CLP - Classification

Methodologies

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Workshop: *"Practical implications of the application of CLP concentration limits on the hazardous properties of waste"*
Vienna, October 25, 2011

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UN – GHS: basis for CLP

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- Agreed principles for harmonization
  a) the level of protection offered to workers, consumers, the general public and the environment should not be reduced as a result of harmonizing the classification and labelling systems;
  b) the hazard classification process refers principally to the hazards arising from the intrinsic properties of substances and mixtures, whether natural or synthetic
  c) harmonization means establishing a common and coherent basis for chemical hazard classification and communication, from which the appropriate elements relevant to means of transport, consumer, worker and environment protection can be selected;
  d) …

CLP: classification principles

"While a manufacturer, importer or downstream user of any substance or mixture should not be obliged to generate new toxicological or eco-toxicological data for the purpose of classification, he should identify all relevant information available to him on the hazards of the substance or mixture and evaluate its quality." (CLP – Rec. (20))

- Classification for substances and mixtures based on all available information (adequate, reliable and scientifically valid) based on
  - expert judgement and
  - weight of evidence

  covering all hazards

CLP: Exemption of waste

Waste as defined in Directive 2006/12/EC of the European Parliament and of the Council of 5 April 2006 on waste (2) is not a substance, mixture or article within the meaning of Article 2 of this Regulation. (CLP Art. 1(3))

- What is waste? Are CLP methods/criteria applicable to waste?

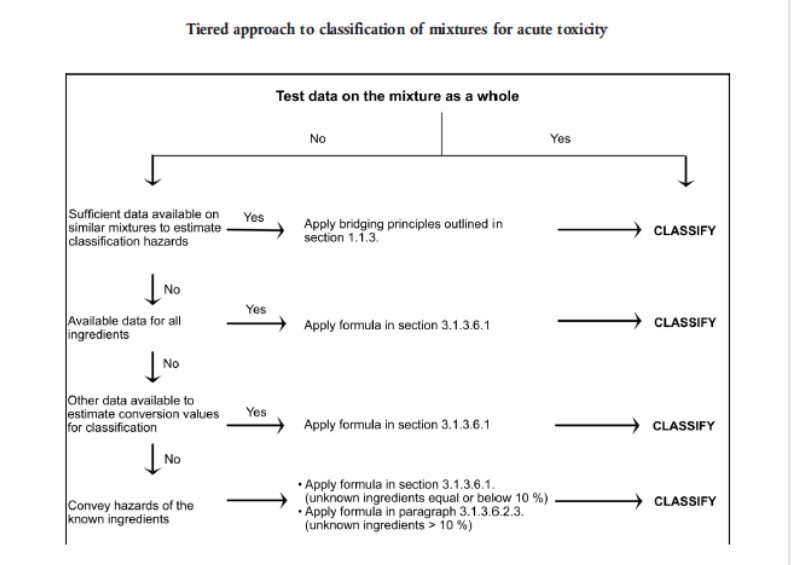
CLP: classification of substances

- Harmonised classification (Annex VI, Table 3.1)
- Self classification
  - Identification and examination of available information - physical, health or environmental hazards (CLP Art. 5)
    - » generated data
    - » epidemiological data and experience on the effects on humans, such as occupational data and data from accident databases;
    - » (Q)SARs, Read across, …
    - » any new scientific information
    - » any other information generated under internationally recognised chemical programmes
  - If no information available → generate data (animal tests only as *"last ressort"*)

CLP: classification of mixtures

- Self classification based on (CLP Art. 6)
  1) available information on the mixture (same as for substances)
  2) application of bridging principles (similar tested mixtures; CLP Annex I, 1.1.3)
  3) calculation based on the information of ingredients (taking cut off limits, concentration limits and additivity in account)
- If no information available (i.e. for physical hazards) – generate data

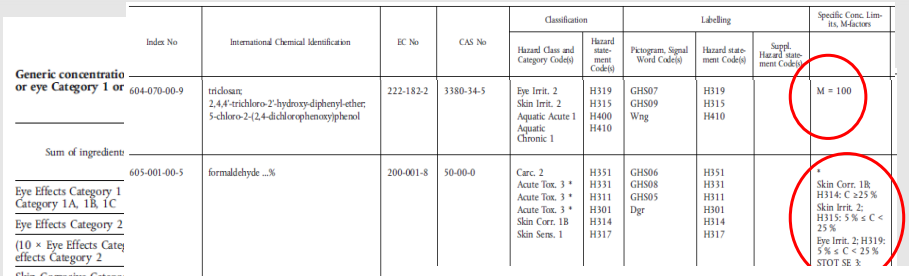
CLP: classification of mixtures



CLP: classification of mixtures

- Calculation method – main definitions:
  - Concentration limit (specific - generic):
    "Specific concentration limits and generic concentration limits are limits assigned to a substance indicating a threshold at or above which the presence of that substance in another substance or in a mixture as an identified impurity, additive or individual constituent leads to the classification of the substance or mixture as hazardous."
  - M-factor:
    "M-factors for substances classified as hazardous to the aquatic environment, acute category 1 or chronic category 1, shall be established …"
  - Cut off limit:
    "Where a mixture contains a substance classified as hazardous, whether as a component or in the form of an identified impurity or additive, this information shall be taken into account for the purposes of classification, if the concentration of that substance is equal to or greater than its cut-off value"

CLP: classification of mixtures



	Index No	International Chemical Identification	EC No	CAS No	Classification: Hazard Class and Category Code(s)	Classification: Hazard statement Code(s)	Labelling: Pictogram, Signal Word Code(s)	Labelling: Hazard statement Code(s)	Labelling: Suppl. Hazard statement Code(s)	Specific Conc. Limits, M-factors
Generic concentratio or eye Category 1 or	604-070-00-9	triclosan; 2,4,4'-trichloro-2'-hydroxy-diphenyl-ether; 5-chloro-2-(2,4-dichlorophenoxy)phenol	222-182-2	3380-34-5	Eye Irrit. 2 Skin Irrit. 2 Aquatic Acute 1 Aquatic Chronic 1	H319 H315 H400 H410	GHS07 GHS09 Wng	H319 H315 H410		M = 100
Sum of ingredient										
	605-001-00-5	formaldehyde ...%	200-001-8	50-00-0	Carc. 2 Acute Tox. 3 * Acute Tox. 3 * Acute Tox. 3 * Skin Corr. 1B Skin Sens. 1	H351 H331 H311 H301 H314 H317	GHS06 GHS08 GHS05 Dgr	H351 H331 H311 H301 H314 H317		* Skin Corr. 1B; H314: C ≥25 % Skin Irrit. 2; H315: 5 % ≤ C < 25 % Eye Irrit. 2; H319: 5 % ≤ C < 25 % STOT SE 3;
Eye Effects Category 1 Category 1A, 1B, 1C										
Eye Effects Category 2										
(10 × Eye Effects Cate effects Category 2										
Skin Corrosive Catego Eye effects Category 1										
10 × (Skin Corrosive (1C + Eye Effects Category 1) + Eye Effects Category 2										

Table 3.3.4

Generic concentration limits of ingredients of a mixture for which the additi apply, that trigger classification of the mixture as hazardous t

Ingredient	Concentration	M
Acid with pH ≤ 2	≥ 1 %	
Base with pH ≥ 11,5	≥ 1 %	
Other corrosive (Category 1) ingredients for which additivity does not apply	≥ 1 %	

Table 1.1

Generic cut-off values

Hazard class	Generic cut-off values to be taken into account
Acute Toxicity:	
— Category 1-3	0,1 %
— Category 4	1 %
Skin corrosion/irritation	1 % (1)
Serious damage to eyes/eye irritation	1 % (2)
Hazardous to Aquatic Environment	
— Acute Category 1	0,1 % (3)
— Chronic Category 1	0,1 % (3)
— Chronic Category 2-4	1 %

(1) Or < 1 % where relevant, see 3.2.3.3.1.
(2) Or < 1 % where relevant, see 3.3.3.3.1.
(3) Or < 0,1 % where relevant, see 4.1.3.1.

CLP: Generating new information

- New information for
  - physical hazards: shall be generated
  - health and environment hazards: may be generated
- Test for generating new information
  - Test method regulation (EC) No 440/2008 (referred to in Article 13(3) of REACH)
  - sound scientific principles that are internationally recognised or methods validated according to international procedures (e.g. for physical hazards - UN manual of tests and criteria)

CLP: Examples - physical hazards

- New information generated for substances and mixtures, e.g.
  - flash-point, viscosity and initial boiling point for flammable liquids

Table 2.6.3

Methods for determining the flash point of flammable liquids

European standards:	EN ISO 1516 as amended Determination of flash/no flash — Closed cup equilibrium method
	EN ISO 1523 as amended Determination of flash point — Closed cup equilibrium method
	(identical to NF M07-036)

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.

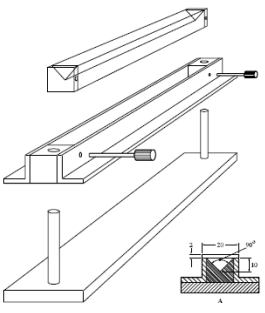
CLP: Examples - physical hazards

- New information generated for substances and mixtures, e.g.
  - flammable solids
    (readily combustible,
    or may cause or contribute
    to fire through friction)
    → method N.1 in 33.2.1
    of UN manual of tests and
    criteria (“burning rate test”)

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



A) Cross-section of 250 mm long mould

Figure 33.2.1.4.1: MOULD AND ACCESSORIES FOR THE PREPARATION OF THE PILE FOR THE BURNING RATE TEST

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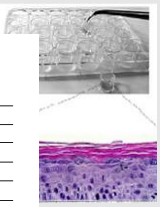
CLP: Examples - health hazards

- New information generated for substances (and mixtures), e.g.
  - corrosive to skin

OECD 404/B.4 – acute dermal (corrosive/irritating)

OECD 430/B.40 – ex-vivo: Transcutenous Electrical Resistance test (corrosive)



OECD 431/B.40 bis – in vitro: human skin model; e.g. EPISKIN corrosive

Table 3.2.1

Skin Corrosive category and subcategories

		Corrosive in > 1 of 3 animals	
	Corrosive subcategories	Exposure	Observation
Category 1: Corrosive	1A	≤ 3 minutes	≤ 1 hour
	1B	> 3 minutes - ≤ 1 hour	≤ 14 days
	1C	> 1 hour - ≤ 4 hours	≤ 14 days

CLP: Examples - health hazards

- Calculation for mixtures, e.g.
  - Acute toxicity (additivity):

$$\frac{100}{ATE_{mix}} = \sum_{n} \frac{C_i}{ATE_i}$$

or with unknown constituents:

$$\frac{100 - (\Sigma C_{unknown})}{ATE_{mix}} = \sum_{n} \frac{C_i}{ATE_i}$$

Table 3.1.2

Conversion from experimentally obtained acute toxicity range values (or acute toxicity hazard categories) to acute toxicity point estimates for classification for the respective routes of exposure

Exposure routes	Classification Category or experimentally obtained acute toxicity range estimate	Converted acute toxicity point estimate (see Note 1)
Oral (mg/kg bodyweight)	0 < Category 1 ≤ 5	0,5
	5 < Category 2 ≤ 50	5
	50 < Category 3 ≤ 300	100
	300 < Category 4 ≤ 2 000	500
Dermal (mg/kg bodyweight)	0 < Category 1 ≤ 50	5
	50 < Category 2 ≤ 200	50
	200 < Category 3 ≤ 1 000	300
	1 000 < Category 4 ≤ 2 000	1 100
Gases (ppmV)	0 < Category 1 ≤ 100	10
	100 < Category 2 ≤ 500	100
	500 < Category 3 ≤ 2 500	700
	2 500 < Category 4 ≤ 20 000	4 500
Vapours (mg/l)	0 < Category 1 ≤ 0,5	0,05
	0,5 < Category 2 ≤ 2,0	0,5
	2,0 < Category 3 ≤ 10,0	3
	10,0 < Category 4 ≤ 20,0	11
Dust/mist (mg/l)	0< Category 1 ≤ 0,05	0,005
	0,05 < Category 2 ≤ 0,5	0,05
	0,5 < Category 3 ≤ 1,0	0,5
	1,0 < Category 4 ≤ 5,0	1,5

Note 1

These values are designed to be used in the calculation of the ATE for classification of a mixture based on its components and do not represent test results.

CLP: Examples - health hazards

- Calculation for mixtures, e.g. eye corrosion /irritation
  - Different calculation depending whether additivity approach applies or whether it doesn't.

Table 3.3.3

Generic concentration limits of ingredients of a mixture classified as Skin corrosive Category 1 and/or eye Category 1 or 2 for effects on the eye that trigger classification of the mixture for effects on the eye (Category 1 or 2)

Sum of ingredients classified as:	Concentration triggering classification of a mixture as:	
	Irreversible Eye Effects	Reversible Eye Effects
	Category 1	Category 2
Eye Effects Category 1 or Skin Corrosive Category 1A, 1B, 1C	≥ 3 %	≥ 1 % but < 3 %
Eye Effects Category 2		≥ 10 %
(10 × Eye Effects Category 1) + Eye effects Category 2		≥ 10 %
Skin Corrosive Category 1A, 1B, 1C + Eye effects Category 1	≥ 3 %	≥ 1 % but < 3 %
10 × (Skin Corrosive Category 1A, 1B, 1C + Eye Effects Category 1) + Eye Effects Category 2		≥ 10 %

Table 3.3.4

Generic concentration limits of ingredients of a mixture for which the additivity approach does not apply, that trigger classification of the mixture as hazardous to the eye

Ingredient	Concentration	Mixture classified as: Eye
Acid with pH ≤ 2	≥ 1 %	Category 1
Base with pH ≥ 11,5	≥ 1 %	Category 1
Other corrosive (Category 1) ingredients for which additivity does not apply	≥ 1 %	Category 1

CLP: Examples - health hazards

- Calculation for mixtures, e.g. eye corrosion/irritation

DPD: Classification and Labelling	%	CLP: Classification and Labelling
≥ 10 %, Xi – *Irritating, R 41*	**10 –100**	**≥ 3 % Eye Cat. 1**
≥ 5 to < 10 %, *Xi – Irritating, R 36*	**5 – 10**	
0 to < 5 %: no classification and labelling	**3 – 5**	
	1 – 3	**≥ 3 bis < 1 % Eye Cat. 2**
	0 – 1	**0 to < 1 %: %: no classification and labelling**

CLP: Examples - health hazards

- Classification of mixtures, e.g. skin/respiratory sensitizers

Table 3.4.3

Generic concentration limits of ingredients of a mixture respiratory sensitisers that trigger classifi

Ingredient classified as:	Concentration trig	
	Skin Sensitiser	
	All physical states	
Skin Sensitiser	≥ 0,1 % (Note 1)	
	≥ 1,0 % (Note 2)	
Respiratory Sensitiser	—	
	—	

(c) Table 3.4.3 and Notes 1, 2 and 3 are replaced by the following:

Table 3.4.5

Generic concentration limits of components of a mixture classified as either respiratory sensitisers or skin sensitisers that trigger classification of the mixture

Component classified as:	Generic concentration limits triggering classification of a mixture as:		
	Respiratory sensitiser Category 1		Skin sensitiser Category 1
	Solid/liquid	Gas	All physical states
Respiratory sensitiser Category 1	≥ 1,0 %	≥ 0,2 %	
Respiratory sensitiser Sub-category 1A	≥ 0,1 %	≥ 0,1 %	
Respiratory sensitiser Sub-category 1B	≥ 1,0 %	≥ 0,2 %	
Skin sensitiser Category 1			≥ 1,0 %
Skin sensitiser Sub-category 1A			≥ 0,1 %
Skin sensitiser Sub-category 1B			≥ 1,0 %'

- 2nd ATP to CLP: new provisions

CLP: Examples - env. hazards

- Classification of substances - main elements:
  - acute aquatic toxicity
  - chronic aquatic toxicity,
  - potential for or actual bioaccumulation, and
  - degradation (biotic or abiotic) for organic chemicals.

Table 4.1.0

Classification categories for hazardous to the aquatic environment

(a) Acute (short-term) aquatic hazard

Category Acute 1: (Note 1)

96 hr LC_{50} (for fish) ≤ 1 mg/l and/or

48 hr EC_{50} (for crustacea) ≤ 1 mg/l and/or

(ii) Rapidly degradable substances (Note 3) for which there are adequate chronic toxicity data available

Category Chronic 1: (Note 1)

Chronic NOEC or EC_x (for fish) ≤ 0,01 mg/l and/or

Chronic NOEC or EC_x (for crustacea) ≤ 0,01 mg/l and/or

Chronic NOEC or EC_x (for algae or other aquatic plants) ≤ 0,01 mg/l.

(iii) Substances for which adequate chronic toxicity data are not available

Category Chronic 1: (Note 1)

96 hr LC_{50} (for fish) ≤ 1 mg/l and/or

48 hr EC_{50} (for crustacea) ≤ 1 mg/l and/or

72 or 96 hr ErC_{50} (for algae or other aquatic plants) ≤ 1 mg/l. (Note 2)

and the substance is not rapidly degradable and/or the experimentally determined BCF ≥ 500 (or, if absent, the log K_{ow} ≥ 4). (Note 3).

Category Chronic 2:

96 hr LC_{50} (for fish) > 1 to ≤10 mg/l and/or

48 hr EC_{50} (for crustacea) > 1 to ≤10 mg/l and/or

72 or 96 hr ErC_{50} (for algae or other aquatic plants) > 1 to ≤10 mg/l (Note 2)

and the substance is not rapidly degradable and/or the experimentally determined BCF ≥ 500 (or, if absent, the log K_{ow} ≥ 4). (Note 3).

Category Chronic 3:

96 hr LC_{50} (for fish) > 10 to ≤ 100 mg/l and/or

48 hr EC_{50} (for crustacea) > 10 to ≤ 100 mg/l and/or

72 or 96 hr ErC_{50} (for algae or other aquatic plants) > 10 to ≤ 100 mg/l. (Note 2)

and the substance is not rapidly degradable and/or the experimentally determined BCF ≥ 500 (or, if absent, the log K_{ow} ≥ 4). (Note 3).

CLP: Examples – env. hazards

- Classification of mixtures

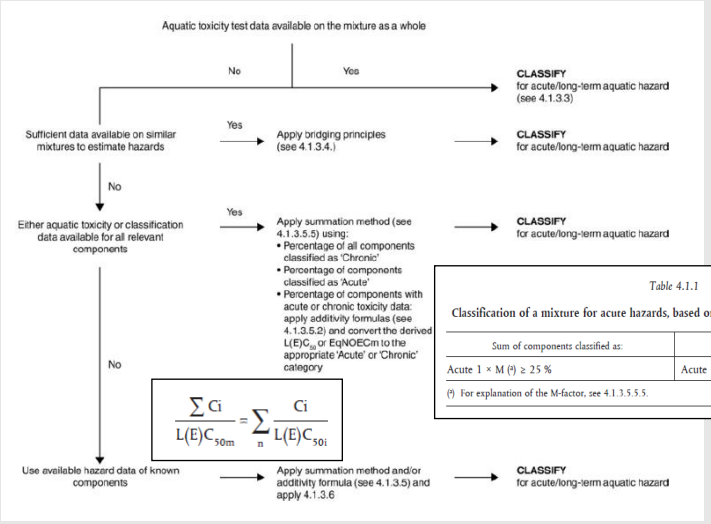


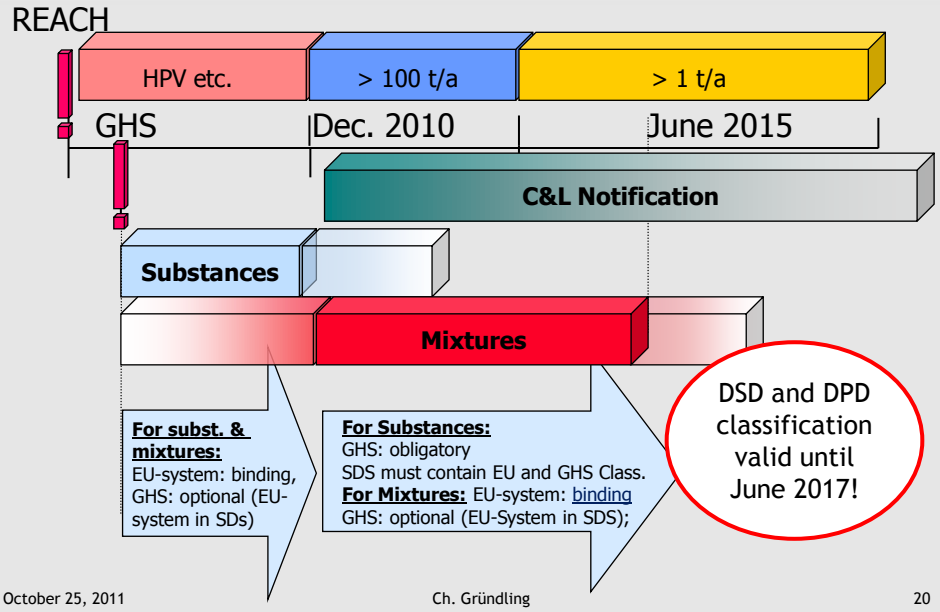
Table 4.1.1

Classification of a mixture for acute hazards, based on summation of classified components

Sum of components classified as:	Mixture is classified as:
Acute 1 × M (*) ≥ 25 %	Acute 1

(*) For explanation of the M-factor, see 4.1.3.5.5.5.

CLP-Reg: Transitional provisions



Thank you …

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