SUMMARY REPORT

NITROGEN ASPHYXIATION
(1 DEATH, 1 INJURY)

UNION CARBIDE CORPORATION
Hahnville, Louisiana
March 27, 1998

KEY ISSUES:

• USE OF NITROGEN IN CONFINED SPACES
• SAFETY OF TEMPORARY ENCLOSURES
Abstract: This summary report explains an incident that occurred March 27, 1998, at Union Carbide Corporation’s Taft/Star Manufacturing Plant in Hahnville, Louisiana. One Union Carbide worker was killed and an independent contractor was seriously injured due to nitrogen asphyxiation. Safety issues discussed in this report include the hazards of temporary enclosures and the use of nitrogen when working in confined spaces. Recommendations concerning these issues were made to Union Carbide Corporation, the Occupational Safety and Health Administration, and others. This summary report also contains a recommendation to the National Institute for Occupational Safety and Health that it conduct a study concerning the feasibility of odorizing nitrogen when it is used in confined spaces.

The Chemical Safety and Hazard Investigation Board (CSB) is an independent federal agency whose mission is to ensure the safety of workers and the public by preventing or minimizing the effects of chemical incidents at industrial facilities. The CSB is a scientific investigatory organization; it is not an enforcement or regulatory body. Established by the Clean Air Act Amendments of 1990, the CSB is responsible for determining the probable causes of incidents, issuing safety recommendations, studying chemical safety issues, and evaluating the effectiveness of other government agencies involved with industrial chemical safety. Section 112(r)(6)(G) of the Clean Air Act prohibits the use of any conclusions, findings, or recommendations of the CSB relating to any chemical incident from being admitted as evidence or used in any lawsuit arising out of any matter mentioned in an investigation report. The CSB makes public its actions and decisions through investigation reports, summary reports, safety studies, safety recommendations, special technical publications, and statistical reviews. A summary report addresses incidents that are within the CSB’s jurisdiction, but because of the limited nature of the issues involved, do not require a more comprehensive investigation and report. More information about the CSB may be found on the World Wide Web (http://www.chemsafety.gov).

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Springfield, Virginia 22161
(703) 487-4600

Salus Populi Est Lex Suprema
People’s Safety is the Highest Law
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1.0 INTRODUCTION

The United States Chemical Safety and Hazard Investigation Board (CSB) is an independent federal agency whose mission is to improve the safety of workers and the public by preventing chemical incidents. One of the CSB’s duties is to conduct investigations of serious incidents to identify the causes and recommend changes to prevent recurrence.

On March 27, 1998, at approximately 12:15 pm, two workers at Union Carbide Corporation’s Taft/Star Manufacturing Plant (the plant) in Hahnville, Louisiana, were overcome by nitrogen gas while performing a black light inspection\(^1\) at an open end of a 48-inch-wide horizontal pipe. The 48-inch pipe was open because chemical-processing equipment had been shut down and opened for major maintenance. Nitrogen was being injected into the process equipment primarily to protect new catalyst in reactors from exposure to moisture. The nitrogen was also flowing through some of the piping systems connected to the reactors. The nitrogen was venting from one side of the open pipe where it had formerly been connected to an oxygen feed mixer. No warning sign was posted on the pipe opening identifying it as a confined space or warning that the pipe contained potentially hazardous nitrogen.

The two workers had placed a sheet of black plastic over the end of the pipe to provide shade to make it easier to conduct the black light test during daylight. While working just outside the pipe opening and inside of the black plastic sheet, the two workers were overcome by nitrogen. One worker died from asphyxiation. The other worker survived but was severely injured.

Nitrogen is an odorless, tasteless, and invisible gas that can cause asphyxiation at high concentrations. When used in confined spaces, nitrogen is especially hazardous because it cannot be detected by human senses but can cause injury or death within minutes by displacing the oxygen that is required to sustain life.

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1 A black light was used to see any residue of organic material, such as grease or oil, on the pipe. Organic residue shines when viewed under a black light.
1.1 BACKGROUND

The plant, which produces chemicals for industry, is located about 30 miles west of New Orleans and employs approximately 1,130 people. The incident occurred in the plant’s Taft Oxide I Unit (the Unit). The Unit primarily produces ethylene oxide, ethylene glycol, and glycol ethers. (See Figure 1 for the numbered locations of the major equipment involved in the Unit’s process.) The Unit uses ethylene and methane as feed gases to produce ethylene oxide. Ethylene and methane are mixed with oxygen (see Figure 1, item 4) and then put in contact with a catalyst located in the reactors (see Figure 1, item 1). A scrubber removes the product while carbon dioxide gas is also removed. The incident occurred at the fifth level of the structure, approximately 60 feet above the ground.

Various plant operations are periodically shut down for a “turnaround.” A turnaround is an industry term describing the time when major maintenance and inspection of process equipment takes place. At the time of the incident, the Unit had been in a turnaround status for about six weeks.

The worker injured in the incident (Worker A) was retained as an independent contractor and was in charge of daily operations in the reaction area during the turnaround. He had retired from Union Carbide after 32 years of service, primarily at the plant. His last position prior to retirement was Reaction Area Specialist for the same Unit.

The worker who died (Worker B) was a Union Carbide employee who had 23 years of service at the plant. He was a Maintenance Skilled Operations Team Technician in the Unit. Worker B was under the general direction of Worker A at the time of the incident.
1.2 EVENTS PRECEDING THE INCIDENT

Two primary maintenance activities were scheduled during the turnaround of the Unit: replacement of the old catalyst in the reactors with new catalyst and cleaning the oxygen feed mixer (see Figure 1, items 1 and 4). The oxygen feed mixer had been removed from the piping system for cleaning. Removing the oxygen feed mixer exposed two open ends on 48-inch piping that had been
connected to the oxygen feed mixer. The two open pipe ends were wrapped with a clear plastic sheet in order to keep the pipe free of debris until the oxygen feed mixer was reinstalled. Figure 2 shows the clear plastic sheet over one of the 48-inch pipe openings and the black plastic sheet lying near the opening.

![Image of clear plastic sheet covering a pipe opening](image)

**Figure 2. Clear Plastic Sheet Covering One Of The Pipe Openings**

The oxygen feed mixer needed to be free of grease, oil, or other organic chemicals because these materials are incompatible with the chemical process that takes place in the oxygen feed mixer. Workers used a cleaning solution containing ethylene trichloride to remove these materials. Later,
workers used a black light to check for any residual deposits of organic chemicals, because the deposits would be seen more clearly under the black light. The parts of the pipe that the workers examined with the black light were the two flange surfaces, which were located at the ends of the pipe that connected to the oxygen feed mixer. Figure 3 shows the north end of the pipe and the flange surface. Although a black light inspection was a typical part of oxygen feed mixer cleaning, it was not needed on the 48-inch pipe flange surfaces. For these flanges, a visual inspection was all that was required. The CSB investigation did not discover any conclusive reason that explained why Workers A and B decided to perform black light inspections on the pipe flanges.

Figure 3. The Flange on the North End of the Pipe
The catalyst used in the ethylene oxide reactors was sensitive to moisture. Therefore, following replacement of the old catalyst, the new catalyst was protected from exposure to moisture-containing air by injecting nitrogen gas into the area around the catalyst. The nitrogen displaced the air in the reactors and blanketed the catalyst.

The evening before the incident, Worker A directed Operations Technicians to add the nitrogen to the piping because the catalyst had been changed. Because nitrogen would retard rust formation in the piping connected to the reactors, two valves (see Figure 1, item 2) were opened to allow the flow of nitrogen into the process piping. The nitrogen vented from the open end of the 48-inch pipe (see Figure 1, item 7) on the north side of where the pipe formerly connected to the oxygen feed mixer.

1.3 THE INCIDENT

On the day of the incident, Workers A and B performed a black light inspection and cleaning of the two flange surfaces on the open 48-inch pipe, beginning with the south flange (see Figure 1, item 6). Because the midday sun made it difficult to see any grease or oil residues with the black light, Workers A and B used a sheet of black plastic to provide a darker working area. The black plastic sheet was fastened over the pipe flange because there was a strong breeze that day. The plastic sheet was held in place by Workers A and B sitting on one edge of the sheet with the remainder of the sheet held over them and against the exterior of the pipe flange by two contractor workers. The contractor workers were in the area because they were waiting for the oxygen feed mixer to be lifted back into place. Though unintended, the plastic sheet created a temporary enclosure around Workers A and B. The inspection and cleaning of the south pipe flange began at approximately 10:45 am and was completed at about 11:35 am. There was no incident because

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2 The specific catalyst used is proprietary information, and it is not necessary to reveal its name for the purposes of this report.
the nitrogen was not venting through the south pipe opening. The south pipe was also connected to the reactors, but a closed valve blocked this piping, thus preventing the flow of nitrogen to the south pipe.

Next, the workers and the contractors placed a plastic sheet in the same fashion on the north pipe flange while Workers A and B conducted an inspection and cleaning. Because this part of the pipe was being purged with nitrogen, it contained a high level of nitrogen. The temporary plastic enclosure trapped a high concentration of the nitrogen, which continued to vent out of the north pipe. Worker A probably did not realize that nitrogen was venting from the pipe even though the evening before he had directed that nitrogen be injected into the piping system. He may have not remembered that nitrogen was in the pipe because the nitrogen was injected at a distant location, 150 feet and several stories in elevation away from the site of the incident.

Contractors, who were on the other side of the black plastic sheet, reported talking with Workers A and B. The last communication with Workers A and B took place just after noon. At approximately 12:20 pm, a contractor noticed blood on one of the worker’s hands when he looked through a gap in the plastic sheet. He alerted his foreman. The foreman called to the two workers behind the sheet and, getting no reply, removed the sheet. Worker B was found in front of the pipe, unconscious and slumped over with his head lying inside the open pipe. Witnesses said that his skin color was purple. Worker A was found seated beside the pipe opening, dazed and leaning against the side of the pipe. His color was described as white.

Emergency assistance was requested. The plant emergency response team arrived and removed the two men from the Unit while administering cardiopulmonary resuscitation to Worker B. The two workers were transported by ambulance to St. Charles Parish Hospital. Worker B was dead on arrival. Worker A was admitted to the hospital in critical condition and given oxygen therapy over the next several days. He was released after five days in the hospital.
2.0 ANALYSIS OF THE INCIDENT

2.1 CONFINED SPACE HAZARD

In 1993, the Occupational Safety and Health Administration (OSHA) confined space entry standard\(^3\) became effective. OSHA defines a confined space as a space that is large enough to enter, has limited or restricted means for entry or exit, and has not been designed for continuous human occupancy. The open pipe involved in the incident may have fit the OSHA definition of a confined space. The temporary enclosure involved in this incident may not have been considered to have a limited or restricted means of exit and, therefore, may not necessarily be considered to be a confined space. In this incident, however, OSHA did cite Union Carbide for violation of the standard.

OSHA defines a permit-required confined space as one that meets all of the above criteria and also contains or has the potential to contain a hazardous atmosphere. In order to enter a permit-required confined space, OSHA requires that personnel monitor the atmosphere in the space and that the company issue a written permit that identifies the hazards present and the precautions that must be taken before entry. Although OSHA may not always consider temporary enclosures that have easy means of exit, such as the one involved in this incident, to be confined spaces, the use of permit-required confined space entry procedures for the temporary enclosure at the plant likely would have prevented this incident.

One factor that makes entering a confined space hazardous is that the space may contain a hazardous atmosphere. A confined space may contain a toxic gas, such as hydrogen sulfide, in concentrations hazardous to health. Other confined spaces may contain a nontoxic gas, such as nitrogen, in concentrations that displace the oxygen in the air in the space. The air we normally

\(^3\) See 29 CFR § 1910.146.
breathe contains about 21% oxygen, 78% nitrogen, and trace amounts of other gases. In this incident, the nitrogen acted as an asphyxiant, causing suffocation by displacing oxygen-containing air.

It is not necessary for nitrogen to displace all of the 21% of oxygen normally found in the air in order to cause harm to people. OSHA requires that oxygen levels be maintained at or above 19.5% in order to prevent injury to workers. According to the Compressed Gas Association, “exposure to atmospheres containing 8-10 percent or less oxygen will bring about unconsciousness without warning and so quickly that the individuals cannot help or protect themselves.” ⁴ Exposure to an atmosphere containing 6-8 percent oxygen can be fatal in as little as 6 minutes. Exposure to an atmosphere containing 4-6 percent oxygen can result in a coma in 40 seconds and subsequent death.

In this incident, no signs were posted at the pipe opening to warn workers and contractors that it was a confined space or that it contained nitrogen. Even if the temporary enclosure had not been erected around the north pipe opening, an employee or a contractor could have been overcome by nitrogen if he or she merely had inserted his or her head into the pipe for a short time. A worker or a contractor could have put his head into the north pipe opening as part of cleaning or inspecting the pipe flange. OSHA has investigated confined space injuries and fatalities at other facilities in which a worker only entered a confined space with his head.

Prior to the incident, the plant’s safety program did not adequately address the control of hazards associated with the creation of temporary enclosures around chemical plant equipment. For example, temporary enclosures that had an easy means of exit were generally not covered by the safety requirements of the plant’s confined space entry policy. After the incident, the plant manager issued a safety notice alerting employees about the incident and banned, pending further review, all inspections of equipment in process units that required a cover or similar method to exclude light. The safety notice was communicated to Union Carbide facilities worldwide.

Union Carbide conducted additional training on nitrogen safety.

\section*{2.2 Control of Secondary Hazards}

It is important that safety management efforts look beyond the immediate task to anticipate secondary hazards. The open pipe was an unrecognized secondary hazard in the oxygen feed mixer cleaning activity. There was no evaluation of the impact of the catalyst change activity and nitrogen purge on the seemingly unrelated oxygen feed mixer cleaning activity. Management should have performed this type of evaluation when it planned to inject nitrogen into the 48-inch pipe and out of the north end of the pipe. Such an evaluation could have revealed the risk to workers from nitrogen in the pipe. Recognition of the nitrogen hazard could have identified the need to post a nitrogen warning sign at the pipe opening where the incident took place.

Interviews with members of the plant management revealed that they did not expect anyone to perform a black light inspection of the pipe flanges. Management personnel said it was unnecessary to clean the flanges because the oxygen feed mixer had been cleaned and an enriched oxygen atmosphere would not contact the flanges.

Although management did not expect the specific job of a black light inspection to be performed, there were other workers in the area who needed to be protected from the potential nitrogen hazard. Earlier during the day of the incident, contractor employees used wire brushes and cleaning solution to clean the same 48-inch pipe flanges that were later inspected with the black light. In order to perform this job, contractors removed the clear plastic sheets covering the pipe openings, thereby exposing themselves to the nitrogen hazard. Because there was a strong breeze that day, the nitrogen venting from the north end of the pipe was quickly dissipated and did not harm the contractors.
2.3 **HISTORY OF NITROGEN-RELATED FATALITIES IN CONFINED SPACES**

According to OSHA’s records, at least 21 people died in the U.S. between 1990 and early 1996 in incidents involving the use of nitrogen in confined spaces. The OSHA confined space entry standard required facilities covered by the law, including the Taft plant, to fully implement its requirements by April 15, 1993. Currently available OSHA fatality data shows that the number of reported fatal incidents involving nitrogen remained about the same in the three-year period following issuance of the confined space entry standard as in the three years preceding issuance of the standard. Nine nitrogen-related incidents resulted in 12 fatalities during the 3-year period preceding issuance of the OSHA confined space entry standard. An additional nine nitrogen-related incidents resulted in nine fatalities during the 3-year period that followed issuance of the standard.\(^5\) Appendix A contains further information on these fatalities.

This fatality data does not take into account the possible increased use in recent years of nitrogen in confined spaces. (Thus, even though the data shows that the number of fatalities has remained fairly constant, if industry used nitrogen more frequently in later years, the rate of fatalities may have actually declined.) Therefore, this data by itself should not be interpreted to mean that there has been no decline in the fatality rate trend. Nonetheless, the OSHA fatality data indicates that the use of nitrogen in confined spaces remains a hazard to workers.

In this incident, the plant had a confined space entry program and a chemical safety-training program. Nonetheless, one very experienced worker died and another was seriously injured because these workers were not aware that they were being exposed to dangerous levels of nitrogen.

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\(^5\) OSHA notes that its statistics may be incomplete. Additional incidents may have taken place which are not reflected in OSHA’s data. In addition, data from earlier years may omit fatality reports from some states that administer their own worker safety programs.
This potentially dangerous substance cannot be detected by the human senses. In addition, high concentrations of nitrogen are dangerous because personnel may not recognize physical or mental symptoms resulting from over-exposure. The two workers involved in the incident were unable to recognize that they were in trouble. They did not try to leave the hazardous work area even though there was an easy means of escape. Also, contractors were located nearby, but the two workers did not ask for help.

2.4 Nitrogen Warning Measures

Like natural gas and propane (two other potentially hazardous gases), nitrogen does not have a naturally occurring odor that can adequately warn people of its presence. Odorant is added to natural gas and propane as a safety measure to provide a warning that a leak has occurred or that the flammable and explosive gas is present.

Odorant is not normally added to nitrogen because a release of nitrogen is not typically a hazardous event. Nitrogen is nontoxic and will not ignite or react with other substances, but it can be very hazardous when used in confined spaces that workers enter. It displaces the oxygen in the space, and at high concentrations, it can cause death. A Material Safety Data Sheet for nitrogen is included in Appendix B.

Posting warning signs to alert personnel of confined space and nitrogen hazards is a useful safety measure. Personnel may occasionally forget to post warning signs or the signs may be accidentally removed, however. If the nitrogen used to purge the reactors at the Taft plant had contained an odorant, the personnel would have been alerted that the gas was present and the incident would have been prevented.

Odorization of nitrogen that is used in confined spaces should not be viewed as a substitute for existing confined space entry safety measures; it would be an additional precaution.
The CSB is aware that technical issues, such as the possible contamination of certain catalysts by the use of an odorant in nitrogen, must be studied. Therefore, research is needed concerning the feasibility of odorizing nitrogen that is used in confined space applications.
3.0 ROOT AND CONTRIBUTING CAUSES

Root Causes

1. Procedures to control potential hazards created by erecting temporary enclosures around nitrogen-containing equipment were inadequate.

The plant did not have adequate procedures in place to address potential hazards created by the use of temporary enclosures. Temporary enclosures erected around tanks, vessels, pipes, or similar equipment that contain hazardous material may trap a dangerous atmosphere if the equipment leaks or vents substances, such as nitrogen, into the enclosure.

2. Nitrogen and confined space hazard warnings were inadequate.

Personnel were not aware of the hazard of the nitrogen flowing out of the open pipe that they were working on, even though one of injured individuals had earlier directed that nitrogen be injected into the equipment. No warning signs were posted identifying the pipe as a confined space or alerting personnel to the presence of nitrogen.

Contributing Cause

Personnel were unable to detect hazardous levels of nitrogen because this gas cannot be detected by human senses.

Odorization of nitrogen could have warned personnel that a hazardous atmosphere was present and thereby prevented the incident.
4.0 RECOMMENDATIONS

Union Carbide Taft Plant

1. Post signs containing the warning “Danger, Confined Space: Do Not Enter Without Authorization” or similar wording at potential entryways when tanks, vessels, pipes, or other similar chemical industry equipment are opened. When nitrogen is added to a confined space, post an additional sign that warns personnel of the potential nitrogen hazard. (98-05-I-LA-R1)

2. Ensure that the plant safety program addresses the control of hazards created by erecting temporary enclosures around equipment that may trap a dangerous atmosphere in the enclosure if the equipment leaks or vents hazardous material. (98-05-I-LA-R2)

National Institute for Occupational Safety and Health

Conduct a study concerning the appropriateness and feasibility of odorizing nitrogen in order to warn personnel of the presence of nitrogen when it is used in confined spaces. (98-05-I-LA-R3)

Occupational Safety and Health Administration

Issue a safety alert that addresses the hazards and provides safety guidelines for the use of temporary enclosures that are erected around equipment containing hazardous substances. (98-05-I-LA-R4)
Center for Chemical Process Safety

Communicate the findings of this report to your membership. (98-05-I-LA-R5)

Compressed Gas Association

Communicate the findings of this report to your membership. (98-05-I-LA-R6)

BY THE CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD

Paul L. Hill, Jr.
Chairman

Gerald V. Poje
Member

Andrea Kidd Taylor
Member

Isadore Rosenthal
Member

February 23, 1999
5.0 REFERENCES


Union Carbide Corporation/Taft Plant Responsible Care Policies Manual (December 1997).
APPENDIX A: List of Other Nitrogen Asphyxiation Cases

The following data is based on publicly available OSHA statistics concerning fatalities in confined spaces due to nitrogen exposure.

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The OSHA Confined Space Entry Standard became effective on April 15, 1993.

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APPENDIX B: Material Safety Data Sheet for Nitrogen

Prepared to U.S. OSHA, CMA, ANSI and Canadian WHMIS Standards

PART I  What is the material and what do I need to know in an emergency?

1. PRODUCT IDENTIFICATION

CHEMICAL NAME: CLASS: NITROGEN - N₂
LIQUEFIED NITROGEN N₂( Cryogenic)

PRODUCT USE: For general analytical/synthetic chemical uses.

SUPPLIER/MANUFACTURER'S NAME: AIRGAS INC.
ADDRESS: 259 Radnor-Chester Road
Suite 100
Radnor, PA 19087-5240

BUSINESS PHONE: 1-610-687-5253
EMERGENCY PHONE: CHEMTREC: 1-800-424-9300
International: 202-483-7616

DATE OF PREPARATION: May 12, 1996
SECOND REVISION: December 11, 1997

2. COMPOSITION and INFORMATION ON INGREDIENTS

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NE = Not Established  C = Ceiling Limit  See Section 16 for Definitions of Terms Used
NOTE: all WHMIS required information is included. It is located in appropriate sections based on the ANSI Z400.1-1993 format.
3. HAZARD IDENTIFICATION

**EMERGENCY OVERVIEW:** Nitrogen is a colorless, odorless, non-flammable gas, or a colorless, odorless, cryogenic liquid. The main health hazard associated with releases of this gas is asphyxiation, by displacement of oxygen. The cryogenic liquid will rapidly boil to the gas at standard temperatures and pressures. The liquefied gas can cause frostbite to any contaminated tissue.

**NITROGEN GAS**

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<td>PROTECTIVE EQUIPMENT</td>
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**LIQUID NITROGEN**

<table>
<thead>
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<td>PROTECTIVE EQUIPMENT</td>
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**SYMPTOMS OF OVEREXPOSURE BY ROUTE OF EXPOSURE:** The most significant route of overexposure for this gas is by inhalation. The following paragraphs describe symptoms of exposure by route of exposure.

**INHALATION:** High concentrations of this gas can cause an oxygen-deficient environment. Individuals breathing such an atmosphere may experience symptoms which include headaches, ringing in ears, dizziness, drowsiness, unconsciousness, nausea, vomiting, and depression of all the senses. The skin of a victim may have a blue color. Under some circumstances, death may occur. The effects associated with various levels of oxygen are as follows:

**CONCENTRATION**  
- 12-16% Oxygen: Breathing and pulse rate increased, muscular coordination slightly disturbed.
- 10-14% Oxygen: Emotional upset, abnormal fatigue, disturbed respiration.
- 6-10% Oxygen: Nausea and vomiting, collapse or loss of consciousness.
- Below 6%: Convulsive movements, possible respiratory collapse, and death.

**OTHER POTENTIAL HEALTH EFFECTS:** Contact with cryogenic liquid or rapidly expanding gases (which are released under high pressure) may cause frostbite. Symptoms of frostbite include change in skin color to white or grayish-yellow. The pain after contact with liquid can quickly subside.

**HEALTH EFFECTS OR RISKS FROM EXPOSURE:** Overexposure to Nitrogen may cause the following health effects:

See Section 16 for Definition of Ratings

For routine industrial applications
**ACUTE:** The most significant hazard associated with this gas is inhalation of oxygen-deficient atmospheres. Symptoms of oxygen deficiency include respiratory difficulty, headache, dizziness and nausea. At high concentrations, unconsciousness or death may occur. Contact with cryogenic liquid or rapidly expanding gases may cause frostbite.

**CHRONIC:** There are currently no known adverse health effects associated with chronic exposure to Nitrogen.

**TARGET ORGANS:** Respiratory system.
PART II  What should I do if a hazardous situation occurs?

4. FIRST-AID MEASURES

RESCUERS SHOULD NOT ATTEMPT TO RETRIEVE VICTIMS OF EXPOSURE TO NITROGEN WITHOUT ADEQUATE PERSONAL PROTECTIVE EQUIPMENT. At a minimum, Self-Contained Breathing Apparatus Personal Protective equipment should be worn.

Remove victim(s) to fresh air, as quickly as possible. Trained personnel should administer supplemental oxygen and/or cardio-pulmonary resuscitation, if necessary. Only trained personnel should administer supplemental oxygen.

In case of frostbite, place the frostbitten part in warm water. DO NOT USE HOT WATER. If warm water is not available, or is impractical to use, wrap the affected parts gently in blankets. Alternatively, if the fingers or hands are frostbitten, place the affected area of the body in the armpit. Encourage victim to gently exercise the affected part while being warmed. Seek immediate medical attention.

Victim(s) must be taken for medical attention. Rescuers should be taken for medical attention, if necessary. Take copy of label and MSDS to physician or other health professional with victim(s).

5. FIRE-FIGHTING MEASURES

NITROGEN GAS

<table>
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LIQUID NITROGEN

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</tbody>
</table>

See Section 16 for Definition of Ratings

FLASH POINT: Not applicable.

AUTOIGNITION TEMPERATURE: Not applicable.

FLAMMABLE LIMITS (in air by volume, %):

Lower (LEL): Not applicable.
Upper (UEL): Not applicable.

FIRE EXTINGUISHING MATERIALS: Non-flammable, inert gas. Use extinguishing media appropriate for surrounding fire.

UNUSUAL FIRE AND EXPLOSION HAZARDS: Nitrogen does not burn; however, containers, when involved in fire, may rupture or burst in the heat of the fire.

RESPONSE TO FIRE INVOLVING CRYOGEN: Cryogenic liquids can be particularly dangerous during fires because of their potential to rapidly freeze water. Careless use of water may cause heavy icing. Furthermore, the relatively warm water greatly increases the evaporation rate of Nitrogen. If large concentrations of Nitrogen gas are present, the water vapor in the surrounding air will condense, creating a dense fog that may make it difficult to find fire exits or equipment. Liquid Nitrogen, when exposed to the atmosphere, will produce a cloud of ice/fog in the air upon its release.

Explosion Sensitivity to Static Discharge: Not Sensitive.
SPECIAL FIRE-FIGHTING PROCEDURES: Structural fire-fighters must wear Self-Contained Breathing Apparatus and full protective equipment. Move fire-exposed cylinders if it can be done without risk to firefighters. Otherwise, cool containers with hose stream and protect personnel. Withdraw immediately in case of rising sounds from venting safety device or any discoloration of tanks due to the fire.

6. ACCIDENTAL RELEASE MEASURES

SPILL AND LEAK RESPONSE: Uncontrolled releases should be responded to by trained personnel using pre-planned procedures. Proper protective equipment should be used. In case of a release, clear the affected area and protect people.

Minimum Personal Protective Equipment should be Level B: protective clothing, mechanically-resistant gloves and Self-Contained Breathing Apparatus. Locate and seal the source of the leaking gas. Allow the gas to dissipate. Monitor the surrounding area for oxygen levels. The atmosphere must have at least 19.5 percent oxygen before personnel can be allowed in the area without Self-Contained Breathing Apparatus. Attempt to close the main source valve prior to entering the area. If this does not stop the release (or if it is not possible to reach the valve), allow the gas to release in-place or remove it to a safe area and allow the gas to be released there.

RESPONSE TO CRYOGENIC RELEASE: Clear the affected area and allow the liquid to evaporate and the gas to dissipate. After the gas is formed, follow the instructions provided in the previous paragraph. If the area must be entered by emergency personnel, SCBA, Kevlar gloves, and appropriate foot and leg protection must be worn.
How can I prevent hazardous situations from occurring?

7. HANDLING and STORAGE

WORK PRACTICES AND HYGIENE PRACTICES: As with all chemicals, avoid getting Nitrogen IN YOU. Do not eat or drink while handling chemicals. Be aware of any signs of dizziness or fatigue; exposures to fatal concentrations of Nitrogen could occur without any significant warning symptoms, due to oxygen deficiency.

STORAGE AND HANDLING PRACTICES: Cylinders should be stored in dry, well-ventilated areas away from sources of heat. Compressed gases can present significant safety hazards. Store containers away from heavily trafficked areas and emergency exits. Post “No Smoking or Open Flames” signs in storage or use areas.

SPECIAL PRECAUTIONS FOR HANDLING GAS CYLINDERS: Protect cylinders against physical damage. Store in cool, dry, well-ventilated, fireproof area, away from flammable materials and corrosive atmospheres. Store away from heat and ignition sources and out of direct sunlight. Do not store near elevators, corridors or loading docks. Do not allow area where cylinders are stored to exceed 52°C (125°F). Isolate from incompatible materials such as magnesium (see Section 10, Stability and Reactivity for more information), which can react violently. Use only storage containers and equipment (pipes, valves, fittings to relieve pressure, etc.) designed for the storage of Liquid Nitrogen. Do not store containers where they can come into contact with moisture. Cylinders should be stored upright and be firmly secured to prevent falling or being knocked over. Cylinders can be stored in the open, but in such cases, should be protected against extremes of weather and from the dampness of the ground to prevent rusting. Keep Dewar flasks covered with loose fitting cap. This prevents air or moisture from entering the container, yet allows pressure to escape. Use only the stopper or plug supplied with the container. Ensure that ice does not form in the neck of flasks. If the neck of Dewar flask is blocked by ice or “frozen” air, follow manufacturer’s instruction for removing it. Ice can also cause pressure release valves to fail. Never tamper with pressure relief devices. The following rules are applicable to situations in which cylinders are being used:

Before Use: Move cylinders with a suitable hand-truck. Do not drag, slide or roll cylinders. Do not drop cylinders or permit them to strike each other. Secure cylinders firmly. Leave the valve protection cap in-place (if provided), until cylinder is ready for use.

During Use: Use designated CGA fittings and other support equipment. Do not use adapters. Do not heat cylinder by any means to increase the discharge rate of the product from the cylinder. Use check valve or trap in discharge line to prevent hazardous backflow into the cylinder. Do not use oils or grease on gas-handling fittings or equipment.

After Use: Close main cylinder valve. Replace valve protection cap (if provided). Mark empty cylinders “EMPTY”.

NOTE: Use only DOT or ASME code containers. Earth-ground and bond all lines and equipment associated with this product. Close valve after each use and when empty. Cylinders must not be recharged except by or with the consent of owner. For additional information refer to the Compressed Gas Association Pamphlet P-1, Safe Handling of Compressed Gases in Containers. For cryogenic liquids, refer to CGA P-12, Safe Handling of Cryogenic Liquids. Also see CGA P-9, the Inert Gases, Argon, Nitrogen, and Helium; CGA P-14, Accident Prevention in Oxygen Rich and Oxygen Deficient Atmospheres; CGA Safety Bulletin SB-2, Oxygen Deficient Atmospheres.

PROTECTIVE PRACTICES DURING MAINTENANCE OF CONTAMINATED EQUIPMENT: Follow practices indicated in Section 6 (Accidental Release Measures). Make certain application equipment is locked and tagged-out safely. Purge gas handling equipment with inert gas (e.g., nitrogen) before attempting repairs.
8. EXPOSURE CONTROLS - PERSONAL PROTECTION

VENTILATION AND ENGINEERING CONTROLS: Use with adequate ventilation to maintain oxygen levels above 19.5% in the workplace. Local exhaust ventilation is preferred, because it prevents Nitrogen dispersion into the workplace by eliminating it at its source. If appropriate, install automatic monitoring equipment to detect the level of oxygen.

RESPIRATORY PROTECTION: Maintain oxygen levels above 19.5% in the workplace. Use supplied air respiratory protection if oxygen levels are below 19.5% or during emergency response to a release of Nitrogen. If respiratory protection is required, follow the requirements of the Federal OSHA Respiratory Protection Standard (29 CFR 1910.134), or equivalent State standards.

EYE PROTECTION: Splash goggles, face-shields or safety glasses. Face-shields must be worn when handling cryogenic Nitrogen.

HAND PROTECTION: Wear mechanically resistant-gloves when handling cylinders of Nitrogen. Use low-temperature protective gloves (e.g., Kevlar) when working with containers of Liquid Nitrogen.

BODY PROTECTION: Use body protection appropriate for task. Transfer of large quantities under pressure may require protective equipment appropriate to protect employees from splashes of liquefied product, as well provide sufficient insulation from extreme cold.

9. PHYSICAL and CHEMICAL PROPERTIES

VAPOR DENSITY: 1.153 kg/m³ (0.072 lb/ft³)  
EVAPORATION RATE (nBuAc = 1): Not applicable.

SPECIFIC GRAVITY (air = 1): 0.967  
FREEZING POINT: -210°C (-345.8°F)

SOLUBILITY IN WATER (v/v): 1.49%  
BOILING POINT @1 atm: -320.4°F (-195.8°C)

EXPANSION RATIO: 696.5 (cryogenic liquid)  
pH: Not applicable.

ODOR THRESHOLD: Not applicable. Odorless.  
VAPOR PRESSURE (psia): Not applicable.

COEFFICIENT WATER/OIL DISTRIBUTION: Log K_{ow} = 0.92.  
SPECIFIC VOLUME (ft³/lb): 13.8

APPEARANCE AND COLOR: Nitrogen is a colorless, odorless gas or a colorless and odorless, cryogenic liquid.

HOW TO DETECT THIS SUBSTANCE (warning properties): There are no unusual warning properties associated with a release of Nitrogen. In terms of leak detection, fittings and joints can be painted with a soap solution to detect leaks, which will be indicated by a bubble formation.

10. STABILITY and REACTIVITY

STABILITY: Normally stable in gaseous state. With cryogenic liquid, when exposed to air, oxygen in the air may condense into the Liquid Nitrogen. Liquid Nitrogen contaminated with oxygen may present the same hazards as Liquid Oxygen and could react violently with organic materials, such as oil and grease.

DECOMPOSITION PRODUCTS: None

MATERIALS WITH WHICH SUBSTANCE IS INCOMPATIBLE: Titanium, neodymium, lithium, zirconium and ozone react with Nitrogen. Calcium, strontium, and barium will react with red heat to form nitrides. Hydrogen reacts on sparking to form ammonia. Liquid Nitrogen in cryogenic grinding of fatty materials can lead to an explosion. A mixture of magnesium powder and Liquid Nitrogen reacts very violently when lit with a fuse, forming magnesium nitride. Liquid Nitrogen is not corrosive to metals.

HAZARDOUS POLYMERIZATION: Will not occur.

CONDITIONS TO AVOID: Contact with incompatible materials. Cylinders exposed to high temperatures or direct flame can rupture or burst.
PART IV  Is there any other useful information about this material?

11. TOXICOLOGICAL INFORMATION

TOXICITY DATA: The following toxicology data for pure Nitrogen are given below.

Eye Irritation (rabbit): Liquid Nitrogen poured into the eye for one or two seconds with the lids held apart, produced no discernible injury. When the exposure was extended to five seconds, slight lesions of the cornea were observed. By the next day, all eyes were entirely normal.

Suspected Cancer Agent: Nitrogen is not found on the following lists: FEDERAL OSHA Z LIST, NTP, CAL/OSHA, IARC; therefore it is not considered to be, nor suspected to be a cancer-causing agent by these agencies.

Irritancy of Product: Contact with rapidly expanding gases can cause frostbite and damage to exposed skin and eyes.

Sensitization of Product: Nitrogen is not a sensitizer upon prolonged or repeated contact.

Reproductive Toxicity Information: Listed below is information concerning the effects of Nitrogen on the human reproductive system.

Mutagenicity: Nitrogen is not expected to cause mutagenic effects in humans.

Embryotoxicity: Nitrogen is not expected to cause embryotoxic effects in humans.

Teratogenicity: Nitrogen is not expected to cause teratogenic effects in humans.

Reproductive Toxicity: Nitrogen is not expected to cause adverse reproductive effects in humans.

A mutagen is a chemical which causes permanent changes to genetic material (DNA) such that the changes will propagate through generation lines. An embryotoxin is a chemical which causes damage to a developing embryo (e.g., within the first eight weeks of pregnancy in humans), but the damage does not propagate across generational lines. A teratogen is a chemical which causes damage to a developing fetus, but the damage does not propagate across generational lines. A reproductive toxin is any substance which interferes in any way with the reproductive process.

Medical Conditions Aggravated by Exposure: Pre-existing respiratory conditions may be aggravated by overexposure to Nitrogen.

Recommendations to Physicians: Administer oxygen, if necessary. Treat symptoms and reduce overexposure.

Biological Exposure Indices (BEIs): Currently, Biological Exposure Indices (BEIs) are not applicable to Nitrogen.

12. ECOLOGICAL INFORMATION

Environmental Stability: Nitrogen occurs naturally in the atmosphere. The gas will be dissipated rapidly in well-ventilated areas.

Nitrogen: Log $K_{ow} = 0.92$; Water solubility = 1.49% v/v (25°C, 1 atm.).

Effect of Material on Plants or Animals: Any adverse effect on animals would be related to oxygen deficient environments. No adverse effect is anticipated to occur to plant-life, except for frost produced in the presence of rapidly expanding gases.

Effect of Chemical on Aquatic Life: No evidence is currently available on the effects of Nitrogen on aquatic life.

13. DISPOSAL CONSIDERATIONS

Preparing Wastes for Disposal: Waste disposal must be in accordance with appropriate Federal, State, and local regulations. Return cylinders with any residual product to Airgas Inc. Do not dispose of locally.
14. TRANSPORTATION INFORMATION

This material is hazardous as defined by 49 CFR 172.101 by the U.S. Department of Transportation.

**PROPER SHIPPING NAME:** Nitrogen Gas: Nitrogen, compressed
Nitrogen Liquid: Nitrogen, refrigerated liquid

**HAZARD CLASS NUMBER and DESCRIPTION:**
Nitrogen Gas: 2.2 (Non-Flammable Gas)

**UN IDENTIFICATION NUMBER:**
Nitrogen Gas: UN 1066
Nitrogen Liquid: UN 1977

**PACKING GROUP:** Not Applicable

**DOT LABEL(S) REQUIRED:** Non-Flammable Gas

**NORTH AMERICAN EMERGENCY RESPONSE GUIDEBOOK NUMBER (1996):** 121 (Gas); 120 (Liquid)

**MARINE POLLUTANT:** Nitrogen is not classified by the DOT as a Marine Pollutant (as defined by 49 CFR 172.101, Appendix B).

**TRANSPORT CANADA TRANSPORTATION OF DANGEROUS GOODS REGULATIONS:** This material is considered as dangerous goods. Use the above information for the preparation of Canadian Shipments.

15. REGULATORY INFORMATION

**U.S. SARA REPORTING REQUIREMENTS:** Nitrogen is not subject to the reporting requirements of Sections 302, 304, and 313 of Title III of the Superfund Amendments and Reauthorization Act.

**U.S. SARA THRESHOLD PLANNING QUANTITY:** Not applicable.

**U.S. CERCLA REPORTABLE QUANTITY (RQ):** Not applicable.

**CANADIAN DSL/NDSL INVENTORY STATUS:** Nitrogen is on the DSL Inventory.

**U.S. TSCA INVENTORY STATUS:** Nitrogen is on the TSCA Inventory.

**OTHER U.S. FEDERAL REGULATIONS:** Not applicable.

**U.S. STATE REGULATORY INFORMATION:** Nitrogen is covered under the following specific State regulations:

- **Alaska - Designated Toxic and Hazardous Substances:** No.
- **California - Permissible Exposure Limits for Chemical Contaminants:** Nitrogen.
- **Florida - Substance List:** No.
- **Illinois - Toxic Substance List:** No.
- **Kansas - Section 302/313 List:** No.
- **Massachusetts - Substance List:** No.
- **Michigan - Critical Materials Register:** No.
- **Minnesota - List of Hazardous Substances:** No.
- **Missouri - Employer Information/Toxic Substance List:** No.
- **New Jersey - Right to Know Hazardous Substance List:** Nitrogen.
- **North Dakota - List of Hazardous Chemicals, Reportable Quantities:** No.
- **Pennsylvania - Hazardous Substance List:** Nitrogen.
- **Rhode Island - Hazardous Substance List:** Nitrogen.
- **Texas - Hazardous Substance List:** No.
- **West Virginia - Hazardous Substance List:** No.
- **Wisconsin - Toxic and Hazardous Substances:** No.
LABELING (For Compressed Gas):

CAUTION: HIGH PRESSURE GAS.
CAN CAUSE RAPID SUFOCATION.
Store and use with adequate ventilation.
Use equipment rated for cylinder pressure.
Close valve after each use and when empty.
Use in accordance with the Material Safety Data Sheet.

FIRST AID: IF INHALED, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Call a physician.
DO NOT REMOVE THIS PRODUCT LABEL.

LABELING (for Liquid):

ALWAYS KEEP CONTAINER IN UPRIGHT POSITION.

WARNING: EXTREMELY COLD LIQUID AND GAS UNDER PRESSURE.
CAN CAUSE RAPID SUFFOCATION.
CAN CAUSE SEVERE FROSTBITE.
Store and use with adequate ventilation.
Do not get liquid in eyes, on skin or clothing.
For liquid withdrawal, wear face shield and gloves.
Do not drop. Use hand truck for container movement.
Close valve after each use and when empty.
Use in accordance with the Material Safety Data Sheet.

FIRST AID: IF INHALED, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Call a physician.
IN CASE OF FROSTBITE, obtain immediate medial attention.
DO NOT REMOVE THIS PRODUCT LABEL.

CANADIAN WHMIS SYMBOLS: Class A: Compressed Gases
The information contained herein is based on data considered accurate. However, no warranty is expressed or implied regarding the accuracy of these data or the results to be obtained from the use thereof. AIRGAS, Inc. assumes no responsibility for injury to the vendee or third persons proximately caused by the material if reasonable safety procedures are not adhered to as stipulated in the data sheet. Additionally, AIRGAS, Inc. assumes no responsibility for injury to vendee or third persons proximately caused by abnormal use of the material even if reasonable safety procedures are followed. Furthermore, vendee assumes the risk in his use of the material.

DEFINITIONS OF TERMS

A large number of abbreviations and acronyms appear on a MSDS. Some of these which are commonly used include the following:

CAS #: This is the Chemical Abstract Service Number which uniquely identifies each constituent. It is used for computer-related searching.

EXPOSURE LIMITS IN AIR:
- ACGIH - American Conference of Governmental Industrial Hygienists, a professional association which establishes exposure limits. TLV - Threshold Limit Value - an airborne concentration of a substance which represents conditions under which it is generally believed that nearly all workers may be repeatedly exposed without adverse effect. The duration must be considered, including the 8-hour Time Weighted Average (TWA); the 15-minute Short Term Exposure Limit, and the instantaneous Ceiling Limit (C). Skin absorption effects must also be considered.
- OSHA - U.S. Occupational Safety and Health Administration.
- PEL - Permissible Exposure Limit - This exposure value means exactly the same as a TLV, except that it is enforceable by OSHA. The OSHA Permissible Exposure Limits are based in the 1989 PELs and the June, 1993 Air Contaminants Rule (Federal Register: 58: 35338-35351 and 58: 40191). Both the current PELs and the vacuum PELs are indicated. The phrase, “Vacated 1989 PEL,” is placed next to the PEL which was vacated by Court Order.
- IDLH - Immediately Dangerous to Life and Health - This level represents a concentration from which one can escape within 30-minutes without suffering escape-preventing or permanent injury. The DFG - MAK is the Republic of Germany’s Maximum Exposure Level, similar to the U.S. PEL. NIOSH is the National Institute of Occupational Safety and Health, which is the research arm of the U.S. Occupational Safety and Health Administration (OSHA). NIOSH issues exposure guidelines called Recommended Exposure Levels (RELs). When no exposure guidelines are established, an entry of NE is made for reference.

HAZARD RATINGS:
- HAZARDOUS MATERIALS IDENTIFICATION SYSTEM:
  - Health Hazard: 0 (minimal acute or chronic exposure hazard); 1 (slight acute or chronic exposure hazard); 2 (moderate acute or significant chronic exposure hazard); 3 (severe acute exposure hazard; onetime overexposure can result in permanent injury and may be fatal); 4 (extreme acute exposure hazard; onetime overexposure can be fatal).
  - Flammability Hazard: 0 (minimal hazard); 1 (materials that require substantial pre-heating before burning); 2 (combustible liquid or solids; liquids with a flash point of 38-93°C [100-200°F]); 3 (Class IB and IC flammable liquids with flash points below 38°C [100°F]); 4 (Class IA flammable liquids with flash points below 23°C [73°F] and boiling points below 80°C [180°F]).
  - Reactivity Hazard: 0 (normal stable); 1 (material that can become unstable at elevated temperatures or which can react slightly with water); 2 (materials that are unstable but do not detonate or which can react violently with water); 3 (materials that can detonate when inhaled or which can react explosively with water); 4 (materials that can detonate at normal temperatures or pressures).
  - NATIONAL FIRE PROTECTION ASSOCIATION: Health Hazard: 0 (material that on exposure under fire conditions would offer no hazard beyond that of ordinary combustible materials); 1 (materials that on exposure under fire conditions could cause irritation or minor residual injury); 2 (materials that on intense or continued exposure under fire conditions could cause temporary incapacitation or possible residual injury); 3 (materials that on short exposure could cause serious temporary or residual injury); 4 (materials that under very short exposure could cause death or major residual injury).

NATIONAL FIRE PROTECTION ASSOCIATION (Continued): Flammability Hazard and Reactivity Hazard: Refer to definitions for “Hazardous Materials Identification System”.

FLAMMABILITY LIMITS IN AIR:
Much of the information related to fire and explosion is derived from the National Fire Protection Association (NFPA). Flash Point - Minimum temperature at which a liquid gives off sufficient vapors to form an ignitable mixture with air. Autoignition Temperature: The minimum temperature required to initiate combustion in air with no other source of ignition. LEL - the lowest percent of vapor in air, by volume, that will explode or ignite in the presence of an ignition source. UEL - the highest percent of vapor in air, by volume, that will explode or ignite in the presence of an ignition source.

ECOLTOXICOLOGICAL INFORMATION:
Possible health hazards as derived from human data, animal studies, or from the results of studies with similar compounds are presented. Definitions of some terms used in this section are: LD₅₀ - Lethal Dose (solids & liquids) which kills 50% of the exposed animals; LC₅₀ - Lethal Concentration (gases) which kills 50% of the exposed animals; TDLo - Lethal Concentration expressed in parts of material per million parts of air or water; mg/m³ concentration expressed in weight of substance per volume of air; mg/kg quantity of material, by weight, administered to a test subject, based on their body weight in kg. Data from several sources are used to evaluate the cancer-causing potential of the material. The sources are: IARC - the International Agency for Research on Cancer; NTP - the National Toxicology Program, RTECS - the Registry of Toxic Effects of Chemical Substances. OSHA and CAL/OSHA. IARC and NTP rate chemicals on a scale of decreasing potential to cause human cancer with rankings from 1 to 4. Subrankings (2A, 2B, etc.) are also used. Other measures of toxicity include TDL Ottawa, the lowest dose to cause a symptom and TCL to the lowest concentration to cause a symptom: TDLo, LDLo, or TC, TCo, LCLo, and LCo, the lowest dose (or concentration) to cause lethal or toxic effects. BEI - Biological Exposure Indices, represent the levels of determinants which are most likely to be observed in specimens collected from a healthy worker who has been exposed to chemicals to the same extent as a worker with inhalation exposure to the TLV. Ecological Information: EC is the effect concentration in water.

REGULATORY INFORMATION:
This section explains the impact of various laws and regulations on the material. EPA is the U.S. Environmental Protection Agency. WHMIS is the Canadian Workplace Hazardous Materials Information System. DOT and TC are the U.S. Department of Transportation and the Transport Canada, respectively. Superfund Amendments and Reauthorization Act (SARA); the Canadian Domestic/Nondomestic Substances List (DSL/NDSL); the U.S. Toxic Substance Control Act (TSCA); Marine Pollutant status according to the DOT; the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund); and various state regulations.