

**Committee of Experts on the Transport of Dangerous Goods  
and on the Globally Harmonized System of Classification  
and Labelling of Chemicals**

27 November 2015

**Sub-Committee of Experts on the Transport of  
Dangerous Goods**

**Forty-eighth session**

Geneva, 30 November – 9 December 2015

Item 10 (c) of the provisional agenda

**Issues relating to the Globally Harmonized  
System of Classification and Labelling of  
Chemicals: classification criteria for flammable  
gases**

**Sub-Committee of Experts on the Globally Harmonized  
System of Classification and Labelling of Chemicals**

**Thirtieth session**

Geneva, 9-11 December 2015

Item 2 of the provisional agenda

**Joint work with the Sub-Committee of Experts on the  
Transport of Dangerous Goods (TDG Sub-Committee)**

## **Low-burning substances and climate change**

### **Transmitted by the European Chemical Industry Council (CEFIC)**

#### **The Montreal Protocol and the Climate Change Convention**

1. The ozone depletion in the stratosphere has clearly been related to the emissions of Chlorinated substances. The Montreal Protocol (1987) and its amendments have led to the phase-out of most ozone depleting substances for developed and developing countries. Those substances were used in aerosols, solvents, blowing agents, fire extinguishers and refrigeration systems. A number of technical options have been proposed, carefully analysed and finally implemented in the relevant industries. As of 1990, fluorinated substances were proposed as substitutes to the chlorinated ones. In parallel the international community prepared significant agreements in order to mitigate the emissions of Green House Gases (GHGs) in the atmosphere; the Rio Convention in 1992 made mandatory the annual declaration of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O emissions, and the Kyoto Protocol added the fluorinated substances.

2. European regulations as well as USA projects are leading the rapid phase down of High Global Warming Potential (GWP) fluorinated substances leading to a need for new substitutes. Similarly “Article 5” countries under the Montreal Protocol, in general, only receive international funding for HCFC phase out management plans if the plans move away from high GWP substances.

#### **New constraints for molecular design**

3. A new paradigm is at the basis of molecular design for blowing agents used worldwide to manufacture insulation foams (polystyrene and polyurethane) and for refrigerants for all applications. This paradigm features low atmospheric life time in order to benefit from low GWP and low flammability in order to limit possible hazards. This compromise led to a decrease in the number of fluorinated atoms, such as solutions like Difluoro-dihydro-methane or substances with double bond molecules, as well as various isomers of tetrafluoropropene. These substances are currently used and integrated in various blends. They have been designed in order to match the specifications of various uses in terms of flammability and achieving global warming mitigation.

#### **Update of standards**

4. The refrigeration industries have been well aware of the need to find new compromises between the global impact of refrigerants' emissions and the issues related to the use of flammable substances in various applications. As of 1995, a series of tests have been carried out under the auspices of ISO and IEC standard committees in order to establish a more appropriate classification between higher and lower flammable substances. In the past the US ASHRAE-34 Standard as well as ISO 5149:1993 and EN 378:2008 made a difference on flammability based on the Lower Flammability Limit and/or the Heat of Combustion. One of the objectives was to differentiate ammonia, which is poorly flammable, from highly flammable gases. The new tests showed that an additional criterion was adequate for an improved flammability classification: Burning Velocity. The burning velocity is "*the rate at which energy is released by the chemical reactions associated with combustion*" (S. Davis).

5. Burning Velocity of flammable substances has been measured for a long time in many different applications; what was new was the measurement of Burning Velocity of lower flammable substances that were historically of no interest for experts in flammability. ASHRAE 34, since 2010, as well as ISO 817:2014 have both adopted the threshold of 10 cm/s Burning Velocity to differentiate lower flammable substances from moderately flammable ones. The videos presented at the IWG meeting in September 2015 clearly demonstrate the wide range of flammability among gases.

#### **Method of tests for burning velocity and related properties**

6. Several methods of tests have been developed to measure Burning Velocity: the vertical tube method, which is the current reference of ASHRAE 34 and ISO 817, and the spherical volume method. Both are based on the measurement of propagation of the flame front. For nearly all highly flammable substances the scientific literature provides values of the Burning Velocity that are consistent independently of the method-of-test used. The only new question is related to substances with a very low Burning Velocity (lower than 4 cm/s), which require the most precise method of test namely the spherical volume method. However this does not constitute a challenge for the proposed 10 cm/s threshold.

7. It should be stressed that other properties are related to the Burning Velocity such as the Minimum Ignition Energy (MIE) and the Quenching Distance ( $d_Q$ ). Quenching distance and MIE are measured since many years by the ASTM Standard E-582-07 and those values are used in many different technical fields.

8. In a recent scientific paper, Dr. Takizawa presented how the ASTM apparatus can be used in a simple Go / No Go test to differentiate flammability of substances. This is because the test is well known, used in many laboratories worldwide and simpler than the direct Burning Velocity measurement methods.

#### **Possible evolution of GHS classification**

9. All the above elements indicate the need for an update of GHS flammable gas classification. It is acknowledged that the implementation of a new method of tests or the validation of a known method of test for a new purpose usually takes time. The creation of a sub-category 1b in order to differentiate low burning substances using the current GHS criteria, with a LFL more than 6% or a burning velocity less than 10 cm/s is simple and allows for the evolution of test methods.

### References

- ANSI:ASHRAE Standard 34-2013 Designation and safety classification of refrigerants, <https://www.ashrae.org/standards-research--technology/standards--guidelines/standards-activities/ashrae-refrigerant-designations>
  - ASTM E582-07 Standard test method for minimum ignition energy and quenching distance in gaseous mixtures, <http://www.astm.org/Standards/E582.htm>
  - ISO 817 Refrigerants – Designation and safety classification – 2014-05-15, [http://www.iso.org/iso/iso\\_catalogue/catalogue\\_tc/catalogue\\_detail.htm?csnumber=52433](http://www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=52433)
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  - Videos presented at the IWG meeting in September 2015: <https://vimeo.com/146174877> (high resolution); <https://vimeo.com/146176112> (low resolution); password: Uj33eJ4ZPw
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