



COMPRESSED GAS ASSOCIATION, INC.

SAFETY BULLETIN

SB-30—2011

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HAZARDS ASSOCIATED WITH THE DECONTAMINATION, DISPOSAL, OR REQUALIFICATION OF CYLINDERS IN DIBORANE, DIBORANE MIXTURE, AND PENTABORANE SERVICE

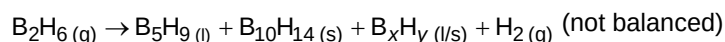
Introduction

The purpose of this bulletin is to raise the awareness of the hazards associated with cleaning of diborane and pentaborane cylinders, and of disposing of or hydrotesting diborane and pentaborane cylinders that have not been properly cleaned. Extreme caution should be observed. Do not dispose of or hydrotest a diborane or pentaborane cylinder unless it has been properly cleaned and decontaminated. It is important to realize that empty cylinders contain hazardous product residue. Diborane, pentaborane, and their decomposition product residue can react with air and water, creating products that could overpressure a cylinder. Serious injury to personnel and property can result. Cylinders can burst emitting highly toxic substances that can cause fatalities. Only specially trained and qualified personnel should attempt to clean or decontaminate a diborane or pentaborane cylinder. Pentaborane has not been commercially available since the 1980s.

Chemistry and hazardous nature of products

Diborane is a compressed gas that is highly toxic and unstable. OSHA lists the Permissible Exposure Limit for an 8-hour Time-Weighted Average (PEL–TWA) of 0.1 ppm (0.1 mg/m³) for diborane. The American Conference of Governmental Industrial Hygienists (ACGIH) has established a Threshold Limit Value–Time-Weighted Average (TLV[®]–TWA) of 0.1 ppm (0.11 mg/m³) [1, 2].

Diborane decomposes slowly into higher boranes and hydrogen at ambient temperature during storage. The amount and rate of decomposition is dependent upon temperature, pressure, and other factors. The decomposition can be described as follows:



Although many higher boranes are formed, the most hazardous decomposition products of diborane are pentaborane, decaborane, and boron hydride polymers.

Pentaborane is a volatile, pyrophoric, highly toxic, and colorless liquid. OSHA lists a PEL–TWA of 0.005 ppm (0.01 mg/m³) for pentaborane. ACGIH has established a TLV–TWA of 0.005 ppm (0.013 mg/m³) and Threshold Limit Value–Short-Term Exposure Limit (TLV[®]–STEL) of 0.015 ppm (0.039 mg/m³). Pentaborane will also decompose into higher boranes.

Decaborane is often recognized by white, needle-like crystals that can appear pale yellow in an impure state. OSHA lists a PEL–TWA of 0.05 ppm (0.3 mg/m³). Decaborane has a TLV–TWA of 0.05 ppm (0.25 mg/m³) and a TLV–STEL of 0.15 ppm (0.75 mg/m³). In addition to the inhalation hazards, decaborane is an extremely toxic dermal poison affecting the central nervous system. The *Registry of Toxic Effects of Chemical Substances* LD₅₀ skin for rabbit is 71 mg/kg [3].

Decaborane can be explosive on contact with flame or heat or with oxygenated or halogenated solvents. Many of these decaborane solutions can decompose very rapidly resulting in a release of heat and hydrogen, often with disastrous results.

All of these higher boranes have the potential to be very reactive and very toxic. Some even form shock-sensitive compounds. Some of these higher boranes react very exothermically with water or base-evolving hydrogen. This combination can create an explosive condition. Others react very slowly with water at ambient temperatures posing a greater risk from their toxicity. Only qualified personnel should handle these chemicals and associated equipment.

Summary

If diborane or pentaborane has been emptied from a cylinder by purging and/or evacuation, the hazards due to decomposition product residue still remain. Cylinders that have been emptied must clearly state that the cylinder was in diborane or pentaborane service. Cylinders must be properly cleaned and decontaminated before processes that require removing the valve from the cylinder including disposal or requalification by hydrotest. Some key points to remember are:

- An "emptied" cylinder could develop considerable pressure over time, due to decomposition of the solid residue. The pressure is due to hydrogen gas, and should be vented properly before attempting to devalue the cylinder;
- A refilled cylinder may develop solid residue accumulation. This accumulation should be monitored and appropriate action taken when accumulation is excessive;
- Purge and evacuate just before devalving; and
- During the cleaning process, never plug or valve a cylinder while water or other solution remains inside.

Never attempt to wash a cylinder with the valve installed unless the consequences of the reaction process are fully understood and provisions are made for the control of pressure so the cylinder does not rupture. The method and the equipment used must be planned, analyzed, tested, and validated to ensure that the process is conducted safely and in an environmentally sound manner. Only specially trained and qualified personnel who are fully aware of all the hazards, proper methods, and equipment should attempt to clean, dispose, or decontaminate a diborane or pentaborane cylinder.

Besides diborane and pentaborane, many other gases are extremely dangerous to handle. One should not attempt to decontaminate, requalify, or remediate gas cylinders without in-depth knowledge of the chemistry, physical properties, toxicity, and hazards of the gas or gases in question and of cylinder and equipment limitations. Refer to CGA P-22, *The Responsible Management and Disposition of Compressed Gases and their Cylinders* for more information [4].

References

[1] *Code of Federal Regulations*, Title 29 (Labor), Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402. www.gpoaccess.gov

[2] *TLVs® and BEIs® Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices*, American Conference of Governmental Industrial Hygienists, 1330 Kemper Meadow Dr., Cincinnati, OH 45240. www.acgih.org

[3] *Registry of Toxic Effects of Chemical Substances (RTECS®)*, Symyx Software, Inc., 2440 Camino Ramon, Suite 300, San Ramon, CA 94583. www.accelrys.com

[4] CGA P-22, *The Responsible Management and Disposition of Compressed Gases and their Cylinders*, Compressed Gas Association, Inc., 4221 Walney Rd., 5th Floor, Chantilly, VA 20151. www.cganet.com