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 **28 November 2011**

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Listing, classification and packing : miscellaneous

Adsorbed Toxic Gases

Transmitted by the Council on Safe Transportation of Hazardous Articles (COSTHA)

Introduction

1. Technology advancements in the areas of toxic gas transportation have resulted in cylinders which operate at a pressure at or below atmospheric conditions. These technologies have been used for several years in the industry to transport toxic gases in an alternate condition to traditional compressed gas or liquefied gas cylinders.

2. Currently, gases transported in these cylinders are classified as Division 2.3 Toxic Gases. However, the nature of the material contained within the cylinder does not meet the definition of a gas (low or negative pressure at 20 ^{o}C). Instead, the material more acts as a toxic solid with vapour emissions at higher temperatures.

3. COSTHA requests comments from the Sub-Committee as to whether these materials meet the definition of a gas and should continue to be offered as a Division 2.3, or whether a better description is available for these consignments. If comments warrant, a formal paper to the Sub-Committee will be prepared for the 41st Session in 2012.

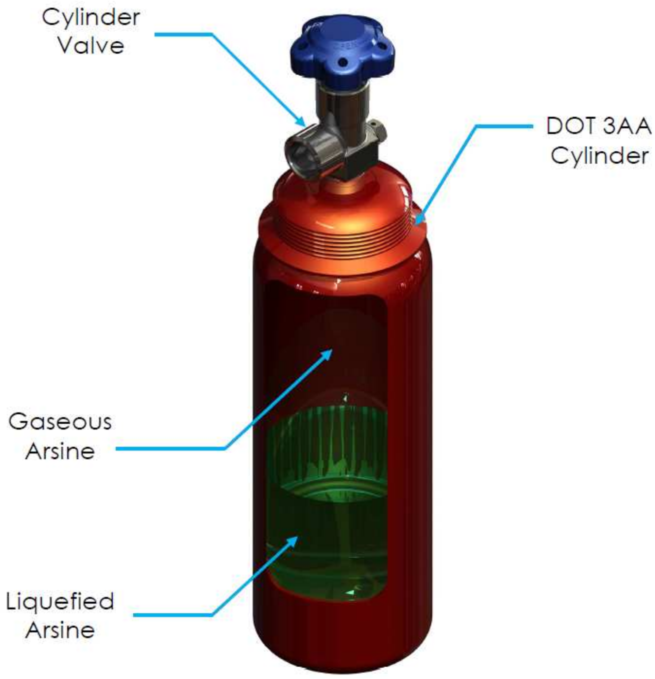
Background

4. Traditionally, gases are compressed or liquefied under high pressures and contained within a pressurized cylinder. Gas under pressure is extremely hazardous as the contents can escape if the cylinder or the valve is damaged during transport, resulting in a release of highly toxic, flammable and/or corrosive gas to the environment. Due to this inherent hazard, the packaging and transportation of hazardous gases is tightly regulated to protect life, property and the environment. In the case of adsorbed gas technology, the gas is adsorbed within a porous, solid material permanently installed in a metal container. The result is a metal container with no pressurized gas at 20 ^{o}C.

5. As an example, transport of Arsine gas is provided.

6. Arsine is a highly toxic (IDLH = 3 ppm) and flammable liquefied gas. In conventional packaging the gas is contained in a UN specification high pressure specification cylinder at 205 PSIG. The arsine in the high pressure cylinder is present in both the liquid and gas phase. The majority of the gas is liquefied. An example of this type of package is shown in Figure 1.

Figure 1



7. In an adsorbed gas container, the arsine is in a substantially different state as it is no longer liquefied but in adsorbed phase due to the addition of an activated carbon adsorbent to the cylinder (See Figure 2). The presence of the adsorbent significantly changes the thermochemical properties of the arsine, most notably the effective vapour pressure and boiling point of the arsine. In other words, the arsine is no longer a gas as the intermolecular forces normally present in the arsine have been perturbed by the adsorbent greatly reducing the normal kinetic energy of the molecule. Table 1 shows the difference in these properties for standard sizes of the two types of gas packages.

Figure 2

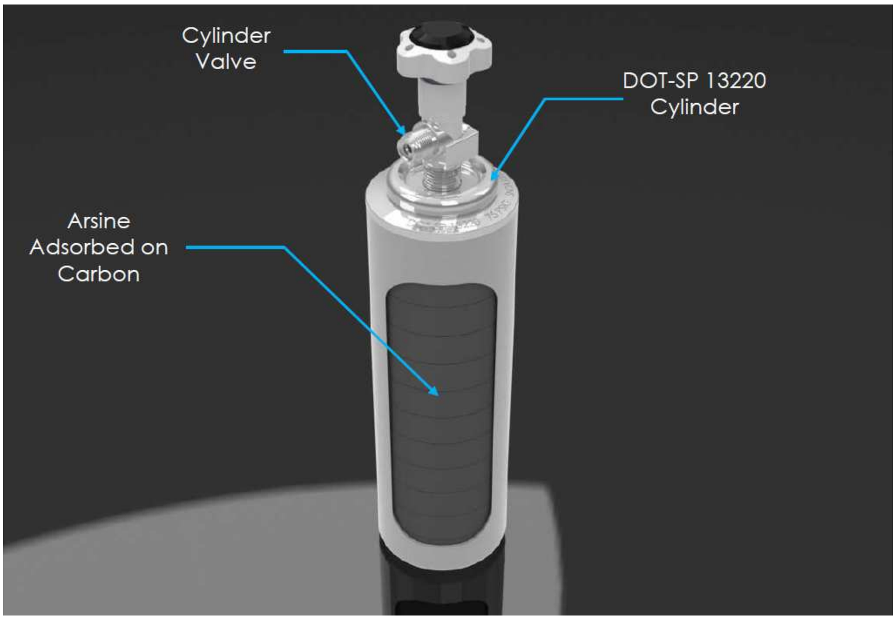


Table 1 - Properties of Arsine and Adsorbed Gas Arsine

Substance	Size of Container	Vapor Pressure @ NTP†	Boiling Point‡
100% Arsine	2 Liter	205 PSIG	-62 □C
Adsorbed Gas Arsine	2 Liter	-5 PSIG	40 □C

†NTP= A temperature of 70 F (21 C) and a pressure of 1 atmosphere [14.7 psia (101.3 kPa)].

‡The boiling point of an element or a substance is the temperature at which the vapor pressure of the liquid equals the environmental pressure surrounding the liquid, normally atmospheric pressure.

8. From a transportation perspective, the differences in the properties shown in Table 1 clearly establish that the two materials are not the same. In fact, the properties of the adsorbed gas arsine are not that of a gas but more closely resemble a high vapor pressure solid or liquid.

9. Further, in reviewing the actual conditions contained within the adsorbed gas container (AGC), the material does not meet the conditions of a gas at all (Table 2).

Table 2 - Justification for adsorbed gas (AG) not Meeting Definition of a Gas

Gas Type	Element	Substantiation
Flammable	Boiling Point < 20 °C	AG Boiling Point is > 20 °C (See Table 1)
Non-Flammable	Pressure > 43.8 psia @ 20 °C	AG Gas Pressure is < 43.8 psia @ 20 °C
Poison	Boiling Point < 20 °C	AG Boiling Point is > 20 °C (See Table 1)

Technology

10. The AGC is based on the reversible adsorption of gases onto a porous media (carbon) contained within a metal cylinder--shown in Figure 2. At NTP (21 ^{o}C and 1 atmosphere) the AGC is at sub-atmospheric pressure and requires an external motive force, e.g., a vacuum, to withdraw the gas from the cylinder. The exposure hazard is significantly reduced as the pressure driver is all but eliminated.

11. Improved sorbent technology incorporated a monolithic, high density microporous carbon disc into container design. This new packaging is currently authorized in the United States under a special permit (DOT-SP 13220), included as Annex 1. DOT-SP 13220 allows the use of a welded metal cylinder with a pressure rating (75 PSIG) consistent with Division 2.3 gases adsorbed at sub-atmospheric pressure. In October 2011, a performance based ISO standard (ISO 11513:2011) was approved for these cylinders.

Proper Shipping Name

12. Today, arsine contained within a AGC ships as a Division 2.3 poison by inhalation hazard gas with a Division 2.1 subsidiary hazard. In reality, the AG arsine is more akin to a toxic solid: the package contains a solid carbon sorbent (approximately 73% by weight) with the arsine molecules associated or bound to the carbon within an extensive pore structure. At NTP, the arsine vapour pressure inside the cylinder is nominally 650 Torr (12.5 PSIA). Hence a description like "arsine adsorbed on carbon", "toxic gas adsorbed on carbon" or "sub-atmospheric pressure arsine (toxic gas) source" would seem like a more appropriate description and carry a corresponding hazard class of 6.1 ascribed to toxic solids.

13. The carbon serving as the adsorbing media is organic, inert, and in the form used, does not meet the definition of a Division 4.2 (spontaneously combustible material). Some of the gases shipped as AG [arsine, phosphine] are flammable but because they are adsorbed, they are self-extinguishing. Backfilling cylinders with air may produce a short lived small flame and smoke at the valve outlet, but not the explosion or fire hazard associated with a compressed gas cylinder.

14. However, we do believe the package could represent a poison by inhalation hazard. An open cylinder, especially one at an elevated temperature can experience a small, partial gas loss (<0.1 to 3%) varying in rate from diffusion to fairly rapid. Gas loss under these circumstances is governed by the adsorption isotherm and is largely a function of temperature and loading density.

15. Alternate existing proper shipping names such as UN2930,Toxic solids, flammable, organic, n.o.s do not identify the material as being poisonous by inhalation. Other entries have also been considered, but suffer similar limitations. For example, UN3383 Toxic by inhalation liquid, flammable, n.o.s. recognizes the inhalation hazard but does not properly describe the physical state of the material; no liquid is contained within an AGC.

Industry Usage

16. The AGC technology is used to provide a safe alternative to pressurized toxic gas transportation to the global semiconductor industry. By replacing high pressure hazardous gases (e.g., arsine, phosphine, boron trifluoride) with an inherently safer gas delivery system, the risk associated with using these highly toxic gases was mitigated. With this hazard diminished, users were more comfortable increasing deliverable quantities, thereby

improving productivity by reducing tool downtime associated with frequent cylinders change-outs.

17. COSTHA welcomes all comments on the technology and possible considerations for classification.

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