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COMMITTEE OF EXPERTS ON THE TRANSPORT OF DANGEROUS GOODS AND ON THE GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION AND LABELLING OF CHEMICALS

Sub-Committee of Experts on the Transport of Dangerous Goods Thirty-sixth session Geneva, 30 November – 9 December 2009 Item 3 of the provisional agenda

### LISTING, CLASSIFICATION AND PACKING

Pressurized adhesives in gas cylinders

Transmitted by the International Council of Chemical Association (ICCA)<sup>1</sup>

#### **Background**

1. Adhesives manufacturers in the United Kingdom, the United States of America, Australia, Canada and other countries, are supplying pressurized adhesive products packed in gas cylinders. The currently most used classification entries are either UN3161, Liquefied flammable gas, n.o.s. for flammable mixtures, or UN3163, Liquefied Gas, n.o.s. for non flammable mixtures.

2. The propellants used add sufficient vapor pressure that the formulated product as packed indeed meets the definition of a gas in 2.2.1.1(a). The precedence of hazard characteristics provisions in section 2.0.3, require for these pressurized adhesives to be assigned to Division 2.1 or 2.2 dependent on flammability of either the adhesive or the propellant.

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In accordance with the programme of work of the Sub-Committee for 2009-2010 approved by the Committee at its fourth session (refer to ST/SG/AC.10/C.3/68, para. 118 (b) and ST/SG/AC.10/36, para. 14).

- 3. Current examples are supplied in refillable cylinders, pressure drums and portable tanks, but also in non-refillable cylinders up to 22.4 L capacity, conforming to ISO 11118:1999, European standard EN 12205, Canadian specification TC-39M or USA specification DOT 39. The spraying equipment itself (connection, hose, spray gun...) is shipped separately. A picture of such a device is shown in Annex.
- 4. Paragraph 4.1.6.1.9(b) states:
  - "Non refillable pressure receptacles shall:
  - (a) Be of a water capacity less than or equal to 1.25 litres when filled with flammable or toxic gas; ..."
- 5. This limitation effectively prohibits the use of > 1.25 L non refillable gas cylinders for flammable gases. However, some countries provide exceptions to this rule. E.g. the Department of Transportaation (DOT) in the United States of America effectively allows carriage of liquefied flammable gases in DOT specification 39 (49 CFR 178.65) cylinders, for sizes up to 55 pounds (1526 cubic inches, 25L) and service pressures of 500 psig or less. DOT did not adopt the capacity limitation, as this would have a negative impact on companies using specification 39 cylinders larger than 75 cubic inches in aerosol applications.
- A 1.25 litres limit is considered by the industry as too restrictive for flammable industrial spray applications, effectively preventing the use of non-refillable cylinders. In contrast, e.g. adhesives or paints of Class 3 (without propellant) are permitted by 4.1.3.6 in cylinders and other pressure receptacles without specific size or type restrictions. Flammable liquids assigned to packing instruction P001 are authorized by the Model Regulations to be safely shipped in ISO 11118:1999 cylinders in capacities up to 150 litres.
- 6. The application of 4.1.6.1.9(b) to non refillable gas cylinders containing a gas/liquid type mixture is seen as questionable. Even though some of these products use a flammable propellant, the propellant usually comprises less than 50 % of the contents of the cylinder. They are not completely filled with a flammable gas. The total potential energy stored in a cylinder of mostly incompressible liquid under pressure, presents significantly less hazard than that of a purely compressed or liquefied gas, yet greater hazard than a purely flammable liquid. It therefore warrants a maximum size larger than 1.25 litres for a flammable gas, but smaller than 150 litres, for a flammable pressurized liquid when packed in non-refillable cylinders.
- 7. Different entries in the Dangerous Goods list can be considered to describe these pressurized chemicals:
  - (a) Liquefied gases (UN3161, UN3163, currently used by adhesive manufacturers or distributors in the United States of America, United Kingdom and Canada): these entries do not accurately describe the aerosol-like properties of the mixtures. In addition, the limitation posed in 4.1.6.1.9(b) effectively prohibits the transport of the flammable mixtures in non-refillable cylinders of capacity > 1.25L.

- (b) Aerosols (UN1950): this entry accurately describes the properties of the pressurized mixture. The non-refillable gas cylinders currently used however do not match the technical requirements of an <u>aerosol dispenser</u>, as described in 6.2.4.2.
- (c) Adhesives (UN1133): this entry takes correctly into account the liquid part of the mixture. It does however not take into account the gaseous component(s). In addition, classification as e.g. UN 1133, class 3 for an adhesive/gas mixture is in conflict with the precedence of hazards provisions in section 2.0.3.
- 8. In conclusion, there is currently no entry in the Dangerous Goods List that suitably describes pressurized adhesives in gas cylinders. Other industries (paints, coatings, and lubricants) face the same problem and therefore it is necessary to have a broad approach to cover as many industries as possible.

## **Proposal**

9. Add a new definition in 1.2.1:

"Pressurized chemical: any refillable or non-refillable cylinder, tube, or pressure drum meeting the requirements of 6.2.1 and 6.2.2 or 6.2.3, and any portable tanks meeting the requirements of 6.7.3, containing a liquid, paste or powder, pressurized with a compressed or liquefied gas or a mixture thereof, under sufficient pressure to eject the contents.

**NOTE:** An example of a pressurized chemical is a pressure receptacle containing a mixture of e.g. an adhesive or paint, and a gas or gas-mixture, which is under sufficient pressure to allow spray application or extrusion.".

- 10. Create 2 new entries (UN 3XXX, UN 3YYY) in Class 2:
  - (a) Add 2 new entries to the Dangerous Goods List, as follows:

UN	Name and description	Class or division	Subsidiary risk	UN Packing group	Special provi- sions	Limited and excepted quantities		Packagings and IBCs		Portable tanks and bulk containers	
No.								Packing instructions	Special packing provisions	Instruc- tions	Special provisions
(1)	(2)	(3)	(4)	(5)	(6)	(7a)	(7b)	(8)	(9)	(10)	(11)
3XXX	PRESSURIZED CHEMICAL, NON FLAMMABLE	2.2			XYZ	0	E0	P2YY	PPYY	T50	
3YYY	PRESSURIZED CHEMICAL, FLAMMABLE	2.1			XYZ	0	E0	P2YY	PPYY	T50	

(b) Add a new Special Provision XYZ in Chapter 3.3:

XYZ: The division of Class 2 and the subsidiary risks depend on the nature of the contents of the pressurized chemical. The following provisions shall apply:

- (a) Division 2.1 applies if the contents include 85% by mass or more flammable components and the chemical heat of combustion is 30 kJ/g or more;
- (b) Division 2.2 applies if the contents contain 1% by mass or less flammable components and the heat of combustion is less than 20 kJ/g;
- (c) Otherwise the product shall be classified based on the components in the different states: the propellant (gas) or mixtures of the propellant with other gases (based on the criteria laid down for Class 2), the liquid (based on the criteria laid down for Class 3 materials) and/or the solid (based on the criteria laid down for Division 4.1 flammable solid material). If one of these components needs to be classified as flammable the pressurized chemical needs to be classified as flammable;
- (d) Gases of Division 2.3 shall not be used as a propellant in a pressurized chemical;
- (e) Where the contents other than the propellant of the pressurized chemical receptacle to be ejected are classified as Division 6.1 packing groups II or III or Class 8 packing groups II or III, the pressurized chemical shall have a subsidiary risk of Division 6.1 or Class 8;
- (f) Pressurized chemicals with contents meeting the criteria for packing group I for toxicity or corrosivity, Division 4.1 self reactive substances and solid desensitized explosives, Division 4.3 substances which, in contact with water, emit flammable gases, Division 5.1 oxidizing substances and Division 5.2 organic peroxides shall be prohibited from transport;
- (g) The appropriate subsidiary risk labels are required.

Flammable components are flammable liquids, flammable solids or flammable gases and gas mixtures as defined in Notes 1 to 3 of sub-section 31.1.3 of Part III of the *UN Manual of Tests and Criteria*. This designation does not cover pyrophoric, self-heating or water-reactive substances. The chemical heat of combustion shall be determined by one of the following methods ASTM D 240, ISO/FDIS 13943: 1999 (E/F) 86.1 to 86.3 or NFPA 30B.

#### 11. Amend 4.1.6.1.5 as follows (new text is underlined):

Prior to filling, the filler shall perform an inspection of the pressure receptacle and ensure that the pressure receptacle is authorized for the gas <u>or pressurized chemical</u> to be transported and that the provisions of these Regulations have been met. Shut-off valves shall be closed after filling and remain closed during transport. The consignor shall verify that the closures and equipment are not leaking.

#### 12. Amend 4.1.6.1.10 as follows (new text is underlined):

Refillable pressure receptacles, other than cryogenic receptacles, shall be periodically inspected according to the provisions of 6.2.1.6 and packing instruction P200 or packing instruction P2YY as applicable. Pressure receptacles shall not be filled after they become due for periodic inspection but may be transported after the expiry of the time limit.

# 13. Add a new packing instruction P2YY as follows:

1211	TACKING INSTRUCTION	1211
P2YY	PACKING INSTRUCTION	P2YY

This instruction applies to UN 3XXX and UN 3YYY

For cylinders, pressure drums and tubes, the general packing requirements of **4.1.6.1** shall be met.

Unless otherwise indicated in these Regulations, cylinders, pressure drums and tubes conforming to:

- (a) The applicable requirements of Chapter 6.2; or
- (b) The national or international standards on the design, construction, testing, manufacturing and inspection, as applied by the country in which the pressure receptacles are manufactured, provided the provisions of 6.2.3 are met; are authorized for the transport of UN 3XXX and UN 3YYY.

For UN 3XXX and UN 3YYY packed in refillable gas receptacles, the maximum test period for periodic inspection shall be 10 years.

Pressure receptacles used for UN 3XXX and UN 3YYY shall not be offered for transport when connected with spray application equipment such as a hose and wand assembly.

The construction materials of the pressure receptacles and their accessories shall be compatible with the contents and shall not react to form harmful or dangerous compounds therewith.

Pressure receptacles shall be so filled that at  $50^{\circ}$ C the non gas phase does not exceed 95% of their water capacity and is not completely filled at  $60^{\circ}$ C. When filled, the internal pressure at  $65^{\circ}$ C shall not exceed the test pressure of the pressure receptacle.

#### **Special packing provisions:**

**PPYY:** Notwithstanding 4.1.6.1.9 (b), non-refillable cylinders used for UN3YYY Pressurized chemical, flammable may have a water capacity in liters not exceeding 1000 divided by the test pressure expressed in bars provided capacity and pressure restrictions of the construction standard are also observed.

### 14. Amend portable tank instruction T50 as follows:

This portable tank instruction applies to non-refrigerated liquefied gases <u>and pressurized chemical UN3XXX and 3YYY.</u>

#### Add UN3XXX and UN3YYY to the instruction as follows:

UN No	Non-refrigerated liquefied gases	Max. allowable working	Openings below liquid level	Pressure-relief requirements	Maximum filling ratio
		pressure (bar)		(see 6.7.3.7)	
<u>UN3XXX</u>	Pressurized	See MAWP	Allowed	<u>Normal</u>	See 4.2.2.7
	chemical, non	definition in			
	<u>flammable</u>	<u>6.7.3.1</u>			
<u>UN3YYY</u>	Pressurized	See MAWP	Allowed	<u>Normal</u>	See 4.2.2.7
	chemical,	definition in			
	<u>flammable</u>	<u>6.7.3.1</u>			

15. Amend 4.2.2.7.2 as follows:

Add:

- a) before the existing text and add a new paragraph:
- b) Portable tanks for Pressurized Chemical, non flammable or flammable (UN3XXX, UN3YYY) shall be so filled that at 50°C the non gas phase does not exceed 95% of their water capacity and is not completely filled at 60°C.
- 16. Amend the headings of chapters 4.2.2 and 6.7.3 and the relevant paragraphs therein, to include "and pressurized chemicals" in addition to the current wording "non-refrigerated liquefied gas".
  - 4.2.2 General provisions for the use of portable tanks for the transport of non-refrigerated liquefied gases <u>and pressurized chemicals</u>
  - 6.7.3 Requirements for the design, construction, inspection and testing of portable tanks intended for the transport of non-refrigerated gases <u>and pressurized chemicals</u>

Annex

Pressure receptacle for pressurized chemical

