

Chapter 17

Dangerous Goods

Transportation

Slide 1

PD1

Pierre David, 3 Jul 2021

Dangerous Goods

- Also known as “Hazardous Materials” in the United States (abbreviated HazMat).
- A fair percentage of international cargo falls in this category (not exactly known).
- Regulations are both international and domestic, and shipments must comply to all.
- International Maritime Organization (*International Maritime Dangerous Goods Code*), International Air Transport Association (*Dangerous Goods Regulations*), United States (*Hazardous Materials Regulations*), European Union (*European Agreement concerning the International Carriage of Dangerous Goods by Road* (ADR)).
- Thankfully, all are coordinated by the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Dangerous Goods

- Hazard Classification
- Degree of Hazard
- Packing Group
- Proper Shipping Name
- United Nations number
- First-responder notification
- Documentation
- Training

Classifications of Dangerous Goods

Dangerous goods are classified according to:

- Their physical characteristics (solid, liquid, gas)
- Their properties (explosive, corrosive, oxidizer, material that combusts when in contact with air or water, radioactive)
- Their boiling point (temperature at which liquid turns into gas)
- Their flash point (the temperature at which vapors ignite)
- Their health hazard

9. Physical and chemical properties

Physical State	Liquid
Appearance	Colorless
Odor	sweet
Odor Threshold	19.8 ppm
pH	7
Melting Point/Range	-95 °C / -139 °F
Boiling Point/Range	56 °C / 132.8 °F
Flash Point	-20 °C / -4 °F
Method -	Closed cup
Evaporation Rate	5.6 (Butyl Acetate = 1.0)
Flammability (solid,gas)	Not applicable
Flammability or explosive limits	
Upper	12.8 vol %
Lower	2.5 vol %
Vapor Pressure	247 mbar @ 20 °C
Vapor Density	2.0
Specific Gravity	0.790
Solubility	Soluble in water
Partition coefficient; n-octanol/water	No data available
Autoignition Temperature	465 °C / 869 °F
Decomposition Temperature	> 4°C
Viscosity	0.32 mPa.s @ 20 °C
Molecular Formula	C3 H6 O
Molecular Weight	58.08
Refractive index	1.358 - 1.359

11. Toxicological information

Acute Toxicity

Product Information

Component Information

Component	LD50 Oral	LD50 Dermal	LC50 Inhalation
Acetone	5800 mg/kg (Rat)	> 15800 mg/kg (rabbit) > 7400 mg/kg (rat)	76 mg/l, 4 h, (rat)

An excerpt of the Safety Data Sheet for a chemical identifies its physical and chemical characteristics.

Source: Fisher Scientific

System of Classification

Dangerous goods are identified using a system of classification that uses labels and placards placed on the goods and on their packaging.

The labels and placards can include local words, but the system is universally understood because the numbering system and colors are universal.



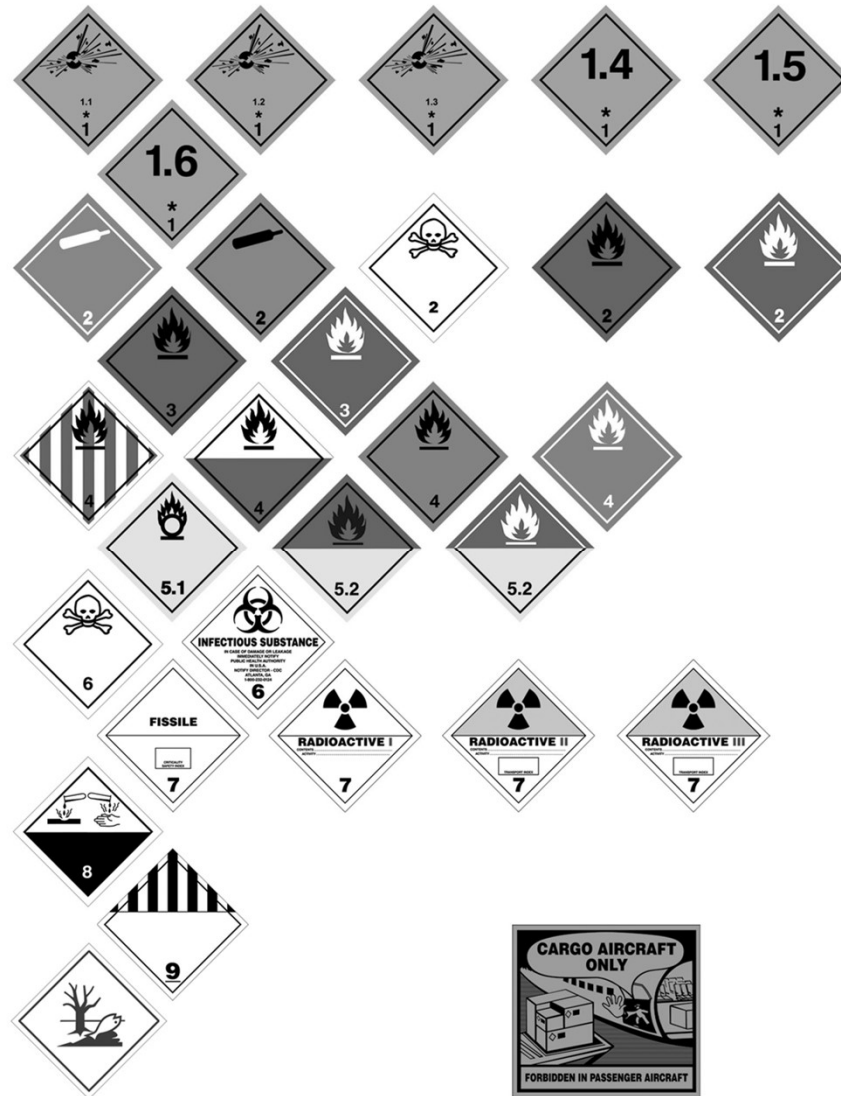
Several examples of labels for dangerous goods.

Source: multiple

Hazard Classes

- Class 1: Explosives
- Class 2: Compressed gases
- Class 3: Flammable liquids
- Class 4: Flammable solids
- Class 5: Oxidizers and peroxides
- Class 6: Toxic substances
- Class 7: Radioactive substances
- Class 8: Corrosive materials
- Class 9: Other dangerous goods (magnetic products, Lithium batteries, ...)

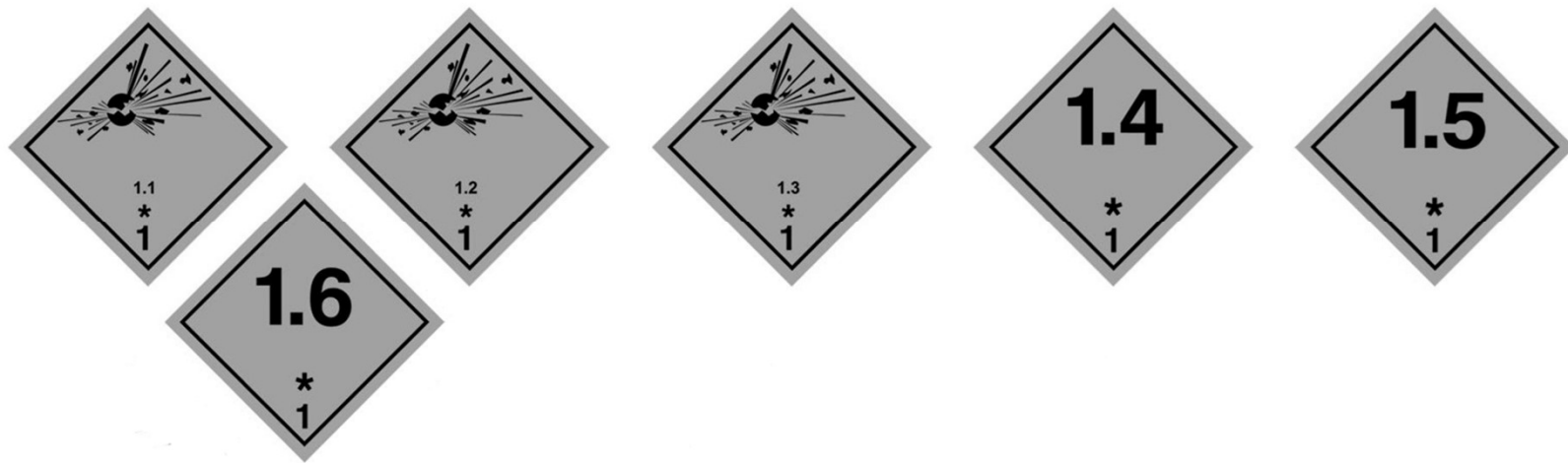
All of the possible labels for dangerous goods.
Source: UNECE



Further classifications (Explosives)

Most of the classes are divided further, in function of the dangers that the goods represent:

- 1.1 Mass explosion risk (the entire shipment would explode at once)
- 1.2 Explosive with a risk of projectiles
- 1.3 Minor explosion or minor projection risk - Fireworks
- 1.4 Small explosion risks - small fireworks
- 1.5 Mass explosion risks, but stable
- 1.6 No mass explosion risk, and stable



The labels used to identify explosive goods, from 1.1 (mass explosion risk) to 1.6 (no mass explosion risk, and stable).

Source: UNECE



A military convoy of explosive goods with mass-explosion risks on a US road.
Source: US Army

Further classification (Compressed Gases)

Class 2 products (compressed gases) are classified as:

2.1 flammable compressed gases (red)

2.2 inert compressed gases (green)

2.3 toxic compressed gases (black and white)

The placard's/label's colors are associated with the product's risks.



The labels used to identify compressed gases, identified by their colors, not their subclassification number.

Source: UNECE



Compressed gases are identified by color rather than by their subclassification number.
Source: Oleksiy Mark

Further classification (Flammable Liquids)

Flammable liquids are not divided any further, but oftentimes, carriers will identify the product transported. What cannot be used is the word “inflammable,” as it can be easily understood for the opposite of what it means.





A truck transporting flammable liquid (diesel fuel) in Russia.
Source: Art Konovalov

Further Classification (Flammable Solids)

Flammable solids are classified as:

- 4.1 Material that combusts readily when presented with a flame (wood fibers, sulfur, matches, ...) marked with vertical white and red lines
- 4.2 Material that is pyrophoric (combusts when in contact with air) and can self ignite (oily rags, powdered metals, magnesium), marked with a red and white placard, horizontally split
- 4.3 Material that is spontaneously flammable when wet (lithium, sodium), marked with a blue placard



The labels used to identify flammable solids, identified by their colors. Again, the subclassification numbers are not used.

Source: UNECE



A truck transporting flammable solids that are both pyrophoric and flammable when wet.
Source: Daniels Training Services



A container of a flammable liquid that is also flammable when wet.
Source: Uwe Aranas

Further Classification (Oxidizers and Peroxides)

Oxidizers and peroxides are classified as:

5.1 Oxidizers (Materials that release Oxygen): Hydrogen Peroxide, Nitric Acid are marked with yellow

5.2 Peroxides (Organic compounds that have oxygen): they contain both the material that burns and the oxygen, and therefore are red and yellow.



The labels used to identify oxidizers and peroxides.
Source: UNECE



A container containing an oxidizer.

Source: Tracy Fox

Further Classification (Toxic Goods)

Toxic Goods are classified as:

6.1 Products dangerous to human and animal life (cyanide, chlorine, nicotine, ...), generally shipped in large quantities

6.2 Infectious products (viruses, human tissues, ...): generally shipped in small quantities



The labels used to identify toxic and infectious goods.
Source: UNECE



A shipment of infectious materials (medical waste from cleaning).
Source: unknown

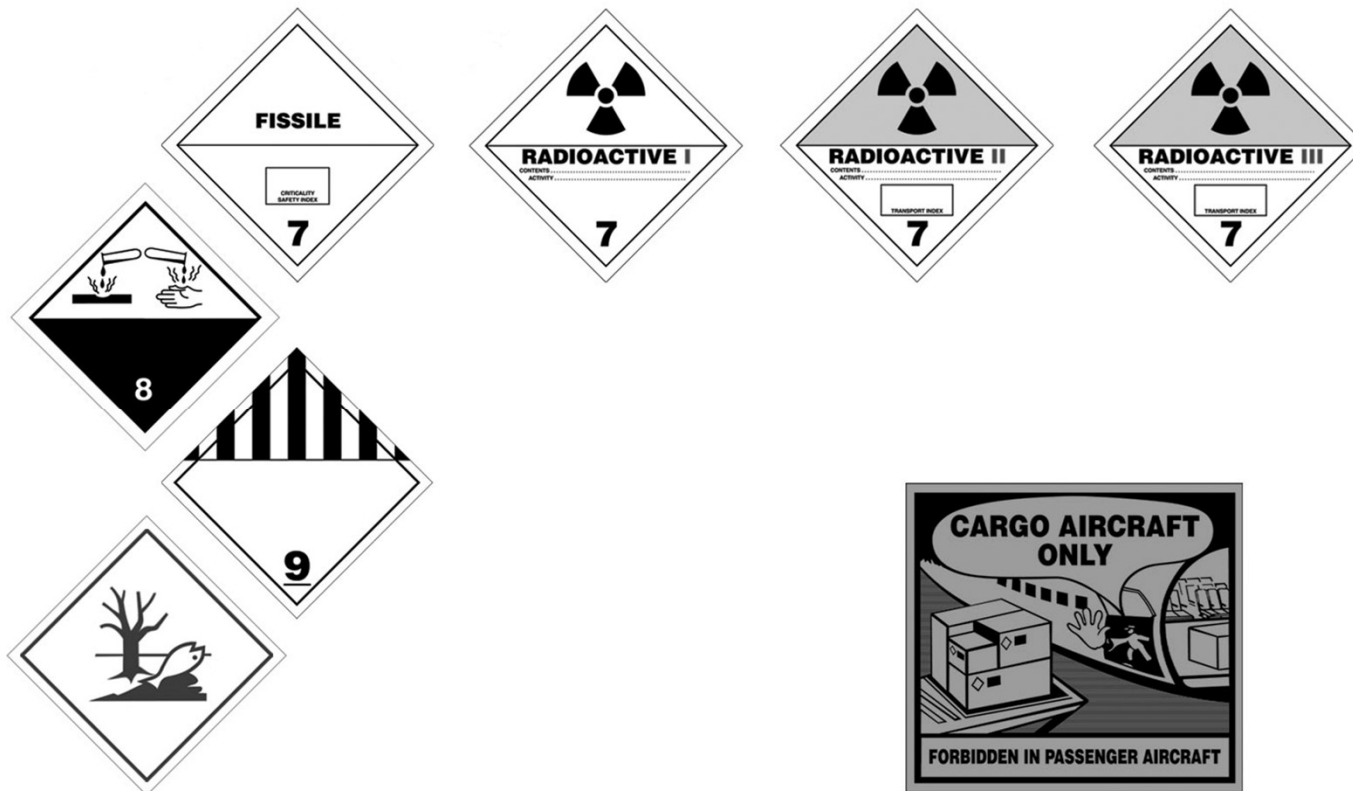
Further Classification (Radioactive Goods [7] and Corrosive Materials [8])

Radioactive Goods are further separated into “fissile” materials and “low-level” (white) and “higher-level” (yellow and white)

Corrosive Materials are not further divided

Class 9 is everything else

Finally, there are placards/labels for environmental damage risks, and passenger-aircraft risks



The labels used to identify radioactive goods, corrosive goods, and other dangerous goods. There are also labels for goods dangerous for the environments and goods that cannot be placed onboard passenger aircrafts.

Source: UNECE



A shipment of radioactive and corrosive material that is dangerous to wildlife (uranium hexafluoride)

Source: National Cargo Bureau

Degrees of Hazard

Almost all classes of dangerous goods are further divided into three different degrees of hazard, marked by their Packing Group:

Packing Group I (PG-I) is for the most dangerous goods

Packing Group II (PG-II) is for very dangerous goods

Packing Group III (PG-III) is for dangerous goods

Degrees of Hazard for Flammable Goods

Packing Group	Boiling Point	Flash Point
I	BP \leq 35° C (95° F)	
II	BP $>$ 35° C (95° F)	FP \leq 23° C (73° F)
III	BP $>$ 35° C (95° F)	FP $>$ 23° C (73° F)

The boiling point is the temperature at which the liquid becomes a gas.

The flash point is the temperature at which the liquid emits vapor that is flammable.

Determination of Packing Group

Here are three examples:

- Pure ethyl alcohol (200 proof) has a boiling point of 78° C and a flash point of 14° C (172° F and 57° F). It is therefore a PG-II product.
- Gasoline has a boiling point (depending on make-up) between 27° C and 226° C (80° F and 440° F), and a flash point of -40° C (-40° F). It is therefore a PG-II product.
- Diesel fuel has a boiling point between 163° C and 371° C (325° F and 700° F), and a flash point of 38° C (100° F). It is therefore a PG-III product.

Degrees of Hazard for Toxic Goods

Packing Group	Oral Toxicity	Dermal Toxicity	Inhalation Toxicity
I	$LD_{50} \leq 5\text{mg/kg}$	$LD_{50} \leq 50\text{mg/kg}$	$LC_{50} \leq 0.2\text{mg/l}$
II	$5\text{mg/kg} < LD_{50} \leq 50\text{mg/kg}$	$50\text{mg/kg} < LD_{50} \leq 200\text{mg/kg}$	$0.2\text{mg/l} < LC_{50} \leq 2\text{mg/l}$
III	$50\text{mg/kg} < LD_{50} \leq 3000\text{mg/kg}$	$200\text{mg/kg} < LD_{50} \leq 1,000\text{mg/kg}$	$2\text{mg/l} < LC_{50} \leq 4\text{mg/l}$

The LD_{50} is the dose that kills 50 percent of a population of rats within 14 days (ingestion) or with 14 days of skin being exposed for 24 hours to the substance (dermal).

The LC_{50} is the concentration that kills 50 percent of a population of rats within 14 days after inhaling the product's mist or dust for an hour.

Determination of Packing Group

Here are three examples:

- Sodium Cyanide (NaCN) has an ingestion LD₅₀ of 4.8 mg/kg. It is a PG-I product. It is also dangerous for wildlife and will be labeled as such.
- Chloroform has an inhalation LC₅₀ of 3.9 mg/l. It is therefore a PG-III product. However, its dermal and ingestion toxicities are low.
- Nicotine has an ingestion LD₅₀ of 50 mg/kg. It is therefore a PG-II product.

Degrees of Hazard for Corrosive Goods

Packing Group	Corrosive Harm
I	Exposure Time \leq 3 minutes Observation Time \leq 60 minutes
II	3 minutes $<$ Exposure Time \leq 60 minutes Observation Time \leq 14 days
III	60 minutes $<$ Exposure Time \leq 4 hours Observation Time \leq 14 days

Corrosive harm is defined as “permanent damage to the skin” after a given exposure period and within a certain observation time.

Determination of Packing Group

Here are three examples:

- Hydrochloric acid (muriatic acid, HCl) is a PG-II or PG-III product depending on its concentration, as it is fully soluble in water.
- Nitric acid (HNO₃) in a concentration greater than 70 percent, is a PG-I product.
- Acetic acid (CH₃OOH) in a concentration between 10 and 50 percent, is a PG-III product.

Proper Shipping Name and UN number

Every dangerous good transported internationally must be identified in two different ways:

- Its Proper Shipping Name

That is an internationally recognized name for this chemical (“Hydrochloric Acid” and not “Muriatic Acid,” for example) displayed on shipping papers.

- Its UN number

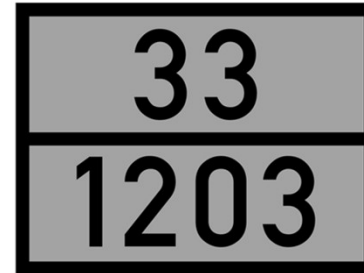
A unique 4-digit code, displayed on shipping papers and placards and labels.

First Responder Notification

Aside from the class number (1 through 9) and the UN number, there is no complete standardization of the warning system for first responders.

- The United States has one system.
- The countries signatory to the ADR (*European Agreement concerning the International Carriage of Dangerous Goods by Road* (ADR)) have another.
- Countries that align with the United Kingdom have yet another.

The remainder of the world follows one of these three systems.



The United States requires the placard and the UN number in orange or on the placard (left two alternatives). The product is gasoline.

The European ADR requires the UN number and the two primary classes/dangers of the product. When doubled, it simply means very flammable.

The British system requires notification of the primary means to fight a spill/fire, the equipment required for first responders, and whether to evacuate the population: these are the codes on the first line on the right.

Packaging Requirements

The Packing Group of a dangerous good (PG-I through PG-III) determines the type of packaging necessary to transport the good.

The packaging requirement is specific to the mode of transportation used and the quantity placed in each packaging unit.

The International Maritime Organization (*International Maritime Dangerous Goods Code*), International Air Transport Association (*Dangerous Goods Regulations*), United States (*Hazardous Materials Regulations*), and the European Union (*European Agreement concerning the International Carriage of Dangerous Goods by Road* (ADR)) regulate the packaging that can be used.

Labeling and Placarding Requirements

The packages must display a label (class), the UN number, and the Proper Shipping Name of the dangerous goods transported.

The means of conveyance (truck trailer, container) must display a placard and the UN number of the dangerous transported.

Since it's possible that goods will be transported by ocean, IMO requirements (that the labels/placards remain in place after three months immersion in salt water) should be respected.

Shipping papers

The documents must accompany the goods (in all cases):

They must include the Proper Shipping Name of the dangerous goods and their UN number

They must contain the name and address of the shipper, the name and address of the consignee, and a phone number that is answered 24 hours a day for assistance for first responders

Training Requirements

Every person handling dangerous goods, whether shipper, carrier, or consignee, must have been trained in DG regulations, and the training must be renewed every two years (IATA), or three years (IMO, DOT, ADR).