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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

Thirtieth session
Geneva, 4-12 (a.m.) December 2006
Item 2(a) of the provisional agenda

**PROPOSALS OF AMENDMENTS TO THE RECOMMENDATIONS
ON THE TRANSPORT OF DANGEROUS GOODS**

Model Regulations on the Transport of Dangerous Goods

P200 filling ratio and working pressure amendments

Transmitted by the Compressed Gas Association (CGA)

Introduction

1. At the twenty-ninth session, a proposal from the expert from the United States of America to increase the filling ratio values for six entries in P200 was adopted (see ST/SG/AC.10/C.3/2006/41 and ST/SG/AC.10/C.3/58, paragraph 30).
2. As described in ST/SG/AC.10/C.3/2006/41, the proposal was based on the results of an independent study commissioned with the United States National Institute of Standards and Technology (NIST) to review the P200 filling ratio values on the basis of the filling criteria provided in P200 and the applicable physical properties of the gases.
3. Also based on the results of that NIST report, *Calculation and Verification of Filling Ratios for Liquefied Gases* (DTRS56-02-X-0049), CGA submitted INF.26 for the twenty-ninth session, introducing additional proposals for increased filling ratio values for tungsten hexafluoride (UN 2196) and dichlorosilane (UN 2189) in P200. In UN/SCETDG/29/INF.26, GE.06-

CGA also proposed to decrease the maximum working pressure value for nitric oxide, compressed (UN 1660) in P200.

4. CGA would like to re-submit those proposals for consideration, as follows.

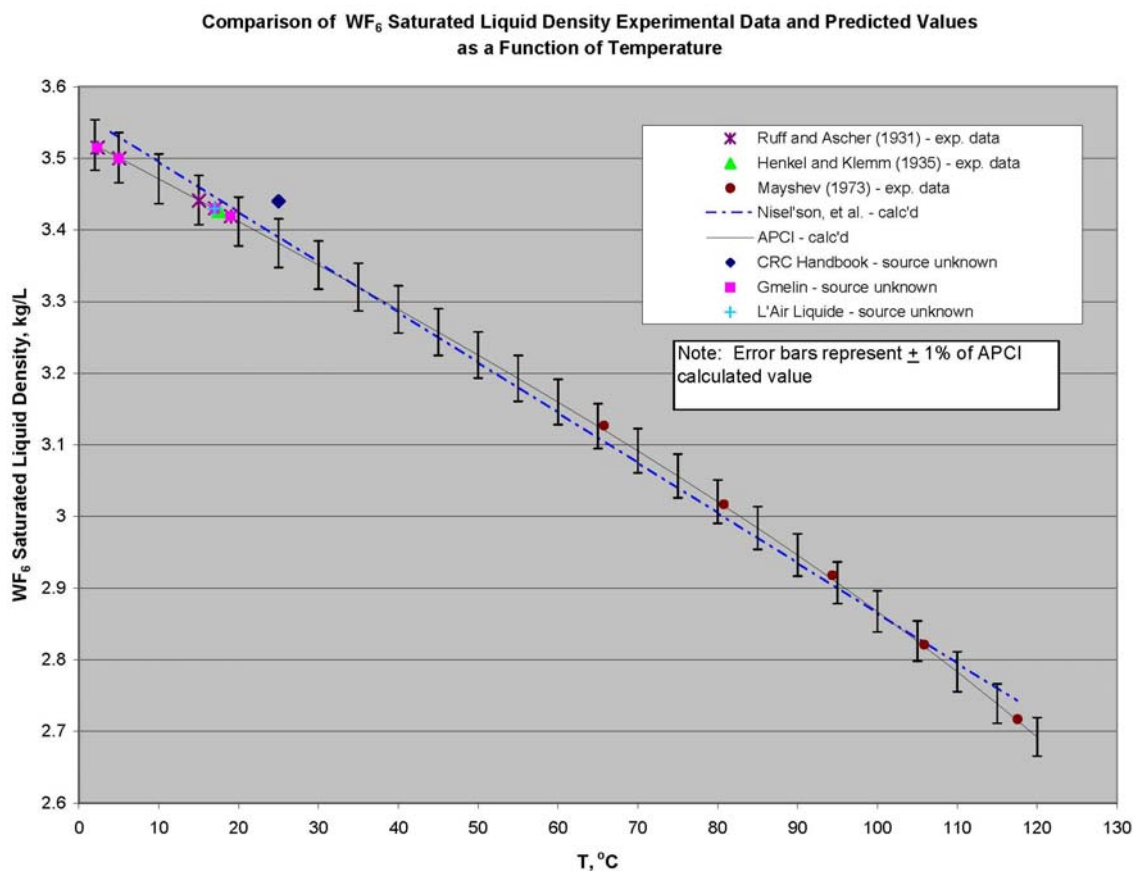
Tungsten hexafluoride (UN 2196)

5. For more than 20 years, tungsten hexafluoride has been safely filled and transported at a filling ratio of 3.19, in accordance with the regulatory requirements of U.S. 49 CFR.

6. In the NIST report, the computed filling ratio for tungsten hexafluoride in a pressure receptacle with a test pressure of 10 bar is 3.13. NIST indicates that there is less than 3% uncertainty in the density value used for this computation.

7. The following shows that a filling ratio of 3.08 is in accordance with the requirements of P200(3)(c):

Subsequent to the NIST report, additional reference data was obtained and compared, resulting in tungsten hexafluoride density values with increased accuracy and less uncertainty. (See the figure below.)



From this data, tungsten hexafluoride, a low pressure liquefied gas, has densities and consequent P200(3)(c) filling conditions as follows:

- Density at 50°C = 3.24 kg/l

$$\begin{aligned} \text{Filling ratio} &= 95\% \text{ density of tungsten hexafluoride at } 50^\circ\text{C} / \text{density of water at } 15^\circ\text{C} \\ &= 0.95 * 3.24 \text{ kg/l} / 0.99910262 \text{ kg/l} \\ &= 3.08 \end{aligned}$$

- Density at 60°C = 3.17 kg/l

$$\begin{aligned} \text{Filling ratio} &= 3.17 \text{ kg/l} / 0.99910262 \text{ kg/l} \\ &= 3.17 \end{aligned}$$

Choosing the lesser of the above two values, the filling ratio for tungsten hexafluoride is 3.08.

At a filling ratio of 3.08, the pressure in the cylinder at 65°C will be 69.9 psia, which is not greater than the pressure receptacle minimum test pressure specified in P200 (i.e. 10 bar = 145 psig ≈ 160 psia).

8. Proposal

In P200, Table 2, increase the filling ratio for UN 2196 (tungsten hexafluoride) from 2.70 to 3.08, for a pressure receptacle with a minimum test pressure of 10 bar:

UN No.	Name and description	Class or Division	Subsidiary risk	LC ₅₀ ml/m ³	Cylinders	Tubes	Pressure drums	Bundles of cylinders	MEGCs	Test period, years	Test pressure, bar	Filling ratio	Special packing provisions
2196	TUNGSTEN HEXAFLUORIDE	2.3	8	160	X			X		5	10	2.70 <u>3.08</u>	a, k

Dichlorosilane (UN 2189)

9. For more than 20 years, dichlorosilane has been safely filled and transported at a filling ratio of 1.11, in accordance with the regulatory requirements of U.S. 49 CFR, in cylinders with test pressures ranging from 32 to 250 bar, commonly 200 bar.

10. In the NIST report, the computed filling ratio for dichlorosilane in a pressure receptacle with a test pressure of 10 bar is 1.10. NIST indicates that there is less than 3% uncertainty in the density value used for this computation.

11. The following calculations show that a filling ratio of 1.08 is in accordance with the requirements of P200(3)(c).

Review of existing reference data indicates that dichlorosilane, a low pressure liquefied gas, has densities and consequent P200(3)(c) filling conditions as follows:

- Density at 50°C = 1.143 kg/l

$$\begin{aligned} \text{Filling ratio} &= 95\% \text{ density of dichlorosilane at } 50^{\circ}\text{C} / \text{density of water at } 15^{\circ}\text{C} \\ &= 0.95 * 1.143 \text{ kg/l} / 0.99910262 \text{ kg/l} \\ &= 1.087 \end{aligned}$$

- Density at 60°C = 1.119 kg/l

$$\begin{aligned} \text{Filling ratio} &= 1.119 \text{ kg/l} / 0.99910262 \text{ kg/l} \\ &= 1.120 \end{aligned}$$

Choosing the lesser of the above two values, and rounding down to the nearest hundredth (as with the other filling ratio values in P200, Table 2), the filling ratio for dichlorosilane is 1.08.

At a filling ratio of 1.08, the pressure in the cylinder at 65°C will be 82.9 psia, which is not greater than the pressure receptacle minimum test pressure currently specified in P200 (i.e. 10 bar = 145 psig \approx 160 psia).

12. Proposal

In P200, Table 2, add a second test-pressure/filling-ratio entry for UN 2189 (dichlorosilane), specifying a filling ratio of 1.08 for a pressure receptacle with a minimum test pressure of 200 bar:

UN No.	Name and description	Class or Division	Subsidiary risk	LC ₅₀ ml/m ³	Cylinders	Tubes	Pressure drums	Bundles of cylinders	MEGCs	Test period, years	Test pressure, bar	Filling ratio	Special packing provisions
2189	DICHLOROSILANE	2.3	2.1 8	314	X	X	X	X	X	5	10 <u>200</u>	0.90 <u>1.08</u>	

Nitric oxide, compressed (UN 1660)

13. On February 1, 1963, when the valve on a 44-litre source cylinder of nitric oxide was opened, the cylinder violently ruptured, killing the operator. The operator was preparing to transfill partially the contents from the 44-litre cylinder into a lecture bottle. The investigation determined that the lecture bottle valve was not open, which caused the gas in the small volume of piping to heat up significantly from the rapid build-up of pressure. The rapid heating caused

the nitric oxide to decompose. The decomposition reaction continued back into the source cylinder, causing it to rupture into four pieces.

14. The investigation discovered a report that noted theoretical decomposition of nitric oxide can cause up to a 15-fold increase in pressure. However, the decomposition reaction requires significant energy to initiate it. In a test cylinder of nitric oxide, a blasting cap was used to trigger decomposition, which led to a 12-fold pressure increase. With a filling pressure of 800 psig (55 bar), the final pressure in the source cylinder may have reached 9600 psig (662 bar).

15. Since the incident in 1963, industry has generally been using a filling density for nitric oxide of 0.0439 kg/l, resulting in a reduced final filling pressure of 500 psig (34 bar) at 70°F (21 °C).

16. The thermodynamic calculation for complete decomposition of nitric oxide at a filling pressure of 500 psig (34 bar) (i.e. 1.93 kg of nitric oxide in a 44-litre cylinder) results in a final pressure of approximately 5250 psig (362 bar). This is around the minimum burst pressure for a cylinder with a test pressure of 225 bar.

17. Proposal

In P200, Table 1, decrease the maximum working pressure for UN 1660 (nitric oxide, compressed) from 50 bar to 33 bar, and increase the minimum test pressure of the pressure receptacle from 200 bar to 225 bar:

UN No.	Name and description	Class or Division	Subsidiary risk	LC ₅₀ ml/m ³	Cylinders	Tubes	Pressure drums	Bundles of cylinders	MEGCs	Test period, years	Test pressure, bar ^a	Maximum working pressure, bar ^a	Special packing provisions
1660	NITRIC OXIDE, COMPRESSED	2.3	5.1 8	115	X			X		5	200 <u>225</u>	50 <u>33</u>	k, o