Use Nitrogen Safely

PAUL YANISKO DENNIS CROLL AIR PRODUCTS Understanding the potential hazards and taking the proper precautions will allow you to reap such benefits as improved product quality and enhanced process safety.

itrogen is valued both as a gas for its inert properties and as a liquid for cooling and freezing. Because of its unique properties, it is used in a wide range of applications and industries to improve yields, optimize performance, protect product quality, and make operations safer (1).

Nitrogen makes up 78% of the atmosphere, with the balance being primarily oxygen (roughly 21%). Most nitrogen is produced by fractional distillation of liquid air in large plants called air separation units (ASUs). Pressure-swing adsorption (PSA) and membrane technologies are also used to produce nitrogen. Nitrogen can be liquefied at very low temperatures, and large volumes of liquid nitrogen can be effectively transported and stored.



▲ Figure 1. Gaseous nitrogen, vaporized from onsite liquid storage into a local distribution system, is used for a wide variety of applications, including blanketing, inerting, purging, stripping, and sparging. Other supply modes ranging from cylinders to onsite generation are also used to deliver nitrogen gas.

Nitrogen does not support combustion, and at standard conditions is a colorless, odorless, tasteless, nonirritating, and inert gas. But, while seemingly harmless, there are hazards associated with the use of nitrogen that require awareness, caution, and proper handling procedures. This article discusses those hazards and outlines the precautions that must be taken to achieve the benefits of using nitrogen in the safest possible manner.

Nitrogen applications

Many operations in chemical plants, petroleum refineries, and other industrial facilities use nitrogen gas to purge equipment, tanks, and pipelines of vapors and gases. Nitrogen gas is also used to maintain an inert and protective atmosphere in tanks storing flammable liquids or air-sensitive materials. It may be delivered in cylinders or tanks, or generated onsite (Figure 1).

Liquid nitrogen is used in a variety of applications, particularly in the food and pharmaceutical industries, to provide safe, efficient, and environmentally friendly freezing and chilling. Liquid nitrogen also is used to freeze materials that are heat-sensitive or soft at room temperature to allow grinding. For example, cryogenic grinding is used to produce finely ground pharmaceuticals, spices, plastics, and pigments (Figure 2).

Properties of nitrogen

Many of nitrogen's physical properties (Table 1) influence its safe handling procedures. The specific gravity (relative vapor density) of a gas is the ratio of the gas density (mass per unit volume) to the density of air. Nitrogen's specific gravity is approximately equal to the ratio of its



▲ Figure 2. Liquid nitrogen is used in certain particle-size-reduction processes to super-refrigerate material, including pigments, plastics, powder coatings, waxes, pharmaceuticals, nutraceuticals, spices, and other food products. Liquid nitrogen makes a material more brittle, allowing it to be easily broken up into small particles using less energy.

molecular weight to that of air $(MW_{N2}/MW_{air} = 28/29 = 0.97)$. A specific gravity less than 1 indicates that the gas is lighter than air and will rise, while a specific gravity greater than 1 indicates that the gas is heavier than air and will tend to settle. Nitrogen gas is only slightly lighter than air and readily mixes with air at room temperature. Cold vapors are more dense and will settle.

Liquid nitrogen, a cryogenic liquid, has a very low boiling point of -320°F. As indicated by its high liquid-to-gas expansion ratio, liquid nitrogen produces large volumes of nitrogen gas when it vaporizes.

Potential hazards of nitrogen

Nitrogen is sometimes mistakenly considered harmless because it is nontoxic and largely inert. However, it can act as a simple asphyxiant by displacing the oxygen in air to levels below that required to support life. In addition, nitrogen gas stored in pressurized containers and systems is stored energy that can cause serious injury or death if released in an uncontrolled manner. Liquid nitrogen also presents hazards due to its extremely low temperature and large expansion ratio.

Oxygen deficiency

Nitrogen can displace oxygen in the air, reducing the percentage of oxygen to below safe levels. Because the brain needs a continuous supply of oxygen to remain active, lack of oxygen prevents the brain from functioning properly, and it shuts down.

Being odorless, colorless, tasteless, and nonirritating, nitrogen has no properties that can warn people of its presence. Inhalation of excessive amounts of nitrogen can cause dizziness, nausea, vomiting, loss of consciousness, and death (Table 2). Death may result from errors in judgment, confusion, or loss of consciousness, which prevent self-rescue. At extremely low oxygen concentrations, unconsciousness and

Table 1. Physical and chemical properties of nitrogen.	
Chemical Formula	N ₂
Molecular Weight	28.01
Boiling Point @ 1 atm	–320.5°F (–195.8°C)
Freezing Point @ 1 atm	–346.0°F (–210°C)
Critical Temperature	–232.5°F (–146.9°C)
Critical Pressure	492.3 psia (33.5 atm)
Density, Liquid, @ Boiling Point, 1 atm	50.45 lb/scf
Density, Gas @ 68°F (20°C), 1 atm	0.0725 lb/scf
Specific Gravity, Gas (air = 1) @ 68°F (20°C), 1 atm	0.967
Specific Gravity, Liquid (water = 1) @ 68°F (20°C), 1 atm	0.808
Specific Volume @ 68°F (20°C), 1 atm	13.80 scf/lb
Latent Heat of Vaporization	2,399 Btu/lb mole
Expansion Ratio, Liquid to Gas, Boiling Point to 68°F (20°C)	1 to 694

Table 2. Effects of oxygen deficiency.		
Oxygen Concentration	Effects	
19.5%	Legal minimum concentration for humans (per OSHA regulation)	
15–19.5%	Decreased ability to perform work; appear- ance of early symptoms in persons with coro- nary, pulmonary or circulation problems	
12–15%	Increased pulse rate and respiration, impaired perception and judgment	
10–12%	Further increase in pulse and respiration, giddiness, poor judgment, blue lips	
8–10%	Mental failure, nausea, fainting, vomiting, unconsciousness	
6–8%	8 minutes, 100% fatalities; 6 minutes, 50% fatalities; 4–5 minutes, recovery expected	
<6%	Coma in 40 seconds, convulsions, breathing stops, death	

death may occur in seconds and without warning.

The U.S. Occupational Safety and Health Administration (OSHA) considers any atmosphere with an oxygen level below 19.5% to be oxygen-deficient and immediately dangerous to life or health. Personnel should not enter an area where the oxygen concentration is below 19.5% unless they are using self-contained breathing apparatus (SCBA) or a supplied-air respirator.

If the atmosphere's oxygen content falls to between

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19.5% and 15%, a person's ability to work strenuously is reduced. Coordination may be impaired. As the oxygen content decreases further, perception and judgment are impaired. When the atmosphere's oxygen content falls to the 6% to 4% range, coma can occur within seconds.

The danger of nitrogen asphyxiation is highest in confined spaces. However, fatalities and injuries can occur in open spaces, including areas with ventilation, laboratories, buildings, and outside in the vicinity of equipment. In these cases, the hazard of asphyxiation is not expected, and personnel can be caught off-guard.

Preventing oxygen deficiency

To prevent oxygen deficiency, areas where nitrogen is used require sufficient ventilation. At least four to six changes of fresh air per hour should be provided, depending on room size, the quantity of nitrogen being used, the presence of an oxygen monitoring system, and the overall area layout. Design features should also include pressure-relief devices to vent nitrogen to a safe area outside.

Because nitrogen lacks properties that warn of its presence (*e.g.*, color, odor), an oxygen monitoring system should be installed in any indoor area where nitrogen is stored or used. Several types of oxygen monitoring systems, including personal monitors, portable handheld monitors, and stationary area monitors, are available.

Cold nitrogen vapors can collect in low areas because the cold gas is denser than air. Evaluate areas where nitrogen is used for the presence of confined spaces, such as tanks and equipment; test chambers; ditches, pits, and trenches (pipe trenches); furnaces; and rooms, especially basements. Display appropriate warnings outside confined-space areas. These spaces should be entered only by trained personnel using the established confined-space entry procedures developed for that facility.

Emergency response personnel should use SCBA or supplied air when entering a potentially oxygen-deficient atmosphere. Emergency response for a victim of oxygen deficiency should be carried out by trained personnel only. After the victim has been moved to an area with fresh air, the rescuer should administer oxygen if the victim is breathing, or start artificial respiration if the victim is not breathing. Unprotected personnel should never attempt to rescue a victim by entering a confined space — such attempts can result in additional victims as the rescuers are also overcome by oxygen deficiency.

Vapor clouds

Two types of vapor clouds can form from liquid nitrogen. Liquid nitrogen in exposed piping may cause moisture in the surrounding air to condense, creating a fog that reduces visibility but is otherwise harmless. However, a discharge of liquid nitrogen itself creates a vapor cloud that is an asphyxiation hazard as well as a visibility hazard. Even outside, asphyxiation can occur in a nitrogen-enriched vapor cloud. Remember, dense nitrogen vapor tends to settle, so a person bending down in a nitrogen vapor cloud increases his or her risk.

Abnormal vapor clouds may be an indication of a leak and should be reported. Plant personnel should be trained to recognize vapor clouds associated with normal operations. For instance, ambient air vaporizers, freezers, grinders, and machine tools generate vapor and fog clouds that are normal. However, venting from trailers, liquid nitrogen tanks, or plant systems that drift onto traveled areas, including walkways, can be harmful.

Unless you are trained and qualified to work near vapor clouds that are formed under normal operations (versus an uncontrolled product release), never walk into or through any vapor cloud. Determine the extent of the hazardous zone by ambient air monitoring before and during nonroutine work near vapor clouds.

Pressurized gas

Nitrogen is typically stored and used in equipment at pressures ranging from 10 to 3,000 psig (0.7 to 207 bar); some pressures can be as high as 10,000 psig (690 bar). Operating pressure should not exceed the design pressure of any component in the system.

Pressure is stored energy. A pressurized nitrogen jet can cause injury to skin, eyes, and ears. A jet can also propel objects, such as dust and dirt, and rupture pipes and equipment. Always wear proper personal protective equipment, including gloves and a faceshield, when working in an area where a high-velocity nitrogen discharge or jet is possible.

To protect against over-pressurization, nitrogen systems must be installed with adequate pressure relief. Pressurerelief devices should be provided anywhere liquid can be trapped, for example between two valves. Never tamper with relief valves. In addition, vent lines should be routed to a safe location outside, and high-pressure lines should be secured to prevent bending or whipping. Portable cylinders should be secured as well.

Never work on pressurized systems or repair or disassemble nitrogen piping or related equipment without depressurizing the system and locking out the nitrogen supply valve. Before investigating any unusual hissing sounds from piping, fittings, controls, etc., ensure that all required precautions are in place.

Liquid nitrogen

Nitrogen is typically liquefied for storage and transportation. Liquid nitrogen, a cryogenic liquid, is extremely cold, with a temperature of -320° F (-196° C) at atmospheric pressure. Upon contact with the skin, liquid nitrogen can produce severe burns that are similar to thermal burns.

When handling cryogenic liquids such as liquid nitrogen, wear loose-fitting gloves that can be quickly removed if the cryogenic liquid is spilled on them. Insulated gloves are not intended to permit the hands to be put into a cryogenic liquid — they only provide short-term protection from accidental contact. Wear a long-sleeved shirt, as well as cuffless pants that extend over high-top safety shoes to prevent any liquid from entering a shoe.

Any cold-contact burn should receive immediate medical attention. To help prevent tissue damage, do not rub or move frozen areas. Flush the area with warm water not exceeding 105°F (40°C). Do not use dry heat! Since these burns can be susceptible to infection, rinse the wound with clean water and cover it with a sterile bandage. The circulatory system will provide internal warming, so remove any clothing that may restrict circulation to the frozen area and move the victim to a warm room.

Cryogenic vapors are also extremely cold. Delicate tissue, such as the eyes, can be damaged by exposure to liquid nitrogen, even when the contact is too brief to affect the skin of the hands or face. Wear safety glasses with side shields at all times, and if splashing or spray may occur, wear a face shield over safety glasses.

Piping, valves, and other components containing liquid nitrogen should be insulated to prevent accidental human contact and the formation of liquid oxygen. If unprotected skin comes into contact with uninsulated piping, the flesh may stick and the skin may tear on removal. Uninsulated equipment can also cause the surrounding air to condense and form an oxygen-enriched liquid, thereby creating a fire hazard. Materials that burn easily will burn more violently in oxygen-enriched environments. to boiling, the water turns into a gas — steam. If this steam is unconfined, it expands and occupies much more volume than the liquid water. If this steam is confined and the boiling process continues, the pressure in the confinement will increase (for example, as in a pressure cooker).

The same physical process occurs when a cryogenic liquid is warmed beyond its boiling point — the gas expands and, if confined, the pressure increases. Keep in mind that at atmospheric pressure, one volume of liquid nitrogen at its boiling point will vaporize to roughly 700 volumes of gas when warmed to room temperature. Thus, a small liquid nitrogen leak can rapidly displace the surrounding air and create an oxygen-deficient atmosphere. If liquid nitrogen is confined, the expansion ratio of liquid to gas can also rapidly over-pressurize equipment and/or piping, resulting in catastrophic failure.

For these reasons, liquid nitrogen should not be placed in any container, piping, or equipment that does not have the appropriate pressure relief protection. Adequate pressurerelief devices, referred to as thermal relief valves, protect systems from over-pressurization anywhere a cryogenic liquid can be trapped, such as between two valves. In addition, liquid nitrogen containers should be used and stored only in well-ventilated areas.

Liquid nitrogen containers

Liquid nitrogen is transported and stored in dewars, cryogenic liquid cylinders, and cryogenic storage tanks. These containers are double-walled, vacuum vessels with multilayer insulation. Dewars are open, nonpressurized vessels that hold cryogenic liquids. Cryogenic liquid cylinders and storage tanks are pressurized vessels.

Although these containers are well-insulated, heat continuously leaks into the product due to the extremely large

It is critical to ensure that any material that comes into contact with liquid nitrogen or cold nitrogen gas is compatible with cryogenic temperatures, because materials change properties at extremely low temperatures. For instance, aluminum becomes stronger, but carbon steel and plastics become brittle and can shatter like glass.

Liquid nitrogen expands significantly when vaporized to nitrogen gas. The simple analogy of heating water to a boil illustrates this hazard. When water in its liquid state is heated

Figure 3. Cryogenic tankers and liquid cylinders are equipped with pressure relief valves to allow the product to periodically vent due to pressure buildup. While this venting is normal and safe, it should always be done in a well-ventilated area to avoid creating an oxygen-deficient atmosphere.



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temperature difference between the cryogenic liquid and the ambient environment. The heat leak causes some vaporization to occur. Vaporized product, if not used, collects in the head space above the cryogenic liquid and builds pressure in closed containers.

Cryogenic containers may periodically vent some product due to pressure buildup. Cryogenic liquid cylinders are equipped with pressure-relief valves for venting excess pressure (Figure 3). A rupture disk is also typically present; it will blow out and vent the entire container if the internal pressure rises above a higher setpoint.

Venting rates through the relief device vary with the container design, ambient conditions, and the volume of product stored. Vaporization rates may be as low as 0.4% or as high as 3% of the container's volume per day. While this venting is a normal and safe function of the container, it is important to ensure that the container is in a well-ventilated area to avoid creating an oxygen-deficient atmosphere.

Product misidentification

Reading the container label is the only reliable method for identifying container contents. Never rely on the container color or outlet connections to identify container contents. All workers storing, handling, and using gas cylinders or cryogenic liquid containers must read the label to identify the contents. They should also review the material safety data sheet (MSDS) to become familiar with necessary safety precautions before performing job duties.

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Industrial incidents have occurred when personnel created an oxygen-deficient atmosphere by mistakenly using nitrogen instead of air to flush equipment prior to entry. In other cases, interchangeable couplings on lines or poor or nonexistent labeling allowed nitrogen to be inadvertently used instead of breathing air.

Emergency plans

Any facility storing or using nitrogen should have an emergency response plan that covers situations such as releases and medical emergencies. Emergency response phone numbers, evacuation procedures, and the frequency of periodic drills are typically included in the plan.

When a leak is discovered or when an alarm sounds, take the following steps:

- · evacuate personnel to safe areas
- if possible to do so safely, shut off the source of the leak
- · monitor oxygen levels and provide maximum ventilation

• initiate the emergency plan and make the required emergency contacts.

Closing thoughts

Nitrogen is a widely used staple of the chemical industry. When the potential hazards of using nitrogen are understood, and the necessary precautions are taken for its safe handling, nitrogen offers benefits in a variety of applications. Its inertness and cold temperature can help to improve product quality and operational performance, extend equipment and/or product life, and increase overall safety of processes involving flammable materials by helping to prevent fire and explosion. With emergency plans in place and ongoing training on the potential hazards associated with oxygen deficiency, pressure release, or exposure to cryogenic temperatures, nitrogen can be used safely.

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