United Nations ST/SG/AC.10/C.3/2012/36

Secretariat

Distr.: General
11 April 2012

Original: English

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

Forty-first session
Geneva, 25 June – 4 July 2012
Item 3 (a) of the provisional agenda
Listing, classification and packing:
Proposals of amendments to the list of dangerous goods of Chapter 3.2

Proposal for classification criteria and packing requirements for gases adsorbed on solids

Transmitted by the Council on Safe Transportation of Hazardous Articles (COSTHA)[1]

Introduction

1. The classification of gases adsorbed onto solid porous materials (adsorbents) was discussed at the fortieth session of the Sub-Committee (see informal document INF.42). These materials are Class 2 gases adsorbed onto a non-hazardous solid porous material at less than 101.3 kPa at a temperature of 20 °C.

2. A summary of the comments resulting from the meeting discussions and background information of the packaging technology is included in the annex to this document.

I. Explanation and justification of proposal

A. The Need for a new transport condition for gases adsorbed on a solid

3. A new transport condition for gases adsorbed onto a porous solid should be included in the regulations to accurately describe the physical state of a gas when in the adsorbed

[1] In accordance with the programme of work of the Sub-Committee for 2011-2012 approved by the Committee at its fifth session (refer to ST/SG/AC.10/C.3/76, para. 116 and ST/SG/AC.10/38, para. 16).

state. The physical properties of a gas in the adsorbed state differ significantly from when the gas is in the compressed or liquefied state due to the forces of attraction between the adsorbent and the adsorbed gas molecules. These attractive forces result in a decrease in the energy normally possessed by gas molecules lessening the pressure of the gas compared to when it is the compressed or liquefied state.

4. Several examples of how the adsorbed gas physical state differs from the state of the gas in other transport conditions are as follows:

(a) **Methane** gas can be transported as either a compressed gas or a refrigerated gas depending on how it is packaged and filled. The UN Model Regulations define a compressed gas as a substance which when packaged under pressure for transport is entirely gaseous at -50 °C; this category includes all gases with a critical temperature less than or equal to -50 °C.

In order to package methane as a compressed gas, mechanical energy via a compressor is applied to the gas in order to increase the number of gas molecules that can be contained in a pressure receptacle. To package methane in practical amounts, the gas must be at relatively high pressures, usually > 5000 kPa.

When methane is adsorbed onto a carbon microporous material the gas does not require compression to fill appreciable amounts of gas into the container. For example, when 1.75 Kg of methane is *compressed* into a 50 liter cylinder, the resultant pressure is 5000 kPa whereas the same amount of methane *adsorbed* into a 50 liter container is < 101.3 kPa at 20 °C.

(b) Adsorbed gas packaging is generally more suited to liquefied gases as the properties of these gases favor more efficient adsorption than compressed gases. Similar to the case of a compressed gas, energy must be provided for a gas to liquefy into a container. For example, certain gases can be liquefied by either compressing or cooling the gas during the filling process. Subsequent to liquefaction, the gas will remain liquefied by the force of its own vapor pressure inside the container.

An example of a gas that exhibits significant differences in the adsorbed state vs. the liquefied state is arsine. Arsine is a highly toxic and flammable gas that is an important commodity used in the microelectronics industry to manufacture semiconductor devices. Most consumer electronics, computers and automobiles incorporate electronic circuits that were fabricated using arsine in the manufacturing process. Most of the arsine used in the microelectronic industry is provided using adsorbed gas packaging technology.

A typical liquefied gas package of arsine is a 2.2 liter cylinder containing 1200 grams of the gas under a pressure of 1400 kPa which is the vapor pressure of the liquid at 20 °C. Since arsine has a critical temperature of 99.85 °C the state of the gas is considered to be a low pressure liquefied gas.

When 1200 grams of arsine is packaged in a 2.2 liter cylinder containing a certain adsorbent, the pressure of the cylinder is < 101.3 kPa at 20 °C. The dramatic reduction in pressure of the adsorbed gas package is a result of the interactive forces between the arsine gas and the adsorbent pores. In this example, the arsine is not in a liquefied state, but is in an adsorbed state. In addition to arsine, the following table shows the pressure comparison for several microelectronic gases in both the adsorbed state and liquefied gas state. In each case the pressure in the adsorbed state is significantly less than the liquefied state.

Adsorbed State		Gas Name	Liquified State	
Pressure (kPa)			Pressure (kPa)	
20 °C	55 °C		20 °C	55 °C
86.2	251	Arsine	1516	2965
86.2	252	Phosphine	3495	6550[1]
86.2	234	Boron Trifluoride[2]	5515	6839

[1] Pressure of liquefied phosphine at the critical temperature (51.6 °C).
[2] For a fill ratio of 0.227

B. New Entries to Dangerous Goods List

5. The proposal adds 6 new entries to the Dangerous Goods List to accommodate the different types of gases that can be adsorbed on porous solids. The justification for these entries are as follows:

(a) Six new entries are necessary to assure that a UN number and a shipping name and description are available for each of the class 2 divisions as well as any subsidiary hazard combination associated with the primary hazard.

(b) Generic descriptions were chosen to limit the number of UN numbers needed as there are many gases that can be adsorbed on solids.

(c) The new generic entries will require a technical name in brackets immediately following the new shipping name and description as indicated by special provision **274** in column 6 for the new dangerous good list entries.

(d) Generic entries would appear more plausible than specific entries for each gas as there are > 10 gases routinely packaged in the adsorbed gas package. We anticipate further proliferation of the technology to other gases over time which would result in additional modifications to the regulations each time a new gas is introduced in the adsorbed gas packaging format. A current list of the commercially important gases shipped in the adsorbed gas state include:

Gas Technical Name	UN Number
Arsine	UN2188
Phosphine	UN2199
Germane	UN2192
Chlorine	UN1017
Silicon Tetrafluoride	UN1859
Germanium Tetrafluoride	UN3308
Phosphorus Pentafluoride	UN2198
Phosphorus Trifluoride	UN3308
Arsenic Pentafluoride	UN3308
Hydrogen Selenide	UN2202
Boron Trifluoride	UN1008

C. New Special Provision “XYZ”

6. A new special provision “XYZ” is needed to set forth proper controls to assure the safe packaging and transportation of adsorbed gas packages.

(a) The purpose of the first statement in the new special provision “XYZ” is to provide controls that limit the pressure of the adsorbed gas package. The control specifies that under the conditions of normal temperature and pressure (NTP), the packaging when completely filled and closed will not exceed an absolute internal pressure of 101.3 kPa at 20 °C. The term “thermally equilibrated” assures the entire contents (gas and adsorbent) of the package are at a uniform temperature of 20 °C. Additionally, when the packaging is completely filled and closed, the pressure cannot exceed 300 kPa at 50 °C; and at any time during the normal condition of transport, the internal pressure of the pressure receptacle cannot exceed the working pressure; and at any time, the pressure of the receptacle cannot exceed the test pressure at 65 °C.

(b) The second and third statement of special provision “XYZ” provide controls to make sure the adsorbent is compatible with the gas and cylinder and that the combined adsorbent-gas system is also compatible with the cylinder.

(c) The fourth statement is necessary to specify the unique leak testing required for an adsorbent gas package containing a Class 2 gas which is described in ISO 11513:2011.

(d) The fifth statement specifies the requirements for filling as specified in ISO 11513:2011

(e) The sixth statement specifies the requirements for periodic inspection and test as specified in ISO 11513:2011.

D. New Packing Instruction “P2YY”

7. The new packing instruction “P2YY” is needed to provide packing instructions unique to gas adsorbed on a microporous solid.

(a) The first instruction specifies which cylinders and pressure receptacles are authorized for packaging adsorbed gases. Competent authority approved cylinders are included in a similar fashion to packing instruction P201. Cylinders meeting the requirements of ISO 11513:2011 are included as this design standard enables the use of monolithic adsorbents that require a welded cylinder design. Cylinders meeting the requirements of ISO 9809-1:1999 are included as these are commonly used for adsorbed gas packages employing granular adsorbents that can be filled into standard cylinder openings.

(b) The packing instruction limits the fill pressure of an adsorbed gas package to < 101.3 kPa at 20°C which is an important control to assure that packages are pressureless.

(c) A minimum test pressure of 21.7 bar has been specified which is seven times greater than the internal pressure the cylinder is allowed to develop at 50°C.

(d) A minimum burst pressure of 94.5 bar is equal to that specified in ISO 11513:2011.

(e) For Division 2.3 gases with a LC50 < 200 mg/m^3 (ppm), the requirements specified in special packaging provision “k” in P200 apply to the new packing instruction.

(f) Gas tight plugs or caps are required for pyrophoric gases adsorbed on a porous solid, which is a prudent practice.

(g) Since the current proposal includes gases where the special provisions a-d of P200 would be applied for compressed gases, it is sensible to apply the same provisions when these gases are adsorbed on a solid to assure the ladings are compatible with the container.

(h) A 10 year periodic inspection interval is suggested as the adsorbed gas packages are pressureless and not prone to failure caused by the combination of pressure and mechanical defects in the cylinder.

8. As a result of the previous justifications and comments made at the fortieth session of the Sub-Committee, COSTHA proposes the following amendments to the Model Regulations.

II. Proposals

9. Amend 2.2.1.2 to include a new transport condition of a gas as follows:

“ (e) Gas adsorbed onto a porous solid—a gas which when packaged for transport is adsorbed onto a solid porous material resulting in an internal receptacle pressure of < 101.3 kPa at 20 °C and less than 300 kPa at 50 °C.”

10. Create six new entries (UN 3XXX, UN 3YYY, UN 3AAA, UN 3BBB, UN 3CCC and 3DDD) in Class 2.

(a) Add six new entries to the Dangerous Goods List, as follows:

UN No.	Name and description	Class or Division	Subsi-diary risk	UN Packing group	Special provi-sions	Limited and excepted quantities		Packagings and IBC's		Portable tanks and bulk containers	
								Packaging instructions	Special packing provisions	Instruc-tions	Special provisions
(1)	(2)	(3)	(4)	(5)	(6)	(7a)	(7b)	(8)	(9)	(10)	(11)
3XXX	GAS ADSORBED ONTO A POROUS SOLID, FLAMMABLE, N.O.S.	2.1			274 XYZ	0	E0	P2YY			
3YYY	GAS ADSORBED ONTO A POROUS SOLID, N.O.S.	2.2			274 XYZ	0	E0	P2YY			
3AAA	GAS ADSORBED ONTO A POROUS SOLID, TOXIC, N.O.S.	2.3			274 XYZ	0	E0	P2YY			
3BBB	GAS ADSORBED ONTO A POROUS SOLID, TOXIC, FLAMMABLE, N.O.S.	2.3	2.1		274 XYZ	0	E0	P2YY			
3CCC	GAS ADSORBED ONTO A POROUS SOLID, TOXIC, CORROSIVE, N.O.S.	2.3	8		274 XYZ	0	E0	P2YY			
3DDD	GAS ADSORBED ONTO A POROUS SOLID, TOXIC, OXIDIZING, CORROSIVE, N.O.S.	2.3	5.1 8		274 XYZ	0	E0	P2YY			

(b) Add the six new N.O.S. entries to Appendix A

11. Add a new special provision XYZ in Chapter 3.3

XYZ: This entry applies to gases of Class 2 adsorbed onto a solid porous material inside a pressure receptacle with a closure.

The pressure receptacle containing the adsorbed gas shall be at a pressure less than 101.3 kPa at the time the filled pressure receptacle is closed and thermally equilibrated to 20 °C. The internal pressure of the filled pressure receptacle shall not exceed 300 kPa at 50 °C. At any time during the normal condition of transport, the internal pressure of the pressure receptacle cannot exceed the working pressure of the cylinder. In no case shall the internal pressure at 65 °C exceed the test pressure of the pressure receptacle.

The adsorbent material shall be compatible with the pressure receptacle and does not form harmful or dangerous compounds with the gas to be adsorbed.

The gas in combination with the adsorbent material shall not affect or weaken the pressure receptacle or cause a dangerous effect (e.g. catalyzing a reaction).

The adsorbent material shall not meet the definition of any of the hazard classes in these Regulations.

Each cylinder shall be leak tested using a helium leak test as specified in ISO 11513:2011.

The filling procedure shall be in accordance with Annex A of ISO 11513:2011.

Periodic inspection and test shall be in accordance with Annex B of ISO 11513:2011.

12. Add a new packing instruction P2YY as follows:

P2YY	PACKING INTRUCTION	P2YY
This instruction applies to UN 3XXX, UN 3YYY, UN 3AAA, UN 3BBB, UN 3CCC, UN 3DDD		
1. The following packagings are authorized provided the general packaging requirements of 4.1.6.1 are met. (a) Compressed gas cylinders and gas receptacles conforming to the construction, testing and filling requirements approved by the competent authority. (b) Cylinders constructed in accordance with ISO 11513:2011 and ISO 9809-1:1999 2. The pressure of each filled gas cylinder or receptacle shall be less than 101.3 kPa at 20 °C. 3. The minimum test pressure of the cylinder is 21.7 bar. 4. The burst pressure of the cylinder shall not be less than 94.5 bar. 5. Requirements for adsorbed gas packages containing toxic gases with an LC_{50} less than or equal to 200 ml/m^3 (ppm). (a) Valve outlets shall be fitted with pressure retaining gas-tight plugs or caps having threads matching those of the valve outlets. (b) Each valve shall either be of the packless type with non-perforated diaphragm, or be of a type which prevents leakage through or past the packing. (c) Each pressure receptacle shall be tested for leakage after filling. (d) Each valve shall be capable of withstanding the test pressure of the pressure receptacle and be directly connected to the pressure receptacle by either a tapered thread or other means which meets the requirements of ISO 10692-2:2001. (e) Pressure receptacles shall not be fitted with a pressure relief device.		

6. Adsorbed gas packages containing pyrophoric gases shall be fitted with gas-tight plugs or caps having threads matching those of the valve outlets.

7. The material compatibility special packaging provisions of P200 (a, b, c and d) apply to adsorbed gas packagings for the specific gas being adsorbed.

8. The interval between test periods for periodic inspection shall be 10 years.

13. Amend 6.2.1.1.5 as follows:

The test pressure of cylinders, tubes, pressure drums and bundles of cylinders shall be in accordance with packing instructions P 200, or, for a chemical under pressure, with packing instruction P206. The test pressure of a closed cryogenic receptacle shall be in accordance with packing instruction P203. The test pressure of a metal hydride storage system shall be in accordance with packing instruction P205. <u>The test pressure of the cylinder for a gas adsorbed on a solid shall be in accordance with P2YY.</u>

14. Add ISO 11513:2011 to the table listing UN cylinders in 6.2.2.1.1

Annex

English only

Discussions Held in Previous UN Meeting and General Product Information

In December 2011, COSTHA presented an informal paper (40/INF.42) to the UN/SCETDG on adsorbed toxic gases. Those commenting on INF 42/COSTHA agreed that adsorbed gases were not adequately addressed in the Model Regulations but preferred retaining a classification calling these materials gases rather than [toxic] solids. A formal summary of comments from the meeting was published and is cited below:

Comments from UN/SCETDG COSHTA Informal Paper

ADSORBED TOXIC GASES

(UN/SCETDG/40/INF.42 – COSTHA) **–** In this information paper COSTHA questioned whether adsorbed gas technology was adequately addressed in the Model Regulations through this INF paper. Specifically, COSTHA requested comments from the Sub-Committee as to whether adsorbed gases should be considered gases or whether they more resemble solids. While time was short, Canada and Austria provided specific comments that adsorbed gases are not adequately addressed, and individual entries for such gases may be necessary to adequately address. However both Canada and Austria were adamant that the material was in fact a gas and should, at least at this stage, remain classified as a toxic gas. These comments were in alignment with comments received earlier in the week from CGA and EIGA. The Chairman noted additional comments would be welcome in the margins of the meeting or following the session via email.

Information on the products being considered

Traditionally, gases are compressed or liquefied under high pressure and contained within a pressure rated 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.

Technology advances in the area of gas stabilization have resulted in packaging systems where internal cylinder pressures are at or below atmospheric conditions. The practice of [reversibly] adsorbing the gas onto a porous solid [adsorbent] has grown as a means to transport hazardous gases in a safer condition, relative to traditional compressed gas or liquefied gas cylinders. In practice, end-users apply a vacuum to the cylinder to provide the motive force to reverse the gas/solid complex and to pull the vapor out. The packaging consists of a metal cylinder shell filled with an adsorbent material, an end cap welded to the cylinder shell and a cylinder valve. Figure 1 is an example of an adsorbed gas packaging system.

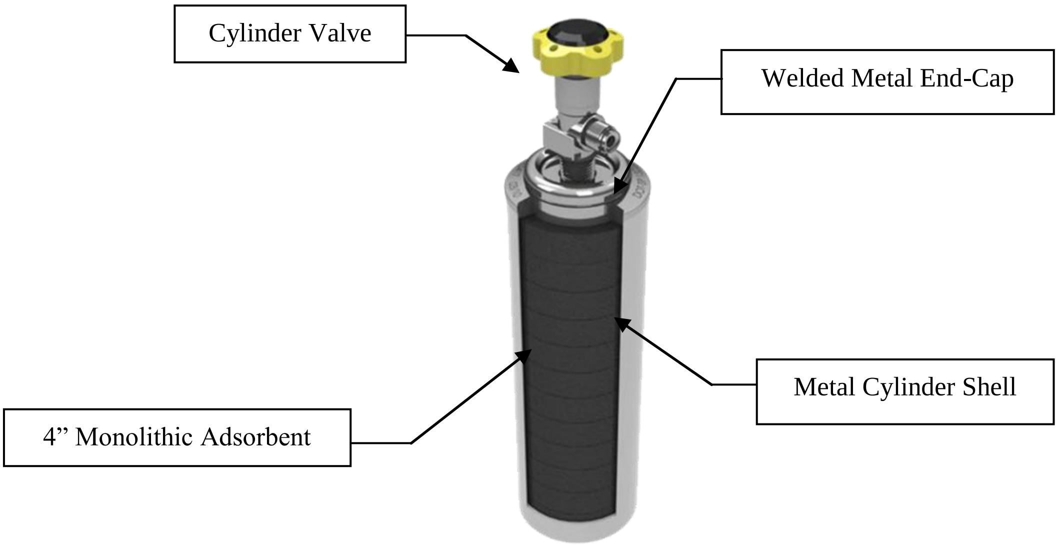

Figure 1

Adsorbed Gas Packaging System

When gases are adsorbed onto a porous solid, the following changes in gas properties and conditions take place.

1. Relative to conventional high pressure gases, when adsorbed on a porous solid, gases exist in a more stable condition within the matrix. Energy is released during the adsorption process. Pressure is dramatically reduced as the gas "complexes" with the solid [typically a highly activated pure carbon]. As a result, the stabilized gas exhibits a reduced chemical reactivity with respect to oxidation and/or deflagration. For example, when germane (UN 2192) is adsorbed on a solid, experiments have shown a deflagration reaction cannot be initiated by an electrical arc. When this same experiment is carried out with pressurized germane, all of the germane decomposes to elemental hydrogen and germanium metal.

2. Maximum pressures expected during transport [50 °C] are low and shown in Figure 2 for a sample of Class 2.3 gases commonly being transported in the adsorbed state. As temperature is increased, the added thermal energy causes some of the adsorbed gas to be desorbed and results in a modest "gas under pressure" condition. Typically this occurs at or above 26 °C. Cooling the cylinder back below this crossover temperature restores the cylinder to a sub-atmospheric pressure state. The maximum pressure reached at 50 °C is ~ 240 kPa (35 psia) for each of the gases

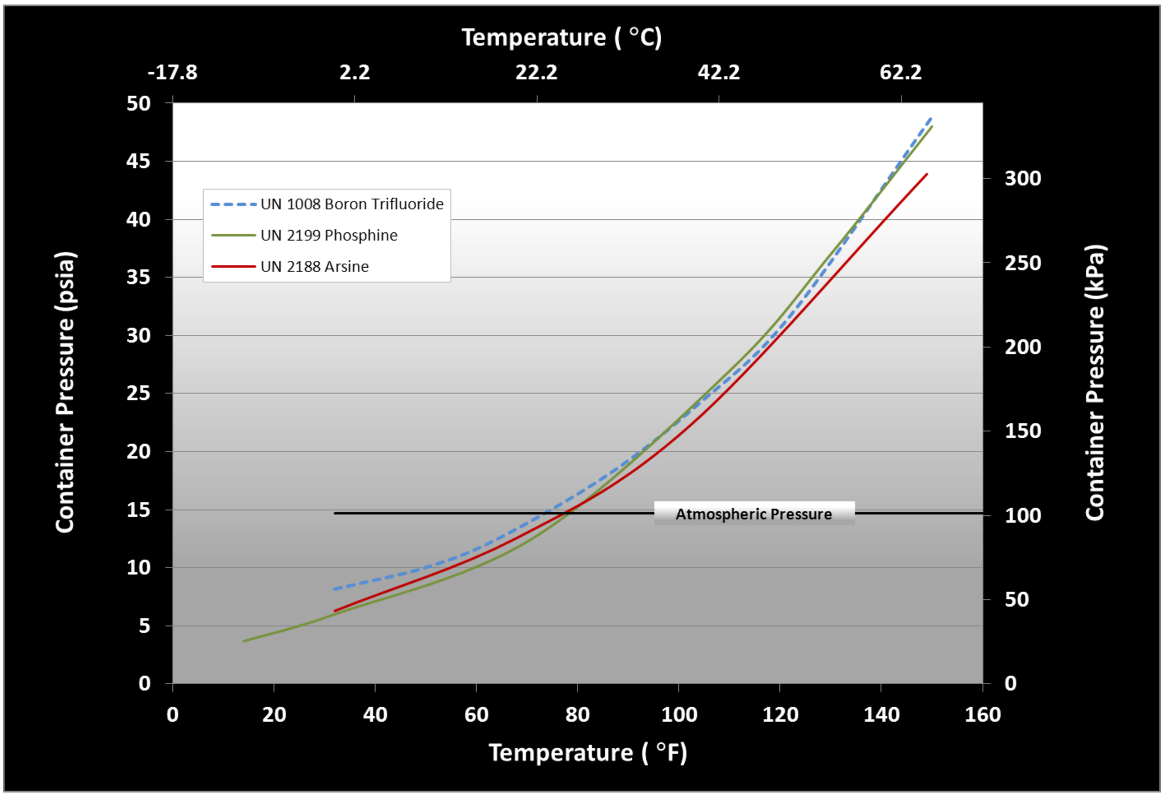

Figure 2

Change in Container Pressure as a Function of Temperature

As the main purpose is to store and transport highly toxic materials, the threat of inhalation and poisoning is present with adsorbed gas packages at temperatures above 26 °C. For that reason, a Class 2 classification is maintained.

3. Another characteristic of adsorbed gases is that only a fraction of the total stored gas inventory would be lost during a release incident. A compressed gas package has the potential to rapidly lose 100% the stored inventory from failed or compromised packaging. In contrast, the adsorbed gas packaging's porous solid exerts attractive forces on the gas and therefore losses to the environment are less. Because the pressure driver is much lower with an adsorbed gas, release rates are also proportionately lower.

4. Adsorbed gas cylinders are less likely to fail in a fire situation because the porous solid acts as both a thermal insulator and a heat sink. In simulated fire testing, cylinders containing gas adsorbed onto a porous solid survived three times longer than comparable high pressure cylinders over a broad range of test temperatures. Figure 3 shows the results of fire testing for standard pressurized liquefied cylinders of phosphine and phosphine adsorbed on a porous solid. The cylinders used in the tests contained equal amounts of phosphine (500 grams) in 2 liter cylinders.

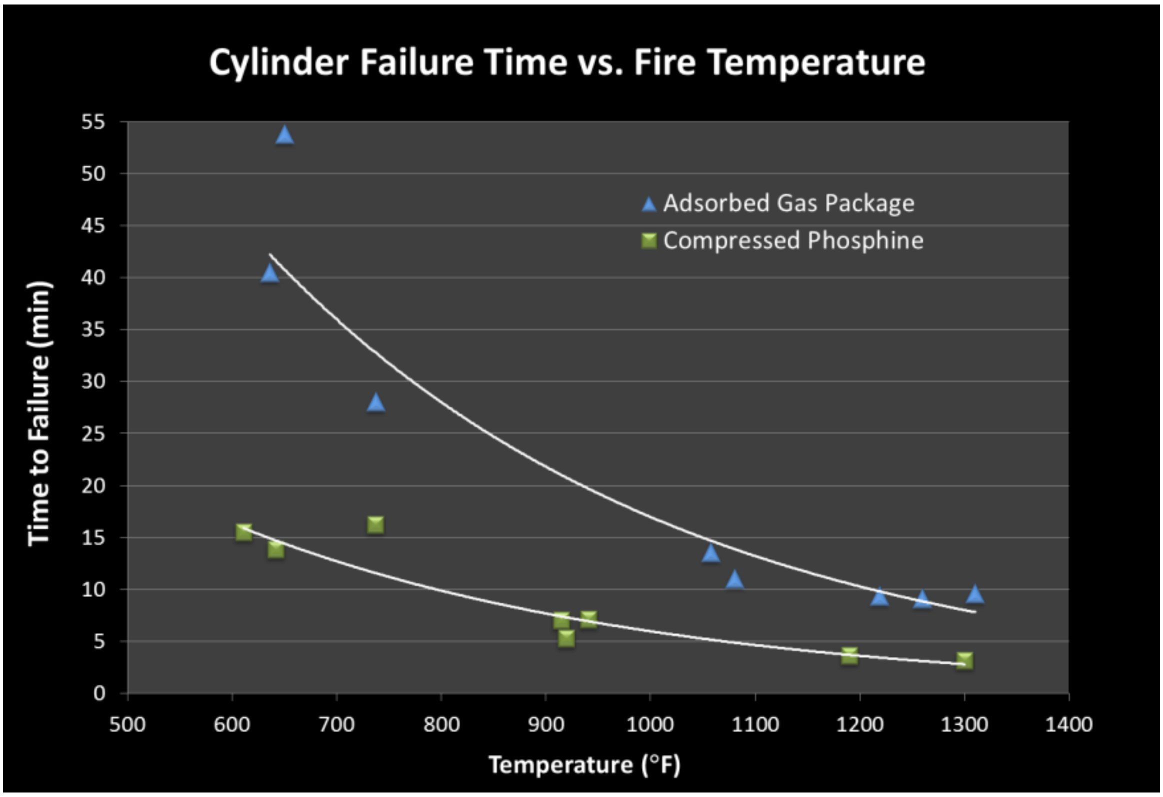

Figure 3

Fire Survivability of Liquefied Phosphine vs. Adsorbed Phosphine

5. The porous solid is typically a high surface area activated carbon. Purity must be high as to not contribute to decomposition of the stored gas. The porous solid can be of many shapes and sizes from granular to shaped monoliths. When shaped sorbents are used, a welded steel cylinder like that specified in ISO 11513:2011 is used for containment. Tests should be run to show the porous solid is stable with any gas to be adsorbed under the conditions of normal transport and use. Figure 4 shows the various adsorbent form factors used in adsorbed gas packagings. The picture shows examples of monolithic, bead, pellet and tablet carbon adsorbents.

6.

Figure 4

Typical Adsorbent Form Factors
