

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

Model Regulations on the Transport of Dangerous Goods

P200 filling ratio amendment for UN 2676 (stibine)

Transmitted by the Compressed Gas Association (CGA)

Introduction

1. A comprehensive review of the P200 filling ratio values has been undertaken by members of this sub-committee's former gases working group, and many results have been presented this biennium. In continuing to review these filling ratio values, CGA has realized that the filling ratio specified in P200 for UN 2676 (stibine) should be decreased.
2. The details that follow are provided for the information of the sub-committee, and it is intended to re-submit this proposal formally at the next session.

Discussion

3. Stibine (antimony hydride, SbH₃) is thermodynamically unstable at room temperature, decomposing into antimony solids and hydrogen gas:



The decomposition is reported to occur even at temperatures of -60°C, which is well below its boiling point of -18°C.ⁱ In a test conducted in a vacuum (5 torr) and at room temperature, the stibine fully decomposed in 3 days.ⁱⁱ At higher pressures or temperatures, the decomposition is more rapid.

The byproduct antimony will have a negligible volume, while the volume of the hydrogen will be 1.5 times the gaseous volume of the stibine. The process is slow enough that the reaction heat is absorbed by the surroundings (non-adiabatic) and is not considered in the final pressure estimate.

Proposal

4. At the twenty-ninth session, a new special packing provision "r" was adopted, as follows, to apply to UN 2192 (germane):

"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."

Special packing provision "r" should also apply to UN 2676 (stibine).

5. To ensure that the byproducts of full decomposition can be contained and not exceed two thirds of the test pressure of the pressure receptacle, the filling ratio for UN 2676 (stibine) in P200, Table 2, should be decreased from 1.20 to 0.49, and the minimum test pressure of the pressure receptacle should be increased from 20 bar to 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
2676	STIBINE	2.3	2.1	20	X			X		5	20 <u>200</u>	1.20 <u>0.49</u>	k _r

6 To address the possible decomposition of gas mixtures containing stibine, the sixth paragraph of special packing provision "z" should be amended as follows:

"z: ...

Mixtures containing UN 1911 diborane or UN2676 stibine shall be filled to a pressure such that, if complete decomposition of the diborane or stibine occurs, two thirds of the test pressure of the pressure receptacle shall not be exceeded."

ⁱ Todd, M.A., Bandari, G., and Buam, T.H., "Synthesis and Stabilization of Stibine for Low Temperature Chemical Vapor Deposition of Carbon Free Antimony Films", *Chem. Mater.*, 02/02/99, 11, 547-551.

ⁱⁱ Knczkowski, A., Schulz, S., and Assenmacher, W., "Growth of GaSb whiskers by thermal decomposition of a single source precursor", *J. Mater. Chem., The Royal Society of Chemistry*, 2001, 11, 3241-3248.