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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

Twenty-ninth session
Geneva, 3-12 (a.m.) July 2006
Item 3 of the provisional agenda

TRANSPORT OF GASES

Filling ratio for germane

Transmitted by the Compressed Gas Association (CGA)

Introduction

1. At the twenty-eighth session, the expert from the United States of America proposed that the P200 filling ratios for certain gases be decreased (see ST/SG/AC.10/C.3/2005/55). This proposal was based on 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.
2. In ST/SG/AC.10/C.3/2005/55, it was proposed that the filling ratio for UN 2192 (germane) be decreased from 1.02 to 1.00. At the twenty-eighth session, there was some discussion that the filling ratio for germane should actually be decreased further, based on industry experience and the possible decomposition of the gas. As a result, the proposal to decrease the filling ratios for certain gases was adopted, with the exception of UN 2192 (germane)

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for which the proposed value of 1.00 was placed in square brackets (see ST/SG/AC.10/C.3/56, paragraph 10).

Discussion

3. After an incident on November 26, 1984, at a facility in Japan, it was determined that pure germane can deflagrate when ignited with a spark in the absence of air, decomposing exothermically to germanium metal and hydrogen.
4. Immediately following this incident, a CGA member company limited the filling ratio of germane to 0.062 based on the test pressure of the cylinder and theoretical calculations assuming full adiabatic decomposition. In these calculations, it was conservatively assumed that all of the energy went into heating the hydrogen produced.
5. Testing was later conducted by Hazards Research Corporation. Based on the equation from Hazards Research Corporation's report no. 6023, "Germane Deflagration Study", dated April 11, 1986, the maximum filling ratio of germane should be 0.096 for a cylinder with a test pressure of 250 bar. This is based on some of the decomposition energy going to melting of the germanium as well as heating of the hydrogen produced. Testing by others closely matched these results and confirmed these calculations.
6. Since the incident in 1984, industry has generally been specifying maximum filling ratios ranging from 0.045 (based on the working pressure of the cylinder filled) to 0.064 (based on the test pressure of the cylinder filled), along with an additional safety margin for actual filling. A survey of germane suppliers indicates that, currently, the actual highest filling ratio being used is 0.053, which is based on a specified maximum filling ratio of 0.064 for a 250-bar-test-pressure cylinder. This specified maximum filling ratio of 0.064 is two thirds of the maximum filling ratio value calculated above in accordance with test data (i.e. 0.096).
7. It should be noted that a maximum filling ratio of 0.064 for a 250-bar-test-pressure cylinder is just one data point, and higher filling ratios could be considered for cylinders with higher test pressures.
8. Possible decomposition of gas mixtures containing germane also need to be addressed. However, experimental testing has shown that mixtures in helium or argon containing up to 28% germane and mixtures in hydrogen or nitrogen containing up to 35% germane will not deflagrate in the presence of a source of ignition. References include the following two papers by S. Horiguchi, Y. Urano, and S. Kondo:
 - **"Decomposition explosion hazards of semiconductor manufacturing gases"**, *Journal of High Pressure Gas Safety Institute of Japan*, 28(3), pp 270-284, 1991.
 - **"Decomposition explosion hazards of semiconductor manufacturing gases"**, *Journal of High Pressure Gas Safety Institute of Japan*, 28(5), pp 351-363, 1991.

Current industry practice for filling cylinders with germane mixtures takes into consideration decomposition of the germane in accordance with the above mixture percentages.

Proposals

The following amendments to the Model Regulations, 14th revised edition, are proposed:

9. In P200, Table 2, decrease the filling ratio for UN 2192 (germane) from 1.02 to 0.064, for a pressure receptacle with a minimum test pressure of 250 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
2192	GERMANE	2.3	2.1	620	X	X	X	X	X	5	250	1.02 <u>0.064</u>	d, q

10. In P200(4), add a new "gas specific" special packing provision, as follows: "r – The filling ratio of this gas shall be limited such that, if complete decomposition occurs, the pressure does not exceed two thirds of the test pressure of the pressure receptacle."

Also, amend the second paragraph of P200(3)(b), as follows: "The use of test pressures and filling ratios other than those in the table is permitted provided that the above criterion is met, except where (4), special packing provision "o" or "r" applies."

Also consequentially, in P200, Table 2, for the entry for UN 2192 (germane), add "r" in the "Special packing provisions" column:

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
2192	GERMANE	2.3	2.1	620	X	X	X	X	X	5	250	1.02 <u>0.064</u>	d, q, <u>r</u>

11. In P200(4), at the end of special packing provision "z", add a new paragraph, as follows: "Mixtures containing UN2192 germane, other than mixtures of up to 35% germane in hydrogen or nitrogen or up to 28% germane in helium or argon, shall be filled to a pressure such that, if complete decomposition of the germane occurs, two thirds of the test pressure of the pressure receptacle shall not be exceeded".