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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**

**Fifty-seventh session**

Geneva, 30 November-8 December 2020  
Item 5 (b) of the provisional agenda

**Transport of gases: miscellaneous**

Gas mixtures containing fluorine (UN 1045)

Transmitted by the expert from Germany[[1]](#footnote-2)

Revision

Introduction

1. During the online informal discussions of the Sub-Committee held in June/July 2020 the proposal of document ST/SG/AC.10/C.3/2020/11 received comments from several experts. Some asked for more information on the technical reasoning for establishing 35 % as limit in paragraph 6.

2. The 35 % limit is a long-standing safety practice in many countries, stated in the EIGA-Code 140/18, last two paragraphs in clause 5.2.5:

*“Mixtures of less than 35% fluorine are less reactive than pure fluorine at a pressure that corresponds to the fluorine partial pressure in the mixtures. Because of the decreased reactivity potential, a concentration of 35% is used as a threshold concentration below which different design criteria are used (materials of construction, shielding, etc.). Mixtures of greater than 35% fluorine in inert gas shall be handled in systems designed for 100% fluorine.”*

3. The document is harmonized among the European Industrial Gas Association (EIGA), the Compressed Gas Association (CGA) and the Japan Industrial and Medical Gases Association (JIMGA). Studies as measurements of pressure-dependent ignition temperatures of bottle and valve materials or similar seem to be not available. Therefore, the proposal should include this internationally accepted limit.

4. Fluorine is a strongly oxidizing gas requiring specific safety measures. It reacts spontaneously with almost all organic materials and many metals. Thus, steel pressure receptacles, for example, have to be passivated before they are filled.

5. Due to the strong chemical reactivity of fluorine, the UN Model Regulations (P200) limit the maximum allowable working pressure for gas cylinders to 30 bar. In addition, a minimum test pressure of 200 bar is required.

6. Unfortunately, the UN Model Regulations do not contain any guidance on the maximum allowable working pressure and minimum test pressure for mixtures containing fluorine and gases that are inert towards fluorine, such as nitrogen. In practice, these mixtures are placed on the market and used. Typical mixtures that are commercially available include 1 % fluorine in noble gases and 10 % or 20 % fluorine in nitrogen.

7. Mixtures of fluorine and inert gases are less reactive towards materials than pure fluorine. For this reason, the maximum allowable working pressure may exceed 30 bar.

Proposal

8. Gas mixtures containing 35 % fluorine or more shall be treated like pure fluorine.

9. For mixtures of fluorine and nitrogen, the maximum allowable working pressure shall be chosen so as to ensure that the partial pressure of fluorine in the mixture does not exceed 31 bar (abs.). For mixtures of fluorine and noble gases, the coefficient of nitrogen equivalency (Kk) in accordance with ISO 10156:2017 shall also be taken into account.

10. The minimum test pressure of the pressure receptacle to be used for a fluorine mixture shall continue to be 200 bar.

11. Based on proposals 5 to 7 above, it is suggested that the following text be added to paragraph (5) z of P200:

“Mixtures of fluorine and nitrogen with a fluorine concentration below 35 % by volume may be filled in pressure receptacles up to a maximum allowable working pressure for which the partial pressure of fluorine does not exceed 31 bar (abs.).

working pressure [bar] < 31/xfluorine - 1  
with xfluorine = fluorine concentration in % by volume/100

Mixtures of fluorine and inert gases with a fluorine concentration below 35 % by volume may be filled in pressure receptacles up to a maximum allowable working pressure for which the partial pressure of fluorine does not exceed 31 bar (abs.), additionally taking the coefficient of nitrogen equivalency in accordance with ISO 10156:2017 into account when calculating the partial pressure.

working pressure [bar] < (31/xfluorine) \* (xfluorine + Kk\*xk) - 1

xfluorine = fluorine concentration in % by volume/100  
Kk = coefficient of equivalency of an inert gas relative to nitrogen (coefficient of nitrogen equivalency)  
xk = inert gas concentration in % by volume/100

However, the working pressure for mixtures of fluorine and inert gases shall not exceed 200 bar. The minimum test pressure of pressure receptacles for mixtures of fluorine and inert gases equals 1.5 times the working pressure or 200 bar, with the greater value to be applied.”

1. 2020 (A/74/6 (Sect.20) and Supplementary, Subprogramme 2) [↑](#footnote-ref-2)