GHS Physical Hazards

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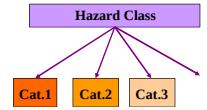
What is a physical hazard?

”Physical hazards” is a term collective term for hazards deriving from:

- Explosivity
- Flammability
- Oxidising abilities
- Decomposition
- Pressure
- (Corrosivity on metals)

The 16 physical hazard classes



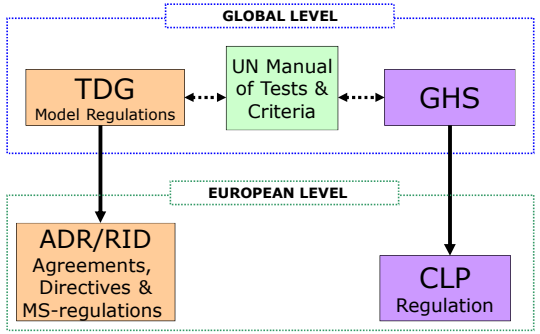
2.1 Explosives	2.9. Pyrophoric liquids
2.2 Flammable gases	2.10 Pyrophoric solids
2.3 Flammable aerosoles	2.11 Self-heating substances and mixtures
2.4 Oxidizing gases	2.12. Substances and mixtures which in contact with water emit flammable gases
2.5 Gases under pressure	
2.6 Flammable liquids	2.13 Oxidizing liquids
2.7 Flammable solids	2.14 Oxidizing solids
2.8 Self-reactive substances and mixtures	2.15 Organic peroxides
	2.16 Corrosive to metals

There are 1-8 Categories (Types/Divisions) for each Hazard Class

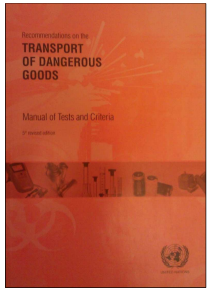
GHS:s physical hazards came from TDG rules

- Since the 1960's there have been internationally developed "rules" for transport of dangerous goods (TDG).
- These so-called "Model Regulations" focus on immediate (acute) hazards.
- The methods and criteria for the hazards of fire, explosion and the like were well-developed in the TDG world.
- So when GHS was written, the system of the TDG domain was taken over for the physical hazards.

How it all fits together:



The UN Test Manual is the core



- For physical hazards, the GHS/CLP refers testing to the methods of the **UN Recommendations on the Transport of Dangerous Goods - Manual of Tests and Criteria**.
- In the business, we usually just call it the **UN Test Manual**…
- It contains (almost) all the tests needed for evaluation of the GHS/CLP physical hazards.

The relation of GHS to TDG

TDG class	GHS Hazard Class
1	Explosives
2	Flammable gases, Oxidizing gases, Flammable aerosols, Gases under pressure
3	Flammable liquids
4.1	Self-reactive substances and mixtures, Flammable solids
4.2	Pyrophoric liquids, Pyrophoric solids, Self-heating substances and mixtures
4.3	Substances and mixtures which in contact with water emit flammable gases
5.1	Oxidizing liquids, Oxidizing solids
5.2	Organic peroxides

Detailed translation TDG – GHS is available in ECHA guidance "Guidance on the Application of the CLP Criteria"

Also the GHS Categories are correlated with TDG packing groups.

A matter of terminology

GHS/CLP TERM	TRANSPORT TERM
Hazard Class	Class/Division
Category	Packing Group (PG)
Pictogram	Warning label

GHS pictograms for physical hazards

GHS01
Explosive

GHS03
Oxidising

GHS02
Flammable

GHS04
Pressurised

GHS05
Corrosive

1. FLAMMABILITY

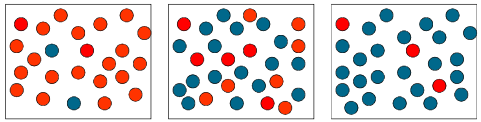
The fire-triangle

The fire-triangle – chemist's version

Flammable gases

A flammable gas can burn when mixed with air.

For flammable gases, the lower and upper explosion limits, LEL and UEL, are used as classification criteria.



Too lean mixture (below LEL) | Combustible mixture (between LEL and UEL) | Too fat mixture (above UEL)

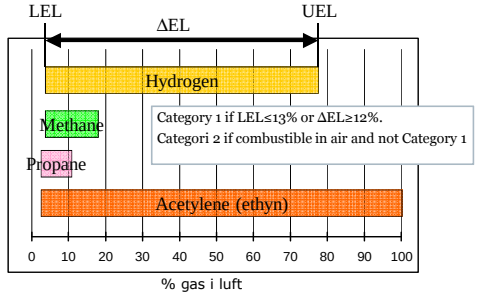
Oxygen (from air)
Flammable gas

Classification of Flammable Gases

All gases that can burn in air are classified as Flammable Gases according to GHS.

- Category 1 if LEL≤13% or UEL-LEL≥12% in air.
- Category 2 if combustible in air and not Cat. 1.

Examles of flammable gases



Labelling of Flammable Gases

Category 1	Category 2
	*(no pictogram)*
DANGER	WARNING
Extremely flammable gas (H220)	Flammable gas (H221)

In practice all pure flammable gases are Category 1.
However, ammonia has been classified as Category 2 in CLP Annex VI.

Flammable liquids

It is the vapour, not the liquid, that burns, since air is needed.

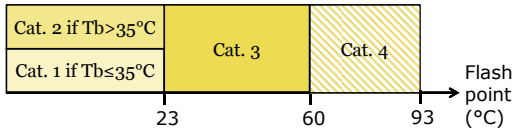
The amount of vapour depends on the molecular details of the liquid and on the **temperature**.

The **flash point** is the lowest temperature where there is enough vapour to burn in air.

The flash- and boiling points are used as classification criteria.

Classification of flammable liquids

Category	Flash point	Boiling point
1	<23°C	≤35°C
2	<23°C	>35°C
3	≥23-60°C	regardless
4	≥60-93°C	regardless



Cat. 1 if flash point <23°C and boiling point ≤35°C.
Cat. 2 if flash point <23°C and boiling point >35°C.
Cat. 3 if flash point ≥23-60°C.
Cat. 4 if flash point >60-93 °C.

Examples of flammable liquids

Liquid	Flash point (°C)	Boiling point (°C)
Acetone	-18	56
Diethyleter	-42	35
Decane	46	174
Ethanol	12	78
Gasoline	<-30	25-200
Cyclohexanone	44	156
Diesel	55-70	180-300

Labelling of Flammable Liquids

Cat. 1		DANGER	Extremely flammable liquid and vapour (H224)
Cat. 2		DANGER	Highly flammable liquid and vapour (H225)
Cat. 3		WARNING	Flammable liquid and vapour (H226)

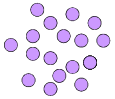
Flammable solids

A combustible particle can only burn on the surface, since air is needed.

Therefore, **particle size** is very important for the flammability.

The speed of burning is the classification criterion.

$$\frac{\text{SURFACE AREA}}{\text{VOLUME}} = \frac{3}{\text{particle radius}}$$



Classification of flammable solids

Category 1 if burning time <45 s or burning velocity >2,2 mm/s, and not stopped by wet-zone.
For metals if burning time ≤5 min.

Category 2 if burning time <45 s or burning velocity >2,2 mm/s, and stopped by wet-zone.
For metals if buring time >5 but ≤10 min.

Labelling of Flammable Solids

Category 1	Category 2
	
DANGER	WARNING
Flammable solid (H228)	Flammable solid (H228)

Pyrophoric substances – self-ignition

Pyrophoric substances self-ignite at room temperature.

The activation energy for the combustion is lower than the energy corresponding to room temperature.


DANGER
Catches fire spontaneously if exposed to air (H250)

Substances which in contact with water generate flammable gases

Some substances/mixtures generate flammable gas upon contact with water. Frequently the gas is hydrogen.

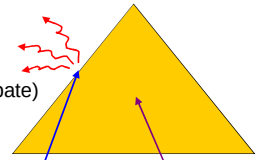
Category 1	Category 2	Category 3
Spontaneous ignition or >10 liter gas/min.	>20 liter gas/hour	>1 liter gas/hour
		
DANGER	DANGER	WARNING
In contact with water releases flammable gases which may ignite spontaneously (H260)	In contact with water releases flammable gases (H261)	In contact with water releases flammable gases (H261)

Self-heating

Self heating is a slow pyrophoric reaction with oxygen in air.

It happens when reaction heat cannot escape (dissipate) to the surroundings.

This usually only happens for solids in large amounts (piles).



Here (at the surface) heat can dissipate to thesurroundings.

Here (inside the pile) heat can not dissipate to the surroundings.

Labelling of Self-heaters

Category 1	Category 2
	
DANGER	WARNING
Self-heating; may catch fire (H251)	Self-heating in large quantities; may catch fire (H252)

2. OXIDISING ABILITY

The oxidiser need not be oxygen/air

$$C_aH_bO_cN_d + [O] \rightarrow CO_2 + H_2O + N_2$$

Examples of oxidisers are:
oxygen, chlorine,
nitric acid,hydrogen peroxide,
chlorate- and perchlorate salts,
nitrate- and nitrite salts

Classification of oxidising liquids and solids

The oxidising ability is measured by mixing the substance with cellulose and igniting.

For classification a comparison is made with reference substance(s).

Category 1	Category 2	Category 3
		
DANGER	DANGER	WARNING
May cause fire or explosion; strong oxidiser (H271)	May intensify fire; oxidiser (H272)	May intensify fire; oxidiser (H272)

Oxidising gases

Gases that are ”more oxidising than air” are classified as Oxidising Gases.

I practice the oxidising ability of gas mixtures is calculated via a method in ISO 10156 and compared to a mixture of 23,5% oxygen and the rest nitrogen.

DANGER

May cause or intensify fire; oxidiser (H270)

3. EXPLOSIVITY

What is an ”explosion”?

- Detonation:
  Super-sonic combustion, 2-10 km/s
  Generates a pressure front
  The pressure front propagates the reaction
  Typical for ”real” explosives

- Deflagration:
  Sub-sonic ”normal” combustion, <100 m/s
  No pressure front
  Typical for pyrotechnic mixtures

Explosive chemistry

Explosive mixtures:

$C_aH_bO_cN_d + [O] \rightarrow CO_2 + H_2O + N_2$

Explosive substances:

$C_aH_bO_cN_d \rightarrow CO_2 + H_2O + N_2$

In explosive substances the oxidative part is built into the molecule, which give a highly effective combustion.

Examples of explosive groups

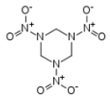
Table A6.1 EXAMPLES OF CHEMICAL GROUPS INDICATING EXPLOSIVE PROPERTIES IN ORGANIC MATERIALS

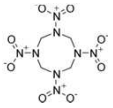
Structural feature	Examples
C-C unsaturation	Acetylenes, acetylides, 1,2-dienes
C-Metal, N-Metal	Grignard reagents, organo-lithium compounds
Contiguous nitrogen atoms	Azides, aliphatic azo compounds, diazonium salts, hydrazines, sulphonylhydrazides
Contiguous oxygen atoms	Peroxides, ozonides
N-O	Hydroxylamines, nitrates, nitro compounds, nitroso compounds, N-oxides, 1,2-oxazoles
N-halogen	Chloramines, fluoroamines
O-halogen	Chlorates, perchlorates, iodosyl compounds

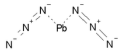
or

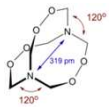
Examples of explosive substances


TNT

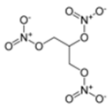

RDX

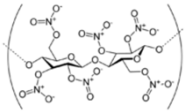

HMX

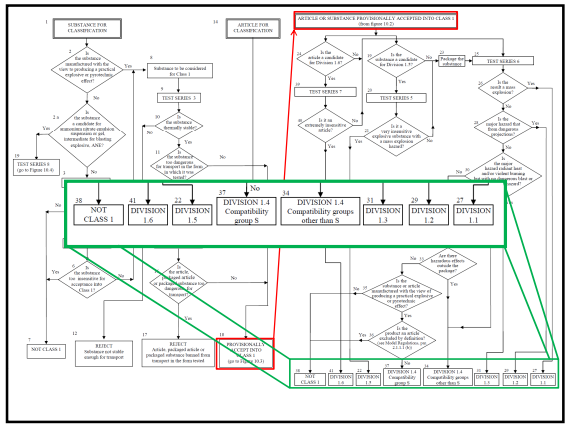

Lead azide



HMTD


Nitroglycerine


Nitrocellulose



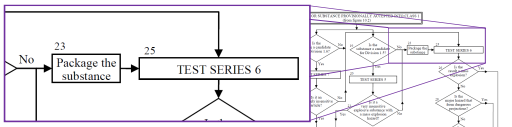
Myndigheten för samhällsskydd och beredskap

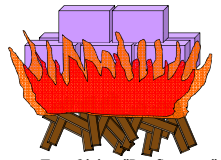
The seven Divisions of Explosives

- Unstable explosives
- 1.1 – mass-detonating
- 1.2 – fragments but not mass-detonating
- 1.3 – fire but not mass-detonating
- 1.4 – small effect, not mass-detonating
- 1.5 – mass-detonating but insensitive
- 1.6 – extremely insensitive not mass-detonating

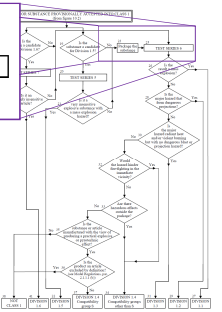
Myndigheten för samhällsskydd och beredskap

Division is package-dependent!





Test 6(c) – "Bonfire test"



Labelling of Explosives

Unstable	Div. 1.1	Div. 1.2	Div. 1.3	Div. 1.4	Div. 1.5	Div. 1.6
					*No pictogram*	*No pictogram*
DANGER	DANGER	DANGER	DANGER	WARNING	DANGER	*No signal word*
Unstable explosive. (H200)	Explosive; mass explosion hazard. (H201)	Explosive; severe projection hazard. (H202)	Explosive; fire, blast or projection hazard. (H202)	Fire or projection hazard. (H204)	May mass explode in fire. (H205)	*No hazard statement*

5. DECOMPOSITION

The decomposition reaction

$C_aH_bO_cN_d$ → all possible fragments + heat

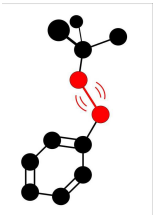
Decomposition may be initiated by heat or contamination.

Reaction may be very violent → **EXPLOSION**

Reaction products are mostly flammable → **FIRE**

Organic peroxides

Organic peroxides contain per definition peroxy-groups, O-O.



They are used as initiators and hardeners:

ROOR → 2RO*
RO* + M → RO + M*
M* + M → MM*
MM* + M → MMM*
… … …. → polymer

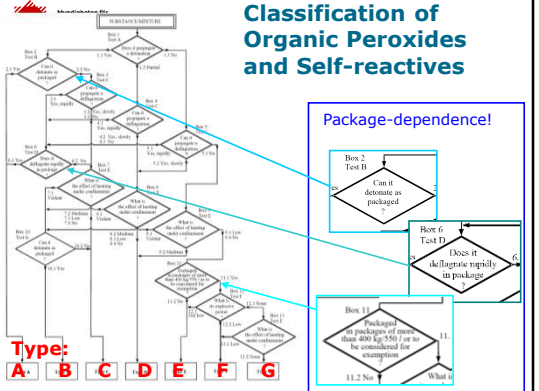
Self-reactives

Examples: Aliphatic azo-compounds (-C-N=N-C-)
Organic azides (-C-N_3)
Diazonium salts (-CN_2+Z-)
N-nitroso-compounds (-N-N=O)
Aromatic sulfohydrazides (-SO_2-NH-NH_2)

Table A6.2: EXAMPLES OF CHEMICAL GROUPS INDICATING SELF-REACTIVE PROPERTIES IN ORGANIC MATERIALS

Structural feature	Examples
Mutually reactive groups	Aminonitriles, haloanilines, organic salts of oxidizing acids
S=O	Sulphonyl halides, sulphonyl cyanides, sulphonyl hydrazides
P-O	Phosphites
Strained rings	Epoxides, aziridines
Unsaturation	Olefins, cyanates

Classification of Organic Peroxides and Self-reactives



Types

Type A: Can detonate or deflagrate rapidly, as packaged.

Type B: Possesses explosive properties and is liable to undergo a thermal explosion in package.

Type C: Possesses explosive properties but cannot undergo a thermal explosion.

Type D: Show no violent effect when heated under confinement, but can deflagrate or partially detonate.

Type E: Neither detonates nor deflagrates and shows low or no effect when heated under confinement.

Type F: Neither detonates nor deflagrates at all, shows low or no effect when heated under confinement as well as low or no explosive power.

Type G: Like Type F with no explosive power and thermally stable.

Labelling of Organic Peroxides and Self-reactives

Type A	Type B	Type C-D	Type E-F	Type G
				*No pictogram*
DANGER	DANGER	DANGER	WARNING	*No signal word*
Heating may cause an explosion (H240)	Heating may cause a fire or explosion (H241)	Heating may cause a fire. (H242)	Heating may cause a fire. (H242)	*No hazard statement*

6. PRESSURE

Pressurised gases

- GHS contains a hazard class for Gases Under Pressure.
- All gases are supplied under pressure, so all gases are classified as Gases Under Pressure.
- Depending on the physical state in the container, division is made into four groups.

Labelling for Gases Under Pressure

Compressed gas	Liquified gas	Refridgerated liquified gas	Dissolved gas
			
WARNING	WARNING	WARNING	WARNING
Contains gas under pressure; may explode if heated (H280)	Contains gas under pressure; may explode if heated (H280)	Contains refridgerated gas; may cause cyogenic burns or injury (H281)	Contains gas under pressure; may explode if heated (H280)

7. CORROSION TO METALS

Corrosive to metals

Criterion:
Corrodes > 6.25 mm/year at 55°C on steel or aluminium.

WARNING
May be corrosive to metals (H290)

Mixtures vs. substances

- There is in general no way to calculate the classification of a mixture from the classification of the component substances.
- Therefore, also mixtures must be tested.

Flammable substance + oxidising substance
=
EXPLOSIVE MIXTURE!

That's it!

There is more to know about Physical Hazards though….

Thanks for the attention!

/Lorens