Voltaix®

Material Safety Data Sheet for: Poisonous* Phosphine (PH_3) Mixtures

In an emergency, call CHEMTREC at 800-424-9300 or 703-527-3887.

Section 1: Chemical Product and Company Identification

Material Name: Poisonous phosphine mixtures:
2.2% or more in argon, helium, hydrogen or nitrogen

Chemical Formula of principal gas: PH_3.

Synonyms of principal gas: Hydrogen phosphide, phosphoretted hydrogen, phosphorus trihydride, phosphorus hydride.

Manufacturer: Voltaix, LLC: Post Office Box 5357, North Branch, New Jersey 08876-5357, USA
Voice:: 908-231-9060 or 800-VOLTAIX, Facsimile: 908-231-9063

This MSDS is Copyrighted, Voltaix, 1994. Permission is hereby granted to duplicate it, in its entirety, for distribution with this material.

Section 2: Composition/Information on Ingredients

Component	CAS Registry Number	Molar (volume) concentration	Exposure Guidelines
Phosphine	7803-51-2	2.2% or more	0.3 ppm TLV-TWA (ACGIH) 1 ppm TLV-STEL (ACGIH)
Argon	7440-37-1	balance	Simple asphyxiant
Helium	7440-59-7	balance	Simple asphyxiant
Hydrogen	1333-74-0	balance	Simple asphyxiant
Nitrogen	7727-37-9	balance	Simple asphyxiant

Section 3: Hazards Identification

Emergency Overview

These phosphine mixtures are colorless gases with no odor or an odor that has been described, by various observers, as similar to that of garlic, rotting fish or stale urine. As exposure deadens the sense of smell, do not use smell to determine phosphine concentration. The mixtures' immediate health hazards are that they are poison gases and may cause thermal burns. They are flammable gases that may be pyrophoric (autoigniting in air) and may form mixtures with air that do not autoignite, but are flammable or explosive. These phosphine mixtures are reactive with oxidizers, halogens, and nitric acid.

NFPA 704 Rating (determined by Voltaix): Health 4 Fire 4 Reactivity 1 Special none

Note: Section 3 is continued on Page 2.

***2.2% or more in argon, helium, hydrogen, or nitrogen.**

Section 3: Hazards Identification (continued)

Potential Health Effects

Routes of Exposure: At low concentrations, the primary route is inhalation. At high concentrations, phosphine autoignites, creating a thermal burn risk, but reducing the toxic hazard.

Lengths of Exposure: Phosphine has been found to be a severe respiratory irritant in short term human exposures. It has been found in animal studies to be toxic in acute (4 hour) tests and subacute (4 hours/day for two months) tests.

Severity of Effect: Depends on concentration and duration.

Target Organs: Respiratory and cardiovascular systems. Neurological and gastrointestinal effects have also been reported, as have renal and hepatic toxicity.

Type of Effect: Respiratory irritation and impairment, pulmonary edema, cardiovascular (including myocardial) injury, gastrointestinal irritation.

Signs and Symptoms of Exposure: Shortness of breath; chest tightness; headache; vertigo; weakness; fatigue; and nausea, vomiting, and diarrhea.

Medical Conditions that may be Aggravated by Exposure: None identified.

Reported Carcinogenic and Reproductive Effects: NTP has not reported genetic or long-term toxicology and carcinogenesis effects studies.

***2.2% or more in argon, helium, hydrogen, or nitrogen.**

Section 4: First Aid Measures

Inhalation

This is the primary route of exposure.

1) Remove the affected person from the gas source or contaminated area. Note: Personal Protective Equipment (PPE), including positive pressure, self contained breathing apparatus, may be required to assure the safety of the rescuer.

2) If the affected person is not breathing spontaneously, administer rescue breathing.

3) If the affected person does not have a pulse, administer CPR.

4) If medical oxygen and appropriately trained personnel are available, administer 100% oxygen to the affected person.

5) Summon an emergency ambulance. If an ambulance is not available, contact a physician, hospital, or poison control center for instruction.

6) Keep the affected person warm, comfortable, and at rest while awaiting professional medical care. *Monitor the breathing and pulse continuously.* Administer rescue breathing or CPR if necessary.

Skin Contact

Flush with a copious stream of water while removing contaminated clothing. Continue flushing until the professional medical assistance arrives, but for no less than fifteen minutes. Assume the patient has also been exposed by inhalation and obtain professional medical assistance immediately. Treat thermal burns by assuring that affected area is cool by flushing with cool water, then apply dry sterile dressings. If the patient is burned on the face, neck, head, or chest, assume that the airway may also have been burned and obtain professional medical assistance immediately.

Eye Contact

Flush continuously with clean water until the professional medical assistance arrives, but for no less than thirty minutes. Continuation of flushing until patient is transferred to an ophthalmologist or emergency physician is recommended.

Ingestion

Ingestion is not an observed route of exposure to gaseous hazardous materials.

Chronic Effects

None is known to Voltaix

Note to Physicians:

The reaction product of phosphine and moist air is phosphoric acid. Therefore, skin and eye burns should be treated as both thermal and chemical.

***2.2% or more in argon, helium, hydrogen, or nitrogen.**

Section 5: Fire Fighting Measures

Flammability and Explosivity

Flash Point: Not applicable, these materials are gases.

Flammability Limits in Air: Unknown.

Autoignition Temperature: Depends on concentration and diluent. The autoignition temperature of pure phosphine, which usually autoignites in moist air, is approximately 38 ^{o}C (100 ^{o}F). The autoignition temperature of pure hydrogen is 500 ^{o}C (932 ^{o}F). The other diluents are nonflammable gases.

Flammability Classification (per 29 CFR 1910.1200): Flammable gas.

Known or Anticipated Hazardous Products of Combustion: Phosphorus oxide, which dissolves in water to form phosphoric acid.

Properties that may Initiate or Intensify Fire: Heating cylinder to the point of initiating decomposition of the phosphine or activating the pressure relief device.

Reactions that Release Flammable Gases: Thermal decomposition of phosphine releases hydrogen.

Extinguishing Media

None.

Fire Fighting Instructions

The only safe way to extinguish a flammable gas fire is to stop the flow of gas. If the flow cannot be stopped, allow the entire contents of the cylinder to burn. Cool the cylinder and surroundings with water from a suitable distance. Extinguishing the fire without stopping the flow of gas may permit the formation of ignitable or explosive mixtures with air. These mixtures may propagate to a source of ignition.

Excessive pressure may develop in gas cylinders exposed to fire, which may result in explosion, regardless of the cylinder's content. Cylinders with pressure relief devices (PRD's) may release their contents through such devices if the cylinder is exposed to fire. Cylinders without PRD's have no provision for controlled release and are therefore more likely to explode if exposed to fire.

Positive pressure, self contained breathing apparatus is required for all fire fighting involving hazardous materials. Full structural fire fighting (bunker) gear is the *minimum* acceptable attire. The need for proximity, entry, and flashover protection and special protective clothing should be determined for each incident by a competent fire fighting safety professional.

***2.2% or more in argon, helium, hydrogen, or nitrogen.**

Section 6: Accidental Release Measures

Containment

These materials are gases at atmospheric conditions. The only means of containment is the enclosure of the space into which the material is released. Such containment is described in Section 7.

Clean Up

Clean up consists of passing the entire gas volume of the enclosure through appropriate exhaust gas treatment equipment (EGTE). Purge the enclosure with a non-reactive gas, such as nitrogen, through the EGTE until an acceptably low level of contamination remains. Equipment contaminated by this material must then be cleaned or decommissioned appropriately.

Evacuation

If the release is not contained in an appropriate device or system, all personnel not appropriately protected (see Section 8) must evacuate the contaminated spaces. Consider evacuation of additional areas, as a precaution against the spread of the release or subsequent explosion or fire.

Special Instructions

Some releases of phosphine mixtures into air will autoignite. As not all leaks will autoignite, consider the formation of ignitable or explosive mixtures with air.

Section 7: Handling and Storage

Handling

Handle this material only in sealed, purged systems. The design of handling systems for hazardous materials is beyond the scope of this MSDS, and should be performed by a competent, experienced professional. Consider the use of doubly-contained piping; diaphragm or bellows sealed, soft seat valves; backflow prevention devices; flash arrestors; and flow monitoring or limiting devices. Gas cabinets, with appropriate exhaust treatment, are recommended, as is automatic monitoring of the secondary enclosures and work areas for release.

Handle sealed gas cylinders in accordance with CGA P-1, *Safe Handling of Compressed Gases in Containers*.

Some material may have accumulated behind the outlet plug. Face the outlet away from you and wear appropriate protective equipment when removing the plug to connect the cylinder to your system.

Never introduce any substance into a gas cylinder. If you believe your cylinder may have been contaminated, notify Voltaix immediately. Provide as much information as possible on the nature and quantity of contamination.

Storage

Store cylinders in accordance with CGA P-1, *Safe Handling of Compressed Gases in Containers*, local building and fire codes and other relevant regulations. Materials should be segregated, by the hazards they comprise, for storage.

Protect the cylinders from direct sunlight, precipitation, mechanical damage, and temperatures above 55 ^{o}C (130 ^{o}F).

Ship and store cylinders with the outlet plug and valve protective cap in place.

***2.2% or more in argon, helium, hydrogen, or nitrogen.**

Section 8: Exposure Control/Personal Protection

Engineering Controls

Local exhaust is required. Secondary containment, with appropriate exhaust gas treatment, is strongly encouraged and is required in some jurisdictions.

Monitor the work area and the secondary containment continuously for release of the material. Automatic alerting of personnel and automatic shutdown of flow are appropriate in most applications and are required in some jurisdictions.

Purge all primary containment systems with a nonreactive gas, such as nitrogen, before introducing a phosphine mixture.

Personal Protective Equipment (PPE)

Respiratory Protection: Positive pressure, full face, air supplied breathing apparatus should be used for work within the secondary containment equipment if a leak is suspected or the primary containment is to be opened, *e.g.*, for a cylinder change. Air supplied breathing apparatus is required for response to demonstrated or suspected releases from the primary containment.

Eye/Face Protection: When using respiratory protection as described above, use a face mask that provides splash and impact protection for the face and eyes. For handling sealed cylinders, wear safety glasses.

Skin Protection: Wear appropriate gloves when handling sealed cylinders. Use gloves and other skin protection, as assigned by a competent safety professional, when working within the secondary enclosure with the primary enclosure compromised, *e.g.*, cylinder changing, to protect both from exposure to the material and from fire that may result from its release to the air.

Other Protection: Wear appropriate protective footwear when moving cylinders.

Exposure Guidelines for Phosphine (The diluents are simple asphyxiants.)

TLV-TWA: 0.3 ppm (ACGIH).

TLV-STEL: 1 ppm (ACGIH).

PEL- TWA: 0.3 ppm (0.4 mg/m^3) (OSHA).

PEL-STEL: 1 ppm (1 mg/m^3) (OSHA).

REL-TWA (10 hour): 0.3 ppm (NIOSH).

REL-STEL: 1 ppm (NIOSH).

IDLH: 50 ppm (Established by NIOSH).

Section 9: Physical and Chemical Properties

Notes: 1) "N/A" means not applicable.
2) Unless otherwise specified, properties are reported at 0 ^{o}C (32 ^{o}F) and 1 atmosphere (1.0 bar, 14.7 psia).

Property	Phosphine	Argon	Helium	Hydrogen	Nitrogen
Appearance	colorless	colorless	colorless	colorless	colorless
Odor	garlic, decomposing fish, stale urine	none	none	none	none
Physical state	gas	gas	gas	gas	gas
pH	N/A	N/A	N/A	N/A	N/A
Vapor Pressure	35.6 bar (517 psia) at 20 ^{o}C (68 ^{o}F)	N/A	N/A	N/A	N/A
Vapor Density	1.53 g/L	1.78 g/L	0.18 g/L	0.082 g/L	1.146 g/L
Boiling point	-87.7 ^{o}C	-122.4 ^{o}C	-268.9 ^{o}C	-252.9 ^{o}C	-195.8 ^{o}C

***2.2% or more in argon, helium, hydrogen, or nitrogen.**

Property	Phosphine	Argon	Helium	Hydrogen	Nitrogen
	(-125 °F)	(-188 °F)	(-458 °F)	(-423 °F)	(-320 °F)
Melting point	-133.8 °C (-208 °F)	N/A	N/A	N/A	N/A
Solubility in water (v/v, at 20 °C)	0.27	0.0337	0.0086	0.0182	0.0149
Specific gravity of liquid (water = 1)	0.74 at-87.7 °C (-125 °F)	N/A	N/A	N/A	N/A
Molecular weight	34.00	39.95	4	2.02	28.01

Section 10: Stability and Reactivity

Chemical Stability: Phosphine is stable at room temperature. At elevated temperature (above 150 °C), phosphine decomposes to phosphorus and hydrogen. Diphosphine may also result from thermal decomposition. The diluents are stable.

Conditions to Avoid: Temperatures above 55 °C, sources of ignition, exposure to air.

Incompatibility with Other Materials: Oxidizers, halogens, nitric acid.

Hazardous Decomposition, Reaction and Oxidation (other than burning) Products: Phosphorus oxide, phosphorus, hydrogen, diphosphine.

Hazardous Polymerization: Not reported to occur.

Section 11: Toxicological Information for Phosphine (The diluents are simple asphyxiants.)

Acute Data (by route): Exposure by inhalation: LC_{50}, 4-hour, rat is reported both as 11 ppm and 57 ppm. The other data, summarized in the table below, are more consistent with the higher of these two values. The primary effect is respiratory irritation and pulmonary edema. Reaction with air may produce irritation or thermal burns to skin, eyes and mucous membranes.

Effect	Species	Time	Concentration (ppm)	Concentration, adjusted to one hour
LC_{50}	Rat	4 hour	11	22
LC_{50}	Rat	4 hour	57	114
LC_{LO}	Human	5 minutes	1000	289
LC_{LO}	Mouse	2 hour	271	383
LC_{LO}	Cat	2 hour	50	71
LC_{LO}	Rabbit	20 minutes	2500	1443
LC_{LO}	Guinea Pig	4 hour	100	200
LC_{LO}	Mammal	5 minutes	1000	289

Chronic and Subchronic Data: Rats exposed to 4 ppm, 4 hr for 9 of 12 days exhibited reduced weight gain and some respiratory irritation, but returned to normal during 2 week recovery. Exposure of unspecified animals to 5 ppm for 4 hours per day for 2 months did not produce fatalities, similarly exposure to 10 ppm for seven days did, but to what fraction of the exposed population was not reported. Phosphine is listed in the *Registry of Toxic Effects of Chemical Substances* (RTECS), but no information on its carcinogenicity is available.

***2.2% or more in argon, helium, hydrogen, or nitrogen.**

Phosphine is suspected as the cause in an acetylene generator operator death; the exposure was estimated to be 8 ppm, for 1 to 2 hours per day. Other, more toxic, hydrides, *e.g.*, arsine and hydrogen selenide, may have been present in that case.

Autopsy findings on humans believed to have died from phosphine exposure include pulmonary edema, diffuse cardiovascular injury, and focal myocardial necrosis.

Diarrhea, nausea and vomiting, chest tightness, cough, headache, dizziness have been reported in intermittent human exposure up to 35 ppm, averaging 10 ppm. No cumulative effects were observed.

Special Studies: None known to Voltaix

Section 12: Ecological Information

Ecotoxicity: None known to Voltaix

Environmental Fate: None known to Voltaix

Section 13: Disposal Considerations

Classification under RCRA, 40 CFR 261: Phosphine has been assigned the Hazardous Waste Number P096. These mixtures may meet the criteria for an "acute hazardous waste".

US EPA waste number and descriptions: P096 (Phosphine), D001 (ignitability).

Special Instructions and Limitations: Treat process and other exhaust streams appropriately before release to the atmosphere.

Notice: The information above is derived from Voltaix's interpretation of the US federal laws, regulations and policies concerning the material, as shipped by Voltaix,, at the time this MSDS was prepared. Federal controls are subject to change and state and local controls may also apply. Proper waste disposal is the responsibility of the owner of the waste. The user is encouraged to consult with appropriate experts in developing a disposal plan.

Section 14: Transport Information

Basic Description: Compressed Gas, Toxic, Flammable, n.o.s. (Phosphine *x%* in *diluent*), Division 2.3 (Toxic Gas, Flammable Gas), UN 1953 Toxic - Inhalation Hazard, Inhalation Hazard Zone *Z*.
Note: Substitute the mixture concentration for *x%*, the proper shipping name of the diluent for *diluent* and, for *Z*, “A” if the concentration is 57.0% or more “B” if the concentration is 11.4% or more, “C” if the concentration is 3.8% or more, or “D” if the concentration is less than 3.8%.

Additional Information for shipment by water: IMDG Page Number 2125-1.

Additional Information for shipment by air: Transportation by air is not permitted.

Section 15: Regulatory Information

TSCA Status: All of the component materials are listed in the index of chemical substances.

CERCLA Reportable Quantity (40CFR302.40): These materials are not listed. The Final Rule Reportable Quantity (RQ) for phosphine is 45.4 kg (100 lb). The Reportable Quantity (RQ) for “Unlisted Hazardous Wastes Characteristic of Ignitability” (D001) is 45.4 kg (100 lbs.).

***2.2% or more in argon, helium, hydrogen, or nitrogen.**

SARA Title III Status (Section 302 (40CFR355), Section 311/312, Section 313 (40CFR372)): No Threshold Planning Quantity (TPQ) or Reportable Quantity (RQ) is listed for these substances. 40CFR355 lists phosphine as an Extremely Hazardous Substance with a Threshold Planning Quantity (TPQ) of 227 kg (500 lbs.) and a Reportable Quantity (RQ) of 45.4 kg (100 lb). Phosphine is listed in 40CFR372. The default federal MSDS submission and inventory requirement filing threshold of 4,540 kg (10,000 lbs.) may also apply.
Note: State and local requirements may be more stringent.

Section 16: Other Information

References

Book of SEMI Standards, Facilities Standards and Safety Guidelines. Mountain View, CA: Semiconductor Equipment and Materials International, 1993.

Borak, Jonathan, M.D., Michael Callan and William Abbott, *Hazardous Materials Exposure: Emergency Response and Patient Care*. Englewood Cliffs, NJ: Prentice-Hall, Inc., 1991.

Documentation of TLV's and BEI's. Cincinatti, Ohio: American Conference of Government Industrial Hygienists, 1992.

Effects of Exposure to Toxic Gases: First Aid and Treatment. Lyndhurst, NJ: Matheson Gas Products, 1977.

Fire Protection Guide on Hazardous Materials. Quincy, MA: National Fire Protection Association, 1991.

Safe Handling of Compressed Gases in Containers (Pamphlet P-1). Arlington, VA: Compressed Gas Association, Inc., 1991.

Revision Indication

Revise to reflect company name change

Disclaimer

Voltaix cannot guarantee that these are the only hazards that exist. Users are solely responsible for the safe storage, handling, use and disposal of this material, and for compliance with the applicable laws, regulations and accepted practices.

Voltaix makes no representations or warranties, either expressed or implied, of merchantability, fitness for a particular purpose, or any other nature.

***2.2% or more in argon, helium, hydrogen, or nitrogen.**