EUROPEAN CHEMICALS AGENCY

GUIDANCE

Guidance on the Application of the CLP Criteria

Part 2: Physical Hazards

Guidance to Regulation (EC) No 1272/2008 on classification, labelling and packaging (CLP) of substances and mixtures

Version 4.0
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LEGAL NOTICE

Guidance on the Application of CLP Criteria

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DOCUMENT HISTORY

Version	Comment	Date
Version 1.0	First edition	August 2009
n.a.	Please note that change between the version published in August 2009 and that of April 2011 are not recorded in this document history.	April 2011
Version 2.0	Revision of the CLP Guidance addressing content in relation to the Part 2: Physical hazards following the 2nd and the 4th Adaptation to Technical Progress to the CLP Regulation (Commission Regulation (EU) No 286/2011 of 10 March 2011 and Commission Regulation (EU) No 487/2013 of 8 May 2013). The revision includes: • Numbering of chapters within CLP Guidance, Part 2 was synchronised with corresponding chapter numbering of CLP, Annex I. • Changes in the legal text due the 2nd and 4th ATPs. • Changes in the legal text due to the 4th ATP were highlighted in orange within all relevant green boxes. All changes are preceded by a note highlighting the changes. (To note: a corrigendum will change the colour of relative legal text boxes from orange to green when the 4th ATP applies). In addition, the revisions to Part 2: Physical hazards include the following: • Chapters 'Pyrophoric liquids and solids' and 'Oxidising liquids and solids' were divided into four chapters: 'Pyrophoric liquids', 'Pyrophoric solids', 'Oxidising liquids' and 'Oxidising solids' respectively. • Based on the 4th ATP the CLP Guidance Chapter 2.2 Flammable gases was extended to take into account the scope of CLP, Annex I, section 2.2 to include chemically unstable gases. • Further, the 4th ATP amended the criteria in CLP Annex I, Section 2.3 Flammable aerosols and renamed it into 2.3 Aerosols. Hence, the CLP Guidance was amended accordingly. • All chapters were rechecked and redundant and/or outdated information were deleted, reorganised and/or revised. For example, 'Introduction' chapters were significantly shortened, however several "examples" sections (i.e. 'Example for classification…') were further elaborated. • Where missing, a new sub-chapter 'Relation to other physical hazards' was added.	November 2013

	- Sub-chapter 2.0.4 'Physical state' was extended with additional information about substance/mixture form and some examples. - In sub-chapter 2.1.5.2 'Additional labelling provisions' within chapter 2.1 'Explosives' further guidance about hazard communication was provided. - In sub-chapter 2.5.6.1 a new recommendation for shot hazard codes to identify the classification of gasses under pressure was added. - Footnotes with references to endorsed or on-going revisions of the GHS which have not yet been implemented into the CLP via a respective ATP were included in relevant sub-chapters of this guidance for information only.	
Version 2.1	Corrigendum to take account of the end of the transition period of the 4th ATP (as foreseen in version 4.0 above): - change the colour of relative legal text boxes from orange to green; - in Part 2, to delete section 2.2.1 Flammable gases and section 2.3.1 Flammable Aerosols (outdated text) and renumber sections 2.2.2 Flammable gases (including chemically unstable gases) and 2.3.2 Aerosols accordingly; In addition, minor editorial errors were corrected and minor reformatting was made.	June 2015
Version 3.0	Partial revision of the Guidance to update the content mainly following the 8th Adaptation to Technical Progress to the CLP Regulation (Commission Regulation (EU) No 286/2011). Revision of few specific additional topics. The update includes the following: (i) Throughout the document: - Revision of legal references and legal text quotations. - Renumbering of some sections. - Deletion of sections regarding the reclassification of substances and mixtures previously classified in accordance with the DSD or DPD. (ii) Revision of the following sections of Part 2: - 2.1 (Explosives): replacement of new figure 2.1.3; update of label elements; addition new note 2 to table 2.1.2 on requirement for SDSs. - 2.3 (Aerosols): update of text on classification criteria; update of decision logic 2.3.1-a; update of section 2.3.6 on the relation to transport classification.	July 2017

	• 2.14 (Oxidising solids): addition of criteria using test 0.3; update of labelling elements. (iii) Minor changes to the following sections in Part 2: • 2.8 (Self-reactive): update of label elements. • 2.12 (Emitting flammable gases): update of label elements. • 2.15 (Organic peroxides): update of decision logic.2.15.1; update of label elements.	
Version 4.0	Substantial update of all hazard classes (sections 2.1 – 2.16) to account for: • CLP ATP 12 • Updates to test guidelines • Developments in science • Clarifications on comparability between EU and UN methods • Removal of references to DSD Addition of section 2.17 on desensitised explosives. CLP Guidance Part 2 re-presented as separate document.	Nov 2024

NOTEs to the reader:

In this document, text cited from Regulation (EC) No 1272/2008 is indicated in green boxes in *italic* font.

⚠ This symbol highlights text to be noted.

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LIST OF ABBREVIATIONS

Standard term / Abbreviation	Explanation
ADD	Directive 75/324/EEC on aerosol dispensers[1]
ADN	European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways (Accord européen relatif au transport international des marchandises dangereuses par voie de navigation intérieure)[2]
ADR	European Agreement concerning the International Carriage of Dangerous Goods by Road (Accord européen relatif au transport international des marchandises dangereuses par route)[3]
ANE	Ammonium Nitrate Emulsion
ANFO	Ammonium Nitrate/Fuel Oil
ASTM	American Society for the Testing of Materials
ATP	Adaptation to Technical Progress (ATP) to the CLP Regulation
BAM	Bundesanstalt für Materialforschung und -prüfung (Federal Institute for Materials Research and Testing)
BP	Boiling point
CLP	Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures[4]

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[1] Directive (75/324/EEC) of the Council on the approximation of the laws of the Member States relating to aerosol dispensers [OJ L 147, 9.6.1975, p.40]. Directive as last amended by Commission Directive 2013/10/EU [OJ L 77, 20.03.2013, p.20].

[2] European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways, concluded at Geneva on 26 May 2000, as amended.

[3] European Agreement concerning the International Carriage of Dangerous Goods by Road, concluded at Geneva on 30 September 1957, as amended.

[4] Regulation (EC) No 1272/2008 of the European Parliament and Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC and amending Regulation (EC) No 1907/2006 [OJ L 353, 31.12.2008, p. 1].

CSA	Chemical Safety Assessment
DDT	Deflagration to Detonation Transition
DIN	Deutsches Institut für Normung (German Institute for Standardisation)
DPD	Directive 1999/45/EC on the classification and labelling of Dangerous Preparations[5]
DSD	Directive 67/548/EEC on the classification and labelling of Dangerous Substances[6]
ECHA	European Chemicals Agency, Helsinki (https://echa.europa.eu/)
EIGA	European Industrial Gases Association
EIS	Extremely Insensitive Substance
EN	A European Standard
EN ISO	European Union International Organization for Standardisation
EU	European Union
EUH	The hazard statements carried through from DSD and DPD, which are not yet included in the GHS are codified as 'EUH'
GHS	Globally Harmonised System of Classification and Labelling of Chemicals[7]
GLP	Good Laboratory Practice

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[5] Directive 1999/45/EC of the European Parliament and of the Council of 31 May 1999 concerning the approximation of the laws, regulations and administrative provisions of the Member States relating to the classification, packaging and labelling of dangerous preparations [OJ L 200, 30.7.1999, p. 1].

[6] Council Directive 67/548/EEC of 27 June 1967 on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances [OJ 196, 16.8.1967, p. 1].

[7] Globally Harmonised System of Classification and Labelling of Chemicals (GHS), Fifth revised edition, United Nations, New York and Geneva, 2013.

IBC	Intermediate Bulk Container
ICAO TI	International Civil Aviation Organization (Technical Instructions for the Safe Transport of Dangerous Goods by Air)
IEC	International Electrotechnical Commission (http://www.iec.ch/)
IMDG Code	International Maritime Dangerous Goods Code
IMO	International maritime Organisation
IR&CSA	Guidance on Information Requirements and Chemical Safety Assessment, ECHA (http://guidance.echa.europa.eu/docs/guidance_document/information_requirements_en.htm)
ISO	International Organisation for Standardization
ITDG	Directive 2008/68 on the Inland Transport of Dangerous Goods[8]
LEL	Lower Explosion Limit
LFL	Lower Flammability Limit
n.a.	Not available
REACH	Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals[9]

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[8] Directive 2008/68/EC of the European Parliament and of the Council of 24 September 2008 on the inland transport of dangerous goods, implementing the European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR), the Regulations concerning the International Carriage of Dangerous Goods by Rail (RID) and the European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways (ADN) [OJ L 260, 30.9.2008, p. 13].

[9] Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and omission of Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC. [OJ L 396, 30.12.2006 p.1.] [Corrigendum: OJ L 136, 29.5.2007 p.3].

RID	Règlement concernant le transport international ferroviaire de marchandises dangereuses (Regulations concerning the International Carriage of Dangerous Goods by Rail)[10]
RTD	Resistance To Detonation
SADT	Self-Accelerating Decomposition Temperature
SDS	Safety Data Sheet
UEL	Upper Explosion Limit
UN	United Nations
UN RTDG Model Regulations	UN Recommendations on the Transport of Dangerous Goods - Model Regulations. It covers all modal transport regulations (ADR, RID, ADN, IMDG and ITDG). It is regularly updated and amended every two years. More information and the latest revision are available at: http://www.unece.org/trans/danger/publi/unrec/rev13/13nature_e.html
UN-MTC	The UN Manual of Tests and Criteria contains criteria, test methods and procedures to be used for classification of dangerous goods according to the provisions of Parts 2 and 3 of the United Nations Recommendations on the Transport of Dangerous Goods, Model Regulations, as well as of chemicals presenting physical hazards according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS). More information and the latest revision are available at: http://www.unece.org/trans/danger/publi/manual/manual_e.html.
VDI	Verein Deutscher Ingenieure (The Association of German Engineers)

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[10] Regulations concerning the International Carriage of Dangerous Goods by Rail, appearing as Appendix C to the Convention concerning International Carriage by Rail (COTIF) concluded at Vilnius on 3 June 1999, as amended.

PART 2: PHYSICAL HAZARDS

2.0. INTRODUCTION

2.0.1 General remarks about the prerequisites for classification and testing

The purpose of this chapter is to give some general guidance with respect to the classification of physical hazards, the generation of test data and their interpretation. The general principles of the classification process are explained Part 1 section 1.1.3, so this section refers to physical hazard specificities.

Test methods for physical hazards are referred to in each physical hazard class chapter of CLP. Most of these test methods can be found in the UN Manual of Tests and Criteria[11] (UN-MTC), see the website http://www.unece.org/trans/danger/publi/manual/manual_e.html. A few of these test methods are contained in standards which are also referred to in CLP (see particularly flammable gases, oxidising gases and flammable liquids). When test results, based on other methods or standards (which are not referred to in CLP) are available, then these data may still be used, provided they are adequate for the purpose of hazard determination. Expert judgement is necessary to conclude whether there is sufficient documentation to assess the suitability of the test method used, and whether the test was carried out using an acceptable level of quality assurance and thus on the adequacy of such data for the purposes of classification according to CLP.

Please note that in practice the physical hazards of a substance or mixture may differ from those shown by tests, e.g., in case of certain ammonium-nitrate-based compounds (explosive / oxidising properties) and certain halogenated hydrocarbons (flammable properties). Such experience must be taken into account for the purpose of classification (CLP, Article 12(a)).

The information available or generated must be checked to determine if it is directly comparable to the respective hazard criteria and if it is, then it can be used to derive the classification immediately. Where the criteria cannot be directly applied to the available data, expert judgement should be used for the evaluation of the available information in a weight of evidence determination (CLP, Article 9(3) and CLP Annex I, section 1.1.1.).

2.0.2 Safety

Special care is required when new or unknown substances or mixtures are tested. If possible, preliminary tests should be carried out before larger quantities are handled. The 'screening procedures', described in Appendix 6 of UN-MTC, allows gathering valuable information about physico-chemical properties based on small-scale tests. Further aspects of safety are given in the general introduction, section 1.4 of the UN-MTC revision 8[12] or within the individual test procedures.

2.0.3 General conditions for testing

Samples offered for testing must in all aspects be representative of the substance or mixture to be classified. Therefore, it is helpful to characterise or specify the sample for the purposes of documentation (i.e. batch number, production code, impurities etc.). Further characterisation (i.e.

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[11] It should be noted that before GHS revision 7, the official name of this manual was "UN Recommendations on the Transport of Dangerous Goods – Manual of Tests and Criteria", which is abbreviated "UN RTDG - Manual of Tests and Criteria" in the CLP Regulation. However, as of GHS revision 7 the official name was changed to "Manual of Tests and Criteria". For this reason, references to this manual are denoted as "Manual of Test and Criteria" or "UN-MTC" when occurring in plain text in this guidance, while they are denoted "UN RTDG - Manual of Tests and Criteria" when occurring in direct quotes from CLP.

[12] Unless otherwise specified, references to sections, tables, figures, etc. are consistent with UN-MTC revision 8 (2023).

analysis) is highly recommended in cases where the presence of diluents, activators, stabilisers or moisture may influence the outcome of the test.

The tests must be performed on the substance or mixture in the appropriate physical form where changes in that form may influence the outcome of the test (CLP, Articles 5 and 6), see CLP Guidance Part 1, Section 1.2.3.1*.* In some cases, test methods as stipulated in the relevant physical hazards sections provide further information on the physical forms that should be tested and whether manipulation of the substance is required (e.g. grinding to decrease particle size).

If additional parameters, such as physical condition, particle size and shape, specific surface area, density, or crystal structure influence the test result, these parameters should be mentioned in the test report.

2.0.4 Physical state

The physical state determines which hazard classes should be considered for testing. As CLP states[13], hazard classification is based on intrinsic properties of the substance or mixture which are determined not only by its physical state but also its form.

The definitions for gases, liquids and solids are given in Annex I, Part 1 of CLP:

Annex I: Part 1, *1.0. Definitions*

Gas means a substance which:

(i) at 50 °C has a vapour pressure greater than 300 kPa (absolute); or

(ii) is completely gaseous at 20 °C at a standard pressure of 101.3 kPa;

Liquid means a substance or mixture which:

(i) at 50 °C has a vapour pressure of not more than 300 kPa (3 bar);

(ii) is not completely gaseous at 20 °C and at a standard pressure of 101,3 kPa; and

(iii) which has a melting point or initial melting point of 20 °C or less at a standard pressure of 101,3 kPa;

Solid means a substance or mixture which does not meet the definitions of liquid or gas.

In some cases (such as viscous substances or mixtures), a specific melting point cannot be determined. Such a substance or mixture must be regarded as a liquid if either the result of the ASTM International[14] D4359-90 test (standard test method for determining whether a material is a liquid or a solid) indicates ‘liquid’ or the result of the test for determining fluidity (penetrometer test) prescribed in section 2.3.4 of Annex A of the European Agreements on the international transport of dangerous goods by road indicates ‘not pasty’. As mentioned in section 1.2, the same solid substance or mixture may have different forms such as flakes, prills, or powder. Furthermore, a powder may contain particles of different size, and particles of the same size may have different shapes, crystallinity or allotropy etc. These differences may result in different intrinsic properties, and consequently, different physical hazards of the powder. Particle size is crucial for several hazard classes such as explosives, flammable solids, solid self-reactive substances and mixtures, pyrophoric solids, self-heating substances and mixtures, solid organic peroxides and solid substances and mixtures which in contact with water emit flammable gases. Therefore, besides the physical state other parameters should also be considered when identifying the form, since they may trigger different classifications of the same substance or mixture.

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[13] CLP, Articles 5(1), 6(1) and 8(6).

[14] ‘ASTM International’ was formerly known as American Society for Testing and Materials, hereafter ASTM

An example of differing classifications due to different intrinsic properties of substance forms is the allotropes red phosphorus (flammable solid) and white phosphorus (pyrophoric solid). Consequently, it is important to evaluate case by case whether available information on the physical properties of the substance or mixture as placed on the market is applicable to the examined form, and whether additional testing should be performed.

The form of a substance or mixture as placed on the market might be such that it is not possible to test it in this form, e.g. if it is in the form of tablets or pellets. In such cases, the physical hazards of the substance or mixture in its granular/powdered form should be considered for classification, especially if it is friable and produces secondary effects due to abrasion or crushing during supply and use. If phase separation occurs, the most hazardous properties of each phase of the substance or mixture must be communicated.

If further testing is required, the choice of the test method should be done after thorough evaluation of its suitability for the substance or mixture, as the properties of the form (e.g. powders particle size and shape) may have a significant effect on the test results.

2.0.5 Quality

The determination of data must be based on the methods named in CLP Annex I, Part 2. Whenever possible, the laboratory should regularly assess its performance with respect to the methods used, e.g. by participating in inter-laboratory testing or by using reference materials. Any deviation from the test procedure or standard should be documented and, if necessary, justified.

The reliability of all test results used for the classification of hazardous substances and mixtures is important so their transparency and comparability must be ensured.

For these purposes, CLP requires in Article 8 the following:

> ***Article 8(5)***
>
> *Where new tests for physical hazards are carried out for the purposes of this Regulation, they shall be carried out, at the latest from 1 January 2014, in compliance with a relevant recognised quality system or by laboratories complying with a relevant recognised standard.*

In general, the following alternative strategies can be pursued:

1. Compliance with the principles of good laboratory practice (GLP);
2. Application of EN ISO[15]/IEC[16] 17025:2017[17] *General requirements for the competence of testing and calibration laboratories* as a relevant recognised standard;
3. Other internationally recognised standards of comparable scope.

Any laboratory that carries out physical hazard tests for classification purposes can choose from these alternatives how to fulfil the quality requirements of CLP. However, it should be noted that GLP is not primarily aimed at physical hazard testing and can only be applied to some physical hazard test methods. Therefore, in general EN ISO/IEC 17025 is more suitable or preferred over GLP for physical hazard testing.

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[15] EN ISO: European Union International Organization for Standardisation

[16] IEC: International Electrotechnical Commission

[17] Hereafter: ISO/IEC 17025

2.1. EXPLOSIVES

2.1.1. Introduction

The requirements in part 2.1 'Explosives' of Annex I of CLP are identical to those in chapter 2.1 of GHS up to revision 8[18]. However, as of revision 9 of GHS the classification system for explosives has been completely altered. It is expected that this new classification system for explosives will be included in CLP, upon which this guidance chapter will have to be substantially reviewed.

Up to revision 8 of GHS, the GHS classification of explosives is almost entirely adopted based on the UN Recommendations on the Transport of Dangerous Goods – Model Regulations (UN RTDG Model Regulations). This classification system, which is currently used in CLP, is appropriate for transport and also for storage of explosives in the transport configuration (e.g. as packaged for transport). In practice, the transport classification normally is simply translated into the corresponding CLP classification without further testing. Note that GHS revision 7 introduced the new hazard class 'desensitised explosives' which is dealt with separately in section 2.17.

The changes in the classification system as of GHS revision 9 were introduced to better reflect the explosive behaviour when the substance, mixture or article is not in the transport configuration. While the overall scope of the class of explosives was retained, new categories 1 and 2A-C were introduced to supplement the divisions used for transport and for classification up to GHS revision 8. For explosives which are transported (which should be virtually all commercial explosives), it is quite straight-forward to derive the new GHS classification from the transport classification.

It should be noted that the explosives hazard class, unlike other hazard classes of CLP, includes articles. According to Article 4(8) of CLP, these articles should be treated as substances and mixtures in the context of CLP.

The classification of substances, mixtures and articles in the explosives hazard class and further allocation to a division is a very complex procedure. References to Part I of the UN-MTC and related expertise are necessary.

2.1.2. Definitions and general considerations for classification of explosives

The following definition is given in CLP for the class of explosives.

Annex I: *2.1.1.1. 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 in points (a) and (b) above which are manufactured with the view to producing a practical, explosive or pyrotechnic effect.

Additional remark related to the applicability of 2.1.1.1(a) (see also the UN RTDG Model Regulations, section 2.1.1.1(a)):

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[18] The twelfth ATP (Commission Regulation (EU) 2019/521) implements the changes introduced by the sixth (2015) and seventh (2017) revisions of the GHS into the CLP Regulation. No changes on chapter 2.1 were included in GHS revision 8. Consequently, if not specified "GHS" indicates "GHS revision 7".

- a substance or mixture which is not itself an explosive (*i.e.* it does not react out of the condensed phase), but which can form an explosive atmosphere of gas, vapour or dust is not included in this class;
- explosive behaviour of organic peroxides and of self-reactive substances and mixtures is covered by those specific hazard classes and therefore not included in the hazard class explosives.

In addition, the following definitions from CLP apply for explosives:

> **Annex I:** *2.1.1.2. For the purposes of this Regulation the following definitions shall apply:*
>
> *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 unstable explosive is an explosive which is thermally unstable and/or too sensitive for normal handling, transport and use.*
>
> *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.*
>
> *An intentional explosive is a substance, mixture or article which is manufactured with a view to produce a practical explosive or pyrotechnic effect.*

2.1.3. Relation to other physical hazards

Substances, mixtures or articles which have already been classified as explosives (Class 1 according to the UN RTDG Model Regulations) should normally not be considered for classification in any other physical hazard classes, as the explosion hazard can be considered to be the most severe of the physical hazards. Furthermore, testing explosives for other physical hazards may pose a severe safety concern for the testing personnel, which must always be avoided.

When considering substances and mixtures for classification within the hazard class explosives, the following checks should be performed with respect to other hazard classes:

- Substances, mixtures and articles that have been manufactured with a view to producing a practical explosive or pyrotechnic effect, are classified as explosives by definition according to 2.1.1.1(c) of Annex I of CLP. It should be checked whether such a substance or mixture is an unstable explosive.
- Thermally unstable substances or mixtures that are not classified as explosives should be considered for classification as self-reactive substances and mixtures.
- Mixtures of oxidising substances and mixtures with combustible material that are not classified as explosives should be considered for classification as self-reactive substances and mixtures, oxidising liquids or oxidising solids.
- Explosive substances or mixtures may be phlegmatised such that, in the phlegmatised state, they meet the criteria for classification as desensitised explosives and should be classified as such instead of as explosives.

Due to the complexity of these issues, expert advice should always be sought when dealing with classification of substances and mixtures and articles with potentially explosive properties.

2.1.4. Classification of substances, mixtures or articles as explosives

2.1.4.1. Identification of hazard information

Information on the following types of hazards is relevant for the evaluation of substances, mixtures and articles for the class of explosives:

- sensitivity to shock;
- effects of heating and ignition under confinement;
- thermal stability;
- sensitiveness to impact and friction;
- mass explosion hazard;
- projection hazard;
- fire and radiant heat hazard.

2.1.4.2. Screening procedures and waiving of testing

The screening procedure is described in CLP Annex I, sections 2.1.4.2 and 2.1.4.3 with references to Appendix 6 of the UN-MTC.

The screening procedure may be used for substances or mixtures which are suspected of having explosive properties. It is not applicable to substances and mixtures manufactured with the intention of producing a practical explosive or pyrotechnic effect, as these are classified as explosives by definition.

Explosive properties are associated with the presence of certain chemical groups in a molecule which can react to produce very rapid increases in temperature and/or pressure. The screening procedure is aimed at identifying the presence of such reactive groups and the potential for rapid energy release.

Examples of groups which may indicate explosive properties in organic materials are:

- C-C unsaturation (*e.g.,* acetylenes, acetylides, 1, 2-dienes);
- C-Metal, N-Metal (*e.g.,* Grignard reagents, organo-lithium compounds);
- Contiguous nitrogen atoms (*e.g.*, azides, aliphatic azo compounds, diazonium salts, hydrazines, sulphonylhydrazides);
- Contiguous oxygen atoms (*e.g.,* peroxides, ozonides);
- N-O (e.g. hydroxyl amines, nitrates, nitro compounds, nitroso compounds, N-oxides, 1,2-oxazoles);
- N-halogen (*e.g.,* chloramines, fluoroamines);
- O-halogen (*e.g.*, chlorates, perchlorates, iodosyl compounds).

A substance or mixture does not have to undergo the acceptance procedure, and is therefore not classified as explosive, if:

a. There are no chemical groups associated with explosive properties present in the molecule (see listing above for indications of chemical groups);

or

b. The substance or mixture 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:

$$C_xH_yO_z + \left[x + \left(\frac{y}{4}\right) - \left(\frac{z}{2}\right)\right]O_2 \rightarrow xCO_2 + \left(\frac{y}{2}\right)H_2O$$

Using the formula:

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

or

c. For an organic substance or a homogenous mixture of organic substances, containing one or more chemical group(s) associated with explosive properties:

- the exothermic decomposition energy is less than 500 J/g; or
- the onset of exothermic decomposition is 500 ºC or above, as indicated in CLP, Annex I, Table 2.1.3 (see below).

  (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 ºC to release more than 500 J/g. Therefore, the measurement is not normally carried out beyond 500 ºC). The exothermic decomposition energy may be determined using a suitable calorimetric technique see section 20.3.3.3 of the UN-MTC.

Annex I: *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*

or

d. for mixtures of inorganic oxidising substances with organic material(s), the concentration of the inorganic oxidising substance is:

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

If the screening procedure identifies the substance or mixture to be a potential explosive or if it is a mixture containing any known explosives, the classification (acceptance) procedure for the class of explosives (see section 2.1.4.5) has to be applied. If the exothermic decomposition energy of organic materials is less than 800 J/g, a UN gap test is not required, neither according to Series 1 Type (a) nor according to Series 2 Type (a).

Note: If explosive properties cannot be rules out according to the above screening procedure, testing is required (at least Test Series 2 of the UN-MTC) unless another valid scientific argumentation is given. EU Test A.14 cannot be used to conclude on classification, including 'no classification'.

2.1.4.3. Classification criteria

The criteria for the classification of explosives are given in the following tables.

Annex I:

2.1.2.1. Substances, mixtures and articles of this class are classified as an unstable explosive on the basis of the flowchart in Figure 2.1.2. The test methods are described in Part I of the UN RTDG, Manual of Tests and Criteria.

2.1.2.2. Substances, mixtures and articles of this class, which are not classified as an unstable explosive, shall be 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.*

2.1.2.3. Explosives, which are not classified as an unstable explosive, shall be classified in one of the six divisions referred to in section 2.1.2.2 of this Annex based on Test Series 2 to 8 in Part I of the UN RTDG, Manual of Tests and Criteria according to the results of the tests laid down in Table 2.1.1:

Table 2.1.1

Criteria for explosives	
Category	*Criteria*
Unstable explosives or explosives of Divisions 1.1 to 1.6	*For explosives of Divisions 1.1 to 1.6, the following are the core set of tests that need to be performed:* *Explosibility: according to UN Test Series 2 (section 12 of the UN RTDG, Manual of Tests and Criteria). Intentional explosives (¹) shall not be subject to UN Test Series 2.* *Sensitiveness: according to UN Test Series 3 (section 13 of the UN RTDG, Manual of Tests and Criteria).* *Thermal stability: according to UN Test 3(c) (sub-section 13.6.1 of the UN RTDG, Manual of Tests and Criteria).* *Further tests are necessary to allocate the correct Division.*
(¹) This comprises substances, mixtures and articles which are manufactured with a view to producing a practical, explosive or pyrotechnic effect.	

2.1.4.4. Testing and evaluation of hazard information

Where test data are available, these must be evaluated against the set criteria for classification.

When the screening procedure indicates that a substance or mixture may possess explosive properties, a cautious approach when performing the tests is necessary to ensure safe handling.

For information on the test procedures see the following section 2.1.4.5 where the individual test series are described in context with the respective decision logic.

The test procedures for the classification of explosives are described in detail in the Part I of the UN-MTC.

Where the test is conducted in the packaged form and the packaging is changed, a further test must be conducted where it is considered that the change in packaging will affect the outcome of the test.

Classification tests must be performed on the substance or mixture as supplied. If 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, where possible.

2.1.4.5. Classification procedure and decision logics

Any substance, mixture or article having, or suspected of having, explosives characteristics must be considered for classification in the explosives hazard class. Substances, mixtures and articles classified in this hazard class must be assigned to the appropriate division or must be classified as unstable explosive.

It should be noted that, as a consequence to the substantial changes to the explosives classification procedure as GHS revision 9 (see introduction, section 2.1.1), the UN-MTC was consequently amended[19]. In essence, the amendments mean that all references to “unstable explosive” and to “too dangerous for transport” in the UN-MTC have been replaced by “too

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[19] These amendments are included in revision 7/amendment 1 of the UN-MTC.

sensitive to assign a division”. A substance, mixture or article that is considered “too sensitive to assign a division” according to the UN-MTC is classified as an unstable explosive according to CLP.

The classification procedure is divided into two stages, the acceptance procedure and the assignment procedure.

In the acceptance procedure, intrinsic explosive properties of a substance, mixture or article are determined through tests of its sensitivity, stability and explosion effects. If the substance, mixture or article is not characterised as unstable explosive and is provisionally accepted into the class of explosives, it is then necessary to ascertain the correct division by applying the assignment procedure. The further subdivision into compatibility groups A to S is described in detail in the UN-MTC, section 2.1.2. The compatibility groups and their recommended combination identify types of explosives which are deemed to be compatible, e.g. for combined storage or transportation and can subsequently be used to distinguish technical requirements (especially) in these sectors. However, assignment of compatibility groups is not part of the classification system according to CLP.

The tests for acceptance and the further tests to determine the correct division are grouped into eight test series. Classification procedures, test methods and criteria are described in detail in Part I of the UN-MTC.

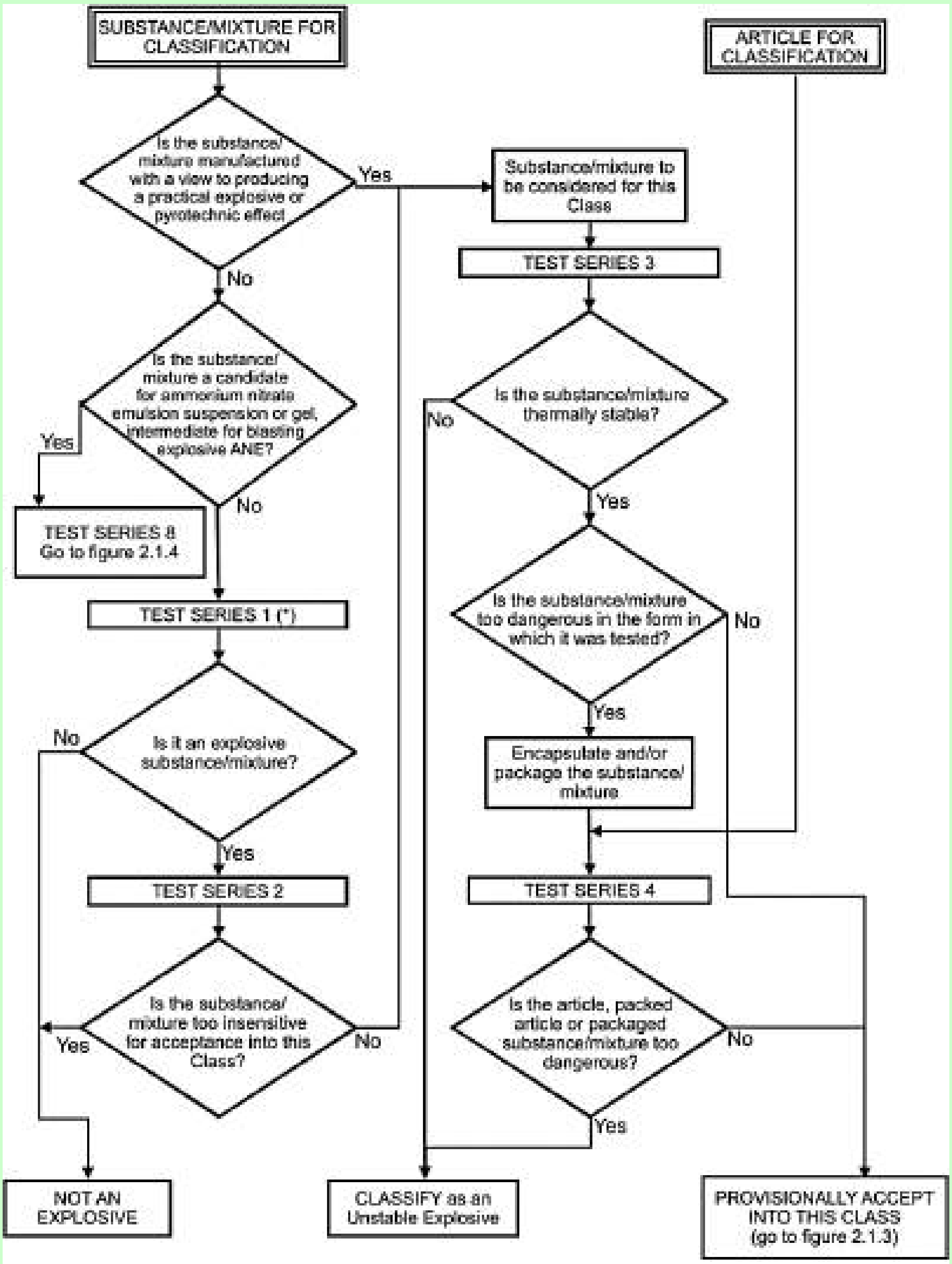
NOTE: The person responsible for the classification of explosives should be experienced in this field and be familiar with the criteria for classification.

2.1.4.5.1. Acceptance procedure

The acceptance procedure is used to determine whether a substance, mixture or article is a candidate for the class of explosives, and whether it is an unstable explosive (which is not allowed for transport).

The test methods used for deciding on provisional acceptance into the class of explosives are grouped into four series, Test Series 1 to 4 (see CLP Annex I, Figure 2.1.2 reported below).

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



(*) For classification purposes, start with Test Series 2.

The numbering of Test Series 1 to 4 relates to the sequence of assessing the results rather than the order in which the tests should be conducted. **It may be important for the safety of test**

personnel that certain tests, using small amounts of material, are conducted first before proceeding to experiment with larger quantities.

Starting the testing procedure with Test Series 3 is highly recommended, because these tests involve relatively small sample sizes, which reduces the risk to test personnel. While Test Series 1 may be waived for the purpose of classification, it can provide useful information on the properties of the substance or mixture.

Test Series 1

Within Test Series 1 the question 'Is it an explosive substance / mixture?' is answered on the basis of the results of three types of tests to assess possible explosive effects. The question is answered 'Yes' if a '+' is obtained in any of the three types of tests. If the answer is 'No', the substance / mixture is rejected from this class; it is not an explosive. Under certain conditions the Test Type 1 (a) can be replaced by certain tests of Test Series F, see UN-MTC, section 11.3.5.

The three types of test used are (recommended test is indicated within brackets):

Type 1 (a): a shock test with defined booster and confinement to determine the ability of the substance to propagate a detonation (UN Gap test, zero gap);

Type 1 (b): a test to determine the effect of heating under confinement (Koenen test); and

Type 1 (c): a test to determine the effect of ignition under confinement (time/pressure test).

Test Series 2

Series 2 tests are used to answer the question 'Is the substance / mixture too insensitive for acceptance into this Class?'. In general, the basic apparatus and method used is the same as that for Test Series 1 but with less stringent criteria, e.g. in the case of gap tests, the gap used is greater than zero. The question is answered 'No' if a '+' is obtained in any of the three types of test. If the answer is 'Yes', the substance / mixture is rejected from this class; it is not an explosive. Under certain conditions Test Type 2 (a) can be replaced by certain tests of Test Series F, see UN-MTC, section 12.3.4.

The following three types of test are used (recommended test is indicated within brackets):

Type 2 (a): a shock test with defined initiation system and confinement to determine sensitivity to shock (UN gap test) (with a defined gap e.g. 50 mm);

Type 2 (b): a test to determine the effect of heating under confinement (Koenen test); and

Type 2 (c): a test to determine the effect of ignition under confinement (Time/pressure test).

If the substance or mixture is manufactured with a view to produce a practical explosive or pyrotechnic effect, it is unnecessary to conduct Test Series 1 and 2 for purposes of classification.

Test Series 3

As stated above, it is recommended to carry out Test Series 3 before Test Series 1 and 2 for safety reasons due to the small sample amount needed. It is also recommended to carry out Test Series 3 even if negative results have been obtained in Test Series 1 and/or 2 because only Test Series 3 gives information about the thermal stability and the sensitivity to mechanical stimuli (impact and friction).

Test Series 3 is used to answer the questions 'Is the substance or mixture thermally stable?' and 'Is the substance / mixture too dangerous in the form in which it was tested (and therefore unstable in that form)?'[20] This involves tests for determining the sensitiveness of the substance or mixture to mechanical stimuli (impact and friction), and to heat and flame.

The following four types of tests are used (recommended test is indicated within brackets):

Type 3 (a):	a falling weight test to determine sensitiveness to impact (BAM Fallhammer);
Type 3 (b):	a friction; or impacted friction test to determine sensitiveness to friction (BAM friction apparatus);
Type 3 (c):	an elevated temperature test to determine thermal stability (thermal stability test at 75 °C); and
Type 3 (d):	an ignition test to determine the response of a substance or mixture to fire (small scale burning test).

The first question is answered 'No' if a '+' is obtained in Test Type 3 (c). Then the substance / mixture is considered as thermally unstable and either classified as an unstable explosive or as a self-reactive substance or mixture.

The second question is answered 'Yes' if a '+' is obtained in any of the Test Types 3 (a), 3 (b) or 3 (d). If a '+' is obtained, the substance / mixture may be encapsulated or packaged to reduce its sensitiveness to external stimuli or is classified as an unstable explosive. Furthermore, the explosive may be desensitised to suppress/reduce its explosive properties in which case the classification procedure has to be restarted.

Test Series 4

Series 4 tests are intended to answer the question 'Is the article, packaged article or packaged substance or mixture too dangerous (and therefore an unstable explosive)?'[21]. Conditions which may occur during supply and use include high / low temperature and high relative humidity, vibration, bumping and dropping.

The two types of test to be carried out are:

Type 4 (a):	a test of thermal stability for articles; and
Type 4 (b):	a test to determine the hazard from dropping.

The question is answered 'Yes' if a '+' is obtained in either Test Type 4 (a) or 4 (b) and the substance or mixture or article is classified as an unstable explosive.

It is important to note that a substance / mixture which fails Test Series 2 (i.e. it is sensitive enough for acceptance into the class of explosives) may still, if properly packaged, leave the class of explosives provided that it is not designed to have an explosive effect and does not exhibit any explosive hazard in Test Series 6 of the assignment procedure (see example for musk xylene). Such an exclusion from the class of explosives is restricted to the specific type and size of package tested.

Especially for substances / mixtures, which have explosive properties according to Test Series 1 and/or 2 but can leave the class of explosives after Test Series 6 due to the type of packaging; these properties should be communicated in the Safety Data Sheet (SDS).

2.1.4.5.2. Assignment procedure to a division

The assignment procedure to one of six divisions, depending on the type of hazard presented, applies to all substances, mixtures and/or articles that are candidates for the class of explosives.

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[20] Through UN-MTC revision 7/ amendment 1, this question has been changed to "Is the substance / mixture too sensitive to assign a division?", see the introduction to section 2.1.4.5.

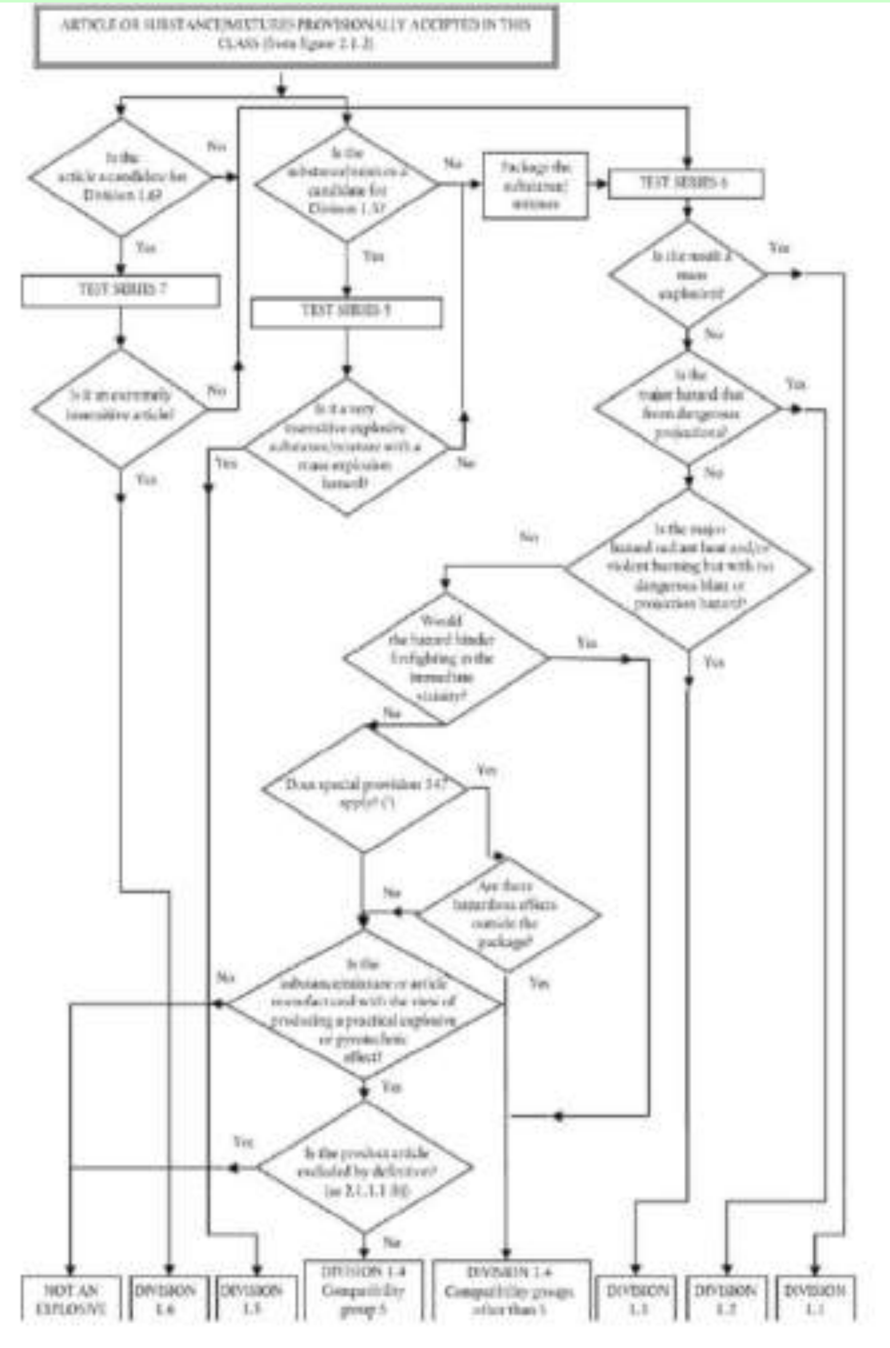
[21] Through UN-MTC revision 7/ amendment 1, this question has been changed to "Is the article, packaged article or packaged substance or mixture too sensitive to assign a division", see the introduction to section 2.1.4.5.

A substance, mixture or article must be assigned to the division which corresponds to the results of the tests to which the substance, mixture or article, as presented for supply and use, has been subjected. Other test results, and data gathered from accidents which have occurred, may also be taken into account.

The test methods used for assignment to a division are grouped into three series – Test Series 5 to 7 – designed to provide the information necessary to answer the questions in Figure 2.1.3 in CLP.

NOTE: The person responsible for the classification of explosives should be experienced in this field and be familiar with the criteria for classification.

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



Test Series 5

Test Series 5 is only carried out for explosive substances / mixtures which are very insensitive and consequent candidates for division 1.5. Typical substances / mixtures are blasting agents such as ammonium nitrate / fuel oil (ANFO), slurries, and emulsion explosives.

The results from three types of series 5 tests are used to answer the question 'Is it a very insensitive explosive substance / mixture with a mass explosion hazard?'.

The test types are (recommended test is indicated within brackets):

Type 5 (a): a shock test to determine the sensitivity to intense mechanical stimulus (cap sensitivity test);

Type 5 (b): thermal tests to determine the tendency of transition from deflagration to detonation (French or USA DDT test); and

Type 5 (c): a test to determine if a substance, when in large quantities, explodes when subjected to a large fire.

The question is answered 'No' if a '+' is obtained in any of the three test types. A candidate for Division 1.5 should pass one test of each type.

Test Series 6

The results from four types of series 6 tests are used to determine which division, amongst Divisions 1.1, 1.2, 1.3 and 1.4, corresponds most closely to the behaviour of the substance, mixture or article to be classified if a load is involved in a fire resulting from internal or external sources or an explosion from internal sources. The results are also necessary to assess whether a substance, mixture or article can be assigned to Compatibility Group S of Division 1.4 and whether or not it may be excluded from this class. Test Series 6 should be applied to packages of substances, mixtures or articles in the condition and form in which they are offered for supply and use.

The four test types are (recommended test is indicated within brackets):

Type 6 (a): a test on a single package to determine if there is mass explosion of the contents (single package test);

Type 6 (b): a test on packages of an explosive substance, mixture or explosive articles, or non-packaged explosive articles, to determine whether an explosion is propagated from one package to another or from a non-packaged article to another (stack test);

Type 6 (c): a test on packages of an explosive substance, mixture or explosive articles, or non-packaged explosive articles, to determine whether there is a mass explosion or a hazard from dangerous projections, radiant heat and/or violent burning or any other dangerous effect when involved in a fire (bonfire test);

Type 6 (d): a test on an unconfined package of explosive articles to which special provision 347 of chapter 3.3 of the UN RTDG Model Regulations applies, to determine if there are hazardous effects outside the package arising from accidental ignition or initiation of the contents.

Test Types 6 (a), 6 (b), 6 (c) and 6 (d) are performed in alphabetical order. However, it is not always necessary to conduct tests of all types. Test Type 6 (a) may be waived if explosive articles are carried without packaging or when the package contains only one article. Test Type 6 (b) may be waived if in each Type 6 (a) test:

- the exterior of the package is undamaged by internal detonation and/or ignition; or
- the contents of the package fail to explode or explode as feebly as would exclude propagation of the explosive effect from one package to another in Test Type 6 (b).

Test Type 6 (c) may be waived if, in a Type 6 (b) test, there is practically instantaneous explosion of virtually the total contents of the stack. In such cases the product is assigned to Division 1.1.

Test Type 6 (d) is a test used to determine whether a Division 1.4 compatibility group S classification is appropriate and is only used if special provision 347 of chapter 3.3 of the UN RTDG Model Regulations applies. The results of Test Series 6 (c) and 6 (d) indicate if division 1.4 compatibility group S is appropriate, otherwise the classification is Division 1.4, compatibility group other than S.

If a substance or mixture gives a '—' result (no propagation of detonation) in the Series 1 Type (a) test, the 6 (a) test with a detonator may be waived.

If a substance gives a '—' result (no or slow deflagration) in a Series 2 Type (c) test, the Test Type 6 (a) test with an igniter may be waived.

Test Series 7

Test Series 7 aims at military explosives (Extremely Insensitive Substance (EIS) or article containing an EIS) and is generally not relevant for explosives for civil use. Therefore, the individual tests are not described here. If needed, they can be found in the UN-MTC, Part I, section 17.

Test Series 8

The question whether a candidate for ammonium nitrate emulsion or suspension or gel (ANE), intermediate for blasting explosives is insensitive enough for classification as oxidising is answered by Test Series 8.

According to CLP, there are three test types for ANE (recommended test is indicated within brackets):

Type 8 (a): a test to determine the thermal stability (Thermal Stability Test for ANE);

Type 8 (b): a shock test to determine sensitivity to intense shock (ANE gap test);

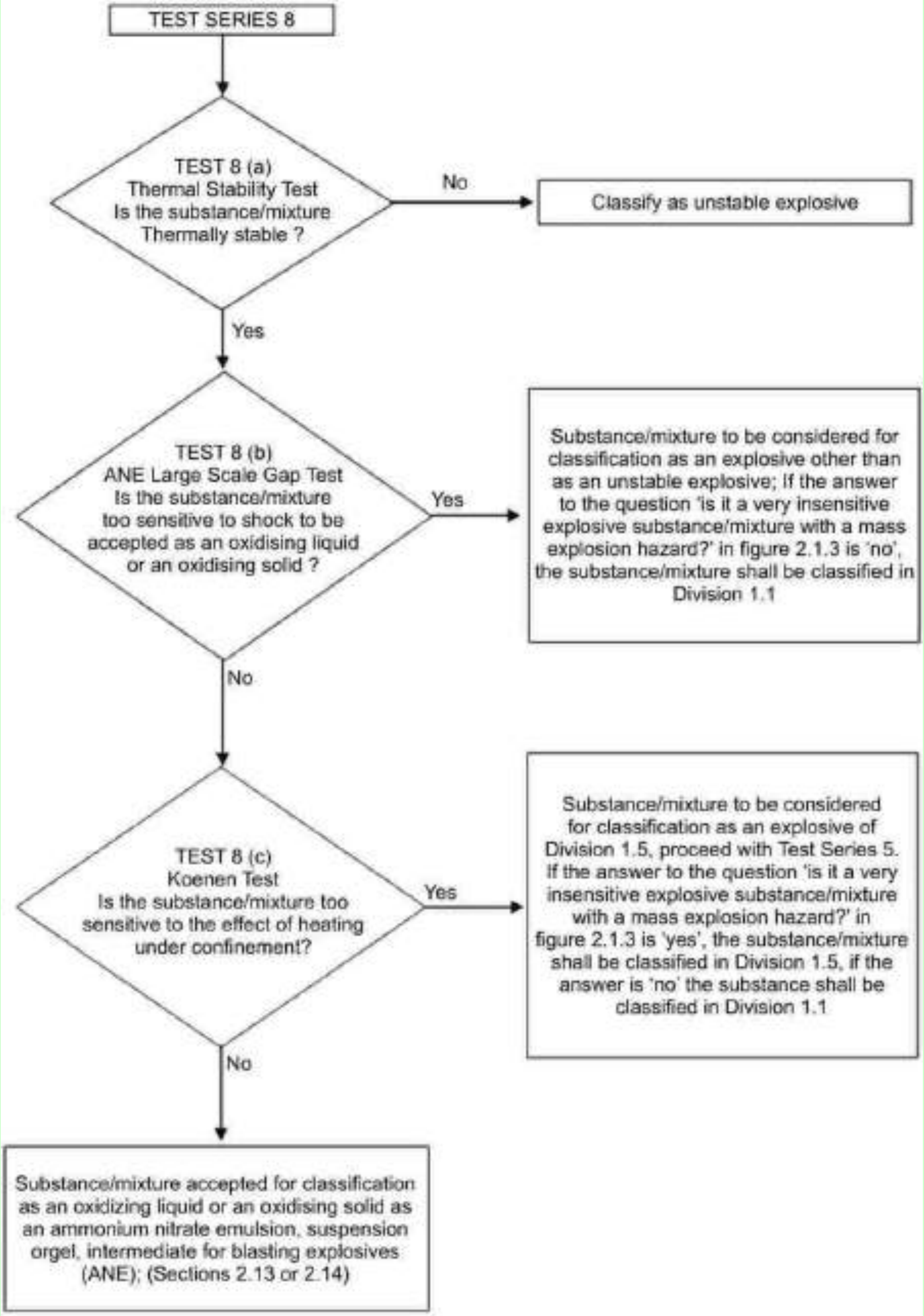
Type 8 (c): a test to determine the effect of heating under confinement (Koenen test).

Test Series 8 is used to establish whether an ANE may leave the class of explosives or not. ANE:s that are allowed to leave the class of explosives are classified as oxidising liquids or oxidising solids (depending on their viscosity).

In the UN-MTC there is an additional classification Test Type 8 (e) (the Minimum Burning Pressure test), which has not yet been introduced into the CLP classification scheme.

Test Type 8 (d) of the UN-MTC is not used for classification and has no relevance for CLP.

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



TEST SERIES 8

TEST 8 (a)
Thermal Stability Test
Is the substance/mixture Thermally stable ?

Classify as unstable explosive

TEST 8 (b)
ANE Large Scale Gap Test
Is the substance/mixture too sensitive to shock to be accepted as an oxidising liquid or an oxidising solid ?

Substance/mixture to be considered for classification as an explosive other than as an unstable explosive; If the answer to the question 'is it a very insensitive explosive substance/mixture with a mass explosion hazard?' in figure 2.1.3 is 'no', the substance/mixture shall be classified in Division 1.1

TEST 8 (c)
Koenen Test
Is the substance/mixture too sensitive to the effect of heating under confinement?

Substance/mixture to be considered for classification as an explosive of Division 1.5, proceed with Test Series 5. If the answer to the question 'is it a very insensitive explosive substance/mixture with a mass explosion hazard?' in figure 2.1.3 is 'yes', the substance/mixture shall be classified in Division 1.5, if the answer is 'no' the substance shall be classified in Division 1.1

Substance/mixture accepted for classification as an oxidizing liquid or an oxidising solid as an ammonium nitrate emulsion, suspension orgel, intermediate for blasting explosives (ANE); (Sections 2.13 or 2.14)

2.1.5. Hazard communication for explosives

2.1.5.1. Pictograms, signal words, hazard statements and precautionary statements[22]

Annex I: *Table 2.1.2* ***Label elements for explosives***

Classification	*Unstable Explosive*	*Division 1.1*	*Division 1.2*	*Division 1.3*	*Division 1.4*	*Division 1.5*	*Division 1.6*
GHS Pictograms							
Signal Word	*Danger*	*Danger*	*Danger*	*Danger*	*Warning*	*Danger*	*No signal word*
Hazard Statement	*H200: Unstable Explosive*	*H201: Explosive; mass explosion hazard*	*H202: Explosive; severe projection hazard*	*H203: Explosive; fire, blast or projection hazard*	*H204: Fire or projection hazard*	*H205: May mass explode in fire*	*No hazard statement*
Pre-cautionary Statement Prevention	*P201* *P250* *P280*	*P210* *P230* *P234* *P240* *P250* *P280*	*P210* *P230* *P234* *P240* *P250* *P280*	*P210* *P230* *P234* *P240* *P250* *P280*	*P210* *P234* *P240* *P250* *P280*	*P210* *P230* *P234* *P240* *P250* *P280*	*No pre-cautionary statement*
Pre-cautionary Statement Response	*P370 + P372 + P380 + P373*	*P370 + P372 + P380 + P373*	*P370 + P372 + P380 + P373*	*P370 + P372 + P380 + P373*	*P370 + P372 + P380 + P373* *P370 + P380 + P375*	*P370 + P372 + P380 + P373*	*No pre-cautionary statement*
Pre-cautionary Statement Storage	*P401*	*P401*	*P401*	*P401*	*P401*	*P401*	*No pre-cautionary statement*
Pre-cautionary Statement Disposal	*P501*	*P501*	*P501*	*P501*	*P501*	*P501*	*No pre-cautionary statement*

The wording of the precautionary statements is found in CLP Annex IV, Part 2.

The intrinsic explosive properties of substances and mixtures regarding their stability and sensitivity are only investigated within Test Series 1, 2 and 3 during the acceptance procedure. Subsequent tests for the assignment to the Divisions 1.1, 1.2, 1.3 and 1.4 (Test Series 6) are

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[22] The combination statement P370+P372+P380+P373 applies to Division 1.4 except for compatibility group S in transport packaging, whereas the combination statement P370+P380+P375 applies to Division 1.4 compatibility group S in transport packaging.

carried out with the packaged substances, mixtures or articles. The type of packaging may significantly influence the test outcome.

Consequently, there are some deficiencies in the hazard communication of GHS for unpacked or repacked explosive substances and mixtures, especially for substances and mixtures, which are provisionally accepted in the class of explosives but are later rejected from this class due to their packaging in the assignment procedure (see CLP Annex I, Figure 2.1.1 and Figure 2.1.3 and section 2.1.4.5). These substances and mixtures have explosive properties but there might be no hazard communication about these properties due to the subsequent classification in a hazard class other than the class of explosives. Musk xylene is an example which illustrates this issue (see section 2.1.7.2). The results of Test Series 6 for musk xylene in the specified packaging led to the exclusion of this substance from the hazard class of explosives. But musk xylene on its own (unpacked) shows explosive properties due to heating under confinement (Koenen test). Also repacking of the substance in a packaging other than the tested one can result in a completely different outcome of Test Series 6.

It is due to this dependence on the transport configuration that the GHS classification of explosives has been thoroughly changed as of GHS revision 9, see the introduction (section 2.1.1).

2.1.5.2. Additional labelling provisions

2.1.5.2.1. Packaging dependence

Explosives are normally classified in their transport packaging. The packaging itself may be crucial for the classification. This is clear from the Figure 2.1.3 in section 2.1.4.5 especially when it comes to Test Series 6. As such, the assignment of an explosive substance or mixture to a particular division within the hazard class of explosives is only valid for the substance and mixture in the packaging in which it was tested, which is usually the transport packaging. Because of the package-dependence of the classification, CLP Annex I, section 2.1.2.4 prescribes:

> **Annex I:** *2.1.2.4. If explosives are unpackaged or repacked in packaging other than the original or similar packaging, they shall be retested.*

Further, according to NOTE 1 to Table 2.1.2 in CLP Annex I, unpackaged explosives or explosives repacked in packaging other than the original or similar packaging must have the following label elements:

> **Annex I: 2.1.3.** ***Hazard communication***
>
> *[…]*
>
> *NOTE 1: Unpackaged explosives or explosives repackaged in packaging other than the original or similar packaging shall include the following label elements:*
>
> *(a) the pictogram: exploding bomb;*
>
> *(b) the signal word: 'Danger'; and*
>
> *I the hazard statement: 'explosive; mass explosion hazard'*
>
> *Unless the hazard is shown to correspond to one of the hazard categories in Table 2.1.2, in which case the corresponding symbol, signal word and/or the hazard statement shall be assigned.*

Normally, if explosives are unpackaged or repacked in packaging other than the original or similar packaging the classification procedure needs to be performed again to determine which Division the explosive belongs to in the new packaging. The label elements prescribed in NOTE 1 to Table 2.1.2, as quoted above, are the same as those of Division 1.1 and in practice this Division constitutes the most severe classification of a repackaged explosive. (Please note that Table 2.1.2

foresees also the hazard category ‘unstable explosive’, which is assigned on the basis of the intrinsic properties of a substance or mixture via Test Series 3 and it is not package dependent). Therefore, CLP allows labelling of a repackaged explosive with labelling corresponding to Division 1.1 instead of retesting. However, this overestimates the hazardous properties unless the explosive in fact belongs to Division 1.1.

Many explosives are supplied in inner packages which are placed together in an outer package and where the entity as a whole, i.e. the combination of inner and outer packages, constitutes the transport packaging. According to the UN RTDG Model Regulations and the modal transport regulations (ADR[23], RID[24], ADN[25] and IMDG[26] Code, ICAO TI[27]) the classification tests are performed in the transport packaging. Under Article 33(1) of CLP where the hazard pictograms(s) required by CLP relate to the same hazard as in the rules for the transport of dangerous goods, the respective CLP hazard pictogram(s) do not need to appear on the outer packaging.

The classification in accordance with rules on the transport of dangerous goods is almost entirely identical to the corresponding classification procedure used in CLP so the CLP classification will automatically be known for the transport packaging. However, the CLP classification for the inner package alone strictly speaking is not known to the manufacturer, importer or downstream user as this will not have been derived from the classification of the transport packaging. On the other hand, it is normally not practicable to perform the required tests on the inner packages. Therefore, normally the same classification as for the transport packaging may be assumed for the inner packages. The labelling requirements for the inner packages are those foreseen in Table 2.1.2 of CLP Annex I. However, the following exceptions apply:

- Transport packages in which the packaging is designed such that mass explosion is prevented by the packaging, e.g. by arranging the individual inner packages crosswise (so that they are not neighbouring each other) and by separating them with specified material. This is especially the case when packing instruction P101 according to section 4.1.5 of the ADR applies. In this case the inner package should be labelled in accordance with Note 1 to Table 2.1.2 of CLP Annex I (i.e. as Division 1.1 unless tested otherwise).
- Packages in which explosives of different divisions are contained (for such cases see especially the mixed packing provisions MP 20 to MP 24 in section 4.1.10 of the ADR).
- Furthermore, they do not apply if the packaging is changed, as stated in Note 1 to Table 2.1.2 of CLP Annex I.

2.1.5.2.2. Supplemental hazard information

Risk phrases carried through from the DSD and DPD, but which are not included in GHS, are codified as EU hazard statements or “EUH”. For explosive properties, EUH044 should be considered.

Annex II:

1.1.4. EUH044 – ‘Risk of explosion if heated under confinement’

For substances and mixtures not in themselves classified as explosive in accordance with section 2.1 of part 2 of Annex I, but which may nevertheless display explosive properties in practice if heated under sufficient confinement. In particular, substances which decompose

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[23] ADR: Agreement concerning the International Carriage of Dangerous Goods by Road

[24] RID: Regulation concerning the International Carriage of Dangerous Goods by Rail

[25] AND: European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways

[26] IMDG: International Maritime Dangerous Goods

[27] ICAO TI: International Civil Aviation Organisation Technical Instructions for the Safe Transport of Dangerous Goods by Air

explosively if heated in a steel drum do not show this effect if heated in less-strong containers.

Some substances and mixtures which may react explosively if heated under confinement are not covered adequately by the classification system. This may *e.g.* be the case for:

- substances or mixtures which are exempted from the class of explosives based on their packaging and according to results of the Test Series 6;
- substances or mixtures with a Self-Accelerating Decomposition Temperature (SADT) of more than 75 °C for a 50 kg package which therefore cannot be classified as self-reactive.

2.1.5.3. Further communication requirements

According to Note 2 to Table 2.1.2, explosive properties of certain substances and mixtures which are exempted from classification as explosives must be communicated to the user via the SDS (when one is required).

Annex I: 2.1.3. ***Hazard communication***

[…]

NOTE 2: Substances and mixtures, as supplied, with a positive result in Test Series 2 in Part I, Section 12, of the UN RTDG, 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 RTDG, Manual of Tests and Criteria,) still have explosive properties. The user shall 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 shall be communicated in Section 2 (Hazards identification) and Section 9 (Physical and chemical properties) of the Safety Data Sheet and other sections of the Safety Data Sheet, as appropriate.

2.1.6. Relation to transport classification

Division 1.1 – 1.6 within Class 1 of the UN RTDG Model Regulations covers explosive substances, mixtures and articles. Normally, the transport classification in accordance with the UN RTDG Model Regulations and the modal transport regulations (ADR, RID, ADN and IMDG Code, ICAO TI) can be used one-to-one when deriving the CLP classification for explosives. Although, strictly speaking, this classification is only valid for the transport configuration, no re-classification or re-testing is normally required to derive the corresponding classification according to CLP. See Annex I for additional information on transport classification in relation to CLP classification.

For the use of other packaging or for unpacked substances and mixtures the additional labelling provisions (see section 2.1.5.2) have to be observed or re-testing is necessary.

2.1.7. Example of classification for explosives

Examples are given below for the classification of substances. Equivalent information would be needed for mixtures.

2.1.7.1. Example of substances and mixtures fulfilling the classification criteria

a. RESULTS FROM APPLICATION OF THE ACCEPTANCE PROCEDURE

Step	Test	Conclusion	Rationale
0. General data: 0.1 Name of the substance / mixture: **Hexanitrostilbene**			
1. Is the substance / mixture a candidate for ammonium nitrate emulsion, suspension or gel, intermediate for blasting explosive (ANE)?		No	
2. Is the substance / mixture manufactured with the view to producing a practical explosive or pyrotechnic effect?		Yes	
3. Test Series 3			
3.1 Thermal stability:	75 °C / 48-hour test (test 3(c))	Result: '—', thermally stable	
3.2 Impact sensitivity:	BAM Fallhammer test (Test Type 3 (a)(ii))	Result: Limiting impact energy 5 J	'—', not too dangerous in form tested
3.3 Friction sensitivity:	BAM friction test (Test Type 3 (b)(i))	Result: Limiting load > 240 N	'—', not too dangerous in form tested
4. Is the substance / mixture thermally stable?		Yes	
5. Is the substance / mixture too dangerous in the form in which it was tested?		No	
6. Conclusion:		**PROVISIONALLY ACCEPT INTO THIS CLASS**	
10.1 Exit:		Apply the assignment procedure	

b. RESULTS FROM APPLICATION OF THE ASSIGNMENT PROCEDURE

Step	Test	Conclusion	Rationale
1. Is the substance a candidate for Division 1.5?		No Result: Package the substance	
2. Test Series 6			
2.1 Effect of initiation in the package:	Test 6 (a) with detonator	Result: detonation, crater	

Step	Test	Conclusion	Rationale
2.2 Effect of propagation:	Type 6 (b) with detonator	Result: detonation of the whole stack of packages, crater	
2.4 Effect of fire engulfment:	Test 6 (c) may be waived because of the result of the Test 6 (b).		
3. Is the result a mass explosion?		Yes	
4. Conclusion:		**Assignment to Division 1.1**	

2.1.7.2. Example of substances and mixtures not fulfilling the classification criteria

This example is taken from the UN-MTC, section 10.5.2, Figure 10.7 (a).

c. RESULTS FROM APPLICATION OF THE ACCEPTANCE PROCEDURE

Step	Test	Conclusion	Rationale
0. General data: 0.1 Name of the substance / mixture: **5-tert-butyl-2,4,6-trinitro-m-xylene (musk xylene)**			
1. Is the substance / mixture a candidate for ammonium nitrate emulsion, suspension or gel, intermediate for blasting explosive ANE?		No	
2. Is the substance / mixture manufactured with the view to producing a practical explosive or pyrotechnic effect?		No	
3. Test Series 1			
3.1 Propagation of Detonation:	UN gap test (Test 1 (a))	Result:'+', propagation of detonation	
3.2 Effect of heating under confinement:	Koenen test (Test 1(b))	Result: Limiting diameter 12.0 mm	Fragmentation type 'F' '+', shows some explosive effects on heating under confinement

Step	Test	Conclusion	Rationale
3.3 Effect of ignition under confinement:	Time/pressure test (test 1(c)(i))	Result: '—', no effect on ignition under confinement	
4. Is it an explosive substance / mixture?		Yes	
5. Test Series 2			
5.1 Sensitivity to shock:	UN gap test (Test 2 (a))	Result: '—', not sensitive to shock	
5.2 Effect of heating under confinement:	Koenen test (Test 2 (b))	Result: Limiting diameter 12.0 mm	Fragmentation type 'F' '+', violent effect on heating under confinement.
5.3 Effect of ignition under confinement:	Time/pressure test (Test 2 (c)(i))	Result: '—', no effect on ignition under confinement	
6. Is the substance / mixture too insensitive for acceptance into this class?		No	
Conclusion:		Substance to be considered for this class	
7. Test Series 3			
7.1 Thermal stability:	75 °C/48-hour test (Test 3 (c))	Result: '—', thermally stable	
7.2 Impact sensitivity:	BAM Fallhammer test (Test 3 (a)(ii))	Result: Limiting impact energy 25 J", not too dangerous in form tested.	
7.3 Friction sensitivity:	BAM friction test (Test 3 (b)(i))	Result: Limiting load > 360 N	'—', not too dangerous in form tested
8. Is the substance / mixture thermally stable?		Yes	
9. Is the substance / mixture too dangerous in the form in which it was tested?		No	
10. Conclusion:		**PROVISIONALLY ACCEPT INTO THIS CLASS**	
10.1 Exit		Apply the assignment procedure	

Step	Test	Conclusion	Rationale
		The explosive properties shall be communicated in the safety data sheet in accordance with section 2.1.5.3 above.	

d. RESULTS FROM APPLICATION OF THE ASSIGNMENT PROCEDURE

Step	Test	Conclusion	Rationale
1. Is the substance a candidate for Division 1.5?		No Result: Package the substance	
2. Test Series 6			
2.1 Effect of initiation in the package:	Test 6 (a) with detonator	Result: Only localised decomposition around detonator	No significant reaction
2.2 Effect of ignition in the package:	Test 6 (a) with igniter	Result: Only localised decomposition around igniter	No significant reaction
2.3 Effect of propagation:	Type 6(b) test not required as no effect outside package between packages in 6(a) test		
2.4 Effect of fire engulfment:	Test 6	Result: Only slow burning with black smoke occurred.	No effects which would hinder fire fighting
3. Is the result a mass explosion?		No	
4. Is the major hazard that from dangerous projections?		No	
5. Is the major hazard radiant heat and/or violent burning but with no dangerous blast or projection hazard?		No	
6. Is there nevertheless a small hazard in the event of ignition or initiation?		No	
7. Is the substance manufactured with the view to producing a practical explosive or pyrotechnic effect?		No	
8. Conclusion:		**NOT AN EXPLOSIVE**	

Step	Test	Conclusion	Rationale
8.1 Exit		Consider for another class (e.g. flammable solid)	

2.2. FLAMMABLE GASES

2.2.1. Introduction

The criteria for 'flammable gases' are found in CLP Annex I, section 2.2 and were taken from those in chapter 2.2 of GHS[18].

2.2.2. Definitions and general considerations for classification of flammable gases

Annex I*: 2.2.1. Definitions*

2.2.1.1 Flammable gas means a gas or gas mixture having a flammable range with air at 20 °C and a standard pressure of 101.3 kPa.

2.2.1.2. A pyrophoric gas means 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 means a flammable gas that is able to explode even in the absence of air or oxygen.

The flammable range of a flammable gas is the range between its lower explosion limit (LEL) and its upper explosion limit (UEL). The term 'explosion limit' is synonymous to 'flammability limit', sometimes used outside the EU.

2.2.3. Relation to other physical hazards

Annex I: *2.2.2. Classification criteria*

[…]

NOTE 1: Aerosols shall not be classified as flammable gases; see Section 2.3.

NOTE 2: In the absence of data allowing classification into Category 1B, a flammable gas that meets the criteria for Category 1A is classified by default in Category 1A.

For flammable gases that are contained in aerosol dispensers see section 2.3 Aerosols. If classified as aerosols, they do not have to be classified as flammable gases in addition.

In many cases, simultaneous classification of gases as flammable and gases under pressure is applicable, since they are often placed on the marked in pressurised containers.

Generally, simultaneous classification of gases as flammable and oxidizing is not applicable when placed on the market and supposed to be transported (UN RTDG Model Regulations, section 2.2.4).

When a gas mixture contains flammable and oxidizing gases, it can be classified as one of the following three categories:

- Gases under pressure, if the oxygen content is less than or equal to 23.5 % and the content of the flammable gases is below the maximum concentration of flammable gas for the mixture to be non-flammable or below the lower explosion limit.
- Oxidizing, if the oxygen content is more than 23.5 % and the content of the flammable gases below the lower explosion limit.
- Flammable, if the content of the flammable gases is more than the maximum concentration of flammable gas for the mixture to be non-flammable and more than the lower explosion limit.

2.2.4. Classification of substances, mixtures or articles as flammable gases

2.2.4.1. Identification of hazard information

Many gaseous substances are classified as flammable gases in Annex VI of CLP and more gases are classified as flammable gases in the UN RTDG Model Regulations.

If the classification of flammable gases given in Annex VI of CLP includes the former category 1 instead of the new categories 1A, 1B, the gas should primarily be classified as 1A, unless there is data available justifying 1B. Please refer to Note 2 on CLP Annex I, Table 2.2.1; see also below in section 2.2.4.3.

Please note that the European Industrial Gases Association (EIGA) document 169 applies the new criteria for a number of flammable gases based on lower explosion limits. However, these classifications should not be applied if they differ from the classification derived based on the CLP criteria, see NOTE 2 in section 2.2.2[28].

For gases that are not listed in Annex VI of CLP or in the UN RTDG Model Regulations, there is ample scientific literature giving the flammability range for most gases (*e.g.,* ISO 10156:2017[29] *Gas cylinders — Gases and gas mixtures — Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets*, or BS EN ISO 80079-20-1:2019[30], *Explosive atmospheres – Part 20-1: Material characteristics for gas and vapour classification – Test methods and data*).

Information on gases classified as pyrophoric can be found in chapter 4.2 of EIGA document 169.

Information on a number of chemically unstable gases can be found in the UN-MTC, section 35. Tables 35.1 and 35.2 within UN-MTC, section 35.3.2.1 contain information on a number of chemically unstable gases together with their classification and category.

To distinguish between the category 1A and 1B, CLP allows the use of lower explosion limit data or of fundamental burning velocity data. For information on fundamental burning velocity see ISO 817:2014 "*Refrigerants-Designation and safety classification, Annex C: - Method of test for burning velocity measurement of flammable gases*".

If no or insufficient information is available, screening and waiving possibilities should be checked. Depending on the results, testing might be necessary, see section 2.2.4.4.

2.2.4.2. Screening procedures and waiving of testing

Gas mixtures are often prepared on demand, so there are numerous gas mixtures containing flammable gases on the market. However, there are a limited number of test reports for the flammability of gas mixtures in the scientific literature. Tests are time consuming and expensive. In most of the cases, a calculation method as described in ISO 10156 (see section 2.2.4.2) may be applied.

If the calculations in accordance with ISO 10156 show that a gas mixture is not flammable, it is also not classified as pyrophoric. Waiving possibilities for pyrophoric gases and chemical instability are given in CLP Annex I, sections 2.2.4.3 and 2.2.4.2, respectively. See also waiving possibilities for chemically instable gases and gas mixtures given in UN-MTC, section 35.

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[28] If there is divergence between the classification in EIGA document 169 and the classification based on Note 2, a CLH dossier can be submitted to modify the classification in Annex VI, see ECHA guidance on the preparation of CLH dossier.

[29] Hereafter: ISO 10156

[30] Hereafter: IEC 80079-20-1

Annex I: ***2.2.4 Additional Classification Considerations***

2.2.4.3. 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, shall be classified as a pyrophoric gas. Expert judgement on the properties and physical hazards of pyrophoric gases and their mixtures shall 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. Chemical instability shall be determined in accordance with the method described in Part III of the UN RTDG, Manual of Tests and Criteria. If the calculations in accordance with ISO 10156 as amended show that a gas mixture is not flammable it is not necessary to carry out the tests for determining chemical instability for classification purposes.

Expert judgement should be applied to decide whether a flammable gas or gas mixture is a candidate for classification as chemically unstable to avoid unnecessary testing of gases where there is no doubt that they are stable. Functional groups indicating chemical instability in gases are triple bonds, adjacent or conjugated double-bonds, halogenated double-bonds and strained rings.

Gas mixtures containing only one chemically unstable gas are not considered as chemically unstable and therefore do not have to be tested for classification purposes if the concentration of the chemically unstable gas is below the higher of the following generic concentration limits:

a. the lower explosion limit (LEL) of the chemically unstable gas; or

b. 3 mole %.

Furthermore, for some gases there are also specific concentration limits available and these are indicated in Tables 35.1 and 35.2 within UN-MTC, section 35.3.2.1.

2.2.4.3. Classification criteria

The criteria for the classification of flammable gases are given in the following table:

Annex I: *Table 2.2.1* ***Criteria for categorisation of flammable gases***

Category			*Criteria*
1A	*Flammable gas*		*Gases, which at 20 °C and a standard pressure of 101.3 kPa are:* *(a) 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* *unless data show they meet the criteria for Category 1B*
	Pyrophoric gas		*Flammable gases that ignite spontaneously in air at a temperature of 54 °C or below*
		A	*Flammable gases which are chemically unstable at 20 °C and a standard pressure of 101.3 kPa*

	Chemically unstable gas	*B*	*Flammable gases which are chemically unstable at a temperature greater than 20 °C and/or a pressure greater than 101.3 kPa*
1B	*Flammable gas*		*Gases which meet the flammability criteria for Category 1A, but which are not pyrophoric, nor chemically unstable, and which have at least either:* *(a) a lower flammability limit of more than 6 % by volume in air; or* *(b) a fundamental burning velocity of less than 10 cm/s;*
2	*Flammable gas*		*Gases, other than those of Category 1A or 1B, which, at 20 °C and a standard pressure of 101,3 kPa, have a flammable range while mixed in air.*
[…] *NOTE 2: In the absence of data allowing classification into Category 1B, a flammable gas that meets the criteria for Category 1A is classified by default in Category 1A.* *NOTE 3: Spontaneous ignition for pyrophoric gases is not always immediate, and there may be a delay.* *NOTE 4: In the absence of data on its pyrophoricity, a flammable gas mixture shall be classified as a pyrophoric gas if it contains more than 1 % (by volume) of pyrophoric component(s)*			

2.2.4.4. Testing and evaluation of hazard information

ISO 10156 describes a test method and a calculation method for the classification of flammable gas mixtures. The test method may be used in all cases but must be used when the calculation method cannot be applied.

The calculation method applies to gas mixtures and can be applied when the T_{Ci} for all flammable components and the K_k for all inert components are available. These are listed for a number for gases in ISO 10156. In the absence of T_{Ci} value for a flammable gas, the value of the LFL can be used. In the absence of a K_k value for a non-flammable and non-oxidising gas with three atoms or more, a K_k value of 1.5 shall be used. The calculation method described in ISO 10156 uses the criterion that a gas mixture is considered non-flammable in air if:

Equation 2.2.4.4.a

$$\sum_{i=1}^{n} \frac{A'_i}{T_{ci}} \leq 1$$

where:

Equation 2.2.3.3.b

$$A'_i = \frac{A_i}{\sum_{i=1}^{n} A_i + \sum_{k=1}^{p} K_k B_k}$$

and where:

A'_i is the equivalent content of the *i*:th flammable gas in the mixture, in %

T_{ci} is the maximum content of flammable gas i which, when mixed with nitrogen, is not flammable in air, in %

A_i is the molar fraction of the *i*:th flammable gas in the mixture, in %

B_k is the molar fraction of the *k*:th inert gas in the mixture, in %

K_k is the coefficient of equivalency of the inert gas *k* relative to nitrogen

n is the number of flammable gases in the mixture

p is the number of inert gases in the mixture

The principle of the calculation method is the following:

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 coefficient for the inert gas K_k. From this the equivalent contents A'_i are then derived through Equation 2.2.3.3.b, which should be viewed as the corresponding concentration of the flammable gases if nitrogen was the only inert gas present in the mixture. In Equation 2.2.4.4.a, the equivalent contents are then compared to the constants T_{Ci}, which have been experimentally found using nitrogen as the (only) inert gas.

It should be noted that ISO 10156 uses molar fractions in some of its equations. For most gases under normal (i.e. non-extreme) conditions the volume fraction can be assumed to be equal to the molar fraction, which is the same as assuming ideal gas behaviour for all gases in the mixture. Furthermore, although normally a fraction is a number ranging from 0 to 1, in this case it is easier to express it as percentage, i.e. the fraction multiplied by 100.

The calculation methods described in ISO 10156 allows the determination of a lower explosion limit and therefore the calculation method can determine whether the mixture is classified as a flammable gas in category 1A or category 1B.

For mixtures of flammable gases, the Le Chatelier's formula is commonly used to predict lower explosion limits. The formula can be applied to flammable mixtures but not to potentially explosive mixtures. Le Chatelier's formula cannot be used for calculation of upper explosion limits. Furthermore, it cannot be used for partially halogenated hydrocarbons or oxidisers other than air.

According to this formula, the lower flammability limit (L_M) of a mixture of flammable gases is given by the following equation:

Equation 2.2.4.4.c

$$\frac{100}{L_M} = \frac{A1}{L1} + \frac{A2}{L2} + \frac{A3}{L3} + \cdots + \frac{An}{Ln}$$

Where *L* is the lower flammability limit in % and *A* is the molar fraction in % of the flammable gas in a mixture of *n* flammable gases.

For mixtures of flammable gases with inert gases other than nitrogen and air, Equation 2.2.4.4.d takes into account the nitrogen equivalent (K_k) of inert gases other than nitrogen.

Equation 2.2.4.4.d

$$L_M = \frac{100}{\sum_{i=1}^{n} A_{\frac{i}{L'_i}}}$$

where L'_i is given by

Equation 2.2.4.4.e

$$L'_i = \frac{\left(100 - L'_M - (1-K) * \frac{\sum_{k=1}^{p} B_k}{\sum_{i=1}^{n} A_i} * L'_M\right)}{(100 - L'_M)} * L_i$$

where:

K is the average of K_k values of the inert gases weighted according to their molar fractions.

The calculation method described in ISO 10156 does not determine a flammability range so the calculation method cannot determine whether the mixture is flammable in category 1A/1B or category 2. Therefore, to be on the safe side, mixtures determined to be flammable according to the calculation method are classified as flammable gas in category 1A or 1B. The gas mixture can be classified as flammable gas category 2 only if it contains flammable gases classified as flammable gas category 2. In these cases, the lower and the upper explosion limits can be determined by using a suitable test method (e.g. EN 1839:2017[31] or ISO 10156).

For mixtures containing both flammable and oxidising components, special calculation methods are described in ISO 10156.

In case a gas or gas mixture needs to be tested for its flammability, a recognised international standard must be used; CLP explicitly refers to ISO 10156. Instead of the test apparatus according to ISO 10156, the test apparatus for the tube method according to clause 4.2 of EN 1839, '*Determination of the explosion limits and the limiting oxygen concentration (LOC) for flammable gases and vapour'* may be used.

Gases (including gas mixtures) that are classified as flammable have to be considered for classification as pyrophoric and/or chemically unstable in addition. If the screening procedures described in section 2.2.4.2 are not conclusive, the gas or gas mixture has to be tested.

Gases do not have to be tested for pyrophoricity for classification purposes (see above in 2.2.4.2) but if tested, the test must be carried out at 54 °C in accordance with either ISO/IEC 80079-20-1:2017 '*Explosive atmospheres – Part 20-1: Material characteristics for gas and vapour classification – Test methods and data*' or DIN[32] 51794 '*Determining the ignition temperature of petroleum products*'.

The test method for chemical instability of gases is described in UN-MTC, section 35. It uses the same equipment as the test method for oxidising gases according to ISO 10156 and so could be applied by laboratories that also carry out the tests for oxidising gases.

If information on other gases or gas mixtures than the ones mentioned in the tables referred to in the last paragraph of 2.2.4.2 is needed, testing should be performed. It should be noted that the test method described in UN-MTC, section 35, does not cover gas mixtures where the components can react dangerously with each other, *e.g.* flammable and oxidising gases. It is not applicable to liquefied gas mixtures because the gaseous phase above a liquefied gas mixture may generally have a different composition than the liquefied phase (except if the mixture is azeotropic and at its azeotropic point), so that the gas may become chemically unstable only after withdrawal. This should be communicated via the SDS.

2.2.4.5. Decision logics

Classification of flammable gases is laid down in the following flow-charts which are applicable according to CLP.

❗ NOTE: The person responsible for the classification of flammable gases should be experienced in this field and be familiar with the criteria for classification.

Decision logic for flammable gases

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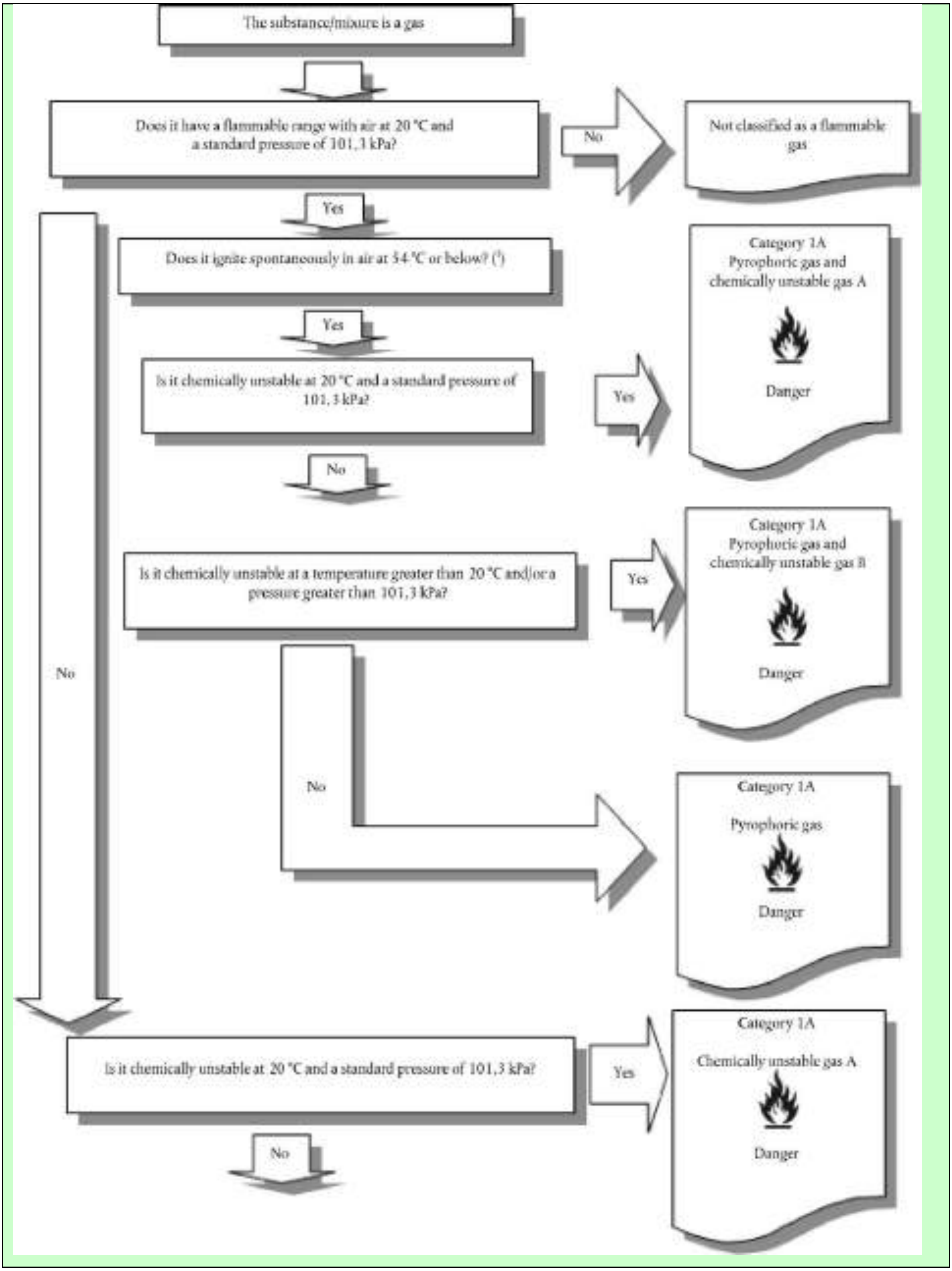
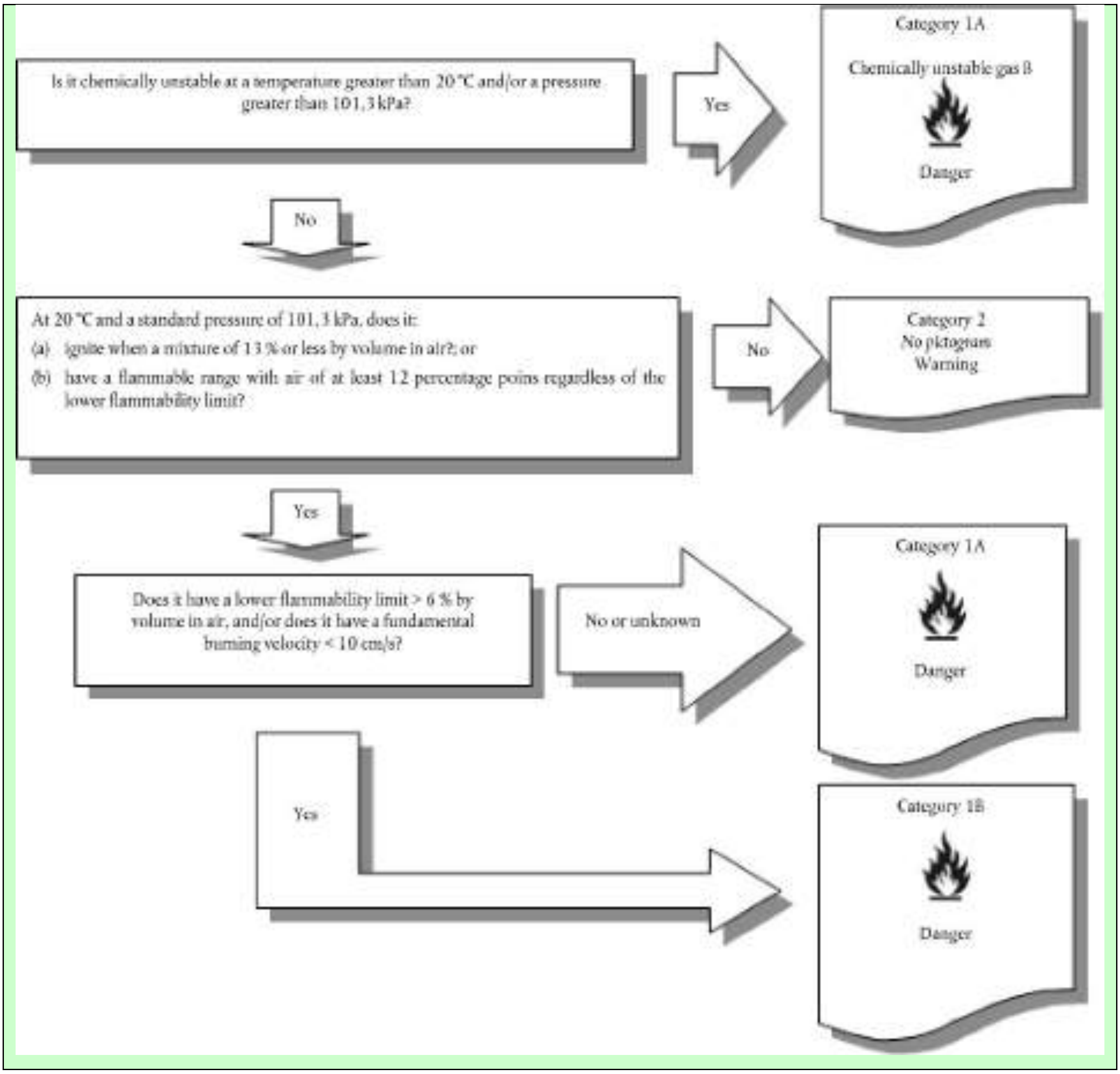
[31] Hereafter: EN 1839

[32] DIN: Deutsches Institut für Normung

Annex I: *Figure 2.2.1* ***Flammable gases***


The substance/mixture is a gas
Does it have a flammable range with air at 20 °C and a standard pressure of 101,3 kPa?
No
Not classified as a flammable gas
Yes
No
Does it ignite spontaneously in air at 54 °C or below? (¹)
Category 1A
Pyrophoric gas and chemically unstable gas A
Danger
Yes
Is it chemically unstable at 20 °C and a standard pressure of 101,3 kPa?
Yes
No
Category 1A
Pyrophoric gas and chemically unstable gas B
Danger
Is it chemically unstable at a temperature greater than 20 °C and/or a pressure greater than 101,3 kPa?
Yes
No
Category 1A
Pyrophoric gas
Danger
Is it chemically unstable at 20 °C and a standard pressure of 101,3 kPa?
Yes
Category 1A
Chemically unstable gas A
Danger
No



Is it chemically unstable at a temperature greater than 20 °C and/or a pressure greater than 101,3 kPa?

At 20 °C and a standard pressure of 101,3 kPa, does it:

(a) ignite when a mixture of 13 % or less by volume in air?; or

(b) have a flammable range with air of at least 12 percentage poins regardless of the lower flammability limit?

Does it have a lower flammability limit > 6 % by volume in air, and/or does it have a fundamental burning velocity < 10 cm/s?

2.2.5. Hazard communication for flammable gases

2.2.5.1. Pictograms, signal words, hazard statements and precautionary statements

Annex I: ***2.2.3.*** *Table 2.2.2* ***Label elements for flammable gases***

	Category 1A	*Gases categorised as 1A meeting pyrophoric or unstable gas A/B criteria*			*Category 1B*	*Category 2*
		Pyrophoric gas	*Chemically unstable gas*			
			Category A	*Category B*		
GHS Pictogram						*No pictogram*
Signal Word	*Danger*	*Danger*	*Danger*	*Danger*	*Danger*	*Warning*
Hazard Statement	*H220: Extremely flammable gas*	*H220: Extremely flammable gas* *H232: May ignite spontaneously if exposed to air*	*H220: Extremely flammable gas* *H230: May react explosively even in the absence of air*	*H220: Extremely flammable gas* *H231: May react explosively even in the absence of air at elevated pressure and/or temperature*	*H221: Flammable gas*	*H221: Flammable gas*
Precautionary Statement Prevention	*P210*	*P210* *P222* *P280*	*P202* *P210*	*P202* *P210*	*P210*	*P210*
Precautionary Statement Response	*P377* *P381*	*P377* *P381*	*P377* *P381*	*P377* *P381*	*P377* *P381*	*P377* *P381*

Precautionary Statement Storage	*P403*	*P403*	*P403*	*P403*	*P403*	*P403*
Precautionary Statement Disposal						

Annex I: ***2.2.3 Hazard Communication***

[…]

If a flammable gas or gas mixture is classified as pyrophoric and/or chemically unstable, then all relevant classification(s) shall be communicated on the safety data sheet as specified in Annex II of Regulation (EC) No 1907/2006, and the relevant hazard communication elements included on the label.

[…]

The wording of the precautionary statements is found in CLP Annex IV, Part 2.

2.2.6. Relation to transport classification

The criteria for flammable gases categories 1A and 1B do not completely correspond to the criteria that are in use for classifying flammable gases in the UN RTDG Model Regulations. Consequently, all gases listed as flammable in the UN RTDG Model Regulations and in the modal transport regulations (ADR, RID, ADN and IMDG Code, ICAO TI) must be classified as Flam. Gas 1A (H220) or 1B (H221). Gases are not classified for chemical instability or for pyrophoricity in the UN RTDG Model Regulations. See Annex I for additional information on transport classification in relation to CLP classification.

2.2.7. Example of classification for flammable gases

EXAMPLE MIXTURE: 2 % (H_2) + 6 % (CH_4) + 27 % (Ar) + 65 % (He)

Calculation steps:

Example for the classification of a gas mixture containing flammable gases based on the calculations of ISO 10156.

***Step 1*: Assign the gases and state their molar fractions, assuming the molar fractions are equal to the volume fractions (ideal gas behaviour for all gases).**

H_2 is flammable gas 1, Press. Gas (Comp), H280; Flam. Gas 1A, H220	yielding A_1 = 2 mole %
CH_4 is flammable gas 2, Press. Gas (Comp), H280; Flam. Gas 1A, H220	yielding A_2 = 6 mole %
Ar is inert gas 1, Press. Gas (Comp), H280;	yielding B_1 = 27 mole %
He is inert gas 2, Press. Gas (Comp), H280	yielding B_2 = 65 mole %
$n=2$	since there are two flammable gases in the mixture
$p=2$	since there are two inert gases in the mixture

Step 2: Assessment of pyrophoricity and chemical instability

As no substance of the mixture is either pyrophoric or chemically unstable the mixture is not pyrophoric and not chemical unstable.

***Step 3:* Look up the values of T_{ci}, K_k and L_i in ISO 10156.**

T_{c1} =	5.5 mole %
T_{c2} =	8.7 mole %
L_{i1} =	4.0 mole %
L_{i2} =	4.4 mole %
K_1 =	0.55
K_2 =	0.9

***Step 4:* Calculate the equivalent gas contents A'_i for the flammable gases according to** Equation 2.2.3.3.b

$$A'_1 = \frac{2}{(2+6)+(0.55\times 27+0.9\times 65)} = 2.46 \text{ mole } \%$$

$$A'_2 = \frac{6}{(2+6)+(0.55\times 27+0.9\times 65)} = 7.38 \text{ mole } \%$$

***Step 5:* Calculate the flammability of the gas mixture according to** Equation 2.2.4.4.a

$$\sum_{i=1}^{2} \frac{A'_i}{T_{ci}} = \frac{A'_1}{T_{c1}} + \frac{A'_2}{T_{c2}} = \frac{2.46}{5.5} + \frac{7.38}{8.7} = 1.29$$

***Step 6*: Compare the outcome to the criterion in** Equation 2.2.4.4.a

Since 1.29 > 1, this particular gas mixture is considered to be flammable.

EXAMPLE MIXTURE: 2 % (H_2) + 6 % (CH_4) + 27 % (Ar) + 65 % (He)

***Step 7*: Calculate the lower explosion limit L_M according to** Equations 2.2.4.4.c, 2.2.4.4.d and 2.2.2.4.e

$$L_M = \frac{100}{\frac{25}{4} + \frac{75}{4.4}} = 4.29 \; mole \; \%$$

$$K = \frac{27 * 0.55 + 65 * 0.9}{(27 + 65)} = 0.797$$

$$L'_{H2} = \frac{\left(100 - 4.29 - (1 - 0.797) * \frac{27+65}{2+6} * 4.29\right)}{(100 - 4.29)} * 4 = 3.58 \; mole \; \%$$

$$L'_{CH4} = \frac{\left(100 - 4.29 - (1 - 0.797) * \frac{27+65}{2+6} * 4.29\right)}{(100 - 4.29)} * 4.4 = 3.94 \; mole \; \%$$

$$L_M = \frac{100}{\frac{2}{3.58} + \frac{6}{3.94}} = 48.04\, mole\ \%$$

Step 8: **Compare the outcome to the criterion in CLP**

As the upper explosion limit cannot be calculated, it is not known if this mixture has a flammable range with air of at least 12 percentage points regardless of the lower flammable limit.

Since L_M is > 6%, this particular gas mixture is classified as a flammable gas category 1B, H221.

In addition, it is classified as gas under pressure, H280.

2.2.8. References

Le Chatelier, H. L., *Note sur le dosage du grisou par les limetes de l'inflammabilité*, Annales des mines 19 (1891) 388–395

2.3. AEROSOLS

2.3.1. Introduction

As of GHS revision 8, chapter 2.3 regarding aerosols has been split into two sub-chapters – one for aerosols and the other for chemicals under pressure. The latter is a new hazard class from GHS revision 8 and onwards, which is not yet implemented in the current version of the CLP Regulation[18]. Other than a renumbering of the paragraphs there was no change for the class of aerosols.

The European Aerosol Dispenser Directive 75/324/EEG (ADD), as regards the flammability and pressure hazards, is fully aligned with the classification (and labelling) of aerosols under CLP.

2.3.2. Definitions and general considerations for classification of aerosols

Annex I: *2.3.1. Definitions*

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.

It should be noted that the type of aerosol container may affect the outcome of flammability tests for aerosols which may, in turn, affect the classification if it is based on testing.

2.3.3. Relation to other physical hazards

As the class of aerosols includes the flammability aspects, they should not be classified as flammables gases, flammable liquids or flammable solids in addition. However, other classifications may apply to aerosols (as for any other container).

Annex I, 2.3.2.1.

[…]

NOTE 2: Aerosols do not fall additionally within the scope of Sections 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.

2.3.4. Classification of aerosols

2.3.4.1. Classification criteria

Annex I:

2.3.2.1. *Aerosols shall be classified in one of the three categories of this hazard class, depending on their flammable properties and their heat of combustion. They shall 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 following criteria set out in this Part:*

– Flammable gases (see Section 2.2);

– Liquids with a flash point ≤ 93 °C, which includes Flammable Liquids according to section 2.6;

– Flammable solids (see Section 2.7);

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

[…]

2.3.2.2. *An aerosol shall be 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) in accordance with Figures 2.3.1(a) to 2.3.1(c) of this Annex and sub-sections 31.4, 31.5 and 31.6 of Part III of the UN RTDG, Manual of Tests and Criteria. Aerosols which do not meet the criteria for inclusion in Category 1 or Category 2 shall be classified in Category 3.*

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 section shall be classified as aerosols, Category 1.

Under the ADD and in UN-MTC, section 31, flammability classification for aerosols refers to ‘extremely flammable’, ‘flammable’ and ‘not classified as flammable aerosol’. This respectively corresponds to the terms ‘Aerosol, category 1’, ‘Aerosol, category 2’ and ‘Aerosol, category 3’ which are used in CLP.

In CLP, the full set of criteria including those based on testing are included only by reference (see CLP Annex I, section 2.3.2.2) and in the decision logic. GHS revision 7 contains the following criteria table with the full set of criteria:

Table 2.1 Criteria for aerosols (Table 2.3.1 of the GHS)

Category	Criteria
1	(a) Any aerosol that contains ≥ 85 % flammable components (by mass) and has a heat of combustion of ≥ 30 kJ/g; (b) Any aerosol that dispenses a spray that, in the ignition distance test, has an ignition distance of ≥ 75 cm; or (c) Any aerosol that dispenses a foam that, in the foam flammability test, has: (i) a flame height of ≥ 20 cm and a flame duration of ≥ 2 s; or (ii) a flame height of ≥ 4 cm and a flame duration of ≥ 7 s.
2	(a) Any aerosol that dispenses a spray that, based on the results of the ignition distance test, does not meet the criteria for Category 1, and which has: (i) a heat of combustion of ≥ 20 kJ/g; (ii) a heat of combustion of < 20 kJ/g along with an ignition distance of ≥ 15 cm; or (iii) a heat of combustion of < 20 kJ/g and an ignition distance of < 15 cm along with either, in the enclosed space ignition test: - a time equivalent of ≤ 300 s/m^3; or - a deflagration density of ≤ 300 g/m^3; or (b) Any aerosol that dispenses a foam that, based on the results of the aerosol foam flammability test, does not meet the criteria for Category 1, and which has a flame height of ≥ 4 cm and a flame duration of ≥ 2 s.
3	(a) Any aerosol that contains ≤ 1 % flammable components (by mass) and that has a heat of combustion < 20 kJ/g; or (b) Any aerosol that contains > 1 % (by mass) flammable components or which has a heat of combustion of ≥ 20 kJ/g but which, based on the results of the ignition distance test, the enclosed space ignition test or the aerosol foam flammability test, does not meet the criteria for Category 1 or Category 2.

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 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.*

NOTE 3: *Aerosols do not fall additionally within the scope of chapter 2.2 (flammable gases), section 2.3.2 (chemicals under pressure), chapters 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.*

The chemical heat of combustion is determined in accordance with CLP Annex I, section 2.3.4.1 which is identical to point 1.10 of the Annex to ADD.

2.3.4.2. Testing and evaluation of hazard information

Results from the ignition distance test, the enclosed space test, and the foam flammability test may be used for classification related to the flammability of aerosols. The enclosed space test should be performed only for spray aerosols and, if no ignition was observed, during the ignition distance test. Performing the enclosed space test erroneously may lead to safety issues. The test methods referred to above are described under point 6.3 of the Annex to ADD and are therefore available in all EU languages. They are also described in the UN-MTC section 31.

After evaluation according to the appropriate criteria (see previous sections) the aerosol is classified in one of the three categories.

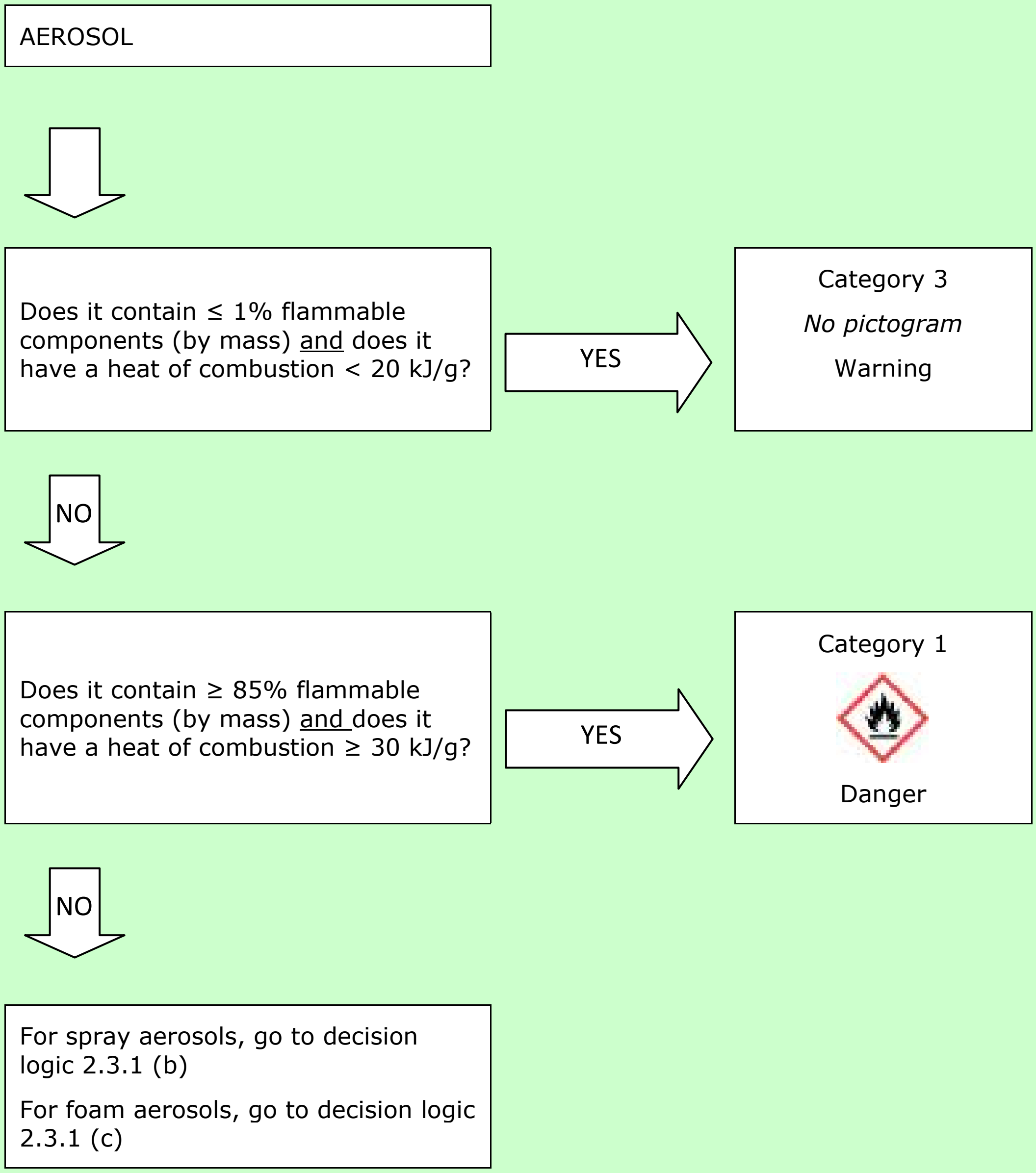
2.3.4.3. Decision logics

The classification procedure is also laid down in the following flow-charts which are applicable according to CLP.

NOTE: The person responsible for the classification of aerosols should be experienced in this field and be familiar with the criteria for classification.

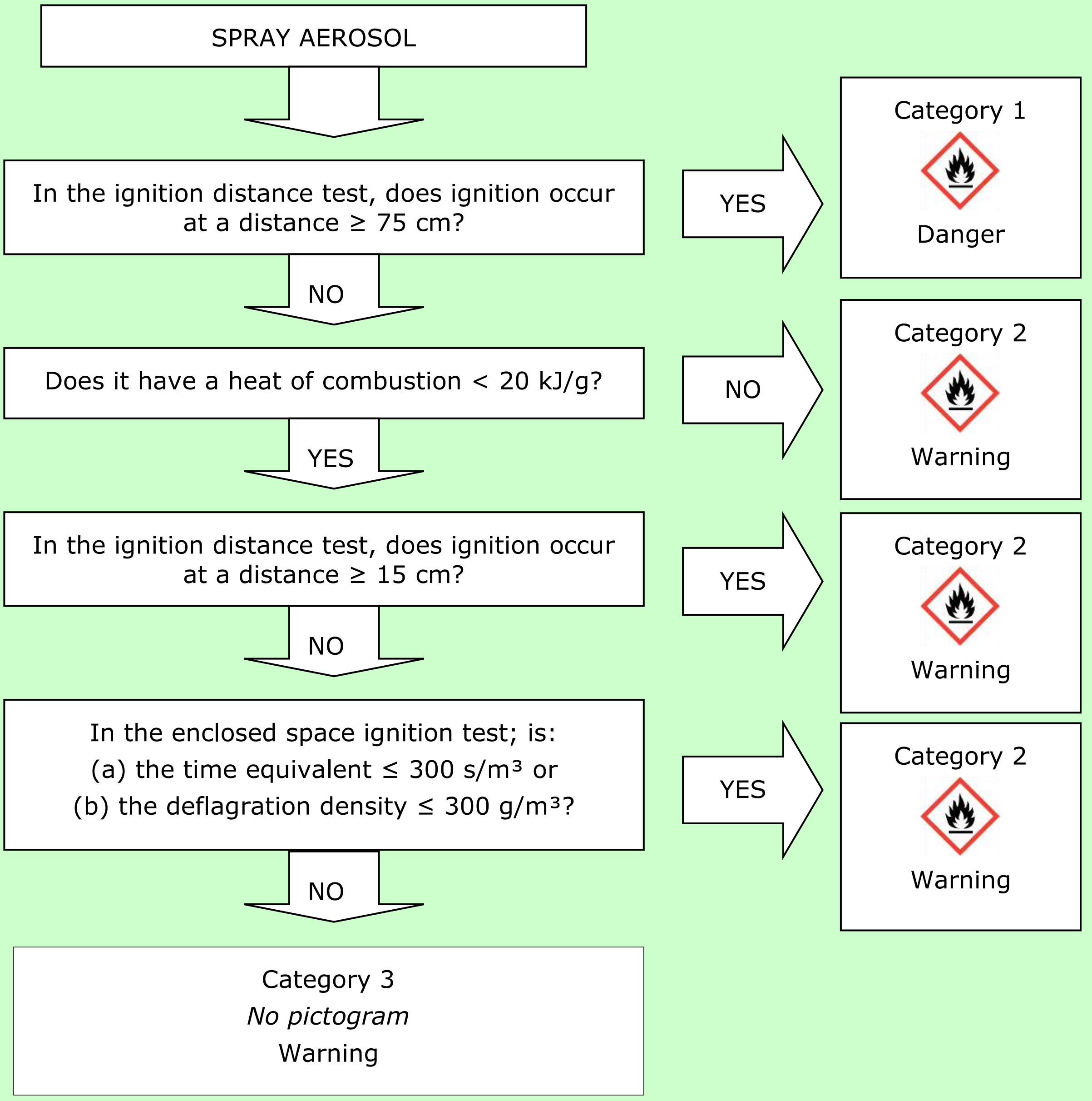
2.3.4.3.1. Decision logics for aerosols

Annex I: *Figure 2.3.1 (a)* **for aerosols**



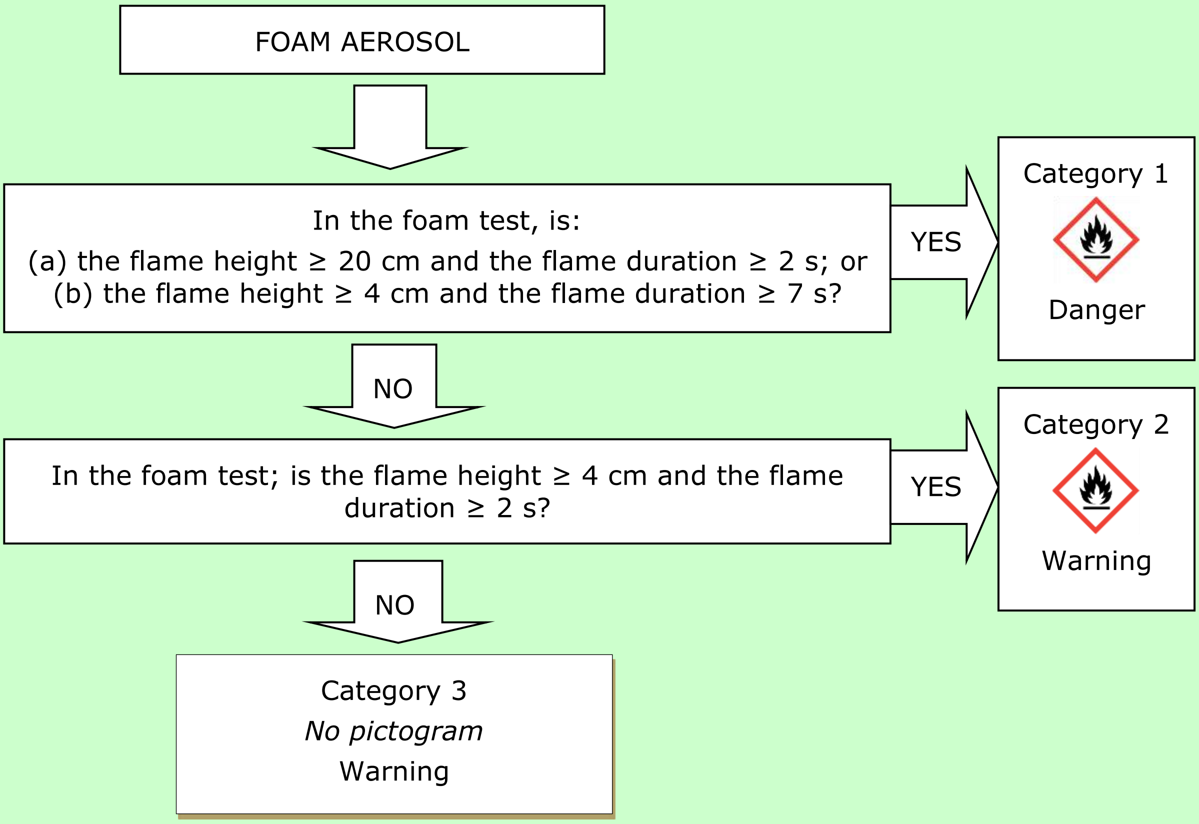
2.3.4.3.2. Decision logics for spray aerosols

Annex I: *Figure 2.3.1 (b)* **Spray aerosols**



2.3.4.3.3. Decision logics for foam aerosols

Annex I: *Figure 2.3.1 (c)* **Foam aerosols**



2.3.5. Hazard communication for aerosols

2.3.5.1. Pictograms, signal words, hazard statements and precautionary statements

Annex I: *Table 2.3.1* ***Label elements for aerosols***

Classification	*Category 1*	*Category 2*	*Category 3*
GHS Pictograms			*No pictogram*
Signal Word	*Danger*	*Warning*	*Warning*
Hazard Statement	*H222: Extremely flammable aerosol* *H229: Pressurised container: May burst if heated.*	*H223: Flammable aerosol* *H229: Pressurised container: May burst if heated.*	*H229: Pressurised container: May burst if heated.*

Precautionary Statement Prevention	*P210* *P211* *P251*	*P210* *P211* *P251*	*P210* *P251*
Precautionary Statement Response			
Precautionary Statement Storage	*P410 + P412*	*P410 + P412*	*P410 + P412*
Precautionary Statement Disposal			

The wording of the precautionary statements is found in CLP Annex IV, Part 2.

2.3.5.2. Additional labelling provisions

The ADD imposes additional labelling requirements on aerosols.

2.3.6. Relation to transport classification

Aerosol dispensers (UN 1950) belong to Class 2 in the UN RTDG Model Regulations and in the modal transport regulations (ADR, RID, ADN and IMDG Code, ICAO TI). Flammability classification criteria are harmonised between CLP and the modal transport regulations (ADR, RID, ADN and IMDG Code, ICAO TI).

Aerosols, categories 1 and 2 fall under Division 2.1 (sometimes referred to as Class 2.1 or Group F, FC, TF or TFC depending on their contents with hazardous properties). Aerosols, category 3 fall under Division 2.2 (sometimes referred to as Class 2.2 or Group A, O, T, C, CO, TC or TOC depending on their contents with hazardous properties). See Annex I for additional information on transport classification in relation to CLP classification.

2.3.7. Example of classification for aerosols

For reasons of simplification, the active materials chosen in the examples have been considered as non-combustible materials ($\Delta H_c = 0$ kJ/g). However, this may not be the case in practice.

2.3.7.1. Example of substances and mixtures fulfilling the classification criteria

Deodorant:

Composition:	
Butane/propane:	70 % (flammable components, ΔHc = 43.5 kJ/g)
Ethanol:	25 % (flammable components, ΔHc = 24.7 kJ/g)
Others:	5 % (non-flammable components, ΔHc = 0 kJ/g)

This spray aerosol contains 95 % of flammable components, and its chemical heat of combustion equals 36.6 kJ/g (= 0.70 * 43.5 + 0.25 * 24.7).

This aerosol is classified as **Aerosol, category 1.**

Air freshener (wet):	
Composition:	
Butane/propane:	**30 % (flammable components, $\Delta Hc = 43.5$ kJ/g)**
Others:	70 % (non-flammable components, $\Delta Hc = 0$ kJ/g)
This spray aerosol contains 30 % of flammable components and its chemical heat of combustion equals 13.1 kJ/g. In the ignition distance test, the ignition occurs at less than 75 cm but more than 15 cm.	
This aerosol is classified as **Aerosol, category 2.**	
Shaving foam:	
Composition:	
Butane/propane:	4 % (flammable components, $\Delta Hc = 43.5$ kJ/g)
Others:	96 % (non-flammable components, $\Delta Hc = 0$ kJ/g)
This foam aerosol contains 4 % of flammable components and its chemical heat of combustion equals 1.7 kJ/g. In the foam test, the flame height is less than 4 cm and the flame duration less than 2 s.	
This aerosol is classified as **Aerosol, category 3**.	

2.3.7.2. Examples of aerosols not fulfilling the classification criteria

By definition, all aerosol dispensers fall under one of the three categories for this hazard class.

2.4. OXIDISING GASES

2.4.1. Introduction

The requirements in chapter 2.4 ‘Oxidising gases’ of Annex I to CLP are identical to those in chapter 2.4 of GHS[18].

2.4.2. Definitions and general considerations for the classification of oxidising gases

> **Annex I:** ***2.4.1.*** *Oxidising gas means any gas or gas mixture which may, generally by providing oxygen, cause or contribute to the combustion of other material more than air does.*

2.4.3. Relation to other physical hazards

Oxidising gases usually do not need to be classified in any other physical hazard class apart from 'Gases under pressure', 'Chemicals under pressure' or 'Aerosol' where appropriate.

2.4.4. Classification of substances and mixtures as oxidising gases

2.4.4.1. Identification of hazard information

There are not many pure gases that are oxidising. Most oxidising gases are identified as such in the UN RTDG Model Regulations and in ISO 10156.

If no or insufficient information is available, screening and waiving possibilities should be checked. Depending on the results testing might be necessary, see section 2.4.4.2.

2.4.4.2. Screening procedures and waiving of testing

Gas mixtures are often prepared on demand, so there are thousands of gas mixtures containing oxidising gases on the market. However, there are very few test reports or data on the oxidising potential of gas mixtures in the scientific literature. Tests according to ISO 10156 to determine the oxidising potential are time consuming and expensive. In most cases, a calculation method as described in ISO 10156 may be applied.

2.4.4.3. Classification criteria

Annex I: *2.4.2*. *Table 2.4.1*	***Criteria for oxidising 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.*
Note: *'Gases which cause or contribute to the combustion of other material more than air does' means pure gases or gas mixtures with an oxidising power greater than 23.5 % as determined by a method specified in ISO 10156 as amended.*	

2.4.4.4. Testing and evaluation of hazard information

ISO 10156 describes a test method and a calculation method for the classification of oxidising gases. The test method may be used in all cases but must be used when the calculation method cannot be applied.

The calculation method applies to gas mixtures and can be applied only when the C_i for all oxidising components and the K_k for all inert components are available. These are listed for a number of gases in ISO 10156. For gas mixtures the calculation method described in ISO 10156 uses the criterion that a gas mixture should be considered as more oxidising than air if the 'Oxidising Power' (OP) of the gas mixture is higher than 0.235 (23.5 %).

The OP is calculated as follows:

Equation 2.4.4.4.a

$$OP = \frac{\sum_{i=1}^{n} x_i C_i}{\sum_{i=1}^{n} x_i + \sum_{k=1}^{p} K_k B_k}$$

Where:

x_i	is the molar fraction of the *i*:th oxidising gas in the mixture, in %
C_i	is the coefficient of oxygen equivalency of the *i*:th oxidising gas in the mixture
K_k	is the coefficient of equivalency of the k:th inert gas relative to nitrogen
B_k	is the molar fraction of the *k*:th inert gas in the mixture, in %
n	is the number of oxidising gases in the mixture
p	is the number of inert gases in the mixture.

For mixtures containing both flammable and oxidising components, special calculation methods are described in ISO 10156.

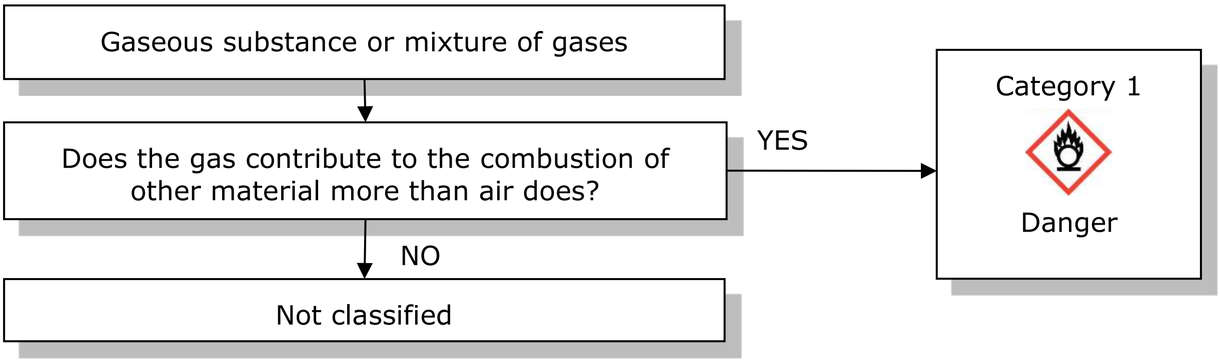
In case a gas or gas mixture needs to be tested for its oxidising potential, a recognised international standard must be used, notes that CLP explicitly refers to ISO 10156.

2.4.4.5. Decision logic

Classification of oxidising gases is done according to decision logic 2.4 in section 2.4.4.1 of GHS.

NOTE: The person responsible for the classification of oxidising gases should be experienced in this field and be familiar with the criteria for classification.

Figure 2.1 Decision logic for oxidising gases (Decision logic 2.4 of GHS)



2.4.5. Hazard communication for oxidising gases

2.4.5.1. Pictograms, signal words, hazard statements and precautionary statements

Annex I: *Table 2.4.2* ***Label elements for oxidising gases***	
Classification	*Category 1*
GHS Pictogram	
Signal word	*Danger*
Hazard statement	*H270: May cause or intensify fire; oxidiser*

Precautionary Statement Prevention	*P220* *P244*
Precautionary Statement Response	*P370 + P376*
Precautionary Statement Storage	*P403*
Precautionary Statement Disposal	

The wording of the precautionary statements is found in CLP Annex IV, Part 2.

2.4.6. Relation to transport classification

Most oxidising gases are classified as gases with subsidiary risk 5.1 in the UN RTDG Model Regulations. Consequently, all gases listed as oxidising in the UN RTDG Model Regulations and in the modal transport regulations (ADR, RID, ADN and IMDG Code, ICAO TI) must be classified as Ox. Gas 1. See Annex I for additional information on transport classification in relation to CLP classification.

2.4.7. Example of classification for oxidising gases

2.4.7.1. Example of substances and mixtures not fulfilling the classification criteria

EXAMPLE OF A CLASSIFICATION USING THE CALCULATION METHOD OF ISO 10156

Example Mixture: 9 % (O_2) + 16 % (N_2O) + 75 % (N_2)

Calculation steps

Step 1: Ascertain the coefficient of oxygen equivalency (C_i) for the oxidising gases in the mixture and the nitrogen equivalency factors (K_k) for the non-flammable, non-oxidising gases.

C_i (N_2O) =	0.6 (nitrous oxide)
C_i (O) =	1 (oxygen)
K_k (N_2) =	1 (nitrogen)

Step 2: Calculate the Oxidising Power (OP) of the gas mixture according to Equation 2.4.4.4.a

$$OP = \frac{\sum_{i=1}^{n} x_i C_i}{\sum_{i=1}^{n} x_i + \sum_{k=1}^{p} K_k B_k} = \frac{0.09 \times 1 + 0.16 \times 0.6}{0.09 + 0.16 + 0.75 \times 1} = 0.186$$

0.186 < 0.235 (18.6 % < 23.5 %), therefore the mixture is <u>not</u> considered as an oxidising gas.

EXAMPLE OF A CLASSIFICATION USING THE CALCULATION METHOD OF ISO 10156

Example Mixture: 9 % (O_2) + 16 % (N_2O) + 75 % (Ar)

Calculation steps

Step 1: Ascertain the coefficient of oxygen equivalency (C_i) for the oxidising gases in the mixture and the nitrogen equivalency factors (K_k) for the non-flammable, non-oxidising gases.

C_i (N_2O) =	0.6 (nitrous oxide)
C_i (O) =	1 (oxygen)
K_k (Ar) =	0.55 (argon)

Step 2: Calculate the Oxidising Power (OP) of the gas mixture according to Equation 2.4.4.4.a

$$OP = \frac{\sum_{i=1}^{n} x_i C_i}{\sum_{i=1}^{n} x_i + \sum_{k=1}^{p} K_k B_k} = \frac{0.09 \times 1 + 0.16 \times 0.6}{0.09 + 0.16 + 0.75 \times 0.55} = 0.281$$

0.281 > 0.235 (28.1 % > 23.5 %), therefore the mixture is considered as an oxidising gas.

2.5. GASES UNDER PRESSURE

2.5.1. Introduction

The requirements in chapter 2.5 'Gases under pressure' of Annex I to CLP are identical to those in chapter 2.5 of GHS[18]. The hazard class 'Gases under pressure' corresponds to Class 2 'Gases' in the UN RTDG Model Regulations.

2.5.2. Definitions and general considerations for classification of gases under pressure

2.5.2.1. Definition of 'gas'

> **Annex I:** ***1.0.*** *Gas means a substance which (i) at 50 °C has a vapour pressure greater than 300 kPa (absolute); or (ii) is completely gaseous at 20 °C at a standard pressure of 101.3 kPa;*

This definition means that substances and mixtures are considered as gases when their boiling point or initial boiling point (BP) is not higher than 20 °C. Substances and mixtures with a boiling point or initial boiling point higher than 20 °C are liquids except those few that develop a vapour pressure higher than 300 kPa at 50 °C; these substances and mixtures are considered as gases because of the pressure hazard when packaged.

Hydrogen fluoride (HF) with a BP of 19.4 °C is a borderline line case that has always been classified as a liquid.

2.5.2.2. Definition of gases under pressure

Annex I:

2.5.1.1. *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.

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

This definition means in practice that compressed gases or dissolved gases that are packaged at a pressure less than 200 kPa are not classified for this hazard.

Dissolved gases packaged at a pressure less than 200 kPa (gauge) are liquids and should be classified as such if they have other hazardous properties, e.g. flammable liquids.

Furthermore, liquids packaged under a layer of inert gas (e.g. nitrogen or helium) remain to be classified as liquids and not as gases under pressure.

2.5.3. Relation to other physical hazards

Gases under pressure may also need to be classified as flammable gases and oxidising gases where relevant.

2.5.4. Classification of substances and mixtures as gases under pressure

2.5.4.1. Identification of hazard information

Many gases are identified as such in the UN RTDG Model Regulations and many flammable gases and some oxidising gases are identified as gases in Annex VI of CLP. Furthermore, the UN RTDG Model Regulations specifies whether the gas can be packaged as a ‘compressed gas’, a ‘liquefied gas’, a ‘refrigerated liquefied gas’ and a ‘dissolved gas’. To determine whether a substance is a gas in case it is not listed in the UN RTDG Model Regulations and in case of doubt, the following physical characteristics are necessary:

- the boiling point;
- the vapour pressure at 50 °C.

See also *IR & CSA, Chapter R.7a: Endpoint specific guidance*, sections R.7.1.3 (Boiling point) and R.7.1.5 (Vapour pressure).

For those substances that meet the definition of a gas (see section 2.5.2), the critical temperature is also necessary. For the classification of gas mixtures based on the pseudo-critical temperature see section 2.5.4.3.

The references according to section 2.6.8 provide good quality data on boiling points, vapour pressure and the critical temperature of substances.

2.5.4.2. Classification criteria

Annex I: *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 ≤ - 50 °C.*

Liquefied gas	*A gas which, when packaged under pressure, is partially liquid at temperatures above - 50 °C. A distinction is made between:* *i) high pressure liquefied gas: a gas with a critical temperature between - 50 °C and + 65 °C; and* *ii) low pressure liquefied gas: a gas with a critical temperature above + 65 °C.*
Refrigerated liquefied gas	*A gas which when packaged is made partially liquid because of its low temperature.*
Dissolved gas	*A gas which when packaged under pressure is dissolved in a liquid phase solvent.*
Note: *Aerosols shall not be classified as gases under pressure. See 2.3.* *NOTE: the distinction between high pressure and low pressure liquefied gas is not relevant for classification, only for transport requirements.*	

2.5.4.3. Testing and evaluation of hazard information

The critical temperature of pure gases is well defined and can be found in technical literature, e.g. EN 13096 *Transportable gas cylinders — Conditions for filling gases into receptacles — Single component gases*.

For gas mixtures, the classification is based on the 'pseudo-critical temperature' which can be estimated as the mole weighted average of the components' critical temperatures.

Pseudo-critical temperature = $\sum_{i=1}^{n} x_i \times T_{Crit_i}$

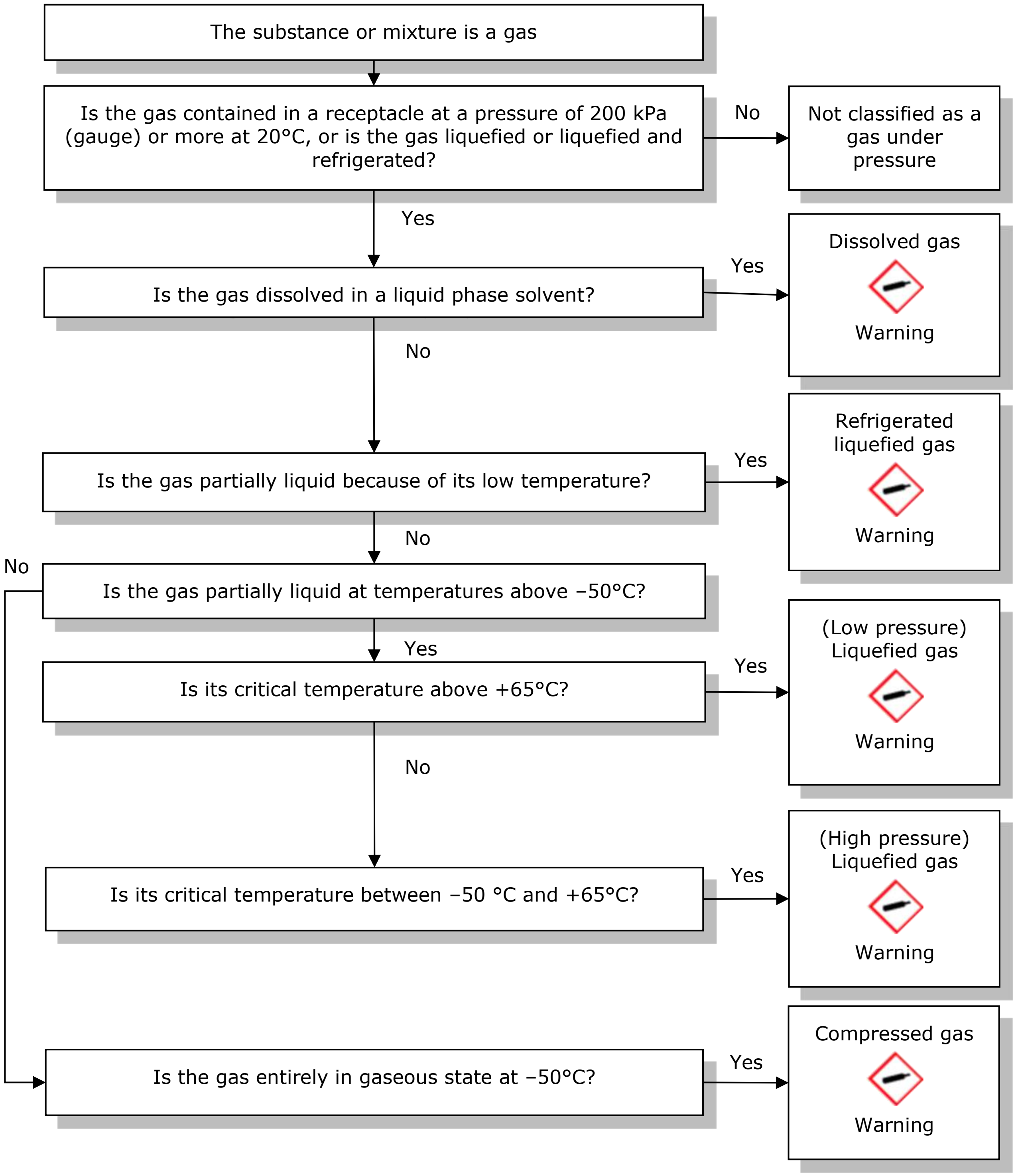
where x_i is the molar concentration of component *i* and T_{Crit_i} is the critical temperature (in °C or in K) of the component *i*.

2.5.4.4. Decision logic

Classification of gases under pressure is done according to decision logic 2.5.4.1 as included in GHS.

NOTE: The person responsible for the classification of gases under pressure should be experienced in this field and be familiar with the criteria for classification.

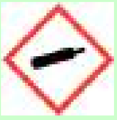
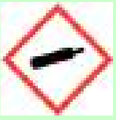
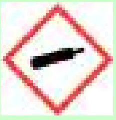
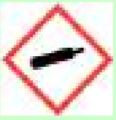
Figure 2.2 Decision logic for gases under pressure (Decision logic 2.5 of GHS)



2.5.5. Hazard communication for gases under pressure

2.5.5.1. Pictograms, signal words, hazard statements and precautionary statements

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

Classification	*Compressed gas*	*Liquefied gas*	*Refrigerated liquefied gas*	*Dissolved gas*
GHS Pictogram				
Signal Word	*Warning*	*Warning*	*Warning*	*Warning*
Hazard Statement	*H280: Contains gas under pressure; may explode if heated*	*H280: Contains gas under pressure; may explode if heated*	*H281: Contains refrigerated gas; may cause cryogenic burns or injury*	*H280: Contains gas under pressure; may explode if heated*
Precautionary Statements Prevention			*P282*	
Precautionary Statements Response			*P336 + P315*	
Precautionary Statements Storage	*P410 + P403*	*P410 + P403*	*P403*	*P410 + P403*
Precautionary Statements Disposal				
Note: Pictogram GHS04 is not required for gases under pressure where pictogram GHS02 or pictogram GHS06 appears.				

The wording of the precautionary statements is found in CLP Annex IV, Part 2.

2.5.6. Relation to transport classification

Gases are listed in the UN RTDG Model Regulations and in the transport regulations (ADR, RID, ADN)[33] with an indication of the physical state in their name for compressed gases (e.g. Argon, compressed), for refrigerated liquefied gas (e.g. Oxygen, refrigerated liquid) and for dissolved gas (e.g. Acetylene, dissolved). These indications of the physical state can be used to identify the group of gases under pressure according to CLP. The gas names without an indication of the physical state are 'liquefied gases' by default. See Annex I for additional information on transport classification in relation to CLP classification.

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[33] The classification codes according to the ADR, sections 2.2.2.1.2 and 2.2.2.1.3 are: 1. Compressed gas; 2. Liquefied gas; 3. Refrigerated liquefied gas; 4. Dissolved gas. An asphyxiant; O oxidizing; F flammable; T toxic; TF toxic, flammable; TC toxic, corrosive; TO toxic, oxidizing; TFC toxic, flammable, corrosive; TOC toxic, oxidizing, corrosive.

2.5.7. Example of classification for gases under pressure

2.5.7.1. Example of substances and mixtures fulfilling the classification criteria

2.5.7.1.1. Example mixture: 9 % (O_2) + 16 % (N_2O) + 75 % (N_2)

EXAMPLE MIXTURE: 9 % (O_2) + 16 % (N_2O) + 75 % (N_2)

Calculation steps:

Step 1: Ascertain the critical temperatures in Kelvin for the gases in the mixture:

Oxygen (O_2):	T_{Crit} = -118.4 °C (= 154.75 K)
Nitrous Oxide (N_2O):	T_{Crit} = +36.4 °C (= 309.55 K)
Nitrogen (N_2):	T_{Crit} = -147 °C (= 126.15 K)

Step 2: Calculate the pseudo-critical temperature:

$$0.09 \times 154.75\ \text{K} + 0.16 \times 309.55\ \text{K} + 0.75 \times 126.15\ \text{K} = 158.7\ \text{Kelvin} = -\ 115.08\ °\text{C}$$

The pseudo-critical temperature is lower than -50 °C, therefore the mixture is a ‘compressed gas’.

2.6. FLAMMABLE LIQUIDS

2.6.1. Introduction

The criteria for 'Flammable liquids' are found in CLP Annex I, section 2.6. For category 1-3, they are identical to those of chapter 2.6 of GHS[18]. However, CLP has not adopted category 4 of GHS (for historical reasons). This means that substances and mixtures classified as flammable liquids category 4 according to GHS are not considered flammable liquids according to CLP.

2.6.2. Definitions and general considerations for classification of flammable liquids

Annex I: ***2.6.1.*** *Flammable liquid means a liquid having a flash point of not more than 60 °C.*

The flash point is the lowest temperature of the liquid, corrected to a barometric pressure of 101.3 kPa, at which application of a test flame causes the vapour of the liquid to ignite momentarily and a flame to propagate across the surface of the liquid under the specified conditions of test. This means, the lower explosion limit is exceeded at the flash point.

2.6.3. Relation to other physical hazards

For flammable liquids in aerosol dispensers, see section 2.3 on aerosols. Aerosols should not be classified as flammable liquids.

2.6.4. Classification of substances and mixtures as flammable liquids

2.6.4.1. Identification of hazard information

For the decision as to whether a substance or mixture is a liquid see section 2.0.4. For the classification of a substance or mixture as a flammable liquid, data on the flash point and on the boiling point (or the initial boiling point) are needed.

Experimentally determined data or data taken from reliable data sources are to be preferred over calculated ones. The references in section 2.6.8 provide good quality data on boiling points (all three references) and flash point (first reference) of substances.

2.6.4.2. Screening procedures and waiving of testing

2.6.4.2.1. Boiling point

Normally calculation methods based on increments give satisfying results for substances and mixtures. With respect to the criterion for distinguishing between category 1 and 2 (boiling point of 35 °C) only that method with a mean absolute error lower than 5 °C could be recommended for screening.

2.6.4.2.2. Flash point

Calculation should work for pure liquids, neglecting impurities, if the vapour pressure curve and lower explosion limit are accurately known. For mixtures, calculation of the flash point is sometimes not reliable, and it is not currently possible to predict the accuracy of a calculated value. Calculation can be used as a screening test for mixtures, and a flash point does not need to be determined experimentally if the calculated value using the method cited in CLP Annex I, section 2.6.4.3 is 5 °C greater than the relevant classification criterion (23 °C and 60 °C, respectively). However, the restrictions outlined in CLP Annex I, section 2.6.4.2 must be taken account of.

Calculation based on structural similarity or properties is often only applicable to a narrowly defined set of substances. For mixtures they are not yet applicable.

Therefore, for both flash point and boiling point experimental determination is normally required.

2.6.4.3. Classification criteria

A flammable liquid has to be classified in one of the 3 categories of this class.

Annex I: *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(1)*
(1) For the purpose of this Regulation gas oils, diesel and light heating oils having a flash point between > 55 °C and ≤ 75 °C may be regarded as Category 3.	
Note: Aerosols shall not be classified as flammable liquids; see section 2.3.	

Annex I: ***2.6.4.5.*** *Liquids with a flash point of more than 35 °C and not more than 60 °C need not be classified in Category 3 if negative results have been obtained in the sustained combustibility test L.2, Part III, section 32 of the UN RTDG, Manual of Tests and Criteria.*

Gas oils, diesel and light heating oils in the flash point range of 55 °C to 75 °C may be regarded as a whole. The reason is that these hydrocarbon mixtures have varying flash points in that range due to seasonal requirements (EN 590 *Automotive fuels – Diesel- Requirements and Test Methods*). If they are regarded as a whole for CLP, they have to be regarded as category 3. However, this states no preliminary decision with respect to downstream regulations and legislation.

2.6.4.4. Testing and evaluation of hazard information

For experimental determination of the flash point, information on the viscosity of the liquid is needed to select a suitable method. Furthermore, to make use of the derogation for classification in category 3 according to CLP Annex I, section 2.6.4.5 (see section 2.6.4.3), information on sustained combustibility is necessary.

Special care is required when viscous substances or mixtures are tested or when halogenated compounds are present (see 'testing' below).

2.6.4.4.1. Testing

Suitable methods are listed in CLP Annex I, Table 2.6.3.

In case of substances with a high decomposition potential, a method using small amounts of liquid (e.g. EN ISO 3679 *Determination of flash point - Rapid equilibrium closed cup method*) is recommended to reduce the amount of substance under test.

The method to be used has to be chosen taking into account the properties of the liquid (viscosity, halogenated compounds present) and the scope of the standard.

For classification purposes it is recommended to use the mean of at least two test runs. One of these runs may be automated. In case of a deviation between manual and automated determination above the tolerance limits of the method, the lower value should be taken, or the determination should be repeated with manual observation. If the experimentally determined flash point is found to be within ± 2 °C a threshold limit when using a non-equilibrium method, it is recommended to repeat the determination with an equilibrium method.

Substances

For non-halogenated substances, the flash point is usually found 80 °C to 130 °C below the boiling point. Special care has to be taken when a sample contains impurities with a lower boiling point than the main compound. Even if their concentration is below 0.5 %, especially if their boiling point is substantially lower, they may have a strong effect on the test result. Impurities with a higher boiling point will normally have no effect on the flash point.

Within the respective scope, every standard is applicable. However, care must be taken to select the appropriate method and standard for the substance being tested.

Mixtures

The flash point may be lower than the lowest flash point of the components and non-volatile components may influence the flash point.

Equilibrium methods are advised if the boiling points of the components of the mixture cover a wide range of temperatures or if their concentrations are very different. They are also advised in case of viscous mixtures (alternatively: test methods with low heating rates (1 °C per min) using a stirrer).

In case of viscous mixtures or if an inerting substance is present at low concentrations and this is a highly volatile compound, the ignitability of the mixture may depend on the temperature at which the tests are started. When an inerting substance is present temperature ranges may exist where the vapour phase is inerted and other temperature ranges where it is not.

Halogenated compounds

The difference between boiling point and flash point may be lower than with non-halogenated compounds.

It is highly recommended to run the tests under careful control with manual observation.

Test results may be very difficult to reproduce. In such cases, classification should be based on the lowest value found (flash or burning inside or outside the cup) or on the value obtained during the screening run if in the main trial performed in accordance with the standard no flash could be found.

2.6.4.4.2. Evaluation of hazard information

Flash points determined by testing or from the mentioned internationally recognised qualified literature are to be preferred over those derived by calculation because of the error of most of the QSAR[34] methods and their limited application range.

If in literature different flash points are found for the same substance, the one found as evaluated or recommended has to be preferred.

If in literature different flash points are found for the same substance where none is found as evaluated/recommended, the lower one has to be preferred because of safety reasons, or an experimental determination should be carried out.

2.6.4.5. Decision logic

Compared to the decision logic 2.6 for flammable liquids contained in GHS chapter 2.6.4.1, this decision logic below is amended to exclude category 4 and to include derogations for gas oil, diesel, light heating, sustained combustibility and for phrases EUH018, EUH209 and EUH209A.

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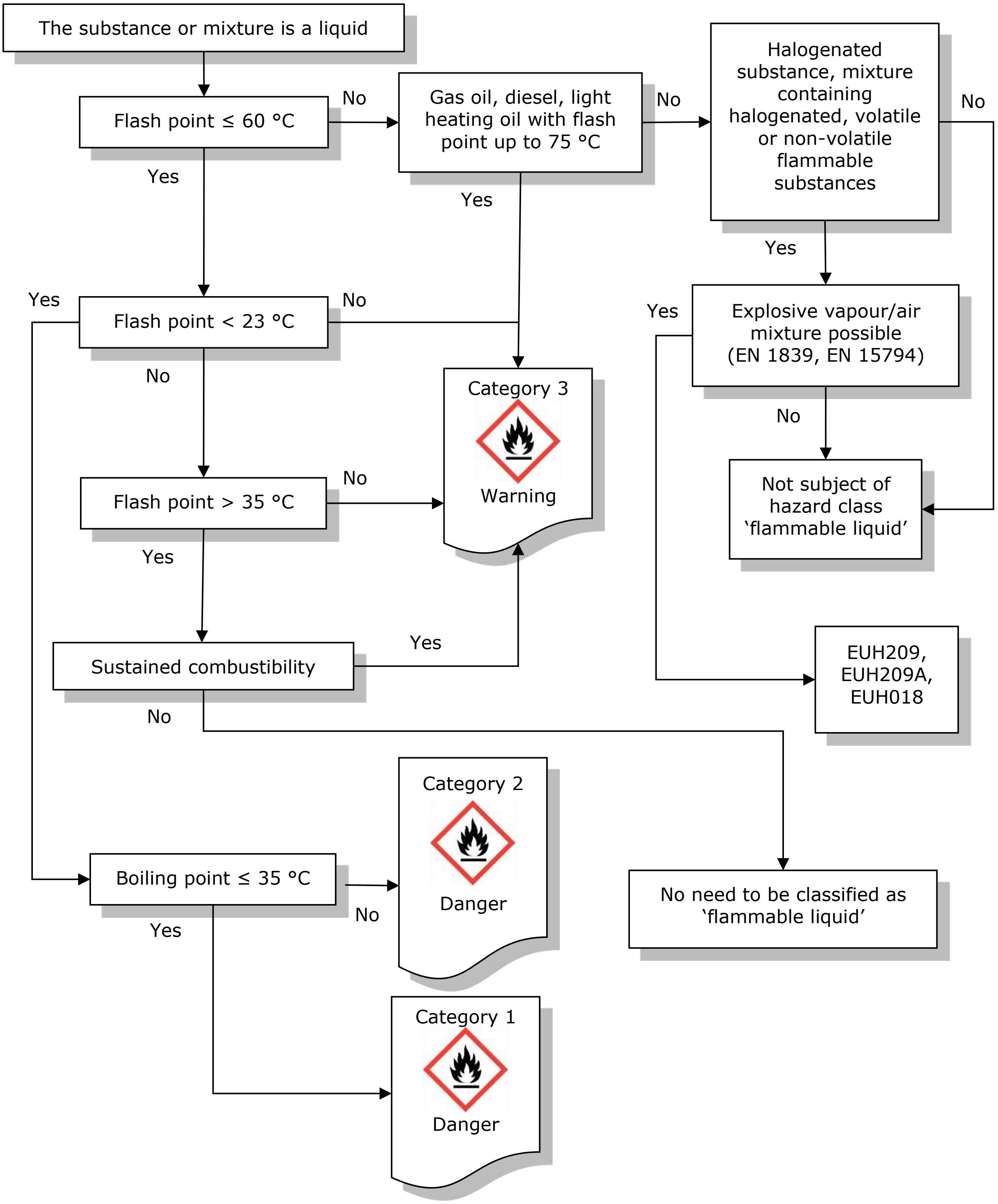
[34] Quantitative structure–activity relationship

NOTE: The person responsible for the classification of flammable liquids should be experienced in this field and be familiar with the criteria for classification.

Figure 2.3 Amended GHS decision logic for flammable liquids to include derogations for gas oil, diesel, light heating, sustained combustibility and for phrases EUH018, EUH209 and EUH209A (see 2.6.5.2 for more information on phrases)



2.6.5. Hazard communication for flammable liquids

2.6.5.1. Pictograms, signal words, hazard statements and precautionary statements

Annex I: *2.6.3.* *Table 2.6.2* ***Label elements for flammable liquids***			
Classification	*Category 1*	*Category 2*	*Category 3*
GHS Pictograms			
Signal Word	*Danger*	*Danger*	*Warning*
Hazard Statement	*H224: Extremely flammable liquid and vapour*	*H225: Highly flammable liquid and vapour*	*H226: Flammable liquid and vapour*
Precautionary Statement Prevention	*P210* *P233* *P240* *P241* *P242* *P243* *P280*	*P210* *P233* *P240* *P241* *P242* *P243* *P280*	*P210* *P233* *P240* *P241* *P242* *P243* *P280*
Precautionary Statement Response	*P303 + P361 + P353* *P370 + P378*	*P303 + P361 + P353* *P370 + P378*	*P303 + P361 + P353* *P370 + P378*
Precautionary Statement Storage	*P403 + P235*	*P403 + P235*	*P403 + P235*
Precautionary Statement Disposal	*P501*	*P501*	*P501*

The wording of the precautionary statements is found in CLP Annex IV, Part 2.

2.6.5.2. Additional labelling provisions for flammable liquids

If no flash point is found up to 60 °C and (partly) halogenated compounds are present, or if there is the possibility of loss of volatile flammable or non-flammable components (i.e. the liquid is a candidate for the assignment of EUH018, EUH209 or EUH209A) or if in doubt, the explosion limits should be determined to decide whether labelling with EUH018, EUH209, or EUH209A, is appropriate. Determination of explosion limits should be carried out according to ISO 10156 or EN 15794:2009[35] *Determination of explosion points of flammable liquids* or EN 1839.

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[35] Hereafter: EN 15794

> **Annex II:** ***1.1.4. EUH018 – 'In use, may form flammable/explosive vapour-air mixture'***
>
> *For substances and mixtures not classified as flammable themselves, which may form flammable/explosive vapour-air mixtures. For substances this might be the case for halogenated hydrocarbons and for mixtures this might be the case due to a volatile flammable component or due to the loss of a volatile non-flammable component.*

Substances or mixtures which do not show a flash point but do have an explosion range or may become flammable in use have to be labelled with EUH018.

> **Annex II:** ***2.9. Liquid mixtures containing halogenated hydrocarbons***
>
> *For liquid mixtures which show no flashpoint or a flashpoint higher than 60 °C but not more than 93 °C and contain a halogenated hydrocarbon and more than 5 % highly flammable or flammable substances, the label on the packaging shall bear one of the following statements, depending on whether the substances referred to above are highly flammable or flammable:*
>
> *EUH209 — 'Can become highly flammable in use' or*
>
> *EUH209A — 'Can become flammable in use'*

Note: EUH209 and EUH209A are limited to special types of mixtures whereas EUH018 covers a wider range of mixtures. In the majority of cases EUH018 covers EUH209 and EUH209A. Information about testing can be found in section 2.6.4.4.

2.6.6. Relation to transport classification

Class 3 of the UN RTDG Model Regulations and the modal transport regulations (ADR, RID, ADN and IMDG Code, ICAO TI) cover flammable liquids based on the same criteria as the CLP hazard class flammable liquids. In general, there is a correspondence between transport packing groups and CLP hazard categories but with exceptions.

Further, the UN RTDG Model Regulations cover substances and mixtures transported above their flash point. In practice the information on flash point and boiling point needed for classification is available and it is recommended to classify based on the data rather than use direct translation.

2.6.7. Example of classification for flammable liquids

2.6.7.1. Example of substances and mixtures fulfilling the classification criteria

2.6.7.1.1. Example 1

MIXTURE OF: N-BUTYLACETATE + P-XYLENE + 1,3,5-TRIMETHYLBENZENE **(7.9 MOL % + 60.3 MOL % + 31.7 MOL %)**	
Initial boiling point (calculated):	140 °C
Flash point (calculated):	26 °C
calculated flash point is within 5 °C to the limiting value of 23 °C ⇨ flash point has to be measured.	

Dyn. Viscosity at 20 °C (DIN 53019):	8 mPa·s
Flash point (EN ISO 3679):	30.0 °C
⇨ According to boiling point and measured flash point result: **Flam. Liq. category 3**	

2.6.7.1.2. Example 2

HYDROCARBONS AND DICHLOROMETHANE (70 VOL % + 30 VOL %)	
Initial Boiling point (calculated):	52 °C
Flash point:	no flash point according to a standard
⇨ Because the hydrocarbon part of the mixture has a flash point by itself (- 12 °C) the question 'Is an explosive vapour/air mixture possible?' (EN 1839, EN 15794) or 'Can it become highly flammable / flammable during use?' has to be answered. **Answer: Yes, an explosion range exists; yes, it can become highly flammable during use.**	
⇨ According to the answer, **the mixture has to be labelled with EUH018 or EUH209** Note 1: In that case EUH018 covers EUH209 Note 2: The EUH018 must only be assigned if the substance or mixture is classified as hazardous (Article 25 (1) of CLP) **Cannot be classified as flammable liquid because the mixture has no flash point.**	

2.6.7.2. Example of substances and mixtures not fulfilling the classification criteria

2.6.7.2.1. Example 3

AQUEOUS FORMULATION OF ALIPHATIC POLYURETHANE RESIN	
Boiling point (EC 440/2008, EU test method A.2):	92 °C
Dyn. Viscosity at 20 °C (DIN 53019):	1938 mPa·s
Sample is highly viscous, use low heating rate for flash point determination (1 °C /min).	
Flash point (EN ISO 13736):	42.5 °C
Sustained combustibility test (UN-MTC L.2) at 60.5 °C:	combustion not sustained
Sustained combustibility test (UN-MTC L.2) at 75 °C:	combustion not sustained
⇨ According to the flash point result: category 3 However, does not necessarily have to be classified as flammable liquid **category 3** because it did not sustain combustion.	

2.6.8. References

Brandes, E. and Möller, W.: *Safety Characteristic Data*, Volume 1, Flammable gases and liquids, nw-Verlag, 2008

Haynes W. M. *et al.* (2012) *CRC Handbook of Chemistry and Physics 93rd Edition*. CRC Press, Taylor and Francis, Boca Raton, FL

O'Neil, M. J. *et al.* © (2016, 2012) *The Merck Index - An Encyclopedia of Chemicals, Drugs, and Biologicals* (14th Edition – Version 14.9). Merck Sharp & Dohme Corp., a subsidiary of Merck & Co., Inc.

2.7. FLAMMABLE SOLIDS

2.7.1. Introduction

The criteria for 'Flammable solids' are found in CLP Annex I, section 2.7 and are identical to those in chapter 2.7 of GHS[18].

2.7.2. Definitions and general considerations for classification of flammable solids

Annex I: *2.7.1.1.* *A flammable solid means a solid which is readily combustible, or may cause or contribute to fire through friction.*

Readily combustible solids are powdered, granular, or pasty substances or mixtures 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.

Special consideration on particle size

Annex I: *2.7.2.3.*

[…]

Note 1: The test shall be performed on the substance or mixture in its physical form 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 shall also be tested in the new form.

[…]

The finer the particle size of a solid substance or mixture, the greater the area exposed to air will be, and since flammability is a reaction with the oxygen in air, the particle size will greatly influence the ability to ignite. Hence, it is very important that flammable properties for solids are investigated on the substance or mixture as it is actually presented (including how it can reasonably be expected to be used, see Article 8(6) of CLP). This is indicated by the Note cited in CLP Annex I, section 2.7.2.3. For further information please see section 1.2 in Part 1.

2.7.3. Relation to other physical hazards

Explosives, organic peroxides, self-reactive substances and mixtures as well as pyrophoric or oxidising solids should normally not be considered for classification as flammable solids.

Flammable solids can present other physical hazards, e.g. they might be self-heating or corrosive to metals or emit flammable gases in contact with water.

For flammable solids that are packaged in aerosol dispensers, see section 2.3. If classified as aerosols, they must not be classified as flammable solids in addition.

2.7.4. Classification of substances and mixtures as flammable solids

2.7.4.1. Identification of hazard information

For the classification of a substance or mixture as a flammable solid, data on the following properties are needed:

- melting point;
- information on water reactivity (due to wetted zone in the test);
- information on flash point for solids containing flammable liquids.

If a solid with a low melting point is handled in the molten state, additional data such as flash point are generally necessary (see Articles 5(1), 6(1) and 8(6)).

See also *IR & CSA, Chapter R.7a: Endpoint specific guidance*, sections R.7.1.2 (Melting/freezing point) and R.7.1.9 (Flash point).

Metal powders (which are powders of metals or metal alloys) may be (highly) flammable depending on their reactivity and particle size. However, most other inorganic solids are not flammable and so are not classified as flammable solids.

2.7.4.2. Screening procedures and waiving of testing

In general, a possible classification as a flammable solid should be considered for any solid organic substance or mixture containing such material. For inorganic material, testing may be waived in cases where the substance is fully oxidised or commonly known to be not flammable (i.e. stable salts or metal oxides) or where a flammability hazard can be excluded by any other scientific reasoning. In many cases, a simple screening test (see section 2.7.4.4) can be used to determine whether a solid should be classified as flammable. Solid substances and mixtures are classified as flammable according to their burning behaviour.

The test method as described in Part III, section 33.2.4.3.1 in the UN-MTC should be applied for screening purposes. Alternatively, the burning index (referred to as 'class number' in VDI 2263) as obtained from the Burning Behaviour test (VDI 2263, part 1) may be used. If a burning index of 3 or less is found, the substance or mixture should not be classified as a flammable solid and no further testing is required. However, if smouldering or a flame is observed, the full test must be carried out.

2.7.4.3. Classification criteria

The classification criteria are identical to the GHS system.

Annex I: *2.7.2.1.* *Powdered, granular or pasty substances or mixtures (except powders of metals or metal alloys – see 2.7.2.2) 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 Part III, sub-section 33.2.1, of the UN RTDG, Manual of Tests and Criteria, is less than 45 seconds 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 (100 mm) in 10 minutes or less.*

2.7.2.3. *A flammable solid shall be classified in one of the two categories for this class using Method N.1 as described in 33.2.1 of the UN RTDG, Manual of Tests and Criteria in accordance with Table 2.7.1:*

Table 2.7.1 ***Criteria for flammable solids***

Category	*Criteria*
1	*Burning rate test* *Substances and mixtures other than metal powders:* *(a) wetted zone does not stop fire and* *(b) burning time < 45 seconds or burning rate > 2,2 mm/s* *Metal powders:* *burning time ≤ 5 minutes*
2	*Burning rate test* *Substances and mixtures other than metal powders:* *(a) wetted zone stops the fire for at least 4 minutes and* *(b) burning time < 45 seconds or burning rate > 2,2 mm/s* *Metal powders:* *burning time > 5 minutes and ≤ 10 minutes*
[…] *Note 2: Aerosols shall not be classified as flammable solids; see section 2.3.*	

2.7.4.4. Testing and evaluation of hazard information

For safety reasons, it is advisable to test for explosive and self-reactive properties first and to rule out pyrophoric behaviour before performing this test. The classification test is described in Part III, section 33.2.4.3.2 of the UN-MTC. The sample should be tested in its commercially relevant form. Special care has to be taken that the sample forms an unbroken strip or powder train in the test mould. Large pieces that do not fit into the mould should be gently crushed. For pasty or sticking substances, it may be helpful to line the mould with a thin plastic foil which is withdrawn after having formed the train. A small gas burner with a non-luminous flame has proven most practical as ignition source; see UN-MTC section 33.2.4.3.1. To detect also smouldering behaviour, it is advisable to dim the light in the laboratory hood during the experiment.

Classification is based upon the fastest burning rate / shortest burning time obtained in six test runs, unless a positive result is observed earlier. For substances and mixtures other than metal powders, the category is assigned depending on whether the wetted zone is able to stop the flame: if the flame passes the wetted zone in at least one trial, category 1 is assigned.

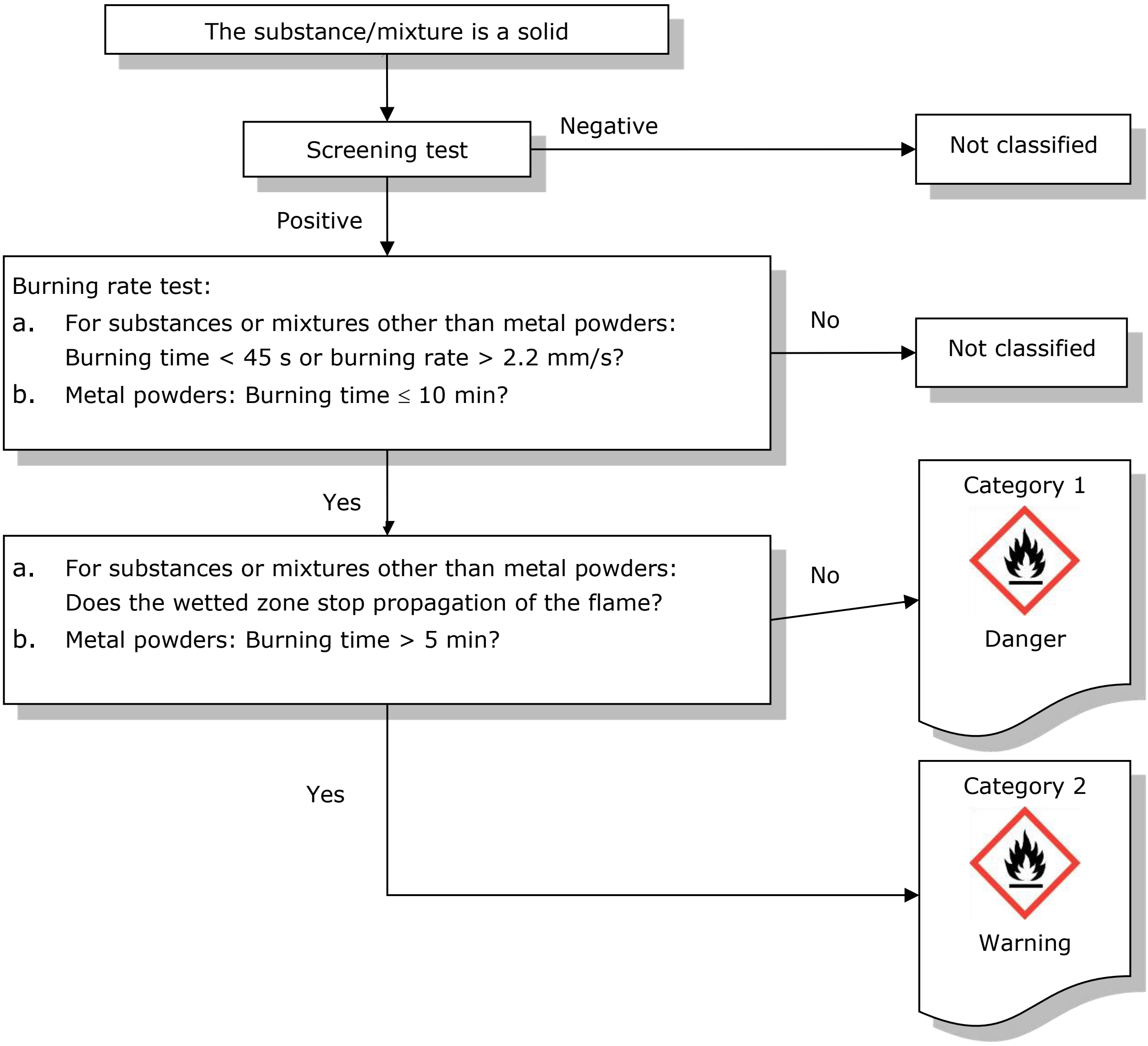
In case the flame propagates rapidly (less than 20 seconds for 100 mm), it is advisable to check for explosive or self-reactive properties. Another possible reason is the presence of flammable liquids in the sample, in which case, labelling with the statement EUH018 — 'In use, may form flammable/explosive vapour-air mixture' following Article 25 of CLP is applicable.

2.7.4.5. Decision logic

Classification of flammable solids is done according to 2.4 (equivalent to the decision logic 2.7 in GHS v.7).

NOTE: The person responsible for the classification of flammable solids should be experienced in this field and be familiar with the criteria for classification.

Figure 2.4 Decision logic for flammable solids (Decision logic 2.7 of GHS)



2.7.5. Hazard communication for flammable solids

2.7.5.1. Pictograms, signal words, hazard statements and precautionary statements

Annex I: 2.7.3. Table 2.7.2 ***Label elements for flammable solids***		
Classification	*Category 1*	*Category 2*
GHS Pictograms		
Signal Word	*Danger*	*Warning*
Hazard Statement	*H228: Flammable Solid*	*H228: Flammable Solid*
Precautionary Statement Prevention	*P210* *P240* *P241* *P280*	*P210* *P240* *P241* *P280*
Precautionary Statement Response	*P370 + P378*	*P370 + P378*
Precautionary Statement Storage		
Precautionary Statement Disposal		

The wording of the precautionary statements is found in CLP Annex IV, Part 2.

2.7.6. Relation to transport classification

Division 4.1 within Class 4 of the UN RTDG Model Regulations covers flammable solids, solid desensitised explosives, self-reactive substances (liquids or solids) and polymerizing substances and mixtures. If a transport classification according to the modal transport regulations (ADR, RID, ADN and IMDG Code, ICAO TI) is available it should be kept in mind that transport classification is based on prioritisation of hazards (see the UN RTDG Model Regulations, section 2.0.3) and that flammable solids have a relatively low rank in the precedence of hazards. Therefore, the translation from transport classification to CLP should be only done if a transport classification for a flammable solid is explicitly available. The conclusion that a substance or mixture not classified as a flammable solid for transport should not be classified as a flammable solid according to CLP is, in general, not correct. See Annex I for additional information on transport classification in relation to CLP classification.

2.7.7. Example of classification for flammable solids

2.7.7.1. Example of substances and mixtures fulfilling the classification criteria

The following example shows a classification based on test data:

TEST SUBSTANCE: ‘FLAMMALENE’ (ORGANIC MATERIAL, SOLID)	
Screening test (VDI 2263, part 1):	burning index: 5 (burning with an open flame or emission of sparks)
Conclusion: Substance is **candidate for classification as a flammable solid, further testing required.**	
UN Test N.1 (Test method for readily combustible solids):	Burning times for a distance of 100 mm (6 runs): 44 s; 40 s; 49 s; 45 s; 37 s; 41 s. Shortest burning time is less than 45 s; substance is a flammable solid. Wetted zone stops the fire, no reignition.
Conclusion: Classify as **flammable solid, category 2.**	

2.7.7.2. Example of substances and mixtures not fulfilling the classification criteria

Many inorganic salts and oxides are not flammable such as NaCl, NaBr, KI, FeO, MnO etc.

Urea or phthalic acid anhydride are examples of organic substances that would not be classified as flammable solids.

2.7.8. References

VDI 2263, part 1, 2022, Dust fires and dust explosions - Hazards - assessment - safety measures - Safety-related parameters of bulk goods

2.8. SELF-REACTIVE SUBSTANCES AND MIXTURES

2.8.1. Introduction

The criteria for ‘Self-reactive substances and mixtures’ are found in CLP Annex I, section 2.8 and are identical to those in chapter 2.8 of GHS.

In general, substances or mixtures classified as self-reactive substances and mixtures can decompose strongly exothermically when 50 kg are exposed to temperatures of 75 °C or lower depending on the SADT of the substance or mixture.

Self-reactive substances and mixtures display a very wide range of properties. The most hazardous type is TYPE A of self-reactive substances and mixtures that, based on their violent decomposition behaviour, are too dangerous to transport commercially though they can be stored safely with appropriate precautions. At the other end of the scale this classification includes substances and mixtures that only decompose very slowly at temperatures well above the normal storage and transport temperatures (e.g. 75 °C).

The decomposition of self-reactive substances and mixtures can be initiated by heat, contact with catalytic impurities (e.g. acids, heavy-metal compounds, and bases), friction, or impact.

The rate of decomposition increases with temperature and varies with the substance or mixture. Decomposition, particularly if no ignition occurs, may result in the production of toxic gases or vapours. For certain self-reactive substances and mixtures, the temperature must be controlled during storage and handling. Some self-reactive substances and mixtures may decompose explosively, particularly if confined. This characteristic may be modified by the addition of diluents or by the use of appropriate packaging. Some self-reactive substances and mixtures burn vigorously.

Additional hazardous properties, resulting in subsidiary labelling, are indicated in the list of already classified self-reactive substances and mixtures included in the UN RTDG Model Regulations, section 2.4.2.3.2.3.

Commercial self-reactive substances and mixtures are commonly formulated by dilution with compatible solid and liquid substances.

2.8.2. Definitions and general considerations for classification of self-reactive substances and mixtures

In CLP the following definition is given for self-reactive substances and mixtures:

Annex I:

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 according to this Part as explosives, organic peroxides or as oxidising.*

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.*

General considerations

Annex I: *2.8.3. Hazard communication*

Type G has no hazard communication elements assigned but shall be considered for properties belonging to other hazard classes.

2.8.3. Relation to other physical hazards

Neither the burning properties nor the sensitivity to impact and friction form part of the classification procedure for self-reactive substances and mixtures in CLP. These properties may be of importance in safe handling of self-reactive substances and mixtures (see additional tests in section 2.8.4.4).

In addition, the explosive properties do not have to be determined according to CLP Annex I, section 2.1, because explosive properties are incorporated in the classification as self-reactive substances and mixtures, see CLP Annex I, section 2.8.2.1 (a). Note that substances and mixtures may have explosive properties when handled under higher confinement.

2.8.4. Classification of substances and mixtures as self-reactive substances and mixtures

2.8.4.1. Identification of hazard information

The classification of a self-reactive substance or mixture in one of the seven categories 'types A to G' is dependent on its detonation, deflagration and thermal explosion properties, its response to heating under confinement, its explosive power and the concentration and the type of diluent added to desensitise the substance or mixture. Specifications of acceptable diluents that can be used safely are given in the UN RTDG Model Regulations, section 2.4.2.3.5.

The classification of a self-reactive substance or mixture as type A, B or C is also dependent on the type of packaging in which the substance or mixture is tested as it affects the degree of confinement to which the substance or mixture is subjected. This has to be considered when handling the substance or mixture; stronger packaging may result in more violent reactions when the substance or mixture decomposes. This is why it is important that storage and transport is done in packaging, allowed for the type of self-reactive substance and mixture, that conforms the requirements of the UN-packaging or IBC instruction (P520/IBC520) or tank instruction (T23).

2.8.4.2. Screening procedures and waiving of testing

The CLP text comprises the following screening considerations.

> ***Annex I: 2.8.4.2 Additional Classification Considerations***
>
> *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*[36] *in Appendix 6 of the UN RTDG, Manual of Tests and Criteria; or*
>
> *(b) For a single organic substance or a homogeneous mixture of organic substances, the estimated SADT for a 50 kg package is greater than 75 o C or the exothermic decomposition energy is less than 300J/g. The onset temperature and decomposition energy can be estimated using a suitable calorimetric technique (see Part II, sub-section 20.3.3.3 of the UN RTDG, Manual of Tests and Criteria).*

Self-reactive substances are, for example, compounds containing the following chemical groups:

a. Aliphatic azo compounds (-C-N=N-C-);
b. Organic azides ($-C-N_3$);
c. Diazonium salts ($-CN_2^+Z^-$);
d. N-nitroso compounds (-N-N=O); and
e. Aromatic sulfohydrazides ($-SO_2-NH-NH_2$).

This list is not exhaustive and substances with other reactive groups, combination of groups and some mixtures of substances may have similar properties. Additional guidance on substances, which may have self-reactive properties, is given in Appendix 6, section 5.1 of the UN-MTC.

For examples of chemical groups associated with explosive properties please refer to the screening procedure under explosives, see section 2.1.4.2.

2.8.4.3. Classification criteria

According to CLP, substances and mixtures must be considered for classification in this hazard class as a self-reactive substance or mixture unless:

> **Annex I:**
>
> ***2.8.2.1.*** *Any self-reactive substance or mixture shall be considered for classification in this class as a self-reactive substance or mixture unless:*
>
> *(a) they are explosives, according to the criteria given in 2.1;*

---

[36] This note is not part of the legal text: following an update of Appendix 6 of the UN-MTC, the correct table reference is A6.3 instead of A6.2 as indicated in the CLP Regulation.

(b) they are oxidising liquids or solids, according to the criteria given in 2.13 or 2.14, except that mixtures of oxidising substances, which contain 5 % or more of combustible organic substances shall be classified as self-reactive substances according to the procedure defined in 2.8.2.2;

(c) they are organic peroxides, according to the criteria given in 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⁽¹⁾

***2.8.2.2**. Mixtures of oxidising substances, meeting the criteria for classification as oxidising substances, which contain 5 % or more of combustible organic substances and which do not meet the criteria mentioned in (a), (c), (d) or (e) in 2.8.2.1, 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 2.8.2.3) shall be classified as a self-reactive substance.

[…]

(1) See UN RTDG, Manual of Test and Criteria, sub-sections 28.1, 28.2, 28.3[37] *and Table 28.3.*

In the CLP decision logic (see section 2.8.4.5), classification of self-reactive substances or mixtures is based on performance-based testing in both small-scale tests and, where necessary, some larger scale tests with the substance or mixture in its packaging. The concept of 'intrinsic properties' is, therefore, not necessarily, applicable to this hazard class.

Self-reactive substances or mixtures are classified in one of the seven categories of 'types A to G' according to the classification criteria given in CLP Annex I, section 2.8.2.3. The classification principles are given in the decision logic in CLP Annex I, Figure 2.8.1 (see section 2.8.4.5) and the Test Series A to H, as described in the Part II of the UN-MTC, should be performed.

---

[37] This note is not part of the legal text: UN-MTC sub-sections 28.4 includes Test Series H description (SADT texts).

Annex I: ***2.8.2.3.*** *Self-reactive substances and mixtures shall be 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, shall 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 shall 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 shall 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;*

shall 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 shall 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 shall 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 (SADT 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 shall 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.

Where the test is conducted in the package form and the packaging is changed, a further test shall be conducted where it is considered that the change in packaging will affect the outcome of the test.

A list of currently classified self-reactive substances and mixtures is included in the UN RTDG Model Regulations, section 2.4.2.3.2.3.

2.8.4.4. Testing and evaluation of hazard information

2.8.4.4.1. Thermal stability and temperature control

In addition to the classification tests given in decision logic Figure 2.8.1 of CLP, the thermal stability of the self-reactive substances and mixtures has to be assessed to determine the SADT.

The SADT is defined as the lowest temperature at which self-accelerating decomposition of a substance or mixture may occur in the packaging as used in transport, handling and storage. It should be emphasised that the SADT is dependent on the nature of the self-reactive substance or mixture itself, together with the volume and heat-loss characteristics of the packaging or vessel in which the substance or mixture is handled. The temperature at which self-accelerating decomposition occurs decreases:

- as the size of the packaging or vessel increases; and
- with increasing efficiency of the insulation on the package or vessel.

The SADT is a measure of the combined effect of the ambient temperature, decomposition kinetics, package size and the heat transfer properties of the substance or mixture and its packaging.

There is no relation between the SADT of a self-reactive substance and mixture and its classification in one of the seven categories 'types A to G'. The SADT is used to derive safe handling, storage and transport temperatures (control temperature) and alarm temperature (emergency temperature).

Depending on its SADT, a self-reactive substance or mixture needs temperature control and the criteria as given in CLP Annex I, section 2.8.2.4, consist of the following elements:

1. Self-reactive substances and mixtures need to be subjected to temperature control when the SADT is ≤ 55 ° C.
2. Derivation of control and emergency temperatures:

Type of receptacle	SADT*	Control temperature	Emergency temperature
Single packaging and IBC's	20 °C or less over 20 °C to 35 °C over 35 °C	20 °C below SADT 15 °C below SADT 10 °C below SADT	10 °C below SADT 10 °C below SADT 5 °C below SADT
Tanks	< 50 °C	10 °C below SADT	5 °C below SADT

*i.e. the SADT of the substance/mixture as packaged for transport, handling and storage.

The SADT is only valid for the substance or mixture as tested and when handled properly. Mixing the self-reactive substances and mixtures with other chemicals or contact with incompatible materials (including incompatible packaging or vessel material) may reduce the thermal stability due to catalytic decomposition and lower the SADT. This may increase the risk of decomposition and has to be avoided.

2.8.4.4.2. Additional consideration and testing

Explosive properties

The sensitivity of self-reactive substances and mixtures to impact (solids and liquids) and friction (solids only) may be of importance for the safe handling of the substances and mixtures, in the event that these substances and mixtures have pronounced explosive properties (e.g. rapid deflagration and/or violent heating under confinement). Test methods to determine these properties are described in Test Series 3 (a) (ii) and 3 (b) (i) of the UN-MTC. This information may be documented in the SDS.

Burning properties

Although there are currently no dedicated storage guidelines for self-reactive substances and mixtures (although in some countries under development), often the regulations for organic peroxides are referred to. For storage classification the burning rate is commonly used, see section 2.15 on organic peroxides.

Flash point

The flash point for liquid self-reactive substances or mixtures is only relevant in the temperature range where the product is thermally stable. Above the SADT of the self-reactive substance or mixture, flash point determination is not relevant because decomposition products have evolved.

NOTE: In case a flash point determination seems reasonable (expected flash point below the SADT) a test method using a small amount of sample is recommended. In case the self-reactive substance or mixture is diluted or dissolved, the diluent may determine the flash point.

Auto-ignition temperature

The determination of the auto-ignition temperature is not relevant for self-reactive substances and mixtures, because the vapours decompose during the execution of the test. Available test methods are for non-decomposing vapour phases. Auto-ignition of vapours of self-reactive substances or mixtures when they decompose, can never be excluded. This information should be documented in the SDS.

Self-ignition temperature

The determination of the self-ignition temperature (test applicable for solids) is not relevant.

The thermal stability of self-reactive substances and mixtures is quantitatively given by the SADT test.

Control and Emergency temperatures

The Control and Emergency temperatures are based on the SADT as determined by UN Test Series H. In UN Test Series H.2 and H.3, the heat loss applied in calculating the SADT should be representative for the packaging, IBC, tank or vessel in which the substance or mixture is handled or stored. In UN Test H.4, the Dewar vessel used is supposed to be representative for the substance or mixture handled in packages. For handling of the substance or mixture in larger quantities (IBCs/tanks/vessels etc.) and/or in better (thermally) insulated containers under more thermally insulated conditions, the SADT has to be determined for that quantity with the given degree of insulation. From that SADT the Control and Emergency temperatures can be derived (see also section 2.8.4.4.1).

2.8.4.4.3. Additional classification considerations

Currently, the following properties are not incorporated in the classification of self-reactive substances and mixtures under CLP:

- mechanical sensitivity *i.e.* impact and friction sensitivity (for handling purposes);
- burning properties (for storage purposes);
- flash point for liquids; and
- burning rate for solids.

In addition to the GHS criteria CLP mentions that:

> **Annex I: *2.8.2.2***
>
> *[…]*
>
> *Where the test is conducted in the package form and the packaging is changed, a further test shall be conducted where it is considered that the change in packaging will affect the outcome of the test.*

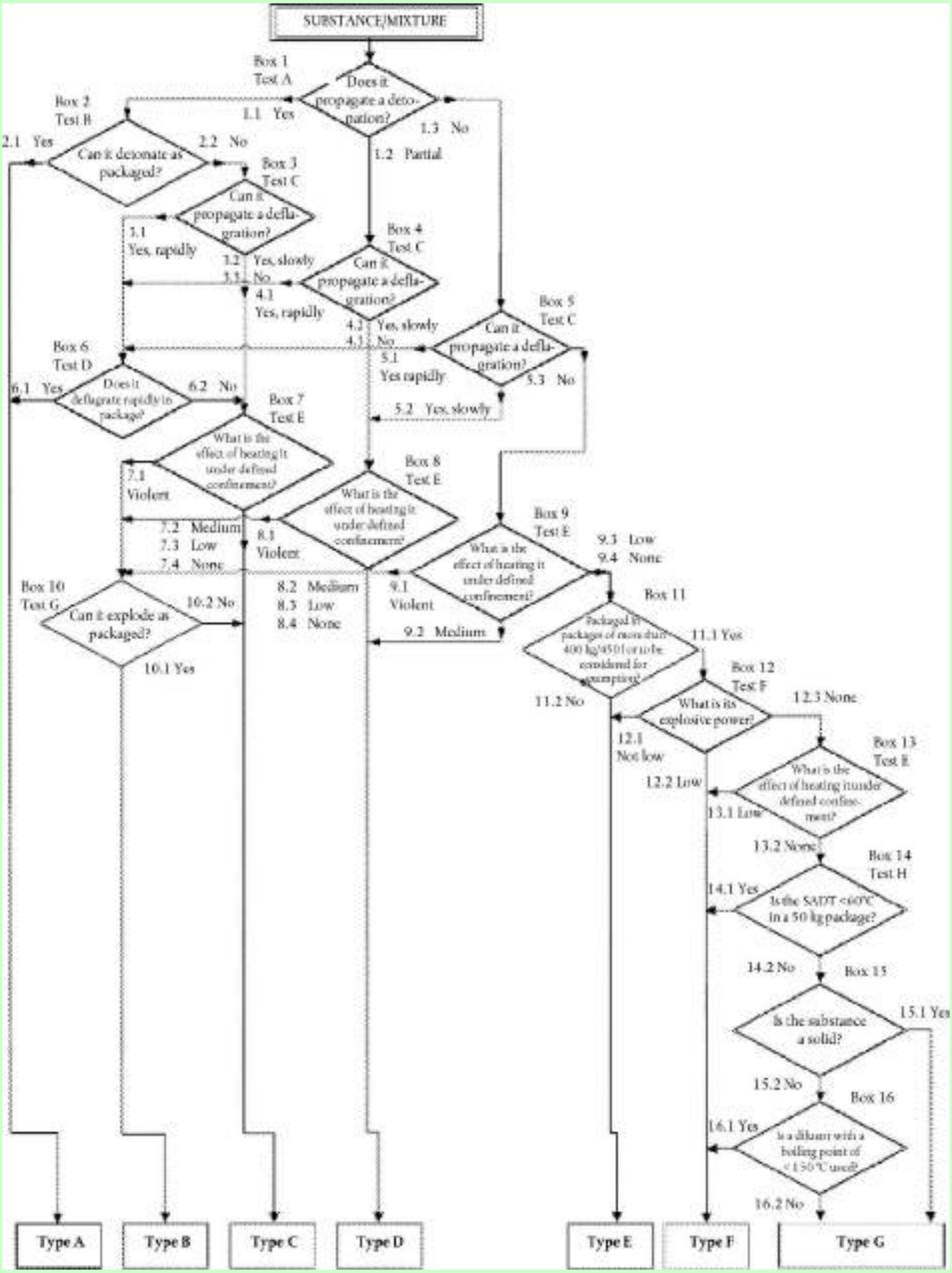
Please note that polymerising substances do not fulfil the criteria for classification as self-reactive substances and mixtures. In transport regulations, they are classified as polymerising substances. These substances are not contained in GHS and therefore not incorporated in CLP.

2.8.4.5. Decision logic

Classification of self-reactive substances and mixtures is done according to decision logic 2.8 as included in GHS.

NOTE: The person responsible for the classification of self-reactive substances and mixtures should be experienced in this field and be familiar with the criteria for classification.

Annex I: *Figure 2.8.1 Self-reactive substances and mixtures*



2.8.5. Hazard communication for self-reactive substances and mixtures

2.8.5.1. Pictograms, signal words, hazard statements and precautionary statements

According to CLP the following label elements must be used for substances and mixtures meeting the criteria for this hazard class:

Annex I: *Table 2.8.1*

Label elements for self-reactive substances and mixtures

Classification	*Type A*	*Type B*	*Type C & D*	*Type E & F*	*Type G(1)*
GHS pictograms		 			*There are no label elements allocated to this hazard category*
Signal Word	*Danger*	*Danger*	*Danger*	*Warning*	
Hazard Statement	*H240: Heating may cause an explosion*	*H241: Heating may cause a fire or explosion*	*H242: Heating may cause a fire*	*H242: Heating may cause a fire*	
Precautionary statement Prevention	*P210* *P234* *P235* *P240* *P280*	*P210* *P234* *P235* *P240* *P280*	*P210* *P234* *P235* *P240* *P280*	*P210* *P234* *P235* *P240* *P280*	
Precautionary statement Response	*P370 + P372 + P380 + P373*	*P370 + P380 + P375 [+P378](2)*	*P370 + P378*	*P370 + P378*	
Precautionary statement Storage	*P403* *P411* *P420*	*P403* *P411* *P420*	*P403* *P411* *P420*	*P403* *P411* *P420*	
Precautionary statement Disposal	*P501*	*P501*	*P501*	*P501*	

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

(2) See the introduction to Annex IV for details on the use of square brackets.

The wording of the precautionary statements is found in CLP Annex IV, Part 2.

2.8.6. Relation to transport classification

Division 4.1 within Class 4 of the UN RTDG Model Regulations covers flammable solids, self-reactive substances, solid desensitised explosives and polymerising substances (not being part of GHS and CLP). A list of already classified self-reactive substances is included in the UN RTDG Model Regulations, section 2.4.2.3.2.3. This table includes self-reactive substances of various types from type B to type F. See Annex I for additional information on transport classification in relation to CLP classification.

2.8.7. Example of classification for self-reactive substances and mixtures

2.8.7.1. Example of substances and mixtures fulfilling the classification criteria

Substance to be classified: NP

Molecular formula: not applicable

The substance has:

- an energy content of 1452 kJ/kg; and
- a SADT of 45 °C (in 50 kg package);

and according to CLP Annex I, section 2.8.2.1, consequently it has to be considered for classification in the hazard class self-reactive substances and mixtures.

Test results and classification according to CLP Annex I, Figure 2.8.1 for self-reactive substances and mixtures and the UN-MTC, Part II, are as follows:

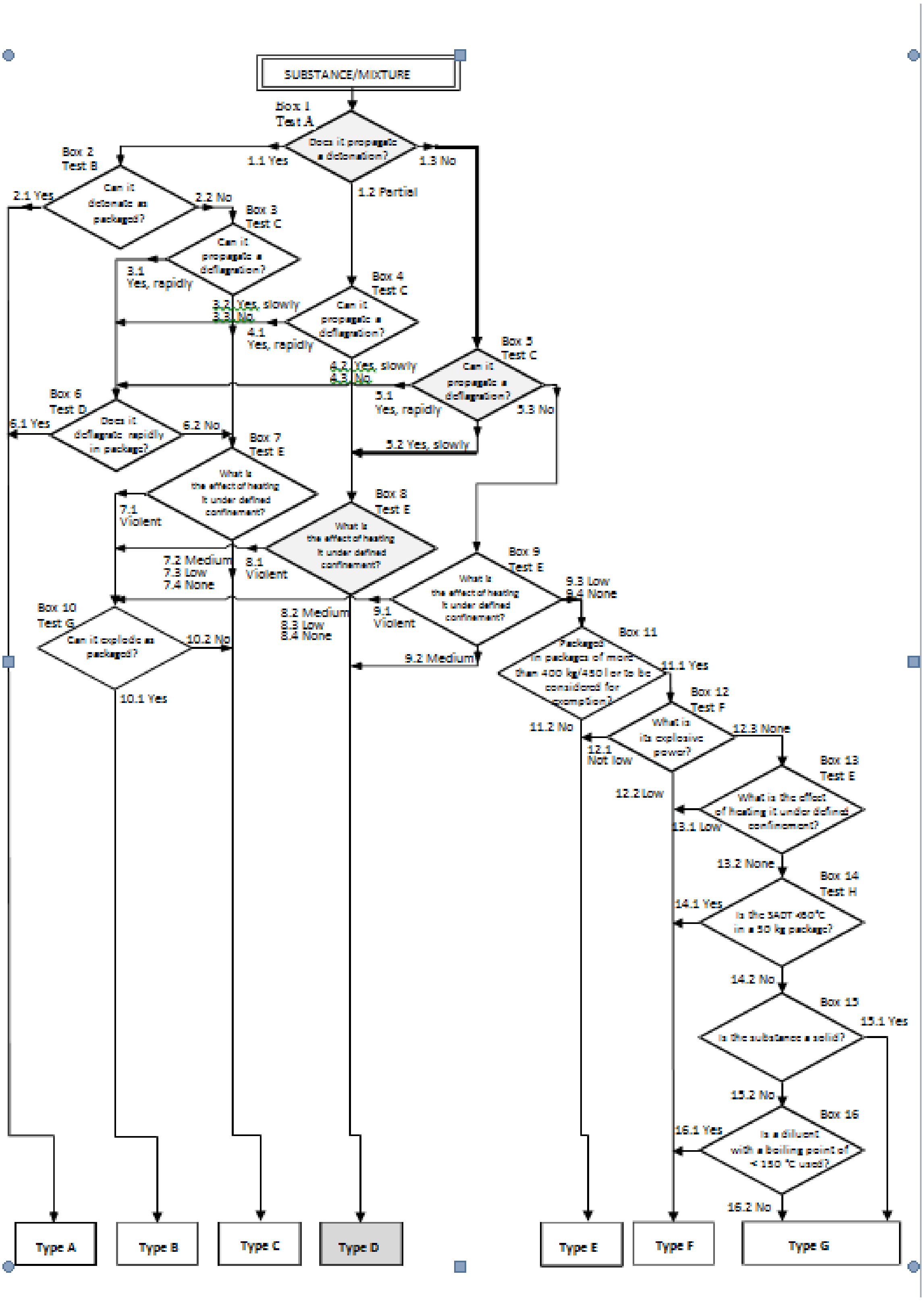
CLASSIFICATION TEST RESULTS		
1. Name of the self-reactive substance or mixture:		NP
2. General data		
2.1.	Composition	NP, technically pure
2.2.	Molecular formula	Not applicable
2.3.	Physical form	Solid, fine powder
2.4.	Colour	Brown
2.5.	Density (apparent)	460 kg/m^3
3. Detonation (Test Series A)		
Box 1 of the decision logic		Does the substance propagate a detonation?
3.1.	Method	UN Test A.1: BAM 50/60 steel tube test
3.2.	Sample conditions	Technically pure substance

CLASSIFICATION TEST RESULTS	
3.3. Observations	Fragmented part of the tube: 12, 18cm
3.4. Result	No
3.5. Exit	1.3
4. Deflagration (Test Series C)	
Box 5 of the decision logic	Does the substance propagate a deflagration?
4.1. Method 1	Time/pressure test (UN Test C.1)
4.1.1. Sample conditions	Ambient temperature
4.1.2. Observations	498, 966, 3395 ms
4.1.3. Result	Yes, slowly
4.2. Method 2	Deflagration test (UN Test C.2)
4.2.1. Sample conditions	Temperature: 20 °C
4.2.2. Observations	Deflagration rate: 0.90, 0.87 mm/s
4.2.3. Result	Yes, slowly
4.3. Final result	Yes, slowly
4.4. Exit	5.2
5. Heating under confinement (Test Series E)	
Box 8 of the decision logic:	What is the effect of heating it under defined confinement?
5.1. Method 1	Koenen test (UN Test E.1)
5.1.1. Sample conditions	
5.1.2. Observations	Limiting diameter: < 1.0 mm, fragmentation type ‘A’
5.1.3. Result	Low
5.2. Method 2	Dutch pressure vessel test (test E.2)
5.2.1. Sample conditions	
5.2.2. Observations	Limiting diameter: <1.0 mm (with 10 g), 1.0 mm (50 g)
5.2.3. Result	Low
5.3. Final result	Low
5.4. Exit	8.3

CLASSIFICATION TEST RESULTS	
6. Thermal stability (outside of the decision logic)	
6.1. Method	Heat accumulation storage test (UN Test H.4)
6.2. Sample conditions:	Mass 232.5 g. Half life time of cooling of Dewar vessel with 400 ml water: 10.0 h (representing substance in package)
6.3. Observations	Self-accelerating decomposition at 45 °C No self-accelerating decomposition at 40 °C
6.4. Result	SADT 45 °C (in 50 kg package)
7. General remarks	The decision logic is given in Figure 2.5
8. Final classification	
Hazard / hazard class:	Self-reactive substance, Type D, solid, temperature controlled
Label	Flame (GHS02)
Signal word	Danger
Hazard statement	H242: Heating may cause a fire
Temperature control	Needed based on SADT (45 °C, in package)
Control temperature*	35 °C (in package)
Emergency temperature*	40 °C (in package)

*See UN-MTC, table 28.3.

Figure 2.5 Decision logic for self-reactive substance example: NP, technically pure



2.9. PYROPHORIC LIQUIDS

2.9.1. Introduction

The criteria for 'Pyrophoric liquids' are found in CLP Annex I, section 2.9 and are identical to those in chapter 2.9 of GHS.

Pyrophoricity, i.e. the ability to spontaneously ignite in air, is the result of a reaction of a substance or mixture with the oxygen in the air and it is a very dangerous property. The reaction is exothermic and has the particularity that it starts spontaneously, i.e. without the aid of a supplied spark, flame, heat or other energy source. Another way of saying this is that the auto-ignition temperature for a pyrophoric substance or mixture is lower than room (ambient) temperature.

2.9.2. Definitions and general considerations for classification of pyrophoric liquids

The definition in CLP for pyrophoric liquids is as follows:

> **Annex I: 2.9.1.** ***Definition***
>
> *Pyrophoric liquid means a liquid substance or mixture which, even in small quantities, is liable to ignite within five minutes after coming into contact with air.*

2.9.3. Relation to other physical hazards

Pyrophoric substances and mixtures will react spontaneously with air already in small amounts and more or less instantaneously (within minutes). This differentiates them from self-heating substances and mixtures, which also react spontaneously with air but only when in larger amounts and after an extended period of time (hours or days). While liquids in themselves generally do not exhibit self-heating properties due to the limited contact with air (which can occur only at the surface), liquids that are adsorbed onto solid particles should, in general, be considered for classification in the hazard class self-heating substances and mixtures, see section 2.11.

Pyrophoricity may be expected for certain reactive metals and some of their compounds (e.g. hydrides and other organo-metal compounds). Many of these substances and mixtures will also react vigorously with water under the production of flammable gases. Such substances and mixtures may therefore be classified in the hazard class substances and mixtures which in contact with water emit flammable gases in addition, see section 2.12. It should be noted in this context that water-reactive substances and mixtures may also to some extent react with the humidity in air, although such a reaction is seldom vigorous. A substance or mixture that spontaneously ignites in air in accordance with the test procedures is to be considered pyrophoric, regardless of the reaction mechanism.

Liquids not classified as pyrophoric but that can burn may belong to the hazard class flammable liquids depending on their flash point and ability to sustain combustion, see section 2.6.

2.9.4. Classification of substances and mixtures as pyrophoric liquids

2.9.4.1. Identification of hazard information

Since the tests to determine pyrophoricity are simple and require no special equipment, see section 2.9.4.4 below, there is in general no reason to go to data sources instead of performing the tests. Furthermore, the possibilities of waiving the tests are ample both for known pyrophores and for substances and mixtures known not to be pyrophoric, see section 2.9.4.2 below. If information nevertheless is taken from literature or other data sources, it is of utmost importance that the correct physical form is considered, see section 2.0.4. Naturally, all data sources should be carefully evaluated with regard to reliability and scientific validity.

2.9.4.2. Screening procedures and waiving of testing

Organo-metals and organo-metalloids may be suspected of being pyrophores, as well as their derivatives. Also, organo-phosphines and their derivatives, hydrides and their derivatives and haloacetylene derivatives may show pyrophoricity. There are also pyrophoric substances or mixtures that do not belong to the above-mentioned groups of chemicals, i.e. the list above is not exhaustive. In case of doubt, it should be thoroughly investigated whether a given substance or mixture is pyrophoric. More information on pyrophoric substances can be found in sources such as *Bretherick's Handbook of Reactive Chemical Hazards* (Urben, 2007).

In case a liquid is known from practical handling to be pyrophoric, no testing is necessary. Such liquids are classified as pyrophoric liquids without testing. This would also be the case if the liquid spontaneously ignites upon opening of the receptacle when trying to perform the tests for classification.

According to the additional classification considerations in CLP:

> **Annex I:** ***2.9.4.1.*** *The classification procedure for pyrophoric liquids need not be applied when experience in manufacture 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)).*

2.9.4.3. Classification criteria

Section 2.9.2.1 of Annex I to CLP specifies the classification criteria:

Annex I: *Table 2.9.1*

Criteria for pyrophoric liquids

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

2.9.4.4. Testing and evaluation of hazard information

In CLP Annex I, section 2.9.2.1 reference to the test-methods is made:

> **Annex I:** ***2.9.2.1.*** *A pyrophoric liquid shall be classified in a single category for this class using test N.3 in part III, sub-section 33.3.1.5*[38] *of the UN RTDG, Manual of Tests and Criteria according to Table 2.9.1:*

The UN Test N.3 for pyrophoricity is quite simple and sufficiently described in Part III, section 33.4.5 of the UN-MTC. No special equipment is needed. Essentially, the substance or mixture is exposed to air to see if it ignites. For liquids which do not spontaneously ignite when poured, the surface in contact with air is increased using a filter paper. Ignition or charring of the filter paper is regarded as a positive response in the test, i.e. such a liquid is considered to be pyrophoric.

It is important that samples for testing of pyrophoric properties are carefully packed and sealed. Furthermore, the material offered for testing should be freshly prepared, since the reactive

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[38] This note is not part of the legal text: following an update on the UN-MTC, the correct reference is 'section 33.4.5' instead of 'section 33.3.1.5' as indicated in CLP.

properties may diminish due to aging or agglomeration. Whenever experiments are to be done one should be careful – a pyrophoric substance or mixture may well ignite already upon opening the receptacle!

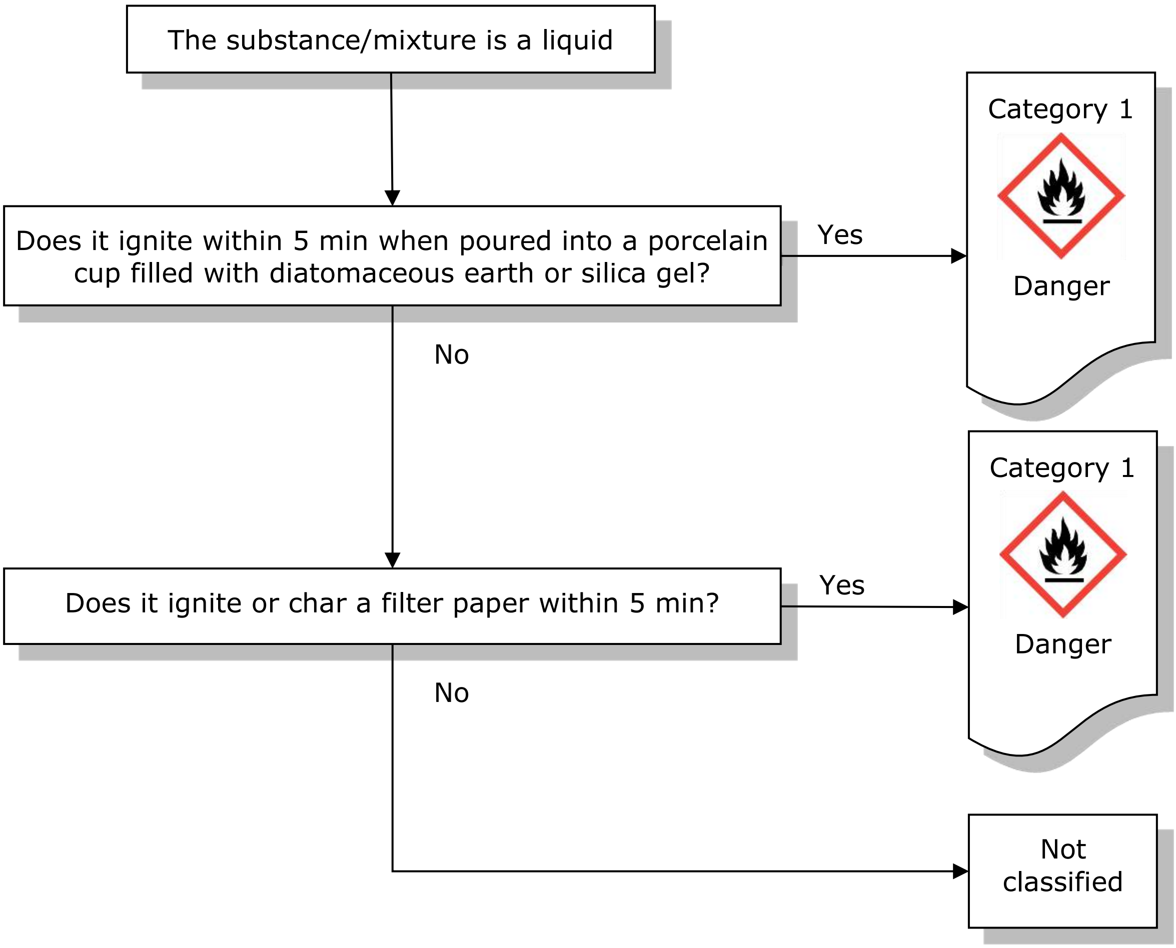
It should be noted that the mechanism of oxidation is, in general, very complex, and that the humidity of air might influence the rate of reaction. Therefore, a false negative may result when performing the tests in an extremely dry environment, and this condition must be avoided when performing the tests for classification for pyrophoricity. The filter paper test of UN Test N.3 for pyrophoric liquids should be carried out at 25 ± 2 °C and a relative humidity of 50 ± 5 % (see UN-MTC, section 33.4.5).

2.9.4.5. Decision logic

Classification of pyrophoric liquids is done according to decision logic 2.9 as included in GHS.

NOTE: The person responsible for the classification of pyrophoric liquids should be experienced in this field and be familiar with the criteria for classification.

Figure 2.6 Decision logic for pyrophoric liquids (Decision logic 2.9 of GHS)



2.9.5. Hazard communication for pyrophoric liquids

2.9.5.1. Pictograms, signal words, hazard statements and precautionary statements

Annex I: *2.9.3* *Table 2.9.2* ***Label elements for pyrophoric liquids***	
Classification	*Category 1*
GHS Pictogram	
Signal Word	*Danger*
Hazard Statement	*H250: Catches fire spontaneously if exposed to air*
Precautionary Statement Prevention	*P210* *P222* *P231 + P232* *P233* *P280*
Precautionary Statement Response	*P302 + P334* *P370 + P378*
Precautionary Statement Storage	
Precautionary Statement Disposal	

The wording of the precautionary statements is found in CLP Annex IV, Part 2.

2.9.6. Relation to transport classification

Division 4.2 within Class 4 of the UN RTDG Model Regulations covers pyrophoric solids, liquids and self-heating substances and mixtures. UN Test N.3 that is used for classification for pyrophoricity for liquids according to CLP is also used for classification in the subdivision pyrophoric substances and mixtures in Division 4.2: Substances liable to spontaneous combustion according to the UN RTDG Model Regulations. The criteria for category 1 according to CLP (which is the only category for pyrophoric liquids) and for packing group I in Division 4.2 according to the modal transport regulations (ADR, RID, ADN and IMDG Code, ICAO TI) are also exactly the same. Furthermore, all pyrophoric substances and mixtures are assigned to packing group I within Division 4.2, which is used exclusively for pyrophoric substances and mixtures.

Therefore, any liquid assigned to Division 4.2, packing group I according to the modal transport regulations (ADR, RID, ADN and IMDG Code, ICAO TI) will be classified in category 1 of the hazard class pyrophoric liquids according to CLP. See Annex I for additional information on transport classification in relation to CLP classification.

2.9.7. Examples of classification for pyrophoric liquids

Please note that the substance and mixture names in this chapter are fictitious.

2.9.7.1. Examples of substances and mixtures fulfilling the classification criteria

2.9.7.1.1. Example 1

Name:	Pyrpherdine
Physical state:	Liquid
Pyrophoric properties:	Unknown, therefore the UN Test N.3 of the UN-MTC was applied. However, when opening the receptacle to perform the test, Pyrpherdine self-ignited spontaneously.
Classification:	Pyrophoric liquid, category 1

2.9.7.1.2. Example 2

Name:	Qulipyr
Physical state:	Liquid
Pyrophoric properties:	Unknown, therefore the UN Test N.3 of the UN-MTC was applied.
Test result:	When poured according to the test procedure, nothing happened. The procedure was repeated six times, each time giving a negative result (i.e. no ignition). Therefore, Qulipyr was supplied to a filter paper in accordance with the test method. In the second trial the filter paper was charred within five minutes.
Classification:	Pyrophoric liquid, category 1

2.9.7.2. Example of substances and mixtures not fulfilling the classification criteria

2.9.7.2.1. Example 3

Name:	Notpyratal
Physical state:	Liquid
Pyrophoric properties:	Unknown, therefore UN Test N.3 of the UN-MTC was applied.
Test result:	When poured according to the test procedure nothing happened in either of six trials. Therefore, Notpyratal was supplied to a filter paper in accordance with the test method, whereupon no ignition or charring occurred in either of three trials.
Classification:	Not a pyrophoric liquid

2.9.8. References

Urben, Peter G. (2007). *Bretherick's Handbook of Reactive Chemical Hazards*, Volumes 1-2 (7th Edition). Elsevier.

2.10. PYROPHORIC SOLIDS

2.10.1. Introduction

The criteria for 'Pyrophoric solids' are found in CLP Annex I, section 2.10 and are identical to those in chapter 2.10 of GHS.

Pyrophoricity, i.e. the ability to spontaneously ignite in air, is the result of a reaction of a substance or mixture with the oxygen in the air and it is a very dangerous property. The reaction is exothermic and has the particularity that it starts spontaneously, i.e. without the aid of a supplied spark, flame, heat or other energy source. Another way of saying this is that the self-ignition temperature for a pyrophoric substance or mixture is lower than room (ambient) temperature.

2.10.2. Definitions and general considerations for classification of pyrophoric solids

The definition in CLP for pyrophoric solids is as follows:

> **Annex I: *2.10.1. Definition***
>
> *Pyrophoric solid means a solid substance or mixture which, even in small quantities, is liable to ignite within five minutes after coming into contact with air.*

Special consideration on particle size

> **Annex I: *2.10.2.1.***
>
> *[…]*
>
> *Note: The test shall be performed on the substance or mixture in its physical form 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 shall also be tested in the new form.*

The finer the particle size of a solid, the greater the area exposed to air will be, and since pyrophoricity is a reaction with the oxygen in air, the particle size will greatly influence the ability to spontaneously ignite. Hence, it is very important that pyrophoric properties for solids are investigated on the substance or mixture as it is actually presented (including how it can reasonably be expected to be used, see Article 8(6) of CLP). This is indicated by the Note in CLP Annex I, section 2.10.2.1.

2.10.3. Relation to other physical hazards

Pyrophoric solids will react spontaneously with air already in small amounts and more or less instantaneously (within minutes). This differentiates them from self-heating substances and mixtures, which also react spontaneously with air but only when in larger amounts and after an extended period of time (hours or days). A solid which is not classified as a pyrophoric solid may therefore belong to the hazard class self-heating substances and mixtures, and should be considered for classification in that hazard class, see section 2.11.

Pyrophoricity may be expected for certain reactive metals and some of their compounds (e.g. hydrides and other organo-metal compounds). Many of these substances will also react vigorously with water under the production of flammable gases. Such substances may therefore be classified in the hazard class substances and mixtures which in contact with water emit flammable gases in addition to pyrophoric solid classification, see section 2.12. It should be noted in this context that water-reactive substances or mixtures may also to some extent react with the humidity in air, although such a reaction is seldom vigorous. A substance that spontaneously ignites in air in accordance with the test procedures is to be considered pyrophoric, regardless of the reaction mechanism.

Solids not classified as pyrophoric may still be able to burn rapidly if subjected to enough initiating energy, such as the flame from a gas burner, to start the reaction. Therefore, they may be subject to classification in the hazard class flammable solids, see section 2.7, i.e. they may be 'flammable solids'.

2.10.4. Classification of substances and mixtures as pyrophoric solids

2.10.4.1. Identification of hazard information

Since the tests to determine pyrophoricity are simple and require no special equipment, see section 2.10.4.4 below, there is in general no reason to go to data sources instead of performing tests. Furthermore, the possibilities of waiving tests are ample both for known pyrophores and for substances and mixtures known not to be pyrophoric, see section 2.10.4.2 below. If information nevertheless is taken from literature or other data sources, it is of utmost importance that the correct physical form is considered, see section 2.0.4. Naturally, all data sources should be carefully evaluated with regard to reliability and scientific validity.

2.10.4.2. Screening procedures and waiving of testing

Organo-metals and organo-metalloids may be suspected of being pyrophores, as well as their derivatives. In addition, organo-phosphines and their derivatives, hydrides and their derivatives, haloacetylene derivatives, and complex acetylides may show pyrophoricity (Urben, 2007). Furthermore, powders or fine particles of metals could be pyrophoric. However, although many solid metallic substances, like e.g. aluminium, would be suspected of being pyrophoric when considering their general reactivity, they form a protective oxide-coat upon reaction with air. This thin coat of metal oxide prevents the metal from reacting further, and hence such substances may not show pyrophoric behaviour in reality. There are also pyrophoric solids that do not belong to the above-mentioned groups of chemicals, i.e. the list above is not exhaustive.

Since pyrophoric solids ignite *spontaneously* in air, pyrophoricity is a very dangerous property. In case of doubt, it should be thoroughly investigated whether a given solid is pyrophoric. More information on pyrophoric solids can be found in sources such as *Bretherick's Handbook of Reactive Chemical Hazards* (Urben, 2007).

In case a solid is known from practical handling to be pyrophoric, no testing is necessary. Such solids are classified as pyrophoric solids without testing. This would also be the case if the solid spontaneously ignites upon opening of the receptacle when trying to perform the tests for classification.

According to the additional classification considerations in CLP:

> **Annex I: *2.10.4.1.*** *The classification procedure for pyrophoric solids need not be applied when experience in manufacture 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)).*

2.10.4.3. Classification criteria

Section 2.10.2.1 of Annex I to CLP specifies the classification criteria:

Annex I: *Table 2.10.1* ***Criteria for pyrophoric solids***	
Category	*Criteria*
1	*The solid ignites within 5 minutes of coming into contact with air.*

2.10.4.4. Testing and evaluation of hazard information

In CLP Annex I, section 2.10.2.1 reference to the test-methods are made:

> **Annex I:** ***2.10.2.1.*** *A pyrophoric solid shall be classified in a single category for this class using test N.2 in part III, sub-section 33.3.1.4*[39] *of the UN RTDG, Manual of Tests and Criteria in accordance with Table 2.10.1:*

UN Test N.2 for pyrophoricity is quite simple and sufficiently described in Part III, section 33.4.4 of the UN-MTC. No special equipment is needed. Essentially the solid is exposed to air to see if it ignites.

It is important that samples for testing of pyrophoric properties are carefully packed and sealed. Furthermore, the material offered for testing should be freshly prepared, since the reactive properties may diminish due to aging or agglomeration. Whenever experiments are to be done one should be careful – a pyrophoric solid may well ignite already upon opening the receptacle!

It should be noted that the mechanism of oxidation is, in general, very complex, and that the humidity of air might influence the rate of reaction. It is known that certain metals will not react in dry air, whereas in the presence of moisture the reaction is almost instantaneous (often even trace amounts of moisture are sufficient). Therefore, a false negative may result when performing the tests in an extremely dry environment, and this condition must be avoided when performing the tests for classification for pyrophoricity.

2.10.4.5. Decision logic

Classification of pyrophoric solids is done according to decision logic 2.10 as included in GHS.

! NOTE: The person responsible for the classification of pyrophoric solids should be experienced in this field and be familiar with the criteria for classification.

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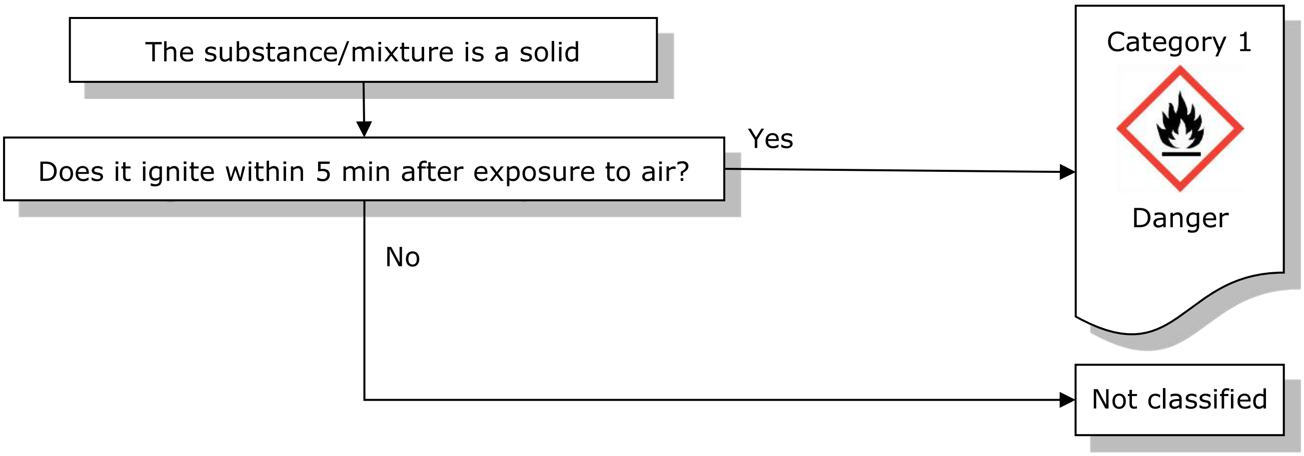
[39] This note is not part of the legal text: following an update on the UN-MTC, the correct reference is 'section 33.4.4' instead of 'section 33.3.1.4' as indicated in the CLP Regulation.

Figure 2.7 Decision logic for pyrophoric solids (Decision logic 2.10 of GHS)



2.10.5. Hazard communication for pyrophoric solids

2.10.5.1. Pictograms, signal words, hazard statements and precautionary statements

Annex I: *2.10.3* *Table 2.10.2* ***Label elements for pyrophoric solids***	
Classification	*Category 1*
GHS Pictogram	
Signal Word	*Danger*
Hazard Statement	*H250: Catches fire spontaneously if exposed to air*
Precautionary Statement Prevention	*P210* *P222* *P231 + P232* *P233* *P280*
Precautionary Statement Response	*P302 + P335 + P334* *P370 + P378*
Precautionary Statement Storage	
Precautionary Statement Disposal	

The wording of the precautionary statements is found in CLP Annex IV, Part 2.

2.10.6. Relation to transport classification

Division 4.2 within Class 4 of the UN RTDG Model Regulations covers pyrophoric solids, liquids and self-heating substances and mixtures. The UN Tests N.2 that is used for classification for pyrophoricity for solids according to CLP is also used for classification in the subdivision pyrophoric substances and mixtures in Division 4.2: substances liable to spontaneous combustion according to the UN RTDG Model Regulations. The criteria for category 1 according to CLP (which is the only category for pyrophoric solids) and for packing group I in Division 4.2 according to the modal transport regulations (ADR, RID, ADN and IMDG Code, ICAO TI) are also exactly the same. Furthermore, all pyrophoric substances and mixtures are assigned to packing group I within Division 4.2, which is used exclusively for pyrophoric substances and mixtures.

Therefore, any solid assigned to Division 4.2, packing group I according to the modal transport regulations (ADR, RID, ADN and IMDG Code, ICAO TI) will be classified in category 1 of the hazard class pyrophoric solids according to CLP. See Annex I for additional information on transport classification in relation to CLP classification.

2.10.7. Examples of classification for pyrophoric solids

Please note that the substance and mixture names in this chapter are fictitious.

2.10.7.1. Examples of substances and mixtures fulfilling the classification criteria

2.10.7.1.1. Example 1

Name:	Pyroferil
Physical state:	Solid
Pyrophoric properties:	Pyroferil is known to self-ignite upon contact with air at ambient conditions.
Classification:	Pyrophoric solid, category 1

2.10.7.1.2. Example 2

Name:	Zorapyrole
Physical state:	Solid
Pyrophoric properties:	Unknown, therefore the UN Test N.2 of the UN-MTC was applied.
Test result:	When poured from one meter height according to the test procedure, Zorapyrole self-ignited after two minutes already in the first trial.
Classification:	Pyrophoric solid, category 1

2.10.7.2. Example of substances and mixtures not fulfilling the classification criteria

2.10.7.2.1. Example 3

Name:	Nonopyr
Physical state:	Solid

Pyrophoric properties:	Nonopyr has been handled extensively in air and has never self-ignited. From the chemical structure no pyrophoricity is expected.
Classification:	Not a pyrophoric solid

2.10.7.2.2. Example 4

Name:	Pyronot
Physical state:	Solid
Pyrophoric properties:	Unknown, therefore UN Test N.2 of the UN-MTC was applied.
Test result:	When poured from one meter height according to the test procedure no ignition occurred within five minutes. The procedure was repeated six times and each time the result was negative.
Classification:	Not a pyrophoric solid

2.10.8. References

Urben, Peter G. (2007). *Bretherick's Handbook of Reactive Chemical Hazards*, Volumes 1-2 (7th Edition). Elsevier.

2.11. SELF-HEATING SUBSTANCES AND MIXTURES

2.11.1. Introduction

The criteria for ‘Self-heating substances and mixtures’ are found in CLP Annex I, section 2.11 and are identical to those in chapter 2.11 of GHS.

Self-heating is the result of an exothermic reaction of a substance or mixture with the oxygen in the air. Initially, the reaction rate may be very low. However, when the heat produced cannot be removed rapidly enough, the substance or mixture will self-heat through heat accumulation, with the possible consequence of self-ignition. The phenomenon can occur only where a large surface of substance or mixture is in contact with air or oxygen (for example, piles of powders, crystals, splinters, any other rough surface etc.). The initiation occurs usually at or near the centre of the substance or mixture pile with the available air in the interspace between the particles.

2.11.2. Definitions and general considerations for classification of self-heating substances and mixtures

The definitions in CLP for self-heating substances and mixtures are as follows:

Annex I: *2.11.1.1.* *A self-heating substance or mixture is a liquid or solid 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).*

2.11.1.2. *Self-heating of a substance or a mixture is a process where the gradual reaction of that substance or mixture with oxygen (in the 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.*

2.11.3. Relation to other physical hazards

Pyrophoric solids and liquids should not be considered for classification as self-heating substances and mixtures.

2.11.4. Classification of substances and mixtures as self-heating

2.11.4.1. Identification of hazard information

Self-heating is a very complex phenomenon which is influenced by many parameters (some of them being volume, temperature, particle shape and size, heat conductivity and bulk density). Therefore, self-heating behaviour cannot be predicted from any theoretical model. In some cases, properties might even differ between material from producers of seemingly identical or similar substances or mixtures. Differences in self-heating behaviour are especially to be anticipated where surface treatment occurs in the production process. Hence, all data sources should be carefully evaluated with regard to reliability and scientific validity.

Self-heating substances and mixtures may include the following:

- many organometallic compounds, especially substances or mixtures containing transition metals;
- many organic substances or mixtures; the tendency to self-heat increases with decreasing particle size;
- many metals, especially catalysts.

Since the surface area of a solid substance or mixture exposed to air increases with decreasing particle size, it follows that particle size and shape will greatly influence the potential of a substance or mixture to self-heat. Therefore, it is very important that self-heating properties for solids, and especially powders, are determined for the substance or mixture in the form it is supplied and expected to be used.

2.11.4.2. Screening procedures and waiving of testing

Annex I: *2.11.4.2.* *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.

Note: Regarding point 'a' in the above table, VDI[40] 2263, part 1 has been updated to a new version: VDI 2263, part 1, 2022, Dust fires and dust explosions - Hazards - assessment - safety measures - Safety-related parameters of bulk goods.

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[40] VDI: Verein Deutscher Ingenieure - Association of German Engineers

EU test method A.16, as described in Regulation (EC) No 440/2008, checks for self-heating properties. However, the method is generally inappropriate for a sound assessment of self-heating, and the findings do not lead to a classification. Therefore, special care must be taken if results from EU test method A.16 are interpreted towards a CLP classification for self-heating substances and mixtures. Even if a temperature rise up to 400 °C due to self-heating is not observed, such behaviour cannot be interpreted as conclusive for "no classification".

In general, the phenomenon of self-heating applies only to solids. The surface of liquids is not large enough for reaction with air and the test method is not applicable to liquids. Therefore, liquids are not classified as self-heating. However, if liquids are adsorbed on a large surface (e.g. on powder particles or a textile mesh), a self-heating hazard should be considered.

Substances or mixtures with a low melting point (< 160 °C) should not be considered for classification as self-heating since the melting process is endothermic and the substance-air surface is drastically reduced. However, this criterion is only applicable if the substance or mixture is **completely molten** up to this temperature (i.e. the test basket of an isothermal Grewer test at 160 °C as mentioned in UN-MTC section 3.12.4.2 a) or in any one of the UN N.4 tests is empty after the test). Sublimation in the same temperature range is also effective in suppressing self-heating. However, if some material remains in the test basket in such a way that the temperature sensor as described in UN-MTC section 33.4.6.2 c) has lost contact, it may be helpful for the interpretation of the findings to repeat the experiment with an additional thermocouple in place.

2.11.4.3. Classification criteria

A self-heating substance or mixture must be classified in one of the two categories for this class if, in a test performed in accordance with UN Test N.4 in Part III, section 33.4.6 of the UN-MTC, the result meets the criteria according to following table:

Annex I: *Table 2.11.1*

Criteria for self-heating substances and mixtures

Category	*Criteria*
1	*A positive result is obtained in a test using a 25 mm sample cube at 140 °C*
2	*(a) a positive result is obtained in a test using a 100 mm sample cube at 140 °C and a negative result is obtained in a test using a 25 mm cube sample at 140 °C <u>and</u> the substance or mixture is to be packed in packages with a volume of more than 3 m^3; or* *(b) a positive result is obtained in a test using a 100 mm sample cube at 140 °C and a negative result is obtained in a test using a 25 mm cube sample at 140 °C, a positive result is obtained in a test using a 100 mm cube sample at 120 °C <u>and</u> the substance or mixture is to be packed in packages with a volume of more than 450 litres; or* *(c) a positive result is obtained in a test using a 100 mm sample cube at 140 °C and a negative result is obtained in a test using a 25 mm cube sample at 140 °C <u>and</u> a positive result is obtained in a test using a 100 mm cube sample at 100 °C.*

Note

The test shall be performed on the substance or mixture in its physical form 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 shall also be tested in the new form.

2.11.2.3. *Substances and mixtures with a temperature of spontaneous combustion higher than 50 °C for a volume of 27 m³ shall not be classified as a self-heating substance or mixture.*

2.11.2.4. *Substances and mixtures with a spontaneous ignition temperature higher than 50 °C for a volume of 450 litres shall not be assigned to Category 1 of this class.*

2.11.4.4. Testing and evaluation of hazard information

A self-heating substance or mixture must be classified in one of the two categories for this class using UN Test N.4 in Part III, section 33.4.6 of the UN-MTC.

2.11.4.4.1. General remarks

If self-heating behaviour cannot be ruled out by a screening test, further testing becomes necessary. UN Test N.4 as described in the latest version of the UN-MTC should be used.

Explosive substances and mixtures should not be tested according to this method. For safety reasons, it is necessary to first test for explosive and self-reactive properties and to rule out pyrophoric behaviour before performing this test. The oven should be equipped with an appropriate pressure-release device in case an energetic decomposition is triggered by a temperature rise. For samples containing flammable solvents explosion protection measures have to be taken.

It is of utmost importance that in compliance with Articles 5 and 6 of CLP authentic and representative material in the correct form and physical state is used for testing.

The tests for self-heating properties may be performed in any order. It is suggested to start with the 25 mm sample cube at 140 °C. If a positive result is obtained, the substance or mixture must be classified as a self-heating substance or mixture, category 1, and no further testing is necessary.

2.11.4.4.2. Sample preparation

The sample (powder or granular) in its commercial form should be used and should not be milled or ground. It should be filled to the brim of the sample container and the container tapped several times. If the sample settles, more is added. If the sample is heaped it should be levelled to the brim. The sample container is placed in the oven as described in the UN-MTC, section 33.4.6.3.

2.11.4.4.3. Test conduction, criteria and evaluation

A positive result is obtained if spontaneous ignition occurs or if the temperature of the sample exceeds the oven temperature by 60 °C. The testing time is 24 hours. The time count starts when the temperature in the centre of the sample has reached a value of 2 °C below the oven temperature. This is especially important when the sample contains solvents which evaporate under the test conditions or when larger test volumes are used for extrapolation purposes (see below).

Before starting UN Test N.4, the decomposition behaviour of the sample should be known. In general, it is sufficient to perform a screening Differential Scanning Calorimetry measurement; see UN-MTC section 20.3.3.3. Test data needs to be interpreted cautiously if exothermic decomposition may occur at the test temperatures. In such cases, a test under an inert atmosphere (i.e. nitrogen) should be run to determine the temperature rise due to decomposition. Thorough flushing with the chosen inert gas is essential in such cases since air may be retained between the crystals of the sample in the container. If endothermic decomposition occurs during testing (for example, release of flammable or toxic gases) the criterion of a 60 °C temperature rise according to UN-MTC section 33.4.6.3 may not be fulfilled because temperature increase is hindered by the endothermic decomposition. However, if such a reaction may be triggered by self-heating the criterion for classification should be considered as fulfilled. An additional thermogravimetric measurement is advisable for assessment under these circumstances.

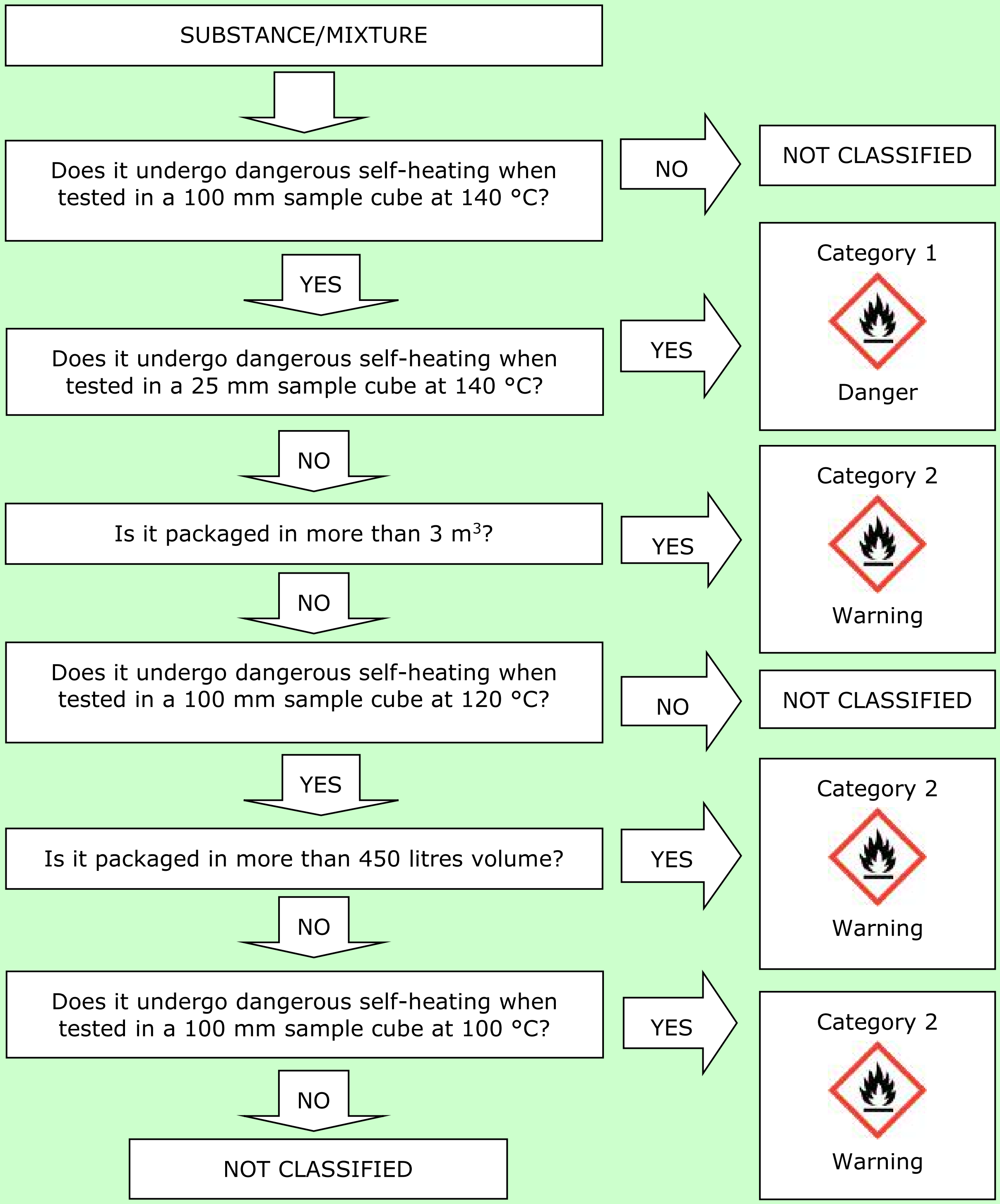
2.11.4.5. Decision logic

The following decision logic for self-heating substances and mixtures is applicable according to CLP.

NOTE: The person responsible for the classification of self-heating substances and mixtures should be experienced in this field and be familiar with the criteria for classification.

Annex I: Figure 2.11.1.

Self-heating substances and mixtures



2.11.4.6. Exemption

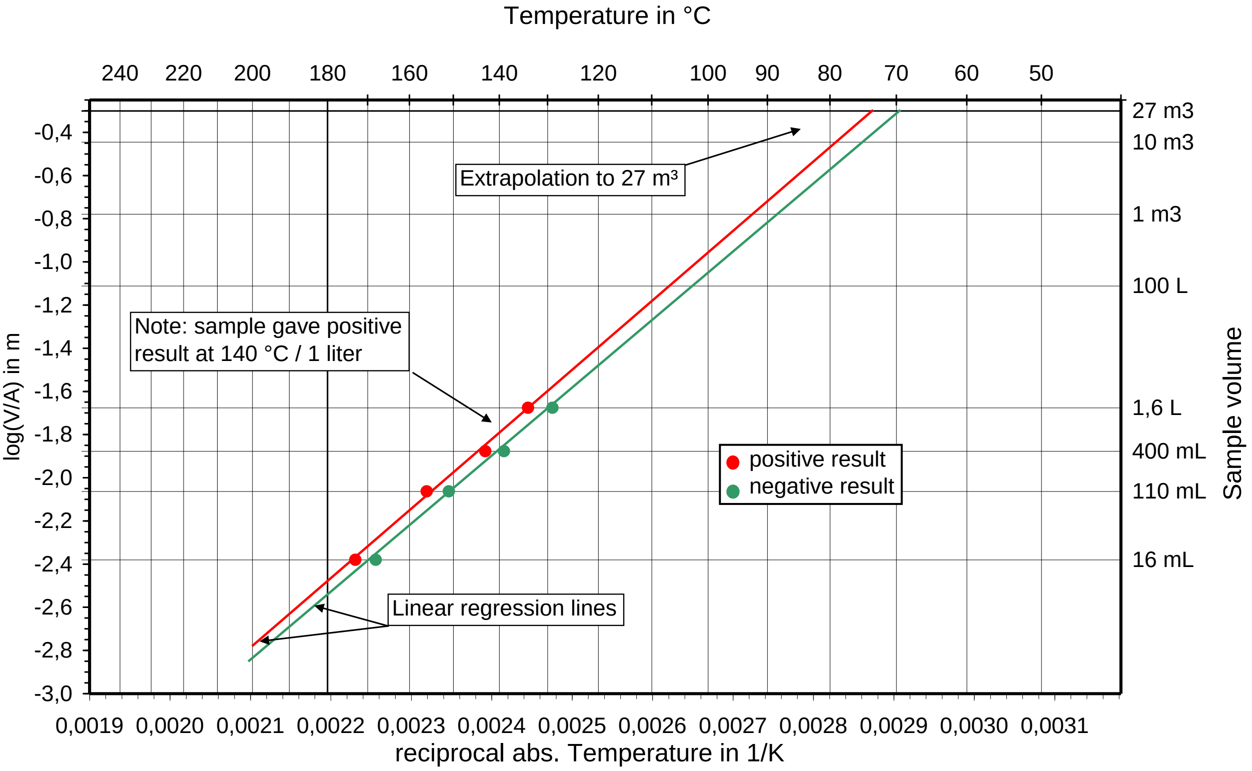
The following exemptions apply (see section 2.11.4.3):

- Substances and mixtures with a temperature of spontaneous combustion higher than 50 °C for a volume of 27 m³ shall not be classified as a self-heating substance or mixture (CLP, 2.11.2.4).
- Substances and mixtures with a spontaneous ignition temperature higher than 50 °C for a volume of 450 litres must not be assigned to category 1 of this class.

However, the UN-MTC does not provide any guidance on how these values should be determined. According to Grewer (Grewer, 1994), plotting the logarithm of the volume to surface ratio (log (V/A)) versus the reciprocal temperature gives good results without knowledge of the Frank-Kamenetskii (Frank-Kamenetskii, 1969) shape factor. This method had first been suggested by Leuschke (Leuschke, 1976 and 1981) as an empirical alternative to the Frank-Kamenetskii approach.

The critical temperature for a volume of 450 l or 27 m³ can be found by extrapolation of the critical temperature in a log (V/A) vs. 1/T plot (see Figure 2.8):

Figure 2.8 Extrapolation towards large volumes



A standardised procedure can be found in BS EN 15188:2020 "*Determination of the spontaneous ignition behaviour of dust accumulations*".

The test setup is essentially the same as in UN Test N.4 of the UN-MTC but now the sample size and possibly the shape are systematically varied. The criteria in section 2.11.4.3 apply as well.

The critical temperature must be determined over a range of at least four different volumes and with a volume not smaller than 16 ml. If possible, larger volumes should be also tested. The borderline temperature should be determined as precisely as possible. For small volumes (< 1 litre), the temperature rise due to self-heating may be considerably less than 60 °C; in this case a noticeable temperature rise is interpreted as a positive result.

A conservative approach is required for the evaluation. The uncertainty of measurement must be taken into account. The extrapolation must be based on a linear regression of the negative and positive borderline data sets in the log (V/A) vs. 1/T diagram. An exemption may be claimed if the more conservative endpoint for the particular volume is well beyond 50 °C (i.e. 55 °C or higher).

It should be noted that the slope of the line in the 1/T vs. volume diagram depends on the individual activation energy of the substance or mixture, so it may vary within certain limits. It must be born in mind that this test regime has been developed to facilitate classification and that it may not suffice to solve safety issues in storage.

A significant increase in the accuracy of the extrapolation can be achieved by conducting tests on a semi-industrial scale. Experiments up to a volume of 1 m^3 are presented in Martin Schmidt *et al*. (2022). For all materials investigated so far, the critical temperatures of the 1 m^3 sample were higher than predicted by the extrapolation of laboratory tests according to Leuschke (1976 and 1981).

In Martin Schmidt *et al*. (2022), a further screening method based on the direct measurement of the heat flows at process temperatures (microcalorimetric low-temperature measurements) is also introduced.

2.11.5. Hazard communication for self-heating substances or mixtures

2.11.5.1. Pictograms, signal words, hazard statements and precautionary statements

Annex I: *Table 2.11.2* ***Label elements for self-heating substances and mixtures***		
Classification	*Category 1*	*Category 2*
GHS Pictograms		
Signal Word	*Danger*	*Warning*
Hazard Statement	*H251: Self-heating; may catch fire*	*H252: Self-heating in large quantities; may catch fire*
Precautionary Statement Prevention	*P235* *P280*	*P235* *P280*
Precautionary Statement Response		
Precautionary Statement Storage	*P407* *P413* *P420*	*P407* *P413* *P420*
Precautionary Statement Disposal		

The wording of the precautionary statements is found in CLP Annex IV, Part 2.

2.11.6. Relation to transport classification

Division 4.2 – substances and mixtures liable to spontaneous combustion – within Class 4 of the UN RTDG Model Regulations comprises the following entries:

a. pyrophoric substances and mixtures;

b. self-heating substances and mixtures.

Whereas pyrophoric substances and mixtures in the modal transport regulations (ADR, RID, ADN and IMDG Code, ICAO TI) are assigned to packing group I, self-heating substances and mixtures are assigned to packing groups II and III. In cases where a substance or mixture is classified in Division 4.2, packing group II or III, the translation into the CLP system is straightforward.

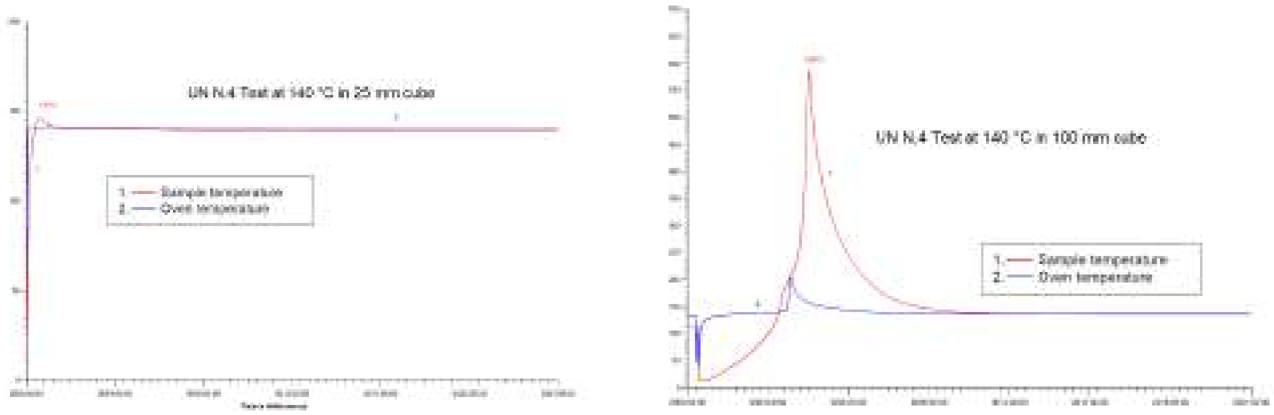
It should be kept in mind that transport classification is based on prioritisation of hazards (see the UN RTDG Model Regulations, section 2.0.3) and that self-heating substances and mixtures have a relatively low rank in the precedence of hazards. Therefore, the translation from the modal transport regulations (ADR, RID, ADN and IMDG Code, ICAO TI) to CLP should be only done if a transport classification as self-heating is explicitly available. The conclusion that a substance or mixture not classified as self-heating for transport should not be classified as a self-heating substance or mixture according to CLP is, in general, not correct. See Annex I for additional information on transport classification in relation to CLP classification.

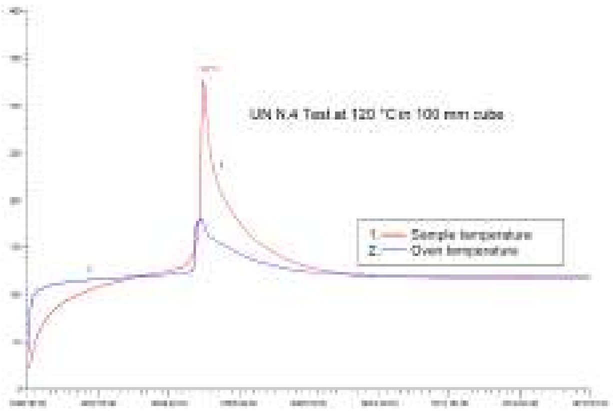
2.11.7. Examples of classification for self-heating substances or mixtures

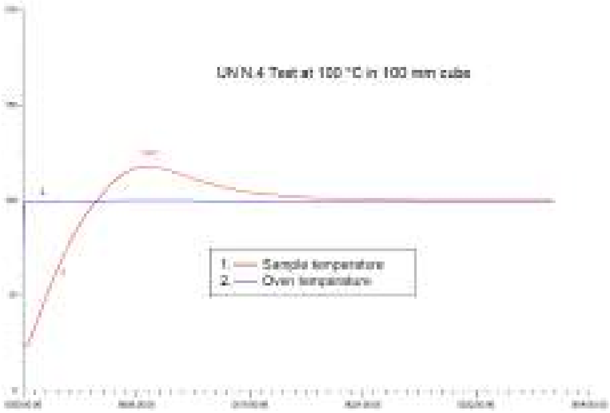
2.11.7.1. Example of substances and mixtures fulfilling the classification criteria

An example for the classification procedure is shown in the following diagrams obtained from performing the UN N.4 test according to the UN-MTC.

Figure 2.9 Results of UN N.4 Test according to the UN-MTC



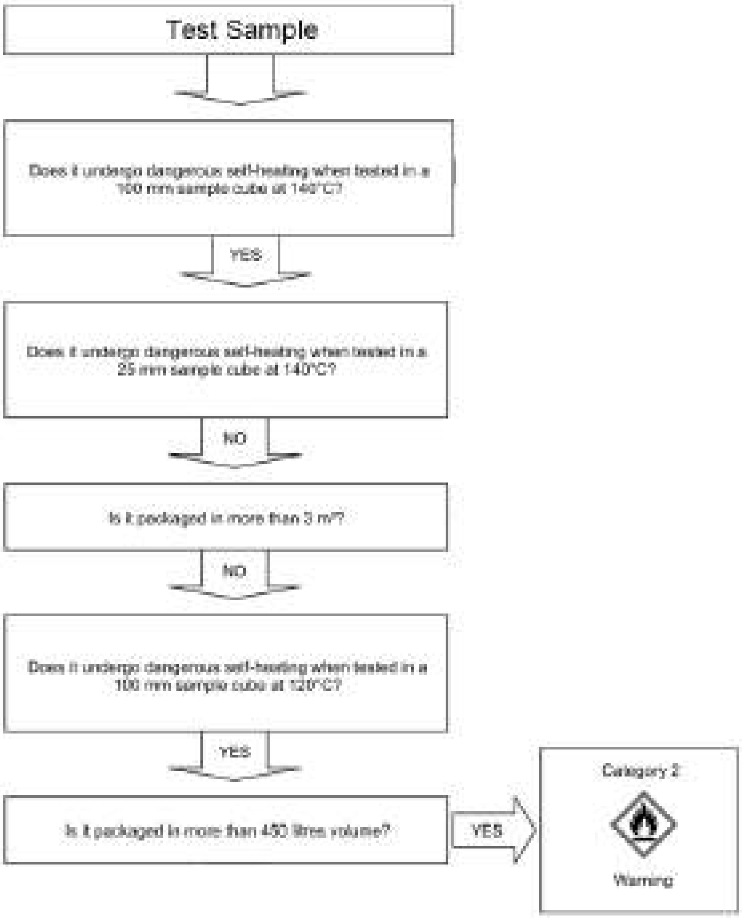




The temperature rises in the 25 mm cube from 140 °C to 146 °C (first diagram) and in the 100 mm cube from 100 °C to 118 °C (last diagram). At 120 °C and 140 °C in the 100 cube, the temperature increase is far beyond 60 °C.

For a substance or mixture packaged in a volume of 1000 litres, the classification comes to the following result.

Figure 2.10 Results of UN N.4 Test according to the UN-MTC



2.11.7.2. Example of substances and mixtures not fulfilling the classification criteria

In general, liquids show no self-heating behaviour unless adsorbed on a large surface.

Scientific background

A basic model for the thermal explosion of solids was first developed by Frank-Kamenetskii (Frank-Kamenetskii, 1969). It is based on the assumption that only the heat loss by thermal conduction is relevant for the phenomenon. In this case, the critical criterion for a thermal runaway reaction can be described as a linear relationship between the reciprocal absolute temperature and the logarithm of volume.

The classification scheme of the UN for self-heating substances and mixtures is based on charcoal as a reference system. The critical temperature for a 1 litre cube of charcoal is 140 °C and for a cube of 27 m³ 50 °C. When a parallel line is drawn in the 1/T vs. logarithm of volume diagram from the reference points 1 litre / 120 °C and 1 litre / 100 °C, the corresponding volumes for a critical temperature of 50 °C are found to be 3 m³ and 450 litre, respectively (see). The black dotted line in separates category 1 from category 2. For examples of results obtained in Test N.4 see section 33.3.4.6.5 of UN-MTC.

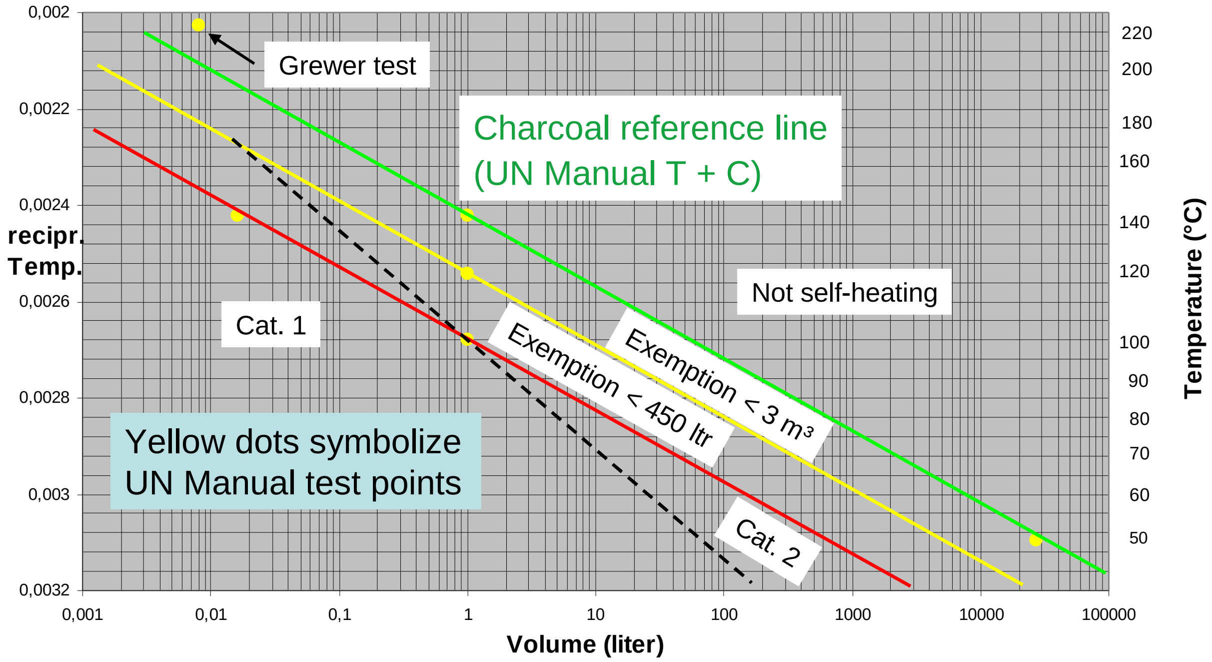


Figure 2.11 Volume dependency of the critical temperature for charcoal

2.11.8. References

Grewer, T. (1994). *Thermal hazards of chemical reactions*, Elsevier.

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Leuschke G. (1976). *Self-Ignition of Powdered Materials*, VFBD 5th International Fire Protection Seminar.

Leuschke, G. (1981). *Experimental investigations on self-ignition of dust deposits in hot environments*, Runaway Reactions, Unstable Products and Combustible Powders, IChemE Symposium Series 68.

Martin Schmidt, Marcus Gödde, Steffen Salg, René Erdt (2022). *Self-ignition Behaviour of Bulk Materials: How Reliable is the Extrapolation of Laboratory Tests?*, Chemical Engineering Transactions, Vol. 90, 289-294, DOI: 10.3303/CET2290049.

2.12. SUBSTANCES OR MIXTURES WHICH, IN CONTACT WITH WATER, EMIT FLAMMABLE GASES

2.12.1. Introduction

The criteria for 'Substances and mixtures which, in contact with water, emit flammable gases' are found in CLP Annex I, section 2.12 and are identical to those in chapter 2.12 of GHS[18].

Depending on the chemical structure and/or the physical state (e.g. particle size) substances or mixtures may be able to react with water (even damp / air humidity) under normal ambient temperature conditions. Sometimes this reaction can be violent and/or with significant generation of heat. Where flammable gases evolve, this reaction may become very dangerous during use. In addition, it is important to know whether a substance or mixture emits flammable gases after contact with water because special precautions are necessary especially with regard to explosion protection.

2.12.2. Definitions and general considerations for classification of substances or mixtures which, in contact with water, emits flammable gases

The following definition is given in CLP for substances and mixtures which, in contact with water, emit flammable gases (CLP Annex I, section 2.12).

> **Annex I:** ***2.12.1.*** *Substances or mixtures which, in contact with water, emit flammable gases means 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.*

2.12.3. Relation to other physical hazards

Gases exhibiting hazards other than flammability may be released by substances in contact with water. Some examples are demonstrated in the following table.

Table 2.2 Examples of hazards, depending on the property of the emitted gas, when substances and mixtures are in contact with water

Type of emitted gas	Example of hazards other than flammability	CLP Reference
Gas (in general)	• Heating up of the substance • Splashing of the substance and for example, contact with skin etc. or additional risk during fire fighting • Pressure rise and bursting of e.g. the packaging, tank	Annex II, section 1.1.3: Supplemental hazard information: EUH014*
Flammable gas	• Ignition • Flash of fire	Annex I, section 2.12: H260/H261
Toxic gas	• Damage to health: intoxication (acute)	Annex II, section1.2.1: Supplemental hazard information:

		EUH029

* For supplemental hazard information: see section 2.12.5.2

If the chemical identity of the emitted gas is unknown, the gas must be tested for flammability (unless it ignites spontaneously). Pyrophoric liquids and pyrophoric solids have to be considered for classification in this hazard class as well and data about pyrophoric properties are needed prior to testing for this hazard class.

2.12.4. Classification of substances and mixtures which, in contact with water, emits flammable gases

2.12.4.1. Identification of hazard information

For the classification of substances and mixtures which, in contact with water, emit flammable gases the following data are needed, if applicable:

- chemical structure;
- water solubility;
- chemical identity and flammability of the emitted gas;
- pyrophoric properties of the tested substance or mixture;
- particle size in case of solids;
- friability in case of solids;
- hazard properties in general;
- information concerning the experience in production or handling.

See also *IR & CSA, Chapter R.7a: Endpoint specific guidance*, section R.7.1.7 (Water solubility) and R.7.1.14 (Granulometry).

Information about the chemical structure is used to check whether the substance or mixture contains metals and/or metalloids.

Many different types of chemicals may belong to the hazard class of substances and mixtures which, in contact with water, emit flammable gases, for example, alkali metals, alkyl aluminium derivatives, alkyl metals, metal hydrides, metal phosphides, certain metal powders. An extensive list can be found in *Bretherick's Handbook of Reactive Chemical Hazards* (Urben, 2007).

The water solubility is used to decide whether the substance or mixture is soluble in water to form a stable mixture. This may also be decided based on information concerning experience in handling or use, e.g. the substance or mixture is manufactured with water or washed with water (see section 2.12.4.4.1).

The chemical identity of the emitted gas is used to decide whether the evolved gas is flammable or not. If the chemical identity of the emitted gas is unknown, the gas must be tested for flammability (see section 2.2).

In case of pyrophoric substances and mixtures the UN Test N.5 of the UN-MTC, Part III, section 33.5.4. must be executed under nitrogen atmosphere. Therefore, data about pyrophoric properties are needed prior to testing.

The melting point, boiling point and information about viscosity are necessary to identify the physical state of the substance or mixture. See also *IR & CSA, Chapter R.7a: Endpoint specific guidance*, sections R.7.1.2 (Melting point/freezing point), R.7.1.3 (Boiling point), and R.7.1.18 (Viscosity). Even though the UN Test N.5 can be applied to both, solids and liquids, these data are necessary to decide whether information concerning the friability (for solids) in accordance with the test method is necessary.

The particle size and the friability of a solid substance or mixture are crucial parameters for the classification of substances and mixtures which, in contact with water, emit flammable gases. These parameters have a significant effect on the test result. Thus, specific requirements regarding the particle size and the friability are prescribed in the UN Test N.5. For further details regarding the test procedure see section 2.12.4.4.1.

The references in section 2.12.8 provide good quality data on physical hazards.

2.12.4.2. Screening procedures and waiving of testing

For the majority of substances and mixtures, flammability as a result of contact with water is not a typical property and testing can be waived based on a consideration of the structure and experiences in handling and use.

Annex I: ***2.12.4.1.*** *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; or

b) experience in handling and use 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.

2.12.4.3. Classification criteria

Annex I: *Table 2.12.1*

Criteria for substances or mixtures which in contact with water emit flammable gas

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

Note:

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

2.12.2.2. *A substance or mixture shall be classified as a substance or mixture which in contact with water emits flammable gases if spontaneous ignition takes place in any step of the test procedure.*

2.12.4.4. Testing and evaluation of hazard information

2.12.4.4.1. Testing procedure

Care must be taken during testing as the emitted gas might be toxic or corrosive.

The testing procedure for substances and mixtures which in contact with water emit flammable gases is sensitive to a number of influencing factors and therefore must be carried out by experienced personnel. Some of these factors are described in the following:

1. Apparatus / measuring technique

In UN Test N.5 no special laboratory apparatus / measuring technique to determine the rate of gas evolution is required and no reference material is prescribed. As demonstrated in the past by a round robin test (Kunath, K. *et al*. 2011), the gas evolution rate measured by different apparatuses may vary widely. Therefore, to avoid measuring and classification errors adequate quality control measures are necessary to validate the results and should be noted in the test report.

2. Particle size and/or friability

The particle size of a solid has a significant effect on the test result. Therefore, if for solids the percentage of powder with a particle size of less than 500 µm constitutes more than 1 % of the total mass, or if the substance or mixture is friable, then the complete sample must be ground to a powder before testing to account for a possible reduction in particle size during handling and transport.

In certain cases, grinding may not be applicable and/or the sample cannot be ground completely to a particle size of less than 500 µm (e.g. metal granules).

Information on these pre-treatments and the respective procedures, the particle size and the friability have to be provided in the test report.

3. Atmospheric parameters

Variations of the atmospheric parameters (mainly air pressure and temperature) during the test have a considerable influence on the test result. Therefore, the substance or mixture must be tested at 20 °C, i.e. make sure that the test apparatus is acclimatised to 20 °C.

However, it is difficult to regulate and stabilise the air pressure during the testing. To characterise this influencing factor and to avoid false positive results, an additional ‘blank test’ is highly recommended. The results of the blank test should be noted in the test report.

4. Test with demineralised (distilled) water

The UN Test N.5 is performed with demineralised (distilled) water. In practice, contact with water can be to water in the liquid state (fresh water, sea water) or humid air, respectively. Note that the reactivity and therefore the gas evolution rate observed in practice may differ from the gas evolution rate value measured using demineralised water. This should be taken into account when handling substances and mixtures which in contact with water emit flammable gases.

5. Stirring procedures during the test

Stirring of the sample or water mixture during the test may have a considerable effect on the test result (e.g. significant increase or decrease of the gas evolution rate). Therefore, the sample or water mixture should not be stirred continuously during the test, e.g. by an automatic magnetic stirrer, even if the test sample has hydrophobic properties and moistening of the sample becomes impossible (see Kunath K. et al., 2011).

6. Spontaneous ignition

Spontaneous ignition of the evolved gas without contact with an additional ignition source, i.e. without the flame of the gas burner results in classification as category 1. This does not necessarily mean that the evolved gas is pyrophoric but often the heat of reaction is sufficient to ignite the evolved gas (e.g. the hydrogen evolved when sodium reacts with water).

2.12.4.4.2. Evaluation of hazard information

To accurately interpret the test results the evaluating person must have sufficient experience in the application of the test methods and in the disturbing / influencing factors as described above.

The evaluation of data comprises two steps:

- evaluation of all available data; and
- identification of the study or studies giving rise to the highest concern (key studies).

The criteria for assignment to categories 2 or 3 are gas evolution rates of 20 and 1 litre per kilogram of substance or mixture per hour, respectively, but for category 1 the relevant criterion is 10 litres per kilogram of substance or mixture over any one minute period (if the gas does not ignite spontaneously). This has to be considered while testing and for correct evaluation of the test results.

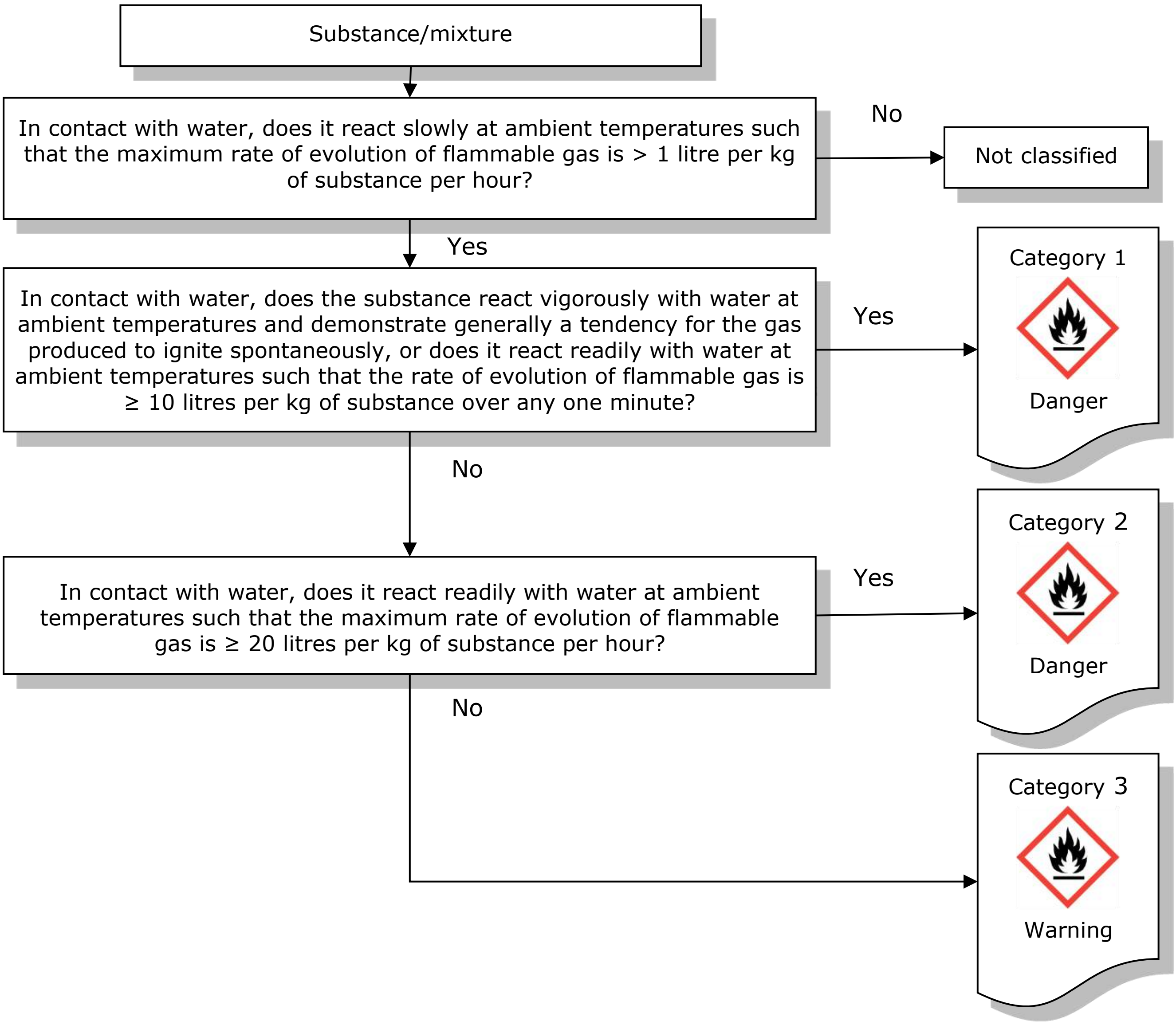
The assignment to the respective hazard class/category will further determine the technical means to be taken to avoid dangerous events which, in combination with other safety characteristics such as i) explosion limits, ii) flash points (applicable only for liquids) or iii) self-ignition temperature, can lead to clear restrictions in the conditions of use.

2.12.4.5. Decision logic

Classification of substances and mixtures which, in contact with water, emit flammable gases is done according to decision logic 2.12.4.1 as included in GHS.

NOTE: The person responsible for the classification of substances and mixtures which, in contact with water, emit flammable gases should be experienced in this field and be familiar with the criteria for classification.

Figure 2.12 Decision logic for substances and mixtures which, in contact with water, emit flammable gases (Decision logic 2.12 of GHS)



2.12.5. Hazard communication for substances or mixtures which, in contact with water, emits flammable gases

2.12.5.1. Pictograms, signal words, hazard statements and precautionary statements

Annex I: *Table 2.12.2*

Label elements for substances or mixtures which in contact with water emit flammable gases

Classification	*Category 1*	*Category 2*	*Category 3*
GHS Pictograms			
Signal Word	*Danger*	*Danger*	*Warning*
Hazard Statement	*H260:* *In contact with water releases flammable gases which may ignite spontaneously*	*H261:* *In contact with water releases flammable gases*	*H261:* *In contact with water releases flammable gases*
Precautionary Statement Prevention	*P223* *P231 + P232* *P280*	*P223* *P231 + P232* *P280*	*P231 + P232* *P280*
Precautionary Statement Response	*P302 + P335 + P334* *P370 + P378*	*P302 + P335 + P334* *P370 + P378*	*P370 + P378*
Precautionary Statement Storage	*P402 + P404*	*P402 + P404*	*P402 + P404*
Precautionary Statement Disposal	*P501*	*P501*	*P501*

The wording of the precautionary statements is found in CLP Annex IV, Part 2.

2.12.5.2. Additional labelling provisions

Annex II to CLP provides the following additional labelling provisions for water-reactive substances and mixtures. These statements must be assigned in accordance with CLP, Article 25(1), to substances and mixtures classified for physical, health or environmental hazards. There are no criteria or test methods provided for these EUH statements.

Annex II: *1.1.1.* *EUH014 – 'Reacts violently with water'*

For substances and mixtures which react violently with water, such as acetyl chloride, alkali metals, titanium tetrachloride.

Annex II: *1.2.1.* *EUH029 - 'Contact with water liberates toxic gas'*

For substances and mixtures which in contact with water or damp air, evolve gases classified for acute toxicity in category 1, 2 or 3 in potentially dangerous amounts, such as aluminium phosphide, phosphorus pentasulphide.

2.12.6. Relation to transport classification

Division 4.3 within Class 4 of the UN RTDG Model Regulations covers substances and mixtures which in contact with water emit flammable gasses. Substances and mixtures which are classified and/or labelled in Division 4.3 in the modal transport regulations (ADR, RID, ADN and IMDG Code, ICAO TI) are classified as substances and mixtures which, in contact with water, emit flammable gases under CLP. See Annex I for additional information on transport classification in relation to CLP classification.

2.12.7. Example of classification for substances or mixtures which, in contact with water, emits flammable gases

2.12.7.1. Example of substances and mixtures fulfilling the classification criteria

2.12.7.1.1. Example 1

SUBSTANCE FULFILLING THE CRITERIA FOR CLP CLASSIFICATION	
Substance:	Magnesium alkyls (Index No. 012-003-00-4)
Chemical structure:	R_2Mg
Flammable gas:	Hydrogen
Gas evolution rate:	Not applicable
Spontaneous ignition:	Not possible due to the nitrogen atmosphere during the UN Test N.5
Transport classification:	-
Reference:	Former Annex I to DSD and Annex VI to CLP
⇒ CLP Classification:	**Water-react. 1; H260** **Pyr. Sol. 1; H250**
Supplemental Hazard Information:	**EUH014**

2.12.7.2. Example of substances and mixtures not fulfilling the classification criteria

2.12.7.2.1. Example 2

SUBSTANCE NOT FULFILLING THE CRITERIA FOR CLP CLASSIFICATION	
Substance Gas evolution rate:	Manganese ethylene bis (dithiocarbamate) complex with zinc salt 88% (Mancozeb) 0 litres per kilogram of substance per hour.
Spontaneous ignition:	Not applicable
Transport classification:	Not Class 4.3
Reference:	UN Test N.5, UN-MTC section 33.5.4.5
⇒ CLP Classification:	**Not classified as substance which, in contact with water, emit flammable gases**

2.12.8. References

Haynes, W. M. *et al.* (2012) *CRC Handbook of Chemistry and Physics 93rd Edition*. CRC Press, Taylor and Francis, Boca Raton, FL

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Urben, Peter G. (2007). *Bretherick's Handbook of Reactive Chemical Hazards*, Volumes 1-2 (7th Edition). Elsevier

2.13. OXIDISING LIQUIDS

2.13.1. Introduction

The criteria for 'Oxidising liquids' are found in CLP Annex I, section 2.13 and are identical to those in chapter 2.13 of GHS[18].

The hazard class oxidising liquids comprises liquid substances and mixtures whose hazard is characterised by the fact that, in contact with other materials, they are able to cause or contribute to the combustion of those materials. The other materials do not necessarily have to belong to a certain hazard class to be able to be affected by the presence of oxidising substances or mixtures. This is for example the case when a solid material (e.g. wood) is soaked with an oxidising liquid.

Certain combinations of combustible materials and oxidising substances or mixtures may even result in spontaneous combustion, thermal instability or form an explosive mixture.

Although widely known as oxidising materials, their hazard and behaviour might be better understood by considering them to be fire enhancing substances or mixtures.

Apart from the combustion hazard, the production of toxic and/or irritating fumes may cause an additional hazard. For example, when nitrates are involved in a fire, nitrous fumes may be formed.

The testing procedure and criteria for oxidising substances or mixtures are not appropriate for ammonium nitrate compounds or solutions, ammonium nitrate-based fertilisers, and ammonium nitrate emulsions, suspensions or gels due to their complex hazard profiles. Therefore, for classification and labelling of substances or mixtures containing ammonium nitrate, experience should be used and expert judgement should be sought. For the classification procedures for intermediates for blasting explosives, such as ammonium nitrate emulsions, suspensions or gels, see section 2.1.

> **Annex I: *2.13.4.3***
>
> *In the event of divergence between test results and known experience in the handling and use of substances or mixtures which shows them to be oxidising, judgments based on known experience shall take precedence over test results.*

2.13.2. Definitions and general considerations for classification of oxidising liquids

The CLP text comprises the following definition for oxidising liquids.

> **Annex I: *2.13.1. Definition***
>
> *Oxidising liquid means a liquid substance or mixture which, while in itself not necessarily combustible, may, generally by yielding oxygen, cause, or contribute to, the combustion of other material.*

2.13.3. Relation to other physical hazards

Oxidising liquids that are mixed with combustible materials or reducing agents may have explosive properties and should be considered for classification in the hazard class explosives (including the applicable screening procedures), see section 2.1 or as self-reactive substances and mixtures, see CLP Annex I, section 2.8.2.1(b) and section 2.8.

The classification procedure and criteria for oxidising substances or mixtures is not applicable for organic peroxides. The majority of the organic peroxides do not possess oxidising properties; their main hazards are reactivity and flammability. Under CLP, organic peroxides are comprised in a separate hazard class (CLP Annex I, section 2.15) and they must not be considered according to the procedures described for oxidising liquids.

Inorganic oxidising liquids are not flammable and therefore do not have to be subjected to the classification procedures for the hazard classes flammable liquids or pyrophoric liquids. Also, other liquids that are classified as oxidising liquids are normally not flammable, although a few exemptions may exist. Expert judgement should be sought in case of doubt.

2.13.4. Classification of substances and mixtures as oxidising liquids

2.13.4.1. Identification of hazard information

Oxidising liquids may cause, or contribute to, the combustion of other material. Although the definition states that they generally do this by yielding oxygen, halogens can behave in a similar way. Therefore, any substance or mixture containing oxygen and/or halogen atoms should in principle be considered for inclusion into the hazard class oxidising liquids. This does not necessarily mean that every substance or mixture containing oxygen and/or halogen atoms should be subjected to the full testing procedure. For example, appropriate testing should be considered when the screening criteria are not met.

2.13.4.2. Screening procedures and waiving of testing

Liquids that are classified as explosives should not be subjected to the testing procedures for oxidising liquids.

Organic peroxides should be considered for classification within the hazard class organic peroxides, see section 2.15. For exceptional cases, in particular low concentrated peroxyacetic acid formulations see 2nd paragraph in section 2.15.6.

Before submitting a substance or a mixture to the full test procedure, an evaluation of its chemical structure may be very useful as it may prevent unnecessary testing. The person applying this procedure should have sufficient experience in testing and in theoretical evaluation of hazardous substances and mixtures. Some substances may react exothermally with the hydroxy groups in the cellulose molecule without affecting its polymeric structure. This reaction occurs spontaneously upon mixing and should not be interpreted as an oxidation. Substances known for such false positive behaviour are isocyanates and acid halides. Further, the following text provides a guideline for the theoretical evaluation of potential oxidising properties on the basis of its composition and chemical structure. In case of doubt, the full test must be performed.

The CLP text comprises the following screening considerations:

Annex I: *2.13.4.1.*

For organic substances or mixtures the classification procedure for this hazard class need not to 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.

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

On the basis of this theoretical evaluation only a distinction can be made between 'potentially oxidising' (i.e. further testing required) and 'non-oxidising' (i.e. no further testing for this hazard class required). It is not possible to assign a hazard category on basis of a theoretical evaluation. Even though for 'potentially oxidising' substances classification cannot be excluded based on theoretical evaluation, in some cases it might not be necessary to test a substance or mixture. However, this decision requires expert judgement.

Any substance or mixture that complies with the above waiving criteria can be safely regarded to have no oxidising properties and, hence, does not to be tested and should not be regarded as an oxidising liquid. However, such a substance or mixture may still possess other hazardous properties that require classification into another hazard class.

In case a mixture of an oxidising substance and a non-hazardous inert substance is offered for classification, the following should be taken into account:

- By definition an inert material does not contribute to the oxidising capability of the oxidising substance. Hence, the mixture can never be classified into a more severe hazard category.
- If an oxidising substance is mixed with an inert material, the oxidising capability of the mixture does not linearly decrease with decreasing content of oxidising substance. The relationship is more or less logarithmic and depends on the characteristics of the oxidising substance. For instance, a mixture containing 50 % of a strong oxidiser and 50 % of an inert material may retain 90 % of the oxidising capability of the original oxidising component. Non-testing classification of mixtures based solely on test data for the original oxidising substance should therefore be done with extreme care and only, if sufficient experience in testing exists.
- The determination of the oxidising properties of an aqueous solution of solid oxidising substances and the classification as an oxidising mixture is not necessary provided that the total concentration of all solid oxidisers in the aqueous solution is less than or equal to 20 % (w/w).

2.13.4.3. Classification criteria

The testing procedures for oxidising liquids are based on the capability of an oxidising liquid to enhance the combustion of a combustible material. Therefore, in the applicable test method substances and mixtures that are submitted for classification testing are mixed with a combustible material. Dried fibrous cellulose is used as a combustible material. The mixture of the potentially oxidising liquid and cellulose is then ignited, and its behaviour is observed and compared to the behaviour of reference materials.

For liquids the mixture with cellulose is ignited under confinement in an autoclave and the pressure rise rate that is caused by the ignition and the subsequent reaction is recorded. The pressure rise rate is compared to that of three reference material mixtures. The higher the pressure rise rate, the stronger the oxidising capability of the liquid tested.

Annex I: *2.13.2.1.*

An oxidising liquid shall be 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 RTDG, Manual of Tests and Criteria in accordance with Table 2.13.1:

Table 2.13.1

Criteria for oxidising 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 (or mixture) 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 Category 1 and 2 are not met.*

For additional information regarding the use of non-testing data see the next section and Urben, 2007 (see section 2.13.7).

2.13.4.4. Testing and evaluation of hazard information

The test methods for oxidising liquids are designed to give a final decision regarding their classification. Apart from testing, also experience in the handling and use of substances or mixtures which shows them to be oxidising is an important additional factor in considering classification in this hazard class. The CLP text comprises the following classification consideration:

> ***Annex I: 2.13.4 Additional Classification Considerations***
>
> *2.13.4.3 In the event of divergence between test results and known experience in the handling and use of substances or mixtures which shows them to be oxidising, judgements based on known experience shall take precedence over test results.*

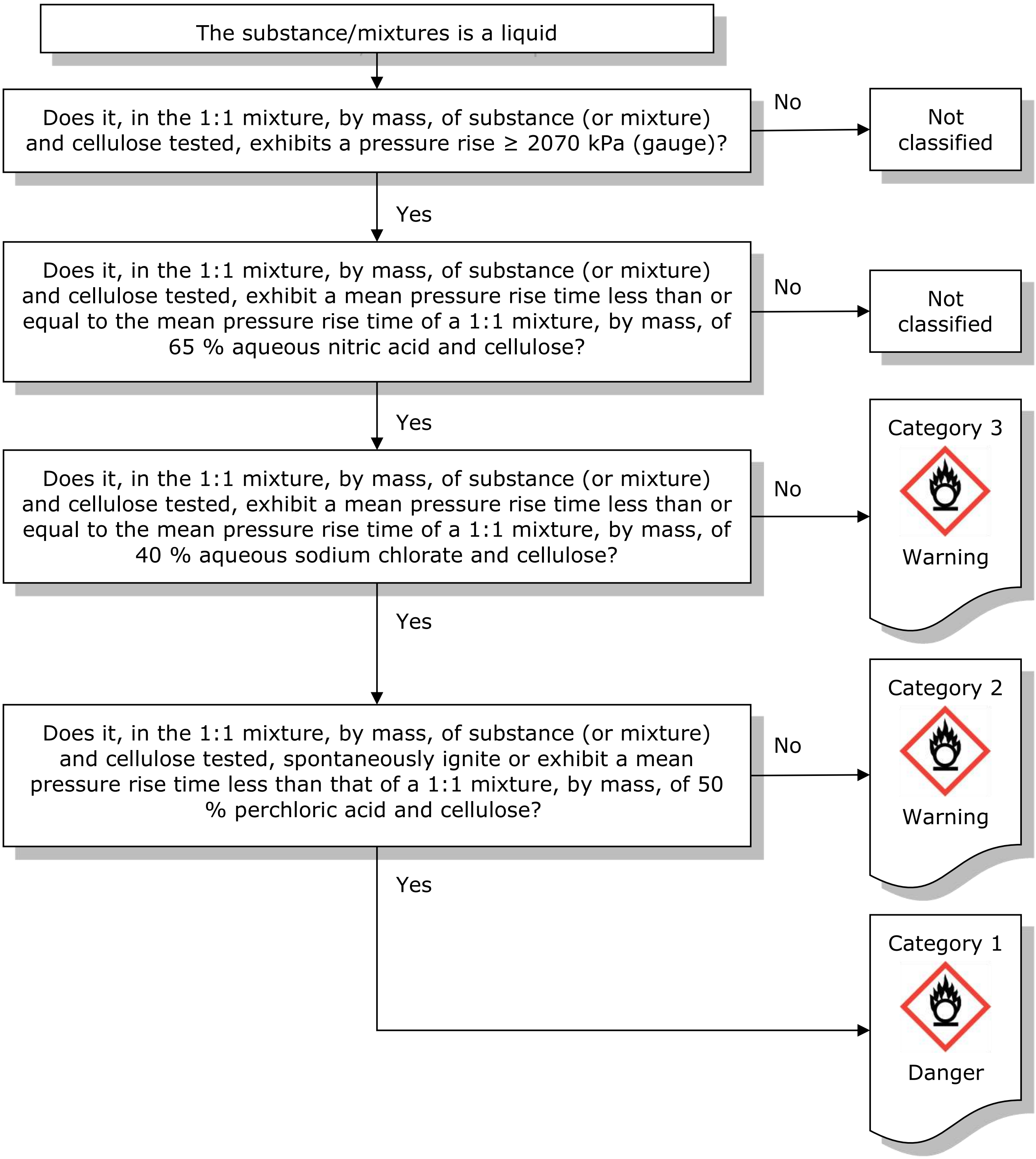
A substance or mixture must not be classified into a less severe category or as non-oxidising based on experience only.

2.13.4.5. Decision logic

Classification of oxidising liquids is done according to decision logic 2.13 as included in GHS.

NOTE: The person responsible for the classification of oxidising liquids should be experienced in this field and be familiar with the criteria for classification.

Figure 2.13 Decision logic for oxidising liquids (Decision logic 2.13 of GHS)



2.13.4.6. Hazard communication for oxidising liquids

2.13.4.6.1. Pictograms, signal words, hazard statements and precautionary statements

The pictograms and hazard statements are designed to indicate that oxidising substances and mixtures may cause or contribute to fire or explosion and therefore in principle should be separated from combustible materials.

Annex I: *Table 2.13.2*

Label elements for oxidising liquids

	Category 1	*Category 2*	*Category 3*
GHS Pictograms			
Signal Word	*Danger*	*Danger*	*Warning*
Hazard Statement	*H271: May cause fire or explosion; strong oxidiser*	*H272: May intensify fire; oxidiser*	*H272: May intensify fire; oxidiser*
Precautionary Statement Prevention	*P210* *P220* *P280* *P283*	*P210* *P220* *P280*	*P210* *P220* *P280*
Precautionary Statement Response	*P306 + P360* *P371 + P380 + P37* *P370 + P378*	*P370 + P378*	*P370 + P378*
Precautionary Statement Storage	*P420*		
Precautionary Statement Disposal	*P501*	*P501*	*P501*

The wording of the precautionary statements is found in CLP Annex IV, Part 2.

2.13.5. Relation to transport classification

Division 5.1 within Class 5 of the UN RTDG Model Regulations covers oxidising liquids and oxidising solids, using the same tests and criteria as CLP. Therefore, a liquid substance or mixture classified as Division 5.1 (sometimes referred to as Class 5.1) according to any of the modal transport regulations (ADR, RID, ADN and IMDG Code, ICAO TI) is normally also classified as an oxidising liquid according to CLP. Packing Groups I, II and III of the transport regulations correspond directly to Categories 1, 2 and 3 of CLP, respectively. See Annex I for additional information on transport classification in relation to CLP classification.

2.13.6. Example of classification for oxidising liquids

2.13.6.1. Example of substances and mixtures fulfilling the classification criteria

The non-exhaustive list of substances and mixtures fulfilling the criteria for classification is only presented for information purposes. For examples of results see section 34.4.2.5 of UN-MTC.

- Ferric nitrate, saturated aqueous solution
- Lithium perchlorate, saturated aqueous solution
- Magnesium perchlorate, saturated aqueous solution
- Perchloric acid, 55 %
- Sodium nitrate, 45 % aqueous solution

2.13.6.2. Example of substances and mixtures not fulfilling the classification criteria

- Nickel nitrate, saturated aqueous solution
- Potassium nitrate, 30 % aqueous solution
- Silver nitrate, saturated aqueous solution

2.13.7. Reference

Urben, Peter G. (2007). *Bretherick's Handbook of Reactive Chemical Hazards, Volumes 1-2* (7th Edition). Elsevier.

2.14. OXIDISING SOLIDS

2.14.1. Introduction

The criteria for 'Oxidising solids' are found in CLP Annex I, section 2.14 and are identical to those in chapter 2.14 of GHS[18].

The hazard class oxidising solids comprises substances and mixtures whose hazard is characterised by the fact that, in contact with other materials, they are able to cause or contribute to the combustion of those materials. The other materials do not necessarily have to belong to a certain hazard class to be affected by the presence of an oxidising solid. This is for example the case when a liquid fuel (e.g. gas oil) mixes with an oxidising solid. Certain combinations of combustible materials and oxidising substances or mixtures may even result in spontaneous combustion, thermal instability or form an explosive mixture.

Although widely known as 'oxidising materials', their hazard and behaviour might be better understood by considering them to be 'fire enhancing substances'.

Apart from the combustion hazard, the production of toxic and/or irritating fumes may cause an additional hazard. For example, when nitrates are involved in a fire, nitrous fumes may be formed.

The testing procedure and criteria for oxidising substances or mixtures are not appropriate for ammonium nitrate-based products. For classification of such products, experience should be applied and expert judgement should be sought.

Ammonium nitrate-based fertilisers are classified based on their composition according to the UN Manual of Tests and Criteria, section 39. For the classification of ammonium nitrate-based emulsions, suspensions or gels (intermediate for blasting explosives), see section 2.1.

2.14.2. Definitions and general considerations for classification of oxidising solids

The CLP text comprises the following definition for oxidising solids.

> **Annex I: *2.14.1. Definition***
>
> *Oxidising solid means a solid substance or mixture which, while in itself is not necessarily combustible, may, generally by yielding oxygen, cause, or contribute to, the combustion of other material.*

Special consideration on particle size

The oxidising properties of a solid depend on its particle size. Smaller particles enable a more intimate contact between the solid oxidiser and a combustible solid. The smaller the particle size, the higher the oxidising capability of the solid. As a consequence, it may happen that large particles of a certain solid are considered to be non-hazardous, while small particles of the same solid need to be classified into the hazard class of oxidising solids. In rare cases, very small particles of a solid oxidiser may even show explosive properties (e.g. ammonium perchlorate).

Hence, it is very important that oxidising properties for solids are investigated on the substance or mixture as it is actually presented (including how it can reasonably be expected to be used, see Article 8 (6) of CLP). This is indicated by the Note 2 cited in CLP Annex I, section 2.14.2.1.

> **Annex I: *2.14.2.1.***
>
> *[…]*
>
> *Note 2: The test shall be performed on the substance or mixture in its physical form 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 shall also be tested in the new form.*

2.14.3. Relation to other physical hazards

Oxidising solids that are mixed with combustible materials or reducing agents may have explosive properties and should be considered for classification in the hazard class explosives (including the applicable screening procedures), see section 2.1. Such mixtures may also exhibit self-reactive behaviour, see section 2.8. Expert judgement should be sought in case of doubt.

The classification procedure and criteria for oxidising substances and mixtures is not applicable for organic peroxides. The majority of the organic peroxides do not possess oxidising properties; their main hazards are reactivity and flammability. Under CLP, organic peroxides comprise a separate hazard class (CLP Annex I, section 2.15) and they must not be considered according to the procedures described for oxidising solids.

Inorganic oxidising solids are not flammable and therefore do not need to be subject to the classification procedures for the hazard classes flammable solids or pyrophoric solids. Also, other solids of organic or partially organic nature that are classified as oxidising solids are normally not flammable, although a few exceptions may exist. Expert judgement should be sought in case of doubt.

2.14.4. Classification of substances and mixtures as oxidising solids

2.14.4.1. Identification of hazard information

Oxidising solids may cause, or contribute to, the combustion of other material. Although the definition in CLP Annex I, section 2.14.1, quoted above, states that they generally do this by yielding oxygen, halogens can behave in a similar way. Therefore, any substance or mixture containing oxygen and/or halogen atoms should in principle be considered for inclusion into the hazard categories oxidising solids. This does not necessarily mean that every substance or mixture containing oxygen and/or halogen atoms should be subjected to the full testing procedure.

2.14.4.2. Screening procedures and waiving of testing

Solids that are classified as explosives should not be subjected to the testing procedures for oxidising solids.

Organic peroxides should be considered for classification within the hazard class organic peroxides, see section 2.15.

Before submitting a substance or a mixture to the full test procedure, an evaluation of its chemical structure may be very useful as it may prevent unnecessary testing. The person applying this procedure should have sufficient experience in testing and in theoretical evaluation of hazardous substances and mixtures. The following text provides a guideline for the theoretical evaluation of potential oxidising properties on the basis of its composition and chemical structure. In case of doubt, the full test must be performed.

The CLP text comprises the following screening considerations:

> **Annex I: *2.14.4.1.***
>
> *For organic substances or mixtures the classification procedure for this hazard class need not to 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.*
>
> ***2.14.4.2.***
>
> *For inorganic substances or mixtures, the classification procedure for this hazard class need not be applied if they do not contain oxygen or halogen.*

On the basis of this theoretical evaluation a distinction can only be made between 'potentially oxidising' (i.e. further testing required) and 'non-oxidising' (i.e. no further testing for this hazard class required). It is not possible to assign a hazard category on the basis of a theoretical evaluation. Even though for 'potentially oxidising' substances, classification cannot be excluded based on theoretical evaluation, in some cases it might not be necessary to test a substance or mixture. However, this decision requires expert judgement.

Any substance or mixture that complies with the above waiving criteria can be safely regarded to have no oxidising properties and, hence, does not to be tested and should not be regarded as an oxidising solid. However, such a substance or mixture may still possess other hazardous properties that require classification into another hazard class.

In case a mixture of an oxidising substance and a non-hazardous inert substance is offered for classification, the following should be taken into account:

- An inert material by definition does not contribute to the oxidising capability of the oxidising substance. Hence, the mixture can never be classified into a more severe hazard category.
- If an oxidising substance is mixed with an inert material, the oxidising capability of the mixture does not linearly decrease with decreasing content of oxidising substance. The relationship is more or less logarithmic and depends on the characteristics of the oxidising substance. For instance, a mixture containing 50 % of a strong oxidiser and 50 % of an inert material may retain 90 % of the oxidising capability of the original oxidising component. Non-testing classification of mixtures based solely on test data for the original oxidising substance should therefore be done with extreme care and only if sufficient experience in testing exists.

2.14.4.3. Classification criteria

The testing procedures for oxidising solids are based on the capability of an oxidising solid to enhance the combustion of a combustible material. Therefore, in the applicable test method solids that are submitted to classification testing are mixed with a combustible material. Dried fibrous cellulose is used as a combustible material. The mixture of the potentially oxidising solid and cellulose is then ignited, and its behaviour is observed and compared to the behaviour of reference material mixtures.

For solids, the mixture with cellulose is ignited at atmospheric conditions and the time necessary for the combustion reaction to consume the mixture is recorded. The faster the combustion rate, the stronger the oxidising capability of the solid tested.

The UN-MTC currently has two methods for the determination of oxidising properties of solids, i.e. tests O.1 and O.3. In test O.1, the reaction between the oxidiser and the combustible material is observed visually while in test O.3 a gravimetric method is applied. Both methods can be used although in certain cases the one or the other method may be preferred. In this case, expert judgement should be sought.

Annex I: ***2.14.2.1.*** *An oxidising solid shall be 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 RTDG, Manual of Tests and Criteria, in accordance with Table 2.14.1:*

Table 2.14.1

Criteria for oxidising solids

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

	mass) tested, exhibits a mean burning time equal to or less than the mean burning time of a 3:7 mixture (by mass) of potassium bromate and cellulose and the criteria for Categories 1 and 2 are not met.	*mass) tested, exhibits a mean burning rate equal to or greater than the mean burning rate of a 1:2 mixture (by mass) of calcium peroxide and cellulose and the criteria for Categories 1 and 2 are not met.*
Note 1 *Some oxidising solids also present explosion hazards under certain conditions (when stored in large quantities). Some types of ammonium nitrate may give rise to an explosion hazard under extreme conditions and the 'Resistance to detonation test' (IMSBC Code (International Maritime Solid Bulk Cargoes Code, IMO), Appendix 2, Section 5) can be used to assess this hazard. Appropriate information shall be made in the SDS.*		

Note 1 may also apply to other oxidising ammonium salts. Experience indicates that the conditions required for ammonium nitrate to present an explosion hazard involve a combination of factors, such as storage in large volumes (multiple tonnes) and either contamination (e.g. with metals, acids, organics) or excessive heat (e.g. under conditions of fire). The resistance to detonation (RTD) test is extensively described in Regulation (EC) No 2019/1009 for ammonium nitrate.

For additional information regarding the use of non-testing data see CLP, Annex I section 2.14.4.3 below and Urben, 2007 (see section 2.14.7).

2.14.4.4. Testing and evaluation of hazard information

The test methods for oxidising solids are designed to give a final decision regarding their classification. Apart from testing, also experience in the handling and use of substances or mixtures which shows them to be oxidising is an important additional factor in considering classification in this hazard class. The CLP text comprises the following classification consideration:

> **Annex I: *2.14.4 Additional Classification Considerations***
>
> *2.14.4.3 In the event of divergence between test results and known experience in the handling and use of substances or mixtures which shows them to be oxidising, judgements based on known experience shall take precedence over test results.*

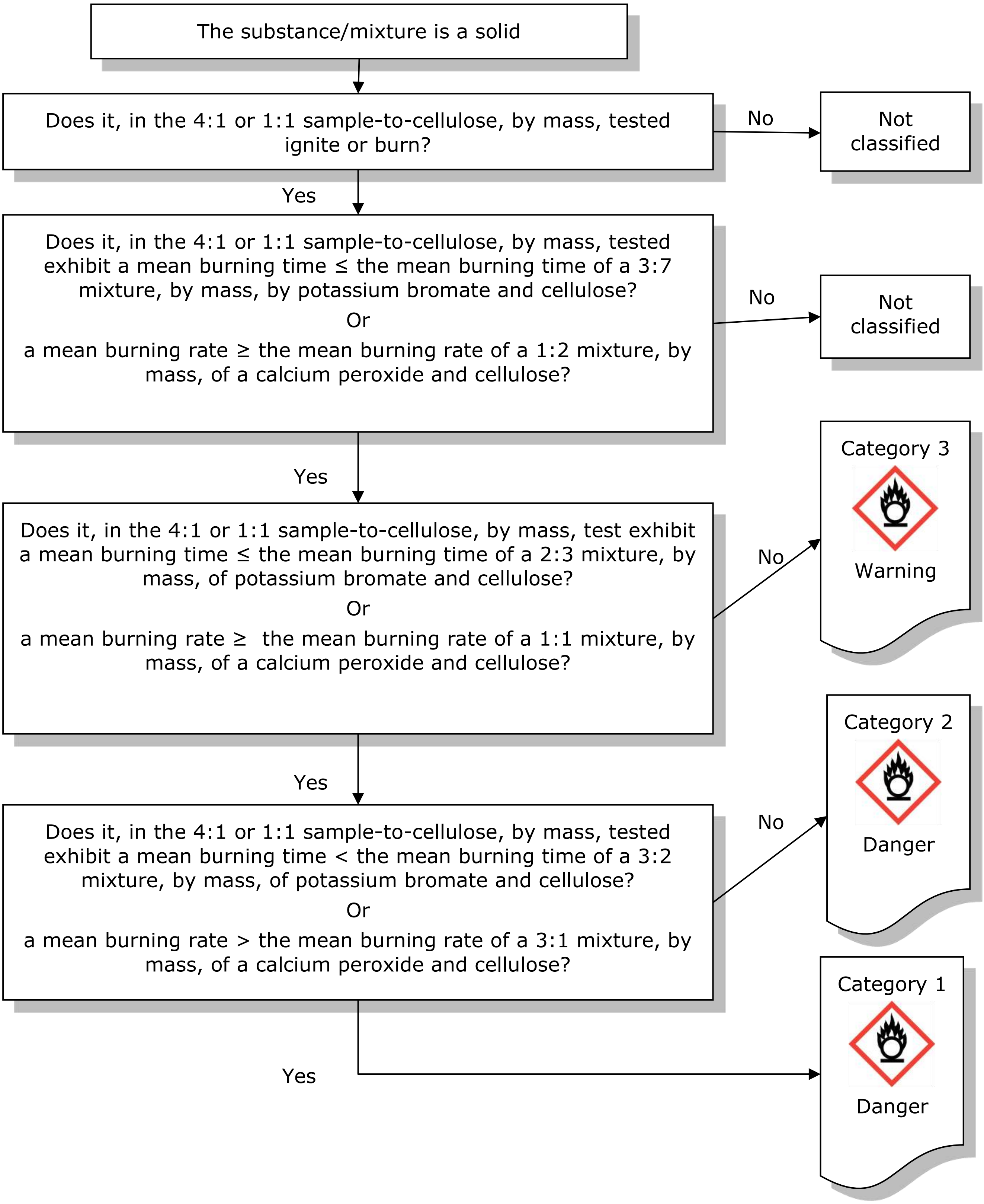
A substance or mixture must not be classified into a less severe category or as non-oxidising based on experience only.

2.14.4.5. Decision logic

Classification of oxidising solids is done according to decision logic 2.14 as included in GHS.

NOTE: The person responsible for the classification of oxidising solids should be experienced in this field and be familiar with the criteria for classification.

Figure 2.14 Decision logic for oxidising solids (Decision logic 2.14 of GHS)



2.14.5. Hazard communication for oxidising solids

2.14.5.1. Pictograms, signal words, hazard statements and precautionary statements

The pictograms and hazard statements are designed to indicate that oxidising substances and mixtures may cause or contribute to fire or explosion and therefore in principle should be separated from combustible materials.

Annex I: *Table 2.14.2*

Label elements for oxidising solids

	Category 1	*Category 2*	*Category 3*
GHS Pictograms			
Signal Word	*Danger*	*Danger*	*Warning*
Hazard Statement	*H271: May cause fire or explosion; strong oxidiser*	*H272: May intensify fire; oxidiser*	*H272: May intensify fire; oxidiser*
Precautionary Statement Prevention	*P210* *P220* *P280* *P283*	*P210* *P220* *P280*	*P210* *P220* *P280*
Precautionary Statement Response	*P306 + P360* *P371 + P380 + P37* *P370 + P378*	*P370 + P378*	*P370 + P378*
Precautionary Statement Storage	*P420*		
Precautionary Statement Disposal	*P501*	*P501*	*P501*

The wording of the precautionary statements is found in CLP Annex IV, Part 2.

2.14.6. Relation to transport classification

Division 5.1 within Class 5 of the UN RTDG Model Regulations covers oxidising liquids and oxidising solids, using the same tests and criteria as CLP. Therefore, a solid substance or mixture classified as Division 5.1 (sometimes referred to as Class 5.1) according to any of the modal transport regulations (ADR, RID, ADN and IMDG Code, ICAO TI) is normally also classified as an oxidising solid according to CLP. Packing Groups I, II and III of the transport regulations correspond directly to Categories 1, 2 and 3 of CLP, respectively. See Annex I for additional information on transport classification in relation to CLP classification.

2.14.7. Example of classification for oxidising solids

2.14.7.1. Example of substances and mixtures fulfilling the classification criteria

The non-exhaustive list of substances and mixtures fulfilling the criteria for classification is only presented for information purposes. Note that oxidising properties of these substances may differ depending on particle size. For examples of results see section 34.4.3.6 of UN-MTC.

- Calcium nitrate, anhydrous
- Chromium trioxide
- Potassium nitrite
- Potassium nitrate
- Potassium perchlorate
- Potassium permanganate
- Sodium chlorate
- Sodium nitrite
- Sodium nitrate
- Strontium nitrate, anhydrous

2.14.7.2. Example of substances and mixtures not fulfilling the classification criteria

- Calcium nitrate, tetrahydrate
- Cobalt nitrate, hexahydrate

2.14.8. Reference

Urben, Peter G. (2007). *Bretherick's Handbook of Reactive Chemical Hazards, Volumes 1-2* (7th Edition). Elsevier.

2.15. ORGANIC PEROXIDES

2.15.1. Introduction

The criteria for ‘Organic peroxides’ are found in CLP Annex I, section 2.15 and are identical to those in chapter 2.15 of GHS[18].

The hazard class organic peroxides is unique in the respect that it is the only category to which chemicals are assigned on the basis of their chemical structure. Being an organic peroxide cannot be seen as an ‘intrinsic property’ *per se* but all organic peroxides have intrinsic properties that are hazardous as they are thermally unstable substances or mixtures, which can undergo exothermic self-accelerating decomposition. However, the hazardous nature of a peroxide is determined by testing.

2.15.2. Definitions and general considerations for classification of organic peroxides

In CLP, the following definition is given for organic peroxides.

> **Annex I: *2.15.1. Definition***
>
> *Organic peroxides means 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 organic peroxide includes organic peroxide mixtures (formulations) containing at least one organic peroxide. Organic peroxides are thermally unstable substances or mixtures, which can undergo exothermic self-accelerating decomposition. In addition, they can 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.*
>
> ***2.15.1.2.** An organic peroxide is regarded as possessing explosive properties when in laboratory testing the mixture (formulation) is liable to detonate, to deflagrate rapidly or to show a violent effect when heated under confinement.*

2.15.3. Relation to other physical hazards

In addition to the definition (CLP Annex I, section 2.15.1), organic peroxides may:

a. be flammable;

b. emit flammable gas when heated.

In general, organic peroxides do not have or have only weak oxidising properties and typically do not require additional classification as oxidising solids or liquids.

The additional (subsidiary) labelling, as indicated in the list of classified organic peroxides included in the UN RTDG Model Regulations, section 2.5.3.2.4, represents the additional hazardous properties.

Neither the burning properties nor the sensitivity to impact and friction form part of the classification procedure for organic peroxides in CLP. However, these properties may be of importance for the safe handling of organic peroxides (see section 2.15.4.3.2 additional testing).

In addition, the following should be noted:

Explosive properties

The explosive properties do not have to be determined according to CLP Annex I, section 2.1, because explosive properties are already incorporated in the classification of organic peroxides.

2.15.4. Classification of substances and mixtures as organic peroxides

2.15.4.1. Identification of hazard information

As a consequence of the hazard class definition, if the chemical structure does not contain the bivalent -O-O- structure, the substance is not classified as organic peroxide.

The classification of an organic peroxide in one of the seven categories ‘Types A to G’ is dependent on its detonation, deflagration and thermal explosion properties, its response to heating under confinement, its explosive power and the concentration and the type of diluent added to desensitise the organic peroxide. Specifications of acceptable diluents that can be used safely are given in the UN RTDG Model Regulations, 2.5.3.5. The classification of an organic peroxide as Type A, B or C is dependent on the type of packaging in which the organic peroxide is tested as it affects the degree of confinement to which the organic peroxide is subjected. This has to be considered when handling the organic peroxide; stronger packaging may result in more violent reactions when the organic peroxide decomposes. This is why it is important that storage and transport is done in packaging, allowed for the type of organic peroxide, that conforms the requirements of the UN-packaging or IBC[41] instruction (P520/IBC520) or tank instruction (T23).

2.15.4.2. Classification criteria

Annex I: ***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.

[…]

In CLP decision logic Annex I, Figure 2.15.1, classification of organic peroxides is based on performance-based testing both small scale tests and, where necessary, some larger scale test with the organic peroxide in its packaging.

Organic peroxides are classified into one of the seven categories of 'Types A to G' according to the classification criteria of CLP. The classification principles are given in decision logic Figure 2.15.1 of CLP and the Test Series A to H, as described in the Part II of the UN-MTC, should be performed.

Annex I: ***2.15.2.2.*** *Organic peroxides shall be 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 shall 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 shall 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 shall 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;

shall be defined as organic peroxide TYPE D;

---

[41] IBC: Intermediate bulk container

(e) any organic peroxide which, in laboratory testing, neither detonates nor deflagrates at all and shows low or no effect when heated under confinement shall 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 shall 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, i.e. the SADT is 60 °C or higher for a 50 kg package(1), and, for liquid mixtures, a diluent having a boiling point of not less than 150 °C is used for desensitisation, shall 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 desensitisation, the organic peroxide shall be defined as organic peroxide TYPE F.

Where the test is conducted in the package form and the packaging is changed, a further test shall be conducted where it is considered that the change in packaging will affect the outcome of the test.

(1) See UN RTDG, Manual of Test and Criteria, sub-sections 28.1, 28.2, 28.3 and Table 28.3.

For reference, a list of currently classified organic peroxides is included in the UN RTDG Model Regulations, section 2.5.3.2.4.

2.15.4.3. Testing and evaluation of hazard information

2.15.4.3.1. Thermal stability tests and temperature control

In addition to the classification tests given in decision logic Figure 2.15.1 of CLP, the thermal stability of the organic peroxide has to be assessed to determine the SADT. For the determination of the SADT, the testing method in UN-MTC, section 28, may be used.

The SADT is defined as the lowest temperature at which self-accelerating decomposition of an organic peroxide may occur in the packaging as used in transport, handling and storage. The SADT is a measure of the combined effect of the ambient temperature, decomposition kinetics, package size and the heat transfer properties of the organic peroxide and its packaging.

There is no relation between the SADT of an organic peroxide and its classification in one of the seven categories 'Types A to G'. The SADT is used to derive safe handling, storage and transport temperatures (control temperature) and alarm temperature (emergency temperature).

Depending on its SADT an organic peroxide needs temperature control and the rules as given in CLP Annex I, section 2.15.2.3, consist of the following two elements:

1. Criteria for temperature control:

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

a. Organic peroxide types B and C with a SADT ≤ 50 °C;

b. Organic peroxide type D showing a medium effect when heated under confinement with a SADT ≤ 50 °C or showing a low or no effect when heated under confinement with a SADT ≤ 45 °C; and

c. Organic peroxide types E and F with a SADT ≤ 45 °C.

2. Derivation of control and emergency temperatures:

Type of receptacle	SADT *	Control temperature	Emergency temperature
Single packaging and IBC's	20 °C or less over 20 °C to 35 °C over 35 °C	20 °C below SADT 15 °C below SADT 10 °C below SADT	10 °C below SADT 10 °C below SADT 5 °C below SADT
Tanks	< 50 °C	10 °C below SADT	5 °C below SADT

* i.e. the SADT of the organic peroxide as packaged for transport, handling and storage

It should be emphasised that the SADT is dependent on the nature of the organic peroxide itself, together with the volume and heat-loss characteristics of the packaging or vessel in which the organic peroxide is handled. The temperature at which self-accelerating decomposition occurs falls:

- as the size of the packaging or vessel increases; and
- with increasing efficiency of the insulation on the package or vessel.

The SADT is only valid for the organic peroxide as tested and when handled properly. Mixing the organic peroxide with other chemicals, or contact with incompatible materials (including incompatible packaging or vessel material) may reduce the thermal stability due to catalytic decomposition, and lower the SADT. This may increase the risk of decomposition and has to be avoided.

2.15.4.3.2. Additional considerations and testing

Explosive properties

The sensitivity of organic peroxides to impact (solids and liquids) and friction (solids only) may be of importance for the safe handling of the organic peroxide if they have pronounced explosive properties (e.g. they are liable to detonate, to deflagrate rapidly or show a violent effect when heated under confinement). Test methods to determine these properties are described in Test Series 3 of the UN-MTC (see Test 3 (a) (ii) and 3 (b) (i)). This information on the mechanical sensitivity could be included in the SDS.

Burning properties

In some national storage guidelines, the burning rate is commonly used for classification for the purposes of storage and consequential storage requirements. Test methods are incorporated in these national storage regulations.

Flash point

The flash point for liquid organic peroxides is only relevant in the temperature range where the organic peroxide is thermally stable. Above the SADT of the organic peroxide, determination of the flash point is not relevant because decomposition products evolve.

NOTE: In case a flash point determination seems reasonable (expected flash point below the SADT) a test method using small amount of sample is recommended. In case the organic peroxide is diluted or dissolved, the diluent may determine the flash point.

Auto-ignition temperature

The determination of the auto ignition temperature is not relevant for organic peroxides. Available test methods are for non-decomposing vapour phases, but the vapours of organic peroxides decompose during execution of the test and auto ignition of these organic peroxide vapours can never be excluded. This information should be included in the SDS.

Self-ignition temperature

The determination of the self-ignition temperature (applicable for solids) is not relevant, since the thermal stability of organic peroxides is quantitatively given by the SADT.

Control and Emergency temperatures

The Control and Emergency temperatures are based on the SADT as in most cases determined by UN Test Series H. In UN Test Series H.2 and H.3, the heat loss applied in the calculating the SADT should be representative for the packaging, IBC, tank or vessel in which the substance or mixture is handled or stored. In UN Test H.4, the Dewar vessel used is supposed to be representative for the organic peroxide handled in packages. For handling the organic peroxide in larger quantities (IBCs/tanks/vessels etc.) and/or in (thermally) insulated containers, the SADT has to be determined for that quantity with that degree of insulation. From that SADT the Control and Emergency temperatures can be derived (see also section 2.15.4.3.1).

2.15.4.3.3. Additional classification considerations

Currently the following properties are not incorporated in the classification of organic peroxides under CLP:

- mechanical sensitivity i.e. impact and friction sensitivity (for handling purposes);
- burning properties (for storage purposes);
- flash point for liquids; and
- burning rate for solids.

Furthermore:

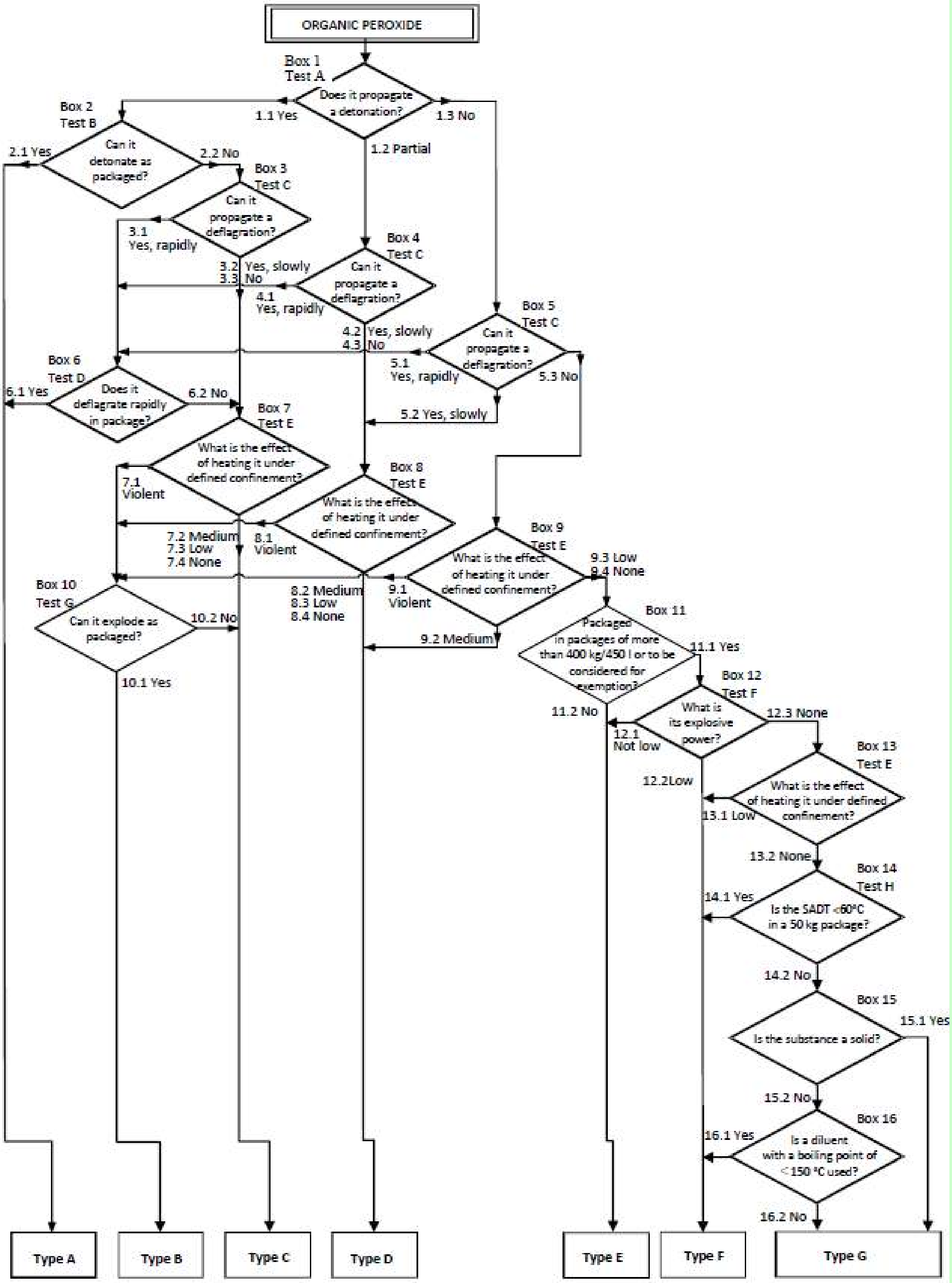
> **Annex I:** ***2.15.4.2.*** *Mixtures of already classified organic peroxides may be classified as the same type of organic peroxide as that of the most dangerous component. However, as two stable components can form a thermally less stable mixture, the SADT of the mixture shall be determined.*
>
> *Note: The sum of the individual parts can be more hazardous than the individual components.*

2.15.4.4. Decision logic

The decision logic for organic peroxides is applicable according to CLP.

NOTE: The person responsible for the classification of organic peroxides should be experienced in this field and be familiar with the criteria for classification.

Annex I: *Figure 2.15.1* ***Organic Peroxide***



2.15.5. Hazard communication for organic peroxides

2.15.5.1. Pictograms, signal words, hazard statements and precautionary statements

According to CLP the following label elements must be used for organic peroxide meeting the criteria for this hazard class:

Annex I: *Table 2.15.1*

Label elements for organic peroxides

Classification	*Type A*	*Type B*	*Type C & D*	*Type E & F*	*Type G*[1]
GHS pictograms		 			*There are no label elements allocated to this hazard category*
Signal Word	*Danger*	*Danger*	*Danger*	*Warning*	
Hazard Statement	*H240: Heating may cause an explosion*	*H241: Heating may cause a fire or explosion*	*H242: Heating may cause a fire*	*H242: Heating may cause a fire*	
Precautionary statement *Prevention*	*P210* *P234* *P235* *P240* *P280*	*P210* *P234* *P235* *P240* *P280*	*P210* *P234* *P235* *P240* *P280*	*P210* *P234* *P235* *P240* *P280*	
Precautionary statement *Response*	*P370 + P372 +* *P380 + P373*	*P370 + P380 +* *P375[+ P378]*[2]	*P370 + P378*	*P370 + P378*	
Precautionary statement *Storage*	*P403* *P410* *P411* *P420*	*P403* *P410* *P411* *P420*	*P403* *P410* *P411* *P420*	*P403* *P410* *P411* *P420*	
Precautionary statement *Disposal*	*P501*	*P501*	*P501*	*P501*	

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

[2] *See introduction to Annex I for details on the use of square brackets.*

The wording of the precautionary statements is found in CLP Annex IV, Part 2.

2.15.5.2. Additional labelling provisions

Additional hazardous properties, resulting in additional (subsidiary) labelling, are indicated in the list of classified organic peroxides included in the UN RTDG Model Regulations, section 2.5.3.2.4.

2.15.6. Relation to transport classification

Division 5.2 within Class 5 of the UN RTDG Model Regulations covers organic peroxides. A list of currently classified organic peroxides is included in the UN RTDG Model Regulations, section 2.5.3.2.4. This table includes organic peroxides Type B - Type F (and some formulations Type G, so-called exempted organic peroxides).

An exceptional case in this respect is a peroxyacetic acid formulation, as currently classified in the UN RTDG Model Regulations under UN 3149, with the following description: HYDROGEN PEROXIDE AND PEROXYACETIC ACID MIXTURE with acid(s), water and not more than 5 % peroxyacetic acid, STABILISED. In the classification procedure for organic peroxides, see decision logic in section 2.15.4.4, this formulation will be assigned to organic peroxide Type G, and consequently no label elements are allocated. In view of the above, this formulation can be classified, also in accordance with CLP, as an oxidising liquid, category 2. See Annex I for additional information on transport classification in relation to CLP classification.

2.15.7. Example of classification for organic peroxides

2.15.7.1. Example of substances and mixtures fulfilling the classification criteria

Substance to be classified: Example Peroxide

Molecular formula: n.a.

According to CLP Annex I, section 2.15.2.1, the substance has an active oxygen content of 7.40 % and has to be considered for classification in the hazard class organic peroxides.

Test results and classification according to CLP decision logic 2.15.1 for organic peroxides and the UN-MTC, Part II, is as follows:

CLASSIFICATION TEST RESULTS	
1. Name of the organic peroxide:	Example Peroxide
2. General data	
2.1. Composition:	Example Peroxide, technically pure (97 %)
2.2. Molecular formula:	Not applicable
2.3. Active oxygen content:	7.18 %
2.4. Physical form:	Liquid
2.5. Colour:	Colourless
2.6. Density (apparent):	900 kg/m^3

CLASSIFICATION TEST RESULTS	
3. Detonation (Test Series A)	
Box 1 of the decision logic:	Does the peroxide propagate a detonation?
3.1. Method:	UN Test A.1: BAM 50/60 steel tube test
3.2. Sample conditions:	Peroxide assay 97 %
3.3. Observations:	Fragmented part of the tube: 18 cm
3.4. Result:	No
3.6. Exit:	1.3
4. Deflagration (Test Series C)	
Box 5 of the decision logic:	Can the peroxide propagate a deflagration?
4.1. Method 1:	Time/pressure test (Test C.1)
4.1.1. Sample conditions:	Ambient temperature
4.1.2. Observations:	4000 ms
4.1.3. Result:	Yes, slowly
4.2. Method 2:	Deflagration test (Test C.2)
4.2.1. Sample conditions:	Temperature: 25 °C
4.2.2. Observations:	Deflagration rate: 0.74 mm/s
4.2.3. Result:	Yes, slowly
4.3. Final result:	Yes, slowly
4.4. Exit:	5.2
5. Heating under confinement (Test Series E)	
Box 8 of the decision logic:	What is the effect of heating it under confinement?
5.1. Method 1:	Koenen test (Test E.1)
5.1.1. Sample conditions:	-
5.1.2. Observations:	Limiting diameter: 2.0 mm Fragmentation type ‘F’
5.1.3. Result:	Violent
5.2. Method 2:	Dutch pressure vessel test (test E.2)
5.2.1. Sample conditions:	-
5.2.2. Observations:	Limiting diameter: 6.0 mm (with 10 g)
5.2.3. Result:	Medium

CLASSIFICATION TEST RESULTS	
5.3. Final result:	Violent
5.4. Exit:	8.1
6. Explosion test in package (Test Series G)	
Box 10 of the decision logic:	Can it explode as packaged?
6.1. Method:	Thermal explosion test in package (Test G.1)
6.2. Sample conditions:	30 litre packaging,
6.3. Observations:	No fragmentation (N.F.)
6.4. Result:	No
6.5. Exit:	10.2
7. Thermal stability (outside of the decision logic)	
7.1. Method:	Heat accumulation storage test (Test H.4)
7.2. Sample conditions:	Mass 380 g. Half-life time of cooling of Dewar vessel with400 ml DMP: 10.0 h (representing substance in package)
7.3. Observations: self	Accelerating decomposition at 35 °C No self-accelerating decomposition at 30 °C
7.4. Result:	SADT 35 °C
8. General remarks:	The decision logic is given in Figure x[42]
9. Final classification	
Hazard class:	Organic peroxide, Type C, liquid, temperature controlled
Label:	Flame (GHS02)
Signal word:	Danger
Hazard statement:	H242: Heating may cause a fire
Temperature control:	Needed based on SADT (35 °C, in package)
Control temperature*:	20 °C (in package)
Emergency temperature*:	25 °C (in package)

*see UN-MTC, table 28.2.

---

[42] Not attached to this example.

2.15.7.2. Additional remarks

Explosive properties

As shown in section 2.15.7.1 a substance and a mixture may have explosive properties when handled under greater confinement and where the packaging in which it was tested in UN Test G.1 (see point 6 of classification test results above) is changed. Such information should be given in the SDS.

The example in section 2.15.7.1 shows a violent effect when heated under confinement (see point 5.3 of the above results). Consequently, also the impact sensitivity according to UN Test Series 3, Test 3 (a) (ii), BAM[43] Fallhammer should be determined. For this example, it amounts to 20 J. Such information should be given in the SDS.

Burning properties

For the example in section 2.15.7.1, the burning properties as determined by the test method described in the storage guidelines, currently in place in France, Germany, Netherlands and Sweden, is 7.0 kg/min/m². Based on this figure and the classification as organic peroxide type C, the storage classification can be assigned in those countries.

Flash point

The example substance thermally decomposes before the temperature at which the vapour can be ignited is reached (see section 2.15.4.3) and consequently a flash point cannot be determined.

2.16. CORROSIVE TO METALS

2.16.1. Introduction

The criteria for ‘Corrosive to metals’ are found in CLP Annex I, section 2.16 and are identical to those in chapter 2.16 of GHS[18].

A substance or a mixture that is corrosive to metal under normal conditions is a substance or a mixture liable to undergo an irreversible electrochemical reaction with metals that leads to significant damage or, in some cases, even to full destruction of the metallic components. The corrosive to metal property is a quite complex property, since it is a substance (or mixture) related as well as a material (metal) related property. This means a corrosive substance or mixture leads to corroded material (metal), according to a number of external conditions. From the material side, many types of corrosion processes may occur, according to configurations, liquid or fluid media inducing the corrosion process, nature of metal, potential passivation occurring by oxide formation during corrosion.

From the substance or mixture side, many parameters may influence the corrosion properties of a substance or mixture, such as the nature of the chemical or the pH. From an electrochemistry point of view, corrosion conditions are often studied using Pourbaix diagrams, which plot the electrochemical potential (in Volt) that develops according to electrical charges transfer versus the pH-value. Such a diagram is shown for the case of iron and applies only for carbon steel corrosion (Jones, 1996).

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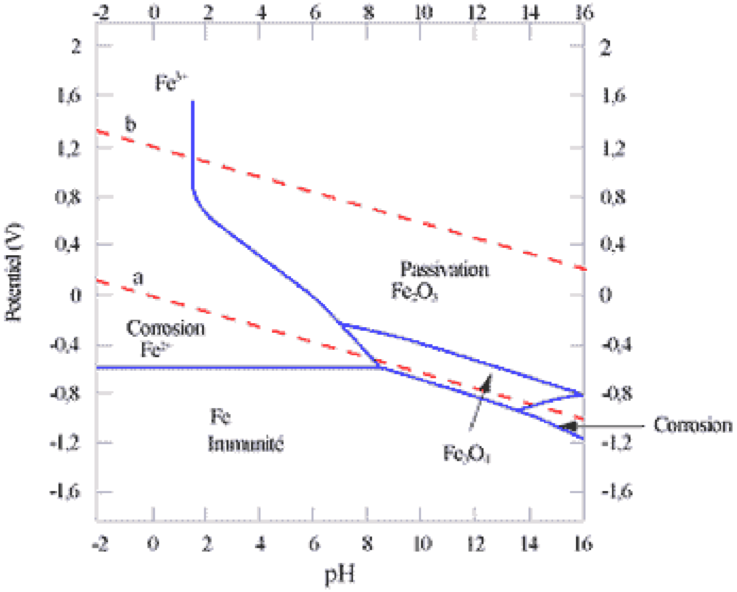
[43] BAM: Bundesanstalt für Materialforschung und -prüfung

Figure 2.15 Potential pH (also called Pourbaix) diagram for iron in water at 25 °C, indicating stable form of the Fe element and implicitly, corrosion domains



For the purposes of CLP, corrosion to metal will only be considered, by pure convention, for substances and mixtures that are liable to attack carbon steel or aluminium, two of the most common metals that may come in contact with chemical substances (containment material, reactor material). The classification scheme applied here must not be considered as a material (metal) classification method for metals regarding resistance to corrosion. By no means steel or aluminium specimens that are treated to resist to corrosion, must be selected for testing.

2.16.2. Definitions and general considerations for classification of corrosive to metals

CLP comprises the following definition for substances and mixtures that are corrosive to metal.

Annex I: *2.16.1. Definition*

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

2.16.3. Relation to other physical hazards

There is no direct relation to other physical hazards.

2.16.4. Classification of substances and mixtures as corrosive to metals

2.16.4.1. Identification of hazard information

Importance of the physical state of the test substance or mixture

There is no reference in the definition (CLP Annex I, section 2.16.1) to the physical state of the substances or mixtures that need consideration for potential classification in this hazard class. According to the test method for considering classification under this hazard class, it can be stated at least that gases are out of the scope of the corrosive to metal hazard class. Neither the corrosivity of gases nor the formation of corrosive gases is currently covered by CLP classes and are consequently **not** applicable here.

Based on practical considerations, only substances and mixtures for which the application of the UN Test C.1 (described in part III, section 37.4.1 of the UN-MTC) is relevant need to be considered. Application of classification criteria in the UN-MTC, Section 37.4 excludes solids, while 'liquids and solids that may become liquids (during transport)', have to be considered for such a classification.

The wording 'solids that may become liquids' was developed for the UN RTDG Model Regulations classification purposes and needs further explanation. One common way by which solids may become liquids is by melting (due to increase in temperature). Solids having a melting point lower than 55 °C (which is the test temperature required in UN Test C.1) must then be taken into consideration. Another common physical way to transform a solid into liquid is by dissolution in water or another solvent. Classification of solid substances that may become liquids, such as through water intake from humid air environments, requires further expert judgement and may need adaptation of the classification criteria or test protocol (see section 2.16.4.4.2). Interaction with liquids may come from air moisture or unintentional contact with water. Other solvent traces may result from the extraction process during manufacturing, and these may induce corrosion in practice, as far as it allows some mobility of subsequent ions. Expert judgement would also be required for low melting point solids that also partially convert into gas phase through sublimation process (e.g. methyl isothiocyanate).

Substances and mixtures in a liquid state must be tested without any modification before testing. It should be specified how such substances or mixtures are prepared (transformed into liquids) to be able to determine their corrosivity to metals. As an example, it is thought that the quantity of solvent (water or any other solvent) to liquefy the test substance before testing would greatly influence results of the UN Test C.1 test and may not necessarily represent the real-life situation of a product during transport, handling or use.

Non-testing data

Following parameters are helpful to evaluate corrosive properties before testing:

- melting points for solids;
- chemical nature of the substances and mixtures under evaluation (e.g. strong acids);
- pH values (liquids).

See also *IR & CSA, Chapter R.7a: Endpoint specific guidance*, section R.7.1.2 (Melting point/freezing point).

Literature may also provide information on widely used substances and liquids 'compatibility tables', taking account of the corrosiveness of the products that may serve to decide whether testing must be conducted before assigning the corrosive to metals hazard class, on basis of expert judgement.

The following substances and mixtures should be considered for classification in this class:

- substances and mixtures having acidic or basic functional groups;
- substances or mixtures containing halogen;
- substances able to form complexes with metals and mixtures containing such substances.

2.16.4.2. Screening procedures and waiving of testing

Experience may have proven the corrosivity of given substances and mixtures. In such cases, no more testing is needed (see examples in Section 2.16.7).

Generally extreme pH-values point to a higher likelihood that the substance or mixture is corrosive. However, it cannot lead to immediate classification in the hazard class corrosive to metals. As a proof of that, Figure 2.15 shows that immunity zones (where steel does not corrode) still exist on the full spectrum of pH values as far as carbon steel is concerned.

Corrosivity is so complex that the evaluation of a mixture cannot be extrapolated from similar behaviour of constituents of a mixture. However, if one significant component of a mixture is corrosive to metals the mixture is likely to be corrosive to metals as well. Testing the actual mixture is therefore highly recommended. As already mentioned, solids are currently difficult to test according to the current CLP requirements, as the UN Test C.1 was designed for liquids.

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.

2.16.4.3. Classification criteria

Substances and mixtures of hazard class corrosive to metals are classified in a single hazard category on the basis of the outcome of the UN Test C.1 (UN-MTC, Part III, Section 37, paragraph 37.4).

Annex I: *Table 2.16.1*

Criteria for substances and mixtures corrosive to metals

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.*

2.16.4.4. Testing and evaluation of hazard information

2.16.4.4.1. General considerations

It is important to point out that the criteria of corrosion rate will never be applied in an absolute way, but by extrapolating the measured rate of corrosion over the test period to the annual assumed correlating corrosion rate. This exercise has to take account of the fact that the corrosion rate is not necessarily constant over time. Expert judgement may be required to consolidate the optimum test duration and to ascertain test results. However, the possibility of increasing the testing period from minimum one week to four weeks as well as the use of two different metals in the UN Test C.1 act as barriers against erroneous classification.

Whatever the result of the classification may be, the classification as corrosive to metals relates to steel and/or aluminium only and does not provide information with regard to the corrosivity potential to other metals than those tested.

Two types of corrosion phenomena need to be distinguished for classification of substances and mixtures in this hazard class, although not reported in CLP: the uniform corrosion attack and the localised corrosion (e.g. pitting corrosion, shallow pit corrosion).

Table 2.3 (Section 37.4.1.4.1 of the UN-MTC) translates the corresponding minimum mass loss rates leading to classify the test substance or mixture as corrosive to metals for standard metal specimens (2 mm of thickness), according to time of exposure, for reasons of uniform corrosion process. In case of use of metal plates of a thickness that differs from the specified 2 mm (see comments in Section 2.16.4.2), the values in Tables 2.3 and 2.4 need adjustments due to the fact that the corrosion process depends on the surface of specimen.

Table 2.3 Minimum mass loss of specimens after different exposure times (corresponding to the criterion of 6.25 mm/year, correspond to Table 37.4.1.1 of UN-MTC)

Exposure time (days)	Mass loss (%)
7	13.5
14	26.5
21	39.2
28	51.5

Table 2.4 (Section 37.4.1.4.2 of the UN-MTC) indicates the criteria leading to classification of the test substance or mixture as corrosive to metals for standard metal specimens, according to time of exposure, for reasons of localised corrosion process.

Table 2.4 Minimum intrusion depths after exposure times (corresponding to the criterion of localised corrosion of 6.25 mm/year, correspond to Table 37.4.1.2 of UN-MTC)

Exposure time (days)	Min. intrusion depth (μm)
7	120
14	240
21	360
28	480

It is not mentioned explicitly in the text that localised corrosion as well as uniform corrosion has also been taken into account. However, localised corrosion, that is entirely part of the UN Test C.1 protocol, has to be taken into account. In addition, although the type of corrosion is not reflected in the classification result, this valuable information should be given in the SDS.

2.16.4.4.2. Additional notes on best practice for testing

Competence required for testing

The overall evaluation of appropriate data for considering the corrosion properties of a substance or a mixture, in particular for testing according to the mentioned criteria for this hazard class, requires certain qualifications and experience. Expertise is often needed for this hazard class, which relates to a complex and multi-faceted hazardous phenomenon.

Selection of metal specimens

CLP refers to two types of metals (carbon steel and aluminium) meeting accurate specifications (technical characteristics of metal sheets and plate thickness). Thicker metal sheets, such as cast materials, of which the thickness is reduced to 2 mm by any form of mechanical treatment, may never be used. Mechanical reduction of sheet (metal) thickness could induce corrosion enhanced process due to cross section heterogeneity in metal grain and impurities. It is far better to use slightly different specifications of metal in the correct thickness or slightly different specimen plate thicknesses. It is recognised that it will not always be easy to obtain metal specimens with the profile as described above.

Regarding the type of aluminium or steel to be used for this test see UN-MTC, Section 37.4.1.2.

Minimum corrosive media volume

To prevent any limitation on the corrosion process due to full consumption of the corrosive media before the end of the testing period, a minimum volume of substance or mixture (1.5 L, according to the UN-MTC) has to be used. (Note: volume/surface ratio of 10 mL/cm² is stated in DIN 50905, similar in ASTM G31–72.)

Adjustment of the test temperature

Corrosion processes are temperature dependent. In the context of CLP, the property corrosive to metals is assessed through testing metal specimens at a specified temperature of 55 °C ± 1 °C. In practice, it may be difficult with standard testing equipment to stay within the temperature window (55 °C ± 1 °C) of the gas phase, all over the test period. In such case, the test can be performed conservatively at a slightly higher temperature and somewhat lower accuracy (e.g. 57 °C ± 3 °C).

Selecting the appropriate test duration

The evaluation of the criterion of 6.25 mm/year is generally based on a test duration not exceeding 1 month. There is the option to stop the test procedure already after 1 week. For the decision on test duration, the non-linear behaviour of the corrosion process must be taken due account of. In borderline cases a non-appropriate test duration may result in either false positive or false negative results.

Specimen cleaning

Attention must be paid to the correct cleaning of the corroded residue before measurement of the corrosion characteristics. In case of adhesive corroded layer, the same cleaning process needs to be carried out on a non-corroded sample to verify if the cleaning procedure is not significantly abrasive. For further information see UN-MTC, section 37.4.1.3.

Testing soluble solids

As said in Section 2.16.4.4.2, for solids that may become liquids through dissolution in water or in a solvent, the adequate testing procedure is more complex (not explicitly described in the UN C.1 test protocol). In no case will simple dilution of the solid substance or mixture in any quantity of water lead to satisfactory testing of the substance or mixture for corrosion to metals.

For the specific case where the corrosion potential is linked to the presence of solvent traces (other than water), expert judgement is needed to determine whether further testing must be performed (where the solid is put in interaction with the metallic part considered).

Example of equipment relevant for the performance UN Test C.1

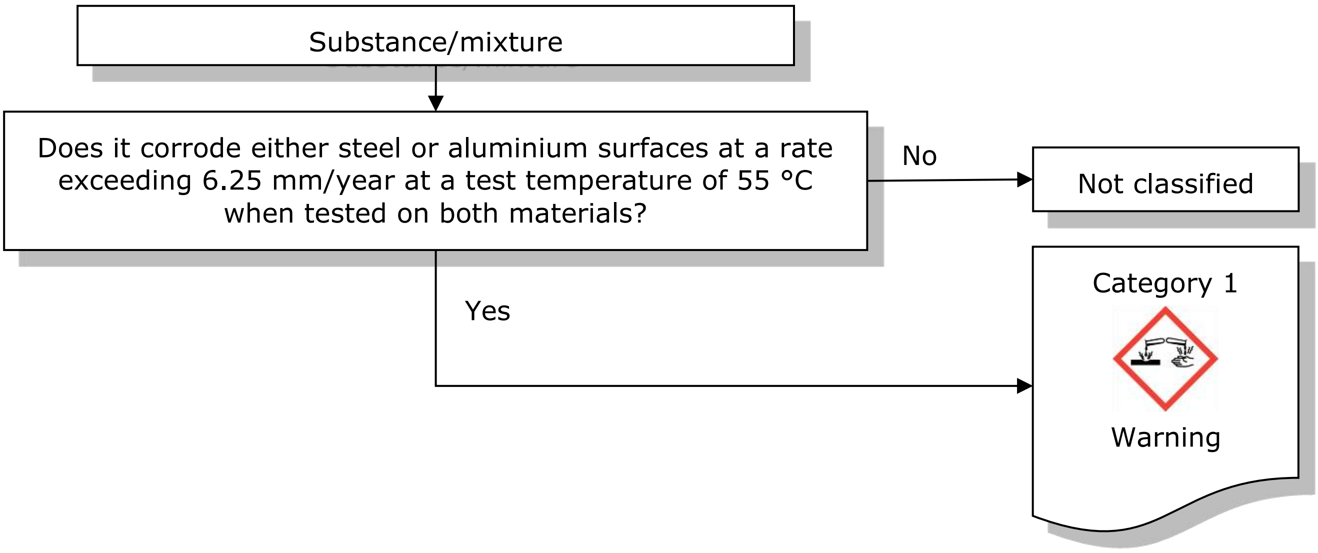
Figure 2.16 Example of testing equipment available on the market to perform UN Test C.1

2.16.4.5. Decision logic

Classification of substances and mixtures corrosive to metals is done according to decision logics 2.16.4.1 as included in GHS.

! NOTE: The person responsible for the classification of substances and mixtures corrosive to metals should be experienced in this field and be familiar with the criteria for classification.

Figure 2.17 Decision logic for substances and mixtures corrosive to metals (Decision logic 2.16 of GHS)



2.16.5. Hazard communication for corrosive to metals

2.16.5.1. Pictograms, signal words, hazard statements and precautionary statements

Table 2.16.2 of CLP Annex I provides the label elements for hazard class corrosive to metals. The hazard statement H290, using the wording 'may', reflects that classification under this hazard class does not cover all metals (testing only considers carbon steel and aluminium). Consequently, we may find examples of substances and mixtures that are classified in this hazard class corrosive to metals but will not induce corrosive action on other more corrosive resistant metals (e.g. platinum) than those serving as reference materials.

Label elements must be used for substances and mixtures meeting the criteria for classification in this hazard class in accordance with Table 2.16.2.

Annex I: *2.16.3.* *Table 2.16.2*

Label elements for substances and mixtures corrosive to metals

Classification	*Category 1*
GHS Pictogram	
Signal Word	*Warning*
Hazard Statement	*H290: May be corrosive to metals*
Precautionary Statement, Prevention	*P234*
Precautionary Statement, Response	*P390*

Precautionary Statement, Storage	*P406*
Precautionary Statement, Disposal	
Note: *Where a substance or mixture is classified as corrosive to metals but not corrosive to skin and/or eyes, the labelling provisions set out in Section 1.3.6 shall be used.*	

The wording of the precautionary statements is found in CLP Annex IV, Part 2.

Furthermore, CLP Annex I, section 1.3.6 provides a derogation from labelling requirements for substances or mixtures classified as corrosive to metals but not corrosive to skin and/or eyes.

> **Annex I: *1.3.6 Substances or mixtures classified as corrosive to metals but not classified as skin corrosion or as serious eye damage (Category 1)***
>
> *Substances or mixtures classified as corrosive to metals but not classified as skin corrosion or as serious eye damage (Category 1) which are in the finished state as packaged for consumer use do not require on the label the hazard pictogram GHS05.*

2.16.6. Relation to transport classification

Class 8 of the UN RTDG Model Regulations covers substances and mixtures that are classified for corrosivity to skin, metals or both. Valuable information can be obtained from the UN RTDG Model Regulations and the modal transport regulations (ADR, RID, ADN and IMDG Code, ICAO TI). Existing test results obtained in the context of the modal transport regulations (ADR, RID, ADN and IMDG Code, ICAO TI) may be applied since the UN Test C.1 serves as reference for testing in both classification systems. See Annex I for additional information on transport classification in relation to CLP classification.

2.16.7. Example of classification for corrosive to metals

The following table lists some examples of substances and mixtures that should be classified, or not, in Class 2.16 (according to known UN Test C.1 results) in comparison with predicted results for skin corrosion hazard.

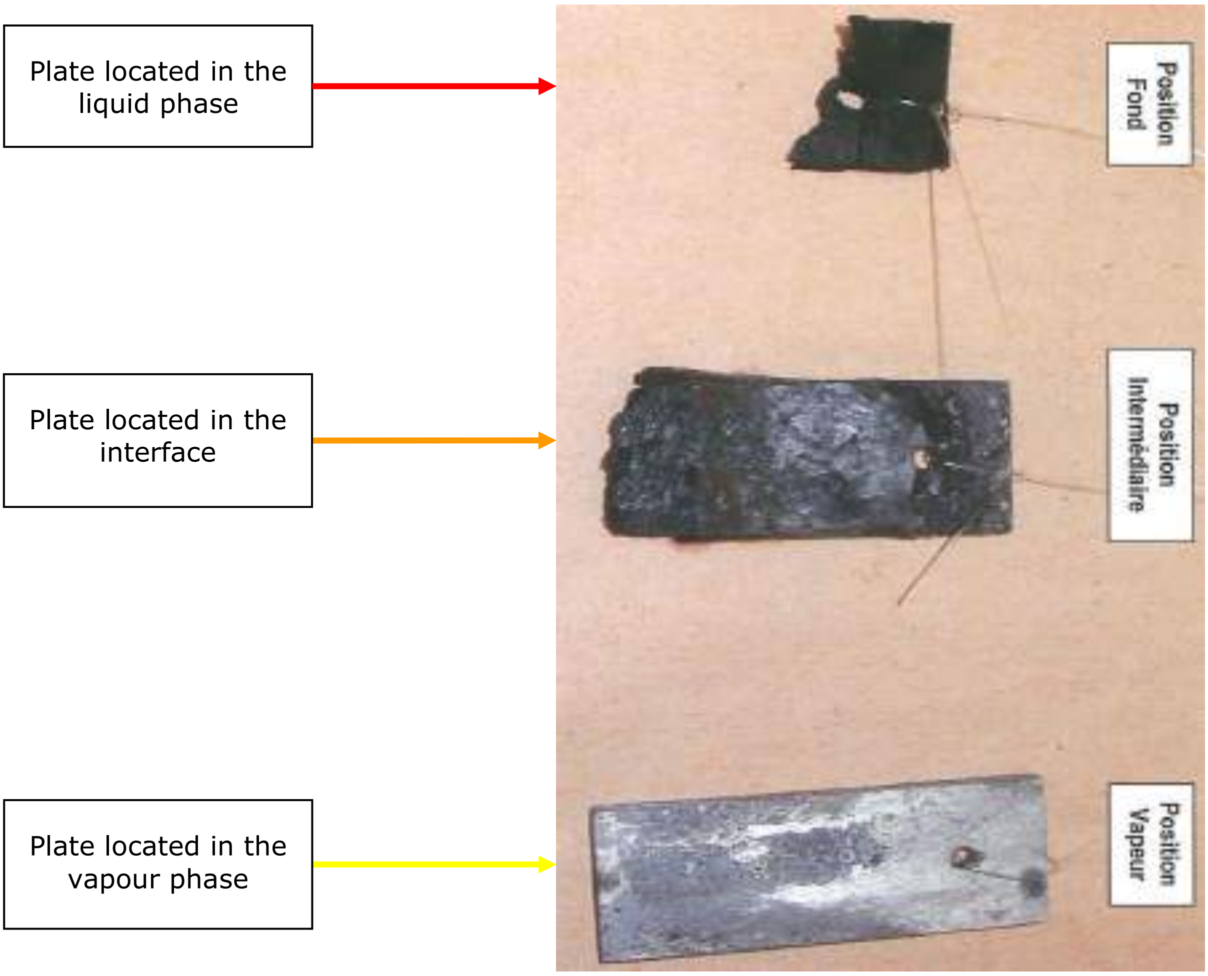
Table 2.5 Examples of classified and non-classified substances and mixtures in Class 2.16

Substance or mixture	Steel	Aluminium	CLP Annex I, 2.16 classification	Skin (for comparison)
Hydrofluoric acid > 70 % (UN1790)	Not corroded	Corroded	Classified	Positive
Highly concentrated nitric acid (97 %) (UN2031)	Not corroded	Corroded	Classified	Positive
HNO_3 red fuming (UN2032)	Not corroded	Not corroded	Not classified	Positive
Hydrochloric acid (diluted) (UN1789)	Corroded	Corroded	Classified	Negative
NaOH solutions (UN1824)	Not corroded	Corroded	Classified	Positive

Note: 'Corroded' means corrosion attack in the sense of UN Test C.1; 'Not corroded' means corrosion resistant in the sense of UN Test C.1; 'Positive' or 'Negative' are results from skin corrosion.

2.16.7.1. Example of metal specimen plates after exposure to a corrosive mixture

Figure 2.18 Example of corroded metal plates after testing according to UN Test C.1 for a classified mixture



This example shows that the corrosion may develop at different rates according to the accurate position of the specimen related to the corroding mixture (sunk in the liquid, placed in the gas phase above liquid or at the liquid/gas interface).

2.16.8. References

ASTM G31-72(2004) *Standard Practice for Laboratory Immersion Corrosion Testing of Metals*.

Jones, D.A., *Principles and Prevention of Corrosion*, 2nd edition, 1996, Prentice Hall, Upper Saddle River, NJ. ISBN 0-13-359993-0 Page 50-52.

DIN 50905-1: 2007, *Corrosion of metals - Corrosion testing – Part 1: General guidance* (Korrosion der Metalle - Korrosionsuntersuchungen - Teil 1: Grundsätze).

2.17. DESENSITISED EXPLOSIVES

2.17.1. Introduction

Desensitised explosives are covered in CLP Annex I, section 2.17. As the definition implies, they are derived from explosive substances and mixtures (see CLP Annex I, section 2.1.1.1(a) and (c)). However, desensitisation of explosive articles (CLP Annex I, section 2.1.1.1(b)) is not possible.

The desensitisation is achieved on the one hand by a dilution effect (reduction of the decomposition energy), on the other hand by disruption of the propagation of a shock wave in combination with an energy-absorbing endothermic evaporation.

As the definition implies, desensitised explosives are generally mixtures consisting of the original explosive substance or mixture and the phlegmatiser or diluent. However, if the phlegmatiser is built directly into the crystal lattice and is therefore chemically bonded (see note in CLP Annex I, section 2.17.1.2(a)), such desensitised explosive would be not a mixture but a substance.

For the "regular" desensitised explosives it is essential that the original explosive and the diluent are HOMOGENEOUSLY mixed. For a solvent-based solid desensitised explosive this means that the diluent has to be evenly distributed among the crystals and not form a wet suspension in the lower part of a package with dry material on the top. Therefore, at least a sufficient amount of liquid has to remain between the crystals to function effectively as desensitiser; separation of excess material is tolerable. For desensitised explosives where a solid phlegmatiser is added to the explosive one has to make sure that the components are permanently homogeneously mixed. This is usually the case if the components have similar crystal sizes and comparable densities. See also note 1 in section 2.17.4.3.

2.17.2. Definitions and general considerations for desensitised explosives

CLP comprises the following definition for substances and mixtures that are desensitised explosives.

Annex I: 2.17.1.1 Definition

Desensitised explosives are solid or liquid explosive substances or mixtures which are phlegmatised 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' (see also paragraph 3 in section 2.1.4.1) (1)

2.17.1.2. The hazard class of desensitised explosives comprises:

> *(a) Solid desensitised 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 desensitisation achieved by formation of hydrates of the substances.*
>
> *(b) Liquid desensitised 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.*

---

(1) *Unstable explosives as defined in Section 2.1 can also be stabilised by desensitisation and consequently may be classified as desensitised explosives, provided all criteria of Section 2.17 are met. In this case the desensitised explosive shall be tested according to test series 3 (Part I of the UN RTDG, 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 shall be communicated in the safety data sheet.*

2.17.3. Relation to other physical hazards

The only possibility to "enter" the class of desensitised explosives is from the class of explosives (section 0) by dilution or phlegmatisation.

Classification as explosive and desensitised explosive are mutually exclusive. Further, note 3 in CLP Annex I, Table 2.17.1 explicitly states that "desensitised explosives do not fall additionally within the scope of sections […] 2.6 (flammable liquids) and 2.7 (flammable solids)."

Explosives may sometimes be an active ingredient in aerosols, specifically used for medical purposes (i.e. nitroglycerin spray for treatment of heart emergencies). However, the concentration is usually so small that the respective aerosol is neither classified as explosive nor as desensitised explosive, because the decomposition energy will fall below the lower limit of 300 J/g of CLP 2.17.2.1(c), so that classification as desensitised explosive does not apply.

Since desensitised explosives are by definition explosives that have been phlegmatised, they cannot be self-reactive substances and mixtures according to CLP Annex I, section 2.8.2.1(a). By definition in CLP Annex I, section 2.15.1.1, organic peroxides cannot be classified as desensitised explosives.

Generally, desensitised explosives will not be classified as oxidising solids or liquids, respectively. It is advisable to also check the chapter about explosives in this guidance.

Although a simultaneous classification as pyrophoric solid / liquid (sections 2.9 and 2.10), self-heating (section 2.11) or water-reactive (section 2.12) cannot be precluded, such combination would be applicable only in extremely rare cases where the resulting intrinsic increase of risk has been intentionally accepted or designed. Substances and mixtures of these chapters usually consist of chemicals that are reactive towards air or water whereas explosives have a certain decomposition energy stored as potential energy in the molecule or mixture that can be released.

In rare cases, desensitised explosives may also be corrosive to metals (section 2.16). However, one has to be aware that metals used in test method UN C.1 of the UN-MTC may trigger decomposition. Therefore, it may not be possible to perform this test. In case of doubt, expert judgement should be applied.

2.17.4. Classification of substances and mixtures as desensitised explosives

Annex I:

2.17.2.1. Any explosive while in a desensitised state shall be considered in this class unless, in that state:

(a) It is intended to produce a practical explosive or pyrotechnic effect;

(b) It has a mass explosion hazard according to test series 6 (a) or 6 (b) or the corrected burning rate according to the burning rate test described in part V, subsection 51.4 of the UN RTDG, Manual of Tests and Criteria is greater than 1 200 kg/min; or

(c) The exothermic decomposition energy is less than 300 J/g.

NOTE 1: Substances or mixtures, which meet the criterion (a) or (b) in their desensitised state shall be classified as explosives (see Section 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 RTDG, Manual of Tests and Criteria).

For a proper classification process, the following questions should be clearly answered:

1. Is the "original" substance or mixture (= substance or mixture before desensitisation) an explosive as defined in section 2.1? If not, a classification as desensitised explosive is not applicable.
2. Is the substance or mixture in the desensitised form intended to produce a practical explosive or pyrotechnic effect? If yes, it remains in the class of explosives.
3. Does the diluent or phlegmatiser fulfil the intended function, especially with respect to a permanent homogeneous distribution (see explanations in section 2.17.1 above)? If not, a classification as desensitised explosive is not possible.
4. What is the value of exothermic decomposition energy? If the answer is less than 300 J/g, the class of desensitised explosives is not applicable; in this case, potential classification as flammable liquids or flammable solids should be checked.
5. Is the phlegmatised explosive too sensitive or thermally unstable in accordance with Test Series 3 of the UN-MTC? If yes, such mixture will remain an explosive of class 2.1. Where a mixture contains nitrocellulose, additional data of the nitrocellulose as described in Appendix 10 of the UN-MTC are needed to be used in nitrocellulose mixtures considered in this class.

Subsequently, testing is required:

Test 6 (a) and 6 (b) according to sections 16.4 and 16.5 of the UN-MTC should be performed to establish that the intended desensitised explosive has no mass explosion hazard.

Alternatively, Test Series 2 according to Part I, section 2 of the UN-MTC may be performed with the phlegmatised explosive. If a negative result ("-") is obtained in each of the three individual tests, it is "too insensitive for inclusion in the class of explosives" and thus may qualify for classification as a desensitised explosive. In this case, Test 6 (a) and 6 (b) need not be performed.

Finally, the burning rate test of section 51.4 of the UN-MTC will confirm the classification as a desensitised explosive and lead to the assignment of the category. However, if the corrected burning rate is found to be 1200 kg/min or more, such material is moved back to the class of explosives.

2.17.4.1. Identification of hazard information

Since desensitised explosives are derived from explosives it is advisable to gather information about these properties first. In a second step, the diluent or phlegmatiser should be checked; key requirements are:

- The diluent (phlegmatiser) has to be chemically inert towards the explosive. This means that this compound does not interact with the explosive in any way that would reduce the thermal or chemical stability.
- Further, the diluent must be effective in its function as a desensitiser (see also section 2.17.1) with a homogeneous distribution over extended periods of time (i.e. duration of storage).

2.17.4.2. Screening procedures and waiving of testing

The screening procedures for explosives are described in section 2.1.4.2.

Phlegmatised mixtures with a decomposition energy below 300 J/g should not be classified as desensitised explosive (see CLP Annex I, section 2.17.2.1(c)).

2.17.4.3. Classification criteria

Substances and mixtures of hazard class desensitised explosives are classified in four hazard categories on the basis of the corrected burning rate (UN-MTC, section 51.4), according to CLP Annex I, Table 2.17.1.

Annex I: *Table 2.17.1*

Criteria for desensitised explosives

Category	*Criteria*
1	*Desensitised explosives with a corrected burning rate (AC) equal to or greater than 300 kg/min but not more than 1 200 kg/min*
2	*Desensitised explosives with a corrected burning rate (AC) equal to or greater than 140 kg/min but less than 300 kg/min*
3	*Desensitised explosives with a corrected burning rate (AC) equal to or greater than 60 kg/min but less than 140 kg/min*
4	*Desensitised explosives with a corrected burning rate (AC) less than 60 kg/min*

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

Note 2: Explosive properties of desensitised explosives shall be determined by test series 2 of the UN RTDG, Manual of Tests and Criteria, and shall be communicated in the safety data sheet.

Note 3: For the purposes of storage, supply and use, desensitised explosives do not fall additionally within the scope of Sections 2.1 (explosives), 2.6 (flammable liquids) and 2.7 (flammable solids).

2.17.4.4. Testing and evaluation of hazard information

General considerations

Due to the high risks relating to the handling of explosives, the testing personnel should be sufficiently qualified and experienced in performing the required tests. Please refer to section 2.1.4.4 for further details.

Additional notes on best practice for testing

Before applying the desensitiser, the explosive properties of the "original" substance or mixture should be known (in general: results of Test Series 2, 3 (a) and 3 (b) of the UN-MTC; further data about thermal stability such as Test 3 (c), or appropriate data determined according to section 20.3.3.3 of the UN-MTC or data from application of microcalorimetric methods).

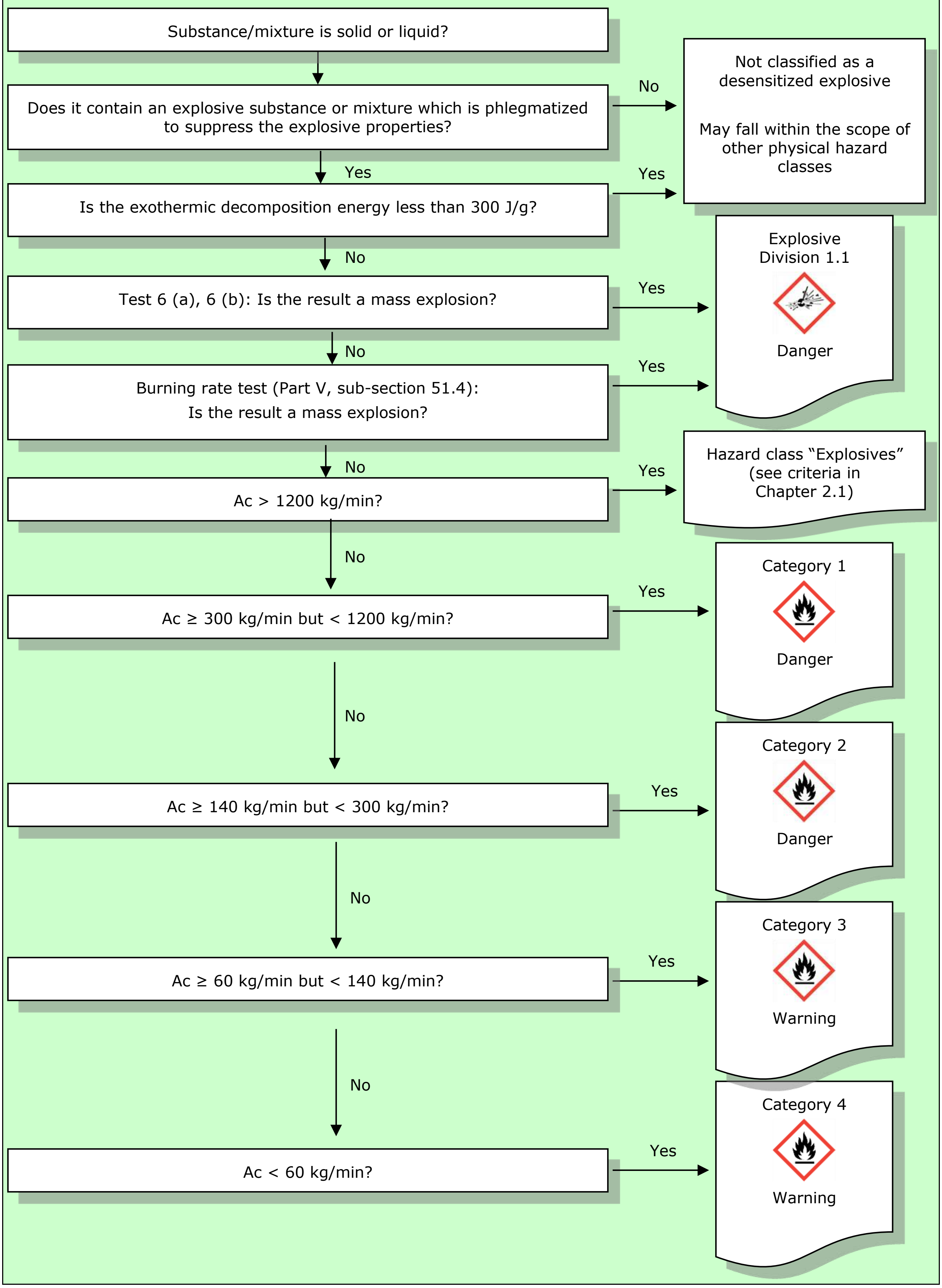
Subsequently, the effect of the diluent/phlegmatiser should be examined; see section 2.17.1.

2.17.4.5. Decision logic

Classification of substances or mixtures as desensitised explosives is done according to decision logics in CLP Annex I, Figure 2.17.1.

NOTE: The person responsible for desensitised explosives should be experienced in this field and be familiar with the criteria for classification.

Annex I: *Figure 2.17.1* *Desensitised explosives*



2.17.5. Hazard communication for desensitised explosives

2.17.5.1. Pictograms, signal words, hazard statements and precautionary statements

Table 2.17.2 of CLP Annex I provides the label elements for hazard class desensitised explosives.

Label elements must be used for substances and mixtures meeting the criteria for classification in this hazard class in accordance with Table 2.17.2.

Annex I: *2.16.3.* *Table 2.17.2* ***Label elements for desensitised explosives***

Classification	*Category 1*	*Category 2*	*Category 3*	*Category 4*
GHS Pictogram				
Signal Word	*Danger*	*Danger*	*Warning*	*Warning*
Hazard Statement	*H206 Fire, blast or projection hazard; increase risk of explosion if desensitising agent is reduced*	*H207 Fire or projection hazard; increased risk of explosion if desensitising agent is reduced*	*H207 Fire or projection hazard; increased risk of explosion if desensitising agent is reduced*	*H208 Fire hazard; increased risk of explosion if desensitising agent is reduced*
Precautionary Statement Prevention	*P210* *P212* *P230* *P233* *P280*	*P210* *P212* *P230* *P233* *P280*	*P210* *P212* *P230* *P233* *P280*	*P210* *P212* *P230* *P233* *P280*
Precautionary Statement Response	*P370 + P380+ P375*	*P370 + P380+ P375*	*P370 + P380+ P375*	*P371 + P380+ P375*
Precautionary Statement Storage	*P401*	*P401*	*P401*	*P401*
Precautionary Statement Disposal	*P501*	*P501*	*P501*	*P501*

The wording of the precautionary statements is found in CLP Annex IV, Part 2.

2.17.6. Relation to transport classification

Since desensitised explosives have a high rank in the precedence tables of the Dangerous Goods Regulations, such substances and mixtures will be classified likewise in CLP. Unlike in CLP, desensitised explosives are not a hazard class of their own for transport. Instead, such substances and mixtures are transported under specific UN-numbers in class 3 (liquids) or division 4.1 (solids).

2.17.7. Examples of classification for desensitised explosives

A detailed example for the classification of a new substance as a desensitised explosive can be found on the UN website using the following link: ST/SG/AC.10/C.3/2021/32 (unece.org).

This document describes in detail testing that has been performed for the original explosive substance, and subsequently the test results in the desensitised form up to the assignment of a category.

ANNEX I: RELATION BETWEEN TRANSPORT AND CLP CLASSIFICATION REGARDING PHYSICAL HAZARDS

Table I.1 on physical hazards only, provided in this annex, contains additional information on transport classifications in relation to CLP classifications that could be of added value. However, these comparisons have certain restrictions with regard to their applicability. In particular, the area of applicability of the transport regulation is different from the CLP Regulation (ADR 49 countries, IMDG-Code, ICAO-TI international regulations). Therefore, the table should be used as reference for deriving CLP classifications and not vice versa.

The transport classification of named substances or mixtures in the transport regulations reflects the transport conditions and therefore were not adapted to take into account the GHS criteria. The transport classifications may be based on experience or certain events that are specific to transport. The transport classification of named substances or mixtures is legally binding for transport and should not be used to derive a CLP classification without an expert review.

The transport regulations include the concept of precedence of hazards which guarantees that information on the most dangerous hazards is communicated with precedence. CLP does not apply a precedence of hazards and therefore substances or mixtures might need to be classified in additional hazard classes under CLP, which in the transport classification are allocated and noted under the respective UN-Number (giving information on subsidiary risks, appropriate packaging and transport conditions).

It needs to be noted that a substance may have more than one entry in the Dangerous Goods List. These are usually within the same class, but transport conditions are different because of different severity of the hazard for different concentrations of this substance.

The following table refers only to physical hazards, as health hazards are not harmonised regarding cut-off values, and/or allowed methods.

Table I.1 Relation between transport and CLP classifications regarding physical hazards

⚠ (NOTE that within transport, the term ‘substances’ covers also mixtures in CLP terms.)

Transport classification		**Physical state**	**CLP-classification**		**Remarks**
Transport class and (sub)division (if applicable)	**Packing group, division, type, group or code**		**Hazard class**	**Hazard category, division, type or group**	
Class 1	Division 1.1	Liquid or solid	Explosives	Division 1.1	Matching criteria. However, if explosives are un-packed or repacked, they have to be assigned to division 1.1 unless the hazard is shown to correspond to one of the other divisions.
	Division 1.2			Division 1.2	
	Division 1.3			Division 1.3	
	Division 1.4			Division 1.4	
	Division 1.5			Division 1.5	
	Division 1.6			Division 1.6	

Class 2* – Gases	1 Compressed gas	Gaseous	Gases under pressure	Compressed gas	A correspondence only applies to the form in which the gas is transported. If it is used in a different form, then the classification has to be amended.
	2 Liquefied gas	Gaseous		Liquefied gas	
	3 Refrigerated liquefied gas	Gaseous		Refrigerated liquefied gas	
	4 Dissolved gas	Gaseous		Dissolved gas	Matching criteria with 2.5. Note: Gases may be packaged in other forms such as "chemical under pressure" or "adsorbed gases" that are not considered in the GHS/CLP.
	5 Aerosol dispensers, Class 2.1 Class 2.2	Not relevant (Articles)	Aerosols	Category 1 Category 2 Category 3	The transport classification does not differentiate between Aerosols Category 1 and 2 (both are classified as class 2.1)
	6 Other articles containing gas under pressure	Gaseous	Flammable gases	Category 1	
	7 Non-pressurised gases subject to special requirements	Gaseous	Oxidising gases	Category 1	
	8 Chemicals under pressure***	Not relevant			
	9 Adsorbed gas	Gaseous			
Class 3	Packing group I	Liquid	Flammable liquid	Category 1	
	Packing group II	Liquid	Flammable liquid	Category 2	
	Packing group III	Liquid	Flammable liquid	Category 3	

Class 4.1	Types B-F	Solid or liquid	Self-reactive substances	Types B-F	
Class 4.1 (solid desensitized explosives)	Packing group I	Solid	Solid desensitized explosives		
Class 4.1 (only readily combustible solids)	Packing group II	Solid	Flammable solids	Category 1	
Class 4.1 (only readily combustible solids)	Packing group III	Solid	Flammable solids	Category 2	
Class 4.2 Pyrophoric substances	Packing group I	Liquid	Pyrophoric liquids	Category 1	
		Solid	Pyrophoric solids	Category 1	
Class 4.2	Packing group II	Solid	Self-heating substances and mixtures	Category 1	
Class 4.2	Packing group III	Solid	Self-heating substances and mixtures	Category 2	
Class 4.3	Packing group I	Liquid or solid	Substances which in contact with water emit flammable gases	Category 1	
	Packing group II			Category 2	
	Packing group III			Category 3	
Class 5.1	Packing group I	Solid	Oxidising solid	Category 1	
	Packing group II			Category 2	
	Packing group III			Category 3	
Class 5.1	Packing group I	Liquid	Oxidising liquid	Category 1	
	Packing group II			Category 2	
	Packing group III			Category 3	
Class 5.2	Types B-F	Solid or liquid	Organic peroxides	Types B-F	
Class 8	Packing group III	Liquid or solid	Corrosive to metals	Category 1	Applies only when the substance or mixture is not classified as

					corrosive to skin and/or eye.

(*) Substances and articles (except aerosols and chemicals under pressure) of Class 2 are assigned to one of the following transport groups according to their hazardous properties, as follows: An asphyxiant, O oxidising, F flammable, T toxic, TF toxic, flammable, TC toxic corrosive, TO toxic, oxidising, TFC toxic, flammable, corrosive, TOC toxic, oxidising, corrosive

(**) Aerosols are assigned to one of the following transport groups according to their hazardous properties, as follows: An asphyxiant, O oxidising, F flammable, T toxic, C corrosive, CO corrosive, oxidising, FC flammable, corrosive, TF toxic, flammable, TC toxic corrosive, TO toxic, oxidising, TFC toxic, flammable, corrosive, TOC toxic, oxidising, corrosive

(***) Chemicals under pressure are assigned to one of the following transport groups according to their hazardous properties, as follows: An asphyxiant, F flammable, T toxic, C corrosive, FC flammable, corrosive, TF toxic, flammable

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