $^{\circ}$ C greater than the relevant classification criterion.

9. For a mixture containing non-volatile components, e.g. polymers or additives, the flash point is calculated from the volatile components. It is considered that a non-volatile component only slightly decreases the partial pressure of the solvents and the calculated flash point is only slightly below the measured value.

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

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

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

<sup>1</sup> 

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

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

International standards: ISO 1516 ISO 1523

ISO 1525 ISO 3679 ISO 3680

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

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

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

Hazard category	Criteria	Hazard communication elements	
			Flame
1	Initial boiling point $\leq 35^{\circ}$ C	Signal word	Danger
1	Initial boining point <u>&lt;</u> 55 C	Hazard statement	Extremely flammable liquid and vapour
		Symbol	Flame
2	Initial boiling point >35°C and	Signal word	Danger
2	flash point $< 23^{\circ}$ C	Hazard statement	Highly flammable liquid and vapour
		Symbol	Flame
3	Initial boiling point >35°C and	Signal word	Warning
3	flash point $\ge 23^{\circ}$ C and $\le 60^{\circ}$ C	Hazard statement	Flammable liquid and vapour
		Symbol	No symbol used
4	Flash point $> 60^{\circ}$ C and $93^{\circ}$ C	Signal word	Warning
		Hazard statement	Combustible liquid

# SUMMARY TABLE FOR FLAMMABLE LIQUIDS

# Chapter 19:

# FLAMMABLE SOLIDS

# DEFINITIONS

1. A *flammable solid* is a solid which is readily combustible, or may cause or contribute to fire through friction.

*Readily combustible solids* are powdered, granular, or pasty substances which are dangerous if they can be easily ignited by brief contact with an ignition source, such as a burning match, and if the flame spreads rapidly.

#### CLASSIFICATION CRITERIA FOR SUBSTANCES

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

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

4. 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.

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

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

#### Table 1: Criteria for flammable solids

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

# CLASSIFICATION CRITERIA FOR MIXTURES

3. The same criteria as for substances apply.

# HAZARD COMMUNICATION

#### **Allocation of Label Elements**

4. The following table contains the harmonized label elements for products classified in this class (for general provisions on labelling see Chapter 4, for precautionary statements see Annex 3).

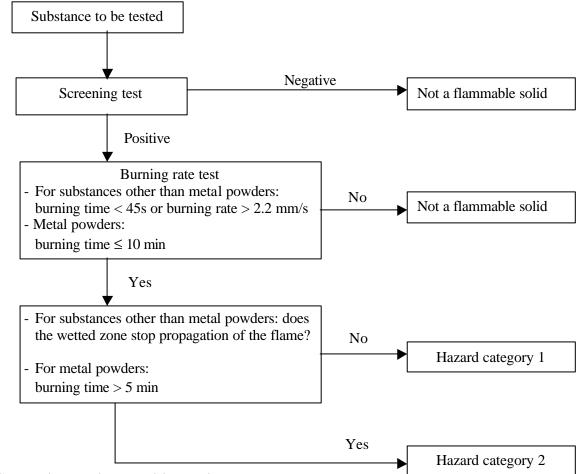
	Category 1	Category 2
Symbol	Flame	Flame
Signal word	Danger	Warning
Hazard statement	Flammable solid	Flammable solid

<b>Table 2: Label elements</b>	for flammable solids
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# **DECISION LOGIC AND GUIDANCE**

# **Decision Logic**

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



6. See previous section - Decision Logic

Guidance

Hazard category	Criteria	Hazard commu	nication elements
	Burning rate test: Substances other than metal powders:	Symbol	Flame
1	<ul> <li>wetted zone does not stop fire and</li> <li>burning time &lt; 45 seconds or burning rate &gt; 2.2 mm/s</li> </ul>	Signal word	Danger
			Flammable solid
	Burning rate test: Substances other than metal powders: - wetted zone stops the fire for at least 4 minutes	Symbol	Flame
2	2 and - burning time < 45 seconds or burning	Signal word	Warning
	rate > 2.2 mm/second Metal powders : - burning time > 5 minutes and ≤ 10 minutes	Hazard statement	Flammable solid

# SUMMARY TABLE FOR FLAMMABLE SOLIDS

#### Chapter 20:

#### SELF-REACTIVE SUBSTANCES

#### DEFINITIONS

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

# CLASSIFICATION CRITERIA FOR SUBSTANCES AND MIXTURES (INCLUDING FORMULATIONS)

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

- (a) They are explosives, according to the GHS criteria of Chapter 15;
- (b) They are oxidizing substances, according to the GHS criteria of Chapters 25 or 26;
- (c) They are organic peroxides, according to the GHS criteria of Chapter 27;
- (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.

3. Self reactive substances are classified in one of the seven categories of "types A to G" for this class, according to the following principles:

- (a) Any self-reactive substance which can detonate or deflagrate rapidly, as packaged, will be defined as self-reactive substance **TYPE A**;
- (b) Any self-reactive substance possessing explosive properties and which, as packaged, neither detonates nor deflagrates rapidly, but is liable to undergo a thermal explosion in that package will be defined as self-reactive substance **TYPE B**;
- (c) Any self reactive substance possessing explosive properties when the substance as packaged cannot detonate or deflagrate rapidly or undergo a thermal explosion will be defined as self-reactive substance **TYPE C**;
- (d) Any self reactive substance which in laboratory testing:
  - (i) detonates partially, does not deflagrate rapidly and shows no violent effect when heated under confinement; or
  - (ii) does not detonate at all, deflagrates slowly and shows no violent effect when heated under confinement; or
  - (iii) does not detonate or deflagrate at all and shows a medium effect when heated under confinement;

will be defined as self reactive substance **TYPE D**;

- (e) Any self reactive substance which, in laboratory testing, neither detonates nor deflagrates at all and shows low or no effect when heated under confinement will be defined as self reactive substance **TYPE E**;
- (f) Any self reactive substance which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows only a low or no effect when heated under confinement as well as low or no explosive power will be defined as self reactive substance **TYPE F**;
- (g) Any self reactive substance which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows no effect when heated under confinement nor any explosive power, provided that it is thermally stable (self-accelerating decomposition temperature is 60 °C to 75 °C for a 50 kg package), and, for liquid mixtures, a diluent having a boiling point not less than 150 °C is used for desensitisation will be defined as self-reactive substance **TYPE G**. If the mixture is not thermally stable or a diluent having a boiling point less than 150 °C is used for desensitisation, the mixture shall be defined as self-reactive substance **TYPE F**.

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

**NOTE 2**: Sub-divisions may not be necessary for all systems.

# HAZARD COMMUNICATION

#### Allocation of label elements

4. The following table contains the harmonized label elements for products classified in this class (for general provisions on labelling see Chapter 4, for precautionary statements see Annex 3).

	Туре А	Туре В	Type C and D	Type E and F	Type G <sup>1</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

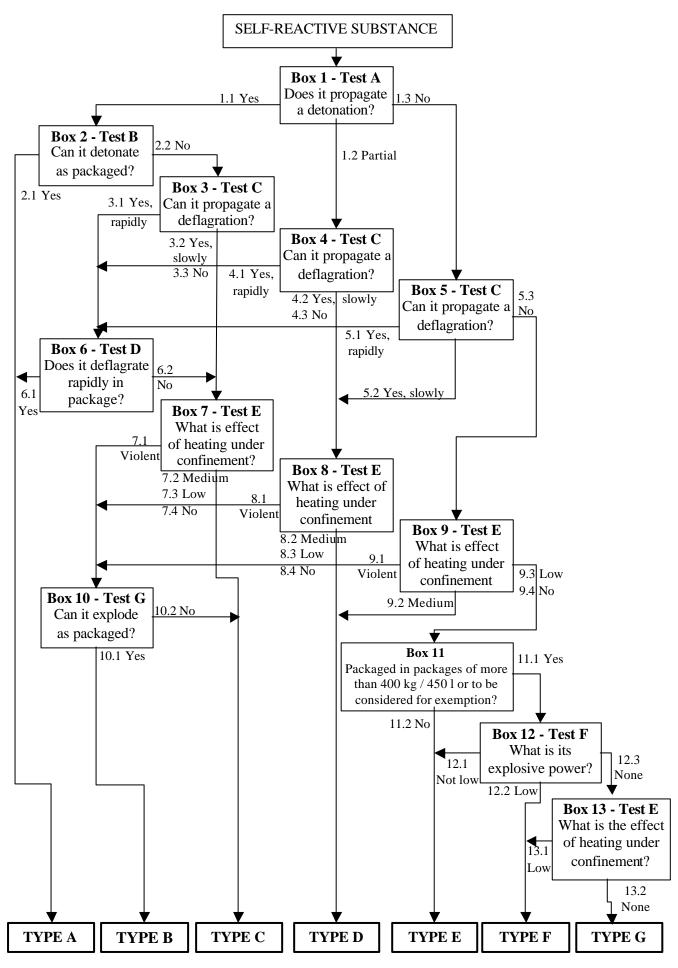
 Table 1: Label elements for self-reactive substances

<sup>1</sup> *Type G has no hazard communication elements assigned but should be considered for properties belonging to other hazard classes.* 

# **DECISION LOGIC AND GUIDANCE**

# **Decision Logic**

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



- 19 -

# Guidance

6. The properties of self-reactive substances which are decisive for their classification should be determined experimentally. Test methods with pertinent evaluation criteria are given in the Manual of Tests and Criteria, Part II (test series A to H).

- 7. The classification procedures for self-reactive substances need not be applied if:
  - (a) There are no chemical groups present in the molecule associated with explosive or selfheating properties; examples of such groups are given in Tables A6.1 and A6.2 in the Manual of Tests and Criteria, Appendix 6; or
  - (b) For a single organic substance or a homogeneous mixture of organic substances, the estimated SADT is greater than 75 °C or the exothermic decomposition energy is less than 300J/g. The onset temperature and decomposition energy may be estimated using a suitable calorimetric technique (see 20.3.3.3 of the Manual of Tests and Criteria).

Hazard category	Criteria	Hazard communi	cation elements
	According to the results of tests in the Manual	Symbol	Exploding bomb
	of Tests and Criteria, Part II and the	Signal word	Danger
Туре А	application of the decision tree in section 5 of this chapter.	Hazard statement	Heating may cause an explosion
	According to the results of tests in the Manual of Tests and Criteria, Part II and the	Symbol	Exploding bomb and Flame
Type B	application of the decision tree in section 5 of	Signal word	Danger
-51	this chapter.	Hazard statement	Heating may cause a fire or explosion
	According to the results of tests in the Manual	Symbol	Flame
Type C	of Tests and Criteria, Part II and the	Signal word	Danger
and D	application of the decision tree in section 5 of this chapter.	Hazard statement	Heating may cause a fire
	According to the results of tests in the Manual	Symbol	Flame
Type E	of Tests and Criteria, Part II and the	Signal word	Warning
and F	application of the decision tree in section 5 of this chapter.	Hazard statement	Heating may cause a fire
	According to the results of tests in the Manual	Signal word	There are no
Type G	of Tests and Criteria, Part II and the	Symbol	label elements
Type G	application of the decision tree in section 5 of this chapter.	Hazard statement	allocated to this hazard category

# SUMMARY TABLE FOR SELF REACTIVE SUBSTANCES

# Chapter 21: PYROPHORIC LIQUIDS

# DEFINITIONS

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

# CLASSIFICATION CRITERIA FOR SUBSTANCES

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

#### Table 1: Criteria for pyrophoric liquids

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

# CLASSIFICATION CRITERIA FOR MIXTURES

3. The same criteria as for substances apply.

# HAZARD COMMUNICATION

#### **Allocation of Label Elements**

4. The following table contains the harmonized label elements for products classified in this class (for general provisions on labelling see Chapter 4, for precautionary statements see Annex 3).

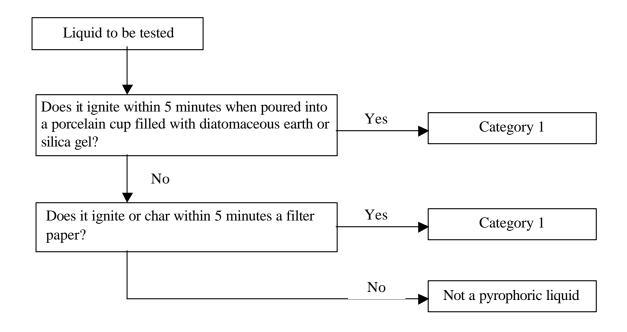
	Category 1	
Symbol	Flame	
Signal word	Danger	
Hazard statement	Catches fire spontaneously if exposed to air	

# Table 2: Label elements for pyrophoric liquids

# DECISION LOGIC AND GUIDANCE

#### **Decision Logic**

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



# **Guidance**

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

Hazard category	Criteria	Hazard comm	unication elements
1		Symbol	Flame
	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	Signal word	Danger
	within 5 min.	Hazard statement	Catches fire spontaneously if exposed to air

# SUMMARY TABLE FOR PYROPHORIC LIQUIDS

# Chapter 22: PYROPHORIC SOLIDS

# DEFINITIONS

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

# CLASSIFICATION CRITERIA FOR SUBSTANCES

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

#### Table 1: Criteria for pyrophoric solids

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

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

# CLASSIFICATION CRITERIA FOR MIXTURES

3. The same criteria as for substances apply.

# HAZARD COMMUNICATION

#### **Allocation of Label Elements**

4. The following table contains the harmonized label elements for products classified in this class (for general provisions on labelling see Chapter 4, for precautionary statements see Annex 3).

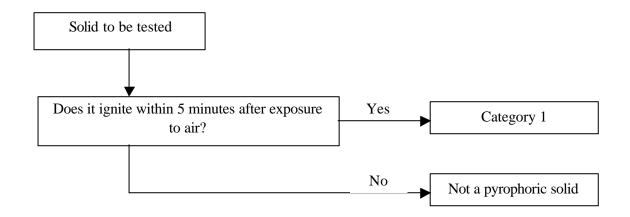
	Category 1
Symbol	Flame
Signal word	Danger
Hazard statement	Catches fire spontaneously if exposed to air

#### Table 2: Label elements for pyrophoric solids

# **DECISION LOGIC AND GUIDANCE**

#### **Decision Logic**

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



# **Guidance**

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

Hazard category	Criteria	Hazard commu	nication elements
1		Symbol	Flame
	The solid ignites within 5 minutes of coming into contact with air.	Signal word	Danger
		Hazard statement	Catches fire spontaneously if exposed to air

# SUMMARY TABLE FOR PYROPHORIC SOLIDS

# Chapter 23: SELF-HEATING SUBSTANCES

# DEFINITIONS

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

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

# CLASSIFICATION CRITERIA FOR SUBSTANCES

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

- (a) A positive result is obtained using a 25 mm cube sample at 140 °C;
- (b) A positive result is obtained in a test using a 100 mm sample cube at 140 °C and a negative result is obtained in a test using a 100 mm cube sample at 120 °C and the substance is to be transported 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 is to be transported 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  $^{\circ}$ C and a positive result is obtained using a 100 mm cube sample at 100  $^{\circ}$ C.

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

# Table 1: Criteria for self-heating substances

Category	Criteria		
1	A positive result is obtained in a test using a 25 mm sample cube at 140 °C		
2	(a) A positive result is obtained in a test using a 100 mm sample cube at 140 °C and a negative result is obtained in a test using a 25 mm cube sample at 140 °C and the substance is to be packed in packages with a volume of more than 3 m <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 is to be packed in packages with a volume of more than 450 litres; or		
	(c) A positive result is obtained in a test using a 100 mm sample cube at 140 °C and a negative result is obtained in a test using a 25 mm cube sample at 140 °C and a positive result is obtained in a test using a 100 mm cube sample at 100 °C.		

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

# CLASSIFICATION CRITERIA FOR MIXTURES

4. The same criteria as for substances apply.

# HAZARD COMMUNICATION

#### **Allocation of Label Elements**

5. The following table contains the harmonized label elements for products classified in this class (for general provisions on labelling see Chapter 4, for precautionary statements see Annex 3).

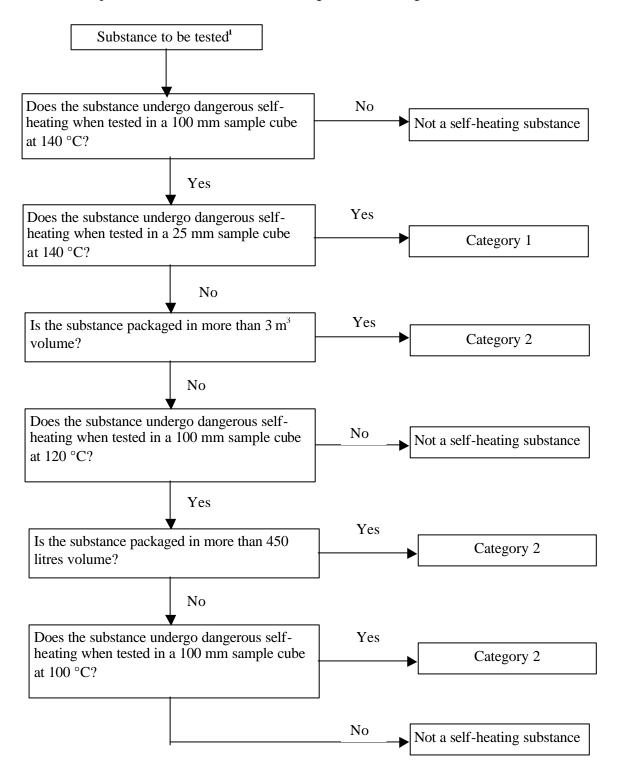
	Category 1	Category 2
Symbol	Flame	Flame
Signal word	Danger	Warning
Hazard statement	Self-heating; may catch fire	Self-heating in large quantities; may catch fire

# Table 2: Label elements for self-heating substances

# DECISION LOGIC AND GUIDANCE

# **Decision Logic**

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



<sup>1</sup> Substances with a self-heating temperature greater than 50 °C for a 27  $m^3$  volume should not be classified in this class. See Manual of Tests and Criteria, 33.3.1.3.3.1.

# **Guidance**

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

- (a) The Grewer Oven test (VDI guideline 2263, part 1, 1990, *Test methods for the Determination of the Safety Characteristics of Dusts*) with an onset temperature 80 K above the reference temperature for a volume of 1 *l*;
- (b) The Bulk Powder Screening Test (Gibson, N. Harper, D. J. Rogers, R. *Evaluation of the fire and explosion risks in drying powders*, Plant Operations Progress, **4** (3), 181 189, 1985) with an onset temperature 60 K above the reference temperature for a volume of 1 *l*.

Hazard category	Criteria Hazard communication eler		nication eleme nts
1	A positive result is obtained in a test using a	Symbol	Flame
	25 mm sample cube at 140°C	Signal word	Danger
		Hazard statement	Self-heating; may catch fire
2	<ul> <li>(a) A positive result is obtained in a test using a 100 mm sample cube at 140 °C and a negative result is obtained in a test using a 25 mm cube sample at 140 °C and the substance is to be packed in packages with a volume of more than 3 m<sup>3</sup>; or</li> </ul>	Symbol	Flame
	(b) A positive result is obtained in a test using a 100 mm sample cube at 140 °C and a negative result is obtained in a test using a 25 mm cube sample at 140 °C, a positive result is obtained in a test using a 100 mm cube sample at 120 °C and the substance is to be packed in packages with a volume	Signal word	Warning
	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	Hazard statement	Self-heating in large quantities; may catch fire

# SUMMARY TABLE FOR SELF-HEATING SUBSTANCES

# Chapter 24:

# SUBSTANCES WHICH IN CONTACT WITH WATER EMIT FLAMMABLE GASES

#### DEFINITIONS

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

# CLASSIFICATION CRITERIA FOR SUBSTANCES

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

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

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

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

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

# **CLASSIFICATION CRITERIA FOR MIXTURES**

3. The same criteria as for substances apply.

# HAZARD COMMUNICATION

# **Allocation of Label Elements**

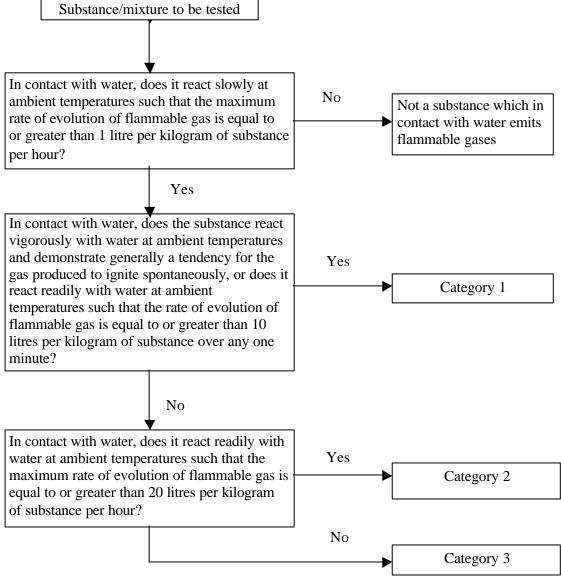
4. The following table contains the harmonized label elements for products classified in this class (for general provisions on labelling see Chapter 4, for precautionary statements see Annex 3).

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

# DECISION LOGIC AND GUIDANCE

# **Decision Logic**

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



# **Guidance**

- 6. Substances or mixtures are not classified in this class if:
  - a) The chemical structure of the substance or mixture does not contain metals or metalloids;
  - b) Experience in production or handling shows that the substance or mixture does not react with water, e.g. the substance is manufactured with water or washed with water; or
  - c) The substance is known to be soluble in water to form a stable mixture.

#### SUMMARY TABLE FOR SUBSTANCES WHICH IN CONTACT WITH WATER EMIT FLAMMABLE GASES

Hazard category	Criteria	Hazard commur	ication elements
1	Any substance which reacts vigorously with	Symbol	Flame
	water at ambient temperatures and	Signal word	Danger
	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.	Hazard statement	In contact with water releases flammable gases which may ignite spontaneously
2	Any substance which reacts readily with water	Symbol	Flame
	at ambient temperatures such that the	Signal word	Danger
	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.	Hazard statement	In contact with water releases flammable gases
3	Any substance which reacts slowly with water	Symbol	Flame
	at ambient temperatures such that the	Signal word	Warning
	maximum rate of evolution of flammable gas is equal to or greater than 1 litre per kilogram of substance per hour, and which does not meet the criteria for categories 1 and 2.	Hazard statement	In contact with water releases flammable gases

# Chapter 25: OXIDIZING LIQUIDS

# DEFINITIONS

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

# CLASSIFICATION CRITERIA FOR SUBSTANCES

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

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

#### Table 1: Criteria for oxidizing liquids

**NOTE:** In the event of divergence between test results and known experience, judgement based on known experience should take precedence over test results.

# CLASSIFICATION CRITERIA FOR MIXTURES

3. The same criteria as for substances apply.

# HAZARD COMMUNICATION

#### **Allocation of Label Elements**

4. The following table contains the harmonized label elements for products classified in this class (for general provisions on labelling see Chapter 4, for precautionary statements see Annex 3).

	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

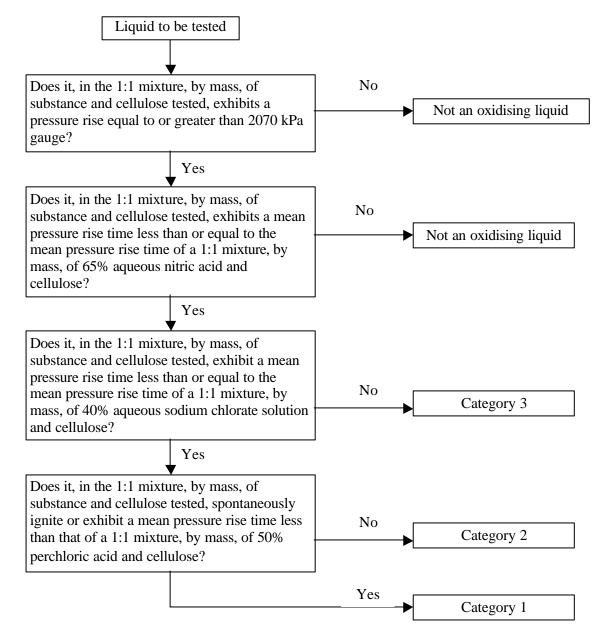
# Table 2: Label elements for oxidizing liquids

# **DECISION LOGIC AND GUIDANCE**

#### **Decision Logic**

ş

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



# **Guidance**

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

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

### 8. Organic substances or mixtures are not classified as oxidizing 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.

Inorganic substances or mixtures are not classified as oxidizing if they do not contain oxygen or halogen atoms.

Hazard category	Criteria	Hazard commun	ication elements
1	Any substance which, in the 1:1 mixture, by	Symbol	Flame over circle
	mass, of substance and cellulose tested,	Signal word	Danger
	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.	Hazard statement	May cause fire or explosion; strong oxidizer.
2	Any substance which, in the 1:1 mixture, by	Symbol	Flame over circle
	mass, of substance and cellulose tested,		Danger
	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.	Hazard statement	May intensify fire; oxidizer.
3	Any substance which, in the 1:1 mixture, by	Symbol	Flame over circle
	mass, of substance and cellulose tested,	Signal word	Warning
	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.	Hazard statement	May intensify fire; oxidizer.

# SUMMARY TABLE FOR OXIDIZING LIQUIDS

# Chapter 26: OXIDIZING SOLIDS

# DEFINITIONS

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

# CLASSIFICATION CRITERIA FOR SUBSTANCES

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

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

#### Table 1: Criteria for oxidizing solids

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

**NOTE 2:** In the event of divergence between test results and known experience, judgement based on known experience should take precedence over test results.

# CLASSIFICATION CRITERIA FOR MIXTURES

3. The same criteria as for substances apply.

# HAZARD COMMUNICATION

# **Allocation of Label Elements**

4. The following table contains the harmonized label elements for products classified in this class (for general provisions on labelling see Chapter 4, for precautionary statements see Annex 3).

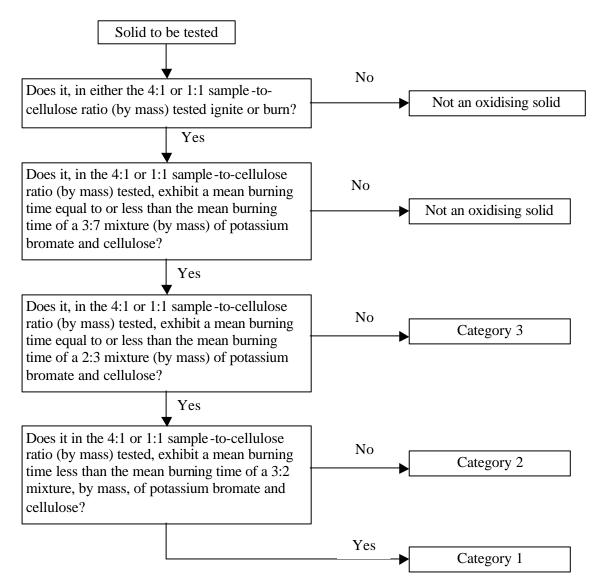
	Category 1	Category 2	Category 3
Symbol	Flame over circle	Flame over circle	Flame over circle
Signal word	Danger	Danger	Warning
Hazard statement	May cause fire or explosion; strong oxidizer	May intensify fire; oxidizer	May intensify fire; oxidizer

Table 2: Label elements for oxidizing solids

# **DECISION LOGIC AND GUIDANCE**

# **Decision Logic**

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



# **Guidance**

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

- 7. Organic substances or mixtures are not classified as oxidizing if:
  - c) The substance or mixture does not contain oxygen, fluorine or chlorine; or
  - d) The substance or mixture contains oxygen, fluorine or chlorine and these elements are chemically bonded only to carbon or hydrogen.

Inorganic substances or mixtures are not classified as oxidizing if they do not contain oxygen or halogen atoms.

Hazard category	Criteria Hazard comm		nication elements
1	Any substance which, in the 4:1 or 1:1 sample -	Symbol	Flame over circle
	to-cellulose ratio (by mass) tested, exhibits a	Signal word	Danger
	mean burning time less than the mean burning time of a 3:2 mixture, by mass, of potassium bromate and cellulose.	Hazard statement	May cause fire or explosion; strong oxidizer
2	Any substance which, in the 4:1 or 1:1 sample -	Symbol	Flame over circle
	to-cellulose ratio (by mass) tested, exhibits a	Signal word	Danger
	mean burning time equal to or less than the mean burning time of a 2:3 mixture (by mass) of potassium bromate and cellulose and the criteria for category 1 are not met.	Hazard statement	May intensify fire; oxidizer
3	Any substance which, in the 4:1 or 1:1 sample -	Symbol	Flame over circle
	to-cellulose ratio (by mass) tested, exhibits a	Signal word	Warning
	mean burning time equal to or less than the mean burning time of a 3:7 mixture (by mass) of potassium bromate and cellulose and the criteria for categories 1 and 2 are not met.	Hazard statement	May intensify fire; oxidizer

# SUMMARY TABLE FOR OXIDIZING SOLIDS

# Chapter 27:

# **ORGANIC PEROXIDES**

#### DEFINITIONS

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

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

# CLASSIFICATION CRITERIA FOR SUBSTANCES AND MIXTURES (INCLUDING FORMULATIONS)

2. Any organic peroxide shall be considered for classification in this class, unless the organic peroxide formulation 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 formulation is given by the formula:

$$16 \, \mathbf{S}(n_i \, \mathbf{c}_i / m_i)$$

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

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

- (a) Any organic peroxide mixture which can detonate or deflagrate rapidly, as packaged, will be defined as organic peroxide **TYPE A**;
- (b) Any organic peroxide mixture possessing explosive properties and which, as packaged, neither detonates nor deflagrates rapidly, but is liable to undergo a thermal explosion in that package will be defined as organic peroxide **TYPE B**;
- (c) Any organic peroxide mixture possessing explosive properties when the substance as packaged cannot detonate or deflagrate rapidly or undergo a thermal explosion will be defined as organic peroxide **TYPE C**;

- (d) Any organic peroxide mixture which in laboratory testing:
  - (i) detonates partially, does not deflagrate rapidly and shows no violent effect when heated under confinement; or
  - (ii) does not detonate at all, deflagrates slowly and shows no violent effect when heated under confinement; or
  - (iii) does not detonate or deflagrate at all and shows a medium effect when heated under confinement;

will be defined as organic peroxide **TYPE D**;

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

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

**NOTE 2**: Sub-divisions may not be necessary for all systems.

# HAZARD COMMUNICATION

# Allocation of label elements

4. The following table contains the harmonized label elements for products classified in this class (for general provisions on labelling see Chapter 4, for precautionary statements see Annex 3).

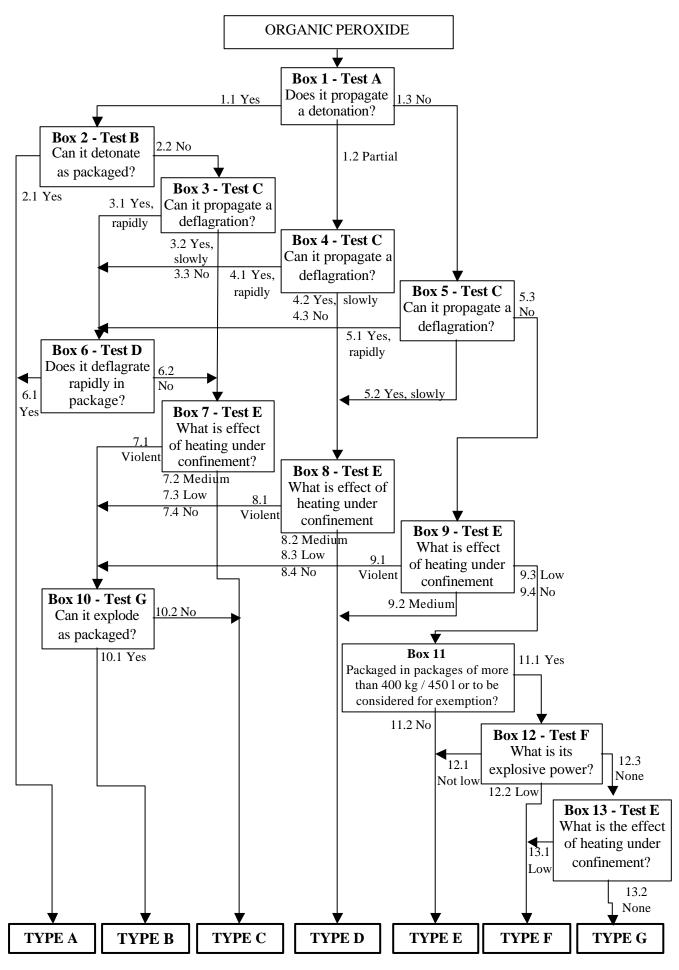
	Type A	Туре В	Type C and D	Type E and F	Type G <sup>1</sup>
Symbol	Exploding bomb	and	Flame over circle	Flame over circle	There are no
		Flame over circle			label elements
Signal word	Danger	Danger	Danger	Warning	allocated to this
Hazard statement	0.00	Heating may cause a fire or explosion	<u> </u>	Heating may cause a fire	hazard category

<sup>1</sup> Type G has no hazard communication elements assigned but should be considered for properties belonging to other hazard classes.

# **DECISION LOGIC AND GUIDANCE**

# **Decision Logic**

5. To classify an organic peroxide test series A to H as described in Part II of the Manual of Tests and Criteria should be performed. Classification is according to the following decision tree:



# **Guidance**

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

7. The properties of organic peroxide which are decisive for their classification should be determined experimentally. Test methods with pertinent evaluation criteria are given in the Manual of Tests and Criteria, Part II (test series A to H).

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

Hazard category	Criteria Hazard communicat		cation elements
Туре А	Type A According to the results of test series A to H in		Exploding bomb
	According to the results of test series A to H in the Manual of Tests and Criteria, Part II and the	Signal word	Danger
	application of the decision tree under point 5 of this chapter	Hazard statement	Heating may cause an explosion
Туре В	According to the results of test series A to H in the Manual of Tests and Criteria, Part II and the application of the decision tree under point 5 of	Symbol	Exploding bomb and Flame over circle
	this chapter	Signal word	Danger
		Hazard statement	Heating may cause a fire or explosion
Type C and	According to the results of test series A to H in	Symbol	Flame over circle
D	the Manual of Tests and Criteria, Part II and the	Signal word	Danger
	application of the decision tree under point 5 of this chapter	Hazard statement	Heating may cause a fire
Type E and	According to the results of test series A to H in	Symbol	Flame over circle
F	the Manual of Tests and Criteria, Part II and the	Signal word	Warning
	application of the decision tree under point 5 of this chapter	Hazard statement	Heating may cause a fire
Type G	According to the results of test series A to H in	Signal word	There are no
	the Manual of Tests and Criteria, Part II and the	Symbol	label elements
	application of the decision tree under point 5 of this chapter	Hazard statement	allocated to this hazard category

# SUMMARY TABLE FOR ORGANIC PEROXIDES

# Chapter 28: CORROSIVE TO METALS

# DEFINITIONS

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

# CLASSIFICATION CRITERIA FOR SUBSTANCES

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

#### Table 1: Criteria for substances corrosive to metal

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

# CLASSIFICATION CRITERIA FOR MIXTURES

3. The same criteria as for substances apply.

# HAZARD COMMUNICATION

# **Allocation of Label Elements**

4. The following table contains the harmonized label elements for products classified in this class (for general provisions on labelling see Chapter 4, for precautionary statements see Annex 3).

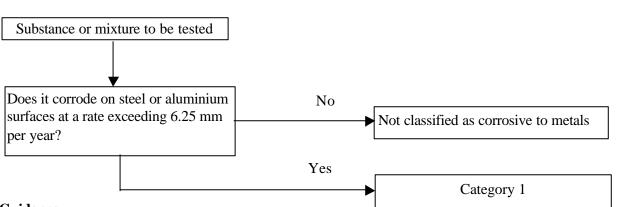
# Table 2: Label elements for substances corrosive to metals

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

# DECISION LOGIC AND GUIDANCE

# **Decision Logic**

```
5.
```



# **Guidance**

6.

- The corrosion rate can be measured with the following tests methods:
  - for the purposes of testing steel, type P235 (ISO 9328 (II):1991) or a similar type shall be used;
  - for testing aluminium, non-clad types 7075-T6 or AZ5GU-T6 shall be used.

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

# SUMMARY TABLE FOR SUBSTANCES CORROSIVE TO METALS

Hazard category	Criteria	Hazard communication elements	
1	Corrosion rate on steel or aluminium surfaces exceeding 6.25 mm per year at a test temperature of 55 °C.	Symbol	Corrosive
		Signal word	Warning
		Hazard statement	May be corrosive to metals