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CODE OF PRACTICE PHOSPHINE

AIGA 051/08

(JIMGA-T—S/37/08/E)

Globally Harmonized Document

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CODE OF PRACTICE PHOSPHINE

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1. Introduction

As a part of a programme of harmonization of industry standards, a working group has been set up under joint lead of AIGA and JIMGA.

Phosphine is a toxic, colourless gas with an odour of decaying fish at room temperature and atmospheric pressure. It is shipped as a liquefied compressed gas under its own vapour pressure of 3.46 MPa. It is also supplied in a gaseous state, diluted with other gases under pressure. It is flammable, pyrophoric and highly toxic.

The use of phosphine has constantly been growing and this usage is expected to continue to escalate throughout the world. The issue of the safe handling of phosphine is a very important and relevant topic to the compressed gas industry as well as the user community of this electronic specialty gas.

Phosphine is used as a doping agent for silicon-based solid-state electronic devices. It is thermally diffused into the silicon layer using furnaces or by an ion implantation system (n-type dopant). It is also used to manufacture compound semiconductors such as light-emitting diodes (LED's) by reaction with a metal organic, such as tri-methyl gallium forming a gallium phosphide layer. Phosphine is also used in the semiconductor industry to grow a capping layer. Phosphine can be inadvertently generated in mining and manufacturing processes involving phosphorous compounds and paints and herbicides containing phosphorous compounds. Phosphine is also used as a fumigant for grain.

Phosphine can be safely handled if equipment is properly designed, maintained and employees are properly trained. As a minimum, all personnel should have access to the phosphine Material Safety Data Sheet (MSDS) and training in the use of the MSDS and other reference material.

Note: In this document, phosphine is understood to be in the gaseous phase unless otherwise stated.

2. Scope and Purpose

2.1 Scope

This document is intended for the suppliers, distributors and users of phosphine and its handling equipment. The document includes guidance for design of equipment, cylinders and valve usage, handling controls and safety. Guidelines on the operational steps associated with the use of phosphine and phosphine mixtures as well as fire protection, gas detection, ventilation and related safeguards are also included. The manufacture, purification and analysis of phosphine are beyond the scope of this documentation, although the general guidance given is also relevant to these processes.

2.2 Purpose

In view of the high toxicity and flammability of phosphine where the consequences of improperly handling of phosphine, could cause injury, death and/or facility damage, this publication has been written. This document will provide a good understanding of the potential hazards involved in handling phosphine and the guidelines to be taken to minimize risk potential.

3. Definitions [1]

Absolute Pressure: is based on a zero reference point, the perfect vacuum. Measured from this reference, the standard atmospheric pressure at sea level is 1.013 bar (101.325 kPa), abs; however, local atmospheric pressure may deviate from this standard value because of weather conditions and the distance above or below sea level.

Apparatus: Accessory equipment, such as valves, pressure relief devices, regulators, non-return valve (check valve) used with compressed gas.

ADR/RID: European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR) and Rail (RID).

Compressed Gas: The definition of a “compressed gas” is not uniformly accepted by all countries and jurisdictions. The definition of United Nations (UN) widely referred is shown below.

(1) UN: A substance or mixture of substances that (1) is a gas at 20 °C (68 °F) or less at an absolute pressure of 0.101 MPa (101.325 kPa, abs) or (14.696 psia) and (2) has a boiling point of 20 °C (68 °F) or less at an absolute pressure of 0.101 MPa (101.325 kPa, abs) or (14.696 psia) and that is liquefied, non-liquefied, or in solution, except those gases that have no other health or physical hazard properties are not considered to be compressed gases until the pressure in the packaging exceed an absolute pressure of 0.280 MPa (280 kPa, abs) or (40.6 psia) at 20 °C (68 °F).

For the reference, the definition of Globally Harmonized Systems (GHS) is also shown as follows.

(2) GHS: Compressed gas means a gas which when packaged under pressure is entirely gaseous at -50 °C; including all gases with a critical temperature \leq -50 °C.

Containers: Vessels of various shapes, sizes, and materials of constructions such as cylinders, portable tanks, or stationary tanks, and of designs meeting the specifications of either the American Society of Mechanical Engineers (ASME), Transport Canada (TC), United States Department of Transportation (DOT), European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR), Japanese Industrial Standard (JIS), or national authorities, and are filled with compressed gases.

Critical Temperature: The critical temperature is the temperature above which the compressed gas cannot exist in the liquid state.

Cylinder: For the purpose of this document, a cylinder is defined as a transportable container having a water capacity that does not exceed 150 litres, that can be filled with a gas under pressure.

Note: For pure phosphine or phosphine mixtures that are classified as highly toxic, some countries prohibit the use of cylinders larger than 57 litres.

Filling Ratio: This is the ratio of the mass of liquefied gas introduced in a container to the mass of water at 15 °C that would fill the same container fitted ready for use. Also known as fill density, filling factor, maximum fill degree, or maximum fill pressure.

Note: (1) For safety reason, filling ratio may be applied to some non-liquefiable gases such as auto-decomposition, e.g. nitrogen trifluoride.

(2) The water capacity stamped on the cylinder may apply to the minimum water capacity designed without internal fittings, in which case, the net water capacity must be ascertained.

Flammable Gas: For the purpose of this document ,a gas is considered flammable when either a mixture of 13 % or less (by volume) with air is ignitable at 0.101 MPa abs or has a flammable range with air of at least 12 % regardless of the lower limit. These limits shall be determined at 0.101 MPa, abs pressure and at a temperature of 20 °C.

Gas Supplier: A business that produces, fills, and/or distributes compressed gases and compressed gas containers.

Handling: Moving, connecting or disconnecting a gas container under normal conditions.

Hazard: Any condition that could potentially cause injury to personnel or property.

Highly Toxic: Gases that have an LC₅₀ in air less than or equal to 200 ppm for a one-hour exposure. See LC₅₀ definition below. National regulations may have additional classifications.

Note: In this document, ppm (parts per million) means ppmv.

Hot Zone: The Hot Zone includes the area immediately around the chemical spill and the surrounding region that may be in serious danger from physical hazards, such as fire or explosion, or chemical exposure. Generally, only fire fighters and emergency response team who are members of a specialized hazmat team will enter the Hot Zone.

Inert Gas: A gas which is not toxic, which doesn't support human breathing and which reacts scarcely or not at all with other substances.

LC₅₀: The median lethal concentration of gas, when administered by continuous inhalation for an hour to 10 albino rats weighing between 200 and 300 grams each, causes death to 50 % of the population within 14 days.

LFL (Lower Flammable Limit or Lower Flammability Limit): The minimum concentration in air of a gas which would burn when ignited. Also referred to as Lower Explosive Limit, LEL.

Material Safety Data Sheet (MSDS): Written or printed information concerning a hazardous material (properties, precautions, etc.) following national regulations. Also referred to as **Safety Data Sheet (SDS)**.

National Standards, Guidelines, Regulations: These are the technical standards set by the regulatory authorities of the country in which the equipment/facility is used, with respect to their design, construction, testing and use. Where available and applicable, these standards shall be followed.

Oxidizer: A substance that in the presence of a fuel, supports and may vigorously accelerate combustion. For example, gaseous oxygen, nitrous oxide or fluorine.

Pressure: The force per unit of area exerted by a gas to its surroundings. The term megapascal (MPa), will be the standard term for pressures used in this document.
1 MPa = 1000 kPa = 20, 885.4 psf = 145 psig = 10 bar.

Pressure Relief Device: A pressure and/or temperature activated device used to prevent the pressure from rising above a predetermined maximum and thereby prevents rupture of a normally charged container when subject to a standard fire test.

Pyrophoric: Materials that can ignite spontaneously in air at a temperature of 54.5 °C (130 °F) or below without an external source of ignition. Regulatory definitions in other jurisdictions may differ.

Shall: The use of the word "shall" in this document implies a strong concern for mandatory instruction.

Should: The use of the word "should" in this document indicates a recommendation.

Tare Weight: The tare weight is the mass of the container and other fittings not removed during the container's fill or use. It would include the valve, dip tube and any permanently or semi-permanently fixed valve protection device.

Test Pressure: The test pressure of a container is the pressure at which the container is hydraulically or pneumatically tested and is the pressure which shall not be exceeded under any foreseeable normal operating conditions (e.g. during filling).

Toxic Gas: A compressed gas that has a LC₅₀ in air of less than or equal to 5,000 parts per million (ppm) but greater than 200 ppm, for a one-hour exposure. National regulations may have additional classifications.

Threshold Limit Value – Time Weighted Average (TLV-TWA): The concentration to which a person may be exposed, 8 hours a day, 40 hours a week, without harm. (This is the definition from ACGIH -American Conference of Governmental Industrial Hygienist).

UFL (Upper Flammable Limit or Upper Flammability Limit): The maximum concentration in air of a gas, which would burn when ignited. Also referred to as Upper Explosive Limit, UEL.

Valve Outlet Caps and Plugs: Removable attachments that usually form a gas-tight seal on valve outlets provided by the gas supplier with certain gases. (Some caps are designed only for valve thread protection and are not gas-tight.)

Valve Protection Cap: A rigid removable cover provided for container valve protection during handling, transportation, and storage.

Valve Protection Device: A device attached to the neck ring or body of the cylinder for the purpose of protecting the cylinder valve from being struck or damaged by impact resulting from a fall or an object striking the cylinder.

4. Gas Properties

4.1 General

Phosphine is a metal hydride gas with the chemical formula PH_3 . It is highly toxic with an established LC_{50} that is less than 200 ppm. In addition to its toxicity, it is also flammable and explosive in air, and can auto ignite at ambient temperatures. It is not considered to be corrosive in the dry gaseous state. It is slightly soluble in water and soluble in most organic solvents. It possesses an odour of decaying fish. [2]

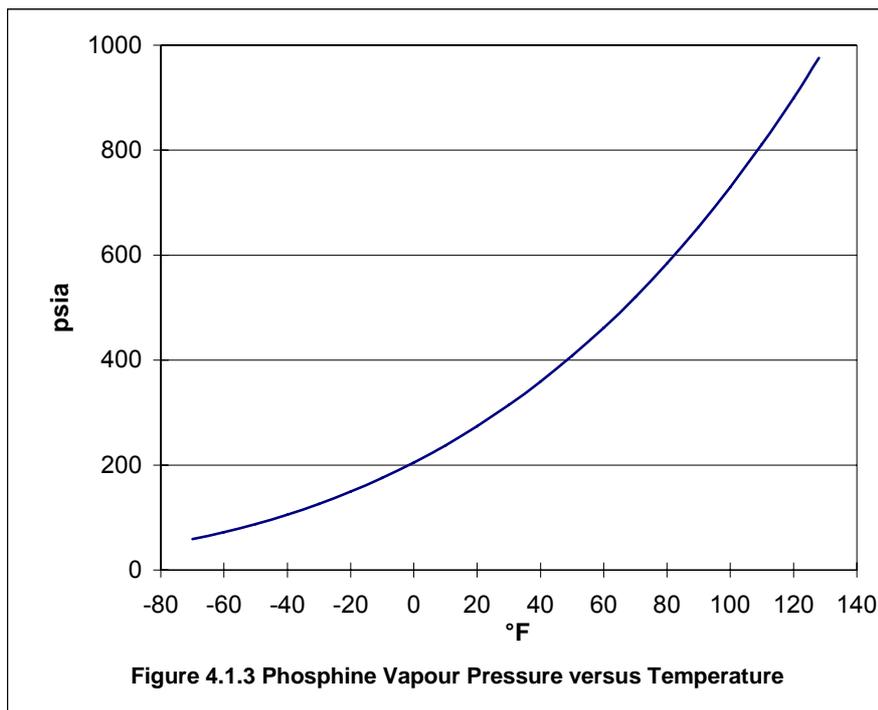
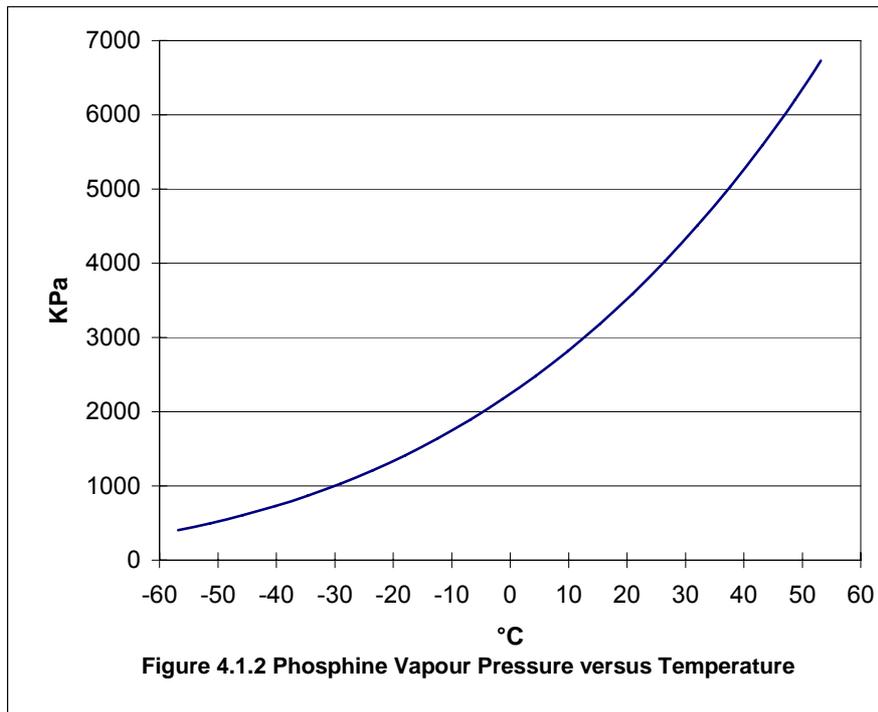
Phosphine is routinely shipped in seamless steel or aluminium alloy cylinders. For reason of safety, cylinders used for phosphine will have a test pressure of 4.2 MPa. Some national bodies mandate higher test pressures. The vapour pressure of phosphine at 20 °C is approximately 3.46 MPa. [3][4]

The table 4.1.1 shows the properties of phosphine.

Table 4.1.1 Properties of Phosphine

Properties	SI	English	Reference
Synonymes	hydrogen phosphide, phosphorous hydride, phosphorated hydrogen		
Molecular Formula	PH ₃		
CAS Nimber	7803-51-2		
UN Number	UN2199		
Physical State	Gas		
Colour	Colourless		
Odour	Decaying Fish		
Molecular Weight	33.998		
Boiling Point	-87.74 °C	-125.93 °F	[5]
Freezing Point	-133.78 °C	-208.8 °F	[5]
Decomposition Temperature Range	375 to 593 °C	707 to 1100 °F	[6]
Critical Temperature	51.6 °C	124.88 °F	[6]
Critical Pressure	6.536 MPa	947.97 psia	[6]
Critical Volume	113.32 cm ³ /mol	6.915 in ³ /mol	[5]
Critical Density	0.3 g/cm ³	18.7 lb/ft ³	[5]
Critical Compressibility Factor	0.274		[5]
Density of Liquid @ 25 °C at 3.46 MPa	0.491 g/cm ³	30.65 lb/ft ³	[5]
Density of Gas @ 21.1 °C at 101325 Pa	1.408 kg/m ³	0.0879 lb/ft ³	[5]
Relative Density Of Gas @ 21.1 °C at 101325 Pa (air=1)	1.174		[5]
Vapour Pressure @ 20 °C	3.46 MPa	501.8 psia	[3][4]
Solubility In Water @ 25 °C and 101325 Pa	269.7 ppm (wt)		[5]
pH	Not applicable		
Volatility	Not applicable		
Odour Threshold (varies with impurities)	0.03 to 3 ppm		[7][8]
Evaporation Rate	Not applicable		
Flash Point	Not applicable		
Lower Flammable Limit (Note : From AIGA & CGA, values vary from source)	1.6 to 1.8 %		[9][10]
Upper Flammable Limit	98 %		[9][10]
Autoignition Temperature	37.8 °C	100 °F	[6][10][11]
Molecular Shape	trigonal pyramidal		
Dipole Moment	0.58 D		[12][13]
Standard Enthalpy Of Formation @ 25 °C, $\Delta_f H_{gas}^0$	+5.4 kJ/mol		[14][15]
Structure			

The figure 4.1.2 and the figure 4.1.3 describe the phosphine vapour pressure versus temperature using its unit of centigrade degree C and Fahrenheit, respectively.



4.2 Physical properties

It is best to avoid sources of ignition, sparks, and flames because of the flammable properties of phosphine. Avoid contact with air as phosphine is considered a pyrophoric and may form explosive mixtures in concentrations of 1.6 % (or greater) in air. Phosphine poses a severe fire hazard and an explosion risk. Phosphine is stable at room temperature and begins to decompose at about 375 °C (707 °F) with complete decomposition at about 593 °C (1100 °F). [6]

4.3 Chemical properties

Phosphine is incompatible with oxidizing materials, members of the halogen family, acids, and other combustible materials. Phosphine is a strong reducing agent and reacts vigorously with oxidizers such as potassium permanganate, sodium hypochlorite, oxygen, ozone, chlorine, fluorine, and nitric oxide. Phosphine will have some reaction with the alkali metal family.

Phosphine is not known to polymerize.

4.4 Health properties

Refer to section "5.2 Toxicology".

4.5 Pyrophoric and flammability properties

Refer to section "5.1 Fire and explosion hazards".

4.6 Environmental properties

With proper control, phosphine can be controlled and pose no threat to human life and the environment. Phosphine presents a low hazard to the general population as accidental emissions into the environment are most unlikely to cause persistent or high concentrations, or to lead to accumulation.

Phosphine released into the atmosphere reacts principally with the HO[•] radical to form HOP[•]. The eventual products will be water and phosphorus oxyacids. Phosphine is also removed from air by soils and oxidized to orthophosphate. Many countries have regulations with measurable action to be taken should a release occur. The users of phosphine should review the regulations that apply.

- Phosphine is considered Hazardous Air Pollutants in certain jurisdictions. It is known or suspected to cause serious health effects, such as reproductive effects or birth defects, or adverse environmental effects.
- Phosphine users should employ a variety of tools to prevent direct pollutant discharges into waterways, municipal wastewater treatment facilities, or allow polluted runoff.
- Emergency response programs are established and at times mandated to eliminate any danger to the public and the environment posed by hazardous substance releases. To help fulfil this mission, local governments may require that the person or organization responsible for a phosphine use notify the government when the amount onsite reaches a pre-determined limit.
- If a release or spill of phosphine occurs, the government may require additional notifications be made. These requirements vary by governments.
- Guidance documents should be obtained from the local government agency to offer direction in following regulations and control emissions. Legal action may be undertaken to pursue those who do not fully comply with the requirements of environmental legislation.
- Risks to human health and the environment will vary considerably depending upon the type and extent of exposure. Phosphine users are strongly encouraged to characterize risk on the basis of locally measured or predicted exposure scenarios.

Risk assessment values or other media quality standards may be used in countries to evaluate the health risks posed by exposures to toxic chemicals. These values are typically specified as concentration limits that must not be exceeded to avoid health risk. These published values can be compared directly to information about the concentration of a chemical in the environment to identify potential health hazards. If a chemical concentration exceeds a relevant media quality standard, action to reduce environmental contamination or exposure is warranted.

5. Gas Major Hazards

5.1 Fire and explosion hazards [16][17][18][19][20][21]

Phosphine is flammable and explosive in air and can auto ignite at ambient temperatures.

The LFL is reported to be 1.6 to 1.8 % [9][10] by volume in air. The Upper Flammable Limit (UFL) is 98 %. [9][10] When phosphine burns it produces a dense white cloud of phosphorus pentoxide, P_2O_5 fume. This fume is a severe respiratory tract irritant due to the rapid formation of orthophosphoric acid, H_3PO_4 , on contact with moisture (water) in human lungs.

Therefore, personnel must wear protective clothing and self-contained breathing apparatus in fighting phosphine fires. Only trained personnel should respond to phosphine fires.

As in the case of a fire of any flammable gas, the flow should be stopped if it is safe and practical to do that. Normally this can be accomplished by shutting off the cylinder valve if safe to do so.

Flammable gases shall not be used near open flames, source of heat, adjacent to oxidizers or non-explosion proof electrical systems. Transportation, storage and use of phosphine should be in well ventilated areas.

In order for a phosphine ignition to occur, two conditions need to occur simultaneously:

- (1) The concentration of phosphine must be within its flammable limits
- (2) The presence of sufficient air or an alternate oxidizing source

Since phosphine is a pyrophoric gas, no source of ignition is required.

Phosphine may begin to slowly decompose into its elements of phosphine and hydrogen at temperatures of 375 °C. [6]

The presence of impurities, particularly diphosphine (PH_2-PH_2), often causes phosphine to ignite spontaneously at room temperature and will form explosive mixtures with air as low as 1.6 %. However, it should be noted that phosphine may diffuse into the atmosphere without autoignition when fume hood, cabinet or other ventilated area exhaust velocity is high.

If the flow of phosphine cannot be stopped, let it burn until the fire stops naturally, keeping adjacent cylinders and equipment cool. If a phosphine fire is extinguished and the flow of phosphine is not stopped, a hazardous combustible mixture may continue to form. It is possible that the mixture can then be auto ignited even under low oxygen concentration and Any unburned phosphine may ignite violently. , explode, cause more damage and restart the fire. Appropriate measures must be taken to protect persons from cylinder rupture in the case of cylinder failure or piping failure.

Although a phosphine fire shall not be extinguished until the flow of phosphine can be stopped, water sprays, etc, should be used to extinguish any secondary fire and to prevent the spread of fires. The phosphine containing equipment may be kept cool by water sprays to decrease the rate of phosphine release or to prevent further damage. This is best done at a distance. A controlled water spray can help knock down and minimize the dispersion of phosphine and phosphine by-products in the gas cloud. Water used in fire fighting could become contaminated when in contact with the oxidized phosphine by-products (phosphorus oxides and/or oxyacids). There should be measures in place to contain and possibly treat such contaminated water.

Remote-controlled water spray equipment is preferable to use of hoses in cooling equipment and to reduce the spread of fire. Should the use of hoses become necessary, operating personnel should remain behind protective structures and upwind of the fire.

Fire-fighting or other emergency personnel should communicate and cooperate with personnel who are familiar with the physical and toxic properties of phosphine. They also should communicate and cooperate with personnel who are familiar with materials in the area of the emergency. Unexpected

conditions may require special actions.

If a cylinder of phosphine or supply piping system is ruptured in such a manner that quantities of phosphine are released and ignited, hazardous conditions will exist.

- **Flame effects:** The major concern is that the generated flames will impinge on surrounding valves and piping thus weakening these structures with the possibility of failure taking place. Hot balls or jet fires may be present. Wind velocity and direction may change the shape of the fire ball or jet to an elliptical shape and push it further downwind of the release.
- **Radiation effect:** The major concern is that radiation effects from the fire can result in the excessive heating of adjacent equipment and process lines.
- **Reaction by-products:** Oxidation of phosphine yields water and phosphorus oxides and oxyacids.

A thorough Process Hazard Analysis with identified sufficient safeguards must be in place to minimize the risk of a potential incident if operating personnel should err in procedures or equipment fails.

5.2 Toxicology

5.2.1 Phosphine exposure

Phosphine is highly toxic to human respiratory system and organs. Phosphine has a decaying fish odour. The odour of phosphine depends on the impurities it contains and the environment it is released in.

The main hazard to man is the possibility of unrecognized occupational exposure to phosphine causing acute poisoning. Neither the smell nor sensory irritation can be relied upon for warning of toxic concentrations, especially in the presence of other fumes, gases, or vapours.

About 20 % to 50 % of attentive persons can detect the odour threshold value of 0.03 ppm to 3 ppm. [7][8]

The predominant pathological feature in acute fatal cases is pulmonary edema. Severe non-lethal cases complain of pain and tightness in the chest. Neurological abnormalities include headache, vertigo, tremors, and unsteady gait, and may progress to convulsions, coma, and death; they may mimic alcoholic intoxication. Gastrointestinal symptoms include loss of appetite, thirst, nausea, vomiting, diarrhoea, epigastric pain, and jaundice. Other effects described include thrombocytopenic purpura and hypotension.

Phosphine is a respiratory tract irritant that attacks primarily the cardiovascular and respiratory systems causing peripheral vascular collapse, cardiac arrest and failure, and pulmonary edema.

There have been no long-term studies on the effects of phosphine on animals or man and there are no data relating to mutagenicity, teratogenicity, or carcinogenicity. [22]

Symptoms are rapid in onset and characterized by: [2]

- Headache
- Dizziness
- Weakness
- Apathy
- Nausea
- Vomiting
- Cough
- Dyspnoea
- Fall in blood pressure
- Change in pulse rate
- Diarrhoea

- Tremors and convulsions
- Intense thirst
- Tightness in the chest
- Restlessness
- Hemoglobinuria
- Paralysis
- Coma

The table 5.2.1.1 shows the toxic information of phosphine.

Table 5.2.1.1 The toxic information of phosphine

Chemical: PHOSPHINE			
CAS Number:	7803-51-2		
Conversion Factor: 1 ppm = 1.39 mg/m ³ 25)			
	Value	Units	Reference
LC ₅₀ /rat 1 hour	20	ppm	[23]
PEL TWA (Permissible Exposure Limit) for General Industry	0.3 0.4	ppm mg/m ³	[24][25]
TLV-TWA (Threshold Limit Value - Time Weighted Average)	0.3 0.42	ppm mg/m ³	[26]
TLV-STEL (Threshold Limit Value – Short Term Exposure Limit)	1 1.4	ppm mg/m ³	[26]
Recommended Exposure Limit (REL) TWA	0.3 0.4	ppm mg/m ³	[24][25]
Recommended Exposure Limit (REL) STEL	1 1	ppm mg/m ³	[24][25]
NIOSH Immediately Dangerous to Life or Health Concentration (IDLH)	50	ppm	[25]
AEGL (Acute Exposure Guideline Levels)			[27]
	AEGL-1 (30 min)	NA	ppm
	AEGL-2 (30 min)	0.38	ppm
	AEGL-3 (30 min)	1.4	ppm
<p>NA: Not appropriate</p> <p>Notes:</p> <p>PEL TWA: OSHA's permissible exposure limit expressed as a time-weighted average is the concentration of a substance to which most workers can be exposed without adverse effects averaged over a normal 8 hours workday or a 40 hours workweek.</p> <p>TLV TWA: ACGIH's threshold limit value expressed as a time-weighted average is the concentration of a substance to which most workers can be exposed without adverse effects.</p> <p>TLV STEL: ACGIH's threshold limit value short-term exposure limit is a 15 minutes TWA exposure which should not be exceeded at any time during a work day.</p> <p>REL TWA: NIOSH's recommended exposure limit expressed as a time-weighted average is a recommended exposure limit for an 8 or 10 hours time-weighted-average exposure and/or ceiling.</p> <p>REL STEL: NIOSH's recommended short-term exposure limit is a 15 minutes TWA exposure which should not be exceeded at any time during a workday.</p> <p>IDLH: NIOSH's immediately dangerous to life or health concentration is NIOSH recommended exposure limit to ensure that a worker can escape from an exposure condition that is likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from the environment.</p>			

5.2.2 Medical treatment for phosphine exposure

Detailed pre-hospital and hospital management practices for treatment of phosphine exposures can be found in the “Medical Management Guidelines for Acute Chemical Exposures” [28].

Key points from these guidelines for Phosphine:

Primary route of entry is inhalation. It is a severe respiratory tract irritant and a highly toxic systemic poison. Phosphine is a multi-system toxicant that can cause pulmonary irritation, Central Nervous System (CNS) depression, and cardiovascular collapse.

Victims exposed only to phosphine gas do not pose substantial risks of secondary contamination to personnel outside the Hot Zone and do not need decontamination.

There is no antidote for phosphine poisoning. Treatment consists of support of respiratory and cardiovascular functions.

5.2.3 Leak or release of phosphine

In view of the toxic nature of phosphine, in the case of a leak all personnel should be immediately evacuated from the affected areas. Only trained emergency response personnel should enter the area, properly equipped with self-contained breathing apparatus.

In the event of the release of a cylinder of phosphine personnel in the immediate area of the release will likely be at risk. As in the case of the release of any toxic gas, first responders should station themselves upwind of the release point. Risk of fire or explosion is a major safety issue and requires the greater evacuation distances.

Because of the high toxicity of the material, any release of the product, whether accidental or intentional, will likely require the filing of a report with the governing agency for environmental protection.

6. Gas Handling Equipment – general considerations

The equipment used to handle phosphine must be designed, constructed and tested in accordance with the regulatory requirements of the country in which the equipment is operated. The equipment must be designed to withstand the maximum pressure and temperature at which it is to be operated. A Process Hazard Analysis (PHA) shall be performed and documented on all phosphine systems. As phosphine is a highly toxic, flammable and pyrophoric gas, consideration should be given to the following issues when designing systems to handle phosphine:

- (1) Materials of construction
- (2) Compatibility of sealing compounds
- (3) System pressures and overpressure protection
- (4) Valve types & filter types
- (5) Tubing
- (6) Purification materials
- (7) System leak tests and purge
- (8) System temperature control
- (9) Use of electrical control and use of explosion proof equipment
- (10) Monitoring system
- (11) Abatement system
- (12) System vent
- (13) Regulators

6.1 Materials of construction

Selection of metals and non-metals shall be made taking into account the compatibility guide listed below. It is extremely important that all gas control equipment be compatible with the gas being passed through it. The use of a device that is not compatible with the service gas may damage the unit and cause a leak that could result in property damage or personal injury. If a material is not listed and is required to be used in phosphine service and is thought to be compatible it should be first tested to confirm suitability prior to use under defined temperature, pressure and flow conditions.

The following table 6.1.1 material compatibility guide is prepared for use with dry phosphine at normal operating temperature of 21.1 °C; information may vary if different operating conditions exist.

Table 6.1.1 Material compatibility guide [29]

		S= Satisfactory			U = Unsatisfactory			? = Unknown or limited data												
MATERIALS OF CONSTRUCTION																				
PHOSPHINE	METALS					PLASTICS					ELASTOMERS									
	Steel	303 SS	304 SS	316 SS	Monel®	Aluminium	Brass	Zinc	Copper	Kynar®	PCTFE	Polycarbonate	PVC	Teflon®	Tefzel®	Buna-N	Kelrez®	Neoprene®	polyurethane	Viton®
	S	S	S	S	S	S	S	U	S	S	S	?	S	S	S	S	S	S	S	S

- Note: (1) Nickel can cause decomposition of phosphine.
 (2) Some plastics and elastomers if used, absorb phosphine.
 (3) While ISO 11114-1 addresses concern for hydrogen embrittlement, and while it is also acknowledged that P-200 requires an “H” stamp for steel cylinders charged with phosphine, there is no conclusive proof that phosphine is an embrittling gas.

6.2 Compatibility of sealing compounds

Consideration should be given to the compatibility of lubricants, seals, greases and sealing compounds which under normal or upset conditions come in contact with phosphine. Refer to vendor supplied data.

6.3 System pressures and overpressure protection

System pressures may be high due to the vapour pressure of phosphine at 20 °C, which is 3.46 MPa. The use of pressure reduction equipment should be used to properly control system pressure (refer to Chapter 10.2. *Regulators*). Proper design should address conditions where system pressure may be subjected to sub-atmospheric conditions and draw in air or other gas stream contamination that is utilized in the system. Due to the hazardous nature of phosphine, a conservative engineering and design approach shall be applied to the system design as applicable whether for pure phosphine or phosphine mixtures.

Gaseous mixtures of phosphine are routinely packaged at pressures at or below the rated cylinder working pressure. Gas panels typically use a gas regulator to reduce the cylinder pressure to the operating condition.

Special care is needed to ensure that all components in the system are rated for these pressures. Due to the hazardous nature of gaseous phosphine mixtures, a conservative engineering and design approach shall be applied to the system design as applicable.

Where system design pressures can be exceeded due to any component failure or operator error, proper overpressure protection shall be provided. Overpressure protection may involve pressure relief devices and/or instrumented systems depending on local code requirements.

Piping system safety relief valve outlet must link to appropriately designed abatement system (see chapter “11. Gas Abatement Systems”).

6.4 Valve types & filter types

Metal diaphragm valves and bellows valves provide a better leak tightness as compared to packed valves. The use of non-metal material for diaphragms or bellows is not recommended due to permeation potential of phosphine thru the non-metal. Ball valves, butterfly valves, gate valves, needle valves, or packed valves are not recommended for use in phosphine service due to a higher leak potential either through or around the valve seat or the valve body.

Mesh filters made of stainless steel work well as do those of Teflon. Sintered metal filters are also recommended. Phosphine has been shown to decompose to phosphorous and hydrogen on the surface of nickel filter media. The decomposition rate was found to be low at ambient temperatures. However, it is recommended that nickel filters not be used in low phosphine concentration applications, <1000 ppm. Over time a solid film growth of nickel phosphides on filter membrane surfaces can increase the pressure drop across a filter and degrade filter performance.

The use of restrictive flow orifices (RFO's) has been a routine practice since the mid 1980's. The restrictor has a small diameter of, for example, 0.152 mm (0.006 inch), 0.254 mm (0.010 inch) and 0.3 mm, and is of stainless steel materials of construction. While early designs had a filter element capable of capturing particles that were greater than two microns, the use of such filters are not currently part of RFO's in service today. The RFO threads into the valve outlet. In the event of a shearing of a process line or a valve being accidentally opened, the RFO significantly reduces the amount of gas that would be released and that would need to be environmentally treated. Some jurisdictions and insurance companies require the use of the RFO.

Also during the 1980's, air actuated valves began to be used. It allowed for remote opening and closing of the cylinder valve, and afforded an extra measure of safety both at the filling as well as at the point of use.

6.5 Tubing

Some national bodies or insurance companies require the use of coaxial tubing when the tubing is outside of an exhausted enclosure. Welded or metal face seal connections are the preferred connection methods due to their leak integrity.

6.6 Purification materials

Phosphine in the electronic industries is offered at high purity by the supplier. Purities offered range from low 99.995 % to 99.9999+ %. Purification materials can be as basic as molecular sieves to remove impurities in the generated phosphine and sophisticated materials such as porous alumina, alumina-silica and silica may be used to also remove other trace impurities pending reaction mechanism used or impurity levels required.

Proper system purge must be done prior to the use of the purifier or removal.

6.7 System leak tests and purge

After system installation or maintenance, they must be leak checked and purged prior to commissioning.

Connections which are routinely re-made in the process (e.g. cylinder pigtail connections) should be leak checked at a pressure higher than maximum usage pressure prior to system purging.

The best purge systems are those that are automated. The number of purge cycles is a function of the inert purge pressure available, the use of vacuum generators, the size of the tubing/piping system to be purged and the desired final dilution value. Common purge gases are nitrogen and helium. Hydrogen is also used as a purge gas. Typical gas delivery systems shall be purged to a safe level of phosphine. The use of manual purge control has a higher potential for operator error and requires clear operator instructions if utilized.

6.8 System temperature control

Systems operate at varying temperatures depending on how the phosphine is being used. Proper design should address conditions where system temperature may vary from room temperature. When working with compressed liquids, refer to the vapour pressure versus temperature relationship shown earlier in this document.

Some systems may require external heating system of the cylinder to maintain system flow. In such

cases, careful engineering review must be taken to ensure the temperature never exceeds 65 °C and creates potential liquid full condition.

Some systems may also require heating to maintain constant temperature and/or prevent condensation of phosphine during use. The preferred method is use of a temperature-controlled environment. Direct heating using of electrical resistance heater on a cylinder has caused accidents and is least preferred method.

Note: Phosphine starts to decompose at the temperature of 375 °C. [6]

6.9 Use of electrical control & use of explosion proof equipment

Since phosphine is flammable and pyrophoric, electrical systems must meet the requirements of the local regulations covering flammable classifications.

These classifications are for generic volatile flammable liquids or flammable gases that if mixed with air may burn or explode. In such cases the liquids, vapours, or gases will normally be confined within closed containers or closed systems from which they can escape only in case of accidental rupture or breakdown. It should be noted that ignitable concentrations of gases or vapours of flammable gas, flammable liquid–produced vapour, or combustible liquid–produced vapour mixed with air are normally prevented by having forced mechanical ventilation, which is under negative pressure. This could become hazardous through the failure or abnormal operation of the ventilating equipment.

Note: Outdoor phosphine installations in the United States generally do not require electrical classification.

6.10 Monitoring system

6.10.1 Gas monitoring

There is a need to ensure that each individual is protected by phosphine detection systems, which are accurate, efficient and easy to use/maintain.

Phosphine is a colourless, flammable, pyrophoric and highly toxic gas. It has a decaying fish odour that can be detected at concentrations of 0.03 to 3 ppm [7][8] and above. This level of detection does not provide adequate warning of hazardous levels. Phosphine is non irritating and produces immediate symptoms. However, persons exposed to hazardous levels may be unaware of its presence. The manifestation of symptoms may be delayed and appear after several hours. A gas monitoring system continuously monitors primary locations for phosphine including but or not limited to the following areas:

- Storage
- Operator areas
- Gas cabinets
- Fume hoods
- Process rooms

The gas monitoring system shall have a backup source of power.
Life safety control is discussed in greater detail in section 7.1.

Detection methods vary, as does their sensitivity to Phosphine. It is desirable to have a system capable of networking existing systems from various manufacturers, and the ability to accommodate ongoing expansion. Typical detector types suitable for phosphine are:

- Photo-absorption
- Photo-ionization
- Electrochemical
- Colorimetric tape
- Thermal conductivity

- Catalytic bead

A gas detection system with a sensing interval not exceeding 5 minutes may be required in certain jurisdictions.

6.10.2 Fire detection

When phosphine burns it produces a dense white cloud of phosphorus pentoxide, P_2O_5 fume. This fume is a severe respiratory tract irritant due to the rapid formation of orthophosphoric acid, H_3PO_4 , on contact with moisture (water) in human lungs.

6.10.2.1 General

The use of ultraviolet/infrared (UV/IR) flame detectors is suitable for phosphine service. Other detectors may offer comparable detection depending on detector location and action required. Temperature rise indicators may also be suitable for indoor use. Such systems work best in Heating Ventilation and Air Conditioning (HVAC) controlled environments.

6.10.2.2 Flame monitoring

Since phosphine is flammable and capable of autoignition (pyrophoric at higher concentrations), monitoring for a flame is applicable. However, an earlier hazard is the high toxicity of the gas at low ppm levels. This toxicity concern occurs well below the **Lower Flammable Limit** of phosphine. Thus, it is recommended that gas monitoring should be directed to ppm emissions in addition to flame monitoring. For higher concentration concerns, a monitoring system capable for detecting a flame is recommended.

Flame detectors suitable for phosphine service shall be located so as to detect fire in potential phosphine leak areas. Whenever flame detection occurs, immediate shutdown of the process is required. This is best achieved with automatic valves controlled with nitrogen instead of air. An alarm should be transmitted so responsible parties will act on the condition.

Refer to section "7.1 Life safety control" for additional gas monitoring considerations.

6.10.2.3 Indoor systems

Flame detectors used indoors shall be located in the room or within gas cabinets depending on cylinder storage requirements and use. Potential leak zones include:

- Cylinder valve (cylinder interface, pressure relief devices and outlet connections)
- Process equipment (reactor, vacuum pump, purification systems)
- Process and purge panels
- Exhaust Ducts

Gas cabinets or fume hoods shall be equipped with automatic sprinkler systems. The sprinkler head(s) should be positioned to keep the cylinder(s) and related gas panel system cool, but not meant to extinguish a fire in the cabinet or hood. There are generally specific requirements on water flow rate and duration of water spray that must be followed. These are national code specific.

6.10.2.4 Outdoor systems

Flame detectors used outdoors should be compatible with the environment. They should be field tested to avoid false alarms due to sunlight, arc welding, artificial lighting or other stray sources that can inadvertently activate the detector.

As noted above, during a fire, phosphine systems and cylinders should be cooled rather than extinguished since the continued leakage of phosphine could result in a latent explosion of accumulated phosphine.

A manual or automatic (where required) deluge water spray system is suitable for outdoor system control.

Systems should be designed and installed in accordance with national regulations to assure proper compliance. There are generally specific requirements on water flow rate and duration of water spray that must be followed. Protection of nearby structures should be considered.

6.11 Abatement system

Refer to section "11. Gas Abatement Systems".

6.12 System vent

All vents in system must be directed to abatement system. These include system pressure relief devices, vacuum pump exhaust, system vent and vacuum venturi exhaust.

6.13 Regulators

Refer to section "10.2 Regulators".

7. Process and Operation

7.1 Life safety control (gas detection and alarm systems)

Sound procedures shall be in place to control worker exposure to phosphine and its by-products. Compliance to such a program will prevent adverse effects of exposure in the workplace through air exposure or through skin exposure. Specific compliance activity may be prescribed by country regulations. The following items should be considered part of a Life Safety Control program

7.1.1 Monitoring

- (1) Environmental workplace air/land monitoring:
Occupational exposure shall be controlled so that no worker is exposed to concentrations greater than allowed either as gas or solid inorganic compound.
- (2) Monitor calibration/inspection:
Routine inspection of monitoring equipment to verify performance and reliability.
- (3) Monitor operation/performance of abatement systems:
Routine inspection of abatement equipment to verify performance and reliability.
- (4) Appropriate leak detection devices should be installed to trigger emergency response actions in compliance with national regulations.

7.1.2 Life safety system

- (1) Periodic review of Heating Ventilation and Air Conditioning (HVAC) air balance through building, fume hoods, gas cabinets and abatement systems:
With time, air flows/exhausts may change and required capture velocities may be under required levels. Ventilation dampers should be locked in place to prevent the altering of required ventilation between air balances.
- (2) Alarm testing and inspection:
Routine testing and inspection of alarm systems to verify performance and reliability.
- (3) Since phosphine is a flammable and pyrophoric gas, fire fighting systems must be considered and should follow national regulations.
- (4) Appropriate gas scrubbing or ventilation systems should be installed to handle gas leaks. National regulations may require gas scrubbing or ventilation to handle gas leaks.
- (5) Gas storage areas should be designed with more than one exit.

7.1.3 Management

- (1) Proper work clothing management:
Daily change outs, place for contaminated clothing, separate locker room from manufacturing environment.
- (2) Training and re-certification in use of proper Personnel Protective Equipment (PPE) for workers who are required to wear respiratory protection must be medically evaluated and fit tested to confirm worker ability and clearance for use.
- (3) Training and emergency response:
Training should be conducted on the proper emergency response to situations that involve the possible release or exposure to phosphine and by-products.
- (4) General awareness training:
Personnel involved in the manufacturing, processing, maintenance, handling, storage and/or transportation shall be trained on the exposure effects (signs, symptoms, medical attention) of phosphine and by-products using MSDS and other safety information on the environment and to personnel. Additional training may be required by local jurisdictions which include personnel safety, preventive maintenance and environmental management programs.
- (5) Record keeping programs:
A program should be documented explaining what to record, when to record, how often to record, place of record storage and length for records to be stored before disposal.
- (6) Periodic medical surveillance must be made available for all workers which meet local government requirements. Documented work history, medical history captured. Some governments may require annual chest X-ray, careful examination of skin for the presence of chronic skin lesions, blood work review.
- (7) Proper labelling of products/containers:
With complete name and applicable hazards as required by regulations.
- (8) Clear, documented work practices/procedures:
Control of equipment, process clean-up, waste disposal, and operations control.
- (9) Emergency Action Plan – response and evacuation protocols for site alarms, releases, and abatement of loss of contaminant.

7.2 Operational procedures and personnel

Clearly defined written work instructions are required to assure safe handling and processing of phosphine. The work instruction should describe in sufficient detail the information needed on how to perform a specific task. These work instructions may exist as text, posted instruction, matrix, or a flowchart. Clarity is the key. Latest versions of the work instructions should be readily available to the operator should questions phosphine.

Operators must be consulted and trained when procedures are changed. All operations involving phosphine shall be covered by “clear language” written operating procedures. A risk assessment should be carried out on all operations involving phosphine.

Components and materials that may be used on phosphine systems shall be clearly identified, carefully stored and handled to ensure that they do not become contaminated. It is recommended that cylinder valve outlet connections gaskets are only handled while wearing approved gloves. This will avoid the risk of:

- Contamination of the gaskets by the natural oils found on the skin
- Contamination of the operator from residue phosphine by-products found on the used gasket

All personnel involved in handling of phosphine and the operations of phosphine systems shall be adequately trained. This training shall include the importance of cleanliness and the need for exclusive use of specified materials and components on phosphine systems.

Personnel who operate gas systems shall have a good understanding of the properties, fire & explosion hazards and toxicity of phosphine. They should also be trained to take appropriate action in the advent of an emergency. Wherever possible, preventive measures shall be considered to protect

operators (e.g. gas cabinets, fume hoods, Personnel Protective Equipment (PPE), remote controlled valves and barrier walls).

7.3 Ventilation

Proper ventilation is required for storage areas, gas cabinets, fume hoods and areas where phosphine is processed, stored or handled.

7.3.1 Direct venting into exhaust systems

Phosphine should not be directly vented into exhaust ventilation systems in concentrations above LFL (1.6 % to 1.8 %) since this can result in a fire or explosion within the exhaust system. [9][10]

A fire or explosion can occur due to autoignition of the phosphine itself, from the ignition of other flammables or from chemical side reactions that may be present in the exhaust system.

Dilution with an inert gas is preferred prior to venting to reduce the risk of fire or explosion.

7.3.2 Dedicated process vent

Phosphine discharged from process panels (or other processes) to an exhaust system should be dedicated to phosphine service.

Vent lines should be constantly purged with inert gas to prevent air (or other back flow of gases) from entering into the vent system.

The venting system should be designed to minimize pressure drop.

Purge systems should be dedicated and isolated systems to curtail the potential back flow of phosphine.

7.3.3 Common Guidelines

Regulations may vary by country and should be verified, but common guidelines are as follows:

7.3.3.1 Necessity of ventilation for phosphine

- (1) Do not vent flammable and toxic gases to the atmosphere except through a properly designed abatement system.
- (2) Mechanical ventilation shall be used to exchange air where phosphine is processed or handled to quickly exhaust any fugitive phosphine emissions.

7.3.3.2 Types of ventilation

- (1) Indoor storage and use areas and storage buildings for compressed gases and cryogenic fluids shall be provided with mechanical exhaust ventilation or natural ventilation, where natural ventilation can be shown to be acceptable for the material as stored. In certain jurisdictions, the use of natural ventilation must be approved by governmental and/or local authorities.
- (2) For indoor storage, forced ventilation is required and should follow national regulations.
- (3) Gas rooms shall be provided with an exhaust ventilation system.
- (4) Where outdoor storage is allowed, forced ventilation is generally not required.

7.3.3.3 Consideration for ventilation design

- (1) The gas cabinet or exhausted enclosure shall be provided with an exhaust ventilation system designed to operate at a negative pressure relative to the surrounding areas.
 1. The velocity at the face of access ports or windows, with the access port or window open, shall be adequate to protect the user from fugitive emissions. In the United Kingdom, a minimum velocity of 1m/s across the face of the small valve manipulation opening is recommended for normal operating conditions.
 2. The number of air exchanges per hour (inside the gas cabinet or exhausted enclosure), may be regulated by local authorities.
- (2) Mechanical ventilation rate shall be adequate. In the United States, the rate of not less than 0.3

cubic meter/minute/square meter (1 cubic foot/minute/square foot) of floor area over the area of storage or use is required.

- (3) The exhaust system shall take into account the density of the potential gases released and leak points.
 1. For gases that are heavier than air, like phosphine, exhaust should be taken near the floor.
 2. Some phosphine mixtures (helium, hydrogen) are lighter than air, exhaust should be taken near the ceiling.
 3. The location of both the exhaust and inlet air openings shall be designed to provide air movement across all portions of the floor or room to prevent the accumulation of vapours.
- (4) Exhaust ventilation should not be re-circulated within the room or building if the cylinders, containers, or tanks stored are capable of releasing hazardous gases, like phosphine.
- (5) Gas cabinets, fume hoods and areas where phosphine is being processed or stored, water sprinkler systems should be installed and properly sized.
- (6) Equipment used to contain or capture phosphine shall be non-flammable.
- (7) Equipment used, like air handling fans, shall be non-sparking by design and construction.
- (8) Ventilation systems shall discharge at an adequate distance from intakes of air-handling systems, air conditioning equipment, and air compressors.
- (9) Storage and use of compressed gases should be located at an adequate distance from air intakes.
- (10) In the United States where powered ventilation is provided, a manual shutoff switch should be provided outside of the room in a position adjacent to the principal access door to the room or in an approved location. The switch shall be the break-glass or equivalent type and shall be labelled as follows: *VENTILATION SYSTEM EMERGENCY SHUTOFF*.
- (11) Where mechanical ventilation is provided, the system shall be operational as minimum during the time the building or space is occupied.
- (12) There shall be an alarm system that will activate in the event of the loss of ventilation.

7.4 On-going maintenance and preventive maintenance (PM) programs

It is essential that equipment in which phosphine is handled is held to a high standard and to assure that this is maintained in a routine, controlled and safe manner. Particular attention should be provided to any replacement parts for compatibility with phosphine and other system products.

Preventive action is directed at eliminating potential causes of equipment failure before they occur. The manufacturer's *Equipment Manual* provides guidelines for preventive maintenance management of their equipment. It is the responsibility of each user to ensure proper control exists. Users of phosphine should have a strong *Preventive Maintenance Program* installed and implemented, at all sites that process or handle phosphine. This program driven by corporate management generally exceeds the equipment manufacturer's recommendations.

8. Gas Cylinder Filling/Packaging

8.1 Filling facility consideration

Good practices for filling facilities should follow those as described under the more general **Storage and Handling** in the section 9 later.

8.2 Containers

8.2.1 Cylinders

Phosphine is routinely packaged in seamless steel cylinders or aluminium alloy cylinders with a minimum test pressure set by the regulatory body. Low pressure welded cylinders may be accepted for this service, with a special approval that has been granted by the regulatory body.

The cylinder size of phosphine and its mixtures are limited by local government regulations. In Japan, maximum cylinder size is 49 L and 57 L in the United States except for mixtures less than 10 vol %.

Cylinders that are used in high purity electronic phosphine service, generally have special internal pre-treatment to maintain gas purity. This treatment is provided by the gas supplier.

Containers shall be certified and tested regularly in compliance with national standards. Container re-test shall follow national standards or the container manufacturer's country laws and regulations, whichever is more stringent. Containers failing to meet these standards must be removed from service. If they can be repaired to meet the standards, they can be put back to use; otherwise they shall be scrapped.

In some countries, phosphine cylinders can not be used in other services.

Prior to fill, care must be exercised to ensure that a container has not been damaged. Pre-fill inspection of containers and correct verification of their pressure rating prior to filling is very important.

8.2.2 Valves and pressure relief devices

It is recommended that diaphragm seal valves be used for phosphine in that it provides a level of leak tightness that is not normally achievable with a packed valve. The diaphragm valve can be either a diaphragm packless or a tied diaphragm valve. Some jurisdictions mandate the use of the diaphragm valve, such as the United States and Europe.

There are different types of valve outlets that are used for phosphine in Asia, North America, and Europe. It is important that the ancillary equipment used to connect to the cylinder valve be of the same thread configuration as the cylinder valve outlet to insure a leak tight connection. Most countries require a gas tight valve outlet cap on the cylinder valve.

There are a variety of different cylinder valve inlets that are in use today for phosphine as well as all gases. There are also a variety of cylinder neck threads that are used worldwide. The threads on the valve inlet must match the threads on the container neck. It is very dangerous to match cylinders and valves that have been manufactured to different national standards since the possibility exists that the valve, under pressure, could be ejected from the cylinder.

The use of pressure relief devices for cylinder valves with phosphine is required in Japan and Korea. However, in the United States and Europe, because of the toxicity of phosphine pressure relief devices are prohibited. In other countries, pressure relief devices are neither required nor prohibited.

8.2.3 Fill density

The United Nations P-200 Packaging Note currently permits a maximum fill density of 0.45 kg/L for phosphine packaged in cylinders with a test pressure of 30 MPa (300 bar) and 0.30 kg/L for a cylinder with a test pressure of 20 MPa (200 bar).

The maximum fill density for phosphine in Japan is 0.207 kg/L.

In the United States the maximum fill density based on liquid full cylinder at 54.4 °C (130 °F) is 0.30 kg/L, however, 0.45 kg/L of fill density with the test pressure of the cylinder over 15.1 MPa (2188 psig) is allowed by the United States DOT under a special permit.

The maximum filling ratio for Europe is 0.3 for 225 bar of the gauge test pressure and 0.45 for 250 bar of the gauge test pressure.

8.3 Filling equipment

Many countries regulate the disposal of phosphine contaminated wastes. Any equipment in contact with phosphine may be treated as a hazardous waste when the time comes for disposal. Proper clean-up procedures and employee protection guidelines should be documented and understood.

The by-products of phosphine oxidization typically are phosphorus oxides or oxyacids, peroxide

washing is a suitable cleaning method of contaminated equipment.

8.3.1 Manifolds

Manifold components in contact with phosphine filling shall be designed with compatible materials listed in this document. When not under phosphine pressure, manifolds should be back-filled with an inert gas (e.g. helium, nitrogen, argon) and plugged to ensure that any contaminants are excluded from the manifold system. Filling manifolds should be located in well-ventilated areas. To reduce potential quantity of gas released in an accident and reduce waste, small diameter tubing and lengths are preferred. The filling manifold should be made utilizing welded fitting and metal face seal fitting. The use of threaded fitting should be avoided.

Refer to section 6.7 for “System leak tests and purge” practices.

8.3.2 Compressors

Since phosphine is a pyrophoric and liquefied gas, compressors are not normally used for pure gas.

8.3.3 Vacuum pumps

Vacuum pumps in contact with phosphine are typically either dry pumps or those using a fluorinated fluid (e.g. Fomblin[®]). There is no hazard to use a hydrocarbon oil pump. However, wet pumps risk oil contamination by phosphine and proper waste management is required. Any possible air reaction will quickly foul the vacuum pump and could cause a serious accident under higher phosphine concentrations.

Dry pumps are recommended due to no oil contamination concern. In addition, wet pumps have the potential for oil back-streaming if proper back-streaming barriers are not maintained properly. If back-streaming occurs, phosphine (and system manifold) contamination will occur and downtime/clean-up can be lengthy. Personnel must exercise care when performing vacuum pump maintenance, especially for wet pumps where the oil may have absorbed phosphine.

8.3.4 Pressure gauges

Pressure gauges are used to monitor the pressure within the phosphine system. Analogue and digital pressure gauges may be used as necessary. However, the pressure gauge dead volume should be considered along with ease of inert gas purge. Gauges shall be placed so they are easily monitored by the operator. Since phosphine is flammable, the use of digital pressure gauges (operated by electricity) should be at low voltage intrinsically safe (via low voltage or electrical barriers) to avoid ignition source potential.

9. Storage and Handling

Good practices for storage and use of phosphine are listed below.

9.1 General guidelines

- (1) All facilities must have an emergency response plan which should include the plan for gas releases and emergency evacuation (more information in AIGA 004/04 and EIGA 30/07).
- (2) Have on hand the MSDS.
- (3) Good housekeeping is essential, e.g. keeping combustible material away from container storage or use areas.
- (4) Check for insects or foreign material before removing the valve protection cap.
- (5) Phosphine cylinder valve outlet caps must be installed except when being filled or in use.
- (6) Always secure (nested, palletized or chained) the containers whether during transportation, storage or use.
- (7) Never strike an arc (with welding electrode) on the container.
- (8) Never allow containers to contact electrical circuits.

- (9) Never expose containers to corrosive chemicals or vapours, e.g. bleach or seawater.
- (10) Container valves must be securely closed, outlet seals tightly installed, and valve protection caps in-place during all storage and handling operation.

9.2 Storage

9.2.1 Segregation

- (1) Full and used containers should be segregated; however, containers with residual gas should be treated as if they were full.
- (2) Group containers according to the gas hazard they pose.
- (3) Phosphine shall be stored in well-ventilated areas, away from incompatible gases (oxidizers, pyrophoric gases, etc.), flammable liquids, open flames, sparks and sources of heat. Incompatible groups shall be separated by appropriate distances or with fire partition. If local jurisdiction does not specify the distance, at least 6 meter separation is recommended.
- (4) A 6 meter separation of phosphine from electrical devices that are not explosion-proof is suggested in the absence of any regulatory direction.

9.2.2 Storage condition

- (1) Practice First-In-First-Out (FIFO) cylinder management.
- (2) Containers should be stored under dry conditions.
- (3) Containers should be stored on level ground to minimize toppling.
- (4) Store containers in such a way as to prevent the temperature of the containers from exceeding the national guideline.
- (5) Quantity of phosphine stored should not exceed the design of the facility and should comply with national regulations.
- (6) Cylinders when stored vertically shall be secured (nested, palletized or chained) to prevent accidental tip-over. Standard compressed gas cylinders are designed to be stored vertically. In these cases, precaution must be taken to ensure that they are secured from falling.
- (7) Other small cylinders such as lecture bottles are more conveniently stored horizontally. However, some local regulations may require vertical storage for toxic liquefied gases, especially when equipped with pressure relief devices.
- (8) An energy relief wall or blast roof should be incorporated into the room design if flammable gases are stored in large quantities indoors. This wall or roof is designed to allow dissipation of pressure arising from an explosion.
- (9) It is noted that there are countries which do not permit outdoor storage of phosphine. In the United States, outdoor storage is allowed under some circumstances.

9.3 Handling

9.3.1 Essentials

- (1) Personnel handling phosphine cylinders should receive appropriate training.
- (2) Use appropriate materials of construction compatible for handling phosphine. This information can be obtained from the MSDS and this document.
- (3) Always wear proper personal protective equipment when handling gas containers. Steel-capped safety shoes, safety glasses with side shields and leather gloves are recommended.
- (4) All piping, cabinet and equipment used to handle phosphine should have electrical continuity sources and should be earthed.

9.3.2 Precautions

- (1) Remove valve outlet cap or connections slowly and look for signs of leakage before removing completely.
- (2) Always stand at the side of the valve outlet cap or connection when removing the cap or breaking a connection.
- (3) Always open valves slowly and carefully.

- (4) Containers with residual gas should be treated as if they were full.
- (5) The filling and use of phosphine shall be done in exhausted enclosures or rooms with the discharge treated properly to below acceptable levels before emission into the atmosphere.

9.3.3 Checking

9.3.3.1 Container

- (1) Check cleanliness of the valve outlet and pigtailed.
- (2) Leak check containers and connection before use.
- (3) Prior to entry, enclosed spaces containing highly toxic gas, including shipping containers, should be checked for leaks of the toxic gas in the absence of a maintained stationary detection system.

9.3.3.2 Piping

- (1) Always purge piping systems with inert gas before introduction of phosphine.
- (2) Always purge piping systems with inert gas before disconnection of phosphine cylinders.

9.3.4 Prohibition and restriction

- (1) Users shall not use adaptors to connect containers.
- (2) Do not over-tighten valves. Follow manufacturer's recommendations.
- (3) Never drag or slide the containers.
- (4) Never lift the container by the valve protection cap.
- (5) Use proper cylinder trolleys or appropriate moving devices to minimize rolling of cylinders over long distances.
- (6) Never use cylinders as a roller to move equipment.
- (7) The use of portable electronic devices, e.g. mobile hand phones and walkie-talkies, is prohibited, unless the devices have been proven to be intrinsically safe.
- (8) Prohibit sources of ignition, e.g. cigarette smoking.
- (9) Electrical equipment in the vicinity of phosphine should be intrinsically safe following zoning guidelines in national regulations. If national regulations are not available, consult IEC (International Electro-technical Commission) or NEC (National Electrical Code).
- (10) Non-sparking tools are recommended to be used when working around phosphine, and are required by some jurisdictions.

9.4 Security

Appropriate security measures should be implemented to prevent access to phosphine cylinders by unauthorized personnel. For more details refer to AIGA Doc. 003/07 *Security Guidelines* or EIGA 907/05 *Security Guidelines*. Phosphine can be used as a weapon of mass destruction (WMD) in the possession of a terrorist.

A sale policy for arsine shall be in place. It shall be ensured by a thorough review prior to the purchase being approved and the delivery being made that the customer has a valid reason to purchase phosphine and that the tracking records during shipment of phosphine shall be issued and kept.

10. Gas Supply to Point-of-use

Gas supply systems shall be located in a well ventilated area. Gas cabinets or ventilated enclosure shall be used for phosphine supply systems. Provision shall be made to deal with emergencies, such as leaks in the supply system.

10.1 Process line control

A purge gas shall be used to purge the phosphine system during commissioning of the system or prior to the maintenance. The purge gas is also used to purge the pigtail prior to and after cylinder change. Appropriate precautions shall be taken to ensure that the purge gas supply does not become

contaminated with phosphine. A dedicated purge gas source shared with other compatible gases, a compressed gas cylinder, shall be used. This will avoid the risk of back-feeding via the purge gas system into another incompatible process gas supply system.

Adequate precautions should be taken to ensure that phosphine does not inadvertently come into contact with any oxidizer or a source of ignition.

10.2 Regulators

Regulators are used in phosphine delivery systems to reduce and control the pressure from a high pressure source to a safe working pressure for use. All internal regulator parts should be compatible with phosphine under normal operating conditions.

A regulator for semiconductor applications is functionally the same, but has different features than those of a regulator designed for general duty use. Regulators designed for controlling phosphine in semiconductor processes are constructed of typically 316 or 316L stainless steel (SS), at times electro-polished. Phosphine being a pyrophoric, requires additional safeguards in material construction. Regulators with stainless steel diaphragms should be used to avoid the potential of phosphine diffusion through porous elastomer diaphragms and the potential diffusion of contaminants that are adsorbed on elastomeric diaphragms. Once a regulator has been used in phosphine service, it should not be used for other gas service.

11. Gas Abatement Systems

Since phosphine is a highly toxic and pyrophoric material, a gas abatement system must be used to control any emission whether anticipated or not.

The best method of abatement depends on whether the phosphine is being handled as a pure product, diluted in a mixture, or mixed with other by-products. Full product recovery tends to be practiced at manufacturing facilities. After use in a process, contamination and other issues utilizing chemical abatement may offer better solutions. Such an abatement system could be capable of dealing with other contaminants in the system. Disposal of phosphine by any means must be done in an environmentally acceptable manner in compliance with all applicable regulations.

A competent person knowledgeable in the handling and processing phosphine should design the equipment.

11.1 Basic principles of abatement

The following are the typical chemical reactions and physical adsorbents.

- (1) Reclamation or recovery
Cryogenic recovery
- (2) Oxidation via incineration
$$2\text{PH}_3 + 4\text{O}_2 \rightarrow \text{P}_2\text{O}_5 + 3\text{H}_2\text{O}$$
- (3) Oxidation via wet scrubber
$$\text{P}_2\text{O}_5 + 3\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}_4$$
 or
$$\text{PH}_3 + 4\text{OCI}^- \rightarrow \text{H}_3\text{PO}_4 + 4\text{Cl}^-$$
- (4) Absorption/adsorption and reaction on a treated solid (with metallic oxides)
$$3\text{CuSO}_4 + 2\text{PH}_3 \rightarrow \text{Cu}_3\text{P}_2 + 3\text{H}_2\text{SO}_4$$
 or
$$6\text{FeCl}_3 + \text{PH}_3 + 3\text{H}_2\text{O} \rightarrow 6\text{FeCl}_2 + \text{H}_3\text{PO}_3 + 6\text{HCl}$$
- (5) Physical adsorption on solid media
$$\text{PH}_3 + \text{C} \rightarrow \text{C}[\text{PH}_3]$$
 (C : Activated Carbon)

11.1.1 Reclamation or recovery

Reclamation of phosphine is not a disposal method, as usually understood. This technique is for reclaiming residual gas and returning the phosphine safely to suitable containers. Once reclaimed, phosphine has to be re-processed, purified and analyzed before being reused. However, the typical phosphine user due to the pyrophoric characteristic of phosphine should not perform reclamation of phosphine.

All types of Reclamation are strongly recommended both in the interests of the environment and the conservation of materials and energy.

The supplier of the material who will have the necessary product handling and container filling expertise is best suited for reclamation of gaseous phosphine. Phosphine should not be reclaimed to a container and returned without the written authority of the owner of the container.

Some users collect the phosphine into the cylinders for treatment off-site.

11.1.2 Oxidation via incineration

While burning the phosphine molecule can be done satisfactorily, capturing the oxidized by-product requires additional equipment. When phosphine burns it produces a dense white cloud of phosphorus pentoxide, P_2O_5 fume. Proper secondary neutralization and clean-up of the phosphorus oxides or oxyacids is critical to employee protection.

Refer to 11.1.3 *Oxidation via wet scrubber* (below) for follow up abatement action to the oxidized phosphine by-product generated.

11.1.3 Oxidation via wet scrubber

The typical wet scrubber use for phosphine is a counter current packed tower.

Suitable arrangements should be made to ensure the system is monitored and shut down in the event of waste gas breakthrough or uncontrolled flammable concerns. Because the phosphine may auto ignite on contact with air, even with low ppm phosphine concentrations (<<1 % concentration to avoid the autoignition point). Factors to be taken into account when utilizing a wet scrubber:

- (1) Phosphine input flow rate
- (2) pH control of the absorbent liquor
- (3) Phosphine concentrations in ppm and <<1 %
- (4) Temperature of the absorbent liquor
- (5) Provisions should be made to monitor both the inlet and outlet stream for phosphine concentration.
- (6) Proper flow control should be installed in the waste phosphine stream to enable the gas flow to be matched to the capacity of the scrubber.
- (7) Proper pressure control should be installed in the waste phosphine stream to enable the gas flow to be matched to the operating capacity of the scrubber.
- (8) Use of inert purge as necessary to facilitate process line clean-up
- (9) Consideration of discharge point from the scrubber exhaust, well away from air intake systems, downdrafts and personnel areas.

To prevent the risk of absorbent liquor sucking back into the system, proper controls should be in place. Consideration should be given to the use of non-sparking equipment as phosphine is flammable. To ensure safe and efficient performance, proper monitoring of process conditions as well as the scrubber gas discharge effectiveness should be carefully considered.

Oxidizing solutions may consist of liquid solutions of potassium permanganate or sodium hypochlorite or caustic solutions and work well for low concentrations of phosphine.

Use of wet scrubber with higher concentrations of phosphine (>1 %) should be carefully engineered to address the pyrophoric characteristic of phosphine.

11.1.4 Absorption/adsorption and reaction on a treated solid (with metallic oxides)

Phosphine is fed directly into a vessel containing a bed of solid adsorbent. It is critical to keep the gas stream under an inert environment to prevent autoignition of the pyrophoric phosphine. There are many solid adsorbents available which strongly and readily adsorb/absorb and react with phosphine. Simplicity and portability of a small solid-state absorber may favour the choice of this method under certain emergency conditions. However, capacity is very limited to the amount of phosphine that can be absorbed/adsorbed on the media.

In this document, the terms absorption and adsorption are used interchangeably.

Factors to be taken into account when utilizing the solid-state absorber include:

- (1) Required phosphine disposal rate
- (2) Quantity of phosphine to be disposed
- (3) Acceptable frequency of changing the adsorbent bed or system
- (4) Concentration of the phosphine stream delivered into the absorber bed
- (5) Temperature rise effects from reaction between the phosphine and the adsorbent
- (6) Distribution system within the absorber bed to prevent channelling and premature breakthrough of un-reacted phosphine
- (7) Adsorbent particle size:
Generally small particles give a high contact area, which corresponds to greater efficiency. However, small particle sizes can lead to pluggage or high pressure drops and a tendency of channelling and premature breakthrough of un-reacted phosphine
- (8) Provisions should be made to monitor both the inlet and outlet stream for phosphine concentration.
- (9) Proper flow control should be installed in the waste phosphine stream to enable the gas flow to be matched to the capacity of the absorber bed.
- (10) Proper pressure control should be installed in the waste phosphine stream to enable the gas flow to be matched to the operating capacity of the absorber bed.
- (11) Use of inert purge as necessary to facilitate process line clean-up
- (12) Consideration of discharge point from the absorber bed exhaust, well away from air intake systems and personnel areas.

11.1.5 Physical adsorption on solid media

Phosphine is fed directly into a vessel containing a bed of solid media. It is critical to keep the gas stream under an inert environment to prevent autoignition of the pyrophoric phosphine gas. There are many types of solid media available which adsorb phosphine. Adsorption capacity varies with solid type, for example using granular activated carbon, phosphine capacities approach to 1-3 % (by weight) of the total carbon weight.

Off-gassing of phosphine from solid media can occur so it is important to have proper controls and phosphine monitoring in place. Heat is generated during phosphine adsorption as a function of adsorption rate and phosphine concentration. Temperature profiles through the bed containing solid media that are flammable must be monitored to prevent the solid media from igniting.

Simplicity and portability of a small solid-state absorber may favour the choice of this method under certain emergency conditions. Factors to be taken into account when adsorption on carbon are similar as those identified in "11.1.4 Absorption/adsorption on a treated solid", listed above.

11.2 User requirements

All personnel involved with the handling of phosphine must be trained in the proper procedures for

abatement control utilized at the site. A thorough knowledge of the product and its associated hazards is required. This would include, but not limited to:

- (1) Physical properties of phosphine
- (2) Physical properties of abatement material
- (3) Toxicological properties of phosphine
- (4) Characteristics of phosphine
- (5) Operating documents

11.3 Waste stream disposal

Dispose in accordance with all applicable regulations. Disposal of pure phosphine is considered a toxic hazardous waste. Waste streams may contain phosphorous oxides or other metallic oxides and be considered a toxic, hazardous waste. Proper management and control of waste is required. Refer to local and government regulations as they apply to waste management.

11.4 Waste Management

Nearly every operational process leaves behind some residual waste. Accelerating pressure on conserving natural resources, the impact of new technologies on resource use, increasing waste generation, and the need for more sustainable approaches to using natural resources represent new challenges to our society.

Local and government authorities tend to regulate all this waste under various programs. Only those companies licensed by the government are allowed to process these waste. Evaluating, selection and monitoring of the waste disposal company is a very important program that the hazardous waste generator must comply with. Full documentation of hazardous waste generation, shipments and final processing is critical to assure proper compliance and control.

The goals of proper waste management are to:

- (1) Protect society from the hazards of waste disposal
- (2) Conserve energy and natural resources by recycling and recovery
- (3) Reduce or eliminate waste
- (4) Clean up waste, which may have spilled, leaked, or been improperly disposed.

Users must promote and encourage the use of combined methods to manage solid waste. These methods are:

- (1) **Source reduction or waste prevention**, which means any practice that reduces the amount or toxicity of waste generated.
- (2) **Recycling**, which conserves disposal capacity and preserves natural resources by preventing potentially useful materials from being thrown away.
- (3) **Land-filling**, landfills are well-engineered facilities that are located, designed, operated, and monitored to ensure compliance with regulations. Solid waste landfills must be designed to protect the environment from contaminants which may be present in the solid waste stream
- (4) **Waste combustion**, can reduce the quantity of waste considerably. However, concerns of what types/quantities of toxics exit the scrubbers can become a local debate.

12. Emergency Response

12.1 Preparation

The purpose of preparation is to establish a system and assign responsibility in the event of an accident or other emergency situation.

The phosphine user shall have procedures in place to address emergency situations that affect public

health and environmental concern in the event of an accident. The **Emergency Plan** is such a document and identifies potential emergencies which are reasonably foreseeable, and specifies actions to prevent, prepare for, respond to, and recover from these. The **Emergency Plan** includes methods used to prevent and mitigate environmental impacts which could be associated with emergency situations.

The **Emergency Plan** shall be reviewed and updated periodically as applicable. Updated copies are provided to the local emergency planning committees and government officials as applicable. Training is provided for all personnel who may be involved with emergency response.

The **Emergency Plan** is tested periodically to ensure its effectiveness, including tests of related leak detection equipment, personnel protective equipment, protective systems and emergency communications. The **Emergency Contact List** is reviewed and updated with each change as applicable. Latest versions shall be maintained.

Phosphine incidents vary considerably and **Emergency Plan** must consider the chemicals and quantities involved, types of hazard, response efforts required, number of responders needed and effects produced. Incidents may require immediate control measures (emergency) or long term activities (remedial action) to restore acceptable conditions. The plan activities are divided into interacting elements:

- (1) Recognition
- (2) Evaluation
- (3) Control
- (4) Information
- (5) Safety

12.1.1 Recognition

Recognizing the type and degree of the hazard presented by phosphine is usually one of the first steps in responding to an incident.

12.1.2 Evaluation

The responder will predict the behaviour and anticipated problems associated with the material. Anticipated problems that may extend beyond the company property will require support/involvement from local officials. Material Safety Data Sheets (MSDS) or other product information will be used to help evaluate the nature and affect to the environment and public health.

12.1.3 Control

Control refers to those methods which prevent or reduce the impact of an incident. Control is addressed by remedial action in the form of documented procedures (plans). It is the responsibility of each facility and its personnel to assure proper procedures are in place and followed.

12.1.4 Information

An integral component of response is information. Notification of internal employees, local emergency response officials, corporate compliance, corporate safety and government agencies is as per established procedures. All accidents are documented and reviewed by the **Safety Committee** and/or **Emergency Response Team**, to determine the root cause and to implement the corrective actions of the accident, the effectiveness of the response, corrective action warranted and notification to prevent repeat occurrence. Reference documents may include:

- (1) Material Safety Data Sheets (MSDS)
- (2) Emergency Plan
- (3) Standard Operating Procedures
- (4) Process Hazard Analysis reviews

(5) Technical Gas Data Books

12.1.5 Safety

All hazardous material responses pose varying dangers (health and safety) to responders, the environment and the neighbourhood. Safety considerations are an input to every activity that is undertaken and are an outcome of each response taken. It is the responsibility of all employees to work in a safe manner and follow established safety rules and regulations.

12.2 Response

Before attempting any emergency situation always ensure that responding personnel are properly trained, adequate and appropriate Personnel Protective Equipment (PPE) equipment is worn. Only those employees trained in responding to an incident shall do so...and only to the level of their training. The company's **Emergency Plan** shall identify the procedures and policies that will be followed in an emergency response [30][31][32]

Off-site response requires interaction with other company's **Emergency Plan**. It could occur during transportation or at the customer site. Whether on-site or off-site, detailed information on how to handle such issues can be found in AIGA document 004/04 *Handling Gas Container Emergencies* and EIGA 80/01/E *Handling Gas Container Emergencies*. Also refer to EIGA document 30/07/E *Disposal of Gases*.

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Conversion Factors

Pressure

To Convert From	To	Multiply by	
atmosphere, standard (atm)	pascal (Pa)	101325	E 0
bar (bar)	pascal (Pa)	1	E 5
pound per square inch (psi)	pascal (Pa)	6.89476	E 3

Weight

To Convert From	To	Multiply by	
pound (lb)	kilogram (kg)	4.5359237	E -1

Length

To Convert From	To	Multiply by	
Inch (in)	meter (m)	2.54	E -2
Foot (ft)	meter (m)	3.048	E -1

Area

To Convert From	To	Multiply by	
square inch (in ²)	square meter (m ²)	6.4516	E -4
square foot (ft ²)	square meter (m ²)	9.290304	E -2

Volume

To Convert From	To	Multiply by	
cubic inch (in ³)	cubic meter (m ³)	1.6387	E -5
cubic foot (ft ³)	cubic meter (m ³)	2.8316	E -2
Liter (L)	cubic meter (m ³)	1	E -3

Density

To Convert From	To	Multiply by	
pound per cubic inch (lb/in ³)	kilogram per cubic meter (kg/m ³)	2.76799	E 4
pound per cubic foot (lb/ft ³)	kilogram per cubic meter (kg/m ³)	1.60185	E 1

Temperature

To Convert From	To	
degree Fahrenheit (°F)	degree Celsius (°C)	$^{\circ}\text{C} = (^{\circ}\text{F} - 32) \times \frac{5}{9}$