**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

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TRANSPORT OF GASES

P200 Filling ratio and working pressure amendments

Transmitted by the Compressed Gas Association (CGA)

**Introduction**

1. In ST/SG/AC.10/C.3/2006/41, the expert from the United States of America proposes to increase the filling ratio values for six entries in P200. CGA supports this proposal.

2. As described in ST/SG/AC.10/C.3/2006/41, the proposal is 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. Based on the results of the NIST final report, *Calculation and Verification of Filling Ratios for Liquefied Gases* (DTRS56-02-X-0049), CGA would like to submit additional proposals for increased filling ratio values for tungsten hexafluoride (UN 2196) and dichlorosilane (UN 2189) in P200.

4. CGA would also like to submit a proposal to decrease the maximum working pressure value for nitric oxide, compressed (UN 1660) in P200.

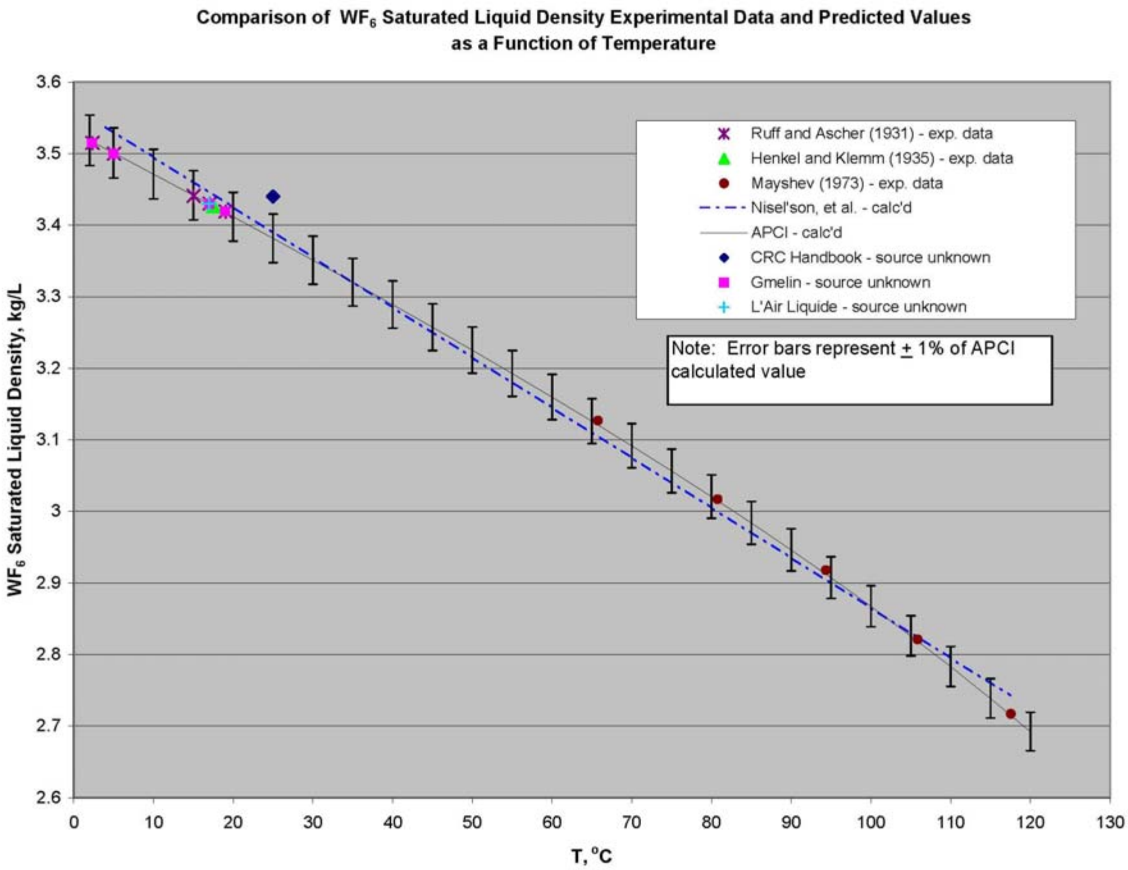
**Tungsten hexafluoride (UN 2196)**

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

  Filling ratio = 95% density of tungsten hexafluoride at 50°C / density of water at 15°C
  = 0.95 * 3.24 kg/l / 0.99910262 kg/l
  = 3.08

- Density at 60°C = 3.17 kg/l

  Filling ratio = 3.17 kg/l / 0.99910262 kg/l
  = 3.17

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 | Specail packing provisions |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2196 | TUNGSTEN HEXAFLUORIDE | 2.3 | 8 | 160 | X | | | X | | 5 | 10 | ~~2.70~~ <u>3.08</u> | a, k |

**<u>Dichlorosilane (UN 2189)</u>**

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

  Filling ratio = 95% density of dichlorosilane at 50°C / density of water at 15°C
  = 0.95 * 1.143 kg/l / 0.99910262 kg/l
  = 1.087

- Density at 60°C = 1.119 kg/l

  Filling ratio = 1.119 kg/l / 0.99910262 kg/l
  = 1.120

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 ≈ 160 psia).

12. <u>Proposal</u>

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 | Specail packing provisions |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2189 | DICHLOROSILANE | 2.3 | 2.1<br>8 | 314 | X | X | X | X | X | 5 | 10<br>200 | 0.90<br>1.08 | |

**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] | Specail packing provisions |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1660 | NITRIC OXIDE, COMPRESSED | 2.3 | 5.1<br>8 | 115 | X | | | X | | 5 | ~~200~~<br>225 | ~~50~~<br>33 | k, o |

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