



APRIL 2015 VOLUME 8 ISSUE 4

Deadly Exposure

The West Virginia DuPont Phosgene Release

January 23, 2010, Belle, West Virginia: A chemical plant owned and operated by DuPont, an industry safety and health role model, suffered three separate anomalous incidents within 33 hours. The last incident, a phosgene release, proved fatal for one plant employee. The worker, wearing minimal PPE, was sprayed across the chest and face with 2 pounds of the deadly chemical when it leaked out of a ruptured flex hose. The worker succumbed to the delayed physiological effects of phosgene exposure approximately 32 hours later.

PROXIMATE CAUSE

- Operator received a lethal dose of phosgene when a hose ruptured

UNDERLYING ISSUES

- Hose failure
- Previous near-miss events

AFTERMATH

- Recommendations to OSHA to revise standards for the storage of highly toxic materials in compressed gas cylinders
- Recommendations to DuPont Belle to improve maintenance management and review all changes to preventative maintenance orders for all critical equipment
- Recommendations to Belle plant to revise emergency response protocol to require that a responsible and accountable employee be available at all times to provide timely and accurate information to emergency dispatchers

BACKGROUND

Phosgene

Phosgene (COCl_2), in liquid and gaseous forms, is colorless and highly toxic. At room temperature, phosgene is a dense, heavier-than-air gas, with inhalation as the primary means of exposure. The odor threshold for phosgene, between 0.4 and 1.0 parts per million (ppm), is higher than the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit of 0.1 ppm. Therefore, the odor of phosgene—reminiscent of freshly cut hay—is not a reliable detection method, as exposure to a harmful concentration of phosgene may occur before noticing its scent.

The properties of phosgene led it to be used as a chemical weapon during WWI before the Geneva Convention ban in 1925. During exposure, phosgene breaks down the proteins in the lung; specifically the delicate alveoli (air sacks) that allow for air transport into the blood stream.

Symptoms from exposure to high concentrations of phosgene may not manifest until 48 hours after initial exposure; however, phosgene poisoning results in respiratory issues such as pulmonary edema, pulmonary emphysema, and potentially death.



Figure 1. German storm troopers emerge from a thick cloud of phosgene poison gas as they attack British trench lines during World War I. Source: Hulton-Deutsch Collection/Corbis Corbis

DuPont Belle's Phosgene Processing

Located in Belle, West Virginia, on the Kanawha River, the DuPont Belle plant produced an assortment of organic chemicals and agricultural products. The plant used phosgene in the creation of five isocyanate intermediate products in the Small Lots Manufacturing (SLM) unit. The phosgene was supplied to the Belle plant in 1-ton cylinders and was stored in the SLM unit in a covered, partially-walled, phosgene shed. Inside the shed, two phosgene cylinders were positioned on scales and each were connected to the manufacturing process via two hoses lined with polytetrafluoroethylene (PTFE) and overbraided with stainless steel. One hose on each cylinder transferred liquid phosgene to a vaporizer while the other pressurized the cylinder with nitrogen.

When a cylinder of phosgene was depleted, the scale notified a board operator to send for a worker to switch the cylinder feed. DuPont required no enhanced Personal Protective Equipment (PPE) (i.e., encapsulated suit and breathing air) for this process because the hoses remained coupled when the worker opened the valves on the full cylinder and closed them on the empty cylinder. Operators only wore enhanced PPE when swapping an empty cylinder with a full one. When switching cylinders, workers cleared the hoses with nitrogen (with the phosgene being pushed to a vacuum and scrubber), isolated the phosgene hose, disconnected the cylinder, then replaced the cylinder and reattached the hoses. Two to three cylinders of phosgene were consumed daily during normal operations.

At the time of the incident, DuPont employed approximately 440 workers at the 105-acre Belle plant. Until the incident, the Belle facility had the best safety record of any DuPont production plant.

WHAT HAPPENED

On Saturday, January 23, 2010, at approximately 1:45 p.m. local time, a phosgene transfer hose connected to a partially filled cylinder burst as an operator was inside the phosgene shed. The operator was checking the status of the cylinders in anticipation of a transfer and was not wearing enhanced PPE. The operator was sprayed across the chest and face as 2 pounds of phosgene inside the hose leaked into the atmosphere. The liquid phosgene had remained in the hose from a previous transfer operation.

Immediately after the incident, the operator called for assistance on the phosgene shed phone. A responding coworker directed the exposed worker to a plant truck and helped transport the worker to the plant's medical center. The two workers were intercepted by a shift supervisor who transported the victim the rest of the way in his vehicle. During this time, the front gate guard was instructed via radio to call emergency services for an ambulance (which occurred at 1:59 p.m.). The guard was unaware of the chemical release and informed emergency services that the response was for a medical emergency. An ambulance was dispatched from the Kanawha County Emergency Ambulance Authority at 2:03 p.m. Five minutes later, responding Emergency Medical Technicians (EMTs) requested more information from dispatch, including whether there was chemical exposure. When dispatchers called DuPont, they encountered busy lines.

EMTs arrived at 2:14 p.m. and met the exposed worker at the DuPont medical center. The exposed worker had washed his face and hands and changed his clothes while waiting at the medical center, but neglected to shower or undergo decontamination activities. While collecting the worker for transport, EMTs were notified of the worker's phosgene exposure and were handed a phosgene treatment protocol for the attending physician at the hospital.

A baseline X-ray revealed no congestion in the victim's lungs; however, almost 4 hours after exposure, the worker's condition rapidly deteriorated. The worker's condition never improved and he died at 9:27 p.m., January 24, 2010.

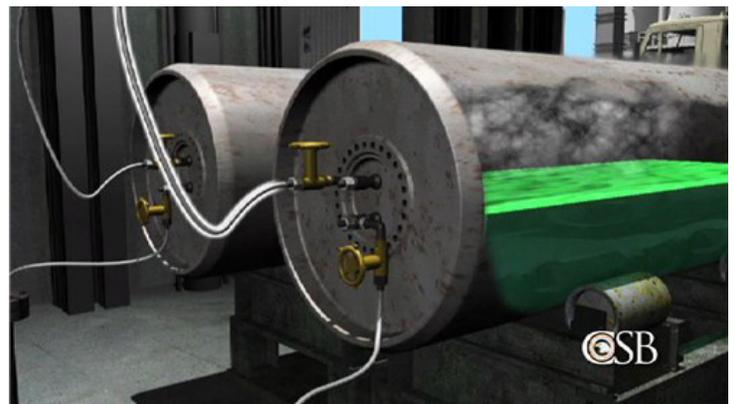


Figure 2. Artist's rendition of the two-tank setup inside the phosgene shed at DuPont Belle. Source: CSB

Although there was one additional confirmed and one possible phosgene exposure (the workers assisting the operator) after the initial release, the workers involved later showed no signs of the adverse effects of exposure. No report of exposure to the public occurred the day of the incident.

PROXIMATE CAUSE

According to U.S. Chemical Safety Board (CSB) calculations, the operator received a lethal dose of phosgene in less than one-tenth of a second.

UNDERLYING ISSUES

Hose Failure

CSB investigators found that the majority of tags attached to the hoses to indicate their intended service were secured in place with plastic ties and metal clamps. However, the manufacturer's tag on the hoses was secured with white plastic adhesive tape. Extensive corrosion was localized under the area covered by the tape. The permeable PTFE and braided 304 stainless steel of the hoses had provided an ideal environment under the tape for phosgene vapor to collect and convert to hydrogen chloride (HCl), which then caused stress corrosion cracking (SCC). Although questions were raised concerning whether or not the hoses used were the ideal choice for phosgene transfer, DuPont previously calculated the risk and cost-effectiveness of purchasing replacement hoses to be too high.

This occurred even though, as of 2010, the Compressed Gas Association (CGA) Standards for PTFE-lined hoses stated that the use of "PTFE-lined [hoses] are not suitable for use with... poisonous, toxic, or pyrophoric gases because permeation of gas through the PTFE wall creates a potential hazard."

At the time of the incident, the isolation valves for the phosgene hose were closed, and the hose retained liquid phosgene between the valves. Corrosion weakened the hose braiding over time, allowing thermal expansion of the isolated liquid phosgene until the hose failed. Although Process Hazard Analyses (PHAs) occurred at the Belle plant in 1994, 1999, 2004, and 2009, the analysis for the phosgene system only included the 1-ton cylinders, nitrogen pressuring system, vaporizer, and all associated piping and controls. While DuPont assessed the potential for a phosgene leak if the hoses were incorrectly connected or inadvertently disconnected while the feed valve was open, they did not assess the potential for the hose to rupture due to thermal expansion. However, the potential for liquid phosgene thermal expansion was evaluated in other process equipment during the 2009 PHA.

Although the maintenance plan for the hoses prescribed a regular change-out schedule of 30 days, work orders show that change-out frequency was neither systematic nor predictable. Between 2006 and 2010, hoses were left in service from 4 to 7 months multiple times. The hose that failed on January 23, 2010 had been in use for over six months. This period included a plant-

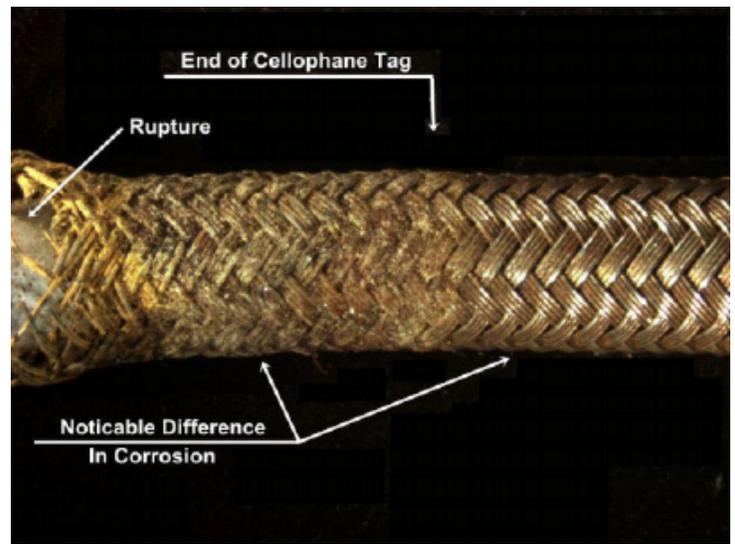


Figure 3. The corroded and ruptured PTFE stainless steel hose from the DuPont Belle phosgene leak. Source: CSB

wide hose change-out and removal of phosgene containers from the phosgene shed.

Change-out frequency was intended to be governed by the facility's automatic System Application and Products (SAP) maintenance program. Some supervisors also relied on the maintenance coordinator remembering to initiate change-out. At some point in 2006, SAP data regarding the change-out frequency was altered. CSB investigators and DuPont Belle were unable to determine exactly when or why this change occurred; only that the change halted hose maintenance notifications. DuPont did not provide a back-up method to ensure timely change-out and the maintenance software was not documented or reviewed in accordance with Management of Change (MOC) processes.

Near-Miss Event

On the morning of the incident, maintenance personnel replaced the phosgene hose on the phosgene tank not involved with the incident because of a suspected flow restriction. As the hose and valve assembly was decontaminated in a water bath, the adhesive ID tag fell off and revealed a corroded section of the stainless steel braid and collapsed PTFE liner. When the worker saw this, he told coworkers that they were lucky in catching the hose before it ruptured. Supervisors were not informed of the issue and it was not captured as a near-miss event. The worker planned to tell the supervisory staff on Monday, when they would return to work after the weekend, and expected a full investigation. This notification would have fallen outside of the DuPont Belle policy for reporting incidents within a 24-hour period.

Though supervisors were not typically onsite on weekends, management and safety and health experts were at the facility that morning of Saturday, January 23, 2010 for a safety pause meeting.

AFTERMATH

The CSB investigators made several recommendations to the involved organizations, specifically to OSHA and DuPont Belle. The CSB recommended that OSHA revise standards for the storage of highly toxic materials in compressed gas cylinders to incorporate provisions that are at least as effective as the National Fire Protection Association (NFPA) 55, Compressed Gases and Cryogenic Fluids Code.

The CSB outlined recommendations for Belle that involve improving the existing maintenance management program by supplementing the computerized system with sufficient redundancies and conducting MOC reviews for all changes to preventative maintenance orders for all Process Safety Management-critical equipment in the computerized maintenance management system. Additionally, revisions were suggested for the near-miss reporting system and investigation policy so that it is operational at all times.

The CSB also recommended that the Belle plant revise their emergency response protocol to require that a responsible and accountable employee be available at all times to provide timely and accurate information to emergency dispatchers. They also recommended that DuPont prohibit the use of hoses with permeable cores and materials susceptible to chlorides corrosion for phosgene transfer. Acceptable corrective action can be found on the CSB website for the incident.

RELEVANCE TO NASA

From Apollo to the Space Shuttle, and now to the next generation of aircraft and spacecraft hardware, many hydraulic pressurized systems have been and continue to be utilized at NASA centers and facilities. Large quantities of ammonia were used at Centers to support and onboard to sustain Shuttle operations. Many leaks occurred during Shuttle processing, which resulted in immediate exposure risks to the surrounding area in addition to larger risks associated with ammonia clouds moving into areas of operation. Although the airborne clouds were lower in toxicity, they still presented a major risk for large populations of workers.

Even more potentially hazardous was the use of highly toxic hydrazine as a hypergolic fuel for Shuttle maneuvering system thrusters. Multiple thrusters on each Shuttle required multiple feed lines throughout the vehicle, support structures, and around processing facilities and the launch pad that all required maintenance. NASA compiled lessons from hypergol spills and fires in NASA/TP-2009-214769, A Summary of NASA and USAF Hypergolic Propellant-Related Spills and Fires:

- Improper configuration control and internal or external human performance shaping factors can lead to being falsely comfortable with a system.
- Communication breakdown can escalate an incident to a level where injuries occur and/or hardware is damaged.

- Improper propulsion system and ground support system designs can destine a system for failure.
- Improper training of technicians, engineers, and safety personnel can put lives in danger.
- Improper PPE, spill protection, and staging of fire extinguishing equipment can result in unnecessary injuries or hardware damage if an incident occurs.
- Improper procedural oversight, development, and adherence to the procedure can be detrimental and quickly lead to an undesirable incident.
- Improper materials cleanliness or compatibility and chemical reactivity can result in fires or explosions.
- Improper established “back-out” and/or emergency safing procedures can escalate an event.

NASA-STD-8719.17A, NASA Requirements for Ground-Based Pressure Vessels and Pressurized Systems provides overall agency guidance. Local maintenance and operating guidance per system manufacturers and certifiers is coordinated by the Pressure System Manager at each NASA Center. NASA personnel and NASA contractors can sign up for informative training courses in Ground-Based Pressure Vessel Safety and High Pressure Systems Operation and Flexible Hose Safety in SATERN, the Agency’s learning management system.

Timely reporting of equipment degradation or damage, or any hazardous condition, to the person with the authority to mitigate the hazard source or eliminate human exposure risk saves lives and enables mission success.

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SYSTEM FAILURE CASE STUDY



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Thanks to W.Frazier, M.Erminger, R.Sweet, and S.Brisbin for their contribution to this study.

This is an internal NASA safety awareness training document based on information available in the public domain. The findings, proximate causes, and contributing factors identified in this case study do not necessarily represent those of the Agency. Sections of this case study were derived from multiple sources listed under References. Any misrepresentation or improper use of source material is unintentional.

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