

GLOBAL HARMONIZATION AND TRANSPORT: PHYSICAL AND OTHER HAZARDS

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Abstract

In developing the Global Harmonized System of Classification, the international regulations governing the transport of dangerous goods were one of the main references.

In particular the development of harmonized criteria for physical hazards was assigned as a task to a joint working group ILO- UN Committee of Experts.

The result, in terms of harmonized criteria, was achieved in 1997, few specific problems still pending.

The criteria are indeed very similar to the ones adopted in transport regulations, so that the impact of GHS on these regulations can be considered quite low.

A more significant impact can be expected in terms of classification of toxic (acute toxicity) substances.

With regard to other dangerous substances, it can be expected that the criteria for environmentally hazardous substances could be adopted in this biennium.

With regard to other toxic effects (irritation, cancer, mutagenicity, etc.), taking care that these hazards are not considered up to now in transport regulations, some discussion can be expected.

With regard to hazard communication, it is expected that the new criteria for labelling will not affect dramatically the existing situation.

However a first effect of the GHS was the restructuring of the existing Committee of Experts on Transport into one Main Committee dealing with transport and GHS and two SubCommittees (one for Transport and the other one for GHS).

A significant point of discussion affecting transport regulations is of course the implementation of GHS.

INTRODUCTION

When, after UNCED, it was decided to develop the Global Harmonized System (GHS) of classification and labelling of hazardous chemicals, reference was made to the necessity of building up the new system on the basis of the existing systems of classification.

On this point it has to be noted that international regulations aimed to establish safety requirements for the transport of dangerous goods have been agreed many years ago, and now largely harmonized on the basis of the UN Recommendations, as prepared and revised by the UN Committee of Experts on the Transport of Dangerous Goods as requested by ECOSOC from 1953.

Transport safety requirements have been developed taking into consideration the hazardous characteristics of the goods, so that the classification system is one of the basis for these requirements.

In conclusion the transport classification system has been adopted decades ago and used worldwide, being then one of the main basis for developing harmonized classification criteria.

TRANSPORT CLASSIFICATION

In transport, dangerous goods are assigned to one of nine classes according to the hazard they present, some of these classes being subdivided into divisions. These classes and division are:

Class 1: Explosives

- Division 1.1: substances and articles which have a mass explosion hazard
- Division 1.2: substances and articles which have a projection hazard but not a mass explosion hazard
- Division 1.3: substances and articles which have a fire hazard and either a minor blast hazard or a minor projection hazard or both, but not a mass explosion hazard
- Division 1.4: substances and articles which present no significant hazard
- Division 1.5: very insensitive substances which have a mass explosion hazard
- Division 1.6: extremely insensitive articles which do not have a mass explosion hazard

Class 2: Gases

- Division 2.1: flammable gases
- Division 2.2: non-flammable, non-toxic gases
- Division 2.3: toxic gases

Class 3: Flammable liquids

Class 4: Flammable solids; substances liable to spontaneous combustion; substances which, in contact with water, emit flammable gases

- Division 4.1: flammable solids, self-reactive substances and desensitized explosives

- Division 4.2: substances liable to spontaneous combustion
- Division 4.3: substances which, in contact with water, emit flammable gases

Class 5: Oxidizing substances and organic peroxides

- Division 5.1: oxidizing substances
- Division 5.2: organic peroxides

Class 6: Toxic and infectious substances

- Division 6.1: toxic substances
- Division 6.2: infectious substances

Class 7: Radioactive material

Class 8: Corrosive substances

Class 9: Miscellaneous dangerous substances and articles

As it is clear, apart from Divisions 2.3, 6.1, 6.2 and, partially, Classes 8 and 9, all the other Classes and Divisions are dealing with physical hazards.

This situation is peculiar to transport, with respect for instance to the classification system used in Europe for consumer goods, where the considered hazards are mainly related to health effects.

It is then quite obvious that the transport system was the basis for the harmonized criteria for classification of physical hazards.

HARMONIZED SYSTEM OF CLASSIFICATION FOR PHYSICAL HAZARDS

The following classes of physical hazards have been identified:

- Flammable liquids
- Flammable solids
- Flammable gases
- Flammable aerosols
- Pyrophoric substances (liquids)
- Pyrophoric substances (solids)
- Self-heating substances
- Substances which, in contact with water, emit flammable gases
- Oxidizing substances (liquids)
- Oxidizing substances (solids)
- Oxidizing substances (gases)
- Organic peroxides
- Self-reactive substances
- Explosive substances (liquids and solids) and explosive articles
- Substances which are corrosive to metals
- Compressed gases

CRITERIA FOR CLASSIFICATION (PHYSICAL HAZARDS)

Flammable liquids

Hazard level	Criteria	Test methods
Very high danger	Flash point < 23 °C and initial boiling point ≤ 35 °C	Closed cup methods to be used, open cup methods only acceptable in special cases
High danger	Flash point < 23 °C and initial boiling point > 35 °C	
Medium danger	Flash point ≥ 23 °C and ≤ 60 °C	
Low danger	Flash point > 60 °C and ≤ 90 °C	

NOTE 1: Gas oils, diesel and light heating oils in the flash point range of 55 °C to 75 °C may be regarded as a special group for some regulatory purposes.

NOTE 2: Liquids with a flash point of more than 35 °C may be regarded as non-flammable liquids for some regulatory purposes (e.g. transport) if negative results have been obtained in the combustibility test L.2 of the Manual of Tests and Criteria.

Flammable solids

Hazard level	Criteria	Test methods
High danger	-	-
Medium danger	<p>Screening test: testing time 2 min (20 min for metal powders)</p> <p>Burning rate test:</p> <ul style="list-style-type: none"> - Substances other than metal powders: wetted zone does not stop fire and burning time < 45 s or burning rate > 2.2 mm/s - Metal powders: burning time ≤ 5 min 	Method as described in section 33.2.1 of the Manual of Tests and Criteria
Low danger	<p>Method and test as described above</p> <p>Burning rate test</p> <ul style="list-style-type: none"> - Substances other than metal powders: wetted zone stops the fire for at least 4 min and burning rate < 45 s - Metal powders : burning time > 5 min and ≤ 10 min 	

Flammable gases

Hazard level	Criteria and test methods
High danger	Gases and gas mixtures, which at 20 EC and a standard pressure of 101.3 kPa, (a) are ignitable when in a mixture of 13 % or less by volume in air; or (b) have a flammable range with air of at least 12 percentage points regardless of the lower flammable limit. Flammability should be determined by tests or by calculation in accordance with methods adopted by ISO (see ISO 10156:1996). Where insufficient data are available to use these methods, tests by a comparable method recognized by the competent authority may be used.
Medium danger	Gases or gas mixtures, other than those of high danger, which, at 20 EC and a standard pressure of 101.3 kPa, have a flammable range in mixture in air.
Low danger	Not applicable

NOTE: Ammonia and methyl bromide may be regarded as special cases for some regulatory purposes.

Flammable aerosols

Criteria for flammability remain to be developed.

Pyrophoric liquids

Hazard level	Criteria	Test methods
High danger	The liquid ignites in the first part of the test, or if it ignites or chars the filter paper.	UN Test N.3 Manual of Tests and Criteria (para. 33.3.1.5.4)
Medium danger	Not applicable	Not applicable
Low danger	Not applicable	Not applicable

Pyrophoric solids

Hazard level	Criteria	Test methods
High danger	The sample ignites in one of the tests.	UN Test N.2 Manual of Tests and Criteria (para. 33.3.1.4.4)
Medium danger	Not applicable	Not applicable
Low danger	Not applicable	Not applicable

Self-heating substances

Hazard level	Criteria	Test methods
High danger	Not applicable	Not applicable
Medium danger	Positive result in a test using a 25 mm sample cube at 140 °C	UN Test N. 4 Manual of Tests and Criteria (para. 33.3.1.6.4.3)
Low danger	<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 is to be packed in packages with a volume of more than 3 m³;</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 is to be packed in packages with a volume of more than 450 litres;</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 <u>and</u> a positive result is obtained in a test using a 100 mm cube sample at 100 °C</p>	UN Test N. 4 Manual of Tests and Criteria (para. 33.3.1.6.4.4)

Substances which, in contact with water, emit flammable gases

Hazard level	Criteria	Test methods
High danger	Any substance which reacts vigorously with water at ambient temperatures and demonstrates generally a tendency for the gas produced to ignite spontaneously, or which reacts readily with water at ambient temperatures such that the rate of evolution of flammable gas is equal to or greater than 10 litres per kilogram of substance over any one minute	UN Test N.5 Manual of Tests and Criteria (para. 33.4.1.4.4.2)
Medium danger	Any substance which reacts readily with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 20 litres per kilogram of substance per hour, and which does not meet the criteria for high danger	UN Test N.5 Manual of Tests and Criteria (para. 33.4.1.4.4.3)
Low danger	Any substance which reacts slowly with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 1 litre per kilogram of substance per hour, and which does not meet the criteria for high and medium danger	UN Test N.5 Manual of Tests and Criteria (para. 33.4.1.4.4.4)

Oxidizing substances (liquids)

Hazard level	Criteria	Test methods
High danger	Any substance which, in the 1:1 mixture, by mass, of substance and cellulose tested, spontaneously ignites; or the mean pressure rise time of a 1:1 mixture, by mass, of substance and cellulose is less than that of a 1:1 mixture, by mass, of 50% perchloric acid and cellulose	UN Test 0.2 Manual of Tests and Criteria (para. 34.4.2.4.2)
Medium danger	Any substance which, in the 1:1 mixture, by mass, of substance and cellulose tested, exhibits a mean pressure rise time less than or equal to the mean pressure rise time of a 1:1 mixture, by mass, of 40% aqueous sodium chlorate solution and cellulose; and the criteria for high danger are not met	UN Test 0.2 Manual of Tests and Criteria (para. 34.4.2.4.2)
Low danger	Any substance which, in the 1:1 mixture, by mass, of substance and cellulose tested, exhibits a mean pressure rise time less than or equal to the mean pressure rise time of a 1:1 mixture, by mass, of 65% aqueous nitric acid and cellulose; and the criteria for high and medium danger are not met	UN Test 0.2 Manual of Tests and Criteria (para. 34.4.2.4.2)

Oxidizing substances (solids)

Hazard level	Criteria	Test methods
High danger	Any substance 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	UN Test 0.1 Manual of Tests and Criteria (para. 34.4.1.4.2)
Medium danger	Any substance 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 high danger are not met	UN Test 0.1 Manual of Tests and Criteria (para. 34.4.1.4.2)
Low danger	Any substance 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 high and medium danger are not met	UN Test 0.1 Manual of Tests and Criteria (para. 34.4.1.4.2)

Oxidizing substances (gases)

Criteria	Test methods
Any gas which may, generally by providing oxygen, cause or contribute to the combustion of other material more than air does.	ISO 10 156: 1996 <i>(NOTE: Improvement of this standard is under consideration by ISO; ISO target date for the revised standard is 2001).</i>

Organic peroxides

Criteria	Test methods
<p>Any organic peroxide, except organic peroxides or organic peroxides formulations:</p> <p>(a) containing not more than 1.0% available oxygen from the organic peroxides when containing not more than 1.0% hydrogen peroxide; or</p> <p>(b) containing not more than 0.5% available oxygen from the organic peroxides when containing more than 1.0% but not more than 7.0% hydrogen peroxide.</p> <p>Organic peroxides in packaged form may be classified under types A to G in accordance with the criteria of the Manual of Tests and Criteria, Part II</p> <p>NOTE 1: Type G is not dangerous for transport.</p>	Test series A to H (Refer to Part II of the Manual of Tests and criteria)

NOTE 2: *Sub-divisions may not be necessary for all systems.*

Self-reactive substances

Criteria	Test methods
<p>Criteria of the Manual of Tests and Criteria, Part II. Self-reactive substances in packaged form may be classified under types A to G in accordance with those criteria</p> <p><i>NOTE 1: Type G is not dangerous for transport.</i></p> <p><i>NOTE 2: Sub-divisions may not be necessary for all systems.</i></p>	<p>Test series A to H (Refer to Part II of the Manual of Tests and criteria)</p>

Explosives and criteria for their classification

Tests and criteria	Comments
<p>Explosibility: according to UN Test series 2 (Section 12)</p> <p>Sensitiveness: according to UN Test series 3 (Section 13)</p> <p>Thermal stability: according to UN Test 3(c) (Sub-section 13.6.1)</p>	<p>Intentional explosives are not subject to UN Test series 2</p> <p><i>NOTE: Explosive substances in packaged form and articles may be classified under divisions 1.1 to 1.6 and compatibility groups A to S to distinguish technical requirements.</i></p>

NOTE 1: *The use of the word "explosive" can have different meanings and interpretations. Reference to "an explosive" or "explosives" is commonly understood to mean substances or articles in Class 1 of the scheme of the UN Recommendations on the Transport of Dangerous Goods, that is those which are intentional explosives or have properties which when assessed under the test procedure of the Manual of Tests and Criteria place them in UN Class 1. The description "explosive" can, however, be used to describe a property and as such it encompasses a wider range of substances than just those in UN Class 1. The Global Harmonized System (GHS) requires that classification is based on intrinsic properties and the word 'explosive' in that context can be used to describe the property of a substance i.e. its ability to explode, as well as referring to a substance or article that has been designed to have explosive properties. This can lead to confusion and difficulty but in the above definition "explosive" refers to explosion hazard of substances and articles and is not limited to those which would be placed in Class 1 of the UN scheme.*

NOTE 2: Some explosive substances are wetted with water or alcohols or diluted with other substances to suppress their explosives properties (Desensitized explosives) . They may be treated differently from explosive substances for some regulatory purposes.

Substances which are corrosive to metals

Hazard level	Criteria	Test method
Low danger	Corrosion rate on steel or aluminium surfaces exceeding 6.25 mm a year at a test temperature of 55 °C.	For the purposes of testing steel, type P235 (ISO 9328 (II):1991) or a similar type, and for testing aluminium, non-clad types 7075-T6 or AZ5GU-T6 shall be used. An acceptable test is prescribed in ASTM G31-72 (Reapproved 1990).

Compressed gases

Gas contained at a pressure not less than 280 kPa at 20°C or as a refrigerated liquid

IMPACT OF GHS ON TRANSPORT REGULATIONS

With regard to physical hazards only few changes are necessary to align transport regulations with the Global Harmonized System of classification, the reason being that the relevant criteria are mainly based on the ones adopted in transport.

The situation is different with regard to health effects.

First of all it has to be noted that the health effects considered in the GHS cover a set of effects very large with respect to transport situation.

Indeed in transport only acute toxicity and corrosivity to skin are considered as relevant hazards . It means that cancerogenicity, mutagenicity, irritation, sensitization, etc. are not considered and consequently no impact is foreseen on transport regulation.

On this point however it has to be mentioned that few substances (asbestos and polyhalogenated biphenyls and terpheniles), which in other regulations are classified as cancerogens, are however classified as dangerous substances in transport regulations and have been assigned to Class 9 (Miscellaneous dangerous substances and articles).

In perspectives it would be possible that some of these health effects (for instance, cancerogenicity, when cancer can develop following a single exposure) are reconsidered in order to introduce them, perhaps as a new class or division, in the transport regulation.

A more significant impact is related to the new criteria for acute toxicity, which will imply changes in the reference values of LD50, LC50 for classification.

With regard to environmentally hazardous substances, it has to be noted that, up to now, no criterion was agreed at the UN Committee of Experts, but different criteria were adopted in the IMDG Code (sea transport) and in RID/ADR (European land transport): however it is possible that the harmonized criteria will be considered for adoption during this biennium.

With regard to hazard communication, it is expected that the new criteria for labelling will not affect dramatically the existing situation.

Apart from the restructuring of the existing Committee of Experts on Transport into one Main Committee dealing with transport and GHS and two SubCommittees (one for Transport and the other one for GHS), another significant issue to be considered is of course the implementation of the full GHS in transport regulation (date for implementation, consideration of the classified

substances, responsibility for future classification, etc., all to be agreed with other regulatory bodies).