

## Safetygram 48

### Safe Handling of Water Reactive Inorganic Halides: Boron Tribromide, Phosphorus Oxychloride, Phosphorus Tribromide, Titanium Tetrachloride

This safetygram provides information on hazards and safe handling procedures for four products that are members of the chemical family called inorganic halides. Boron tribromide (BBr<sub>3</sub>), phosphorus oxychloride (POCl<sub>3</sub>) and phosphorus tribromide (PBr<sub>3</sub>) are used in semiconductor, flat-panel and solar cell manufacturing as dopants to introduce impurities into silicon to change electrical properties. Titanium tetrachloride (TiCl<sub>4</sub>) is used as the titanium source for titanium nitride, titanium dioxide and titanium metal in the semiconductor industry. These inorganic halides exhibit similar hazards, including exothermic reactivity with water and the potential to be corrosive to the respiratory tract and skin. It is important to recognize these hazards so that appropriate precautions can be

taken for storage, when working with the materials, and when responding to emergencies.

The water reactivity exhibited by these products extends to reaction with moisture found in skin perspiration and mucous membranes, tears, and atmospheric humidity. The reaction with water is exothermic, generating heat and inorganic acids. Injury can result from the combined thermal and acid burns.

End users should conduct their own formal risk assessment to identify all hazards and evaluate the controls needed to ensure the safety of workers. Typical controls include training, use of protective equipment, implementing safety procedures for work and posting of warning signs.

#### Chemical and Physical Properties

Table 1 shows some of the physical properties of these water-reactive liquids. These products are generally colorless, volatile, fuming liquids with pungent odors. Boron tribromide discolors when exposed to light. These liquids are corrosive to metals, skin and other tissue. Fuming of these products increases with increasing humidity.

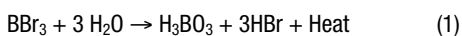
#### Hazards

##### Water Reactivity and Formation of Acidic Hydrolysis Products

Water reacts violently and exothermically with these inorganic halides, scattering the material and creating significant fumes of inorganic acids.

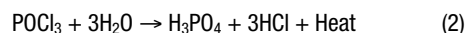
**Warning:** Containers, especially quartz bubblers, should not be rinsed or washed with water under any circumstances!

**Boron tribromide** may explode on contact with water. Boric acid, hydrogen bromide and heat are formed.



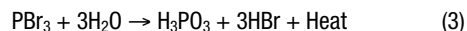
**Warning:** This reaction is very fast, and the energy released may be sufficient to cause a detonation.

**Phosphorus oxychloride** reacts violently with water to produce phosphoric acid, hydrogen chloride and heat.

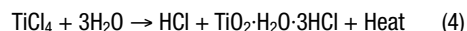


In experiments at room temperature when phosphorus oxychloride is added carefully without agitation to water, the more dense phosphorus oxychloride liquid will submerge, forming two layers. The hydrolysis reaction may be delayed for several minutes. After the initial contact with water, the water reaction begins slowly but will progress to a rapid acceleration with spattering.

**Phosphorus tribromide** reacts violently with water to produce phosphorous acid, hydrogen bromide and heat.



**Titanium tetrachloride** reacts violently with water to form hydrogen chloride and a solid complex of titanium oxychloride, resulting in heavy smoke.



If vapors of the solid complex are inhaled, the particulate can travel into the deeper parts of the lungs where the hydrolysis process may continue and lead to more severe damage.



## Flammability

These inorganic halides and the products resulting from their reactivity with water are not flammable.

## Material Incompatibility

If packing materials made from wood and cellulose come in contact with inorganic halides, these materials become hot and char. Papers and cartons will frequently become black. The severity of this reaction is highest with boron tribromide. If spilled liquids contact steel packaging, the corrosion will be significant. This can be avoided by absorbing any liquid spill or leak (See Emergency Operations).

## Health Effects

### Inhalation

Based on the low exposure limits shown in Table 2, breathing of vapors or aerosols of these materials must be prevented. These inorganic halides and their hydrolysis products can cause severe burns to the respiratory tract. These products must be used only in closed systems.

A person breathing a low concentration of the corrosive vapors of these substances may experience symptoms similar to a sore throat. Following minor exposure to these products, a person may notice a foul smell or taste. Saline nose drops may be used to flush out the odor.

Symptoms of overexposure may include breathing difficulties, headache, dizziness, nausea and vomiting. Greater exposure can cause a buildup of fluid in the lungs (pulmonary edema) and severe shortness of breath that results in a medical emergency. Symptoms of pulmonary edema may be delayed for 6 to 24 hours after exposure. Severe cases of overexposure can result in respiratory failure. Other symptoms of overexposure may include bronchitis, bronchopneumonia and kidney inflammation.

### Skin and Eye Contact

Contact with these materials must be avoided. Exposure to these materials can cause severe thermal and chemical burns to the skin and eye.

## First Aid

Before performing first aid measures, first remove contaminated clothing and residual chemical to reduce the interaction with water. While the use of water for first aid in the case of skin and eye exposure may at first seem counter-intuitive for water reactive materials, the flushing accomplishes three things:

**Table 1**

### Physical Properties

Property	Boron Tribromide	Phosphorus Oxychloride	Phosphorus Tribromide	Titanium Tetrachloride
Molecular Formula	BBr <sub>3</sub>	POCl <sub>3</sub>	PBr <sub>3</sub>	TiCl <sub>4</sub>
CAS Number	10294-33-4	10025-87-3	7789-60-8	7550-45-0
Molecular Weight	250.54	153.33	270.73	189.69
Relative Liquid Density (Water = 1)	2.6	1.7	2.8	1.7
Vapor Pressure @ 20°C [mm Hg]	54.5	25.0	2.2	9.6
Relative Vapor Density (Air = 1)	8.6	5.3	9.3	6.5
Water Solubility	Reacts Very Violently	Reacts Violently	Reacts Violently	Reacts Violently
Boiling Point, 1 atm.*	91°C (196°F)	107°C (225°F)	173.2°C (344°F)	136.4°C (278°F)
Freezing Point, 1 atm.*	-46°C (-51°F)	1.2°C (34°F)	-41.5°C(-43°F)	-25°C(-13°F)

**Table 2**

### Exposure Limits

	OSHA PEL	ACGIH TLV	Inhalation LC50 (Rat, 1 h)
Boron Tribromide	1 ppm (Ceiling)	1 ppm (Ceiling)	953 ppm *
Phosphorus Oxychloride	-	0.1 ppm (TWA)	64 ppm **
Phosphorus Tribromide	-	-	> 267 ppm ** < 740 ppm **
Titanium Tetrachloride	-	-	118 ppm **

### Hydrolysis Products

Hydrogen Bromide	3 ppm (TWA)	2 ppm (Ceiling)	2,858 ppm
Hydrogen Chloride	5 ppm (Ceiling)	2 ppm (Ceiling)	3,120 ppm
Phosphoric Acid	1 mg/m3 (TWA)	1 mg/m3 (TWA) 3 mg/m3 (STEL)	-

Ceiling: Ceiling limit value

TWA: Time weighted average

STEL: Short Term Exposure Limit

\* Estimated from Inhalation LC50 (Rat) of hydrolysis product HBr

\*\* Estimated from Inhalation LC50 (Rat) for 4 hours

1. The flushing action, such as water from a safety shower, helps to remove the chemical from the skin or eyes.
2. Water helps to remove the heat that may be generated by the initial reaction of the chemical with the moisture in skin or eyes.
3. Any residual material (after removal of extraneous chemical from clothing and skin) reacts with the water used for flushing, instead of with moisture in the skin or eyes.

### Inhalation

A person who has been exposed to the vapors or is experiencing any of the initial exposure symptoms should be moved to fresh air. If the person is not breathing, perform artificial respiration. If the person is having difficulty breathing, provide supplemental oxygen. Seek immediate medical assistance while continuing to administer oxygen. Continue to monitor for respiratory distress for 24 to 48 hours.

### **Skin Contact**

If skin contact occurs, immediately remove contaminated clothing and shoes. Before using a safety shower or water spray, remove any liquid from the skin with a clean, dry cloth and gloved hands to reduce the interaction of the chemical with water. The exposed skin should be flushed with plenty of water. Obtain medical attention immediately; however, if not promptly available, continue to flush the skin for one hour.

### **Eye Contact**

If these materials get into the eyes, wipe away excess liquid from the skin area around the eye using a clean, dry cloth. Flush with plenty of water, such as from an eyewash station, for at least 30 minutes. In order to ensure that irrigation is complete, hold the eyelids open while flushing. Get medical care immediately, but if not promptly available, continue to irrigate for one hour.

### **Exposure Control**

#### **Containers**

Boron tribromide, phosphorus oxychloride and phosphorus tribromide are packaged in sealed quartz bubblers (see Figure 1) to prevent contamination and subsequent material degradation. Titanium tetrachloride is packaged in stainless steel bubblers. Potential for exposure increases when installing and removing the bubbler systems. To minimize the risk of exposure and bubbler damage, follow the recommendations in Air Products' Safetygram 43, "Air Products Bubbler Installation and Removal Procedures."

#### **Personal Protective Equipment**

For skin protection wear acid-resistant gloves, a long-sleeved acid-resistant apron smock or splash suit, and rubber boots. For acid-forming products, Silver Shield® gloves as a liner under nitrile gloves provide chemical resistance.

When exposure is possible but not expected, use a NIOSH/MSHA approved respirator with acid gas/HEPA cartridges. These liquids have a pungent odor. Leave the area immediately if, while wearing a cartridge respirator, you can smell, taste, or otherwise detect these materials. Check to make sure the respirator-to-face seal is still good. If it is, replace the cartridge. If the seal is no longer good, you may need a new respirator.

When product vapors are known to be present, such as during an emergency or when the airborne concentration is unknown, use a full-face supplied air respirator (airline or self-contained) for respiratory, eye and face protection.

Eyewash stations and safety showers must be readily accessible.

**Figure 1**

#### **Quartz Bubbler**



### **Emergency Operations**

Only qualified emergency responders, thoroughly familiar with the product and package, should respond to an incident. Emergency responders should use self-contained breathing apparatus and chemically protective clothing.

Because of the corrosive effects of these products on skin, eyes and lungs, the hazard area for leaks and spills should be isolated. Operating personnel not involved in emergency response should leave immediately. Do not touch damaged containers or spilled material unless wearing appropriate protective clothing. Fumes are much heavier than air and will drift downwind into low-lying areas.

Liquid spills from a bubbler can be diked and absorbed with inert absorbent material such as kiln-dried vermiculite, dry sand, polyethylene or treated polypropylene. Since acidic hydrolysis products will continue to form for up to 12 hours, allow the spill to completely absorb and react before placing into an appropriate chemical waste container. Consider using additional absorbent if fuming is visible. A licensed hazardous waste disposal company should be contacted to arrange for disposal of the absorbed material. Contact Air Products' Emergency Response Center for technical assistance.

### **Quartz Bubbler Stem Breaks**

In the event of a quartz bubbler stem break, please contact the Air Products Emergency Response Center for technical assistance (see last page for detailed contact information). Except for qualified emergency responders, all other employees should be evacuated from the area. After consulting with the Air Products Emergency Response Center, the appropriate personal protective equipment should be donned. If it can be done safely, carefully place the bubbler in a clean, dry salvage drum with enough appropriate absorbent (dry vermiculite or other compatible material) to completely surround the bubbler. If a salvage drum is not available, the original packaging may be suitable for this purpose. Isolate the bubbler in a well-ventilated area, away from other chemicals and sources of moisture. After isolating the bubbler, the lid should be secured to the secondary container, but not so that it is air tight, to avoid any buildup of pressure while it is being stored. In preparation for shipping, firmly secure lid for shipment back to Air Products. Comply with all Dangerous Goods and Environmental regulations when transporting and disposing of damaged containers and residual product.

### **Firefighting**

These inorganic halides do not burn, but can decompose on heating, and containers may explode. For small fires, dry chemical or carbon dioxide extinguishers should be used. Do not use water on these materials or bubblers due to the water reactivity hazard. For large fires impacting inorganic halide bubblers, flood fire area with water from a safe distance.

### **Additional Information**

If further details are required on these products, please contact the Air Products Technical Information Center. In addition, product material safety data sheets and Safetygram 43, "Air Products Bubbler Installation and Removal Procedures," are available at [www.airproducts.com/safetygrams](http://www.airproducts.com/safetygrams).

#### *Emergency Response System*

- For assistance involving products from Air Products and Chemicals, Inc.
- 24 hours a day, 7 days a week
- Tel 1-800-523-9374 (Continental U.S. and Puerto Rico)
- Tel +1-610-481-7711 (other locations)

#### *Product Safety Information*

Look for more information on our websites:

- Material Safety Data Sheets  
[www.airproducts.com/msds](http://www.airproducts.com/msds)
- Safetygrams  
[www.airproducts.com/safetygrams](http://www.airproducts.com/safetygrams)
- Product Safety Information  
[www.airproducts.com/productsafety](http://www.airproducts.com/productsafety)

#### *Technical Information Center*

- Tel 1-800-752-1597 (U.S.)
- Tel +1-610-481-8565 (other locations)
- Monday–Friday, 8:00 a.m.–5:00 p.m. ET
- Fax: 1-610-481-8690
- E-mail [gastech@airproducts.com](mailto:gastech@airproducts.com)

#### *Information Sources*

- Compressed Gas Association (CGA)  
[www.cganet.com](http://www.cganet.com)
- European Industrial Gases Association (EIGA)  
[www.eiga.org](http://www.eiga.org)
- American Chemistry Council (ACC)  
[www.americanchemistry.com](http://www.americanchemistry.com)

### *For More Information*

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