

Understanding Cut-off Value and Concentration Limits in CLP Regulation and China GHS



*Enabling Chemical Compliance
for A Safer World*

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About the Presenter



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About Us (CIRS-瑞旭技术)

- Chemical regulatory consulting + hazardous substances testing
- **100** employees, **15** chemists and toxicologists, **2** large operations (China & Ireland)
- REACH, CLP, China REACH, China GHS for industrial chemicals
- Consulting services for food additives, cosmetics, and pesticides
- Hazardous substances testing for articles

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A Few Polls

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- Classification of Substances and Mixtures
- Intro to Cut-off Value and Concentration Limits
- CLP Regulation vs China GHS
- Transform REACH SDS into Chinese GHS SDS

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- **Classification of Substances and Mixtures**
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Classification: Identification of hazard classes for substance and mixture

<p>Physical Hazards 16 Classes</p> 	<p>Explosive, Flammable gases, Flammable aerosols, Oxidising gases, Gas under pressure, Flammable liquids, Flammable solids, Pyrophoric liquids, Pyrophoric solids, Self-heating substances and mixtures, substances and mixtures which are in contact with water emit flammable gases, Oxidising liquids, Oxidising solids, Organic peroxides, Corrosive to metals, Self-reactive substances and mixtures.</p>
<p>Health Hazards 10 Classes</p> 	<p>Acute toxicity, Skin corrosion/irritation, Serious eye damage/irritation, Respiratory or skin sensitization, Germ cell mutagenicity, Carcinogenicity, Reproductive toxicity, Specific target organ toxicity- single exposure, Specific target organ toxicity-repeated exposure, <i>Aspiration Hazard</i>(*)</p>
<p>Environmental Hazards 2 Classes</p> 	<p>Hazardous to the aquatic environment <i>Hazardous to ozone layer</i>(*)</p>

* Does not exist in China GHS

Classification determines hazard communication elements (SDS + label)

■ Example, Respiratory or skin sensitisation

Classification	Respiratory sensitisation	Skin sensitisation
	Category 1 and sub-categories 1A and 1B	Category 1 and sub-categories 1A and 1B
GHS pictograms		
Signal word	Danger	Warning
Hazard statement	H334: May cause allergy or asthma symptoms or breathing difficulties if inhaled	H317: May cause an allergic skin reaction
Precautionary statement prevention	P261 P285	P261 P272 P280
Precautionary statement response	P304 + P341 P342 + P311	P302 + P352 P333 + P313 P321 P363
Precautionary statement storage		
Precautionary statement disposal	P501	P501'

↓

❖ **Harmonized Hazard Description, Pictogram and Precautionary Statements**

❖ **Elements in Safety Data Sheet and Chemical Safety Label**

Classification Criteria for Substances

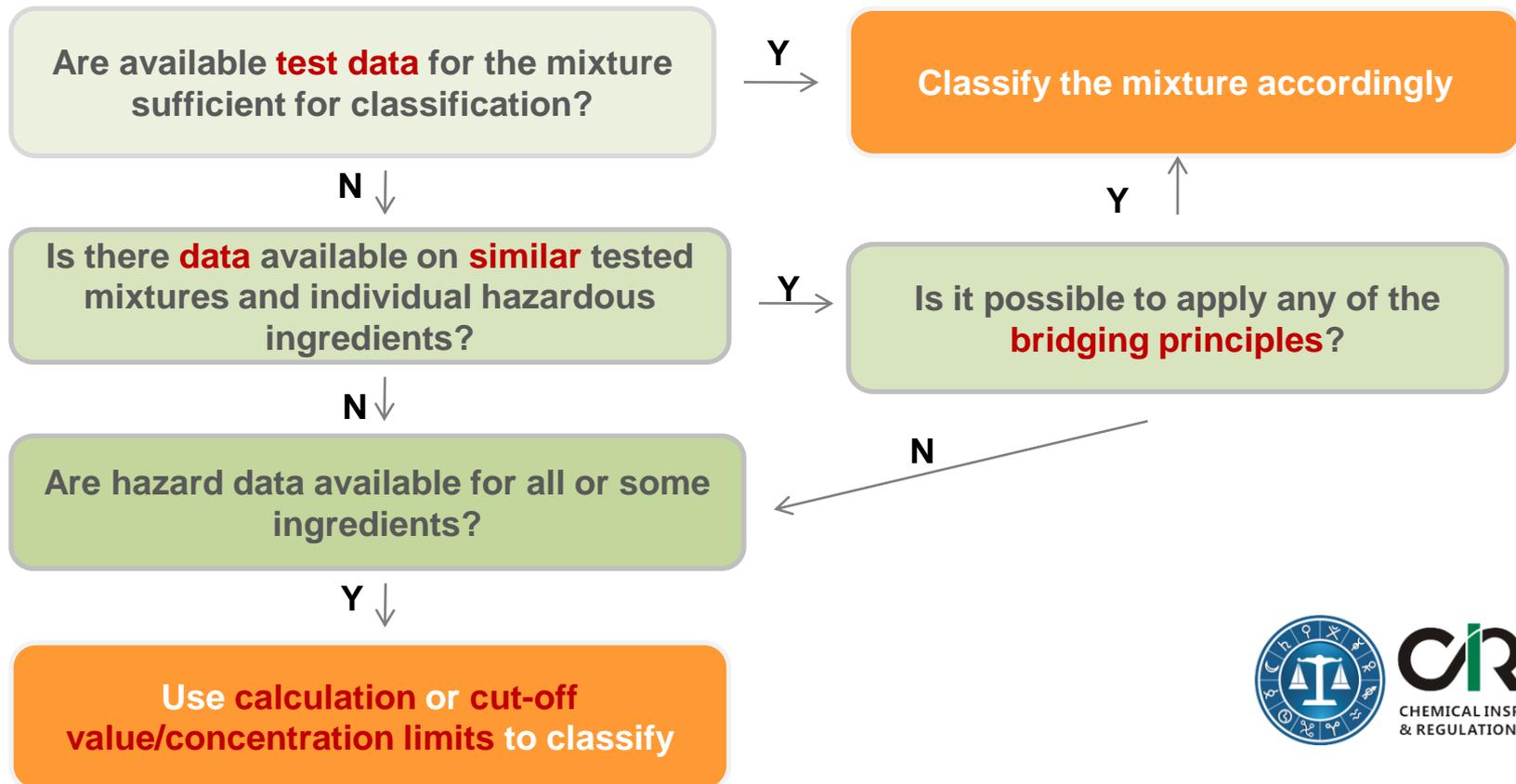
- Based on available data such as test data & QSAR(*)
- Classification Criteria for Acute Toxicity Category 3,4

3	Oral LD ₅₀ > 50 but ≤ 300 mg/kg bodyweight; or Dermal LD ₅₀ > 200 but ≤ 1000 mg/kg bodyweight; or Inhalation (gas) LC ₅₀ > 500 but ≤ 2500 ppm; or Inhalation (vapour) LC ₅₀ > 2.0 but ≤ 10.0 mg/l; or Inhalation (dust, mist) LC ₅₀ > 0.5 but ≤ 1.0 mg/l	Symbol	
		Signal word	Danger
		Hazard statement	Toxic if swallowed (oral) Toxic in contact with skin (dermal) Toxic if inhaled (gas, vapour, dust, mist)
4	Oral LD ₅₀ > 300 but ≤ 2000 mg/kg bodyweight; or Dermal LD ₅₀ > 1000 but ≤ 2000 mg/kg bodyweight; or Inhalation (gas) LC ₅₀ > 2500 but ≤ 20000 ppm; or Inhalation (vapour) LC ₅₀ > 10.0 but ≤ 20.0 mg/l; or Inhalation (dust, mist) LC ₅₀ > 1.0 but ≤ 5.0 mg/l	Symbol	
		Signal word	Warning
		Hazard statement	Harmful if swallowed (oral) Harmful in contact with skin (dermal) Harmful if inhaled (gas, vapour, dust, mist)

* Classification criteria for substances containing additives and impurities are similar to criteria for mixtures.

Classification of Mixtures

- Classifi. of majority of physical hazards based on testing
- Health and environ. hazards: test data not easily available



Classification of Mixtures: Bridging Principles

■ Dilution

- Tested mixture A is diluted with less or equally hazardous ingredient B. $A+B=A$;

■ Batching

- Mixture A & B are two batches produced under same conditions. $A=B$;

■ Concentration of highly hazardous mixtures

- Mixture A is classified at its highest hazard category, for example, acute toxicity category 1. B is more concentrated mixture of A. $B=A$;

■ Interpolation within one toxicity category

- Mixture A and B share the same classifi. and active hazardous ingredient. If the concent. of the hazardous ingredient in mixture C is in-between, $C=A=B$;

■ Substantially similar mixtures

- Mixtures $A+B$, $C+B$, $A=C$ in concent. & classification. $A+B=B+C$.



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Classification of Mixtures: Calculation Method

■ Acute Toxicity

$$\frac{100}{ATE_{\text{mix}}} = \sum_n \frac{C_i}{ATE_i}$$

where:

C_i = concentration of ingredient i (% w/w or % v/v)

i = the individual ingredient from 1 to n

n = the number of ingredients

ATE_i = Acute Toxicity Estimate of ingredient i .

Total concentration of the ingredient(s) with unknown toxicity is **$\leq 10\%$** ;

$$\frac{100 - \sum C_{\text{unknown}} \text{ if } > 10\%}{ATE_{\text{mix}}} = \sum_n \frac{C_i}{ATE_i}$$

Total concentration of the ingredient(s) with unknown toxicity is **$> 10\%$** ;

Classification of Mixtures: Use of Cut-off Value and Concentration Limits

- Used when test data on mixture is not available or abridging principle cannot be applied;
- Also used to classify substances containing hazardous additives or impurities;
- Available only for health hazards and environmental hazards;

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Definition of Cut-off Value

- Cut-off values are the minimum concentrations for a substance (either as additive, impurity or an individual constituent of mixture) **to be taken into account** for classification purposes.
- A classified substance present in a concentration above the cut-off value **might not trigger classification** of the substance or mixture.

Generic Cut-off Value - Table 1.1 of Annex I to CLP

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 %

❖ Note 1,2: There is a presumption that an ingredient present at a concentration of less than 1% can still be relevant for classifying the mixture for skin irritation or eye irritation.

❖ Note 3: Generally, for substances classified as 'Acute Category 1' or 'Chronic Category 1' the concentration to be taken into account is $(0,1/M)$ %; M= M-factor.

Examples: How Cut-off Value Is Used?

Ingredient	w%	LD50(mg/kg)	Classification
Anionic surfactant	9.2	>5000	Not classified
Thickening agent	0.8	3600	Skin Irrit. 2
Water	90		Not classified

❖ Example 1: **Below cut-off value 1%.**

❖ The mixture is **not classified as Skin Irrit. 2.**

Ingredient	w%	LD50(mg/kg)	Classification
Anionic surfactant	8.2	>5000	Not classified
Thickening agent	1.8		Skin Irrit. 2
Water	90		Not classified

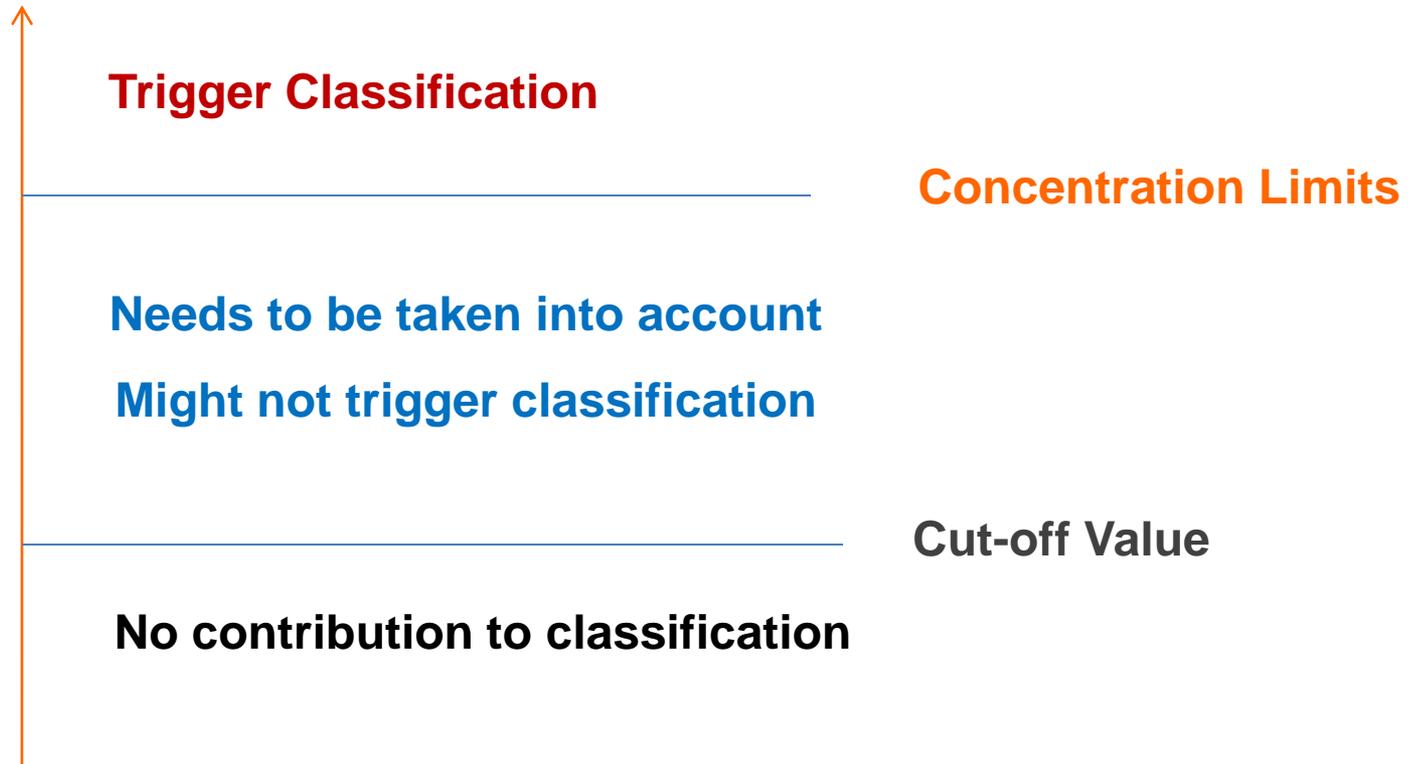
❖ Example 2: **Above cut-off value 1%.**

❖ The mixture **might be classified.**

Definition of Concentration Limits

- Concentration limits are the minimum concentrations for a substance which **trigger the classification** of a mixture if exceeded by the **individual concentration** or the **sum of concentrations** of relevant substances
- Additivity concepts (the sum of concentrations) are not applicable to all hazard classes.

Cut-off Value vs Concentration Limits



Generic Concentration Limits - Part 3-5 of CLP

■ Example: Respiratory/Skin Sensitiser from CLP

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 %

Example 1: How Concentration Limits Are Used for Classification?

Ingredient	w%	LD50(mg/kg)	Classification
Anionic surfactant	8.2	>5000	Not classified
Thickening agent	1.8	3600	Skin Sens. 1 Skin Irrit. 2
Water	90		Not classified

- ❖ Above concentration limit 1% for Skin Sens. 1.
- ❖ The mixture is classified as Skin Sens 1

Generic concentration limits of ingredients classified for skin corrosive/irritant hazard (Category 1 or 2) that trigger classification of the mixture as corrosive/irritant to skin

Sum of ingredients classified as:	Concentration triggering classification of a mixture as:	
	Skin Corrosive	Skin Irritant
	Category 1 (see note below)	Category 2
Skin Corrosive Categories 1A, 1B, 1C	≥ 5 %	≥ 1 % but < 5 %
Skin irritant Category 2		≥ 10 %
(10 × Skin Corrosive Category 1A, 1B, 1C) + Skin irritant Category 2		≥ 10 %

- ❖ Above cut-off value 1%;
- ❖ Below concentration limit 10% for Skin Irrit. 2;
- ❖ The mixture is not classified as Skin Irrit 2

Example 2: How Concentration Limits Are Used for Classification?

Ingredient	w%	LD50(mg/kg)	Classification
Anionic surfactant	9.2	>5000	Not classified
Thickening agent	1.8	3600	Skin Sens. 1 Skin Irrit. 2
Solvent A	9		Skin Irrit. 2
Water	80		Not classified

- ❖ The sum of concentration exceeds concentration limit for Skin Irrit. 2 – 10%;
- ❖ The mixture is classified as Skin Irrit 2;

! Additivity concepts are not applicable to every hazard class.

Additivity concepts are not applied to the following classes:

- skin and respiratory sensitisers;
- germ cell mutagenicity;
- carcinogenicity;
- reproductive toxicity;
- specific target organ toxicity, single and repeated exposure, categories 1 and 2;
- aspiration hazard (plus consideration of viscosity of the final mixture);
- skin corrosion/irritation in some special cases (for example strong acid and base, see CLP Annex I, 3.2.3.3.4); and
- serious eye damage/eye irritation in some special cases (see CLP Annex I, 3.3.3.3.4).

Additivity concepts are used for the following hazard classes:

- skin corrosion/irritation (besides the cases mentioned in CLP Annex I, 3.2.3.3.4);
- serious eye damage/eye irritation (besides the cases mentioned in CLP Annex I, 3.3.3.3.4);
- specific target organ toxicity, single exposure Category 3 (respiratory tract irritation);
- specific target organ toxicity, single exposure Category 3 (narcotic effects); and
- acute and chronic aquatic hazards.

Specific Concentration Limits

- Substance specific;
- Takes precedence over any other concentration limits;
- Could be **lower** or **higher** than generic concentration limits if proven by data;
- Only available for health hazards;

Example: Specific Concentration Limits in CLP

006-003-00-3	carbon disulphide	200-843-6	75-15-0	Flam. Liq. 2 Repr. 2 STOT RE 1 Eye Irrit. 2 Skin Irrit. 2	H225 H361fd H372 ** H319 H315	GHS02 GHS08 GHS07 Dgr	H225 H361fd H372 ** H319 H315	Repr. 2; H361fd. C ≥ 1 % STOT RE 1; H372: C ≥ 1 % STOT RE 2; H373: 0,2 % ≤ C < 1 %
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Example

- Carbon Disulphide, Reproductive Toxicant Category 2
- Generic Concentration Limit: $C \geq 3\%$;
- Specific Concentration Limit: $C \geq 1\%$;

Setting Specific Concentration Limits

Table 1.5.1 Possibilities for setting SCL for health hazards as addressed in sections of the guidance.

Hazard class	Category	Lower SCL than GCL	Higher SCLs than GCL in exceptional circumstances	Guidance
Acute toxicity	all	not applicable	not applicable	not necessary
Skin corrosion/irritation	all	yes	yes	based on data
Serious eye damage/eye irritation	all	yes	yes	based on data
Respiratory sensitisation	1	yes	no	based on data. See also Section 3.4
Skin sensitisation	1	yes	yes	available in Section 3.4
Germ cell mutagenicity	all	no	no	currently not possible
Carcinogenicity	all	yes	yes	available in Section 3.6
Reproductive toxicity	all	under discussion	under discussion	currently not available
STOT-SE	1	yes	no	available in Section 3.8
	2	no	no	see Section 3.8
	3	yes	yes	available in Section 3.8
STOT-RE	1	yes	no	available in Section 3.9
	2	no	no	see Section 3.9
Aspiration hazard	1	not applicable	not applicable	not necessary

- ❖ Not available for all health hazards
- ❖ Set by manufacturer, importer or downstream user



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CLP Regulation vs China GHS

Items	China GHS	EU CLP Regulation
UN Version	UN GHS 2003+2007	UN GHS 2009 3rd Rev
Hazard Classes	26 classes, no aspiration hazard	28 classes, aspiration hazard, hazardous to ozone layer.
Unique Building Blocks	Acute Toxicity, Cate. 5 Acute Aquatic Cate. 2 & 3 Flammable Liquids Cate. 4 Skin Corrosion/Irritant 3 Serious eye damage/eye irritation, Cate. 2B (Do not exist in CLP)	H304: May be fatal if swallowed and enters airways H335: STOT— Single Exposure Category 3, Respiratory tract irritation H336: STOT— Single exposure, Category 3, Narcosis EUxx: Hazardous to the ozone layer and other supplemental hazards (Do not exist in China GHS)
Pictogram	Frame: Both red and black	Frame: Red; Minimum size requirement;
Acute Toxicity for Gases Category 4	Inhalation(Gas) LC50>2500ppm, <5000ppm	H332: Inhalation(Gas) LC50>2500ppm, <20000ppm
Simplified label	Yes	No

China GHS vs CLP: Cut-off Value and Concentration Limits

- No generic cut-off value or cut-off value and concentration limits are combined;
- Concentration limits are usually consistent with generic concentration limits in CLP regulation;
- No substance specific concentration limits due to lack of data and harmonized inventory (annex VI of CLP);
- For one hazard class, multiple concentration limits might be available (example, reproductive toxicant);

China GHS vs CLP: Cut-off Value and Concentration Limits

- Example: Reproductive Toxicant (from GB 20598-2006)

Ingredients classified as:	Cut-off/concentration limits triggering clas	
	Category 1 reproductive toxicant	Category 2 reproductive toxicant
Category 1 reproductive toxicant	≥ 0.1% (note 1)	
	≥ 0.3% (note 2)	
Category 2 reproductive toxicant		≥ 0.1 % (note 3)
		> 3.0% (note 4)
Additional category for effects on or via lactation		

❖ UN GHS gives two concentration limits. China does the same.

China GHS vs CLP: Cut-off Value and Concentration Limits

■ Example: Reproductive Toxicant (from CLP)

Ingredient classified as:	Generic concentration limits triggering classification of a mixture as:			
	Category 1A reproductive toxicant	Category 1B reproductive toxicant	Category 2 reproductive toxicant	Additional category for effects on or via lactation
Category 1A reproductive toxicant	≥ 0,3 % [Note 1]			
Category 1B reproductive toxicant		≥ 0,3 % [Note 1]		
Category 2 reproductive toxicant			≥ 3,0 % [Note 1]	
Additional category for effects on or via lactation				≥ 0,3 % [Note 1]

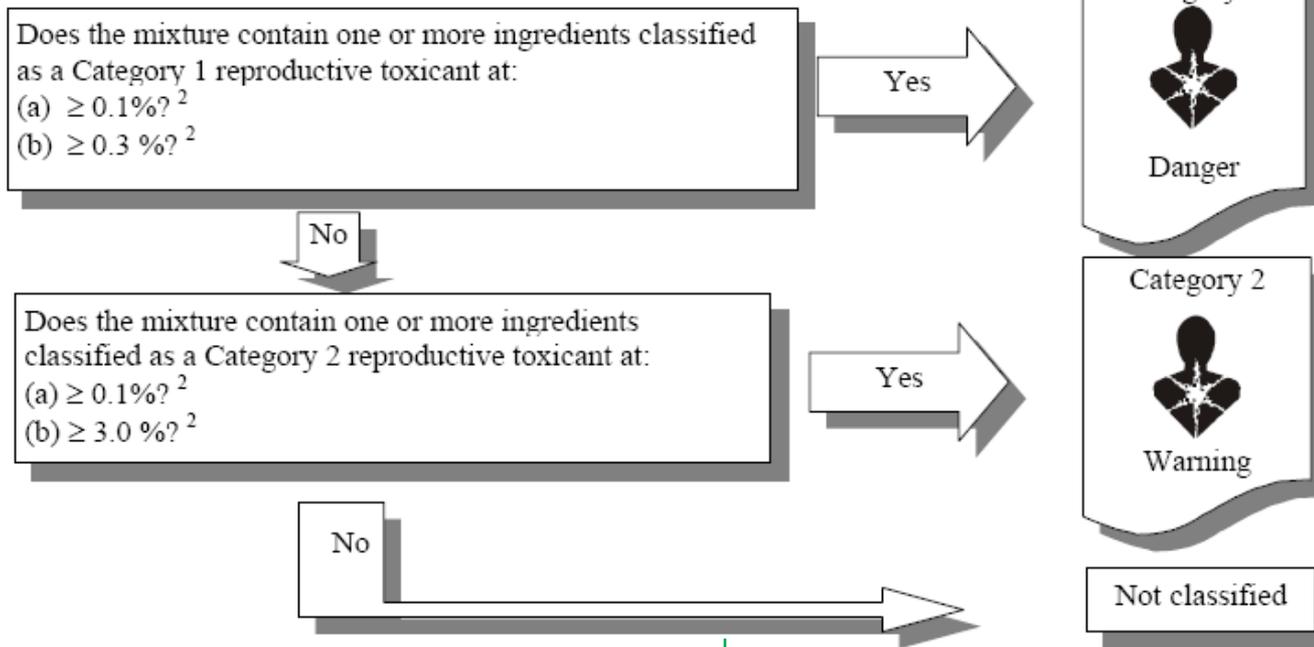
- ❖ CLP differentiates cut-off value and concentration limits;
- ❖ Concentration limit are 0.3% and 3% under CLP. More clearly defined.



China GHS vs CLP: Cut-off Value and Concentration Limits

■ Example: Reproductive Toxicant (from GB 20598-2006)

Classification based on individual ingredients of the mixture



- ❖ CIRS's suggestion: consistent with CLP – 0.3% and 3%;
- ❖ 0.1% is the minimum concentration for SDS (from note);



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China GHS vs CLP: Required Ingredient Info in SDS for Un-classified Mixture Under CLP

- a substance posing human health or environmental hazards with a concentration of $>1\%w/w$ for non-gaseous mixtures or $0.2\%v/v$ for gas;
- a substance that is PBT, or vPvB, or SVHC in an individual concentration of $\geq 0.1\%$ by weight for mixtures that are solid or liquids (i.e., non-gaseous mixtures);
- Similar to China's requirement

China GHS vs CLP: Required Ingredient Info in SDS for Classified Mixture Under CLP

1.1. — Hazard class and category	Concentration limit (%)
Acute toxicity, category 1, 2 and 3	≥ 0,1
Acute toxicity, category 4	≥ 1
Skin corrosion/irritation, category 1A, 1B, 1C and 2	≥ 1
Serious damage to eyes/eye irritation, category 1 and 2	≥ 1
Respiratory/skin sensitisation	≥ 0,1
Germ cell mutagenicity category 1A and 1B	≥ 0,1
Germ cell mutagenicity category 2	≥ 1
Carcinogenicity category 1A, 1B and 2	≥ 0,1
Reproductive toxicity, category 1A, 1B, 2 and effects on or via lactation	≥ 0,1
Specific target organ toxicity (STOI) — single exposure, category 1 and 2	≥ 1
Specific target organ toxicity (STOI) — repeated exposure, category 1 and 2	≥ 1
Aspiration hazard	≥ 10
Hazardous to the aquatic environment — Acute, category 1	≥ 0,1
Hazardous to the aquatic environment — Chronic, category 1	≥ 0,1
Hazardous to the aquatic environment — Chronic, category 2, 3 and 4	≥ 1
Hazardous for the ozone layer	≥ 0,1

❖ A combined list of generic cut-off value and concentration limit in CLP

❖ The difference between EU and China is marked in red

❖ If specific concentration limit or M-factor is available, the lowest of concentration limit in this table, specific concentration limit or specific cut-off value shall be used.

China GHS vs CLP: Required Ingredient Information in SDS under China GHS

Table 1 Threshold Values/Concentration Limits for Each Health and Environmental Hazard Class

Hazard Class	Threshold Value/Concentration Limit
Acute Toxicity	$\geq 1.0\%$
Skin Corrosion/Irritation	$\geq 1.0\%$
Serious Eye Damage/Eye Irritation	$\geq 1.0\%$
Respiratory/Skin Sensitization	$\geq 1.0\%$
Germ Cell Mutagenicity: Category 1	$\geq 0.1\%$
Germ Cell Mutagenicity: Category 2	$\geq 1.0\%$
Carcinogenicity	$\geq 0.1\%$
Reproductive Toxicity	$\geq 0.1\%$
Target Organ Systemic Toxicity (Single Exposure)	$\geq 1.0\%$
Target Organ Systemic Toxicity (Repeated Exposure)	$\geq 1.0\%$
Hazardous to the Aquatic Environment	$\geq 1.0\%$

❖ From GB 13690 – 2009: General Rule for Classification and Hazard Communication of Chemicals;

❖ If other cut-off value or concentration limit is used for classification, those ingredients shall be indicated for SDSs;

❖ The difference between EU and China is marked in red

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Transform REACH/CLP SDS into Compliant Chinese GHS SDS

- Remove REACH reg. number, DSD/DPD classification, CSA/exposure scenario;
- Provide 24h domestic emergency telephone number (could be Chinese trading partner's phone or professional service provider in China);
- Review classification (attention should be paid to specific concentration limits and H304, H332, H335 and H336);
- Translation of P/H statements using standard phrase from Chinese GB standards;
- Add relevant info in section 15;
- Supplemental hazards could be put in section 16.

Upcoming Events

- 7-8 Sep, CIR, Barcelona, Spain, pre-conference workshop speaker
- 27-28 Sep, The Chemical Management Summit 2011, Sweden (TBA)
- 3-4 Oct, exhibitor booth 9, SCHC Fall Meeting, Virginia, USA
- 3-4 Nov, Summit Meeting on Chemical Regulations in China, Korea and Japan, Shanghai, China – Hosted by CIRS & KTR

Invited Speaker

- China: MEP, AQSIQ, SAWS, CRC & NRCC;
- Korea: MOE, NIER, KCMA
- Japan: METI, JEMAI
- CIRS, KTR, 3ECOMPANY, CCCMPHIE & AICM (TBA)

More info at <http://www.cirs-reach.com>



Thank you for your time!

谢谢您的时间！

시간 내주셔서 감사합니다!

お時間をいただき！