



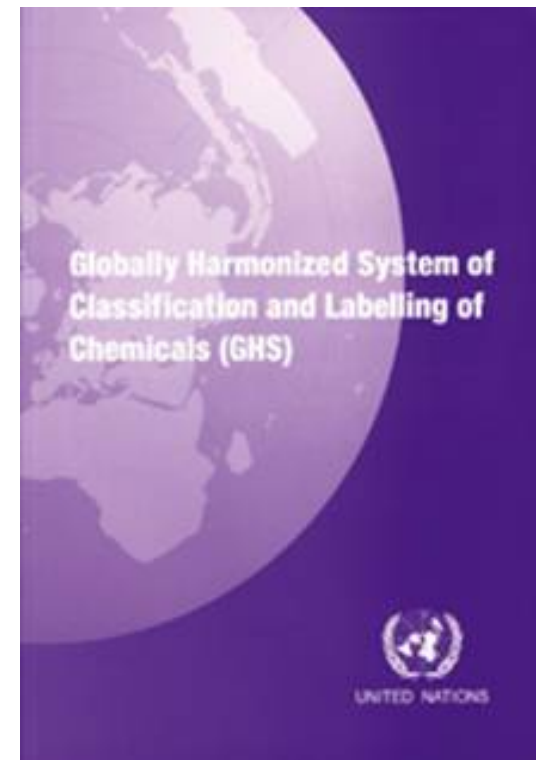
# **Classification and Labelling based on physical hazards**

**CIPAC Symposium 2018, Panama**

## *UN GHS Purple Book*

*Rev 7, 2017*

- The UN GHS Purple Book is a guidance document published by the United Nations on the Globally Harmonized System of Classification and Labelling of Chemicals (GHS);
- it defines **physical**, **health** and **environmental** hazards of chemicals and harmonizes classification criteria;
- it standardizes the content and format of chemical **labels** and **Safety Data Sheets**.



- The UN GHS Purple Book is **not** a regulation and it is not legally binding in any country;
- countries adopting GHS have to take basic GHS elements from the Purple Book and issue their own regulations or standards for implementation;
- each country/region may set extra requirements on chemical classification and labelling.

- REGULATION (EC) No 1272/2008 on Classification, Labelling and Packaging of Substances and Mixtures, „**CLP Regulation**“, entered into force in January 2009 (**EU**);
- OSHA's Hazard Communication Standard 2012 (**US**);
- **China** has fully implemented GHS for all hazardous substances and mixtures from 1 May 2011: GB 15258-2009
- **Mexico** has published **NOM-018-STPS-2015** Harmonized system for the identification and communication of hazards and risks from hazardous chemicals in the workplace on 8 Oct 2015. NOM-018-STPS-2015 will fully come into force on 8 Oct 2018.

# *UN Transport of dangerous Goods (UN TDG) Orange Book*

- The Globally Harmonized System of Classification and Labelling of Chemicals ([GHS](#)) and the UN Recommendations on the Transport of Dangerous Goods Model Regulations (TDG) are the most important guidance documents on chemical hazard communication in the world;
- Orange Book Rev.20 (Model Regulations on the Transport of Dangerous Goods) – 2017;
- Not all dangerous goods are chemicals or GHS classified (i.e. batteries, airbags) .

## *Classification*

- Classification is the starting point for hazard communication;
- It involves the identification of the hazard(s) of a chemical or mixture by assigning a category of hazard/danger using defined criteria

## *Hazard classes*

- **29 classes of hazards**
    - 17 physical hazard,
    - 10 health hazard and
    - 2 on environmental hazards)
  - **Each class has different categories or divisions (RTDG)**
- Classification**
- **Signal words (Danger or Warning);**
  - **Pictogram (9);**
  - **Hazard statement (H<sup>2</sup>xx);**
  - **Precautionary statement (Pxxx).**
- and Labelling**

## *Hazard classes* *Physical*

- Explosives
- Flammable Gases
- Flammable Aerosols
- Oxidizing Gases
- **Gases Under Pressure**
- **Flammable Liquids**
- Flammable Solids
- Self-Reactive Substances
- Pyrophoric Liquids
- Pyrophoric Solids
- **Self-Heating Substances**
- **Substances which, in contact with water emit flammable gases**
- **Oxidizing Liquids**
- Oxidizing Solids
- Organic Peroxides
- **Corrosive to Metals**
- Desensitized explosives



**Oxidizers**



**Flammables, Self Reactives,  
Pyrophorics, Self-Heating, Emits  
Flammable Gas, Organic  
Peroxides**



**Explosives, Self Reactives,  
Organic Peroxides**



**Acutely Toxic  
(severe)**



**Burns Skin, Damages  
Eyes, Corrosive to Metals**



**Gases Under Pressure**



**Carcinogen, Respiratory  
Sensitizer, Reproductive  
Toxicity, Target Organ  
Toxicity, Mutagenicity  
Aspiration Toxicity**



**Toxic to aquatic  
environment**



**Acutely toxic(harmful),  
Irritant to skin, eyes or  
respiratory tract, Skin  
sensitizer, Hazardous to  
the Ozone layer.**

## *Data requirements for registration*

Flammability

Oxidising properties

Self-heating

*Explosive properties*

## *Example – Flammable liquids*

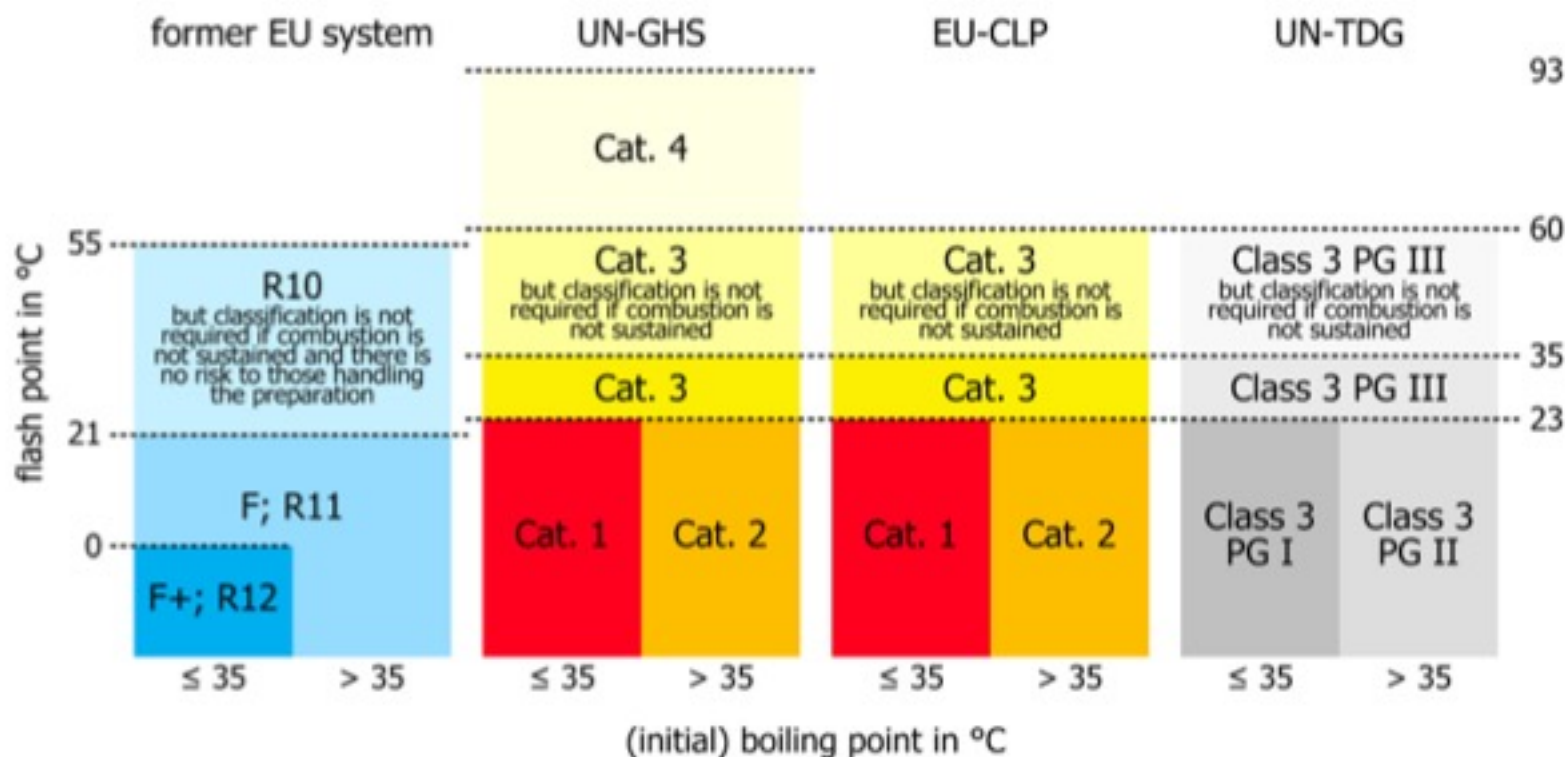
- A liquid with a flash point between 23 and 60 °C will be classified as **flammable liquid category 3**.
- A liquid with a flash point above 93 °C is not regarded as a hazardous chemical.

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
<del>4</del>	<del>Flash point &gt; 60 °C and ≤ 93 °C</del>

Source: UN GHS Purple Book



## Example – Flammable liquids



Source: C. Wilrich et al., Classification of chemicals according to UN GHS and EU CLP ..., OSJ, 2018

## *Example – Flammable liquids*

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

## *Example – Oxidising properties*

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

*- Same is valid for solids -*

## Example – Oxidizing solids

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

## *Example – Oxidizing solids*

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

## *Example – Self-heating substances and mixtures*

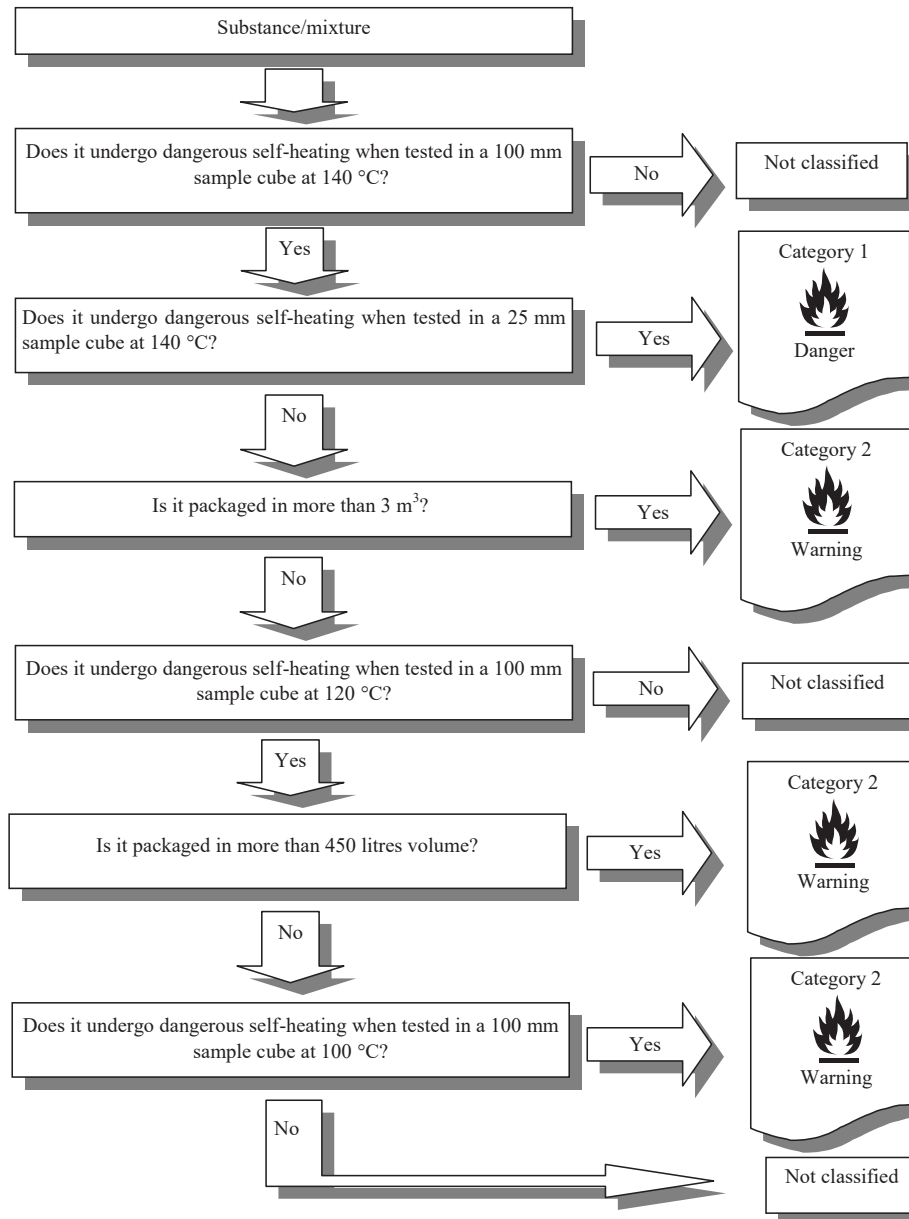
A self-heating substance or mixture is a solid or liquid substance or mixture, which by reaction with air and without energy supply, is liable to self-heat.

Effect: gradual **reaction with oxygen** (air) generates heat; **rate of heat production exceeds rate of heat loss**;  
may lead to self-ignition.

*Difference to pyrophoric: only ignite in large amounts and after long periods of time.*

## *Example – 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	<p>(a) A positive result is obtained in a test using a 100 mm sample cube at 140 °C and a negative result is obtained in a test using a 25 mm cube sample at 140 °C <u>and</u> the substance or mixture is to be packed in packages with a volume of more than 3 m<sup>3</sup>; or</p> <p>(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</p> <p>(c) A positive result is obtained in a test using a 100 mm sample cube at 140 °C and a negative result is obtained in a test using a 25 mm cube sample at 140 °C and a positive result is obtained in a test using a 100 mm cube sample at 100 °C.</p>



## *Example – Self-heating substances and mixtures*

former EU system

no classification based on this hazard

UN-GHS / EU-CLP

Cat. 2

Cat. 1

UN-TDG

Division 4.2 PG III

Division 4.2 PG II

propensity to self-heat  
(dependent on volume and temperature)

Source: C. Willrich et al, Classification of chemicals according to UN GHS and EU CLP ..., OSJ, 2018

## *Screening procedures (Guidance)*

### *Manual on Tests and criteria, Appendix 6*

Oxidising properties	Structure does not contain <b>O, F or Cl</b> or these are bound only to carbon or hydrogen
Flammability	
Self-heating	
Explosive properties	Decomposition energy < 500 J/g Onset temperature > 500 °C

# Data requirements for active substance

## 2.9. Flammability and self-heating - Flammability

Methods A.10 Flammability (solids), A.11 Flammability (gases), A.12 Flammability (contact with water), as appropriate

Test N.1: test method for readily combustible solids (UN RTDG Manual of Tests and Criteria ST/SG/AC.10/11/Rev. 5 – Part III, section 33.2.1.4)

Methods A.15 Auto-ignition temperature (liquids and gases), A.16 Relative self-ignition temperature for solids,, as appropriate.

Test N.4: test method for self-heating substances (UN RTDG Manual of Tests and Criteria ST/SG/AC.10/11/Rev. 5 – Part III, section 33.3.1.6)

## 2.10. Flash point

Method A.9 Flash-point

Test methods according to table 2.6.3 of Annex I, Part 2 of Regulation (EC) No 1272/2008 (liquids)

## 2.11. Explosive properties

Method A.14 Explosive properties

United Nations Recommendations on the Transport of Dangerous Goods (UN RTDG) Manual of Tests and Criteria ST/SG/AC.10/11/ Rev. 5 – Part I (Test series), section 11.

## 2.13. Oxidising properties

Solids: Method A.17 Oxidising properties (solids)

Liquids: Method A.21 Oxidising properties (liquids)

Test O.1: Test for oxidizing solids (UN RTDG Manual of Tests and Criteria ST/SG/AC.10/11/Rev. 5 – Part III, section 34.4.1)

Test O.2: Test for oxidizing liquids (UN RTDG Manual of Tests and Criteria ST/SG/AC.10/11/Rev. 5 – Part III, section 34.4.2)

# Data requirements for formulations

<b>2.2. Explosive and oxidising properties - Explosive properties</b>	<b>Method A.14 Explosive properties</b>
	<b>United Nations Recommendations on the Transport of Dangerous Goods (UN RTDG) Manual of Tests and Criteria ST/SG/AC.10/11/Rev. 5 – Part I (Test series), section 11.</b>
<b>2.2. Explosive and oxidising properties - Oxidising properties</b>	<b>Method A.17 Oxidising properties (solids)</b>
	<b>Method A.21 Oxidising properties (liquids)</b>
	<b>Test O.1: Test for oxidizing solids (UN RTDG)</b>
	<b>Test O.2: Test for oxidizing liquids (UN RTDG)</b>
<b>2.3. Flammability and self-heating</b>	<b>Method A.9 Flash-point (liquids)</b>
	<b>Methods A.10 Flammability (solids), A.11 Flammability (gases), A.12 Flammability (contact with water)</b>
	<b>Test N.1: Test method for readily combustible solids (UN RTDG)</b>
	<b>Methods A.15 Auto-ignition temperature (liquids and gases) and A.16 Relative self-ignition temperature for solids</b>
	<b>Test N.4: test method for self-heating substances (UN RTDG)</b>

# Conversion

	Data requirement	CLP regulation 1272/2008	
<b>explosibility</b>	A.14 UN Part 1 sec. 11 theoretical assessment	UN-Test series	A direct 'translation' from a classification according to DSD or DPD to CLP is not possible. <i>test series 3 similar to A14</i>
<b>oxidising properties</b>	A.17 A.21 UN O.2	UN O.1 UN O.2	questionable UN O.2 = A.21
<b>flammability/ flash point</b>	A.9 A.10 UN N.1 theoretical assessment	N.1	Liquids: closed cup - comparable  <i>Solids: comparable</i>
<b>self-heating</b>	A.15 A.16 UN Test N.4 Part III section 33.3.1.6	UN Test N.4 Part III section 33.3.1.6	A.16 has no influence on C&L

# Thank You / Gracias!

## Questions?

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