Phosphine

From Swamp Gas to Applications in the Clean Room

By Eugene Ngai

Phosphine (phosphorus hydride, CAS# 7803-51-2; UN 2199) is one of the key metal hydride gases used in semiconductor processing as well as a grain fumigant. Lavoisier (1789) recognized phosphine as a combination of phosphorus with hydrogen by describing it as "hydruyet of phosphorus, or phosphuret of hydrogen." Phosphine is sometimes found in nature in low concentrations. Researchers have reported that biological sources may be emitting over 40,000 metric tons of phosphine per year. Co-produced with methane, phosphine is the cause of the glow found in swamps. Commonly known as Will-o'-the-Wisp, swamp gas is found in peat bogs, mud flats, marshes, and swamps — wherever stagnant water coincides with the decay of organic matter. Phosphine ignites the methane causing the mysterious glow reported at night.

Physical Properties

Pure phosphine (PH_3) is a colorless, pyrophoric liquefied gas with a vapor pressure of 513 psig (3.64 MPa) at 70°F (21°C). Although pure samples of phosphine are odorless, the gas often has an odor of garlic or decaying fish due to the presence of substituted phosphine and diphosphine (P_2H_4). It is highly toxic gas with a permissible exposure limit (PEL) of 300 ppb, a lethal concentration value (LC_{50}) of 20 ppm and an immediately dangerous to life or health (IDLH) value of 50 ppm. Phosphine is slightly heavier than air (specific gravity: 1.18) and is not soluble in water. Phosphine is thermally stable up to 707°F (375°C) with complete dissociation reported at 1112°F (600°C) or in some reports, at even higher temperatures.

Phosphine has a low auto-ignition temperature <32°F (<0°C) so it ignites spontaneously on contact with air at atmospheric pressure and ambient temperature of 70°F (21°C). It has an extremely wide flammable range of 1.6–95 percent in air. It burns in air with an orange flame forming white phosphorous pentoxide as a byproduct, which is a severe respiratory irritant. Under certain conditions, phosphine will form red phosphorus as a byproduct.

Health and Safety

Phosphine can sometimes be detected by its odor of decaying fish, or some report it to be an odor similar to "halitosis" — bad breath. Acute exposures to phosphine cause respiratory tract irritation that attacks primarily the cardiovascular and respiratory systems causing peripheral vascular collapse, cardiac arrest and failure, and pulmonary edema. Inhalation is the primary exposure route, and there is no known dermal exposure route. Symptoms may include restlessness, irritability, drowsiness, tremors, vertigo, double vision (diplopia), ataxia, cough, dyspnea, retrosternal discomfort, abdominal pain, and vomiting. There is no antidote for phosphine exposures; treatment is supportive. Guidance on proper medical treatment is available from the US Health Department Agency for Toxic Substances and Disease Registry (ATSDR) sheet on phosphine. The author is not aware of any phosphine fatalities related to semiconductor use.

Phosphine can cause fatalities. People who illegally manufacture methamphetamine (Angel Dust) heat pure phosphorus, which produces traces of phosphine. Many cookers are unaware of this hazard and become acutely exposed.

Suicide pellets are made from aluminum phosphide, and they kill either after being ingested or when the phosphine offgased from the pellets is inhaled. Medical personnel must beware, because the body of one who has committed suicide in this way will continue offgassing phosphine until all of the phosphide has reacted in the stomach.

Phosphine also is produced as an impurity in some industrial processes and workers can be unintentionally exposed. For example, acetylene for welding is typically produced by reacting calcium carbide with water. Most calcium carbides have varying amounts of calcium phosphide as an impurity. This will also react with the water used to react the calcium carbide to form phosphine, which gives acetylene its characteristic odor. Impurity levels of over 300 ppm are common. Acetylene suppliers try to reduce this below 200 ppm as levels above this can have a significant effect on its flammability. Wet scrubbers are commonly used to reduce this level.

In two other examples: sodium hypophosphite ($NaPO_2H_2$, also known as sodium phosphinate), used in electroless nickel plating processes, decomposes when heated, producing phosphine gas; and, during phosphoric acid manufacturing, trace amounts of phosphine also may be produced.

Production

Phosphine may be prepared in a variety of ways. Industrially it is produced by reacting white phosphorus with sodium hydroxide, producing sodium hypophosphite and sodium phosphite as byproducts. This is the most common route to produce phosphine used for fumigation. Other methods include water or hydrochloric acid on calcium phosphide or zinc phosphide, or hot alkaline solutions on elemental phosphorus.

For semiconductor applications, a very high purity (99.9999 percent pure) phosphine is required. This is manufactured by the high temperature disproportionation of polyphosphoric acid yielding phosphine and phosphoric acid.

Applications

The two main applications for phosphine are in semiconductor manufacturing processes and in crop fumigation.

Pure phosphine is used in silicon semiconductor processing as a phosphorus (N-type dopant) source in ion implantation. Phosphine mixtures are used as dopants in diffusion ovens. Phosphine can also be reacted with trimethylborate to form a capping layer on a semiconductor device to prevent atmospheric moisture from permeating into the device. In crystalline silicon PV fabrication, phosphine mixtures are used to dope polysilicon bricks with phosphorus before they are sawed into wafers.

In compound semiconductor applications, phosphine is a raw material in organometallic vapor phase epitaxy (OMVPE) or metal organic chemical vapor deposition (MOCVD) reactors to grow crystal structures epitaxially or deposit films onto substrates. Phosphine (Group V) is typically reacted with an organometallic such as trimethylgallium or trimethyindium (Group III) to form optically active semiconductor layers (GaP, InP, GaInP). These form discrete optoelectronic devices such as lasers, photodiodes, or light emitting diodes (LEDs). These crystalline layers respond to or emit different wavelengths: InGaP — 650 nm; AlGaInP — 635–650 nm; AlInGaP — 565 nm; InP — 1300 nm. Compound semiconductor photovoltaic cells use multiple layers to absorb more sunlight, which increases the cells efficiency. In 2009 a record 41.6 percent efficiency was recorded for a tandem junction photovoltaic cell using a triple layer GaInAs/GaInP/Ge for earth-bound applications.

For space applications the most efficient is a four-layer design with phosphorus as the top layer. InGaP absorbs yellow-green wavelengths; GaAs absorbs green-deep red wavelengths; InGaAsN absorbs deep red-infrared wavelengths; and Ge absorbs infrared-far infrared wavelengths.

Phosphine also is the raw material used to form phosphine derivative products, including phosphonium salts used in pharmaceutical catalysts and biocides. A key segment is the organo phosphorus compounds. These are used primarily as intermediates and catalyst ligands for organic and chemical synthesis in the pharmaceutical and chemical industries.

In a completely different market, phosphine is widely used as a grain fumigant and has been for the last 50 years. In Australia it is used on over 80 percent of the grain. Like methyl bromide it does not leave a residue on the grain. It is also used as a rodenticide. Phosphine is delivered as a gas in cylinders or generated at the location using a solid such as: aluminum phosphide (AlP) for product fumigation and occasionally for rodent control; magnesium phosphide (Mg_3P_2) for product fumigation and occasionally for rodent control; or zinc phosphide (Zn_3P_2) (more stable chemically than aluminum phosphide, it forms phosphine gas only when ingested by the animal) for rodent control. Typically the solid is a tablet coated in paraffin to delay the reaction with moisture in the air.

As insects are becoming more resistant to phosphine, phosphine mixtures in cylinders are more commonly used (ECO_2 FUME® or nitrogen FRISIN®). These allow a more precise concentration to be delivered throughout the silo and can be maintained for a period of time, which increases effectiveness. ■

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Air Products worker assembles a gas cabinet in a cleanroom environment at the company's Semiconductor Equipment Manufacturing Center located in Allentown, Pennsylvania.